Metal-free carboxamidation of P(O)H compounds with in

situ formed isocyanates from dioxazolones: a convenient

access to carbamoylphosphine oxides

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1. General information

All reactions were carried out under dry argon (unless otherwise noted). All the heating experiments were performed in an oil bath. ¹H NMR, ¹³C NMR and ³¹P NMR spectra were recorded on a Bruker Av400 or Av500 spectrometer using tetramethylsilane (TMS) in CDCl₃ or DMSO-*d6* as the internal standard. Chemical shifts were reported in ppm on the scale relative to CDCl₃ and DMSO-*d6* (¹H NMR: TMS at 0.00 ppm, CHCl₃ at 7.26 ppm, DMSO-*d6* at 2.50 ppm; ¹³C NMR: CDCl₃ at 77.2 ppm, DMSO-*d6* at 39.5 ppm) and P(O)Ph₃ as external standard for 31P NMR. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz). HRMS spectra of compounds were carried out with Waters Micromass LCT Premier TOF-MS apparatus. Crystallographic data were collected on XtaLAB Synergy, Dualflex, HyPix diffractometer. Absorption corrections were applied by using the spherical harmonics program (multi-scan type). Silica gel column chromatography was performed using 300-400 mesh.

2. General procedure for the preparation of compounds 3

$$\begin{array}{c} N^{-O} & O \\ R_{1} & O \\ R_{1} & O \end{array} + \begin{array}{c} R_{2} - P - H \\ R_{3} \\ 1 \end{array} \xrightarrow{Na_{2}CO_{3}} R_{1} \\ MTBE, \ 60 \ ^{\circ}C \end{array} + \begin{array}{c} R_{1} \\ R_{1} \\ H \\ H \\ 0 \\ 0 \\ 3 \end{array}$$

To a Schlenk tube equipped with a magnetic stir bar was added dioxazolones 1 (0.3 mmol), P(O)H compounds 2 (0.2 mmol), and Na₂CO₃ (0.03 mmol) in MTBE (0.2 mL) under argon, and the mixture was kept stirring at 60 °C in an oil bath for 9 h. Upon completion, the reaction mixture was concentrated in vacuum. The residue was purified by silica gel column chromatography using a petroleum ether/EtOAc (4 / 1) as the eluent to give the corresponding products **3**.

3. General procedure for the preparation of dioxazolones 1

$$\begin{array}{c} O \\ H \\ H \\ OH \\ \hline ii) NH_2OH \\ HCI \\ \hline HCI \\ HCI \\ \hline H \\$$

To a solution of a carboxylic acid (10 mmol, 1.0 equiv.) in freshly distilled THF (20 mL, 0.5 M) was added 1,1' carbonyldiimidazole (CDI, 2.43 g, 15 mmol, 1.5 equiv.) at room temperature. The reaction mixture was stirred for 1 h. Then, hydroxylamine hydrochloride (1.40 g, 20 mmol, 2.0 equiv.) was added. After stirring overnight, the resulting mixture was quenched with 5% aqueous KHSO₄ solution (20 mL), extracted with EtOAc, dried over Na₂SO₄ and concentrated under reduced pressure. The crude hydroxamic acid (10 mmol, 1.0 equiv.) in freshly distilled DCM (100 mL, 0.1 M) was added CDI (1.62 g, 10 mmol, 1.0 equiv.) in one portion. The reaction mixture was stirred at room temperature for 30 min. Then, a cold aqueous HCl solution (50 mL, 1 N) was added, and the aqueous phase was extracted with DCM (3×20 mL). The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. The crude pressure. The desired dioxazolones **1** was purified quickly by short silica gel flash chromatography.¹

4. Procedure for the application studies

$$\begin{array}{c} N^{-0} \longrightarrow 0 \\ Ph \end{array} + Ph - P-H \\ Ph \end{array} + \begin{array}{c} Na_2CO_3 (15 \text{ mol } \%) \\ MBTE, 60 \ ^\circ C \end{array} + \begin{array}{c} Ph \\ N \\ H \\ 0 \\ 3a, 2.34 \text{ g}, 73\% \end{array}$$

An oven - dried 50 mL Schlenk flask was charged with a stirring bar, dioxazolone **1a** (2.44 g, 15.0 mmol), diphenylphosphine oxide **2a** (2.02 g, 10 mmol), MTBE (10 ml) and Na₂CO₃ (0.16 g, 1.5 mmol) was added and the mixture was heated at 60 °C for 9 h. After cooling to room temperature, the solution was then diluted with EtOAc (50 mL) and water, extracted with EtOAc. The combined organic extracts were dried over anhydrous Na₂SO₄, filtered, and concentrated. The crude product was purified by silica gel column chromatography using a petroleum ether/EtOAc (5 / 1) as the eluent to give the corresponding products **3a** (2.34 g, 73% yield).

$$\begin{array}{cccc} Ph & & & & \\ Ph & & & \\ N & & P - Ph \\ H & & & \\ 3a \end{array} \xrightarrow{\begin{subarray}{c} n-BuLi \\ THF, rt, 12 h \end{array}} Ph & & \\ Ph & & \\ N & H \\ H & \\$$

A stirred solution of compound **3a** (0.2 mmol) in anhydrous THF (2.0 mL) was added n-BuLi (320 μ L, 2.5 M in hexane) at 0 °C. Then the mixture was stirred at room temperature overnight. TLC monitored the reaction to reach completion. The reaction was quenched by addition of saturated NH₄Cl solution (3.0 mL). Extracted with EtOAc (3×5.0 mL), the combined organic layers were washed with brine, dried over Na₂SO₄. The concentrated residue was purified by column chromatography to afford the desired product **4** as a white solid (19.8 mg, 56% yield).

$$\begin{array}{c} Ph \underbrace{N}_{H} \underbrace{Ph}_{O} \underbrace{Ph}_{H} \underbrace{Lawesson's \ reagent}_{O} Ph \underbrace{N}_{H} \underbrace{Ph}_{O} \underbrace{Ph}_{H} \underbrace{N}_{H} \underbrace{Ph}_{H} \underbrace{Ph}_{H$$

3a (0.20 mmol) and Lawesson's reagent (242.6 mg, 0.4 mmol) in toluene (2.0 mL) in an oven-dried 25 mL Schlenk tube was refluxed with vigorous stirring for 12 h under Ar atmosphere. After cooling to room temperature, the reaction mixtures were then diluted with water (5.0 mL) and extracted with EtOAc (3×10 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel to give the pure product **5** (55.1 mg, 78% yield).²

5. Investigation of the reaction mechanism



To a Schlenk tube equipped with a magnetic stir bar was added 2a (0.2 mmol), 4methylphenyl isocyanate (0.3 mmol), and Na₂CO₃ (0.03 mmol) in MTBE (0.2 mL) under argon, and the mixture was kept stirring at 60 °C in an oil bath for 9 h. Upon completion, the reaction mixture was concentrated in vacuum. The resulting mixture was cooled down to room temperature and purified by flash chromatography to give **3b** (51.8 mg, 73% yield).



To a Schlenk tube equipped with a magnetic stir bar was added 1a (0.2 mmol) and Na₂CO₃ (0.02 mmol) in MTBE (0.2 mL) under argon, and the mixture was kept stirring at 60 °C in an oil bath for 9 h. Upon completion, the reaction mixture was concentrated in vacuum. The resulting mixture was cooled down to room temperature and purified by flash chromatography to give **6** (19.5 mg, 46% yield).

6. Characterization data for products 3-6

1-(diphenylphosphoryl)-N-phenylformamide 3a

$$Ph \underset{H}{\overset{O}{\overset{}}} Ph \underset{H}{\overset{H}{\overset{}}} Ph$$

Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 4:1); **3a** was obtained as a white solid (55.8 mg, 87% yield).

¹**H NMR** (400 MHz, CDCl₃): δ 10.06 (s, 1H), 8.01-7.96 (m, 4H), 7.78 (d, *J* = 7.6 Hz, 2H), 7.60-7.58 (m, 2H), 7.52-7.48 (m, 4H), 7.34 (t, *J* = 8.4 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 1H).

