Supporting Information

Palladium-Catalyzed Regioselective C–H Alkynylation of Indoles with Haloalkynes: Access to Functionalized 7-Alkynylindoles

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Table of Contents

A. General Information..............................................................................................................S2
B. General Procedure for the Synthesis of Starting Materials...............................................S2
C. Optimization of Reaction Conditions...................................................................................S9
D. General Procedure for the Synthesis of 3..........................................................................S12
E. Mechanistic Studies .............................................................................................................S12
F. Further Synthetic Applications............................................................................................S13
G. Reference ..............................................................................................................................S14
H. Characterization Data for All Products ..............................................................................S15
I. X-ray Crystallographic Analysis ........................................................................................S24
J. Copies of $^1$H, $^{13}$C, $^{19}$F and $^{31}$P NMR Spectra ...............................................................S25

S1
A. General Information

All purchased reagents and solvents were used without further purification unless otherwise noted. Analytical thin layer chromatography was performed by using commercially prepared 100-400 mesh silica gel plates (GF254) and visualization was effected at 254 nm. All the haloalkynes were prepared according to known procedures. $^1$H and $^{13}$C NMR spectra were recorded using a Bruker DRX-400 spectrometer using CDCl3 as solvent. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively. Mass spectra were recorded on a Thermo Scientific ISQ gas chromatograph-mass spectrometer. The data of HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker TENSOR 27 spectrometer. Melting points were determined with a Büchi Melting Point B-545 instrument.

B. General Procedure for the Synthesis of Starting Materials

**General Procedure for Synthesis of Starting Materials 1-3**

![Chemical Reaction](attachment:image.png)

To a two-neck flask contained indole (3.0 mmol, 1.0 equiv) was added anhydrous THF (8 mL) under nitrogen. The reaction vessel was fitted with a rubber stopper and a three-way valve with nitrogen balloon, and was evacuated and back-filled with nitrogen. Subsequently, a solution of $n$-BuLi (solution in hexanes, 3.6 mmol, 1.2 equiv) was added dropwise. After stirring for 15 min, chloro-dialkyl phosphine (3.6 mmol, 1.2 equiv) was added dropwise. The mixture was allowed to stir and warm to room temperature until complete by TLC analysis. Then, 1.2 mL of MeOH was added and most of the solvent was removed under reduced pressure. The residue was dissolved in 20 mL of MeOH (some DCM could be added to help dissolve) and cooled to 0 °C. Slow addition of excess H$_2$O$_2$ (0.6 mL of 30% solution, approx. 6 mmol) caused the completion of oxidation process. After adding 4.8 mL of Na$_2$SO$_3$ (2 M solution) dropwise, the solution was stirred for 2 h, allowed to warm to room temperature, treated with 7.2 mL of HCl (10% solution), and stirred for another hour. Most of MeOH was removed under reduced pressure, and the remaining residue was poured into 30 mL of H$_2$O and extracted with DCM (3 × 25 mL). The combined organics were dried over Na$_2$SO$_4$ and evaporated to give the crude product. Further purification was carried out by recrystallization or column chromatography (silica gel, petroleum ether /EtOAc /DCM).

**Di-tert-butyl(1H-indol-1-yl)phosphine oxide (1a)**

White solid (81%, 673.1 mg); Isolated by recrystallization; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.52 (d, $J = 8.0$ Hz, 1H), 7.57 (d, $J = 7.6$ Hz, 1H), 7.24-7.15 (m, 3H), 6.68 (t, $J = 2.2$ Hz, 1H), 1.34 (d, $J = 14.8$ Hz, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 141.6, 129.3 (d, $J = 5.4$ Hz), 126.4 (d, $J = 5.0$ Hz), 123.4, 121.5, 120.1, 116.2, 107.1 (d, $J = 4.9$ Hz), 38.6 (d, $J = 68.8$ Hz), 26.7; $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 63.25-62.34 (m).
Di-tert-butyl(4-methyl-1H-indol-1-yl)phosphine oxide (1b)<sup>2</sup>

White solid (80%, 698.4 mg); Isolation by recrystallization; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.35 (d, <i>J</i> = 8.4 Hz, 1H), 7.23 (d, <i>J</i> = 2.8 Hz, 1H), 7.15-7.11 (m, 1H), 6.97 (d, <i>J</i> = 7.8 Hz, 1H), 6.71 (s, 1H), 2.53 (s, 3H), 1.34 (d, <i>J</i> = 14.4 Hz, 18H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.4, 129.4, 129.0 (d, <i>J</i> = 5.4 Hz), 125.8 (d, <i>J</i> = 4.8 Hz), 123.5, 121.8, 113.8, 105.5 (d, <i>J</i> = 5.1 Hz), 38.6 (d, <i>J</i> = 68.9 Hz), 26.7, 18.7; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 63.00-62.09 (m).

Di-tert-butyl(4-methoxy-1H-indol-1-yl)phosphine oxide (1c)

White solid (60%, 552.6 mg); Isolation by recrystallization; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.13 (d, <i>J</i> = 8.4 Hz, 1H), 7.14 (t, <i>J</i> = 7.6 Hz, 2H), 6.81 (s, 1H), 6.59 (d, <i>J</i> = 8.0 Hz, 1H), 3.93 (s, 3H), 1.32 (d, <i>J</i> = 14.8 Hz, 18H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 152.5, 142.8, 124.9 (d, <i>J</i> = 4.7 Hz), 124.0, 119.8 (d, <i>J</i> = 5.8 Hz), 109.4, 104.0 (d, <i>J</i> = 4.9 Hz), 101.3, 55.1, 38.5 (d, <i>J</i> = 68.8 Hz), 26.6; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 63.14-62.24 (m). HRMS (ESI) m/z: calcd for C<sub>17</sub>H<sub>22</sub>No<sub>3</sub>P [M+H]<sup>+</sup>, 308.1774; found 308.1775.

(4-(Benzyloxy)-1H-indol-1-yl)di-tert-butylphosphine oxide (1d)

White solid (81%, 930.7 mg); Isolation by recrystallization; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.14 (d, <i>J</i> = 8.4 Hz, 1H), 7.50 (d, <i>J</i> = 7.2 Hz, 2H), 7.39 (t, <i>J</i> = 7.2 Hz, 2H), 7.34-7.31 (m, 1H), 7.15-7.11 (m, 2H), 6.86 (s, 1H), 6.67 (d, <i>J</i> = 7.8 Hz, 1H), 5.19 (s, 2H), 1.34 (d, <i>J</i> = 14.4 Hz, 18H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 151.8, 143.0, 137.4, 128.4, 127.8, 127.4, 124.9 (d, <i>J</i> = 4.9 Hz), 124.1, 120.2 (d, <i>J</i> = 5.8 Hz), 109.7, 104.3 (d, <i>J</i> = 5.1 Hz), 102.8, 69.9, 38.5 (d, <i>J</i> = 68.8 Hz), 26.7; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 63.29-62.36 (m). HRMS (ESI) m/z: calcd for C<sub>25</sub>H<sub>28</sub>NOP [M+H]<sup>+</sup>, 384.2087; found 384.2093.

Di-tert-butyl(4-phenyl-1H-indol-1-yl)phosphine oxide (1e)

White solid (60%, 635.4 mg); Isolation by recrystallization; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.57 (d, <i>J</i> = 8.0 Hz, 1H), 7.62 (d, <i>J</i> = 7.2 Hz, 2H), 7.43 (t, <i>J</i> = 7.2 Hz, 2H), 7.34-7.27 (m, 2H), 7.23 (s, 2H), 6.82 (s, 1H), 1.31 (d, <i>J</i> = 14.8 Hz, 18H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.8, 140.7, 133.8, 128.6, 128.2, 127.3 (d, <i>J</i> = 5.2 Hz), 126.7, 126.5 (d, <i>J</i> = 4.6 Hz), 123.4, 121.3, 115.1, 106.2 (d, <i>J</i> = 4.8 Hz), 38.4 (d, <i>J</i> = 68.7 Hz), 26.5; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 63.44-62.54 (m). HRMS (ESI) m/z: calcd for C<sub>22</sub>H<sub>2</sub>NOP [M+H]<sup>+</sup>, 354.1981; found 354.1987.

