Electronic Supplementary Information (ESI)

Tunable Synthesis of Chalcophosphinic Amides and Tertiary Phosphinates Using *tert*-Butyl N, N-Dialkylperoxyamidate

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1. General information

Reactions were monitored by using thin-layer chromatography (TLC) on commercial silica gel plates (GF254). Visualization of the developed plates was performed under UV lights (254 nm). Flash column chromatography was performed on silica gel (200-300 mesh). ¹H, ¹³C and ³¹P NMR spectra were recorded on a Bruker AV300, 400 and 500 spectrometer. Chemical shifts (δ) were reported in ppm referenced to the CDCl₃ residual peak (δ 7.26) or the DMSO-d₆ residual peak (δ 2.50) for ¹H NMR. Chemical shifts of ¹³C NMR were reported relative to CDCl₃ (δ 77.0) or D₆-DMSO (δ 39.5). Chemical shifts of ³¹P NMR were reported relative to 85% H₃PO₄ (δ = 0). The following abbreviations were used to describe peak splitting patterns when appropriate: br s = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constant, *J*, was reported in Hertz unit (Hz). Melting points (mp) were taken on a MEL-TEMP® apparatus and were uncorrected. High resolution mass spectra (HRMS) were obtained on an ESI-LC-MS/MS spectrometer.

2. General procedure and product characterization

2.1 General procedure

Procedure A: Typical procedure for the synthesis of chalcophosphinic amides **3**.



A 15 mL schlenk tube was charged with a mixture of **1** (0.2 mmol), **2** (0.6 mmol), catalyst (0.04 mmol) in DCM (1.0 mL) and was stirred at 80 °C for 3 h. After the reaction was complete (as determined by TLC analysis), the reaction was cooled to room temperature and EtOAc (20 mL) was added to the solution and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (ethanol/hexane = 1:10) to afford the targeted products **3**.

Procedure B: Typical procedure for the synthesis of phosphinates 4.



A 15 mL schlenk tube was charged with a mixture of **1** (0.2 mmol), **2** (0.6 mmol), catalyst (0.04 mmol) in THF (1.0 mL) and was stirred at 80 °C for 5 h. After the reaction was complete (as determined by TLC analysis), the reaction was cooled to room temperature and EtOAc (20 mL) was added to the solution and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (EtOAc/hexane = 1:2) to afford the targeted products **4**.

Procedure C: Gram-scale synthesis of phosphinates 4a.

A 100 mL schlenk tube was charged with a mixture of **1a** (5.0 mmol), **2a** (15.0 mmol), catalyst (1.0 mmol) in THF (20.0 mL) and was stirred at 80 °C for 5 h. After the reaction was complete (as determined by TLC analysis), the reaction was cooled to room temperature and EtOAc (100 mL) was added to the solution and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (EtOAc/hexane = 1:2) to afford the targeted products **4a** in 78% yield.



2.2 Product Characterization

N,N-dimethyl-1,1-diphenylphosphanamine (3a)¹



Following procedure A, which purified using mixture of ethanol/hexane (1:10) as

eluent, obtained (39.2 mg, 80% yield) as a white solid; Mp 73-74 °C. ¹H NMR (300 MHz, DMSO): δ 7.82-7.75 (m, 4H), 7.60-7.48 (m, 6H), 2.55 (s, 3H), 2.52 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 132.5, 132.4, 132.3, 131.8, 131.7, 131.2, 128.6, 128.5, 37.2, 37.1; ³¹P NMR (162 MHz, CDCl₃): δ 31.40; HRMS (ESI): Exact mass calcd for C₁₄H₁₆NOP [M+Na]⁺: 268.0682; Found: 268.0683.

N,N-dimethyl-P-(m-tolyl)-P-(p-tolyl)phosphinic amide (3b)



Following procedure A, which purified using mixture of ethanol/hexane (1:10) as eluent, obtained (44.8 mg, 82% yield) as a yellow oil. ¹H NMR (500 MHz, CDCl₃): δ 7.73 (dd, *J* = 11.5, 8.0, 4H), 7.27-7.24 (m, 4H), 2.65 (s, 3H), 2.63 (s, 3H), 2.37 (s, 6H); ¹³C NMR (125 MHz, CDCl₃): δ 137.9, 137.8, 135.1, 134.0, 133.2, 128.9, 128.8, 31.0, 21.3; ³¹P NMR (202 MHz, CDCl₃): δ 27.18; HRMS (ESI): Exact mass calcd for C₁₆H₂₀NOP [M+H]⁺: 274.1355; Found: 274.1356.

P,P-bis(4-(tert-butyl)phenyl)-N,N-dimethylphosphinic amide (3c)



Following procedure A, which purified using mixture of ethanol/hexane (1:10) as eluent, obtained (60.8 mg, 85% yield) as a white solid; Mp 132-134 °C. White solid. ¹H NMR (300 MHz, CDCl₃): δ 7.80-7.75 (m, 4H), 7.47-7.44 (m, 4H), 2.67 (s, 3H), 2.64 (s, 3H), 1.31 (s, 18H); ¹³C NMR (100 MHz, CDCl₃): δ 155.0, 132.3, 132.2, 129.4, 128.1, 125.6, 125.4, 37.2, 37.1, 34.9, 31.1; ³¹P NMR (162 MHz, CDCl₃): δ 31.56; HRMS (ESI): Exact mass calcd for C₂₂H₃₂NOP [M+H]⁺: 358.2294; Found: 358.2293.

