Supporting Information

K$_2$S$_2$O$_8$-mediated metal-free direct P-H/C-H functionalization: a convenient route to benzo[b]phosphole oxides from unactivated alkynes

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Table of Contents

Page 2 1. General information and experimental section
Page 3 2. Gram-scale synthesis of 3a
Page 3 3. Application for the synthesis of 3u
Page 3 4. Radical trapping study
Page 4-14 5. Spectral data and characterization of 3a-3u
Page 14 6. References
Page 15-46 7. NMR spectra of 3a-3u
1. General information and experimental section

General information:

Substrates (1b-1q and 1u) were prepared according to the known reference: Org. Lett. 2015, 17, 2522–2525. Other reagents were purchased from commercial sources and used without further purification. Spectroscopy data of the known compounds matches with the data reported in the corresponding references. $^1$H, $^{13}$C and $^{31}$P NMR spectra were recorded on a Bruker Av500 spectrometer using tetramethylsilane (TMS) in CDCl$_3$ as the internal standard for $^1$H, and $^{13}$C NMR (1H NMR: TMS at 0.00 ppm, CHCl$_3$ at 7.26 ppm; $^{13}$C NMR: CDCl$_3$ at 77.16 ppm) and 85% H$_3$PO$_4$ as external standard for $^{31}$P NMR. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration. ESI mass spectra was aquired on a Bruker Dalton Esquire3000 Plus mass spectrometer. HRMS spectra of new compounds were recorded on a Waters Micromass LCT Premier TOF-MS apparatus. Infrared spectra were recorded on a Nicollet Avatar 330 spectrometer. Melting points were recorded on a WRS-1B Digital Melting-Point apparatus. The products were purified by column chromatography on silica gel 300-400 mesh.

Experimental section:

General procedure for the synthesis of 3: K$_2$S$_2$O$_8$ (405 mg, 1.5 mmol), alkyne 1 (0.3 mmol) and diarylphosphine oxide 2 (0.9 mmol) were added to a sealed tube equipped with a magnetic stir bar under argon, and then CH$_3$CN (2 mL) were added to the sealed reaction tube by syringe. The resulting reaction mixture was kept stirring at 90 °C for 24 h. After required reaction time, the mixture was cooled down to room temperature and purified by flash chromatography (petroleum ether/ethyl acetate) to afford the corresponding product.
2. Gram-scale synthesis of 3a

\[
\begin{align*}
\text{Ph} & \equiv \text{Ph} + \text{PhCO}_2\text{H} + \text{K}_2\text{S}_2\text{O}_8 \quad \text{in CH}_3\text{CN at 90 °C for 36 h}\quad \text{Scheme 1} \\
\end{align*}
\]

K\textsubscript{2}S\textsubscript{2}O\textsubscript{8} (2.7 g, 100 mmol), 1a (20 mmol, 3.6 g) and diphenylphosphine oxide 2a (12 g, 100 mmol) were added to a round flask equipped with a magnetic stir bar under argon, and then CH\textsubscript{3}CN (140 mL) were added by syringe. The resulting reaction mixture was kept stirring at 90 °C for 36 h. After 36 h, the mixture was cooled down to room temperature and purified by flash chromatography (petroleum ether/ethyl acetate) to afford the corresponding product.

3. Application for the synthesis of 3u

\[
\begin{align*}
\text{EtO}_2\text{C} & \equiv \text{Ph} + \text{PhCO}_2\text{H} + \text{K}_2\text{S}_2\text{O}_8 \quad \text{in CH}_3\text{CN at 90 °C for 24 h}\quad \text{Scheme 2} \\
\end{align*}
\]

K\textsubscript{2}S\textsubscript{2}O\textsubscript{8} (810 mg, 3 mmol), 1u (81 mg, 0.3 mmol) and diphenylphosphine oxide 2a (362 mg, 1.8 mmol) were added to a sealed tube equipped with a magnetic stir bar under argon. Under argon, CH\textsubscript{3}CN (4 mL) were added to the sealed reaction tube by syringe. The resulting reaction mixture was kept stirring at 90 °C for 24 h. After required reaction time, the mixture was cooled down to room temperature and purified by flash chromatography (petroleum ether/ethyl acetate) afforded the corresponding product.

4. Radical Trapping Study

\[
\begin{align*}
\text{Ph} & \equiv \text{Ph} + \text{PhCO}_2\text{H} + \text{K}_2\text{S}_2\text{O}_8 \quad \text{in CH}_3\text{CN at 90 °C for 24 h}\quad \text{Scheme 3} \\
\end{align*}
\]

The reaction was carried out according to the general procedure, except 6 equiv of TEMPO
(280 mg, 1.8 mmol) or BHT (396 mg, 1.8 mmol) was added. At the end of the reaction, the isolated yield revealed formation of the target product 3a decreased dramatically. The adduct 10 was detected by ESI-HRMS measurement of the crude reaction mixture (HRMS (ESI): C$_{27}$H$_{33}$O$_2$P$^+$, Calcd: 421.2291, Found: 421.2296).

5. Spectral data and characterization of 3a-3u

1,2,3-Triphenyl-1H-phosphindole 1-oxide (3a, CAS 1478603-26-7)\(^1\)

![Image of 3a]