Di-tert-butyl(4-fluoro-1H-indol-1-yl)phosphine oxide (1f)<sup>3</sup>

White solid (78%, 690.3 mg); Isolation by recrystallization; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.31 (d, <i>J</i> = 8.4 Hz, 1H), 7.21 (d, <i>J</i> = 2.0 Hz, 1H), 7.14 (dd, <i>J</i> = 14.0, 7.6 Hz, 1H), 6.87-6.82 (m, 1H), 6.79 (s, 1H), 1.34 (d, <i>J</i> = 14.8 Hz, 18H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 155.7 (d, <i>J</i> = 245.1 Hz), 143.8 (d, <i>J</i> = 9.3 Hz), 126.2 (d, <i>J</i> = 4.7 Hz), 123.8 (d, <i>J</i> = 7.3 Hz), 118.4 (dd, <i>J</i> = 21.9, 5.7 Hz), 112.3 (d, <i>J</i> = 3.7 Hz), 106.3 (d, <i>J</i> = 18.0 Hz), 102.8 (d, <i>J</i> = 4.8 Hz), 38.6 (d, <i>J</i> = 68.4 Hz), 26.6; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -122.75 (dd, <i>J</i> = 9.7, 5.8 Hz); <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 63.96-63.06 (m).
Di-tert-butyl(4-chloro-1H-indol-1-yl)phosphine oxide (1g)

White solid (78%, 727.7 mg); Isolation by recrystallization; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.44 (d, $J = 8.0$ Hz, 1H), 7.27 (s, 1H), 7.19-7.12 (m, 2H), 6.81 (s, 1H), 1.33 (d, $J = 14.8$ Hz, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 142.2, 128.1 (d, $J = 5.3$ Hz), 126.9 (d, $J = 4.6$ Hz), 125.3, 124.0, 121.3, 114.8, 105.4 (d, $J = 4.7$ Hz), 38.6 (d, $J = 68.3$ Hz), 26.6; $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 64.22-63.31 (m).

(4-Bromo-1H-indol-1-yl)di-tert-butylphosphine oxide (1h)

White solid (79%, 841.4 mg); Isolation by recrystallization; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.49 (d, $J = 8.4$ Hz, 1H), 7.34 (d, $J = 7.6$ Hz, 1H), 7.28 (d, $J = 4.8$ Hz, 1H), 7.09 (t, $J = 8.0$ Hz, 1H), 6.76 (s, 1H), 1.33 (d, $J = 14.8$ Hz, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 141.8, 129.9 (d, $J = 5.2$ Hz), 126.9 (d, $J = 5.2$ Hz), 124.5, 124.4, 115.4, 113.8, 107.2 (d, $J = 4.7$ Hz), 38.6 (d, $J = 68.1$ Hz), 26.6; $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 64.32-63.41 (m).

Methyl 1-(di-tert-butylphosphoryl)-1H-indole-4-carboxylate (1i)

White solid (68%, 683.4 mg); Isolation by recrystallization; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.81 (d, $J = 8.4$ Hz, 1H), 7.95 (d, $J = 7.6$ Hz, 1H), 7.42 (s, 1H), 7.39 (s, 1H), 7.29 (d, $J = 7.2$ Hz, 1H), 3.97 (s, 3H), 1.34 (d, $J = 14.8$ Hz, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.6, 142.2, 129.0 (d, $J = 5.1$ Hz), 128.2 (d, $J = 4.4$ Hz), 124.7, 122.7, 121.2, 121.1, 107.8 (d, $J = 4.6$ Hz), 51.7, 38.5 (d, $J = 68.3$ Hz), 26.5; $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 64.29-63.37 (m). HRMS (ESI) m/z: calcd for C$_{18}$H$_{27}$NO$_3$P [M+H]$^+$, 336.1723; found 336.1724.

Di-tert-butyl(4-(trifluoromethyl)-1H-indol-1-yl)phosphine oxide (1j)

White solid (32%, 331.2 mg); Isolation by recrystallization; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.76 (d, $J = 8.4$ Hz, 1H), 7.47 (d, $J = 7.6$ Hz, 1H), 7.36 (s, 1H), 7.28 (s, 1H), 6.89 (s, 1H), 1.35 (d, $J = 14.8$ Hz, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 142.1, 128.0 (d, $J = 4.4$ Hz), 125.6 (d, $J = 5.2$, 2.0 Hz), 124.8 (q, $J = 270.2$ Hz), 122.6, 121.4 (q, $J$ = 32.1 Hz), 119.9, 118.9 (q, $J = 4.7$ Hz), 105.5, 38.6 (d, $J = 68.1$ Hz), 26.5; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -61.18 (s); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 64.75-63.83 (m). HRMS (ESI) m/z: calcd for C$_{17}$H$_{24}$F$_3$NOP [M+H]$^+$, 346.1542; found 346.1545.

Di-tert-butyl(5-methyl-1H-indol-1-yl)phosphine oxide (1k)

White solid (72%, 628.6 mg); Isolation by recrystallization; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.39 (d, $J = 8.8$ Hz, 1H), 7.36 (s, 1H), 7.19 (d, $J = 2.4$ Hz, 1H), 7.05 (d, $J = 8.8$ Hz, 1H), 6.60 (s, 1H), 2.42 (s, 3H), 1.33 (d, $J = 14.8$ Hz, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 139.8, 130.8, 129.4 (d, $J = 5.5$ Hz), 126.3 (d, $J = 4.8$ Hz), 124.9, 119.8, 115.8, 106.7 (d, $J = 5.0$ Hz), 38.5 (d, $J = 69.0$ Hz), 26.6, 21.2; $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 62.90-62.00 (m).
Di-tert-butyl(5-methoxy-1H-indol-1-yl)phosphine oxide (1l)

White solid (56%, 515.7 mg); Isolation by recrystallization; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.40 (d, $J = 9.2$ Hz, 1H), 7.21 (d, $J = 3.2$ Hz, 1H), 7.03 (d, $J = 2.0$ Hz, 1H), 6.87 (dd, $J = 9.2$, 2.4 Hz, 1H), 6.62–6.60 (m, 1H), 3.83 (s, 3H), 1.33 (d, $J = 14.8$ Hz, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.1, 136.5, 129.8 (d, $J = 5.5$ Hz), 126.9 (d, $J = 4.7$ Hz), 116.9, 112.9, 106.9 (d, $J = 4.9$ Hz), 102.1, 55.6, 38.5 (d, $J = 69.0$ Hz), 26.6; $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 63.00–62.10 (m).

Di-tert-butyl(5-ethoxy-1H-indol-1-yl)phosphine oxide (1m)

White solid (79%, 760.8 mg); Isolation by recrystallization; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.39 (d, $J = 9.2$ Hz, 1H), 7.19 (s, 1H), 7.01 (s, 1H), 6.86 (d, $J = 9.2$ Hz, 1H), 6.59 (s, 1H), 4.04 (q, $J = 6.8$ Hz, 2H), 1.41 (t, $J = 6.8$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 154.2, 136.2, 129.7 (d, $J = 5.6$ Hz), 126.7 (d, $J = 4.7$ Hz), 116.7, 113.3, 106.8 (d, $J = 5.0$ Hz), 102.8, 63.6, 38.3 (d, $J = 69.0$ Hz), 26.4, 14.8; $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 63.05–62.15 (m). HRMS (ESI) m/z: calcd for C$_{18}$H$_{29}$NO$_2$P [M+H]$^+$, 322.1930; found 322.1935.

Di-tert-butyl(5-fluoro-1H-indol-1-yl)phosphine oxide (1n)

White solid (83%, 734.5 mg); Isolation by recrystallization; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.47 (dd, $J = 9.2$, 4.8 Hz, 1H), 7.27 (s, 1H), 7.20 (dd, $J = 8.9$, 1.8 Hz, 1H), 6.96 (td, $J = 9.2$, 2.4 Hz, 1H), 6.64 (s, 1H), 1.33 (d, $J = 14.8$ Hz, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.7 (d, $J = 235.6$ Hz), 137.9, 129.8 (d, $J = 5.5$ Hz), 127.9 (d, $J = 4.4$ Hz), 117.1 (d, $J = 9.0$ Hz), 111.5 (d, $J = 24.8$ Hz), 107.0 (t, $J = 4.6$ Hz), 105.0 (d, $J = 23.4$ Hz), 38.6 (d, $J = 68.7$ Hz), 26.6; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -122.85 (td, $J = 9.1$, 4.8 Hz); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 63.73–62.82 (m).

Di-tert-butyl(5-chloro-1H-indol-1-yl)phosphine oxide (1o)

White solid (70%, 653.1 mg); Isolation by recrystallization; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.46 (d, $J = 8.8$ Hz, 1H), 7.54 (s, 1H), 7.26 (d, $J = 4.4$ Hz, 1H), 7.17 (d, $J = 9.2$ Hz, 1H), 6.63 (s, 1H), 1.33 (d, $J = 14.8$ Hz, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 139.9, 130.4 (d, $J = 4.9$ Hz), 127.6 (d, $J = 4.4$ Hz), 127.2, 123.7, 119.6, 117.3, 106.6 (d, $J = 4.9$ Hz), 38.6 (d, $J = 68.5$ Hz), 26.6; $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 64.08–63.17 (m). HRMS (ESI) m/z: calcd for C$_{16}$H$_{24}$ClNOP [M+H]$^+$, 312.1279; found 312.1279.