P,P-bis(4-fluorophenyl)-N,N-dimethylphosphinic amide (3d)



Following procedure A, which purified using mixture of ethanol/hexane (1:10) as eluent, obtained (46.1 mg, 82% yield) as a yellow solid; Mp 88-89 °C. ¹H NMR (300 MHz, DMSO): δ 7.88-7.80 (m, 4H), 7.40-7.33 (m, 4H), 2.54 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 165.1 (d, ¹*J*_{CF} = 251.8 Hz), 134.8 (dd, ³*J*_{CF} = 10.3 Hz, ³*J*_{CF} = 8.9 Hz), 127.0, 116.0 (dd, ²*J*_{CF} = 21.1 Hz, ²*J*_{CF} = 13.6 Hz), 37.1; ³¹P NMR (162 MHz, CDCl₃): δ 29.53; ¹⁹F NMR (376 MHz, CDCl₃) δ -107.03; HRMS (ESI): Exact mass calcd for C₁₄H₁₄F₂NOP [M+H]⁺: 282.0854; Found: 282.0854.

P,P-bis(4-chlorophenyl)-N,N-dimethylphosphinic amide (3e)



Following procedure A, which purified using mixture of ethanol/hexane (1:10) as eluent, obtained (47.1 mg, 75% yield) as a yellow oil. ¹H NMR (300 MHz, DMSO): δ 7.82-7.75 (m, 4H), 7.60 (dd, *J* = 8.7 Hz, 2.4 Hz, 4H), 2.55 (s, 3H), 2.52 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 138.6, 133.8, 133.7, 130.6, 129.3, 129.2, 129.0, 37.1; ³¹P NMR (162 MHz, CDCl₃): δ 29.60; HRMS (ESI): Exact mass calcd for C₁₄H₁₄Cl₂NOP [M+H]⁺: 314.0263; Found: 314.0266.

P,P-bis(4-methoxyphenyl)-N,N-dimethylphosphinic amide (3f)



Following procedure A, which purified using mixture of ethanol/hexane (1:10) as eluent, obtained (47.0 mg, 77% yield) as a yellow oil. ¹H NMR (300 MHz, CDCl₃): δ 7.78-7.71 (m, 4H), 6.94 (d, *J* = 6.6 Hz, 4H), 3.81 (s, 6H), 2.64 (s, 3H), 2.61 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 162.3, 162.2, 134.1, 134.0, 132.9, 132.8, 124.0, 122.7, 114.2, 114.0, 113.5, 113.4, 55.3, 55.1, 37.1, 37.0; ³¹P NMR (162 MHz, CDCl₃): δ

31.60; HRMS (ESI): Exact mass calcd for $C_{16}H_{20}NO_3P [M+H]^+$: 306.1254; Found: 306.1259.

N,N-dimethyl-P,P-di-m-tolylphosphinic amide (3g)



Following procedure A, which purified using mixture of ethanol/hexane (1:10) as eluent, obtained (41.5 mg, 76% yield) as a white solid; Mp 113-114 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.72 (d, *J* = 12.3 Hz, 2H), 7.62 (t, *J* = 6.9 Hz, 2H), 7.37-7.31 (m, 4H), 2.68 (s, 3H), 2.65 (s, 3H), 2.39 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 138.5, 138.4, 133.0, 132.9, 132.5, 132.3, 131.1, 129.3, 129.2, 128.5, 128.3, 37.2, 21.4; ³¹P NMR (162 MHz, CDCl₃): δ 31.88; HRMS (ESI): Exact mass calcd for C₁₆H₂₀NOP [M+H]⁺: 274.1355; Found: 274.1358.

N,N-dimethyl-P,P-di-o-tolylphosphinic amide (3h)



Following procedure A, which purified using mixture of ethanol/hexane (1:10) as eluent, obtained (38.8 mg, 71% yield) as a white solid; Mp 110-112 °C. ¹H NMR (300 MHz, DMSO): δ 7.50-7.45 (m, 2H), 7.37-7.19 (m, 6H), 2.65 (s, 3H), 2.61 (s, 3H), 2.43 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 143.1, 143.0, 132.7, 132.6, 131.9, 131.8, 131.7, 131.4, 131.3, 130.1, 125.4, 125.3, 36.9, 36.8, 21.5, 21.4; ³¹P NMR (162 MHz, CDCl₃): δ 37.00; HRMS (ESI): Exact mass calcd for C₁₆H₂₀NOP [M+H]⁺: 274.1355; Found: 274.1351.

