Supporting Information

Copper-Catalyzed P-H Insertions of α-Imino Carbenes for the Preparation of 3-Phosphinoylindoles


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General Remarks and Materials:

All $^1$H NMR, and $^{13}$C NMR spectra were recorded using a Brucker 600 MHz spectrometer in CDCl$_3$. Tetramethylsilane (TMS) served as an internal standard (δ = 0) for $^1$H NMR, and CDCl$_3$ was used as internal standard (δ = 77.0) for $^{13}$C NMR. $^{31}$P NMR spectra and $^{19}$F NMR were recorded on the same instrument. Chemical shifts are reported in parts per million as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad). HRMS (ESI) Mass spectra were recorded on Thermo Fisher Scientific LTQ FT Ultra. The starting materials were purchased from Aldrich, Macklin and Energy Chemicals used without further purification. Solvents were dried and purified according to the procedure from “Purification of Laboratory Chemicals book”. Column chromatography was carried out on silica gel (particle size 200-300 mesh ASTM). Substrates 1 were prepared according to the published procedures$^1$.

General Procedures

General Procedure for Optimization of Reaction Conditions (Table 1 and Table S1):
A solution of the 1a (65.2 mg, 0.2 mmol) in 0.4 mL CHCl$_3$ was slowly added to a mixture solution of 2a (40.4 mg, 0.2 mmol) and catalyst (0.01 mmol) in 0.4 mL CHCl$_3$. The reaction mixture under an argon atmosphere was stirred under the indicated temperature in table 1. Upon completion, the solvent was removed in vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 3:1) to give the product 3a.

Table S1. Optimization of the Reaction Conditions$^a$

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$^a$
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* Reaction conduction: 1a (0.2 mmol), 2a (0.2 mmol), catalyst (0.01 mmol), solvent (0.8 mL). * Isolated yield. * catalyst (0.001 mol). * The reaction was carried out for 24 h. * catalyst (0.002 mol). * catalyst (0.006 mol).

**General procedure for the synthesis of compounds 3a-t (Scheme 2, Scheme 3):**
A solution of the 1 (0.2 mmol) in 0.4 mL CHCl$_3$ was slowly added to a mixture solution of 2 (0.2 mmol) and Cu(CH$_3$CN)$_4$PF$_6$ (0.01 mmol) in 0.4 mL CHCl$_3$. The reaction mixture under an argon atmosphere was stirred for 1 hour at 50 °C. Upon completion, the solvent was removed in vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 3:1) to give the product 3.

**A typical procedure for the preparation of optically pure H-phosphinates 4:**
The mixture of (L)-(−)-menthol (100 g, 641 mmol) and pyridine (51.3 mL, 641 mmol) in Et$_2$O (200 mL) was added dropwise with stirring to a PhPCl$_2$ (87.2 mL, 641 mmol) solution in Et$_2$O (400 mL) at 0°C and then stirred at room temperature overnight. Water (12 mL, 667 mmol) was added, and the reaction mixture was washed with water and extracted with hexane. The hexane layer was dried over magnesium sulfate, filtered, and concentrated. Recrystallization of the mixture in hexane (twice) at -30 °C gave pure H-Phosphinates 4 a white crystal (66.4 g) in 37% yield (RP/SP>99/1).

**General procedure for stereoselective synthesis of chiral 3-methoxyl-arylphosphoinoles 5a-f (Scheme 4):**
A solution of the 1 (0.2 mmol) in 0.4 mL CHCl$_3$ was slowly added to a mixture solution of optically pure H-Phosphinate (56.0 mg, 0.2 mmol) and Cu(CH$_3$CN)$_4$PF$_6$ (7.5 mg, 0.02 mmol) in 0.4 mL CHCl$_3$. The reaction mixture was stirred for 8 hours at 50 °C. Upon completion, the solvent
was removed in vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 6:1) to give the product 5.

**General procedure for the synthesis of 2-free amino indole 6:**

\[
\begin{align*}
\text{Ph}_2\text{P=O} & \quad \text{H}_2\text{SO}_4 \quad 2\text{h} \quad \text{Me} \\
\text{NHTs} & \quad \rightarrow \\
\text{Ph}_2\text{P=O} & \quad \text{Me} \\
\text{N}\text{H}_2
\end{align*}
\]

To 3a (50 mg, 0.1 mmol) was added cold 18 M H\textsubscript{2}SO\textsubscript{4} (0.5 mL) slowly at 0 °C and stirred at room temperature for 2 hours. The reaction mixture was cooled to 0 °C and quenched by cool water (50 mL) and then saturated aqueous NaHCO\textsubscript{3} (10 mL) slowly, extracted with CHCl\textsubscript{3} (20 mL × 3), dried over Na\textsubscript{2}SO\textsubscript{4} and concentrated under vacuum. The residue was purified by column chromatography (DCM/CH\textsubscript{3}OH 3:1) on silica gel to give 2-free amino indole 6 (31.4 mg) in 91% yield.

**References:**

Analysis data of new compounds:

(3a): White solid; 82.0 mg; yield: 82%; $^1$H NMR (600 MHz, Chloroform-d) δ 10.21 (s, 1H), 7.51–7.46 (m, 3H), 7.43 (d, $J = 8.3$ Hz, 1H), 7.41–7.30 (m, 8H), 7.29–7.25 (m, 1H), 6.99 (t, $J = 7.6$ Hz, 1H), 6.78 (d, $J = 8.0$ Hz, 1H), 6.73 (d, $J = 8.1$ Hz, 2H), 4.03 (s, 3H), 2.08 (s, 3H); $^{13}$C NMR (151 MHz, Chloroform-d) δ 143.65, 143.15 (d, $J = 12.5$ Hz), 136.75 (d, $J = 11.2$ Hz), 134.23, 133.29 (d, $J = 109.5$ Hz), 131.73 (d, $J = 2.7$ Hz), 131.39 (d, $J = 11.0$ Hz), 129.03, 128.26 (d, $J = 12.7$ Hz), 128.01, 126.97 (d, $J = 9.9$ Hz), 122.56, 121.73, 119.75, 110.61, 90.24 (d, $J = 125.1$ Hz), 32.40, 21.70, 14.40; $^{31}$P NMR (243 MHz, CDCl$_3$) δ 28.18; HRMS (ESI) Calcd. for C$_{28}$H$_{26}$N$_2$O$_3$PS (M+H)$^+$ 501.1396, Found: 501.1395.