(5-Bromo-1H-indol-1-yl)di-tert-butylphosphine oxide (1p)

White solid (63%, 670.9 mg); Isolation by recrystallization; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.42 (d, $J = 8.8$ Hz, 1H), 7.54 (s, 1H), 7.30 (d, $J = 9.2$ Hz, 1H), 7.24 (s, 1H), 6.62 (s, 1H), 1.32 (d, $J = 14.8$ Hz, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 140.2, 130.9 (d, $J = 5.6$ Hz), 127.4 (d, $J = 4.5$ Hz), 126.2, 122.7, 117.7, 114.9, 106.4 (d, $J = 4.4$ Hz), 38.5 (d, $J = 68.4$ Hz), 26.5; $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 64.18–63.26 (m). HRMS (ESI) m/z: calcd for C$_{16}$H$_{25}$BrNOP [M+H]$^+$, 356.0773; found 356.0771.
Methyl 1-(di-tert-butylphosphoryl)-1H-indole-5-carboxylate (1q)

White solid (67%, 673.4 mg); Isolation by recrystallization; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.57 (d, $J = 9.2$ Hz, 1H), 8.33 (s, 1H), 7.92 (d, $J = 9.2$ Hz, 1H), 7.30 (s, 1H), 6.77 (s, 1H), 3.92 (s, 3H), 1.34 (d, $J = 14.8$ Hz, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.7, 144.3, 128.9 (d, $J = 5.4$ Hz), 127.6 (d, $J = 4.6$ Hz), 124.5, 123.5, 122.8, 115.8, 107.9 (d, $J = 4.5$ Hz), 51.8, 38.5 (d, $J = 68.1$ Hz), 26.5; $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 64.47-63.56 (m).

Di-tert-butyl(6-methyl-1H-indol-1-yl)phosphine oxide (1r)

White solid (57%, 497.7 mg); Isolation by recrystallization; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.35 (s, 1H), 7.45 (d, $J = 8.0$ Hz, 1H), 7.15 (d, $J = 3.0$ Hz, 1H), 2.45 (s, 3H), 1.33 (d, $J = 15.0$ Hz, 18H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 142.0, 133.2, 126.9 (d, $J = 5.5$ Hz), 125.7 (d, $J = 4.8$ Hz), 123.2, 119.6, 116.1, 106.9 (d, $J = 5.1$ Hz), 38.5 (d, $J = 68.7$ Hz), 26.9, 26.7, 21.9; $^{31}$P NMR (202 MHz, CDCl$_3$) $\delta$ 62.93-62.21 (m). HRMS (ESI) m/z: calcd for C$_{17}$H$_{27}$NOP [M+H]$^+$, 292.1825; found 292.1830.

Di-tert-butyl(6-fluoro-1H-indol-1-yl)phosphine oxide (1s)

White solid (60%, 531.1 mg); Isolation by recrystallization; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.29 (dd, $J = 11.5$, 2.5 Hz, 1H), 7.47 (dd, $J = 8.5$, 5.5 Hz, 1H), 7.24-7.18 (m, 1H), 6.93 (td, $J = 9.0$, 2.5 Hz, 1H), 1.34 (d, $J = 14.5$ Hz, 18H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 160.2 (d, $J = 237.0$ Hz), 141.6 (d, $J = 13.1$ Hz), 126.7 (t, $J = 4.1$ Hz), 125.5 (d, $J = 5.4$ Hz), 120.5 (d, $J = 10.0$ Hz), 110.2 (d, $J = 24.6$ Hz), 107.0 (d, $J = 4.8$ Hz), 102.9 (d, $J = 28.4$ Hz), 38.6 (d, $J = 68.5$ Hz), 26.6; $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -114.05 – -122.58 (m); $^{31}$P NMR (202 MHz, CDCl$_3$) $\delta$ 63.90-61.50 (m). HRMS (ESI) m/z: calcd for C$_{16}$H$_{24}$FNOP [M+H]$^+$, 296.1574; found 296.1580.

Di-tert-butyl(3-methyl-1H-indol-1-yl)phosphine oxide (1t)

White solid (46%, 401.5 mg); Isolation by recrystallization; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.49 (d, $J = 8.4$ Hz, 1H), 7.49 (d, $J = 7.6$ Hz, 1H), 7.23-7.15 (m, 2H), 6.98 (s, 1H), 2.32 (s, 3H), 1.32 (d, $J = 14.4$ Hz, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 142.0, 129.8 (d, $J = 5.4$ Hz), 123.3 (d, $J = 4.5$ Hz), 120.9, 118.1, 116.2, 115.9 (d, $J = 4.9$ Hz), 38.40 (d, $J = 69.3$ Hz), 26.6, 9.7; $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 62.40-61.50 (m).

Di-tert-butyl(3-chloro-1H-indol-1-yl)phosphine oxide (1u)

White solid (66%, 615.7 mg); Isolation by recrystallization; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.52 (d, $J = 8.0$ Hz, 1H), 7.58 (d, $J = 7.6$ Hz, 1H), 7.31-7.24 (m, 2H), 7.21 (s, 1H), 1.34 (d, $J = 14.8$ Hz, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 140.7, 126.7 (d, $J = 4.5$ Hz), 124.6, 122.4 (d, $J = 4.7$ Hz), 122.1, 117.8, 116.5, 111.4 (d, $J = 5.3$ Hz), 38.6 (d, $J = 68.0$ Hz), 26.1; $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 64.70-63.79 (m).
Ethyl 2-(1-(di-tert-butylphosphoryl)-1H-indol-3-yl)acetate (1v)

White solid (77%, 838.5 mg); Isolation by recrystallization; 1H NMR (400 MHz, CDCl3) δ 8.49 (d, J = 8.0 Hz, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.32 (s, 1H), 7.24-7.16 (m, 2H), 4.17 (q, J = 7.2 Hz, 2H), 3.76 (s, 2H), 1.33 (d, J = 14.8 Hz, 18H), 1.24 (t, J = 7.0 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 171.0, 141.5, 128.6 (d, J = 5.1 Hz), 124.8 (d, J = 5.0 Hz), 123.4, 121.2, 117.9, 116.1, 112.6 (d, J = 5.1 Hz), 60.6, 38.3 (d, J = 68.7 Hz), 30.7, 26.4, 14.0; 31P NMR (162 MHz, CDCl3) δ 63.49-62.58 (m). HRMS (ESI) m/z: calcd for C20H30NNaO3P [M+H]+, 386.1856; found 386.1857.

Methyl 1-(di-tert-butylphosphoryl)-1H-indole-3-carboxylate (1w)

White solid (62%, 623.1 mg); Isolation by recrystallization; 1H NMR (400 MHz, CDCl3) δ 8.55 (d, J = 7.2 Hz, 1H), 8.16 (d, J = 6.8 Hz, 1H), 7.94 (s, 1H), 7.33-7.27 (m, 2H), 3.95 (s, 1H), 1.36 (d, J = 15.2 Hz, 18H); 13C NMR (100 MHz, CDCl3) δ 164.8, 142.1, 132.5 (d, J = 4.7 Hz), 126.4 (d, J = 4.3 Hz), 124.4, 123.1, 120.8, 116.4, 112.5 (d, J = 4.6 Hz), 51.3, 38.6 (d, J = 66.9 Hz), 26.5; 31P NMR (162 MHz, CDCl3) δ 66.13-65.21 (m).

1-(Di-tert-butylphosphoryl)-1H-indole-3-carbaldehyde (1x)

White solid (49%, 448.3 mg); Isolation by recrystallization; 1H NMR (400 MHz, CDCl3) δ 10.15 (s, 1H), 8.56-8.54 (m, 1H), 8.27-8.26 (m, 1H), 7.85 (s, 1H), 7.35-7.28 (m, 2H), 1.39 (d, J = 15.2 Hz, 18H); 13C NMR (100 MHz, CDCl3) δ 185.2, 142.7, 136.5 (d, J = 4.1 Hz), 125.5, 125.2 (d, J = 4.2 Hz), 123.9, 122.2 (d, J = 4.1 Hz), 121.0, 116.6, 38.8 (d, J = 66.5 Hz), 26.6; 31P NMR (162 MHz, CDCl3) δ 66.41-65.67 (m). HRMS (ESI) m/z: calcd for C17H25NO2P [M+H]+, 306.1617; found 306.1623.

1-(1-(Di-tert-butylphosphoryl)-1H-indol-3-yl)ethan-1-one (1y)

White solid (56%, 535.9 mg); Isolation by recrystallization; 1H NMR (400 MHz, CDCl3) δ 8.55 (d, J = 6.8 Hz, 1H), 8.30 (d, J = 6.8 Hz, 1H), 7.87 (s, 1H), 7.32-7.30 (m, 2H), 2.59 (s, 3H), 1.39 (d, J = 15.2 Hz, 18H); 13C NMR (100 MHz, CDCl3) δ 193.2, 142.3, 132.6 (d, J = 4.3 Hz), 126.0 (d, J = 4.1 Hz), 124.7, 123.6, 121.5, 121.3 (d, J = 3.6 Hz), 116.3, 38.7 (d, J = 66.8 Hz), 28.0, 26.6; 31P NMR (162 MHz, CDCl3) δ 65.89-64.96 (m). HRMS (ESI) m/z: calcd for C18H27NO2P [M+H]+, 320.1774; found 320.1771.