P,P-bis(3,5-dimethylphenyl)-N,N-dimethylphosphinic amide (3i)



Following procedure A, which purified using mixture of ethanol/hexane (1:10) as eluent, obtained (42.2 mg, 70% yield) as a white solid; Mp 117-118 °C. ¹H NMR (300

MHz, CDCl₃): δ 7.47 (s, 2H), 7.43 (s, 2H), 7.08 (s, 2H), 2.65 (s, 3H), 2.61 (s, 3H), 2.31 (s, 12H); ¹³C NMR (100 MHz, CDCl₃): δ 138.2, 138.1, 133.4, 132.3, 131.0, 129.9, 37.2, 21.3; ³¹P NMR (162 MHz, CDCl₃): δ 32.34; HRMS (ESI): Exact mass calcd for [M+H]⁺: 302.1668; Found: 302.1662.

N,N-dimethyl-P,P-di(naphthalen-2-yl)phosphinic amide (3j)



Following procedure A, which purified using mixture of ethanol/hexane (1:10) as eluent, obtained (49.7 mg, 72% yield) as a yellow oil. ¹H NMR (300 MHz, CDCl₃): δ 8.58 (d, *J* = 13.5 Hz, 2H), 7.96-7.84 (m, 8H), 7.59-7.53 (m, 4H), 2.78 (s, 3H), 2.75 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 134.8, 134.1, 132.7, 131.8, 129.6, 129.0, 128.8, 128.5, 128.4, 128.1, 127.7, 127.0, 126.9, 126.8, 126.2, 37.3, 37.2, 34.6; ³¹P NMR (162 MHz, CDCl₃): δ 31.34; HRMS (ESI): Exact mass calcd for C₂₂H₂₀NOP [M+H]⁺: 346.1355; Found: 346.1354.

N,N-dimethyl-P-phenyl-P-(p-tolyl)phosphinic amide (3k)



Following procedure A, which purified using mixture of ethanol/hexane (1:10) as eluent, obtained (26.4 mg, 51% yield) as a yellow oil. ¹H NMR (300 MHz, CDCl₃): δ 7.87-7.80 (m, 2H), 7.73 (dd, J = 11.7 Hz, 8.1 Hz, 2H), 7.47-7.42 (m, 3H), 7.26-7.23 (m, 2H), 2.66 (s, 3H), 2.62 (s, 3H), 2.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 142.3, 142.2, 132.7, 132.4, 132.3, 132.2, 131.7, 131.6, 131.4, 129.4, 129.3, 129.0, 128.6, 128.5, 127.7, 37.1, 21.6; ³¹P NMR (162 MHz, CDCl₃): δ 31.81; HRMS (ESI): Exact mass calcd for C₁₅H₁₈NOP [M+H]⁺: 260.1199; Found: 260.1191.

P-(4-chlorophenyl)-N,N-dimethyl-P-phenylphosphinic amide (3l)



Following procedure A, which purified using mixture of ethanol/hexane (1:10) as eluent, obtained (29.6 mg, 53% yield) as a yellow oil. ¹H NMR (300 MHz, CDCl₃): δ 7.86-7.76 (m, 4H), 7.51-7.41 (m, 5H), 2.67 (s, 3H), 2.63 (s, 3H) ; ¹³C NMR (100 MHz, CDCl₃): δ 138.4, 133.8, 133.7, 132.3, 132.2, 132.0, 131.1, 130.7, 129.8, 129.0, 128.9, 128.8, 128.7, 37.1; ³¹P NMR (162 MHz, CDCl₃): δ 30.56; HRMS (ESI): Exact mass calcd for C₁₄H₁₅CINOP [M+H]⁺: 280.0653; Found: 280.0652.

N-ethyl-N-methyl-P,P-diphenylphosphinic amide (30)



Following procedure A, which purified using mixture of ethanol/hexane (1:10) as eluent, obtained (42.0 mg, 81% yield) as a white solid; Mp 93-94 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.82-7.75 (m, 4H), 7.57-7.48 (m, 6H), 2.90-2.85 (m, 2H), 2.54 (s, 3H), 1.06 (t, *J* =6.9 Hz, 3H) ; ¹³C NMR (100 MHz, CDCl₃): δ 132.8, 132.4, 132.3, 131.7, 131.5, 128.6, 128.5, 43.9, 43.8, 33.3, 33.2, 13.6; ³¹P NMR (162 MHz, CDCl₃): δ 31.23; HRMS (ESI): Exact mass calcd for C₁₅H₁₈NOP [M+Na]⁺: 282.1018; Found: 282.1017.

diphenyl(pyrrolidin-1-yl)phosphine oxide (3p)



Following procedure A, which purified using mixture of ethanol/hexane (1:10) as eluent, obtained (22.8 mg, 42% yield) as a colorless oil. ¹H NMR (300 MHz, CDCl₃): δ 7.91-7.84 (m, 4H), 7.44-7.41 (m, 6H), 3.11-3.09 (m, 4H), 1.88-1.83 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 131.2, 131.1, 130.2, 128.0, 127.9, 44.3, 24.3; ³¹P NMR (162 MHz, CDCl₃): δ 21.43; HRMS (ESI): Exact mass calcd for C₁₆H₁₈NOP [M+H]⁺: 272.1199; Found: 272.1198.