White solid, 90% yield. \(^1\)H NMR (500 MHz, CDCl$_3$): δ 7.80 (dd, J = 12.5, 7.2 Hz, 2 H), 7.69 (dd, J = 9.3, 7.9 Hz, 1 H), 7.45-7.32 (m, 10 H), 7.24-7.20 (m, 3 H), 7.08-7.07 (m, 3 H). \(^{13}\)C NMR (125 MHz, CDCl$_3$): δ 149.9 (d, J$_{C,P}$ = 21.3 Hz), 143.6 (d, J$_{C,P}$ = 26.8 Hz), 134.0 (d, J$_{C,P}$ = 14.9 Hz), 134.1 (d, J$_{C,P}$ = 95.8 Hz), 132.8 (d, J$_{C,P}$ = 1.4 Hz), 132.5 (d, J$_{C,P}$ = 9.8 Hz), 132.1 (d, J$_{C,P}$ = 2.6 Hz), 131.9 (d, J$_{C,P}$ = 121.4 Hz), 130.8 (d, J$_{C,P}$ = 10.6 Hz), 129.7 (d, J$_{C,P}$ = 99.7 Hz), 129.0 (d, J$_{C,P}$ = 11.0 Hz), 128.9 (d, J$_{C,P}$ = 2.7 Hz), 128.87, 128.84, 128.7 (d, J$_{C,P}$ = 12.5 Hz), 128.6, 128.1, 127.7, 123.9 (d, J$_{C,P}$ = 10.9 Hz). \(^{31}\)P NMR (202 MHz, CDCl$_3$): δ 39.2. MS-ESI: m/z 379 [M + H]$^+$. IR (film) $\nu_{max}$: 3057, 2921, 1587, 1437, 1198 (P=O), 779, 634 cm$^{-1}$.

1-Phenyl-2,3-di-p-tolyl-1H-phosphindole 1-oxide (3b, CAS 1537189-01-7)\(^1\)

![Image of 3b]

Pale yellow solid, 75% yield. \(^1\)H NMR (500 MHz, CDCl$_3$): δ 7.79-7.75 (m, 2 H), 7.68 (dd, J = 9.3, 7.4 Hz, 1 H), 7.45-7.32 (m, 5 H), 7.24-7.19 (m, 5 H), 7.15 (d, J = 7.8 Hz, 2 H), 6.90 (d, J = 8.1 Hz, 2 H), 2.40 (s, 3 H), 2.18 (s, 3 H). \(^{13}\)C NMR (125 MHz, CDCl$_3$): δ 148.5 (d, J$_{C,P}$ = 21.7 Hz), 143.1 (d, J$_{C,P}$ = 27.2 Hz), 137.6, 136.7, 132.8 (d, J$_{C,P}$ = 96.0 Hz), 131.9, 131.14 (d, J$_{C,P}$ = 2.6 Hz), 131.13 (d, J$_{C,P}$ = 105.5 Hz), 130.5, 130.02 (d, J$_{C,P}$ = 98.0 Hz), 130.03 (d, J$_{C,P}$ = 10.6 Hz), 128.9 (d, J$_{C,P}$ = 10.0 Hz), 128.8 (d, J$_{C,P}$ = 8.3 Hz), 128.7, 128.1, 128.01, 128.02, 127.9 (d, J$_{C,P}$ = 1.6 Hz), 127.88 (d, J$_{C,P}$ = 6.5 Hz), 123.0 (d, J$_{C,P}$ = 10.9 Hz), 20.5, 20.3. \(^{31}\)P NMR (202 MHz, CDCl$_3$): δ 39.2. MS-ESI: m/z 407 [M + H]$^+$. IR (film) $\nu_{max}$: 3054, 2921, 1586, 1437, 1197 (P=O), 732, 522 cm$^{-1}$. 


2,3-Bis(4-ethylphenyl)-1-phenyl-1H-phosphindole 1-oxide (3c, new compound)

Yellow solid, 63% yield. mp 48.6-49.5 °C. 1H NMR (500 MHz, CDCl₃): δ 7.80-7.76 (m, 2 H), 7.68 (dd, J = 9.3, 7.6 Hz, 1 H), 7.47-7.30 (m, 7 H), 7.25-7.15 (m, 5 H), 6.91 (d, J = 8.2 Hz, 2 H), 2.71 (q, J = 7.6 Hz, 2 H), 2.49 (q, J = 7.5 Hz, 2 H), 1.28 (t, J = 7.6 Hz, 3 H), 1.10 (t, J = 7.6 Hz, 3H). 13C NMR (125 MHz, CDCl₃): δ 149.9 (d, JC-P = 21.6 Hz), 144.8, 144.2 (d, JC-P = 27.3 Hz), 143.9, 133.7 (d, JC-P = 96.1 Hz), 132.9 (d, JC-P = 1.6 Hz), 132.13 (d, JC-P = 105.6 Hz), 132.14 (d, JC-P = 2.6 Hz), 131.7 (d, JC-P = 15.3 Hz), 131.0 (d, JC-P = 10.7 Hz), 130.3 (d, JC-P = 98.9 Hz), 130.1 (d, JC-P = 10.0 Hz), 129.1 (d, JC-P = 1.7 Hz), 129.0 (d, JC-P = 4.0 Hz), 128.97, 128.90 (d, JC-P = 1.5 Hz), 128.88 (d, JC-P = 2.6 Hz), 128.5, 127.8, 124.0 (d, JC-P = 10.9 Hz), 28.8, 28.6, 15.4, 15.1. 31P NMR (202 MHz, CDCl₃): δ 39.2. IR (film) νmax: 3055, 2964, 1587, 1437, 1196 (P=O), 732, 519 cm⁻¹. HRMS: [M + H]⁺ m/z calcd for C₃₀H₂₄OPH⁺: 435.1878, found: 435.1875.

2,3-Bis(4-(tert-butyl)phenyl)-1-phenyl-1H-phosphindole 1-oxide (3d, new compound)

Yellow solid, 70% yield. mp 85.3-87.6 °C. 1H NMR (500 MHz, CDCl₃): δ 7.82-7.76 (m, 2 H), 7.67 (dd, J = 9.2, 7.4 Hz, 1 H), 7.50-7.39 (m, 6 H), 7.34-7.26 (m, 3 H), 7.20-7.14 (m, 3 H), 7.09 (d, J = 8.5 Hz, 2 H), 1.38 (m, 9 H), 1.19 (m, 9 H). 13C NMR (125 MHz, CDCl₃): δ 151.8, 150.8, 149.4 (d, JC-P = 21.6 Hz), 144.4 (d, JC-P = 27.4 Hz), 133.3 (d, JC-P = 96.2 Hz), 132.9 (d, JC-P = 1.8 Hz), 132.2 (d, JC-P = 105.9 Hz), 132.1 (d, JC-P = 2.7 Hz), 131.7 (d, JC-P = 15.4 Hz), 131.1 (d, JC-P = 10.4 Hz), 130.2, 129.8, 129.4 (d, JC-P = 95.5 Hz), 129.0 (d, JC-P = 11.9 Hz), 128.9 (d, JC-P = 3.6 Hz), 128.8 (d, JC-P = 8.7 Hz), 128.78 (d, JC-P = 2.4 Hz), 126.0, 125.3, 124.1 (d, JC-P = 10.9 Hz), 34.9, 34.6, 31.5, 31.2. 31P NMR (202 MHz, CDCl₃): δ 39.3. IR (film) νmax: 3057, 2963, 1587, 1437, 1197 (P=O), 773, 523 cm⁻¹. HRMS: [M + H]⁺ m/z calcd for C₃₄H₃₅OPH⁺: 491.2504, found: 491.2500.
2,3-Bis(4-fluorophenyl)-1-phenyl-1H-phosphindole 1-oxide (3e, CAS 1478603-94-9)²