¹³**C NMR** (101 MHz, CDCl₃): δ 168.2 (d, *J* = 123.2 Hz), 137.0 (d, *J* = 9.5 Hz), 132.7 (d, *J* = 2.9 Hz), 131.8 (d, *J* = 9.6 Hz), 129.0, 128.9 (d, *J* = 100.6 Hz), 128.8 (d, *J* = 12.5 Hz), 125.5, 120.2.

³¹**P NMR** (162 MHz, CDCl₃): δ 15.51.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₉H₁₆NaNO₂P⁺ 344.0811; found 344.0804.

1-(diphenylphosphoryl)-N-(p-tolyl)formamide 3b

Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 2:1); **3b** was obtained as a white solid (56.9 mg, 86% yield).

¹**H NMR** (400 MHz, CDCl₃): δ 9.63 (d, *J* = 14.7 Hz, 1H), 8.01-7.97 (m, 4H), 7.63-7.60 (m, 4H), 7.55-7.51 (m, 4H), 7.17 (d, *J* = 7.9 Hz, 2H), 2.35 (s, 3H),

¹³**C NMR** (101 MHz, CDCl₃): δ 167.8 (d, *J* = 128.5 Hz), 135.4, 134.3 (d, *J* = 7.5 Hz), 132.8, 131.9 (d, *J* = 8.4 Hz), 129.6, 128.9 (d, *J* = 100.1 Hz), 128.8 (d, *J* = 11.5 Hz), 120.0, 21.1.

³¹**P NMR** (162 MHz, CDCl₃): δ 15.63.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{18}NaNO_2P^+$ 336.1148; found 336.1140.

1-(diphenylphosphoryl)-N-(m-tolyl)formamide 3c



Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 2:1); **3c** was obtained as a white solid (59.6 mg, 90% yield). ¹**H NMR** (400 MHz, CDCl₃): δ 9.75 (s, 1H), 8.00-7.97 (m, 4H), 7.65-7.60 (m, 3H), 7.54-7.51 (m, 5H), 7.25 (t, *J* = 7.8 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 2.35 (s, 3H). ¹³**C NMR** (101 MHz, CDCl₃): δ 168.1 (d, *J* = 127.0 Hz), 139.1, 136.8 (d, *J* = 9.6 Hz), 132.8 (d, *J* = 8.0 Hz), 131.8 (d, *J* = 9.9 Hz), 128.9, 128.9 (d, *J* = 12.8 Hz), 128.9 (d, *J* = 100.2 Hz), 126.4, 120.7, 117.2, 21,5. ³¹**P NMR** (162 MHz, CDCl₃): δ 15.58. **HRMS** (ESI) m/z: [M+Na]⁺ Calcd for C₂₀H₁₈NaNO₂P⁺ 336.1148; found 336.1140.

1-(diphenylphosphoryl)-N-(o-tolyl)formamide 3d



Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 2:1); **3d** was obtained as a white solid (60.5 mg, 91% yield). ¹**H NMR** (400 MHz, CDCl₃): δ 9.48 (s, 1H), 8.08-8.00 (m, 5H), 7.62 (m, 2H), 7.56-7.52 (m, 4H), 7.24 (d, *J* = 6.6 Hz, 2H), 7.15-7.12 (m, 1H), 2.39 (s, 3H). ¹³**C NMR** (101 MHz, CDCl₃): δ 168.0 (d, *J* = 126.4 Hz), 134.6 (d, *J* = 7.2 Hz), 132.9 (d, *J* = 2.7 Hz), 131.8 (d, *J* = 9.5 Hz), 130.8, 128.7, 128.9 (d, *J* = 100.5 Hz), 128.8 (d, *J*

= 12.3 Hz), 126.9, 126.0, 121.9, 17.6.

³¹**P NMR** (162 MHz, CDCl₃): δ 15.87.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₀H₁₈NaNO₂P⁺ 336.1148; found 336.1139.

N-([1,1'-biphenyl]-4-yl)-1-(diphenylphosphoryl)formamide 3e



Following general procedure, purification by flash column chromatography (petroleum

ether/EtOAc = 3:1); **3e** was obtained as a white solid (60.4 mg, 76% yield).

¹H NMR (400 MHz, DMSO): δ 11.15 (s, 1H), 7.93-7.86 (m, 6H), 7.71-7.60 (m, 10H), 7.45 (t, J = 7.4 Hz, 2H), 7.34 (t, J = 7.5 Hz, 1H).

¹³C NMR (101 MHz, DMSO): δ 169.2 (d, J = 122.5 Hz), 139.9, 137.3, 137.2 (d, J =9.1 Hz), 133.2 (d, J = 2.9 Hz), 131.9 (d, J = 9.4 Hz), 130.24 (d, J = 99.2 Hz), 129.4 (d,

J = 11.7 Hz), 129.4, 127.8, 127.3, 126.9, 121.8.

³¹**P NMR** (162 MHz, DMSO): δ 15.19.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₅H₂₀NaNO₂P⁺ 420.1124; found 420.1115.

1-(diphenylphosphoryl)-N-(4-fluorophenyl)formamide 3f

Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 2:1); **3f** was obtained as a white solid (49.5 mg, 73% yield).

¹H NMR (400 MHz, DMSO): δ 11.14 (s, 1H), 7.89-7.82 (m, 6H), 7.70-7.67 (m, 2H), 7.62-7.60 (m, 4H), 7.19 (t, J = 8.8 Hz, 2H).

¹³C NMR (101 MHz, DMSO): δ 173.8 (d, J = 123.4 Hz), 164.3 (d, J = 241.1 Hz), 138.9 (d, J = 12.3 Hz), 137.5 (d, J = 2.5 Hz), 136.6 (d, J = 9.0 Hz), 134.9 (d, J = 99.1 Hz),134.2 (d, *J* = 11.8 Hz), 128.2, 120.6 (d, *J* = 22.1 Hz).

³¹**P NMR** (162 MHz, DMSO): δ 14.60.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{15}FNaNO_2P^+$ 362.0717; found 362.0706.

N-(4-chlorophenyl)-1-(diphenylphosphoryl)formamide 3g

Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 1:1); 3g was obtained as a white solid (44.9 mg, 64% yield). ¹**H NMR** (400 MHz, CDCl₃): δ 9.78 (s, 1H), 7.92-7.88 (m, 4H), 7.73 (d, J = 7.8 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 4H), 7.40-7.36 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 167.3 (d, J = 127.8 Hz), 139.9 (d, J = 3.1 Hz), 136.6 (d, *J* = 9.5 Hz), 133.1 (d, *J* = 10.5 Hz), 129.3 (d, *J* = 12.5 Hz), 129.2, 127.0 (d, *J* = 101.9 Hz), 125.9, 120.2.

³¹**P NMR** (162 MHz, CDCl₃): δ 14.66.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₉H₁₅ClNaNO₂P⁺ 378.0421; found 378.0411.

N-(4-bromophenyl)-1-(diphenylphosphoryl)formamide 3h



Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 2:1); **3h** was obtained as a white solid (50.2 mg, 63% yield).

¹**H NMR** (400 MHz, CDCl₃): δ 9.95 (s, 1H), 7.99-7.94 (m, 4H), 7.68-7.61 (m, 4H), 7.55-7.51 (m, 4H), 7.47 (d, *J* = 8.9 Hz, 2H).

¹³**C NMR** (101 MHz, CDCl₃): δ 168.3 (d, *J* = 122.8 Hz), 136.0 (d, *J* = 9.5 Hz), 133.0 (d, *J* = 2.7 Hz), 132.1, 131.8 (d, *J* = 10.0 Hz), 128.9 (d, *J* = 12.5 Hz), 128.6 (d, *J* = 101.3 Hz), 121.7, 118.3.

³¹**P NMR** (162 MHz, CDCl₃): δ 15.93.

HRMS (ESI) m/z: $[M+H^+]$ Calcd for $C_{19}H_{16}BrNO_2P^+$ 400.0097; found 400.0087.

1-(diphenylphosphoryl)-N-(4-methoxyphenyl)formamide 3i

Μ

Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 1:1); **3i** was obtained as a white solid (57.5 mg, 82% yield).

¹**H NMR** (400 MHz, CDCl₃): δ 9.66 (s, 1H), 8.00-7.95 (m, 4H), 7.67 (d, *J* = 8.6 Hz, 2H), 7.63-7.59 (m, 2H), 7.53-7.51 (m, 4H), 6.86 (d, *J* = 8.9 Hz, 2H), 3.81 (s, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 167.3 (d, *J* = 123.3 Hz), 157.1, 133.8 (d, *J* = 2.4 Hz), 131.8 (d, *J* = 9.8 Hz), 129.9 (d, *J* = 100.6 Hz), 128.8 (d, *J* = 12.8 Hz), 121.6, 114.2, 55.5.