diphenyl(piperidin-1-yl)phosphine oxide (3q)



Following procedure A, which purified using mixture of ethanol/hexane (1:10) as eluent, obtained (34.8 mg, 61% yield) as a yellow solid; Mp 103-104 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.92-7.85 (m, 4H), 7.50-7.42 (m, 6H), 3.06-3.00 (m, 4H), 1.61-1.58 (m, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 132.7, 132.4, 132.3, 131.4, 128.6, 128.5, 45.8, 26.3, 26.2, 24.6; ³¹P NMR (162 MHz, CDCl₃): δ 29.06; HRMS (ESI): Exact mass calcd for C₁₇H₂₀NOP [M+H]⁺: 286.1355; Found: 286.1356.

morpholinodiphenylphosphine oxide (3r)



Following procedure A, which purified using mixture of ethanol/hexane (1:10) as eluent, obtained (31.0 mg, 54% yield) as a yellow oil. ¹H NMR (300 MHz, CDCl₃): δ 7.92-7.85 (m, 4H), 7.53-7.44 (m, 6H), 3.72 (t, *J* = 4.2 Hz, 4H), 3.11-3.05 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 132.5, 132.4, 132.1, 132.0, 131.4, 130.2, 128.8, 128.7, 67.3, 67.2, 45.0; ³¹P NMR (162 MHz, CDCl₃): δ 29.24; HRMS (ESI): Exact mass calcd for C₁₆H₁₈NO₂P [M+H]⁺: 288.1148; Found: 288.1149.

N,N-dimethyl-P,P-diphenylphosphinothioic amide (3s)



Following procedure A, which purified using mixture of ethanol/hexane (1:10) as eluent, obtained (40.8 mg, 78% yield) as a white solid; Mp 78-79 °C. ¹H NMR (300 MHz, DMSO): δ 8.04-7.97 (m, 4H), 7.56-7.53 (m, 6H), 2.42 (s, 3H), 2.38 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 133.3, 132.3, 132.1, 132.0, 131.7, 131.6, 128.5, 128.4, 37.5; ³¹P NMR (162 MHz, CDCl₃): δ 71.13; HRMS (ESI): Exact mass calcd for

C₁₄H₁₆NPS [M+NH₄]⁺: 279.1079; Found: 279.1079.

diphenyl(pyrrolidin-1-yl)phosphine sulfide (3t)



Following procedure A, which purified using mixture of ethanol/hexane (1:10) as eluent, obtained (21.3 mg, 37% yield) as a yellow solid; Mp 92-93 °C. ¹H NMR (300 MHz, CDCl₃): δ 8.12-8.04 (m, 4H), 7.49-7.44 (m, 6H), 3.02 (t, *J* = 2.7 Hz, 4H), 1.92-1.88 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 134.3, 133.3, 132.1, 132.0, 131.5, 128.4, 128.3, 47.3, 47.2, 26.4, 26.3; ³¹P NMR (162 MHz, CDCl₃): δ 65.08; HRMS (ESI): Exact mass calcd for C₁₆H₁₈NPS [M+H]⁺: 288.0970; Found: 288.0971.

diphenyl(piperidin-1-yl)phosphine sulfide (3u)



Following procedure A, which purified using mixture of ethanol/hexane (1:10) as eluent, obtained (30.7 mg, 51% yield) as a white solid; Mp 77-79 °C. ¹H NMR (300 MHz, CDCl₃): δ 8.12-8.04 (m, 4H), 7.49-7.44 (m, 6H), 2.84 (d, *J* = 3.0 Hz, 4H), 1.63 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 133.4, 132.4, 132.0, 131.9, 131.5, 128.5, 128.4, 46.0, 25.9, 25.8, 24.3; ³¹P NMR (162 MHz, CDCl₃): δ 67.56; HRMS (ESI): Exact mass calcd for C₁₇H₂₀NPS [M+H]⁺: 302.1127; Found: 302.1121.

morpholinodiphenylphosphine sulfide (3v)



Following procedure A, which purified using mixture of ethanol/hexane (1:10) as eluent, obtained (27.9 mg, 46% yield) as a white solid; Mp 90-91 °C. ¹H NMR (300 MHz, CDCl₃): δ 8.12-8.04 (m, 4H), 7.52-7.47 (m, 6H), 3.77 (t, *J* = 3.9 Hz, 4H), 2.92-2.87 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 132.3, 132.2, 132.1, 131.9, 131.3,

128.7, 128.6, 66.8, 66.7, 45.1; ³¹P NMR (162 MHz, CDCl₃): δ 67.60; HRMS (ESI): Exact mass calcd for C₁₆H₁₈NOPS [M+H]⁺:304.0847; Found: 304.0851.