White solid, 51% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.74-7.68 (m, 3 H), 7.48-7.34 (m, 5 H), 7.30-7.27 (m, 2 H), 7.21-7.18 (m, 3 H), 7.14-7.10 (m, 2 H), 6.80-6.77 (m, 2 H). ¹³C NMR (125 MHz, CDCl₃): δ 162.7 (d, J_C= 249.1 Hz), 162.1 (d, J_C= 248.9 Hz), 148.7 (d, J_C= 21.7 Hz), 143.3 (d, J = 26.6 Hz), 133.7 (d, J_C= 96.0 Hz), 133.0 (d, J = 1.4 Hz), 132.3 (d, J = 2.6 Hz), 131.6 (d, J_C= 106.0 Hz), 130.9 (d, J = 7.6 Hz), 130.8 (d, J = 9.2 Hz), 130.7 (dd, J = 6.2, 3.5 Hz), 130.1 (d, J = 103.9 Hz), 129.7 (dd, J = 15.2, 3.7 Hz), 129.2 (d, J = 24.9 Hz), 129.1 (d, J = 4.5 Hz), 128.8 (d, J = 12.5 Hz), 128.5 (dd, J = 10.0, 2.9 Hz), 123.8 (d, J = 10.9 Hz), 116.2 (d, J = 21.6 Hz), 115.4 (d, J = 21.5 Hz). ³¹P NMR (202 MHz, CDCl₃): δ 38.9. MS-ESI: m/z 415 [M + H]⁺. IR (film) ν_max: 3057, 2982. 1716, 1505, 1160 (P=O), 743, 561 cm⁻¹.

2,3-Bis(4-chlorophenyl)-1-phenyl-1H-phosphindole 1-oxide (3f, CAS 1537198-04-0)¹

Pale yellow solid, 55% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.73-7.70 (m, 3 H), 7.51-7.47 (m, 2 H), 7.44-7.38 (m, 5 H), 7.26-7.25 (m, 2 H), 7.20-7.15 (m, 3 H), 7.09 (d, J = 8.6 Hz, 2 H). ¹³C NMR (125 MHz, CDCl₃): δ 149.2 (d, J_C= 21.6 Hz), 143.3 (d, J_C= 26.6 Hz), 135.1, 134.0 (d, J_C= 95.4 Hz), 134.18, 134.19, 133.3 (d, J_C= 1.8 Hz), 132.6 (d, J_C= 2.6 Hz), 132.4 (d, J_C= 15.0 Hz), 131.9 (d, J_C= 107.5 Hz), 131.0 (d, J_C= 10.7 Hz), 130.6, 130.3 (d, J_C= 5.5 Hz), 129.65 (d, J_C= 8.4 Hz), 129.61, 129.5 (d, J_C= 9.6 Hz), 129.3 (d, J_C= 100.5 Hz), 129.1 (d, J = 12.5 Hz), 128.9, 124.0 (d, J_C= 10.7 Hz). ³¹P NMR (202 MHz, CDCl₃): δ 39.0. MS-ESI: m/z 446 [M + H]⁺. IR (film) ν_max: 3048, 2941, 1585, 1483, 1197 (P=O), 773, 565 cm⁻¹.
2,3-Bis(4-bromophenyl)-1-phenyl-1H-phosphindole 1-oxide (3g, CAS 1537198-05-1)

Pale yellow solid, 57% yield. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.73-7.57 (m, 5 H), 7.47-7.39 (m, 5 H), 7.25-7.18 (m, 5 H), 7.10 (d, $J$ = 8.3 Hz, 2 H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 149.1 (d, $J_{C,P}$ = 21.6 Hz), 143.1 (d, $J_{C,P}$ = 26.4 Hz), 133.9 (d, $J_{C,P}$ = 95.5 Hz), 133.2 (d, $J_{C,P}$ = 1.4 Hz), 132.7 (d, $J_{C,P}$ = 14.7 Hz), 132.50 (d, $J_{C,P}$ = 12.8 Hz), 132.51, 131.8 (d, $J_{C,P}$ = 106.1 Hz), 131.7, 131.4 (d, $J_{C,P}$ = 9.9 Hz), 130.9 (d, $J_{C,P}$ = 10.6 Hz), 130.7, 130.5 (d, $J_{C,P}$ = 5.5 Hz), 129.6 (d, $J_{C,P}$ = 10.3 Hz), 129.4 (d, $J_{C,P}$ = 9.7 Hz), 129.2 (d, $J_{C,P}$ = 100.7 Hz), 129.0 (d, $J_{C,P}$ = 12.6 Hz), 124.0 (d, $J_{C,P}$ = 10.8 Hz), 123.2, 122.5. $^{31}$P NMR (202 MHz, CDCl$_3$): $\delta$ 38.9. MS-ESI: m/z 537 [M + H]$^+$. IR (film) $\nu_{\text{max}}$: 3058, 2986, 1583, 1481, 1196 (P=O), 733, 540 cm$^{-1}$.