(3b): White solid; 78.1 mg; yield: 76%; $^1$H NMR (600 MHz, Chloroform-d) δ 10.24 (s, 1H), 7.55–7.47 (m, 5H), 7.40–7.30 (m, 8H), 7.24 (t, $J = 7.4$ Hz, 1H), 6.99–6.94 (m, 1H), 6.76 (d, $J = 8.0$ Hz, 1H), 6.72 (d, $J = 8.0$ Hz, 2H), 4.71–4.63 (m, 2H), 2.07 (s, 3H), 1.56 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (151 MHz, Chloroform-d) δ 143.61, 142.63 (d, $J = 12.3$ Hz), 135.74 (d, $J = 11.2$ Hz), 134.12, 133.31 (d, $J = 109.5$ Hz), 131.72 (d, $J = 2.7$ Hz), 131.42 (d, $J = 11.0$ Hz), 128.99, 128.26 (d, $J = 12.6$ Hz), 128.11, 127.49 (d, $J = 9.9$ Hz), 122.45, 121.56, 119.96, 111.20, 90.69 (d, $J = 124.5$ Hz), 40.18, 21.70, 14.40; $^{31}$P NMR (243 MHz, CDCl$_3$) δ 28.33; HRMS (ESI) Calcd. for C$_{29}$H$_{28}$N$_2$O$_3$PS (M+H)$^+$ 515.1553, Found: 515.1553.

(3c): White solid; 74.9 mg; yield: 71%; $^1$H NMR (600 MHz, Chloroform-d) δ 10.27 (s, 1H), 7.72 (d, $J = 8.4$ Hz, 1H), 7.55–7.45 (m, 4H), 7.40–7.30 (m, 8H), 7.20 (t, $J = 7.5$ Hz, 1H), 6.94 (t, $J = 7.6$ Hz, 1H), 6.77 (d, $J = 8.0$ Hz, 1H), 6.71 (d, $J = 8.0$ Hz, 2H), 5.61–5.51 (m, 1H), 2.07 (s, 3H), 1.76 (d, $J = 7.0$ Hz, 6H); $^{13}$C NMR
(151 MHz, Chloroform-d) δ 143.58, 142.44 (d, J = 12.3 Hz), 134.34 (d, J = 11.0 Hz), 134.05, 133.33 (d, J = 109.5 Hz), 131.67 (d, J = 2.6 Hz), 131.43 (d, J = 10.9 Hz), 128.97, 128.28, 128.20, 128.11, 121.89, 121.14, 120.26, 113.48, 90.35 (d, J = 124.8 Hz), 49.24, 21.71, 21.21; $^{31}$P NMR (243 MHz, CDCl$_3$) δ 28.37; HRMS (ESI) Calcd. for C$_{30}$H$_{30}$N$_2$O$_3$PS (M+H)$^+$ 529.1709, Found: 529.1711.

(3d): Yellow solid; 83.1 mg; yield: 79%; $^1$H NMR (600 MHz, Chloroform-d) δ 10.26 (s, 1H), 7.56–7.46 (m, 5H), 7.41–7.31 (m, 8H), 7.21 (t, J = 7.7 Hz, 1H), 6.96 (t, J = 7.6 Hz, 1H), 6.76 (d, J = 8.0 Hz, 1H), 6.72 (d, J = 8.1 Hz, 2H), 6.17–6.08 (m, 1H), 5.31 (d, J = 11.1 Hz, 1H), 5.25–5.19 (m, 3H), 2.07 (s, 3H); $^{13}$C NMR (151 MHz, Chloroform-d) δ 143.66, 142.85 (d, J = 12.4 Hz), 136.43 (d, J = 11.1 Hz), 134.04, 133.53, 133.22 (d, J = 109.6 Hz), 131.76 (d, J = 2.7 Hz), 131.40 (d, J = 10.9 Hz), 129.00, 128.29 (d, J = 12.7 Hz), 128.14, 127.30 (d, J = 9.8 Hz), 122.52, 121.74, 119.84, 117.45, 111.91, 91.00 (d, J = 123.9 Hz), 48.15, 21.70; $^{31}$P NMR (243 MHz, CDCl$_3$) δ 28.27; HRMS (ESI) Calcd. for C$_{30}$H$_{28}$N$_2$O$_3$PS (M+H)$^+$ 527.1553, Found: 527.1551.

(3e): Yellow solid; 66.8 mg; yield: 58%; $^1$H NMR (600 MHz, Chloroform-d) δ 10.31 (s, 1H), 7.58–7.49 (m, 4H), 7.45–7.34 (m, 8H), 7.34–7.30 (m, 2H), 7.29–7.24 (m, 2H), 7.17–7.09 (m, 3H), 6.94 (t, J = 7.5 Hz, 1H), 6.78 (d, J = 8.0 Hz, 1H), 6.75 (d, J = 8.1 Hz, 2H), 5.88 (s, 2H), 2.09 (s, 3H); $^{13}$C NMR (151 MHz, Chloroform-d) δ 143.72, 143.31 (d, J = 12.4 Hz), 136.88 , 136.14 (d, J = 11.0 Hz), 134.12, 133.25 (d, J = 109.6 Hz), 131.81 (d, J = 2.6 Hz), 131.42 (d, J = 10.9 Hz), 129.04, 128.62, 128.34 (d, J = 12.7 Hz), 128.21, 127.47, 127.41, 126.74, 122.69, 121.82, 119.93, 112.07, 91.56 (d, J = 123.4 Hz), 48.82, 21.73; $^{31}$P NMR (243 MHz, CDCl$_3$) δ 28.31; HRMS (ESI) Calcd. for C$_{34}$H$_{30}$N$_2$O$_3$PS (M+H)$^+$ 577.1709, Found: 577.1708.
(3f): Yellow solid; 76.8 mg; yield: 74%; \(^1H\) NMR (600 MHz, Chloroform-\(d\)) \(\delta\) 10.19 (s, 1H), 7.53–7.48 (m, 4H), 7.37–7.32 (m, 9H), 7.02–6.95 (m, 1H), 6.75 (d, \(J = 8.0\) Hz, 2H), 6.38 (dd, \(J = 9.5, 2.5\) Hz, 1H), 4.01 (s, 3H), 2.09 (s, 3H); \(^{13}C\) NMR (151 MHz, Chloroform-\(d\)) \(\delta\) 158.70 (d, \(J = 237.6\) Hz), 144.12 (d, \(J = 12.4\) Hz), 143.77, 134.25, 133.19, 132.91 (d, \(J = 109.5\) Hz), 131.91 (d, \(J = 2.7\) Hz), 131.33 (d, \(J = 10.9\) Hz), 129.07, 128.38 (d, \(J = 12.7\) Hz), 127.95, 127.42 (t, \(J = 10.0\) Hz), 111.49 (d, \(J = 9.7\) Hz), 110.87 (d, \(J = 26.0\) Hz), 105.07 (d, \(J = 25.0\) Hz), 90.51 (d, \(J = 129.3\) Hz), 32.65, 21.70; \(^{31}P\) NMR (243 MHz, CDCl\(_3\)) \(\delta\) 27.89; \(^{19}F\) NMR (565 MHz, CDCl\(_3\)) \(\delta\) -12.09; HRMS (ESI) Calcd. for C\(_{28}\)H\(_{25}\)FN\(_2\)O\(_3\)PS (M+H)\(^+\) 519.1302, Found:519.1302.