N,N-dimethyl-P,P-diphenylphosphinoselenoic amide (3w)



Following procedure A, which purified using mixture of ethanol/hexane (1:10) as eluent, obtained (41.3 mg, 67% yield) as a pink solid; Mp 78-79 °C. ¹H NMR (300 MHz, DMSO): δ 8.08-8.01 (m, 4H), 7.57-7.54 (m, 6H), 2.36 (s, 3H), 2.31 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 132.6, 132.4, 132.3, 131.8, 131.7, 128.5, 128.4, 38.1; ³¹P NMR (162 MHz, CDCl₃): δ 72.82; HRMS (ESI): Exact mass calcd for C₁₄H₁₆NPSe [M+H]⁺: 310.0258; Found: 310.0259.

N-ethyl-N-methyl-P,P-diphenylphosphinoselenoic amide (3x)



Following procedure A, which purified using mixture of ethanol/hexane (1:10) as eluent, obtained (38.0 mg, 59% yield) as a white solid; Mp 86-87 °C. ¹H NMR (300 MHz, CDCl₃): δ 8.13-8.06 (m, 4H), 7.49-7.42 (m, 6H), 2.87-2.77 (m, 2H), 2.48 (d, *J* = 15.3 Hz, 3H), 1.17 (t, *J* =7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 133.1, 132.3, 132.2, 132.1, 131.7, 128.4, 128.3, 45.0, 34.1, 12.9, 12.8; ³¹P NMR (162 MHz, CDCl₃): δ 71.17; HRMS (ESI): Exact mass calcd for C₁₅H₁₈NPSe [M+H]⁺: 324.0415; Found: 324.0411.

diphenyl(pyrrolidin-1-yl)phosphine selenide (3y)



Following procedure A, which purified using mixture of ethanol/hexane (1:10) as eluent, obtained (27.4 mg, 41% yield) as a yellow solid; Mp 109-110 °C. ¹H NMR (300 MHz, DMSO): δ 8.07-8.00 (m, 4H), 7.56-7.52 (m, 6H), 2.87-2.79 (m, 4H),

1.85-1.81 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 133.6, 132.7, 132.3, 132.2, 131.7, 128.4, 128.3, 47.9, 26.2, 26.1; ³¹P NMR (162 MHz, CDCl₃): δ 66.42; HRMS (ESI): Exact mass calcd for C₁₆H₁₈NPSe [M+Na]⁺: 358.0234; Found: 358.0235.

diphenyl(piperidin-1-yl)phosphine selenide (3z)



Following procedure A, which purified using mixture of ethanol/hexane (1:10) as eluent, obtained (30.7 mg, 44% yield) as a ywllow solid; Mp 81-82 °C. ¹H NMR (300 MHz, CDCl₃): δ 8.14-8.07 (m, 4H), 7.48-7.42 (m, 6H), 2.77 (t, *J* = 3.9 Hz, 4H), 1.64 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 132.6, 132.3, 132.2, 132.1, 131.7, 128.5, 128.4, 128.3, 46.6, 25.7, 25.6, 24.2; ³¹P NMR (162 MHz, CDCl₃): δ 68.22; HRMS (ESI): Exact mass calcd for C₁₇H₂₀NPSe [M+H]⁺: 350.0571; Found: 350.0570.

morpholinodiphenylphosphine selenide (3aa)



Following procedure A, which purified using mixture of ethanol/hexane (1:10) as eluent, obtained (35.0 mg, 50% yield) as a brown solid; Mp 113-114 °C. ¹H NMR (300 MHz, CDCl₃): δ 8.14-8.07 (m, 4H), 7.52-7.44 (m, 6H), 3.79 (t, *J* = 4.2 Hz, 4H), 2.86-2.81 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 132.5, 132.4, 132.1, 131.6, 130.6, 128.7, 128.5, 66.6, 66.4, 45.6; ³¹P NMR (162 MHz, CDCl₃): δ 68.61; HRMS (ESI): Exact mass calcd for C₁₆H₁₈NOPSe [M+H]⁺:352.0291; Found: 352.0296.

tert-butyl diphenylphosphinate (4a)

Following procedure B, which purified using mixture of EtOAc/hexane (1:2) as eluent,

obtained (44.4 mg, 81% yield) as a white solid; Mp 102-103 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.82-7.75 (m, 4H), 7.43-7.35 (m, 6H), 1.49 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 135.4, 134.0, 131.5, 131.4, 131.3, 128.3, 128.2, 83.7, 83.6, 31.0, 30.9; ³¹P NMR (162 MHz, CDCl₃): δ 25.77; HRMS (ESI): Exact mass calcd for C₁₆H₁₉O₂P [M+Na]⁺: 297.1015; Found: 297.1016.

tert-butyl di-p-tolylphosphinate (4b)



Following procedure B, which purified using mixture of EtOAc/hexane (1:2) as eluent, obtained (52.0 mg, 86% yield) as a white solid; Mp 118-119 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.70-7.63 (m, 4H), 7.21-7.17 (m, 4H), 2.34 (s, 6H), 1.49 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 141.8, 132.5, 131.4, 131.3, 131.1, 129.1, 128.9, 83.2, 31.0, 31.0, 30.9, 21.6; ³¹P NMR (162 MHz, CDCl₃): 26.71; HRMS(ESI): Exact mass calcd for for C₁₈H₂₃O₂P [M+Na]⁺: 325.1328; Found: 325.1321.