Di-tert-butyl(3-(2-hydroxyethyl)-1H-indol-1-yl)phosphine oxide (1z)

White solid (30%, 288.9 mg); Isolation by recrystallization; 1H NMR (400 MHz, CDCl3) δ 8.47 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 7.2 Hz, 1H), 7.22-7.14 (m, 2H), 7.12 (s, 1H), 3.93 (t, J = 5.6 Hz, 2H), 3.02 (t, J = 6.0 Hz, 2H), 2.79 (s, 1H), 1.32 (d, J = 14.8 Hz, 18H); 13C NMR (100 MHz, CDCl3) δ 141.9, 129.0 (d, J = 4.9 Hz), 124.2 (d, J = 7.4 Hz), 123.5, 121.2, 118.2, 117.1 (d, J = 4.9 Hz), 116.2, 62.1, 38.5 (d, J = 68.8 Hz), 28.5, 26.6; 31P NMR (162 MHz, CDCl3) δ 63.42-62.51 (m). HRMS (ESI) m/z: calcd for C19H29NO3P [M+H]+, 322.1930; found 322.1933.
Di-tert-butyl(3-chloro-4-fluoro-1H-indol-1-yl)phosphine oxide (1aa)

White solid (75%, 740.2 mg); Isolation by recrystallization; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.33 (d, $J$ = 8.4 Hz, 1H), 7.20-7.15 (m, 2H), 6.87 (d, $J$ = 9.2 Hz, 1H), 1.35 (d, $J$ = 14.8 Hz, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.5 (d, $J$ = 238.1 Hz), 143.0 (d, $J$ = 7.6 Hz), 125.0 (d, $J$ = 7.5 Hz), 123.0 (d, $J$ = 4.2 Hz), 115.6 (dd, $J$ = 17.5, 4.7 Hz), 114.1 (d, $J$ = 4.1 Hz), 108.5 (d, $J$ = 4.2 Hz), 107.5 (d, $J$ = 17.8 Hz), 38.7 (d, $J$ = 67.5 Hz), 26.6; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -126.51 (dd, $J$ = 10.6, 5.3 Hz); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 65.48-64.55 (m). HRMS (ESI) m/z: calcd for C$_{16}$H$_{23}$ClFNOP [M+H]$^+$, 330.1184; found 330.1178.

Di-tert-butyl(3-chloro-5-methyl-1H-indol-1-yl)phosphine oxide (1ab)

White solid (68%, 663.3 mg); Isolation by recrystallization; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.39 (d, $J$ = 8.8 Hz, 1H), 7.36 (s, 1H), 7.17 (s, 1H), 7.11 (d, $J$ = 8.8 Hz, 1H), 2.45 (s, 3H), 1.33 (d, $J$ = 14.8 Hz, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 138.9, 131.6, 126.7 (d, $J$ = 4.4 Hz), 126.2, 122.4 (d, $J$ = 4.6 Hz), 117.3, 116.1, 110.9 (d, $J$ = 5.3 Hz), 38.5 (d, $J$ = 68.1 Hz), 26.5, 21.2; $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 64.26-63.35 (m). HRMS (ESI) m/z: calcd for C$_{17}$H$_{26}$ClNOP [M+H]$^+$, 326.1435; found 326.1445.

Di-tert-butyl(indolin-1-yl)phosphine oxide (1ac)

$n$-BuLi (7.2 mmol, 2.4 equiv), di-tert-butylchlorophosphane (3.6 mmol, 1.2 equiv) and H$_2$O$_2$ (1.2 mL of 30% solution, approx. 12 mmol). White solid (26%, 441.5 mg); Isolation by column chromatography (petroleum ether/EtOAc/DCM: 10/1/2); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.50 (d, $J$ = 8.4 Hz, 1H), 7.53 (d, $J$ = 7.6 Hz, 1H), 7.24 (t, $J$ = 7.5 Hz, 1H), 7.16 (t, $J$ = 7.5 Hz, 1H), 6.86 (s, 1H), 4.22 (s, 1H), 1.23 (d, $J$ = 14.0 Hz, 36H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 142.1, 128.7 (d, $J$ = 5.2 Hz), 124.1 (d, $J$ = 5.2 Hz), 123.5, 118.9 (d, $J$ = 4.8 Hz), 118.5, 116.2, 38.3 (d, $J$ = 69.4 Hz), 26.5, 21.2; $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 62.80-61.90 (m). HRMS (ESI) m/z: calcd for C$_{33}$H$_{49}$N$_2$O$_2$P$_2$ [M+H]$^+$, 567.3264; found 567.3272.

Di-tert-butyl(indolin-1-yl)phosphine oxide (1ad)

White solid (50%, 418.5 mg); Isolation by column chromatography (petroleum ether/EtOAc/DCM: 10/1/2); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.83 (d, $J$ = 8.0 Hz, 1H), 7.10 (d, $J$ = 7.2 Hz, 1H), 7.03 (t, $J$ = 7.8 Hz, 1H), 6.79 (t, $J$ = 7.4 Hz, 1H), 3.86 (d, $J$ = 8.4, 1.6 Hz, 2H), 3.07 (t, $J$ = 8.2 Hz, 2H), 1.35 (d, $J$ = 14.0 Hz, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.7, 129.5 (d, $J$ = 6.7 Hz), 127.5, 123.8, 120.3, 115.1, 50.1, 38.6 (d, $J$ = 72.0 Hz), 30.3, 27.2; $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 59.16-58.64 (m). HRMS (ESI) m/z: calcd for C$_{16}$H$_{27}$NOP [M+H]$^+$, 280.1825; found 280.1832.
Di-tert-butyl(9H-carbazol-9-yl)phosphine oxide (1ae)

White solid (18%, 176.6 mg); Isolation by column chromatography (petroleum ether/EtOAc/DCM: 10/1/2); 'H NMR (400 MHz, CDCl₃) δ 8.87 (d, J = 8.8 Hz, 1H), 8.02 (d, J = 7.6 Hz, 1H), 7.96 (d, J = 7.6 Hz, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.38 (q, J = 7.2 Hz, 2H), 7.27 (t, J = 7.2 Hz, 2H), 1.42 (d, J = 15.2 Hz, 18H); 13C NMR (100 MHz, CDCl₃) δ 145.1, 140.2 (d, J = 3.3 Hz), 126.7 (d, J = 4.6 Hz), 126.5, 125.5 (d, J = 4.1 Hz), 124.9, 121.5, 121.2, 119.9, 118.8, 118.0, 114.8, 40.5 (d, J = 65.8 Hz), 27.3; 31P NMR (162 MHz, CDCl₃) δ 69.66-68.73 (m). HRMS (ESI) m/z: calcd for C₂₀H₂₇NOP [M+H]+, 328.1825; found 328.1826.

C. Optimization of Reaction Conditions

(a) Screening of ligand

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*a Conditions: unless otherwise noted, all reactions were performed with 1 (0.1 mmol), 2a (2 equiv), Pd₂(dba)₃ (10 mol %), L (20 mol %), Ag₂CO₃ (2.0 equiv) and Cu(OTf)₂ (1.0 equiv) in toluene (1.5 mL), 90 °C, 12 h.*
(b) Optimization of additive amounts

\[
\begin{align*}
\text{1a} & \quad + \quad \text{TIPS} \quad \text{Br} \\
\text{2a} & \quad \rightarrow \quad \text{3a}
\end{align*}
\]

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\(^a\) Conditions: unless otherwise noted, all reactions were performed with 1a (0.1 mmol), 2a (2 equiv), \(\text{Pd}_2(\text{dba})_3\) (10 mol %), \(\text{L5}\) (20 mol %), Ag\(_2\text{CO}_3\), Cu(OTf)\(_2\) in solvent (1.0 mL) under air at 90 °C for 12 h.

\(^b\) Monitored by NMR using CH\(_2\)Br\(_2\) as the internal standard.

(c) Optimization of substrate amounts

\[
\begin{align*}
\text{1a} & \quad + \quad \text{TIPS} \quad \text{Br} \\
\text{2a} & \quad \rightarrow \quad \text{3a}
\end{align*}
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\(^a\) Conditions: unless otherwise noted, all reactions were performed with 1a (0.1 mmol), 2a, Pd\(_2\)(dba)\(_3\) (10 mol %), L5 (20 mol %), Ag\(_2\)CO\(_3\) (1.8 equiv), Cu(OTf)\(_2\) (1.5 equiv) in solvent (1.0 mL) under air at 90 °C for 12 h. \(^b\) Monitored by NMR using CH\(_2\)Br\(_2\) as the internal standard.

**d) Optimization by varying toluene amounts**

\[ \text{1a} \quad \text{2a} \quad \text{3a} \]

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<td>Ag(_2)CO(_3)/Cu(OTf)(_2)</td>
<td>1.5</td>
<td>83</td>
</tr>
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</table>

\(^a\) Conditions: unless otherwise noted, all reactions were performed with 1a (0.1 mmol), 2a (1.8 equiv), Pd\(_2\)(dba)\(_3\) (10 mol %), L5 (20 mol %), Ag\(_2\)CO\(_3\) (1.8 equiv), Cu(OTf)\(_2\) (1.5 equiv) in toluene under air at 90 °C for 12 h. \(^b\) Monitored by NMR using CH\(_2\)Br\(_2\) as the internal standard.