2,3-Bis(4-methoxyphenyl)-1-phenyl-1H-phosphindole 1-oxide (3h, CAS 1537189-02-8)

Yellow solid, 50% yield. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.76 (dd, $J$ = 12.3, 7.8 Hz, 2 H), 7.67 (dd, $J$ = 8.4, 7.4 Hz, 1 H), 7.48-7.31 (m, 5 H), 7.28-7.20 (m, 5 H), 6.97 (d, $J$ = 8.0 Hz, 2 H), 6.64 (d, $J$ = 8.3 Hz, 2H), 3.86 (s, 3 H), 3.70 (s, 3 H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 159.7, 159.0, $\delta$ 148.1 (d, $J_{C,P}$ = 21.9 Hz), 144.2 (d, $J_{C,P}$ = 27.5 Hz), 133.1 (d, $J_{C,P}$ = 96.8 Hz), 132.8, 132.0 (d, $J_{C,P}$ = 2.7 Hz), 131.9 (d, $J_{C,P}$ = 106.0 Hz), 130.9 (d, $J_{C,P}$ = 10.7 Hz), 130.46, 130.4 (d, $J_{C,P}$ = 3.8 Hz), 130.38, 130.3 (d, $J_{C,P}$ = 99.6 Hz), 128.8 (d, $J_{C,P}$ = 34.7 Hz), 128.79 (d, $J_{C,P}$ = 12.5 Hz), 126.5 (d, $J_{C,P}$ = 15.5Hz), 125.3 (d, $J_{C,P}$ = 10.1 Hz), 123.7 (d, $J_{C,P}$ = 10.7 Hz), 114.5, 113.8, 55.3, 55.1. $^{31}$P NMR (202 MHz, CDCl$_3$): $\delta$ 38.9. MS-ESI: m/z 439 [M + H]$^+$. IR (film) $\nu_{\text{max}}$: 3058, 2930, 1606, 1501, 1195 (P=O), 736, 522 cm$^{-1}$.
1-Phenyl-2,3-bis(4-(trifluoromethyl)phenyl)-1H-phosphindole 1-oxide (3i, new compound)

Pale yellow solid, 43% yield. mp 69.0-71.0 °C. 1H NMR (500 MHz, CDCl3): δ 7.77-7.71 (m, 4 H), 7.53-7.40 (m, 8 H), 7.37 (d, J = 8.3, 2 H), 7.31 (d, J = 8.3 Hz, 2 H), 7.18-7.16 (m, 1 H). 13C NMR (125 MHz, CDCl3): δ 150.0 (d, J = 21.4 Hz), 142.8 (d, J = 26.2 Hz), 137.5 (d, J = 14.9 Hz), 136.0 (d, J = 10.1 Hz), 134.7 (d, JCP = 94.9 Hz), 133.4, 132.8 (d, JCP = 2.5 Hz), 131.8 (d, JCP = 106.9 Hz), 131.3 (q, JCP = 33.2 Hz), 131.2 (d, J = 10.8 Hz), 130.1 (q, JCP = 32.3 Hz), 129.7 (d, J = 10.1 Hz), 129.6, 129.3 (d, J = 1.8 Hz), 129.2 (d, J = 4.8 Hz), 128.9 (d, J = 101.2 Hz), 128.7 (d, J = 12.2 Hz), 126.3 (d, J = 3.5 Hz), 125.6 (dd, J = 7.6, 3.4 Hz), 124.3 (d, J = 10.7 Hz), 123.9 (q, JCP = 272.4 Hz), 123.7 (q, JCP = 272.4 Hz). 31P NMR (202 MHz, CDCl3): δ 39.0. IR (film) νmax: 3059, 2928, 1615, 1325, 1124 (P=O), 722, 562 cm⁻¹. HRMS: [M + H]+ m/z calcd for C38H17F6OPH: 515.0999, found: 515.1001.

Methyl 1,3-diphenyl-1H-phosphindole-2-carboxylate 1-oxide (3j, new compound)

Yellow solid, 53% yield. mp 38.1-39.4 °C. 1H NMR (500 MHz, CDCl3): δ 7.77-7.73 (m, 2 H), 7.71-7.67 (m, 1 H), 7.54-7.48 (m, 6 H), 7.46-7.35 (m, 4 H), 7.20-7.18 (m, 1 H), 3.55 (s, 3 H). 13C NMR (125 MHz, CDCl3): δ 164.5 (d, JCP = 18.3 Hz), 163.0 (d, JCP = 12.0 Hz), 142.1 (d, JCP = 25.2 Hz), 133.1 (d, JCP = 1.4 Hz), 133.0, 132.49 (d, JCP = 2.8 Hz), 132.46 (d, JCP = 105.4 Hz), 131.9 (d, JCP = 10.9 Hz), 130.9 (d, JCP = 10.9 Hz), 129.5 (d, JCP = 9.6 Hz), 129.4, 128.8 (d, JCP = 13.1 Hz), 128.9 (d, JCP = 106.2 Hz), 128.3, 127.9, 126.5 (d, JCP = 10.5 Hz), 125.7 (d, JCP = 98.0 Hz), 52.0. 31P NMR (202 MHz, CDCl3): δ 35.7. IR (film) νmax: 3058, 2968, 1722, 1562, 1202 (P=O), 721, 549 cm⁻¹. HRMS: [M + H]+ m/z calcd for C22H13O3P: 361.0994, found: 361.0999.
Ethyl 1,3-diphenyl-1H-phosphindole-2-carboxylate 1-oxide (3K, CAS 1478604-03-3) \(^{2}\)

![Diagram](image)