(3g): Yellow solid; 69.4 mg; yield: 65%; \(^1H\) NMR (600 MHz, Chloroform-\(d\)) \(\delta\) 10.23 (s, 1H), 7.56–7.47 (m, 4H), 7.39–7.31 (m, 9H), 7.20 (dd, \(J = 8.7, 2.0\) Hz, 1H), 6.75 (d, \(J = 8.0\) Hz, 2H), 6.68 (d, \(J = 1.9\) Hz, 1H), 4.01 (s, 3H), 2.09 (s, 3H); \(^{13}C\) NMR (151 MHz, Chloroform-\(d\)) \(\delta\) 144.10 (d, \(J = 12.3\) Hz), 143.80, 135.16 (d, \(J = 10.9\) Hz), 134.21, 132.86 (d, \(J = 109.8\) Hz), 131.95 (d, \(J = 2.7\) Hz), 131.33 (d, \(J = 11.0\) Hz), 129.09, 128.41 (d, \(J = 12.7\) Hz), 127.95, 127.91, 127.51, 122.98, 119.02, 111.67, 90.21 (d, \(J = 124.2\) Hz), 32.63, 21.70; \(^{31}P\) NMR (243 MHz, CDCl\(_3\)) \(\delta\) 27.80; HRMS (ESI) Calcd. for C\(_{28}\)H\(_{25}\)ClN\(_2\)O\(_3\)PS (M+H)\(^+\) 535.1007, Found:535.1005.

(3h): Yellow solid; 68.2 mg; yield: 59%; \(^1H\) NMR (600 MHz, Chloroform-\(d\)) \(\delta\) 10.25 (s, 1H), 7.56–7.47 (m, 4H), 7.40–7.31 (m, 10H), 6.83 (d, \(J = 1.8\) Hz, 1H), 6.75 (d, \(J = 8.0\) Hz, 2H), 4.00 (s, 3H), 2.09 (s, 3H); \(^{13}C\) NMR (151 MHz, Chloroform-\(d\)) \(\delta\) 143.99 (d, \(J = 12.3\) Hz), 143.80, 135.46 (d, \(J = 10.9\) Hz), 134.24, 132.86 (d, \(J = 109.9\) Hz), 131.95 (d, \(J = 2.7\) Hz), 131.33 (d, \(J = 11.0\) Hz), 129.09, 128.53 (d, \(J = 9.5\) Hz), 128.41 (d, \(J = 12.7\) Hz), 127.94, 125.57, 122.04, 115.09, 112.07, 90.16 (d, \(J = 124.4\) Hz), 32.60, 21.71;
\[^{31}\text{P NMR}\] (243 MHz, CDCl\(_3\)) \(\delta\) 27.79; \[\text{HRMS (ESI) Calcd. for C}_{28}\text{H}_{25}\text{BrN}_{2}\text{O}_{3}\text{PS} (\text{M+H})^+ 579.0501, \text{Found:} 579.0501.\]

(3i): Yellow solid; 54.5 mg; yield: 53%; \[^1\text{H NMR}\] (600 MHz, Chloroform-\(d\)) \(\delta\) 10.19 (s, 1H), 7.54–7.45 (m, 4H), 7.41–7.29 (m, 9H), 7.08 (d, \(J = 8.4\) Hz, 1H), 6.73 (d, \(J = 8.1\) Hz, 2H), 6.54 – 6.51 (m, 1H), 4.00 (s, 3H), 2.22 (s, 3H), 2.08 (s, 3H); \[^{13}\text{C NMR}\] (151 MHz, Chloroform-\(d\)) \(\delta\) 143.58, 142.99 (d, \(J = 12.7\) Hz), 135.06 (d, \(J = 11.4\) Hz), 134.26, 133.36 (d, \(J = 109.4\) Hz), 131.67 (d, \(J = 2.7\) Hz), 131.41 (d, \(J = 10.9\) Hz), 131.17, 129.01, 128.23 (d, \(J = 12.6\) Hz), 128.00, 127.19 (d, \(J = 9.8\) Hz), 124.07, 119.50, 110.25, 89.58 (d, \(J = 125.5\) Hz), 32.40, 21.69, 21.53; \[^{31}\text{P NMR}\] (243 MHz, CDCl\(_3\)) \(\delta\) 28.39; \[\text{HRMS (ESI) Calcd. for C}_{29}\text{H}_{28}\text{N}_{2}\text{O}_{3}\text{PS} (\text{M+H})^+ 515.1553, \text{Found:} 515.1552.\]

(3j): Yellow solid; 73.3 mg; yield: 65%; \[^1\text{H NMR}\] (600 MHz, Chloroform-\(d\)) \(\delta\) 10.31 (s, 1H), 7.55 (m, 2H), 7.49–7.43 (m, 3H), 7.40–7.35 (m, 8H), 7.30–7.27 (m, 1H), 7.06–7.03 (m, 2H), 7.02–6.99 (m, 1H), 6.79 (d, \(J = 8.0\) Hz, 1H), 4.02 (s, 3H); \[^{13}\text{C NMR}\] (151 MHz, Chloroform-\(d\)) \(\delta\) 142.44 (d, \(J = 12.5\) Hz), 136.72 (d, \(J = 11.1\) Hz), 136.21, 132.97 (d, \(J = 109.7\) Hz), 132.22 (d, \(J = 2.7\) Hz), 131.64, 131.21 (d, \(J = 11.0\) Hz), 129.55, 128.55, 128.46, 126.88 (d, \(J = 9.8\) Hz), 122.81, 121.93, 119.83, 110.68, 90.71 (d, \(J = 124.5\) Hz), 32.36; \[^{31}\text{P NMR}\] (243 MHz, CDCl\(_3\)) \(\delta\) 28.39; \[\text{HRMS (ESI) Calcd. for C}_{29}\text{H}_{28}\text{N}_{2}\text{O}_{3}\text{PS} (\text{M+H})^+ 565.0345, \text{Found:} 565.0344.\]