³¹**P NMR** (162 MHz, CDCl₃): δ 15.82.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₀H₁₈NaNO₃P⁺ 352.1097; found 352.1088.

N-(4-(tert-butyl)phenyl)-1-(diphenylphosphoryl)formamide 3j



Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 2:1); **3j** was obtained as a white solid, mp 200-202 °C. (57.3 mg, 76% yield).

¹**H NMR** (400 MHz, CDCl₃): δ 9.55 (s, 1H), 8.01-7.97 (m, 4H), 7.67-7.60 (m, 4H), 7.55-7.53 (m, 4H), 7.39 (d, *J* = 7.9 Hz, 2H), 1.33 (s, 9H)

¹³**C NMR** (101 MHz, CDCl₃): δ 167.8 (d, *J* = 123.2 Hz), 148.7, 134.2 (d, *J* = 8.6 Hz), 132.8 (d, *J* = 2.4 Hz), 131.8 (d, *J* = 9.7 Hz), 128.9 (d, *J* = 99.5 Hz), 128.7 (d, *J* = 12.3 Hz), 126.0, 119.6, 34.5, 31.3.

³¹**P NMR** (162 MHz, CDCl₃): δ 15.74.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{24}NaNO_2P^+$ 400.1437; found 400.1428.

1-(diphenylphosphoryl)-N-(4-(trifluoromethyl)phenyl)formamide 3k

Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 2:1); **3k** was obtained as a white solid (40.4 mg, 52% yield).

¹**H NMR** (400 MHz, CDCl₃): δ 10.18 (s, 1H), 7.99-7.90 (m, 6H), 7.66-7.60 (m, 4H), 7.55-7.52 (t, *J* = 7.3 Hz, 4H).

¹³**C NMR** (101 MHz, CDCl₃): δ 168.8 (d, J = 123.4 Hz), 139.8 (d, J = 10.4 Hz), 133.1 (d, J = 2.4 Hz), 131.8 (d, J = 10.2 Hz), 128.9 (d, J = 12.5 Hz), 128.4 (d, J = 101.3 Hz), 127.3 (q, J = 34.2 Hz), 126.3 (q, J = 3.6 Hz), 124.1 (q, J = 271.3 Hz).

³¹**P NMR** (162 MHz, CDCl₃): δ 16.02.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{15}F_3NaNO_2P^+$ 412.0685; found 412.0677.

1-(diphenylphosphoryl)-N-(2-(trifluoromethyl)phenyl)formamide 31



Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 2:1); **3l** was obtained as a white solid, mp 108-110 °C. (36.4 mg, 47% yield).

¹**H NMR** (400 MHz, CDCl₃): δ 9.85 (s, 1H), 8.28 (d, J = 7.9 Hz, 1H), 8.03-7.98 (m, 4H), 7.74 (d, J = 7.8 Hz, 1H), 7.65-7.60 (m, 2H), 7.58-7,53 (m, 5H), 7.34-7.29 (m, 1H). ¹³**C NMR** (101 MHz, CDCl₃): δ 169.2 (d, J = 122.4 Hz), 133.8 (d, J = 9.9 Hz), 133.0 (d, J = 2.8 Hz), 132.8, 131.9 (d, J = 9.8 Hz), 128.9 (d, J = 12.4 Hz), 128.5 (d, J = 100.4 Hz), 126.4 (q, J = 5.2 Hz), 125.8, 124.0, 124.9 (q, J = 273.3 Hz), 121.3 (q, J = 30.3 Hz). ³¹**P NMR** (162 MHz, CDCl₃): δ 16.25.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₀H₁₅F₃NaNO₂P⁺ 412.0685; found 412.0675.

N-(3-cyanophenyl)-1-(diphenylphosphoryl)formamide 3m



Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 1:1); **3m** was obtained as a white solid, mp 197-199 °C. (28.3 mg, 41% yield).

¹**H NMR** (400 MHz, CDCl₃): δ 10.68 (s, 1H), 8.32 (s, 1H), 8.04-7.94 (m, 5H), 7.66-7.63 (m, 2H), 7.55-7.53 (m, 4H), 7.47-7.42 (m, 2H).

¹³**C NMR** (101 MHz, CDCl₃): δ 169.1 (d, *J* = 125.1 Hz), 138.3 (d, *J* = 9.7 Hz), 133.1, 131.8 (d, *J* = 9.8 Hz), 129.8, 129.0 (d, *J* = 12.0 Hz), 128.6, 128.6 (d, *J* = 99.8 Hz), 124.6, 124.0, 118.3, 113.0.

³¹**P NMR** (162 MHz, CDCl₃): δ 16.29.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{15}NaN_2O_2P^+$ 369.0763; found 369.0754.

N-(4-((diphenylphosphoryl)formamido)phenyl)acetamide 3n



Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 1:3); **3n** was obtained as a white solid, mp 296-298 °C. (28.3 mg, 38% yield).

¹**H NMR** (500 MHz, CDCl₃): δ 9.79 (s, 1H), 8.16 (s, 1H), 7.94-7.90 (m, 4H), 7.63-7.57 (m, 4H), 7.50-7.48 (m, 6H), 2.08 (s, 3H),

¹³C NMR (101 MHz, CDCl₃): δ 168.8, 167.7 (d, *J* = 123.5 Hz), 135.8, 132.9 (d, *J* = 1.9 Hz), 132.8 (d, *J* = 9.4 Hz), 131.8 (d, *J* = 9.6 Hz), 128.8 (d, *J* = 12.4 Hz), 128.6 (d, *J* = 101.1 Hz), 120.7, 120.4, 24.3.

³¹**P NMR** (162 MHz, CDCl₃): δ 16.14.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{19}N_2NaO_3P^+$ 401.1026; found 401.1022.

1-(diphenylphosphoryl)-N-(naphthalen-2-yl)formamide 3o



Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 1:1); **30** was obtained as a white solid (49.7 mg, 62% yield). ¹H NMR (400 MHz, CDCl₃): δ 9.98 (s, 1H), 8.50 (s, 1H), 8.04 (t, *J* = 9.7 Hz, 4H), 7.85-7.81 (m, 3H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.65-7.62 (m, 2H), 7.57-7.44 (m, 6H). ¹³C NMR (101 MHz, CDCl₃): δ 168.3 (d, *J* = 122.4 Hz), 134.3 (d, *J* = 9.3 Hz), 133.6, 132.9, 131.9 (d, *J* = 9.5 Hz), 131.2, 129.0 128.9 (d, *J* = 100.4 Hz), 128.9 (d, *J* = 12.2 Hz), 127.9, 127.7, 126.7, 125.6, 119.6, 117.4. ³¹P NMR (162 MHz, CDCl₃): δ 15.72.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₃H₁₈NaNO₂P⁺ 394.0967; found 394.0959.

1-(diphenylphosphoryl)-N-(4-ethynylphenyl)formamide 3p



Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 1:1); **3p** was obtained as a white solid, mp 184-186 °C (51.7 mg, 75% yield).

¹**H NMR** (400 MHz, CDCl₃): δ 10.32 (s, 1H), 7.98-7.93 (m, 4H), 7.79 (d, *J* = 8.6 Hz, 2H), 7.62-7.59 (m, 2H), 7.53-7.43 (m, 6H), 3.09 (s, 1H).

¹³C NMR (101 MHz, CDCl₃): δ 168.4 (d, J = 122.6 Hz), 137.5 (d, J = 9.8 Hz), 132.1,
131.8 (d, J = 10.0 Hz), 128.9 (d, J = 12.0 Hz), 128.7 (d, J = 101.0 Hz), 120.0, 119.0.
83.2, 77.4.

³¹**P NMR** (162 MHz, CDCl₃): δ 15.83.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{16}NaNO_2P^+$ 368.0811; found 368.0802.