**e) Investigations of reaction atmosphere**

\[ \text{1a} \quad \text{2a} \quad \text{3a} \]

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>atmosphere</th>
<th>toluene (mL)</th>
<th>yield of 3a (%) (^b)</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>Pd(_2)(dba)(_3)</td>
<td>N(_2)</td>
<td>1.5</td>
<td>56</td>
</tr>
<tr>
<td>2</td>
<td>Pd(_2)(dba)(_3)</td>
<td>O(_2)</td>
<td>1.5</td>
<td>76</td>
</tr>
<tr>
<td>3</td>
<td>Pd(_2)(dba)(_3)</td>
<td>air</td>
<td>1.5</td>
<td>83</td>
</tr>
</tbody>
</table>

\(^a\) Conditions: unless otherwise noted, all reactions were performed with 1a (0.1 mmol), 2a (1.8 equiv),
Pd$_2$(dba)$_3$ (10 mol %), L$_5$ (20 mol %), Ag$_2$CO$_3$ (1.8 equiv), Cu(OTf)$_2$ (1.5 equiv) in toluene (1.5 mL) at 90 °C for 12 h. Monitored by NMR using CH$_2$Br$_2$ as the internal standard.

D. General Procedure for the Synthesis of 3

A mixture of substrate 1 (0.1 mmol), haloalkyne (2, 0.18 mmol), Pd$_2$(dba)$_3$ (10 mol %), Cu(OTf)$_2$ (1.5 equiv), Ag$_2$CO$_3$ (1.8 equiv), L$_4$ or L$_5$ (20 mol %) and 1.5 mL of toluene was added to a test tube equipped with a magnetic stirring bar. The mixture was then stirred at 90 °C under air for 2~12 h. After the reaction was completed (monitored by TLC), the resulting mixture was cooled to room temperature and extracted with ethyl acetate. The combined organic layers were evaporated under vacuum. The desired product 3 was obtained in the corresponding yield after purified by column chromatography on silica gel with mixture of petroleum ether and ethyl acetate.

E. Mechanistic Studies

A mixture of di-tert-butyl(1H-indol-1-yl)phosphine oxide (1a, 0.05 mmol), di-tert-butyl(1H-indol-1-yl-4,5,6,7-d$_4$)phosphine oxide (d$_4$-1a, 0.05 mmol), bromoalkyne (2a, 0.18 mmol), Pd$_2$(dba)$_3$ (10 mol %), Ag$_2$CO$_3$ (1.8 equiv), Cu(OTf)$_2$ (1.5 equiv), L$_5$ (20 mol %) and 1.5 mL of toluene was added to a test tube equipped with a magnetic stirring bar. The mixture was then stirred at 90 °C under air for 20 min. Then, the resulting mixture was cooled to room temperature and extracted with ethyl acetate. The combined organic layers were evaporated under vacuum. The desired product was obtained in 26% yield after purified by column chromatography on silica gel with mixture of petroleum ether and ethyl acetate (v/v = 30/1).
F. Further Synthetic Applications

(a) Di-tert-butyl(7-((trisopropylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3a, 0.1 mmol), TBAF (1 M in THF, 0.2 mL) and THF (3.5 mL) were added in a test tube under air atmosphere. Then the mixture was stirred at 45 °C for 1 h. After the reaction was completed (monitored by TLC), the resulting mixture was extracted with ethyl acetate. The combined organic layers were evaporated under vacuum. The desired product 4a was obtained in 86% yield after purified by column chromatography on silica gel with a mixture of petroleum ether/ethyl acetate (v/v = 5/1).

(b) Di-tert-butyl(7-((trisopropylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3a, 0.1 mmol), TBAF (1 M in THF, 0.2 mL) and THF (3.0 mL) were added in a test tube under air atmosphere. After this, the mixture was stirred at 65 °C for 12 h. After the reaction was completed (monitored
by TLC), the resulting mixture was extracted with ethyl acetate. The combined organic layers were evaporated under vacuum. The desired product 5a was obtained in 93% yield after purified by column chromatography on silica gel with a mixture of petroleum ether/ethyl acetate (v/v = 30/1).

(c) To a resealable Schlenk tube or alternatively, a screw-cap pressure tube, were added 4a (0.1 mmol), 1-iodo-4-methylbenzene (0.1 mmol, 1 equiv), Pd(PPh₃)₂Cl₂ (10 mol %), CuI (20 mol %), MeCN (1.0 mL), Et₃N (0.5 mL) and a stir bar. The reaction vessel was fitted with a rubber septum, and was evacuated and back-filled with nitrogen. The reaction tube was sealed and immersed in a preheated oil bath at 70 °C for 10 h and the solution was stirred with the aid of a magnetic stirrer. After the reaction was completed (monitored by TLC), the resulting mixture was cooled to room temperature and extracted with ethyl acetate. The desired product 6a was obtained in 67% yield after purified by column chromatography on silica gel with a mixture of petroleum ether/ethyl acetate (v/v = 30/1).

(d) 7-Ethynyl-1H-indole (5a, 0.12 mmol, 1.2 equiv), BnN₃ (0.1 mmol), CuI (20 mol %), MeCN (1.5 mL) were added in a test tube under air atmosphere and stirred at 80 °C for 12 h. After the reaction was completed (monitored by TLC), the resulting mixture were cooled to room temperature and extracted with ethyl acetate. The desired product 7a was obtained in 65% yield after purified by column chromatography on silica gel with a mixture of petroleum ether/ethyl acetate (v/v = 5/1).

G. Reference

H. Characterization Data for All Products

Di-tert-butyl(7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3a)

Brown solid (81%, 37.0 mg); mp: 83-84 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 30/1); 1H NMR (400 MHz, CDCl₃) δ 7.58-7.53 (m, 2H), 7.29 (s, 1H), 7.11 (t, J = 7.6 Hz, 1H), 6.69 (d, J = 3.2 Hz, 1H), 1.35 (d, J = 14.4 Hz, 18H), 1.17 (s, 21H); 13C NMR (100 MHz, CDCl₃) δ 138.3, 133.6, 131.5 (d, J = 4.1 Hz), 128.1 (d, J = 4.8 Hz), 121.6, 121.2, 112.4, 108.0 (d, J = 5.1 Hz), 107.5, 94.8, 39.2 (d, J = 67.3 Hz), 27.1, 18.8, 11.6; 31P NMR (162 MHz, CDCl₃) δ 62.51-61.61 (m); IR: νmax(KBr) = 2943, 2868, 2143, 1467, 1387, 1243, 1129, 993, 879, 738, 659, 474 cm⁻¹; HRMS (ESI) m/z: calcd for C₇₂H₈₄NOPSi [M+H]+, 458.3003; found 458.3008.

Di-tert-butyl(4-methyl-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3b)

Brown solid (82%, 38.6 mg); mp: 105-106 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 30/1); 1H NMR (400 MHz, CDCl₃) δ 7.48 (d, J = 7.6 Hz, 1H), 7.29 (s, 1H), 6.91 (d, J = 7.2 Hz, 1H), 6.71 (s, 1H), 2.50 (s, 3H), 1.35 (d, J = 14.8 Hz, 18H), 1.16 (s, 21H); 13C NMR (100 MHz, CDCl₃) δ 138.0, 133.6, 131.0 (d, J = 4.0 Hz), 130.7, 127.6 (d, J = 4.9 Hz), 122.2, 109.9, 107.8, 106.1 (d, J = 5.1 Hz), 93.8, 39.2 (d, J = 67.3 Hz), 27.1, 18.8, 11.6; 31P NMR (162 MHz, CDCl₃) δ 62.17-61.28 (m); IR: νmax(KBr) = 2945, 2867, 2141, 1471, 1355, 1242, 1122, 1003, 881, 813, 663, 474 cm⁻¹; HRMS (ESI) m/z: calcd for C₃₂H₃₄NOPSi [M+H]+, 472.3159, found 472.3161.

Di-tert-butyl(4-methoxy-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3c)

Brown oil (42%, 20.5 mg); Isolation by column chromatography (petroleum ether/ethyl acetate: 10/1); 1H NMR (400 MHz, CDCl₃) δ 7.53 (d, J = 8.4 Hz, 1H), 7.20 (s, 1H), 6.82 (d, J = 1.6 Hz, 1H), 6.57 (d, J = 8.0 Hz, 1H), 3.92 (s, 3H), 1.35 (d, J = 14.4 Hz, 18H), 1.16 (s, 21H); 13C NMR (100 MHz, CDCl₃) δ 153.3, 139.5, 134.9, 126.6 (d, J = 4.5 Hz), 121.7 (d, J = 4.6 Hz), 107.7, 105.5, 104.7 (d, J = 4.9 Hz), 102.2, 92.4, 55.3, 39.2 (d, J = 67.2 Hz), 27.1, 18.8, 11.6; 31P NMR (162 MHz, CDCl₃) δ 62.47-61.57 (m); IR: νmax(KBr) = 2941, 2864, 2139, 1482, 1364, 1272, 1119, 881, 756, 659, 476 cm⁻¹; HRMS (ESI) m/z: calcd for C₃₄H₃₆NO₃PSi [M+H]+, 488.3108, found 488.3111.