tert-butyl bis(4-(tert-butyl)phenyl)phosphinate (4c)



Following procedure B, which purified using mixture of EtOAc/hexane (1:2) as eluent, obtained (63.4 mg, 82% yield) as a white solid; Mp: 144-146 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.76-7.70 (m, 4H), 7.45-7.42 (m, 4H), 1.52 (s, 9H), 1.32 (s, 18H); ¹³C NMR (100 MHz, CDCl₃): δ 154.7, 131.2, 131.1, 131.0, 125.3, 125.2, 83.2, 83.1, 34.9, 31.2, 31.0; ³¹P NMR (162 MHz, CDCl₃): δ 26.66; HRMS (ESI): Exact mass calcd for C₂₄H₃₅O₂P [M+Na]⁺: 409.2267; Found: 409.2266.

tert-butyl bis(4-fluorophenyl)phosphinate (4d)



Following procedure B, which purified using mixture of EtOAc/hexane (1:2) as eluent, obtained (47.2 mg, 76% yield) as a white solid; Mp 69-71 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.81-7.72 (m, 4H), 7.12-7.05 (m, 4H), 1.49 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 164.9 (d, $J_{CF} = 251.3$ Hz), 133.7 (dd, ${}^{3}J_{CF} = 11.5$ Hz, ${}^{3}J_{CF} = 8.7$ Hz), 131.3, 131.2, 129.9, 129.8, 115.7 (dd, ${}^{2}J_{CF} = 21.3$ Hz, ${}^{2}J_{CF} = 14.3$ Hz), 84.3, 84.2, 30.9; ³¹P NMR (162 MHz, CDCl₃): δ 23.98; ¹⁹F NMR (376 MHz CDCl₃): δ -111.11; HRMS (ESI): Exact mass calcd for C₁₆H₁₇F₂O₂P [M+Na]⁺:333.0934; Found: 333.0931.

tert-butyl bis(4-chlorophenyl)phosphinate (4e)



Following procedure B, which purified using mixture of EtOAc/hexane (1:2) as eluent, obtained (47.4 mg, 69% yield) as a white solid; Mp 79-80 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.74-7.67 (m, 4H), 7.43-7.39 (m, 4H), 1.52 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 138.3, 133.5, 132.7, 132.6, 132.1, 128.9, 128.7, 84.7, 84.6, 31.0, 30.9; ³¹P NMR (162 MHz, CDCl₃): δ 23.85; HRMS (ESI): Exact mass calcd for C₁₆H₁₇Cl₂O₂P [M+Na]⁺:365.0235; Found:365.0234.

tert-butyl bis(4-methoxyphenyl)phosphinate (4f)



Following procedure B, which purified using mixture of EtOAc/hexane (1:2) as eluent, obtained (55.5 mg, 83% yield) as a white solid; White solid. ¹H NMR (300 MHz,

CDCl₃): δ 7.64-7.57 (m, 4H), 7.04-7.00 (m, 4H), 3.79 (s, 6H), 1.40 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 162.0, 133.2, 133.1, 127.2, 125.8, 113.8, 113.7, 83.1, 83.0, 55.3, 31.0, 30.9; ³¹P NMR (162 MHz, CDCl₃): δ 26.59; HRMS (ESI): Exact mass calcd for C₁₈H₂₃O₄P [M+H]⁺: 335.1407; Found: 335.1404.

tert-butyl di-m-tolylphosphinate (4g)



Following procedure B, which purified using mixture of EtOAc/hexane (1:2) as eluent, obtained (46.0 mg, 76% yield) as a white solid; Mp 70-71 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.64-7.54 (m, 4H), 7.32-7.25 (m, 4H), 2.36 (s, 6H), 1.51 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 138.1, 138.0, 135.3, 134.0, 132.3, 132.2, 131.8, 131.7, 128.5, 128.4, 128.2, 128.1, 83.5, 83.4, 31.0, 30.9, 21.4; ³¹P NMR (162 MHz, CDCl₃): δ 26.49; HRMS (ESI): Exact mass calcd for C₁₈H₂₃O₂P [M+Na]⁺: 325.1328; Found: 325.1322.

tert-butyl (3,4-dimethylphenyl)(3,5-dimethylphenyl)phosphinate (4h)



Following procedure B, which purified using mixture of EtOAc/hexane (1:2) as eluent, obtained (39.6 mg, 60% yield) as a white solid; Mp 86-87 °C. ¹H NMR (500 MHz, CDCl₃): δ 7.43 (s, 2H), 7.39 (s, 2H), 7.09 (s, 2H), 2.33 (s, 12H), 1.52 (s, 9H); ¹³C NMR (125 MHz, CDCl₃): δ 137.8, 137.8, 135.1, 134.0, 133.2, 133.1, 128.9, 128.8, 83.3, 83.2, 31.0, 21.3; ³¹P NMR (202 MHz, CDCl₃): δ 27.18; HRMS (ESI): Exact mass calcd for C₂₀H₂₇O₂P [M+Na]⁺: 353.1641; Found: 353.1646.

tert-butyl di-o-tolylphosphinate(4i)