(E)-1-(diphenylphosphoryl)-N-styrylformamide 3q



Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 4:1); **3q** was obtained as a white solid (49.3 mg, 71% yield). ¹**H NMR** (400 MHz, CDCl₃): δ 10.33 (d, J = 10.0 Hz, 1H), 8.00-7.95 (m, 4H), 7.64-7.53 (m, 7H), 7.33-7.23 (m, 4H), 7.25-7.21 (m, 1H), 6.63 (d, J = 15.0 Hz, 1H). ¹³**C NMR** (101 MHz, CDCl₃): δ 167.3 (d, J = 124.7 Hz), 135.7, 133.1 (d, J = 2.1 Hz), 131.9 (d, J = 10.1 Hz), 129.0 128.9 (d, J = 102.3 Hz), 128.9 (d, J = 6.0 Hz), 127.5, 126.2, 120.9 (d, J = 6.7 Hz), 117.6. ³¹**P NMR** (162 MHz, CDCl₃): δ 16.12.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₁H₁₈NaNO₂P⁺ 370.0967; found 370.0960.

1-(diphenylphosphoryl)-N-(furan-2-yl)formamide 3r

 $\bigcirc \begin{matrix} O \\ Ph \\ P-Ph \\ H \\ \square \end{matrix}$

Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 4:1); **3r** was obtained as a white solid, mp 129-131 °C (43.6 mg, 70% yield).

¹**H NMR** (400 MHz, CDCl₃): δ 10.60 (s, 1H), 8.00-7.96 (m, 4H), 7.63-7.60 (m, 2H), 7.55-7.51 (m, 4H), 7.11 (dd, *J* = 1.8, 0.9 Hz, 1H), 6.52 (d, *J* = 2.9 Hz, 1H), 6.41-6.40 (m, 1H).

¹³C NMR (101 MHz, CDCl₃): δ 166.1 (d, J = 125.3 Hz), 144.3 (d, J = 12.6 Hz), 136.1, 133.0, 131.8 (d, J = 9.5 Hz), 128.9 (d, J = 12.7 Hz), 128.6 (d, J = 102.1 Hz), 111.5, 96.5.
³¹P NMR (162 MHz, CDCl₃): δ 15.98.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₇H₁₄NaNO₃P⁺ 334.0604; found 334.0596.

1-(diphenylphosphoryl)-N-(thiophen-2-yl)formamide 3s



Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 4:1); **3s** was obtained as a white solid, mp 197-199 °C (39.9 mg, 61% yield).

¹**H NMR** (400 MHz, CDCl₃): δ 11.65 (s, 1H), 8.00-7.95 (m, 4H), 7.63-7.59 (m, 2H), 7.53-7.49 (m, 4H), 7.11 (m, 1H), 6.96 (d, *J* = 5.3 Hz, 1H), 6.91-6.88 (m, 1H).

¹³C NMR (101 MHz, CDCl₃): δ 165.4 (d, *J* = 124.5 Hz), 137.8 (d, *J* = 9.3 Hz), 132.9 (d, *J* = 2.5 Hz), 131.8 (d, *J* = 10.1 Hz), 129.0 (d, *J* = 12.6 Hz), 128.7 (d, *J* = 102.5 Hz) 124.3, 118.8, 114.5.

³¹**P NMR** (162 MHz, CDCl₃): δ 16.17.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₇H₁₄NNaO₂SP⁺ 350.0375; found 350.0368.

N-(6-chloropyridin-3-yl)-1-(diphenylphosphoryl)formamide 3t

Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 2:1); **3t** was obtained as a white solid, mp 199-201 °C (35.7 mg, 50% S14

yield).

¹**H NMR** (400 MHz, CDCl₃): δ 10.87 (s, 1H), 8.85 (s, 1H), 8.29 (d, *J* = 8.2 Hz, 1H), 7.92-7.88 (m, 4H), 7.63-7.60 (m, 2H), 7.51-7.49 (m, 4H), 7.28-7.27 (m, 1H), .

¹³C NMR (101 MHz, CDCl₃): δ 169.1 (d, *J* = 126.0 Hz), 147.0, 141.6, 138.4, 133.2 (d, *J* = 2.3 Hz), 131.8 (d, *J* = 9.7 Hz), 130.3, 129.0 (d, *J* = 12.4 Hz), 128.2 (d, *J* = 102.0 Hz), 124.2.

³¹**P NMR** (162 MHz, CDCl₃): δ 16.51.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₀H₁₈NaNO₂P⁺ 336.1148; found 336.1140.

N-cyclobutyl-1-(diphenylphosphoryl)formamide 3u

Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 4:1); **3u** was obtained as a white solid, mp 148-150 °C (38.3 mg, 64% yield).

¹**H NMR** (400 MHz, CDCl₃): δ 8.27 (s, 1H), 7.95-7.90 (m, 4H), 7.58-7.48 (m, 6H), 4.55-4.50 (m, 1H), 2.34-2.32 (m, 2H), 2.21-2.20 (m, 2H), 1.77-1.68 (m, 2H).

¹³C NMR (101 MHz, CDCl₃): δ 168.5 (d, *J* = 119.5 Hz), 132.6 (d, *J* = 2.1 Hz), 131.7 (d, *J* = 9.6 Hz), 129.5 (d, *J* = 99.9 Hz), 128.7 (d, *J* = 12.1 Hz), 44.8 (d, *J* = 4.5 Hz), 30.8, 12.6.

³¹**P NMR** (162 MHz, CDCl₃): δ 14.47.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{19}NO_2P^+$ 300.1148; found 300.1138.

N-cyclopentyl-1-(diphenylphosphoryl)formamide 3v

$$\bigcirc \mathsf{Ph}_{\mathsf{H}} \overset{\mathsf{O}}{\underset{\mathsf{O}}{\overset{\mathsf{P}}}} \mathsf{Ph}_{\mathsf{P}} \mathsf{Ph}_{\mathsf{H}} \\ \mathsf{P} \mathsf{Ph}_{\mathsf{O}} \mathsf{Ph}_$$

Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 4:1); 3v was obtained as a white solid, mp 144-146 °C (44.5 mg, 71% yield).

¹**H NMR** (400 MHz, CDCl₃): δ 7.95-7.90 (m, 4H), 7.73 (s, 1H), 7.60-7.56 (m, 2H),

7.52-7.48 (m, 4H), 4.39-4.30 (m, 1H), 2.05-2.00 (m, 2H), 1.77-1.70 (m, 2H), 1.66-1.49 (m, 4H).

¹³C NMR (101 MHz, CDCl₃): δ 169.5 (d, J = 121.6 Hz), 132.6 (d, J = 2.8 Hz), 131.7 (d, J = 9.6 Hz), 129.4 (d, J = 99.5 Hz), 128.7 (d, J = 12.0 Hz), 51.5 (d, J = 5.0 Hz), 33.0,24.0.

³¹**P NMR** (162 MHz, CDCl₃): δ 14.81.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{20}NaNO_2P^+$ 336.1124; found 336.1132.

N-cyclohexyl-1-(diphenylphosphoryl)formamide 3w



Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 4:1); 3w was obtained as a white solid (47.8 mg, 73% yield).

¹H NMR (400 MHz, CDCl₃): δ 7.95-7.91 (m, 4H), 7.75-7.73 (m, 2H), 7.53-7.48 (m, 4H), 3.96-3.89 (m, 1H), 2.00-1.94 (m, 2H), 1.79-1.71 (m, 2H), 1.66-1.59 (m, 1H), 1.42-1.11 (m, 5H).

¹³C NMR (101 MHz, CDCl₃): δ 168.6 (d, J = 120.6 Hz), 132.6 (d, J = 2.4 Hz), 131.7 (d, J = 9.6 Hz), 129.4 (d, J = 99.8 Hz), 128.7 (d, J = 12.3 Hz), 49.1 (d, J = 4.9 Hz), 32.8,25.3, 24.8.

³¹**P** NMR (162 MHz, CDCl₃): δ 14.94.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for C₁₉H₂₃NaNO₂P⁺ 328.1461; found 328.1453.

N-(cyclopent-3-en-1-yl)-1-(diphenylphosphoryl)formamide 3x

Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 4:1); 3x was obtained as a white solid, mp 142-144 °C (41.1 mg, 66%) yield).

¹H NMR (400 MHz, CDCl₃): δ 7.96-7.91 (m, 4H), 7.60-7.57 (m, 2H), 7.52-7.49 (m, 4H), 5.72-5.66 (m, 2H), 4.71-4.70 (m, 1H), 2.83-2.77 (m, 2H), 2.32 (d, J = 17.3 Hz, 2H).