White solid, 60% yield. \(^{1}\)H NMR (500 MHz, CDCl\(_{3}\)): \(\delta\) 7.79-7.74 (m, 2 H), 7.73-7.69 (m, 1 H), 7.55-7.47 (m, 6 H), 7.45-7.36 (m, 4 H), 7.22-7.19 (m, 1 H), 4.08-3.94 (m, 2 H), 0.95 (t, \(J = 7.1\) Hz, 3 H). \(^{13}\)C NMR (125 MHz, CDCl\(_{3}\)): \(\delta\) 156.2, 120.9 (P=O), 7.13, 131.8 Hz). \(^{13}\)C NMR (125 MHz, CDCl\(_{3}\)): \(\delta\) 164.0 (d, \(J_{CP} = 18.3\) Hz), 162.6 (d, \(J_{CP} = 12.5\) Hz), 142.3 (d, \(J_{CP} = 24.8\) Hz), 133.2, 133.1, 132.6 (d, \(J_{CP} = 106.1\) Hz), 132.5 (d, \(J_{CP} = 2.9\) Hz), 131.8 (d, \(J_{CP} = 10.6\) Hz), 131.1 (d, \(J_{CP} = 11.2\) Hz), 129.6 (d, \(J_{CP} = 9.3\) Hz), 129.4, 129.1 (d, \(J_{CP} = 106.4\) Hz), 128.8 (d, \(J_{CP} = 12.8\) Hz), 128.3, 128.0, 126.5 (d, \(J_{CP} = 10.7\) Hz), 126.4 (d, \(J_{CP} = 98.3\) Hz), 60.9, 13.7. \(^{31}\)P NMR (202 MHz, CDCl\(_{3}\)): \(\delta\) 35.8. MS-ESI: m/z 375 [M + H]\(^{+}\). IR (film) \(\nu_{max}\): 3048, 2981, 1716, 1562, 1208 (P=O), 752, 550 cm\(^{-1}\).

Ethyl 1-phenyl-3-(p-tolyl)-1H-phosphindole-2-carboxylate 1-oxide (3l, new compound)

![Diagram](image)

White solid, 61% yield. mp 159.0-159.8 °C. \(^{1}\)H NMR (500 MHz, CDCl\(_{3}\)): \(\delta\) 7.78-7.74 (m, 2 H), 7.73-7.69 (m, 1 H), 7.56-7.49 (m, 3 H), 7.46-7.42 (m, 2 H), 7.32-7.25 (m, 5 H), 4.11-3.96 (m, 2 H), 2.44 (s, 3 H), 0.97 (t, \(J = 7.1\) Hz, 3 H). \(^{13}\)C NMR (125 MHz, CDCl\(_{3}\)): \(\delta\) 164.5 (d, \(J_{CP} = 18.6\) Hz), 162.7 (d, \(J_{CP} = 12.0\) Hz), 142.5 (d, \(J_{CP} = 25.0\) Hz), 139.7, 133.1, 132.5 (d, \(J_{CP} = 2.7\) Hz), 131.9 (d, \(J_{CP} = 104.6\) Hz), 131.8 (d, \(J_{CP} = 10.7\) Hz), 131.2 (d, \(J_{CP} = 11.0\) Hz), 130.1 (d, \(J_{CP} = 12.8\) Hz), 129.3 (d, \(J_{CP} = 105.6\) Hz), 129.6 (d, \(J_{CP} = 9.7\) Hz), 129.1, 128.8 (d, \(J_{CP} = 12.8\) Hz), 128.2, 126.6 (d, \(J_{CP} = 10.4\) Hz), 125.9 (d, \(J_{CP} = 98.3\) Hz), 60.9, 21.6, 13.8. \(^{31}\)P NMR (202 MHz, CDCl\(_{3}\)): \(\delta\) 35.7. IR (film) \(\nu_{max}\): 3038, 2981, 1719, 1562, 1209 (P=O), 768, 562 cm\(^{-1}\). HRMS: [M + H]\(^{+}\) m/z calcd for C\(_{24}\)H\(_{21}\)O\(_{3}\)P: 389.1307, found: 389.1310.
**Ethyl 1-phenyl-3-(m-tolyl)-1H-phosphindole-2-carboxylate 1-oxide (3m, new compound)**

Yellow solid, 48% yield. mp 158.2-160.0 °C. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.80-7.78 (m, 2 H), 7.73-7.71 (m, 1 H), 7.57-7.51 (m, 3 H), 7.47-7.38 (m, 3 H), 7.30-7.29 (m, 1 H), 7.23-7.18 (m, 3 H), 4.11-3.96 (m, 2 H), 2.43 (s, 3 H), 0.97 (t, $J=7.1$ Hz, 3 H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 162.7 (d, $J_{C\beta}$ = 18.3 Hz), 162.7 (d, $J_{C\beta}$ = 12.3 Hz), 142.5 (d, $J_{C\beta}$ = 25.2 Hz), 139.1, 133.21, 133.19 (d, $J_{C\beta}$ = 1.5 Hz), 132.7 (d, $J_{C\beta}$ = 106.6 Hz), 132.5 (d, $J_{C\beta}$ = 3.4 Hz), 131.8 (d, $J_{C\beta}$ = 10.8 Hz), 131.2 (d, $J_{C\beta}$ = 10.9 Hz), 130.2, 129.6 (d, $J_{C\beta}$ = 9.5 Hz), 129.3 (d, $J_{C\beta}$ = 106.2 Hz), 128.8 (d, $J_{C\beta}$ = 12.9 Hz), 128.3, 126.6 (d, $J_{C\beta}$ = 10.7 Hz), 126.3 (d, $J_{C\beta}$ = 98.2 Hz), 60.9, 21.6, 13.8. $^{31}$P NMR (202 MHz, CDCl$_3$): $\delta$ 35.8. IR (film) $\nu_{max}$: 3038, 2920, 1718, 1559, 1211 (P=O), 751, 554 cm$^{-1}$. HRMS: [M + H]$^+$ m/z calcd for C$_{24}$H$_{21}$O$_3$P$^+$: 389.1307, found: 389.1300.