(3k): Yellow solid; 77.5 mg; yield: 70%; \[^1\text{H NMR}\] (600 MHz, Chloroform-\(d\)) \(\delta\) 10.44 (s, 1H), 7.80–7.78 (m, 2H), 7.52–7.48 (m, 2H), 7.47–7.44 (m, 1H), 7.39–7.32 (m, 8H), 7.31–7.27 (m, 1H), 7.22 (d, \(J = 8.3\) Hz, 2H).
Hz, 2H), 7.01 (t, J = 7.6 Hz, 1H), 6.79 (d, J = 8.0 Hz, 1H), 4.04 (s, 3H); $^{13}$C NMR (151 MHz, Chloroform-$d$) δ 142.16 (d, J = 12.2 Hz), 140.95, 136.73 (d, J = 11.1 Hz), 134.51, 134.29, 133.11 (d, J = 109.8 Hz), 132.24 (d, J = 2.7 Hz), 131.18 (d, J = 11.0 Hz), 128.75, 128.44 (d, J = 12.7 Hz), 126.80 (d, J = 9.7 Hz), 125.38 (d, J = 3.7 Hz), 122.91, 122.00, 119.87, 110.71, 90.73 (d, J = 124.1 Hz), 32.40; $^{31}$P NMR (243 MHz, CDCl$_3$) δ 28.53; $^{19}$F NMR (565 MHz, CDCl$_3$) δ 062.87; HRMS (ESI) Calcd. for C$_{28}$H$_{23}$F$_{3}$N$_{2}$O$_{3}$PS (M+H)$^+$ 555.1114, Found:555.1113.

(3l): White solid; 107.7 mg; yield: 88%; $^1$H NMR (600 MHz, Chloroform-$d$) δ 10.45 (s, 1H), 7.55–7.46 (m, 6H), 7.41 (d, J = 8.3 Hz, 1H), 7.38–7.33 (m, 4H), 7.24 (t, J = 7.4 Hz, 1H), 7.07 (s, 2H), 7.02–6.98 (m, 1H), 6.85 (d, J = 8.0 Hz, 1H), 3.96 (s, 3H), 3.94–3.87 (m, 2H), 2.90–2.85 (m, 1H), 1.25 (d, J = 6.9 Hz, 6H), 1.11 (d, J = 6.7 Hz, 12H); $^{13}$C NMR (151 MHz, Chloroform-$d$) δ 153.04, 151.11, 143.58 (d, J = 12.6 Hz), 136.62 (d, J = 11.3 Hz), 133.62, 133.04 (d, J = 42.4 Hz), 131.83 (d, J = 2.7 Hz), 131.66 (d, J = 11.0 Hz), 128.28 (d, J = 12.6 Hz), 127.06 (d, J = 10.0 Hz), 123.85, 122.29, 121.59, 119.57, 110.29, 90.31 (d, J = 125.9 Hz), 33.96, 32.23, 30.51, 24.81, 23.48; $^{31}$P NMR (243 MHz, CDCl$_3$) δ 28.55; HRMS (ESI) Calcd. for C$_{36}$H$_{42}$N$_{2}$O$_{3}$PS (M+H)$^+$ 613.2646, Found:613.2646.

(3m): White solid; 74.9 mg; yield: 71%; $^1$H NMR (600 MHz, Chloroform-$d$) δ 10.41 (s, 1H), 7.55–7.49 (m, 2H), 7.45–7.35 (m, 3H), 7.26–7.14 (m, 3H), 7.07–7.01 (m, 2H), 6.88 (m, 3H), 6.66 (d, J = 8.0 Hz, 2H), 6.48 (d, J = 8.0 Hz, 1H), 4.04 (s, 3H), 2.36 (s, 6H), 2.05 (s, 3H); $^{13}$C NMR (151 MHz, Chloroform-$d$) δ 143.39, 142.89 (d, J = 12.9 Hz), 136.50 (d, J = 10.9 Hz), 134.53, 132.20, 131.73, 131.54, 128.80, 127.84, 126.84 (d, J = 9.4 Hz), 125.39 (d, J = 13.7 Hz), 122.48, 121.62, 119.44, 110.34, 90.60 (d, J = 123.3 Hz), 32.04, 21.70, 21.14; $^{31}$P NMR (243 MHz, CDCl$_3$) δ 33.51; HRMS (ESI) Calcd. for C$_{36}$H$_{38}$N$_{2}$O$_{3}$PS (M+H)$^+$ 529.1709, Found:529.1707.
(3n): White solid; 61.1 mg; yield: 57%; $^1$H NMR (600 MHz, Chloroform-<i>d</i>) δ 10.04 (s, 1H), 7.51–7.44 (m, 3H), 7.40–7.33 (m, 4H), 7.31–7.26 (m, 1H), 7.07–6.98 (m, 5H), 6.78 (d, <i>J</i> = 8.1 Hz, 2H), 6.71 (d, <i>J</i> = 8.0 Hz, 1H), 4.03 (s, 3H), 2.13 (s, 3H); $^{13}$C NMR (151 MHz, Chloroform-<i>d</i>) δ 164.92 (dd, <i>J</i> = 253.8, 3.1 Hz), 143.89, 143.15 (d, <i>J</i> = 12.8 Hz), 136.76 (d, <i>J</i> = 11.3 Hz), 134.31, 133.89 (dd, <i>J</i> = 12.6, 8.8 Hz), 129.24 (d, <i>J</i> = 107.0 Hz), 128.98, 128.05, 126.71 (d, <i>J</i> = 10.0 Hz), 126.37, 122.42 (d, <i>J</i> = 118.5 Hz), 119.34, 115.76 (dd, <i>J</i> = 21.4, 13.9 Hz), 110.85, 89.92 (d, <i>J</i> = 127.5 Hz), 32.44, 21.50; $^{31}$P NMR (243 MHz, CDCl<sub>3</sub>) δ 26.34; $^{19}$F NMR (565 MHz, CDCl<sub>3</sub>) δ 0106.27; HRMS (ESI) Calcd. for C<sub>28</sub>H<sub>24</sub>F<sub>2</sub>N<sub>2</sub>O<sub>3</sub>PS (M+H)<sup>+</sup> 537.1208, Found:537.1207.

(3o): White solid; 132.8 mg; yield: 86%; $^1$H NMR (600 MHz, Chloroform-<i>d</i>) δ 9.48 (s, 1H), 8.06 (s, 2H), 7.91–7.80 (m, 4H), 7.59–7.47 (m, 3H), 7.38 (t, <i>J</i> = 7.8 Hz, 1H), 7.13 (t, <i>J</i> = 7.3 Hz, 1H), 6.79 (d, <i>J</i> = 8.0 Hz, 2H), 6.70 (d, <i>J</i> = 8.0 Hz, 1H), 4.09 (s, 3H), 1.98 (s, 3H); $^{13}$C NMR (151 MHz, Chloroform-<i>d</i>) δ 144.03 (d, <i>J</i> = 13.8 Hz), 143.80, 136.90 (d, <i>J</i> = 12.2 Hz), 136.03, 135.31, 134.15, 132.63 (d, <i>J</i> = 13.0 Hz), 132.40 (d, <i>J</i> = 12.8 Hz), 132.17 (d, <i>J</i> = 12.8 Hz), 131.05 (d, <i>J</i> = 11.8 Hz), 128.98, 128.21, 126.15, 125.76 (d, <i>J</i> = 10.4 Hz), 123.79, 123.40, 123.12, 121.59, 118.15, 111.66, 86.41 (d, <i>J</i> = 132.6 Hz), 32.66, 21.13; $^{31}$P NMR (243 MHz, CDCl<sub>3</sub>) δ 23.60; $^{19}$F NMR (565 MHz, CDCl<sub>3</sub>) δ -63.15; HRMS (ESI) Calcd. for C<sub>32</sub>H<sub>22</sub>F<sub>12</sub>N<sub>2</sub>O<sub>3</sub>PS (M+H)<sup>+</sup> 773.0892, Found:773.0891.