¹³**C NMR** (101 MHz, CDCl₃): δ 169.1 (d, *J* = 121.0 Hz), 132.6 (d, *J* = 2.1 Hz), 131.7 (d, *J* = 9.7 Hz), 129.3 (d, *J* = 100.1 Hz), 128.7 (d, *J* = 12.1 Hz), 48.9 (d, *J* = 5.0 Hz), 40.1.

³¹**P NMR** (162 MHz, CDCl₃): δ 14.79.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₈H₁₈NaNO₂P⁺ 334.0967; found 334.0960.

1-(diphenylphosphoryl)-N-(2-(furan-2-yl)ethyl)formamide 3y



Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 2:1); **3y** was obtained as a white solid (42.7 mg, 63% yield). **¹H NMR** (400 MHz, CDCl₃): δ 8.02 (s, 1H), 7.91-7.89 (m, 4H), 7.62-7.58 (m, 2H), 7.52-7.49 (m, 4H), 7.31 (d, *J* = 1.0 Hz, 1H), 6.27 (t, *J* = 2.2 Hz, 1H), 6.06 (d, *J* = 3,0 Hz, 1H), 3.71 (t, *J* = 5.7 Hz, 2H), 2.94 (t, *J* = 6.4 Hz, 2H). **¹³C NMR** (101 MHz, CDCl₃): δ 170.0 (d, *J* = 115.5 Hz), 152.1, 141.8, 132.7, 131.8 (d,

J = 2.3 Hz), 129.4 (d, *J* = 99.9 Hz), 128.7 (d, *J* = 9.2 Hz), 110.3, 106.7, 38.2, 28.0.

³¹**P NMR** (162 MHz, CDCl₃): δ 15.41.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₉H₁₈NaNO₃P⁺ 362.0917; found 362.0907.

N-(5-bromopentyl)-1-(diphenylphosphoryl)formamide 3z

Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 1:1); 3z was obtained as a white solid, mp 98-100 °C (49.5 mg, 63% yield).

¹**H NMR** (400 MHz, CDCl₃): δ 8.00-7.83 (m, 4H), 7.60 (t, *J* = 7.5 Hz, 2H), 7.52 (t, *J* = 7.12 Hz, 4H), 3.44-3.37 (m, 4H), 1.92-1.85 (m, 2H), 2.65-1.60 (m, 2H), 1.54-1.46 (m, 2H).

¹³**C NMR** (101 MHz, CDCl₃): δ 169.1 (d, J = 121.0 Hz), 132.6, 131.7 (d, J = 9.7 Hz),

129.3 (d, *J* = 100.1 Hz), 128.7 (d, *J* = 10.5 Hz), 49.4 (d, *J* = 2.8 Hz), 34.2, 34.1, 28.5, 28.4.

³¹**P NMR** (162 MHz, CDCl₃): δ 15.34.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₈H₂₁BrNaNO₂P⁺ 416.0385; found 416.0377.

N-benzyl-1-(diphenylphosphoryl)formamide 3aa

Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 2:1); **3aa** was obtained as a white solid (44.0 mg, 62% yield). ¹**H NMR** (400 MHz, CDCl₃): δ 8.57 (s, 1H), 7.95-7.90 (m, 4H), 7.60 (t, *J* = 7.3 Hz, 2H), 7.51-7.48 (m, 4H), 7.34-7.29 (m, 5H), 4.60 (d, *J* = 4.8 Hz, 2H). ¹³**C NMR** (101 MHz, CDCl₃): δ 169.6 (d, *J* = 122.0 Hz), 137.0, 132.7 (d, *J* = 2.4 Hz), 131.7 (d, *J* = 9.4 Hz), 129.2 (d, *J* = 100.6 Hz), 128.8 128.7 (d, *J* = 11.1 Hz), 128.1, 127.7, 43.7 (d, *J* = 5.1 Hz).

³¹**P NMR** (162 MHz, CDCl₃): δ 15.30.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₀H₁₈NaNO₂P⁺ 358.0967; found 358.0960.

Tert-butyl 3-((diphenylphosphoryl)formamido)propanoate 3ab



Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 2:1); **3ab** was obtained as a white solid, mp 297-299 °C (33.6 mg, 45% yield).

¹H NMR (400 MHz, CDCl₃): δ 8.21 (s, 1H), 7.94-7.89 (m, 4H), 7.57-7.55 (m, 2H), 7.50-7.46 (m, 4H), 3.64 (q, *J* = 6.16 Hz, 2H), 2.52 (d, *J* = 6.5 Hz, 2H), 1.42 (s, 9H),
¹³C NMR (101 MHz, CDCl₃): δ 170.5, 169.8 (d, *J* = 121.2 Hz), 132.6 (d, *J* = 2.7 Hz), 131.7 (d, *J* = 9.6 Hz), 129.2 (d, *J* = 100.2 Hz), 128.7 (d, *J* = 12.3 Hz), 81.4, 35.4 (d, *J* = 5.2 Hz), 35.0, 28.0.

³¹**P NMR** (162 MHz, CDCl₃): δ 16.11.

N-tert-butyl-1-(diphenylphosphoryl)formamide 3ac

$$\searrow \overset{O}{\underset{H}{\overset{}}} \overset{Ph}{\underset{H}{\overset{}}} \overset{Ph}{\underset{H}{\overset{Ph}{\overset{}}} \overset{Ph}{\underset{H}{\overset{Ph}{\underset{H}{\overset{}}} \overset{Ph}{\underset{H}{\overset{Ph}}} \overset{Ph}{\underset{H}{\overset{Ph}{\overset{}}} \overset{Ph}{\underset{H}{\overset{Ph}{\overset{}}} \overset{Ph}{\underset{H}{\overset{Ph}{\overset{}}} \overset{Ph}{\underset{H}{\overset{Ph}}} \overset{Ph}{\underset{H}{\overset{Ph}{\overset{Ph}}} \overset{Ph}{\underset{H}{\overset{Ph}}} \overset{Ph}{\overset{Ph}}} \overset{Ph}{\overset{Ph}}} \overset{Ph}{\overset{Ph}} \overset{Ph}{\overset{Ph}} \overset{Ph}{\overset{Ph}}} \overset{Ph}{\overset{Ph}} \overset{Ph}} \overset{Ph}{\overset{Ph}} \overset{Ph}{\overset{Ph}} \overset{Ph}{\overset{Ph}} \overset{Ph} \overset{Ph}} \overset{Ph} \overset{Ph} \overset{Ph}} \overset{Ph}{\overset{Ph}} \overset{Ph}} \overset{Ph} \overset{Ph} \overset{Ph}$$

Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 3:1); **3ac** was obtained as a white solid (28.9 mg, 48% yield).

¹**H NMR** (400 MHz, CDCl₃): δ 7.93-7.88 (m, 4H), 7.59-7.55 (m, 2H), 7.51-7.45 (m, 4H), 1.4 (s, 9H).

¹³C NMR (101 MHz, CDCl₃): δ 168.3 (d, *J* = 120.1 Hz), 132.5 (d, *J* = 2.9 Hz), 131.6 (d, *J* = 10.3 Hz), 129.5 (d, *J* = 99.1 Hz), 128.7 (d, *J* = 12.0 Hz), 53.4 (d, *J* = 6.9 Hz), 28.6.

³¹**P NMR** (162 MHz, CDCl₃): δ 15.32.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₇H₂₀NaNO₂P⁺ 324.1124; found 324.1116.

N-(((3r,5r,7r)-adamantan-1-yl)methyl)-1-(diphenylphosphoryl)formamide 3ad

Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 4:1); **3ad** was obtained as white solid, mp 168-170 °C (34.6 mg, 44% yield).

¹**H NMR** (400 MHz, CDCl₃): δ 7.94-7.90 (m, 4H), 7.77 (s, 1H), 7.58-7.56 (m, 2H), 7.50-7.47 (m, 4H), 3.08 (d, *J* = 8.3 Hz, 2H), 1.96 (s, 3H), 1.70-1.58 (m, 6H), 1.50 (s, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 169.7 (d, J = 124.2 Hz), 132.6 (d, J = 2.7 Hz), 131.7 (d, J = 9.7 Hz), 129.6 (d, J = 99.9 Hz), 128.6 (d, J = 12.1 Hz), 51.0 (d, J = 5.1 Hz), 40.2, 36.7, 34.0, 28.1.