(4-Benzoyloxy)-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)di-tert-butylphosphine oxide (3d)

Brown solid (82%, 46.2 mg); mp: 115-116 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 30/1); 1H NMR (400 MHz, CDCl₃) δ 7.52-7.45 (m, 3H), 7.38 (t, J = 7.3 Hz, 2H), 7.34-7.30 (m, 1H), 7.20 (s, 1H), 6.88 (s, 1H), 6.63 (d, J = 8.4 Hz, 1H), 5.18 (s, 2H), 1.35 (d, J = 14.8 Hz, 18H), 1.16 (s, 21H); 13C NMR (100 MHz, CDCl₃) δ 152.5, 139.6, 137.0, 134.9, 128.5, 127.9, 127.3, 126.6 (d, J = 4.7 Hz), 122.1 (d, J = 4.5 Hz), 107.6, 105.7, 104.9 (d, J = 5.1 Hz), 103.6, 92.6, 70.0, 39.2 (d, J = 67.2 Hz), 27.1, 18.8, 11.6; 31P NMR (162 MHz, CDCl₃) δ 62.56-61.66 (m); IR: νmax(KBr) = 2940, 2864, 2139, 1481, 1366, 1275, 1117, 1018, 881, 747, 657, 473 cm⁻¹; HRMS (ESI) m/z: calcd for C₃₄H₃₆NO₃PSi [M+H]+, 564.3421, found 564.3429.

S15
**Di-tert-butyl(4-phenyl-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3e)**

White solid (79%, 42.1 mg); mp: 175-176 ℃; Isolation by column chromatography (petroleum ether/ethyl acetate: 20/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.64 (d, \(J = 7.6\) Hz, 1H), 7.58 (d, \(J = 7.2\) Hz, 2H), 7.46 (t, \(J = 7.4\) Hz, 2H), 7.37 (d, \(J = 7.0\) Hz, 1H), 7.33 (s, 1H), 7.16 (d, \(J = 7.6\) Hz, 1H), 6.85 (s, 1H), 1.37 (d, \(J = 14.4\) Hz, 18H), 1.18 (s, 21H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 140.4, 138.7, 135.0, 133.8, 129.8 (d, \(J = 3.8\) Hz), 128.9, 128.5, 128.4, 127.2, 121.8, 111.4, 107.6, 107.3 (d, \(J = 5.0\) Hz), 95.2, 39.4 (d, \(J = 67.1\) Hz), 27.2, 18.8, 11.6; \(^31\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) 62.78-62.05 (m); IR: \(\nu_{\text{max}}\) (KBr) = 3431, 2939, 2140, 1642, 1468, 1364, 1233, 1124, 1002, 891, 783, 663, 486 cm\(^{-1}\); HRMS (ESI) m/z: calcd for C\(_{33}\)H\(_{40}\)NNaOPSi [M+Na]\(^+\), 556.3135, found 556.3141.

**Di-tert-butyl(4-fluoro-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3f)**

Brown solid (78%, 37.1 mg); mp: 96-97 ℃; Isolation by column chromatography (petroleum ether/ethyl acetate: 30/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.53-7.49 (m, 1H), 7.27 (s, 1H), 6.83-6.79 (m, 2H), 1.36 (d, \(J = 14.8\) Hz, 18H), 1.16 (s, 21H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 156.1 (d, \(J = 248.8\) Hz), 140.5 (d, \(J = 9.4\) Hz), 134.4 (d, \(J = 7.4\) Hz), 128.0 (d, \(J = 4.6\) Hz), 120.4 (dd, \(J = 22.2, 4.5\) Hz), 108.7 (d, \(J = 4.0\) Hz), 107.1 (d, \(J = 18.8\) Hz), 106.7, 103.3 (d, \(J = 5.0\) Hz), 94.2, 39.3 (d, \(J = 66.8\) Hz), 27.1, 18.8, 11.5; \(^19\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -120.43 (t, \(J = 7.0\) Hz); \(^31\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) 63.40-62.48 (m); IR: \(\nu_{\text{max}}\) (KBr) = 2946, 2871, 2143, 1593, 1479, 1361, 1247, 1116, 1007, 882, 799, 662, 480 cm\(^{-1}\); HRMS (ESI) m/z: calcd for C\(_{27}\)H\(_{34}\)FNOPSi [M+H]\(^+\), 476.2908, found 476.2910.

**Di-tert-butyl(4-chloro-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3g)**

Brown solid (60%, 29.5mg); mp: 99-100 ℃; Isolation by column chromatography (petroleum ether/ethyl acetate: 30/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.49 (d, \(J = 8.0\) Hz, 1H), 7.34 (s, 1H), 7.12 (d, \(J = 8.0\) Hz, 1H), 6.84 (d, \(J = 2.0\) Hz, 1H), 1.35 (d, \(J = 14.8\) Hz, 18H), 1.16 (s, 21H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 138.8, 133.9, 130.2 (d, \(J = 4.1\) Hz), 128.7 (d, \(J = 4.5\) Hz), 126.3, 121.5, 111.2, 106.6, 106.2 (d, \(J = 4.8\) Hz), 95.9, 39.3 (d, \(J = 66.6\) Hz), 27.1, 18.8, 11.5; \(^31\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) 63.49-62.60 (m); IR: \(\nu_{\text{max}}\) (KBr) = 2946, 2868, 2144, 1468, 1348, 1239, 1122, 998, 884, 812, 751, 657, 472 cm\(^{-1}\); HRMS (ESI) m/z: calcd for C\(_{27}\)H\(_{36}\)ClINaOPSi [M+Na]\(^+\), 514.2432, found 514.2438.

(4-Bromo-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)di-tert-butylphosphine oxide (3h)

Brown solid (53%, 28.4 mg); mp: 100-101 ℃; Isolation by column chromatography (petroleum ether/ethyl acetate: 30/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.42 (d, \(J = 8.2\) Hz, 1H), 7.34 (s, 1H), 7.28 (d, \(J = 8.0\) Hz, 1H), 6.80 (d, \(J = 2.0\) Hz, 1H), 1.35 (d, \(J = 14.8\) Hz, 18H), 1.16 (s, 21H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 138.3, 134.0, 132.0 (d, \(J = 3.9\) Hz), 128.6 (d, \(J = 4.6\) Hz), 124.7, 115.0, 111.7, 108.1 (d, \(J = 4.6\) Hz), 106.6, 96.1, 39.3 (d, \(J = 66.6\) Hz), 27.1, 18.8, 11.5; \(^31\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) 63.60-62.70 (m); IR: \(\nu_{\text{max}}\) (KBr) = 2942, 2866, 2142, 1466, 1342, 1238, 1123, 993, 878, 811, 744, 657, 473 cm\(^{-1}\); HRMS (ESI) m/z: calcd for C\(_{27}\)H\(_{36}\)BrNNaOPSi [M+H]\(^+\), 558.1927, found 558.1931.

**S16**
Methyl 1-(di-tert-butylphosphoryl)-7-((triisopropylsilyl)ethynyl)-1H-indole-4-carboxylate (3i)

Brown solid (45%, 23.2 mg); mp: 153-154 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 10/1); 1H NMR (400 MHz, CDCl₃) δ 7.84 (d, J = 7.6 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.51 (s, 1H), 7.44 (s, 1H), 3.95 (s, 3H), 1.35 (d, J = 14.8 Hz, 18H), 1.16 (s, 21H); 13C NMR (100 MHz, CDCl₃) δ 167.1, 139.1, 132.5, 131.8 (d, J = 3.9 Hz), 130.2 (d, J = 4.6 Hz), 124.3, 121.3, 117.2, 108.7 (d, J = 4.7 Hz), 106.8, 99.2, 51.8, 39.4 (d, J = 66.7 Hz), 27.1, 18.8, 11.5; 31P NMR (162 MHz, CDCl₃) δ 63.61-62.72 (m); IR: νₗmax(KBr) = 2940, 2142, 1710, 1570, 1462, 1361, 1248, 1102, 1007, 891, 806, 656, 522 cm⁻¹; HRMS (ESI) m/z: calcld for C₉₂H₇₁NO₃PSi [M+H]+, 516.3057, found 516.3061.

Di-tert-butyl(4-(trifluoromethyl)-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phospine oxide (3j)

Brown solid (30%, 15.7 mg); mp: 71-72 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 10/1); 1H NMR (400 MHz, CDCl₃) δ 7.61 (d, J = 7.8 Hz, 1H), 7.43 (s, 1H), 7.39 (d, J = 7.6 Hz, 1H), 6.91 (s, 1H), 1.36 (d, J = 14.4 Hz, 18H), 1.17 (s, 21H); 13C NMR (100 MHz, CDCl₃) δ 138.9, 132.6, 129.8 (d, J = 4.3 Hz), 128.3 (q, J = 19.3 Hz), 124.52 (q, J = 270.4 Hz), 121.6 (q, J = 32.5 Hz), 118.8 (q, J = 4.8 Hz), 116.3, 106.3, 106.2 (d, J = 2.7 Hz), 98.3, 39.4 (d, J = 66.4 Hz), 27.1, 18.8, 11.5; 31F NMR (376 MHz, CDCl₃) δ -61.24 (s); 31P NMR (162 MHz, CDCl₃) δ 64.07-63.16 (m); IR: νₗmax(KBr) = 2943, 2144, 1590, 1468, 1318, 1228, 1119, 1001, 896, 813, 655, 474 cm⁻¹; HRMS (ESI) m/z: calcld for C₅₂H₄₅F₃NaNOPSi [M+Na]+, 548.2696, found 548.2697.