**Ethyl 3-(4-fluorophenyl)-1-phenyl-1H-phosphindole-2-carboxylate 1-oxide (3n, new compound)**

Yellow solid, 51% yield. mp 54.0-55.7 °C. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.77-7.72 (m, 3 H), 7.56-7.51 (m, 3 H), 7.45-7.38 (m, 4 H), 7.21-7.18 (m, 3 H), 4.10-3.95 (m, 2 H), 0.98 (t, $J=7.1$ Hz, 3 H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 163.4 (d, $J_{C\beta}$ = 249.7 Hz), 163.0 (d, $J=18.9$ Hz), 162.5 (d, $J=12.1$ Hz), 142.2 (d, $J=25.0$ Hz), 133.3 (d, $J=1.2$ Hz), 132.57 (d, $J_{C\beta}$ = 105.8 Hz), 132.58 (d, $J=2.6$ Hz), 132.0 (d, $J=10.7$ Hz), 131.2 (d, $J=11.0$ Hz), 130.2, 129.8 (d, $J=9.6$ Hz), 129.0 (d, $J_{C\beta}$ = 106.6 Hz), 128.9 (d, $J=11.3$, 3.5 Hz), 128.8 (d, $J=12.9$ Hz), 126.7 (d, $J_{C\beta}$ = 96.0 Hz), 126.3 (d, $J=10.5$ Hz), 115.6 (d, $J=21.8$ Hz), 61.1, 13.7. $^{31}$P NMR (202 MHz, CDCl$_3$): $\delta$ 35.8. IR (film) $\nu_{max}$: 3057, 2982, 1716, 1505, 1160 (P=O), 743, 561 cm$^{-1}$. HRMS: [M+H]$^+$ m/z calcd for C$_{23}$H$_{18}$FO$_3$P$^+$: 393.1056, found: 393.1052.
Ethyl 3-(4-bromophenyl)-1-phenyl-1H-phosphindole-2-carboxylate 1-oxide (3o, new compound)

White solid, 33% yield. mp 154.2-155.1 °C. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.76-7.71 (m, 3 H), 7.62-7.61 (m, 2 H), 7.53-7.43 (m, 5 H), 7.26-7.17 (m, 3 H), 4.07-3.96 (m, 2 H), 0.97 (t, $J$ = 6.8 Hz, 3 H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 162.6 (d, $J_{C-P}$ = 18.7 Hz), 162.3 (d, $J_{C-P}$ = 11.8 Hz), 141.8 (d, $J_{C-P}$ = 24.7 Hz), 133.2, 132.4 (d, $J_{C-P}$ = 103.6 Hz), 132.6 (d, $J_{C-P}$ = 2.2 Hz), 132.0 (d, $J_{C-P}$ = 10.6 Hz), 131.9 (d, $J_{C-P}$ = 13.4 Hz), 131.6, 131.1 (d, $J_{C-P}$ = 11.0 Hz), 129.74, 129.70 (d, $J_{C-P}$ = 9.2 Hz), 128.8 (d, $J_{C-P}$ = 106.4 Hz), 128.7 (d, $J_{C-P}$ = 12.8 Hz), 126.8 (d, $J_{C-P}$ = 97.4 Hz), 126.2 (d, $J_{C-P}$ = 10.4 Hz), 123.7, 61.0, 13.7. $^{31}$P NMR (202 MHz, CDCl$_3$): $\delta$ 35.9. IR (film) $\nu_{max}$: 3057, 2981, 1716, 1557, 1207 (P=O), 744, 550 cm$^{-1}$. HRMS: [M + H]$^+$ m/z calcd for C$_{23}$H$_{18}$BrO$_3$P$^+$ : 453.0255, found: 453.0260.

Ethyl 3-(4-methoxyphenyl)-1-phenyl-1H-phosphindole-2-carboxylate 1-oxide (3p, new compound)

Yellow solid, 53% yield. mp 137.0-137.7 °C. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.76-7.69 (m, 3 H), 7.51-7.26 (m, 8 H), 7.01 (m, $J$ = 7.8 Hz, 2 H), 4.09-3.95 (m, 2 H), 3.85 (s, 3 H), 0.96 (t, $J$ = 6.5 Hz, 3 H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 164.0 (d, $J_{C-P}$ = 18.6 Hz), 162.7 (d, $J_{C-P}$ = 12.0 Hz), 160.7, 142.4 (d, $J_{C-P}$ = 25.2 Hz), 133.0, 132.7 (d, $J_{C-P}$ = 105.2 Hz), 132.4 (d, $J_{C-P}$ = 2.5 Hz), 131.7 (d, $J_{C-P}$ = 10.6 Hz), 131.09 (d, $J_{C-P}$ = 11.0 Hz), 131.05, 129.5 (d, $J_{C-P}$ = 9.6 Hz), 129.3 (d, $J_{C-P}$ = 106.4 Hz), 128.7 (d, $J_{C-P}$ = 12.9 Hz), 126.5 (d, $J_{C-P}$ = 10.5 Hz), 125.3 (d, $J_{C-P}$ = 98.8 Hz), 124.8 (d, $J_{C-P}$ = 13.1 Hz), 113.7, 60.8, 55.4, 13.7. $^{31}$P NMR (202 MHz, CDCl$_3$): $\delta$ 35.4. IR (film) $\nu_{max}$: 3028, 2980, 1716, 1508, 1180 (P=O), 768, 552 cm$^{-1}$. HRMS: [M + H]$^+$ m/z calcd for C$_{24}$H$_{21}$O$_4$P$^+$ : 405.1256, found: 405.1251.
Ethyl 1-phenyl-3-(4-(trifluoromethyl)phenyl)-1H-phosphindole-2-carboxylate 1-oxide (3q, new compound)

White solid, 38% yield. Mp 177.6-178.8 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.78-7.71 (m, 5 H), 7.56-7.43 (m, 7 H), 7.11-7.10 (m, 1 H), 4.08-3.94 (m, 2 H), 0.95 (t, \(J = 7.1\) Hz, 3 H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 162.3 (d, \(J = 4.2\) Hz), 162.2 (d, \(J = 2.0\) Hz), 141.7 (d, \(J = 24.8\) Hz), 137.0 (d, \(J = 13.1\) Hz), 133.4 (d, \(J = 1.3\) Hz), 132.4 (d, \(J_{CP} = 106.1\) Hz), 132.7 (d, \(J = 2.7\) Hz), 132.2 (d, \(J = 10.9\) Hz), 131.3 (q, \(J_{CF} = 32.4\) Hz), 131.1 (d, \(J = 10.9\) Hz), 129.9 (d, \(J = 9.4\) Hz), 128.8 (d, \(J = 12.9\) Hz), 128.7 (d, \(J_{CP} = 106.6\) Hz), 128.5, 127.5 (d, \(J_{CP} = 96.9\) Hz), 126.2 (d, \(J = 10.6\) Hz), 125.4 (d, \(J = 2.9\) Hz), 123.9 (d, \(J_{CF} = 272.4\) Hz), 61.2, 13.6. \(^{31}\)P NMR (202 MHz, CDCl\(_3\)): \(\delta\) 35.8. IR (film) \(\nu_{max}\): 3028, 2968, 1716, 1324, 1206 (P=O), 768, 549 cm\(^{-1}\). HRMS: [M + H]\(^+\) m/z calcd for C\(_{24}\)H\(_{18}\)F\(_3\)O\(_2\)P\(^+\): 443.1024, found: 443.1028.