³¹**P NMR** (162 MHz, CDCl₃): δ 15.83.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{28}NaNO_2P^+$ 416.1750; found 416.1740..

1-(diphenylphosphoryl)-N-undecylformamide 3ae



Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 2:1); **3ae** was obtained as a white solid (45.5 mg, 57% yield).

¹**H NMR** (400 MHz, CDCl₃): δ 7.96-7.91 (m, 4H), 7.60-7.56 (m, 2H), 7.51-7.48 (m, 4H), 3.40 (q, *J* = 6.7 Hz, 2H), 1.62-1.55 (m, 2H), 1.31-1.26 (m, 16H), 0.90 (t, *J* = 7.2 Hz, 3H).

¹³**C NMR** (101 MHz, CDCl₃): δ 169.5 (d, *J* = 123.9 Hz), 132.6, 131.7 (d, *J* = 9.4 Hz), 129.4 (d, *J* = 100.0 Hz), 128.7 (d, *J* = 12.3 Hz), 39.7 (d, *J* = 4.6 Hz), 31.9, 29.6, 29.5, 29.5, 29.5, 29.3, 29.3, 29.2, 26.8, 22.7, 14.1.

³¹**P NMR** (162 MHz, CDCl₃): δ 15.11.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₄H₃₄NaNO₂P⁺ 422.2219; found 422.2208.

(Z)-1-(diphenylphosphoryl)-N-(heptadec-8-en-1-yl)formamide 3af



Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 4:1); **3af** was obtained as a white solid (43.3 mg, 45% yield).

¹**H NMR** (400 MHz, CDCl₃): δ 7.97-7.92 (m, 4H), 7.73 (s, 1H), 7.62-7.58 (m, 2H), 7.54-7.50 (m, 4H), 5.42-5.32 (m, 2H), 3.41 (q, *J* = 6.8 Hz, 2H), 2.04-2.00 (m, 4H), 1.62-1.56 (m, 2H), 1.35-1.26 (m, 20H), 0.91 (t, *J* = 6.2 Hz, 3H).

¹³**C NMR** (101 MHz, CDCl₃): δ 169.5 (d, *J* = 123.9 Hz), 132.6, 131.7 (d, *J* = 9.4 Hz), 129.4 (d, *J* = 100.0 Hz), 128.7 (d, *J* = 12.3 Hz), 39.7, 31.9, 29.8, 29.7, 29.6, 29.5, 29.3, 29.3, 29.1, 29.0, 27.2, 27.1, 26.8, 22.7, 14.1.

³¹**P** NMR (162 MHz, CDCl₃): δ 15.04.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₀H₄₄NaNO₂P⁺ 504.3002; found 504.2992.

(S)-N-(1-(1,3-dioxoisoindolin-2-yl)-2-phenylethyl)-1-(diphenylphosphoryl)forma mide 3ag



Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 1:1); **3ag** was obtained as a white solid, mp 183-185 °C (55.3 mg, 56% yield).

¹**H NMR** (400 MHz, CDCl₃): δ 8.56 (d, J = 9.2 Hz, 1H), 7.90-7.86 (m, 2H), 7.81-7.78 (m, 2H), 7.71-7.66 (m, 4H), 7.59-7.50 (m, 2H), 7.47-7.39 (m, 4H), 7.30-7.26 (m, 2H), 7.23-7.13 (m, 3H), 6.57 (q, J = 8.4 Hz, 1H), 3.46 (d, J = 8.1 Hz, 2H). ¹³**C NMR** (101 MHz, CDCl₃): δ 169.5 (d, J = 120.0 Hz), 167.1, 134.9, 134.3, 132.7 (dd, J = 1.7, 2.7 Hz), 132.0 (d, J = 9.6 Hz), 131.6 (d, J = 10.0 Hz), 131.4, 129.3, 129.1 (d, J = 100.5 Hz), 128.8, 128.7 (d, J = 5.8 Hz), 128.2 (d, J = 102.6 Hz), 127.3, 123.7, 56.5 (d, J = 5.8 Hz), 39.1.

³¹**P NMR** (162 MHz, CDCl₃): δ 15.56.

HRMS (ESI) m/z: [M+Na⁺] Calcd for C₂₉H₂₃NaN₂O₄P⁺ 517.1288; found 517.1280.

1-(diphenylphosphoryl)-N-((11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)methyl)f ormamide 3ah



Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 2:1); **3ah** was obtained as a white solid, mp 210-212 °C (29.8 mg, 32% yield).

¹**H NMR** (400 MHz, DMSO): δ 9.92 (s, 1H), 8.07 (d, *J* = 2.2 Hz, 1H), 7.84-7.80 (m, 5H), 7.71-7.67 (m, 3H), 7.62-7.57 (m, 6H), 7.52-7.48 (m, 1H), 7.08 (d, *J* = 8.5 Hz, 1H), 5.3 (s, 2H), 4.43 (d, *J* = 6.2 Hz, 2H).

¹³**C NMR** (101 MHz, DMSO): δ 190.6, 169.7 (d, *J* = 121.0 Hz), 160.5, 140.5, 136.4, 135.6, 133.6, 133.1 (d, *J* = 2.3 Hz), 132.70, 131.7 (d, *J* = 9.7 Hz), 130.6, 130.5 (d, *J* = 99.0 Hz), 129.7, 129.3 (d, *J* = 11.8 Hz), 129.3, 128.8, 125.0, 121.3, 73.2, 42.2 (d, *J* = 6.5 Hz).

³¹**P NMR** (162 MHz, DMSO): δ 13.76.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₈H₂₂NNaO₄P⁺ 490.1179; found 490.1171.

N-(2-(4,5-diphenyloxazol-2-yl)ethyl)-1-(diphenylphosphoryl)formamide 3ai



Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 3:1); **3ai** was obtained as a white solid (42.3 mg, 43% yield).

¹**H NMR** (400 MHz, CDCl₃): δ 8.55 (s, 1H), 7.96-7.91 (m, 4H), 7.67 (d, *J* = 7.9 Hz, 2H), 7.60-7.54 (m, 4H), 7.48-7.45 (m,4H), 7.41-7.36 (m, 6H), 3.96 (q, *J* = 6.37 Hz, 2H), 3.18 (t, *J* = 6.4 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃): δ 169.9 (d, J = 120.1 Hz), 160.5, 145.8, 135.2, 132.7 (d, J = 2.7 Hz), 132.3, 131.8 (d, J = 9.7 Hz), 129.0 (d, J = 102.2 Hz), 128.8, 128.7 (d, J = 10.4 Hz), 128.7, 128.6, 128.1, 128.0, 127.4, 126.6. 36.7 (d, J = 5.4 Hz), 28.1.
³¹P NMR (162 MHz, CDCl₃): δ 15.64.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{25}N_2NaO_3P^+$ 515.1495; found 515.1486.

1-(diphenylphosphoryl)-N-(1-(4-isobutylphenyl)ethyl)formamide 3aj



Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 3:1); **3aj** was obtained as a white solid, mp 141-143 °C (41.3 mg, 51% yield).

¹**H NMR** (400 MHz, CDCl₃): δ 8.40 (d, *J* = 9.0 Hz, 1H), 9.00-7.95 (m, 2H), 7.86-7.80 (m, 2H), 7.60-7.50 (m, 4H), 7.44-7.41 (m, 2H), 7.27 (d, *J* = 7.6 Hz, 2H), 7.10 (d, *J* = 7.7 Hz, 2H), 5.29-5.22 (m, 1H), 2.47 (d, *J* = 7.1 Hz, 2H), 1.89-1.83 (m, 1H), 1.59 (d, *J* = 6.9 Hz, 3H), 0.92 (d, *J* = 6.9 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 168.7 (d, J = 120.6 Hz), 141.1, 139.3, 135.6 (dd, J =

2.0, 7.2 Hz), 131.8 (d, *J* = 9.5 Hz), 131.7 (d, *J* = 9.7 Hz), 129.6 (d, *J* = 99.8 Hz), 129.4, 129.3 (d, *J* = 100.4 Hz), 128.7 (d, *J* = 12.0 Hz), 126.1, 49.3 (d, *J* = 5.0 Hz), 45.1, 30.2, 22.4 (d, *J* = 2.6 Hz), 21.6.