(3p): Yellow solid; 98.6 mg; yield: 88%; $^1$H NMR (600 MHz, Chloroform-<i>d</i>) δ 10.38 (s, 1H), 7.53–7.50 (m, 2H), 7.42 (d, <i>J</i> = 8.3 Hz, 1H), 7.31–7.23 (m, 5H), 6.99 (t, <i>J</i> = 7.6 Hz, 1H), 6.84–6.81 (m, 4H), 6.79–6.76 (m, 3H), 4.01 (s, 3H),
3.83 (s, 6H), 2.10 (s, 3H); $^{13}$C NMR (151 MHz, Chloroform-$d$) δ 162.18, 143.60, 142.93 (d, $J = 12.6$ Hz), 136.72 (d, $J = 11.1$ Hz), 134.29, 133.28 (d, $J = 12.4$ Hz), 128.95, 128.06, 127.05 (d, $J = 9.6$ Hz), 125.18 (d, $J = 116.1$ Hz), 122.39, 121.58, 119.79, 113.71 (d, $J = 13.7$ Hz), 110.51, 91.13 (d, $J = 125.3$ Hz), 55.27, 32.36, 21.48; $^{31}$P NMR (243 MHz, CDCl$_3$) δ 27.17; HRMS (ESI) Calcd. for $\text{C}_{30}\text{H}_{30}\text{N}_{2}\text{O}_{5}\text{PS}$ (M+H)$^+$ 561.1608, Found: 561.1606.

(3q): Yellow solid; 116.9 mg; yield: 87%; $^1$H NMR (600 MHz, Chloroform-$d$) δ 10.60 (s, 1H), 7.45–7.37 (m, 5H), 7.23 (t, $J = 7.7$ Hz, 1H), 7.07 (s, 2H), 7.00 (t, $J = 7.1$ Hz, 1H), 6.87–6.82 (m, 5H), 3.95 (s, 3H), 3.94–3.88 (m, 2H), 3.82 (s, 6H), 2.91–2.82 (m, 1H), 1.25 (d, $J = 6.9$ Hz, 6H), 1.11 (d, $J = 6.7$ Hz, 12H); $^{13}$C NMR (151 MHz, Chloroform-$d$) δ 162.22 (d, $J = 2.7$ Hz), 152.93, 151.12, 143.30 (d, $J = 12.7$ Hz), 136.59 (d, $J = 11.1$ Hz), 133.57 (d, $J = 12.3$ Hz), 133.25, 127.15 (d, $J = 9.9$ Hz), 125.02 (d, $J = 115.6$ Hz), 123.81, 122.14, 121.44, 119.60, 113.76 (d, $J = 13.7$ Hz), 110.19, 91.14 (d, $J = 126.4$ Hz), 55.25, 33.95, 32.20, 30.52, 24.82, 23.47; $^{31}$P NMR (243 MHz, CDCl$_3$) δ 27.59; HRMS (ESI) Calcd. for $\text{C}_{38}\text{H}_{46}\text{N}_{2}\text{O}_{5}\text{PS}$ (M+H)$^+$ 673.2860, Found: 673.2856.

(3r): White solid; 68.9 mg; yield: 67%; $^1$H NMR (600 MHz, Chloroform-$d$) δ 9.37 (s, 1H), 8.08–7.98 (m, 2H), 7.79 (d, $J = 8.3$ Hz, 2H), 7.64 (t, $J = 7.7$ Hz, 1H), 7.44 (d, $J = 8.3$ Hz, 1H), 7.38 (t, $J = 7.7$ Hz, 1H), 7.33–7.29 (m, 3H), 7.26 (t, $J = 7.7$ Hz, 1H), 7.18–7.13 (m, 1H), 7.08 (d, $J = 7.9$ Hz, 1H), 6.93 (t, $J = 7.5$ Hz, 1H), 6.64 (dd, $J = 15.1$, 7.2 Hz, 1H), 6.60 (d, $J = 8.0$ Hz, 1H), 4.06 (s, 3H), 2.45 (s, 3H); $^{13}$C NMR (151 MHz, Chloroform-$d$) δ 148.98 (d, $J = 8.1$ Hz), 144.41, 143.77 (d, $J = 18.3$ Hz), 136.75 (d, $J = 13.2$ Hz), 135.23 (d, $J = 6.0$ Hz), 134.64, 132.88 (d, $J =$
2.2 Hz), 130.59 (d, \( J = 13.7 \) Hz), 130.32, 129.64, 128.89, 127.77 (d, \( J = 15.0 \) Hz), 126.52 (d, \( J = 10.3 \) Hz), 125.44 (d, \( J = 137.1 \) Hz), 125.04, 124.57, 123.61 (d, \( J = 9.8 \) Hz), 123.06, 122.11, 121.97 (d, \( J = 11.7 \) Hz), 120.55 (d, \( J = 5.9 \) Hz), 119.64, 110.63, 88.76 (d, \( J = 176.5 \) Hz), 32.59, 21.79; \( ^{31} \)P NMR (243 MHz, CDCl\(_3\)) \( \delta \) 21.39; HRMS (ESI) Calcd. for C\(_{28}\)H\(_{24}\)N\(_2\)O\(_4\)PS (M+H)\(^+\) 515.1189, Found: 515.1186.