Diethyl (1-oxido-1,3-diphenyl-1H-phosphindol-2-yl)phosphonate (3r, CAS 1537189-12-0)

Colorless solid, 57% yield. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.80 (dd, \(J = 12.9, 7.6\) Hz, 2 H), 7.67-7.64 (m, 1 H), 7.52-7.42 (m, 10 H), 7.17-7.16 (m, 1 H), 3.93-3.78 (m, 3 H), 3.69-3.61 (m, 1 H), 1.05 (t, \(J = 7.0\) Hz, 3 H), 0.93 (t, \(J = 7.0\) Hz, 3 H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 167.0 (dd, \(J_{CP} = 13.1, 7.2\) Hz), 142.5 (dd, \(J_{CP} = 27.5, 20.8\) Hz), 133.9 (dd, \(J_{CP} = 104.8, 7.4\) Hz), 133.4 (dd, \(J_{CP} = 11.6, 3.3\) Hz), 133.0, 132.4 (d, \(J_{CP} = 3.0\) Hz), 131.3 (d, \(J_{CP} = 10.6\) Hz), 131.2 (d, \(J_{CP} = 11.0\) Hz), 129.7, 129.2 (d, \(J_{CP} = 9.8\) Hz), 129.0 (d, \(J_{CP} = 105.6\) Hz), 128.7 (d, \(J_{CP} = 12.8\) Hz), 128.4, 128.2, 125.9 (d, \(J_{CP} = 11.3\) Hz), 125.4 (dd, \(J_{CP} = 188.7, 80.5\) Hz), 62.3 (d, \(J_{CP} = 6.0\)Hz), 61.9 (d, \(J_{CP} = 5.8\) Hz), 16.0 (d, \(J_{CP} = 7.2\) Hz), 15.9(d, \(J_{CP} = 6.4\) Hz). \(^{31}\)P NMR (202 MHz, CDCl\(_3\)): \(\delta\) 40.8 (d, \(J = 39.7\) Hz), 11.2 (d, \(J = 39.7\) Hz). MS-ESI: m/z 439 [M + H]\(^+\). IR (film) \(\nu_{max}\): 3068, 2982, 1546, 1438, 1206 (P=O), 1111 (P=O), 721, 575 cm\(^{-1}\).
5-Chloro-1-(4-chlorophenyl)-2,3-diphenyl-1H-phosphindole 1-oxide compound with 6-chloro-1-(4-chlorophenyl)-2,3-diphenyl-1H-phosphindole 1-oxide (3s, 1:1, CAS 1478603-76-7, 1478603-73-4)

![Diagram]

White solid, 61% yield. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.71 (m, 5 H), 7.45-7.35 (m, 9 H), 7.31-7.30 (m, 3 H), 7.22-7.14 (m, 5 H), 7.11-7.09 (m, 4 H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 149.6 (d, $J_{CP} = 20.8$ Hz), 149.1 (d, $J_{CP} = 20.7$ Hz), 145.8 (d, $J_{CP} = 28.8$ Hz), 142.0 (d, $J_{CP} = 27.2$ Hz), 140.0 (d, $J_{CP} = 2.7$ Hz), 139.3 (d, $J_{CP} = 3.3$ Hz), 139.2 (d, $J_{CP} = 3.1$ Hz), 135.8, 135.7, 135.6 (d, $J_{CP} = 95.8$ Hz), 134.4-133.4 (m), 133.1 (d, $J_{CP} = 1.8$ Hz), 132.4 (d, $J_{CP} = 11.6$ Hz), 132.2 (d, $J_{CP} = 10.0$ Hz), 132.1, 130.2 (d, $J_{CP} = 10.8$ Hz), 127.7 (d, $J_{CP} = 101.6$ Hz), 125.4 (d, $J_{CP} = 11.8$ Hz), 124.7 (d, $J_{CP} = 11.7$ Hz).

$^{31}$P NMR (202 MHz, CDCl$_3$): $\delta$ 37.3 (s), 37.0.

Ethyl 1-ethyl-3-phenyl-1H-phosphindole-2-carboxylate 1-oxide (3t, new compound)

![Diagram]

White solid, 63% yield. Mp 139.7-140.0 °C. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.83 (t, $J = 8.0$ Hz, 1 H), 7.55-7.51 (m, 1 H), 7.48-7.47 (m, 4H), 7.33-7.27 (m, 2 H), 7.14-7.12 (m, 1 H), 4.23-4.10 (m, 2 H), 2.49-2.22 (m, 2 H), 1.16-1.04 (m, 6 H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 163.2 (d, $J_{CP} = 3.1$ Hz), 163.1 (d, $J_{CP} = 7.4$ Hz), 141.9 (d, $J_{CP} = 23.6$ Hz), 133.3 (d, $J_{CP} = 11.9$ Hz), 133.0, 131.4 (d, $J_{CP} = 10.1$ Hz), 131.1 (d, $J_{CP} = 99.5$ Hz), 129.2, 129.0 (d, $J_{CP} = 9.3$ Hz), 128.3, 128.0, 126.4 (d, $J_{CP} = 9.8$ Hz), 124.7 (d, $J_{CP} = 93.5$ Hz), 61.1, 22.1 (d, $J_{CP} = 71.6$ Hz), 14.0, 6.2 (d, $J_{CP} = 3.7$ Hz). $^{31}$P NMR (202 MHz, CDCl$_3$): $\delta$ 49.9. IR (film) $\nu_{\max}$: 3392, 2919, 1720, 1645, 1195 (P=O), 766, 700 cm$^{-1}$. HRMS: [M + H]$^+$ m/z calcd for C$_{19}$H$_{19}$O$_3$P$^+$: 372.1150, found: 372.1145.
Diethyl 3,3’-(1,4-phenylene)bis(1-phenyl-1H-phosphindole-2-carboxylate 1-oxide) (3u, CAS 1478604-30-6)²