³¹**P NMR** (162 MHz, CDCl₃): δ 15.06.

HRMS (ESI) m/z: [M+Na⁺] Calcd for C₂₅H₂₈NaNO₂P⁺ 444.1489; found 444.1481.

(Z)-1-(diphenylphosphoryl)-N-((5-fluoro-2-methyl-1-(4-(methylsulfinyl)benzylide ne)-1H-inden-3-yl)methyl)formamide 3ak



Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 1:2); **3ak** was obtained as a yellow solid, mp 239-241 °C (47.3 mg, 43% yield).

¹**H NMR** (400 MHz, CDCl₃): δ 8.40 (s, 1H), 7.87-7.83 (m, 4H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.62-7.55 (m, 4H), 7.47-7.43 (m, 4H), 7.15-7.12 (m, 2H), 6.92 (dd, *J* = 2.3, 8.9 Hz, 1H), 6.55 (td, *J* = 2.3, 8.7 Hz, 1H), 4.56 (d, *J* = 5.7 Hz, 2H), 2.82 (s, 3H), 2.19 (s, 3H).

¹³**C NMR** (101 MHz, CDCl₃): δ 169.8 (d, *J* = 120.2 Hz), 163.3 (d, *J* = 246.9 Hz), 145.7 (d, *J* = 8.8 Hz), 145.6, 141.7, 139.5, 139.0, 134.1 (d, *J* = 1.8 Hz), 132.7 (d, *J* = 2.5 Hz), 131.7 (d, *J* = 9.7 Hz), 130.5 (d, *J* = 9.6 Hz), 130.2, 129.5 (d, *J* = 2.6 Hz), 129.0, 128.9 (d, *J* = 100.7 Hz), 128.7 (d, *J* = 12.3 Hz), 123.9, 123.7, 111.0 (d, *J* = 22.5 Hz), 106.4 (d, *J* = 24.8 Hz), 43.9, 34.0 (d, *J* = 5.4 Hz), 10.4.

³¹**P NMR** (162 MHz, CDCl₃): δ 14.84.

HRMS (ESI) m/z: [M+Na⁺] Calcd for C₃₂H₂₇FNNaO₃PS⁺ 578.1326; found 578.1317.

1-(bis(4-methoxyphenyl)phosphoryl)-N-phenylformamide 3al



Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 6:1); **3al** was obtained as a white solid, mp 158-161 °C (62.5 mg, 82% yield).

¹**H NMR** (400 MHz, CDCl₃): δ 9.43 (s, 1H), 7.88 (t, *J* = 9.6 Hz, 4H), 7.72 (d, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 6.3 Hz, 4H), 3.8 (s, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 168.7 (d, *J* = 124.0 Hz), 163.3 (d, *J* = 2.9 Hz), 136.8 (d, *J* = 9.4 Hz), 133.8 (d, *J* = 12.0 Hz), 129.2, 125.5, 119.9 (d, *J* = 107.3 Hz), 119.8, 114.4 (d, *J* = 13.4 Hz), 55.4.

³¹**P NMR** (162 MHz, CDCl₃): δ 16.96.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₁H₂₀NaNO₄P⁺ 420.0762; found 420.0752.

1-(bis(4-(tert-butyl)phenyl)phosphoryl)-N-phenylformamide 3am



Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 4:1); **3am** was obtained as a white solid, mp 230-232 °C (53.7 mg, 62% yield).

¹**H NMR** (400 MHz, CDCl₃): δ 9.55 (s, 1H), 7.95-7.90 (m, 4H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.55 (dd, *J* = 6.7, 10.7 Hz, 4H), 7.37 (t, *J* = 7.9 Hz, 2H), 7.19 (t, *J* = 6.6 Hz, 1H), 1.36 (s, 18H).

¹³**C NMR** (101 MHz, CDCl₃): δ 168.6 (d, *J* = 123.0 Hz), 156.4 (d, *J* = 2.5 Hz), 136.9 (d, *J* = 9.4 Hz), 131.8 (d, *J* = 9.5 Hz), 129.1, 125.8 (d, *J* = 12.4 Hz), 125.5 (d, *J* = 104.4 Hz), 125.5, 119.9, 35.1, 31.1.

³¹**P NMR** (162 MHz, CDCl₃): δ 16.17.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₇H₃₂NaNO₂P⁺ 472.1802; found 472.1794.

1-(bis(4-chlorophenyl)phosphoryl)-N-phenylformamide 3an



Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 2:1); **3an** was obtained as a white solid (57.5 mg, 74% yield). ¹H NMR (400 MHz, CDCl₃): δ 9.78 (s, 1H), 7.92-7.88 (m, 4H), 7.73 (d, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 7.6 Hz, 4H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃): δ 167.3 (d, *J* = 124.9 Hz), 139.9 (d, *J* = 3.0 Hz), 136.6 (d, *J* = 9.7 Hz), 133.1 (d, *J* = 10.6 Hz), 129.4, 127.1 (d, *J* = 101.6 Hz), 125.9, 120.1. ³¹P NMR (162 MHz, CDCl₃): δ 13.82.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{14}Cl_2NaNO_2P^+$ 390.0212; found 390.0204.

1-(di-p-tolylphosphoryl)-N-phenylformamide 3ao



Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 3:1); **3ao** was obtained as a white solid (53.7 mg, 77% yield).

¹**H NMR** (400 MHz, CDCl₃): δ 9.45 (s, 1H), 7.88-7.82 (m, 4H), 7.70 (d, *J* = 7.8 Hz, 2H), 7.38-7.33 (m, 6H), 7.19 (t, *J* = 7.4 Hz, 1H). 2.43 (s, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 168.7 (d, J = 124.0 Hz), 163.3 (d, J = 2.9 Hz), 136.8 (d, J = 9.4 Hz), 133.8 (d, J = 12.0 Hz), 129.2, 125.5, 119.9 (d, J = 107.3 Hz), 119.8, 114.4 (d, J = 13.4 Hz), 55.4.

³¹**P NMR** (162 MHz, CDCl₃): δ 16.96.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₂₁H₂₀NaNO₂P⁺ 340.2247; found 340.2250.

1-(butyl(phenyl)phosphoryl)-N-phenylformamide 3ap



Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 2:1); **3ap** was obtained as a white solid (24.6 mg, 41% yield). ¹H NMR (400 MHz, CDCl₃): δ 9.55 (s, 1H), 8.00-7.95 (m, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.61-7.57 (m, 1H), 7.53-7.50 (m, 2H), 7.35 (t, *J* = 7.9 Hz, 2H), 7.18 (t, *J* = 7.9 Hz, 1H), 2.45-2.21 (m, 2H), 1.69-1.61 (m, 2H), 1.51-1.44 (m, 2H), 0.92 (t, *J* = 6.8 Hz, 3H) ¹³C NMR (101 MHz, CDCl₃): δ 169.2 (d, *J* = 116.3 Hz), 136.8 (d, *J* = 8.7 Hz), 132.7 (d, *J* = 2.7 Hz), 131.0 (d, *J* = 7.9 Hz), 129.1, 125.5, 123.4 (d, *J* = 106.8 Hz), 120.0, 27.3 (d, *J* = 70.0 Hz), 23.8 (d, *J* = 12.5 Hz), 23.3 (d, *J* = 4.0 Hz), 13.6.

³¹**P NMR** (162 MHz, CDCl₃): δ 26.25.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{20}NaNO_2P^+$ 324.1124; found 324.1124.

1-(dibutylphosphoryl)-N-phenylformamide 3aq



Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 2:1); **3aq** was obtained as a white solid (25.8 mg, 46% yield).

¹**H NMR** (400 MHz, CDCl₃): δ 9.23 (s, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 2.06-1.95 (m, 4H), 1.76-1.78 (m, 2H), 1.63-1.55 (m, 2H), 1.50-1.41 (m, 4H), 0.95 (t, *J* = 7.3 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 169.5 (d, J = 109.3 Hz), 136.8 (d, J = 8.7 Hz), 129.2, 125.6, 119.8, 26.5 (d, J = 62.7 Hz), 23.9 (d, J = 14.6 Hz), 23.5 (d, J = 4.4 Hz), 13.5.
³¹P NMR (162 MHz, CDCl₃): δ 41.66.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₅H₂₄NaNO₂P⁺ 304.1437; found 304.1430.