**(3s):** White oil; 39.3 mg; yield: 42%; \(^1\)H NMR (600 MHz, Chloroform-\( d \)) \( \delta \) 9.65 (s, 1H), 7.55 (d, \( J = 8.1 \) Hz, 2H), 7.49–7.43 (m, 3H), 7.41–7.32 (m, 3H), 7.32–7.25 (m, 2H), 7.20 (t, \( J = 7.6 \) Hz, 1H), 6.87 (d, \( J = 8.1 \) Hz, 2H), 4.01 (s, 3H), 3.90–3.82 (m, 1H), 3.66–3.56 (m, 1H), 2.15 (s, 3H), 1.20 (t, \( J = 7.1 \) Hz, 3H); \(^{13}\)C NMR (151 MHz, Chloroform-\( d \)) \( \delta \) 143.93, 143.20 (d, \( J = 17.1 \) Hz), 136.69 (d, \( J = 12.1 \) Hz), 134.47, 132.39 (d, \( J = 152.1 \) Hz), 131.52 (d, \( J = 2.9 \) Hz), 130.17 (d, \( J = 11.3 \) Hz), 129.26, 128.10, 128.01 (d, \( J = 14.2 \) Hz), 126.76 (d, \( J = 9.2 \) Hz), 122.93, 122.12, 119.96, 110.61, 90.29 (d, \( J = 155.8 \) Hz), 60.89 (d, \( J = 6.1 \) Hz), 32.57, 21.62, 16.36 (d, \( J = 7.0 \) Hz); \( ^{31} \)P NMR (243 MHz, CDCl\(_3\)) \( \delta \) 31.55; HRMS (ESI) Calcd. for C\(_{24}\)H\(_{26}\)N\(_2\)O\(_4\)PS (M+H)\(^+\) 469.1345, Found: 469.1345.

**(3t):** White oil; 54.7 mg; yield: 57%; \(^1\)H NMR (600 MHz, Chloroform-\( d \)) \( \delta \) 10.09 (s, 1H), 7.48 (t, \( J = 8.2 \) Hz, 4H), 7.41–7.28 (m, 5H), 7.25 (d, \( J = 7.9 \) Hz, 1H), 7.18 (t, \( J = 7.5 \) Hz, 1H), 6.79 (d, \( J = 8.1 \) Hz, 2H), 4.00 (s, 3H), 2.09 (s, 3H), 2.06–1.97 (m, 1H), 1.93–1.85 (m, 1H), 1.49–1.40 (m, 1H), 1.32–1.21 (m, 3H), 0.79 (t, \( J = 7.1 \) Hz, 3H); \(^{13}\)C NMR (151 MHz, Chloroform-\( d \)) \( \delta \) 143.71, 143.07 (d, \( J = 11.3 \) Hz), 136.80 (d, \( J = 11.0 \) Hz), 134.11 (d, \( J = 103.5 \) Hz), 131.28 (d, \( J = 2.5 \) Hz), 129.81 (d, \( J = 10.6 \) Hz), 129.04, 128.27 (d, \( J = 12.1 \) Hz), 128.10, 126.36 (d, \( J = 10.1 \) Hz), 122.68, 121.83, 119.44, 110.85, 89.84 (d, \( J = 117.5 \) Hz), 32.35 (d, \( J = 75.3 \) Hz), 32.27, 23.76 (d,
\[ J = 15.5 \text{ Hz}, 23.29 \text{ (d, } J = 4.2 \text{ Hz), 21.62 , 13.49; } ^{31}\text{P NMR (243 MHz, CDCl}_3\text{)} \delta 35.36; \text{ HRMS (ESI) Calcd. for C}_{26}\text{H}_{30}\text{N}_2\text{O}_3\text{PS (M+H)}^+ 481.1631, \text{ Found: 481.1631.} \]

(5a): Yellow oil; 54.9 mg; yield: 42%; dr >20:1; \textit{^1H NMR (600 MHz, Chloroform-}d\textit{)} \delta 9.97 \text{ (s, 1H), 7.62 \text{ (d, } J = 8.0 \text{ Hz, 2H), 7.48–7.44 \text{ (m, 1H), 7.30–7.22 \text{ (m, 9H), 7.17–7.12 \text{ (m, 3H), 7.04 \text{ (t, } J = 7.5 \text{ Hz, 1H), 6.92 \text{ (d, } J = 8.0 \text{ Hz, 2H), 6.15 \text{ (d, } J = 16.4 \text{ Hz, 1H), 5.54 \text{ (d, } J = 16.4 \text{ Hz, 1H), 4.06–3.97 \text{ (m, 1H), 2.30–2.24 \text{ (m, 1H), 2.17 \text{ (s, 3H), 1.72–1.65 \text{ (m, 2H), 1.63–1.59 \text{ (m, 1H), 1.56–1.51 \text{ (m, 1H), 1.42–1.24 \text{ (m, 2H), 0.91 \text{ (d, } J = 6.5 \text{ Hz, 3H), 0.82 \text{ (t, } J = 10.7 \text{ Hz, 2H), 0.58 \text{ (d, } J = 7.0 \text{ Hz, 3H), -0.06 \text{ (d, } J = 6.8 \text{ Hz, 3H); } ^{13}\text{C NMR (151 MHz, Chloroform-}d\text{)} \delta 144.04, 142.87 \text{ (d, } J = 16.7 \text{ Hz), 136.76, 135.97 \text{ (d, } J = 11.8 \text{ Hz), 134.26, 133.20 \text{ (d, } J = 150.1 \text{ Hz), 131.47 \text{ (d, } J = 14.2 \text{ Hz), 127.44, 127.24 \text{ (d, } J = 9.1 \text{ Hz), 126.93, 122.86, 121.58, 120.62, 111.76, 92.54 \text{ (d, } J = 155.1 \text{ Hz), 77.73 \text{ (d, } J = 7.2 \text{ Hz), 48.91, 48.51 \text{ (d, } J = 6.4 \text{ Hz), 44.07, 34.02, 31.68, 24.96, 22.65, 22.02, 21.66, 20.74, 14.73; } ^{31}\text{P NMR (243 MHz, CDCl}_3\text{)} \delta 31.30; \text{ HRMS (ESI) Calcd. for C}_{38}\text{H}_{44}\text{N}_2\text{O}_4\text{PS (M+H)}^+ 655.2754, \text{ Found:655.2753.} \]

(5b): White solid; 70.4 mg; yield: 51%; dr >20:1; \textit{^1H NMR (600 MHz, Chloroform-}d\textit{)} \delta 10.31 \text{ (s, 1H), 7.59–7.52 \text{ (m, 2H), 7.43 \text{ (t, } J = 7.0 \text{ Hz, 1H), 7.36–7.29 \text{ (m, 3H), 7.26–7.20 \text{ (m, 2H), 7.18 \text{ (s, 2H), 7.06 \text{ (t, } J = 7.5 \text{ Hz, 1H), 4.30–4.20 \text{ (m, 1H), 4.09–4.02 \text{ (m, 2H), 3.85 \text{ (s, 3H), 2.99–2.90 \text{ (m, 1H), 2.38 \text{ (d, } J = 12.6 \text{ Hz, 1H), 1.9–1.85 \text{ (m, 1H), 1.66–1.56 \text{ (m, 2H), 1.48–1.26 \text{ (m, 15H), 1.06 \text{ (d, } J = 6.7 \text{ Hz, 6H), 0.93 \text{ (d, } J = 6.4 \text{ Hz, 3H), 0.92–0.82 \text{ (m, 2H), 0.69 \text{ (d, } J = 7.0 \text{ Hz, 3H), 0.09 \text{ (d, } J = 6.8 \text{ Hz, 3H); } ^{13}\text{C NMR (151 MHz, Chloroform-}d\textit{)} \delta 153.36 , 151.24 , 143.16 \text{ (d, } J = 16.5 \text{ Hz), 136.46 \text{ (d, } J = 12.2 \text{ Hz), 133.66 \text{ (d, } J = 150.7 \text{ Hz), 133.50, 131.54 \text{ (d, } J = 2.7 \text{ Hz), 130.90 \text{ (d, } J = 11.1 \text{ Hz), 128.12 \text{ (d, } J = 13.9 \text{ Hz), 126.76 S13}}