White solid, 40 % yield. ¹H NMR (500 MHz, CDCl₃): δ 7.80-7.74 (m, 6 H), 7.58-7.55 (m, 10 H), 7.48-7.45 (m, 4 H), 7.33-7.30 (m, 2 H), 4.14-4.01 (m, 4 H), 1.02 (td, J = 7.1, 3.7 Hz, 6 H).

¹³C NMR (125 MHz, CDCl₃): δ 163.2 (d, Jₑ₋ₑ = 18.7 Hz), 162.6 (dd, Jₑ₋ₑ = 11.7, 8.2 Hz), 142.0 (dd, Jₑ₋ₑ = 24.7, 3.9 Hz), 134.3 (dd, Jₑ₋ₑ = 25.2, 2.6 Hz), 133.4, 132.65 (d, Jₑ₋ₑ = 2.4 Hz), 132.62 (d, Jₑ₋ₑ = 106.1 Hz), 132.1 (d, Jₑ₋ₑ = 11.0 Hz), 131.2 (d, Jₑ₋ₑ = 11.0 Hz), 129.9 (dd, Jₑ₋ₑ = 9.2, 1.7 Hz), 129.0 (d, Jₑ₋ₑ = 106.4 Hz), 128.9 (dd, Jₑ₋ₑ = 12.9, 1.7 Hz), 128.2, 127.4 (d, Jₑ₋ₑ = 7.6 Hz), 127.0 (d, Jₑ₋ₑ = 90.1 Hz), 126.6 (dd, Jₑ₋ₑ = 11.0, 5.1Hz), 61.2, 13.8. ³¹P NMR (202 MHz, CDCl₃): δ 35.7. MS-ESI: m/z 671 [M + H]⁺. IR (film) νmax: 3050, 2982, 1719, 1438, 1206 (P=O), 1113 (P=O), 724, 551 cm⁻¹.

6. References
7. NMR Spectra of the Compounds of 3a-3u

$^1$H NMR spectrum of compound 3a.

$^{13}$C NMR spectrum of compound 3a.
$^{31}$P NMR spectrum of compound 3a.

$^1$H NMR spectrum of compound 3b.
$^{13}$C NMR spectrum of compound 3b.

$^{31}$P NMR spectrum of compound 3b.
$^{1}H$ NMR spectrum of compound 3c.

$^{13}C$ NMR spectrum of compound 3c.
$^{31}$P NMR spectrum of compound 3c.

$^1$H NMR spectrum of compound 3d.
13C NMR spectrum of compound 3d.

31P NMR spectrum of compound 3d.
\(^1\)H NMR spectrum of compound 3e.

\(^{13}\)C NMR spectrum of compound 3e.
The 31P NMR spectrum of compound 3e.

The 1H NMR spectrum of compound 3f.
$^{13}$C NMR spectrum of compound 3f.

$^{31}$P NMR spectrum of compound 3f.
$^1$H NMR spectrum of compound 3g.

$^{13}$C NMR spectrum of compound 3g.
$^{31}$P NMR spectrum of compound 3g.

$^1$H NMR spectrum of compound 3h.
$^{13}$C NMR spectrum of compound 3h.

$^{31}$P NMR spectrum of compound 3h.
$^1$H NMR spectrum of compound 3i.

$^{13}$C NMR spectrum of compound 3i.
\[ \text{\textsuperscript{31}P NMR spectrum of compound 3i.} \]

\[ \text{\textsuperscript{1}H NMR spectrum of compound 3j.} \]
$^{13}$C NMR spectrum of compound 3j.

$^{31}$P NMR spectrum of compound 3j.
$^1$H NMR spectrum of compound 3k.

$^{13}$C NMR spectrum of compound 3k.
$^{31}$P NMR spectrum of compound 3k.

$^1$H NMR spectrum of compound 3l.
\textsuperscript{13}C NMR spectrum of compound 3l.

\textsuperscript{31}P NMR spectrum of compound 3l.
$^1$H NMR spectrum of compound 3m.

$^{13}$C NMR spectrum of compound 3m.
$^3$P NMR spectrum of compound 3m.

$^1$H NMR spectrum of compound 3n.
$^{13}$C NMR spectrum of compound 3n.

$^{31}$P NMR spectrum of compound 3n.
\[ \text{H NMR spectrum of compound 3o.} \]

\[ \text{\(^1\)H NMR spectrum of compound 3o.} \]

\[ \text{\(^{13}\)C NMR spectrum of compound 3o.} \]
$^{31}$P NMR spectrum of compound 3o.

$^1$H NMR spectrum of compound 3p.
$^{13}$C NMR spectrum of compound 3p.

$^{31}$P NMR spectrum of compound 3p.
$^1$H NMR spectrum of compound 3q.

$^{13}$C NMR spectrum of compound 3q.
$^{31}\text{P}$ NMR spectrum of compound 3q.

$^1\text{H}$ NMR spectrum of compound 3r.
\[ \text{\(^{13}\)C NMR spectrum of compound 3r.} \]

\[ \text{\(^{31}\)P NMR spectrum of compound 3r.} \]
$^1$H NMR spectrum of compound 3s.

$^{13}$C NMR spectrum of compound 3s.
$^{31}$P NMR spectrum of compound 3s.

$^1$H NMR spectrum of compound 3t.
$^{13}$C NMR spectrum of compound $3t$.

$^{31}$P NMR spectrum of compound $3t$. 
$^1$H NMR spectrum of compound 3u.

$^{13}$C NMR spectrum of compound 3u.
31P NMR spectrum of compound 3u.