Diethyl (phenylcarbamoyl)phosphonate 3ar

Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 2:1); **3ar** was obtained as a colorless oil (41.1 mg, 80% yield).

¹**H NMR** (400 MHz, CDCl₃): δ 9.11 (s, 1H), 7.70 (d, J = 8.0 Hz, 2H), 7.40-7.35 (m,

2H), 7.21 (t, *J* = 7.5 Hz, 1H), 4.37-4.26 (m, 4H), 1.43 (t, *J* = 7.0 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃): δ 164.1 (d, *J* = 226.4 Hz), 136.6 (d, *J* = 13.3 Hz), 129.2,

125.6, 120.2, 64.8 (d, *J* = 6.3 Hz), 16.3 (d, *J* = 5.8 Hz).

³¹**P NMR** (162 MHz, CDCl₃): δ -1.72.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₁H₁₆NNaO₄P⁺ 280.0709; found 280.0711.

Ethyl phenyl(phenylcarbamoyl)phosphinate 3as

Following general procedure, purification by flash column chromatography (petroleum ether/EtOAc = 2:1); **3as** was obtained as a yellow oil (45.1 mg, 78% yield).

¹**H NMR** (400 MHz, CDCl₃): δ 9.45 (s, 1H), 8.06-8.02 (m, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.67-7.63 (m, 1H), 7.56-7.51 (m, 2H), 7.37-7.35 (m, 2H), 7.20-7.16 (m, 1H), 4.44-4.23 (m, 2H), 1.47 (t, *J* = 7.0 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 166.4 (d, *J* = 160.0 Hz), 136.8 (d, *J* = 10.7 Hz), 133.6 (d, *J* = 2.4 Hz), 132.6 (d, *J* = 10.3 Hz), 129.1, 128.7 (d, *J* = 13.5 Hz), 126.7 (d, *J* = 137.7 Hz), 125.6, 120.0, 63.2 (d, *J* = 6.6 Hz), 16.4 (d, *J* = 6.4 Hz).

³¹**P NMR** (162 MHz, CDCl₃): δ 20.32.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{16}NNaO_3P^+$ 312.0760; found 312.0758.

N-phenylpentanamide 4

Ph

Following **P1**, purification by flash column chromatography (petroleum ether/EtOAc = 30:1); **4** was obtained as a colorless oil (28.6 mg, 56% yield).

¹**H NMR** (400 MHz, CDCl₃): δ 7.96 (s, 1H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.10 (t, *J* = 7.3 Hz, 1H), 2.36 (t, *J* = 7.1 Hz, 2H), 1.71 (dt, *J* = 15.1, 7.4 Hz, 2H), 1.43-1.35 (m, 2H), 0.94 (t, *J* = 9.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃): δ 172.1, 138.1, 128.9, 124.2, 120.1, 37.4, 27.8, 22.4, 13.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{15}ON^+$ 163.1117; Found 163.1116.

1-(diphenylphosphorothioyl)-N-phenylmethanethioamide 5

$$Ph \underbrace{N}_{H} \underbrace{Ph}_{H} \underbrace{Ph}_{S}$$

Following **P1**, purification by flash column chromatography (petroleum ether/EtOAc = 20:1); **5** was obtained as a yellow solid. (28.6 mg, 78% yield).

¹**H NMR** (400 MHz, CDCl₃): δ 12.0 (d, *J* = 8.9 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 2H), 8.10-8.05 (m, 4H), 7.63-7.58 (m, 2H), 7.54-7.46 (m, 6H), 7.35 (t, *J* = 7.4 Hz, 1H).

¹³**C NMR** (101 MHz, CDCl₃): δ 189.0 (d, *J* = 67.1 Hz), 138.5 (d, *J* = 13.2 Hz), 133.1 (d, *J* = 10.3 Hz), 132.3 (d, *J* = 3.3 Hz), 131.0 (d, *J* = 90.0 Hz), 129.1, 128.4 (d, *J* = 13.3 Hz), 127.6, 121.2.

³¹**P NMR** (162 MHz, CDCl₃): δ 45.75.

HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₁₉H₁₆NNaPS₂⁺ 376.0354; found 376.0346.

diphenylurea 6



Purification by flash column chromatography (petroleum ether/EtOAc = 1:1); **6** was obtained as a white solid (28.6 mg, 46% yield).

¹**H NMR** (400 MHz, CDCl₃): δ 8.62 (s, 2H), 7.41 (d, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.1 Hz, 4H), 6.92 (t, *J* = 7.4 Hz, 4H).

¹³C NMR (101 MHz, CDCl₃): δ 157.8, 144.9, 134.0, 127.0, 123.4.

HRMS (ESI) m/z: $[M+K]^+$ Calcd for $C_{13}H_{12}N_2KO^+$ 251.0581; found 251.0573.

7. References

- 1 (a) J. Park, A. U. Krishnapriya, Y. Park, M. Kim, T. W. Reidl, R. Kuniyil and J. Son, *Adv. Synth. Catal.*, 2023, **365**, 4495-4501; (b) J.-J. Tang, N. Yan, Y. Zhang, Y. Wang, M. Bao and X. Yu, *Green Chem.*, 2023, **25**, 7529-7533.
- 2 G. Lu, X. Huangfu, Z. a. Wu, G. Tang and Y. Zhao, *Adv. Synth. Catal.*, 2019, **361**, 4961-4965.

8. ¹H, ¹³C, ³¹P NMR spectra of compounds 3 and 4-6



¹³C NMR (101 MHz, CDCl₃) spectrum of compound **3a**









 ^1H NMR (400 MHz, CDCl₃) spectrum of compound 3d



³¹P NMR (162 MHz, CDCl₃) spectrum of compound **3d**



¹³C NMR (101 MHz, DMSO) spectrum of compound **3e**




³¹P NMR (162MHz, DMSO) spectrum of compound **3f**











 ^{13}C NMR (101 MHz, CDCl₃) spectrum of compound **3i**





 ^{31}P NMR (162 MHz, CDCl₃) spectrum of compound 3j









 ^{31}P NMR (162 MHz, CDCl₃) spectrum of compound **31**





 ^1H NMR (500 MHz, CDCl₃) spectrum of compound 3n











 ^{31}P NMR (162 MHz, CDCl₃) spectrum of compound $\boldsymbol{3p}$



 ^{13}C NMR (101 MHz, CDCl₃) spectrum of compound 3q



 ^1H NMR (400 MHz, CDCl₃) spectrum of compound 3r



³¹P NMR (162 MHz, CDCl₃) spectrum of compound **3r**



 ^{13}C NMR (101 MHz, CDCl₃) spectrum of compound 3s









¹³C NMR (101 MHz, CDCl₃) spectrum of compound **3u**



 ^1H NMR (400 MHz, CDCl₃) spectrum of compound 3v



 ^{31}P NMR (162 MHz, CDCl₃) spectrum of compound 3v







 ^{13}C NMR (101 MHz, CDCl₃) spectrum of compound 3w









 ^{13}C NMR (101 MHz, CDCl₃) spectrum of compound 3y



 ^1H NMR (400 MHz, CDCl₃) spectrum of compound 3z



 ^{31}P NMR (162 MHz, CDCl₃) spectrum of compound $\boldsymbol{3z}$











S72


¹H NMR (400 MHz, CDCl₃) spectrum of compound **3ad**



³¹P NMR (162 MHz, CDCl₃) spectrum of compound **3ad**



¹³C NMR (101 MHz, CDCl₃) spectrum of compound **3ae**



¹H NMR (400 MHz, CDCl₃) spectrum of compound **3af**



³¹P NMR (162 MHz, CDCl₃) spectrum of compound **3af**











¹H NMR (400 MHz, DMSO) spectrum of compound **3ah**



³¹P NMR (162 MHz, DMSO) spectrum of compound **3ah**





S82









¹H NMR (400 MHz, CDCl₃) spectrum of compound **3al**





¹³C NMR (101 MHz, CDCl₃) spectrum of compound **3am**



¹H NMR (400 MHz, CDCl₃) spectrum of compound **3an**





S90





S92



S93



¹H NMR (400 MHz, CDCl₃) spectrum of compound 3ar



 ^{31}P NMR (162 MHz, CDCl₃) spectrum of compound **3ar**







S96