Following procedure B, which purified using mixture of EtOAc/hexane (1:2) as eluent, obtained (40.5 mg, 67% yield) as a white solid; Mp 82-84 °C. ¹H NMR (300 MHz, CDCl₃): δ 8.03-7.95 (m, 2H), 7.40-7.34 (m, 2H), 7.30-7.27 (m, 2H), 7.16-7.12 (m, 2H), 2.32 (s, 6H), 1.51 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 141.2, 141.1, 133.5, 133.4, 133.3, 132.1, 131.7, 131.3, 131.2, 125.4, 125.3, 83.9, 83.8, 30.9, 30.8, 21.2; ³¹P NMR (162 MHz, CDCl₃): δ 25.72; HRMS (ESI): Exact mass calcd for C₁₈H₂₃O₂P [M+Na]⁺: 325.1328; Found: 325.1323.

tert-butyl di(naphthalen-1-yl)phosphinate (4j)



Following procedure B, which purified using mixture of EtOAc/hexane (1:2) as eluent, obtained (57.7 mg, 77% yield) as a white solid; Mp 144-145 °C. ¹H NMR(300 MHz, DMSO): δ 8.44 (d, *J* =14.1 Hz, 2H), 8.10 (d, *J* = 7.2 Hz, 2H), 8.04-7.95 (m, 4H), 7.83-7.76 (m, 2H), 7.64-7.59 (m, 4H), 1.50 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 134.7, 134.6, 133.0, 132.9, 132.6, 132.5, 132.4, 131.1, 129.0, 128.2, 128.0, 127.9, 127.7, 126.7, 126.6, 126.5, 84.0, 83.9, 31.1, 31.0; ³¹P NMR (162 MHz, CDCl₃): δ 25.96; HRMS (EI): Exact mass calcd for C₂₄H₂₃O₂P [M+Na]⁺: 397.1328; Found: 397.1320.

tert-butyl phenyl(p-tolyl)phosphinate (4k)



Following procedure B, which purified using mixture of EtOAc/hexane (1:2) as eluent, obtained (47.3 mg, 82% yield) as a yellow solid; Mp 70-72 °C. ¹H NMR (300 MHz,

CDCl₃): δ 7.82-7.66 (m, 4H), 7.47-7.40 (m, 3H), 7.24-7.22 (m, 2H), 2.38 (s, 3H), 1.52 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 141.9, 135.7, 134.3, 132.2, 131.5, 131.4, 131.3, 131.2, 130.8, 129.1, 129.0, 128.3, 128.2, 83.5, 83.4, 31.0, 30.9, 21.6; ³¹P NMR (162 MHz, CDCl₃): δ 26.26; HRMS (ESI): Exact mass calcd for C₁₇H₂₁O₂P [M+Na]⁺: 311.1171; Found: 311.1171.

tert-butyl (4-chlorophenyl)(phenyl)phosphinate (4l)



Following procedure B, which purified using mixture of EtOAc/hexane (1:2) as eluent, obtained (45.1 mg, 73% yield) as a white solid; Mp 117-119 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.79-7.67 (m, 4H), 7.45-7.34 (m, 5H), 1.49 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 138.1, 138.0, 134.8, 133.9, 133.4, 132.8, 132.7, 132.6, 131.8, 131.7, 131.3, 131.2, 128.7, 128.6, 128.5, 128.4, 84.2, 84.1, 30.9; ³¹P NMR (162 MHz, CDCl₃): δ 24.84; HRMS (ESI): Exact mass calcd for C₁₆H₁₈ClO₂P [M+H]⁺:309.0987; Found: 309.0989.

tert-butyl methyl(phenyl)phosphinate (4m)

Following procedure B, which purified using mixture of EtOAc/hexane (1:2) as eluent, obtained (19.9 mg, 47% yield) as a colorless oil. ¹H NMR (300 MHz, CDCl₃): δ 7.78-7.71 (m, 2H), 7.57-7.51 (m, 3H), 1.56 (d, J = 14.4 Hz, 3H), 1.35 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 135.8, 134.5, 131.6, 130.9, 130.8, 128.4, 128.3, 82.7, 30.8, 19.1, 18.1; ³¹P NMR (162 MHz, CDCl₃): δ 37.15; HRMS (ESI): Exact mass calcd for C₁₁H₁₇O₂P [M+H]⁺:213.0977; Found: 213.0972.

tert-pentyl diphenylphosphinate (40)



Following procedure B, which purified using mixture of EtOAc/hexane (1:2) as eluent, obtained (34.6 mg, 60% yield) as a white solid; Mp 68-69 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.83-7.76 (m, 4H), 7.49-7.37 (m, 6H), 1.81 (d, *J* = 7.5 Hz, 2H), 1.46 (s, 6H), 0.99 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 135.5, 134.2, 131.5, 131.4, 131.3, 128.3, 128.2, 86.4, 36.6, 28.1, 8.8; ³¹P NMR (162 MHz, CDCl₃): δ 25.49; HRMS (ESI): Exact mass calcd for C₁₇H₂₁O₂P [M+Na]⁺: 311.1171; Found: 311.1171.