\textit{S13}
(d, J = 9.9 Hz), 124.05, 122.37, 121.38, 119.92, 109.83, 91.79 (d, J = 156.1 Hz), 77.40 (d, J = 7.1 Hz), 48.83 (d, J = 6.6 Hz), 44.01, 34.13, 34.10, 32.07, 31.56, 30.36, 25.10, 24.79 (d, J = 20.4 Hz), 23.57 (d, J = 15.6 Hz), 22.64, 22.09, 21.02, 14.80; $^{31}$P NMR (243 MHz, CDCl$_3$) δ 29.32; HRMS (ESI) Calcd. for C$_{40}$H$_{56}$N$_2$O$_4$PS (M+H)$^+$ 691.3693, Found: 691.3687.

(5c): White solid; 80.6 mg; yield: 56%; dr >20:1;

$^1$H NMR (600 MHz, Chloroform-d) δ 10.18 (s, 1H), 7.58–7.53 (m, 2H), 7.45–7.41 (m, 1H), 7.33–7.29 (m, 2H), 7.21 (dd, J = 8.9, 1.7 Hz, 1H), 7.17 (s, 2H), 6.86 (dd, J = 8.9, 2.5 Hz, 1H), 6.66 (d, J = 2.4 Hz, 1H), 4.29–4.22 (m, 1H), 4.09–4.03 (m, 2H), 3.80 (s, 3H), 3.67 (s, 3H), 2.98–2.90 (m, 1H), 2.40 (d, J = 12.6 Hz, 1H), 1.98–1.90 (m, 1H), 1.66–1.61 (m, 1H), 1.61–1.56 (m, 1H), 1.49–1.25 (m, 15H), 1.07 (d, J = 6.7 Hz, 6H), 0.93 (d, J = 6.5 Hz, 3H), 0.91–0.82 (m, 2H), 0.72 (d, J = 7.0 Hz, 3H), 0.09 (d, J = 6.8 Hz, 3H); $^{13}$C NMR (151 MHz, Chloroform-d) δ 155.14, 153.35, 151.26, 143.06 (d, J = 16.5 Hz), 133.63 (d, J = 150.3 Hz), 133.43, 131.54 (d, J = 2.8 Hz), 131.47 (d, J = 12.2 Hz), 130.92 (d, J = 11.0 Hz), 128.10 (d, J = 13.8 Hz), 127.41 (d, J = 9.6 Hz), 124.03, 111.82, 110.57, 102.50, 91.59 (d, J = 156.6 Hz), 77.30 (d, J = 7.1 Hz), 55.63, 48.86 (d, J = 6.6 Hz), 44.06, 34.14, 34.10, 32.13, 31.54, 30.32, 25.18, 24.81 (d, J = 14.6 Hz), 23.56 (d, J = 16.1 Hz), 22.65, 22.09, 21.05, 14.76; $^{31}$P NMR (243 MHz, CDCl$_3$) δ 29.19; HRMS (ESI) Calcd. for C$_{41}$H$_{58}$N$_2$O$_5$PS (M+H)$^+$ 721.3799, Found: 721.3798.

(5d): White solid; 72.2 mg; yield: 51%; dr >20:1;

$^1$H NMR (600 MHz, Chloroform-d) δ 10.30 (s, 1H), 7.52 (dd, J = 13.3, 7.6 Hz, 2H), 7.47–7.43 (m, 1H), 7.34–7.30 (m, 2H), 7.26 (dd, J = 9.0, 4.2 Hz, 1H), 7.18 (s, 2H), 6.99–6.95 (m, 1H), 6.88 (d, J = 9.5, 2.4 Hz, 1H), 4.27–4.20 (m, 1H), 4.06–4.01 (m, 2H), 3.84 (s, 3H), 3.00–2.91 (m, 1H), 2.35 (d, J = 12.7 Hz, 1H), 1.90–1.84 (m, 1H), 1.66–1.57 (m, 2H), 1.44–1.27 (m, 15H), 1.06 (d, J = 6.7 Hz, 6H), 0.92 (d, J = 6.4 Hz, 3H), 0.90–0.83 (m, 2H), 0.73 (d, J = 7.0 Hz, 3H), 0.15 (d, J = 6.7 Hz, 3H); $^{13}$C
NMR (151 MHz, Chloroform-d) δ 158.72 (d, J = 237.1 Hz), 153.48, 151.23, 144.18 (d, J = 16.3 Hz), 133.40, 133.27 (d, J = 150.8 Hz), 132.93 (d, J = 11.9 Hz), 131.74 (d), 130.82 (d, J = 11.1 Hz), 128.24 (d, J = 13.9 Hz), 127.30 (t, J = 10.1 Hz), 124.10, 110.71 (d, J = 9.7 Hz), 110.52 (d, J = 26.0 Hz), 105.30 (d, J = 24.8 Hz), 92.16 (d, J = 160.3 Hz), 77.57 (d, J = 7.1 Hz), 48.78 (d, J = 6.5 Hz), 43.96, 34.10, 34.08, 32.37, 31.58, 30.39, 25.20, 24.79 (d, J = 18.7 Hz), 23.56 (d, J = 17.5 Hz), 22.62, 22.06, 21.03, 14.78; 31P NMR (243 MHz, CDCl3) δ 28.70; 19F NMR (565 MHz, CDCl3) δ -121.62; HRMS (ESI) Calcd. for C40H55FN2O4PS (M+H)+ 709.3599, Found:709.3593.