Di-tert-butyl(5-methyl-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phospine oxide (3k)

Brown solid (79%, 37.2 mg); mp: 116-117 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 30/1); 1H NMR (400 MHz, CDCl₃) δ 7.37 (s, 1H), 7.33 (s, 1H), 7.25 (s, 1H), 6.61 (d, J = 2.0 Hz, 1H), 2.38 (s, 3H), 1.34 (d, J = 14.4 Hz, 18H), 1.17 (s, 21H); 13C NMR (100 MHz, CDCl₃) δ 136.8, 134.6, 131.8 (d, J = 4.2 Hz), 130.9, 128.2 (d, J = 4.9 Hz), 121.3, 111.9, 107.6, 107.6 (d, J = 5.7 Hz), 94.2, 39.2 (d, J = 67.5 Hz), 27.1, 20.7, 18.8, 11.6; 31P NMR (162 MHz, CDCl₃) δ 61.92-61.02 (m); IR: νₗmax(KBr) = 2944, 2867, 2143, 1466, 1381, 1239, 1124, 991, 878, 753, 661, 608, 473 cm⁻¹; HRMS (ESI) m/z: calcld for C₅₂H₄₅NOPSi [M+H]+, 472.3159, found 472.3163.

Di-tert-butyl(5-methoxy-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phospine oxide (3l)

Brown oil (52%, 25.3 mg); Isolation by column chromatography (petroleum ether/ethyl acetate: 10/1); 1H NMR (400 MHz, CDCl₃) δ 7.27 (d, J = 2.4 Hz, 1H), 7.19 (d, J = 2.4 Hz, 1H), 7.03 (d, J = 2.4 Hz, 1H), 6.61 (d, J = 3.2 Hz, 1H), 3.81 (s, 3H), 1.33 (d, J = 14.4 Hz, 18H), 1.16 (s, 21H); 13C NMR (100 MHz, CDCl₃) δ 154.4, 133.5, 132.4 (d, J = 4.2 Hz), 128.8, 121.8, 113.0, 107.8 (dd, J = 4.4, 3.3 Hz), 107.0, 104.0 (d, J = 1.4 Hz), 94.8, 55.6 (d, J = 5.8 Hz), 39.2 (d, J = 67.3 Hz), 27.1, 18.8, 11.5; 31P NMR (162 MHz, CDCl₃) δ 62.13-61.21 (m); IR: νₗmax(KBr) = 2945, 2870, 2145, 1679, 1595, 1467, 1387, 1228, 1047, 805, 660, 472 cm⁻¹; HRMS (ESI) m/z: calcld for C₅₂H₄₇NO₃PSi [M+H]+, 488.3108, found 488.3111.
Di-tert-butyl(5-ethoxy-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3m)

Brown solid (58%, 29.1 mg); mp: 93-94 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 10/1); 1H NMR (400 MHz, CDCl3) δ 7.26 (s, 1H), 7.19 (s, 1H), 7.03 (s, 1H), 6.61 (s, 1H), 4.05 (q, J = 6.9 Hz, 2H), 1.42 (t, J = 6.9 Hz, 3H), 1.34 (d, J = 14.8 Hz, 18H), 1.16 (s, 21H); 13C NMR (100 MHz, CDCl3) δ 153.8, 133.5, 132.5 (d, J = 4.2 Hz), 128.8 (d, J = 4.7 Hz), 122.4, 113.0, 108.0 (d, J = 5.0 Hz), 107.1, 105.0, 94.8, 64.0, 39.3 (d, J = 67.3 Hz), 27.1, 18.9, 14.9, 11.6; 31P NMR (162 MHz, CDCl3) δ 62.38-61.49 (m); IR: νmax(KBr) = 2943, 2145, 1604, 1468, 1381, 1231, 1156, 1004, 807, 660, 491 cm⁻¹; HRMS (ESI) m/z: calcd for C29H49NO2PSi [M+H]+, 502.3265, found 502.3271.

Di-tert-butyl(5-fluoro-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3n)

Brown solid (56%, 26.6 mg); mp: 117-118 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 30/1); 1H NMR (400 MHz, CDCl3) δ 7.34 (s, 1H), 7.28 (d, J = 9.6 Hz, 1H), 7.20 (d, J = 8.0 Hz, 1H), 6.65 (s, 1H), 1.34 (d, J = 14.8 Hz, 18H), 1.16 (s, 21H); 13C NMR (100 MHz, CDCl3) δ 157.7 (d, J = 237.4 Hz), 135.1, 132.4 (dd, J = 10.3, 4.1 Hz), 129.7 (d, J = 4.6 Hz), 120.4 (d, J = 25.6 Hz), 113.3 (d, J = 10.2 Hz), 107.9 (t, J = 4.6 Hz), 106.7 (d, J = 22.9 Hz), 106.2 (d, J = 2.0 Hz), 96.3, 39.3 (d, J = 67.0 Hz), 27.1, 18.8, 11.5; 19F NMR (376 MHz, CDCl3) δ -123.43 (t, J = 9.0 Hz); 31P NMR (162 MHz, CDCl3) δ 62.90-62.00 (m); IR: νmax(KBr) = 2945, 2870, 2147, 1581, 1467, 1381, 1234, 1138, 985, 871, 802, 476 cm⁻¹; HRMS (ESI) m/z: calcd for C27H44FNOPSi [M+H]+, 476.2908, found 476.2913.

Di-tert-butyl(5-chloro-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3o)

Brown solid (46%, 22.6 mg); mp: 140-141 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 30/1); 1H NMR (400 MHz, CDCl3) δ 7.49 (d, J = 8.0 Hz, 1H), 7.32 (s, 1H), 7.12 (d, J = 8.0 Hz, 1H), 6.84 (d, J = 2.0 Hz, 1H), 1.35 (d, J = 14.8 Hz, 18H), 1.16 (s, 21H); 13C NMR (100 MHz, CDCl3) δ 137.0, 132.8 (d, J = 3.9 Hz), 132.5, 129.4 (d, J = 4.7 Hz), 126.8, 120.6, 113.5, 107.4 (d, J = 4.9 Hz), 106.0, 96.5, 39.3 (d, J = 66.8 Hz), 27.1, 18.8, 11.5; 31P NMR (162 MHz, CDCl3) δ 63.25-62.40 (m); IR: νmax(KBr) = 2939, 2145, 1719, 1456, 1368, 1233, 1115, 1006, 873, 669 cm⁻¹; HRMS (ESI) m/z: calcd for C27H43ClNNaOPSi [M+Na]+, 514.2432, found 514.2435.

(5-Bromo-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)di-tert-butylphosphine oxide (3p)

Brown solid (39%, 20.8 mg); mp: 141-142 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 30/1); 1H NMR (400 MHz, CDCl3) δ 7.66 (s, 1H), 7.61 (s, 1H), 7.30 (s, 1H), 6.63 (s, 1H), 1.34 (d, J = 14.8 Hz, 18H), 1.16 (s, 21H); 13C NMR (100 MHz, CDCl3) δ 137.4, 135.0, 133.2 (d, J = 4.3 Hz), 129.3 (d, J = 4.7 Hz), 123.7, 114.2, 114.0, 107.3 (d, J = 4.9 Hz), 105.9, 96.6, 39.1 (d, J = 66.7 Hz), 27.1, 18.8, 11.5; 31P NMR (162 MHz, CDCl3) δ 63.25-62.40 (m); IR: νmax(KBr) = 2939, 2145, 1719, 1456, 1368, 1233, 1115, 1006, 873, 669 cm⁻¹; HRMS (ESI) m/z: calcd for C27H43BrNOPSi [M+H]+, 536.2108, found 536.2110.
Methyl 1-(di-tert-butylphosphoryl)-7-((triisopropylsilyl)ethynyl)-1H-indole-5-carboxylate (3q)

Brown solid (52%, 26.8 mg); mp: 132-133 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 20/1); 1H NMR (400 MHz, CDCl3) δ 8.25 (s, 1H), 8.22 (s, 1H), 7.4 (s, 1H), 6.8 (s, 1H), 3.93 (s, 3H), 1.35 (d, J = 14.8 Hz, 18H), 1.18 (s, 21H); 13C NMR (100 MHz, CDCl3) δ 166.0, 139.9, 133.3, 130.5 (d, J = 4.2 Hz), 128.3 (d, J = 4.8 Hz), 122.8, 122.0, 111.3, 107.6 (d, J = 4.5 Hz), 105.4, 94.8, 51.0, 38.3 (d, J = 66.6 Hz), 26.1, 17.8, 10.5; 31P NMR (162 MHz, CDCl3) δ 63.57-62.66 (m); IR: νmax (KBr) = 2944, 2146, 1721, 1590, 1464, 1215, 1115, 998, 896, 664, 509 cm⁻¹; HRMS (ESI) m/z: calcd for C29H47NO3PSi [M+H]+, 516.3057, found 516.3059.