3. Mechanistic studies

3.1 The radical-trapping experiment



A 15 mL schlenk tube was charged with a mixture of **1a** (0.2 mmol), **2a** (0.6 mmol), TEMPO (0.6 mmol), catalyst (0.04 mmol) in DCM (1.0 mL) and was stirred at 80 °C for 3 h. After the reaction was complete (as determined by TLC analysis), the reaction was cooled to room temperature and EtOAc (20 mL) was added to the solution and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (ethanol/hexane = 1:10) to afford the product **3a** in 75% yield.



A15 mL schlenk tube was charged with a mixture of **1a** (0.2 mmol), **2a** (0.6 mmol), TEMPO (0.6 mmol), catalyst (0.04 mmol) in THF (1.0 mL) and was stirred at 80 $^{\circ}$ C

for 5 h. After the reaction was complete (as determined by TLC analysis), the reaction was cooled to room temperature and EtOAc (20 mL) was added to the solution and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (EtOAc/hexane = 1:2) to afford the targeted products **4a** in 77% yield.

3.2 Exporing possible reaction pathway



A 15 mL schlenk tube was charged with a mixture of **1a** (0.2 mmol), **7** (0.6 mmol), catalyst (0.04 mmol) in DCM (1.0 mL) and was stirred at 80 $^{\circ}$ C for 3 h. Then the reaction was monitored by TLC and the targeted product **3r** was not detected.



A 15 mL schlenk tube was charged with a mixture of **1a** (0.2 mmol), **8** (0.6 mmol), catalyst (0.04 mmol) in DCM (1.0 mL) and was stirred at 80 °C for 3 h. After the reaction was complete (as determined by TLC analysis), the reaction was cooled to room temperature and EtOAc (20 mL) was added to the solution and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (ethanol/hexane = 1:10) to afford the targeted products **3r** in 64% yield.

$$\begin{array}{cccc} Ph \\ O_{S}P' \\ Ph' H \\ 1a \\ 9 \\ \end{array} + t-Bu O' \\ THF, 80 °C, 5h \\ HF, 80 °C, 5h \\ \end{array} + t-Bu O' \\ Ph' O' \\ Ph' O' \\ HF, 80 °C, 5h \\ \end{array}$$

-

A 15 mL schlenk tube was charged with a mixture of oxidant **1a** (0.2 mmol), **9** (0.6 mmol), catalyst (0.04 mmol) in THF (1.0 mL) and was stirred at 80 °C for 5 h. Then the reaction was monitored by TLC and only trace of **4a** was detected.



A 15 mL schlenk tube was charged with a mixture of oxidant **1a** (0.2 mmol), **10** (0.6 mmol), catalyst (0.04 mmol) in THF (1.0 mL) and was stirred at 80 °C for 5 h. After the reaction was complete (as determined by TLC analysis), the reaction was cooled to room temperature and EtOAc (20 mL) was added to the solution and washed with brine, dried over Na₂SO₄, concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (EtOAc/hexane = 1:2) to afford the product **4a** in 23% yield.



A 15 mL schlenk tube was charged with a mixture of **11** (0.2 mmol), **2a** (0.6 mmol), catalyst (0.04 mmol) in DCM (1.0 mL) and was stirred at 80 $^{\circ}$ C for 3 h. Then the reaction was monitored by TLC and the targeted product **3a** was not detected.

A 15 mL schlenk tube was charged with a mixture of oxidant **11** (0.2 mmol), **2a** (0.6 mmol), catalyst (0.04 mmol) in THF (1.0 mL) and was stirred at 80 °C for 5 h. Then the reaction was monitored by TLC and only trace of **4a** was detected.

4. References

 (a) Zhu, R.; Pan, C.; Gu, Z. Org. Lett. 2015, 17, 5862-5865; (b) Wang, Y.; Qian, P.; Su, J.-H.; Li, Y.; Bi, M.; Zha, Z.; Wang, Z. Green Chem. 2017, 19, 4769-4773; (c) Dong, X.; Wang, R.; Jin, W.; Liu, C. Org. Lett. 2020, 22, 3062-3066; (d) Tan, C.; Liu, X. Y.; Jia, H. X.; Zhao, X. W.; Chen, J.; Wang, Z. Y.; Tan, J. J. Chem.-Eur. J. 2020, 26, 881-887; (e) Wu, Y.; Chen, K.; Ge, X.; Ma, P.; Xu, Z.; Lu, H.; Li. G. Org. Lett. 2020, 22, 6143-6149.



5. Copies of ¹H NMR, ¹³C NMR and ³¹P NMR Spectra

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)



-31.403









-31.556



140 110 80 60 40 20 0 -10 -30 -50 -70 -90 -110 -140 -170 -200 -230 fl (ppm)







210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)



-31.598







-36.997







-31.339






-30.557







-21.427



150 130 110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -100 -120 -140 -160 -180 -200 -220 -240 f1 (ppm)





-29.243



















-71.166













-25.773









-140 -170 -200



---111.108



-14 -18





-26.591







-27.176






-25.958







-24.841