(5e): White solid; 69.5 mg; yield: 48%; dr >20:1;

1H NMR (600 MHz, Chloroform-d) δ 10.33 (s, 1H), 7.54–7.49 (m, 2H), 7.47–7.44 (m, 1H), 7.35–7.30 (m, 2H), 7.26 (dd, J = 9.4, 1.8 Hz, 1H), 7.21–7.16 (m, 4H), 4.23–4.16 (m, 1H), 4.05–3.99 (m, 2H), 3.84 (s, 3H), 2.97–2.91 (m, 1H), 2.37–2.33 (m, 1H), 1.92–1.85 (m, 1H), 1.66–1.57 (m, 2H), 1.44–1.26 (m, 15H), 1.05 (d, J = 6.8 Hz, 6H), 0.92 (d, J = 6.4 Hz, 3H), 0.89–0.83 (m, 2H), 0.74 (d, J = 7.0 Hz, 3H), 0.14 (d, J = 6.9 Hz, 3H); 13C NMR (151 MHz, Chloroform-d) δ 153.52, 151.22, 144.18 (d, J = 16.3 Hz), 134.86 (d, J = 11.8 Hz), 133.33, 133.24 (d, J = 151.3 Hz), 131.77, 130.76 (d, J = 11.1 Hz), 128.27 (d, J = 14.0 Hz), 127.72 (d, J = 9.4 Hz), 127.25, 124.11, 122.72, 119.38, 110.92, 91.70 (d, J = 155.4 Hz), 77.77 (d, J = 7.2 Hz), 48.79 (d, J = 6.7 Hz), 43.95, 34.10, 34.05, 32.37, 31.58, 30.39, 25.27, 24.79 (d, J = 14.0 Hz), 23.55 (d, J = 17.1 Hz), 22.62, 22.05, 21.05, 14.75; 31P NMR (243 MHz, CDCl3) δ 28.67; HRMS (ESI) Calcd. for C40H55ClN2O4PS (M+H)+ 725.3303, Found:725.3302.

(5f): White solid; 79.9 mg; yield: 52%; dr >20:1;

1H NMR (600 MHz, Chloroform-d) δ 10.34 (s, 1H), 7.54–7.49 (m, 2H), 7.48–7.44 (m, 1H), 7.36 (d, J = 1.9 Hz, 1H), 7.35–7.31 (m, 3H), 7.21 (dd, J
= 8.6, 1.7 Hz, 1H), 7.18 (s, 2H), 4.22–4.16 (m, 1H), 4.05–4.00 (m, 2H), 3.84 (s, 3H), 2.97–2.92 (m, 1H), 2.38–2.33 (m, 1H), 1.93–1.86 (m, 1H), 1.66–1.57 (m, 2H), 1.45–1.25 (m, 15H), 1.05 (d, J = 6.8 Hz, 6H), 0.92 (d, J = 6.4 Hz, 3H), 0.91–0.85 (m, 2H), 0.76 (d, J = 7.1 Hz, 3H), 0.13 (d, J = 6.8 Hz, 3H); $^{13}$C NMR (151 MHz, Chloroform-$d$) δ 153.54, 151.22, 144.08 (d, J = 16.4 Hz), 135.17 (d, J = 11.7 Hz), 133.32, 133.22 (d, J = 151.4 Hz), 131.80 (d, J = 2.8 Hz), 130.75 (d, J = 11.1 Hz), 128.28 (d, J = 14.0 Hz), 128.27, 125.34, 124.11, 121.84, 114.85, 111.33, 91.59 (d, J = 155.1 Hz), 77.81 (d, J = 7.2 Hz), 48.79 (d, J = 6.7 Hz), 43.97, 34.11, 34.06, 32.35, 31.59, 30.39, 25.29, 24.79 (d, J = 12.6 Hz), 23.55 (d, J = 17.0 Hz), 22.63, 22.05, 21.08, 14.76; $^{31}$P NMR (243 MHz, CDCl$_3$) δ 28.69; HRMS (ESI) Calcd. for C$_{40}$H$_{55}$BrN$_2$O$_4$PS (M+H)$^+$ 769.2798, Found: 769.2798.

(6): Organe solid; 31.5 mg; yield: 91%; $^1$H NMR (600 MHz, Chloroform-$d$) δ 7.80–7.73 (m, 4H), 7.55–7.50 (m, 2H), 7.46–7.40 (m, 4H), 7.14 (d, J = 8.1 Hz, 1H), 7.06–7.01 (m, 1H), 6.92–6.86 (m, 1H), 6.64 (d, J = 7.8 Hz, 1H), 5.74 (s, 2H), 3.56 (s, 3H); $^{13}$C NMR (151 MHz, Chloroform-$d$) δ 154.28 (d, J = 13.7 Hz), 135.17, 135.10, 134.61 (d, J = 107.7 Hz), 131.67 (d, J = 10.8 Hz), 128.83 (d, J = 11.4 Hz), 128.40 (d, J = 12.3 Hz), 120.81, 119.29, 117.66, 107.95, 76.02 (d, J = 136.5 Hz), 27.95; $^{31}$P NMR (243 MHz, CDCl$_3$) δ 29.13; HRMS (ESI) Calcd. for C$_{21}$H$_{30}$N$_2$OP (M+H)$^+$ 347.1308, Found: 347.1306.
Single Crystal X-ray Structure Determinations of Compounds 3e (CCDC: 1486528)

Bond precision: C-C = 0.0054 Å  Wavelength=0.71073 Å

Cell: a=32.921(7)  b=11.658(2)  c=20.290(4)
      alpha=90  beta=118.58(3)  gamma=90

Temperature: 293 K

Calculated  Reported
Volume       6838(3)      6838(3)
Space group  C 2/c        C 1 2/c 1
Hall group   -C 2yc       -C 2yc
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Correction method = # Reported T Limits: Tmin=0.667 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness = 0.997
Theta(max) = 27.523
R(reflections) = 0.0610(4948)
wr2(reflections) = 0.1836(7851)
S = 1.036
Npar = 426
Single Crystal X-ray Structure Determinations of Compounds 5f (CCDC: 1501118)

Bond precision:  
C-C = 0.0059 Å  
Wavelength = 0.71073 Å

Cell:  
a = 10.7121(11) Å  
b = 9.9230(11) Å  
c = 19.323(2) Å  
alpha = 90°  
beta = 97.966(3)°  
gamma = 90°

Temperature:  
293 K

Calculated  
Reported

Volume  
2034.1(4) Å³  
2034.1(4) Å³

Space group  
P 21  
P 21

Hall group  
P 2yb  
?

Moiety formula  
C₄₀ H₅₄ Br N₂ O₄ P S  
?

Sum formula  
C₄₀ H₅₄ Br N₂ O₄ P S  
C₄₀ H₅₄ Br N₂ O₄ P S

Mr  
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769.79

Dx, g cm⁻³  
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Correction method = # Reported T Limits: Tmin=0.603 Tmax=0.683

AbsCorr = MULTI-SCAN

Data completeness = 1.87/1.00  Theta(max) = 25.010

R(reflections) = 0.0500(6057)  wR2(reflections) = 0.1375(7135)

S = 1.034  Npar = 464
$^1\text{H NMR}, ^{13}\text{C NMR}, ^{31}\text{P NMR} \text{ and } ^{19}\text{F NMR spectra for new compounds}$
3r

\[ \text{Structure Image} \]

3r

\[ \text{Structure Image} \]