Di-tert-butyl(6-fluoro-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3s)

Brown oil (26%, 12.4 mg); Isolation by column chromatography (petroleum ether/ethyl acetate: 30/1); 1H NMR (400 MHz, CDCl3) δ 7.45 (dd, J = 8.5, 5.5 Hz, 1H), 7.28 (dd, J = 3.4, 2.0 Hz, 1H), 6.99 (t, J = 9.0 Hz, 1H), 6.66 (dd, J = 3.5, 1.0 Hz, 1H), 1.35 (d, J = 14.5 Hz, 18H), 1.17 (s, 21H); 13C NMR (100 MHz, CDCl3) δ 164.0 (d, J = 242.9 Hz), 138.9, 128.4, 127.5, 121.1 (d, J = 10.1 Hz), 110.6, 110.4, 107.8 (d, J = 4.5 Hz), 101.8 (dd, J = 63.3, 14.4 Hz), 98.6, 39.3 (d, J = 66.9 Hz), 27.1, 18.7, 11.5; 19F NMR (471 MHz, CDCl3) δ -109.59 (dd, J = 9.3, 5.7 Hz); 31P NMR (202 MHz, CDCl3) δ 63.06-62.55 (m); IR: νmax (KBr) = 2942, 2148, 1583, 1468, 1393, 1230, 1128, 1013, 918, 808, 729, 655 cm⁻¹; HRMS (ESI) m/z: calcd for C27H44FNOPSi [M+H]+, 476.2908, found 476.2914.

Di-tert-butyl(3-methyl-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3t)

Brown solid (84%, 39.6 mg); mp: 104-105 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 30/1); 1H NMR (400 MHz, CDCl3) δ 7.57 (d, J = 7.2 Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.12 (t, J = 7.2 Hz, 1H), 7.04 (s, 1H), 2.29 (s, 3H), 1.34 (d, J = 14.8 Hz, 18H), 1.16 (s, 21H); 13C NMR (100 MHz, CDCl3) δ 138.9, 133.5, 132.3 (d, J = 3.9 Hz), 125.2 (d, J = 2.5 Hz), 121.1, 119.1, 116.6 (d, J = 5.2 Hz), 112.4, 107.6, 94.6, 39.1 (d, J = 67.7 Hz), 27.1, 18.8, 11.5, 9.7; 31P NMR (162 MHz, CDCl3) δ 61.79-61.08 (m); IR: νmax (KBr) = 2943, 2141, 1466, 1390, 1320, 1112, 1013, 918, 808, 729, 664, 474 cm⁻¹; HRMS (ESI) m/z: calcd for C28H47NOPSi [M+H]+, 472.3159, found 472.3161.

Di-tert-butyl(3-chloro-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3u)

Brown solid (52%, 25.5 mg); mp: 102-103 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 30/1); 1H NMR (400 MHz, CDCl3) δ 7.63 (d, J = 7.6 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.26 (s, 1H), 7.20 (t, J = 7.6 Hz, 1H), 1.36 (d, J = 14.8 Hz, 18H), 1.16 (s, 21H); 13C NMR (100 MHz, CDCl3) δ 137.6, 134.7, 129.0 (d, J = 3.1 Hz), 124.3 (d, J = 4.6 Hz), 122.1, 118.7, 112.9, 112.0 (d, J = 5.5 Hz), 106.7, 95.9, 39.3 (d, J = 66.4 Hz), 27.1, 18.8, 11.5; 31P NMR (162 MHz, CDCl3) δ 63.97-63.07 (m); IR: νmax (KBr) = 2944, 2145, 1467, 1388, 1247, 1123, 1069, 1002, 884, 739, 661, 518 cm⁻¹; HRMS (ESI) m/z: calcd for C27H47ClNNaOPSi [M+Na]+, 516.2432, found 514.2433.
Ethyl 2-(1-(di-tert-butylphosphoryl)-7-((triisopropylsilyl)ethynyl)-1H-indole-3-yl)acetate (3v)

Brown solid (83%, 45.1 mg); mp: 116-117 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 10/1); 1H NMR (400 MHz, CDCl3) δ 7.58 (d, J = 7.2 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.38 (s, 1H), 7.14 (t, J = 7.5 Hz, 1H), 4.17 (q, J = 6.8 Hz, 2H), 3.73 (s, 2H), 1.35 (d, J = 14.4 Hz, 18H), 1.25 (t, J = 6.9 Hz, 3H), 1.16 (s, 21H); 13C NMR (100 MHz, CDCl3) δ 171.1, 138.7, 133.6, 131.1 (d, J = 3.5 Hz), 127.0 (d, J = 4.7 Hz), 121.5, 118.8, 113.4 (d, J = 5.1 Hz), 112.7, 107.3, 95.0, 60.9, 39.2 (d, J = 67.2 Hz), 30.8, 27.1, 18.8, 14.2, 11.5; 31P NMR (162 MHz, CDCl3) δ 62.76-62.04 (m); IR: δ 65.51-64.78 (m); IR: $\nu_{\text{max}}$(KBr) = 2943, 2141, 1733, 1466, 1390, 1222, 1012, 899, 797, 651, 514 cm$^{-1}$; HRMS (ESI) m/z: calcd for C31H33NO3PSi [M+H]+, 544.3370, found 544.3376.

Methyl 1-(di-tert-butylphosphoryl)-7-((triisopropylsilyl)ethynyl)-1H-indole-3-carboxylate (3w)

Brown solid (72%, 37.1 mg); mp: 85-86 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 10/1); 1H NMR (400 MHz, CDCl3) δ 8.20 (d, J = 7.6 Hz, 1H), 8.00 (s, 1H), 7.64 (d, J = 7.2 Hz, 1H), 7.24 (t, J = 7.8 Hz, 1H), 3.93 (s, 3H), 1.38 (d, J = 14.8 Hz, 18H), 1.16 (s, 21H); 13C NMR (100 MHz, CDCl3) δ 164.5, 138.7, 134.6, 134.5 (d, J = 4.9 Hz), 128.6 (d, J = 3.5 Hz), 123.1, 121.8, 112.6 (d, J = 5.0 Hz), 106.8, 99.9, 95.9, 51.4, 39.4 (d, J = 65.4 Hz), 27.2, 18.8, 11.5; 31P NMR (162 MHz, CDCl3) δ 65.03-64.30 (m); IR: $\nu_{\text{max}}$(KBr) = 2940, 2144, 1718, 1582, 1469, 1377, 1221, 1094, 998, 894, 794, 651, 502 cm$^{-1}$; HRMS (ESI) m/z: calcd for C29H30NO3PSi [M+H]+, 516.3057, found 516.3059.

1-(Di-tert-butylphosphoryl)-7-((triisopropylsilyl)ethynyl)-1H-indole-3-carbaldehyde (3x)

Brown solid (47%, 22.8 mg); mp: 172-173 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 5/1); 1H NMR (400 MHz, CDCl3) δ 10.14 (s, 1H), 8.31 (d, J = 7.6 Hz, 1H), 7.92 (s, 1H), 7.68 (d, J = 7.2 Hz, 1H), 7.27 (t, J = 7.6 Hz, 1H), 1.41 (d, J = 14.8 Hz, 18H), 1.17 (s, 21H); 13C NMR (100 MHz, CDCl3) δ 185.0, 139.2, 138.3 (d, J = 4.5 Hz), 135.5, 127.3 (d, J = 3.4 Hz), 123.8, 122.1 (d, J = 4.1 Hz), 121.9, 112.7, 106.5, 96.5, 39.5 (d, J = 64.9 Hz), 27.2, 18.8, 11.5; 31P NMR (162 MHz, CDCl3) δ 65.51-64.78 (m); IR: $\nu_{\text{max}}$(KBr) = 2942, 2147, 1662, 1469, 1390, 1232, 1014, 906, 800, 663, 501 cm$^{-1}$; HRMS (ESI) m/z: calcd for C29H44NO2PSi [M+H]+, 486.2952, found 486.2955.

1-(1-(Di-tert-butylphosphoryl)ethyl)-7-((triisopropylsilyl)ethyl)-1H-indol-3-yl)ethan-1-one (3y)

Brown solid (29%, 14.5 mg); mp: 111-112 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 10/1); 1H NMR (400 MHz, CDCl3) δ 8.39 (d, J = 7.6 Hz, 1H), 7.94 (s, 1H), 7.64 (d, J = 7.6 Hz, 1H), 7.26 (t, J = 6.6 Hz, 1H), 2.57 (s, 3H), 1.40 (d, J = 14.8 Hz, 18H), 1.16 (s, 21H); 13C NMR (100 MHz, CDCl3) δ 192.9, 138.9, 134.9, 134.8 (d, J = 4.8 Hz), 128.3 (d, J = 3.3 Hz), 123.6, 122.6, 121.2 (d, J = 4.1 Hz), 112.5, 106.7, 96.0, 39.5 (d, J = 65.3 Hz), 27.9, 27.2, 18.8, 11.5; 31P NMR (162 MHz, CDCl3) δ 64.74-64.01 (m); IR: $\nu_{\text{max}}$(KBr) = 2944, 2143, 1667, 1388, 1220, 1000, 888, 806, 651, 506 cm$^{-1}$; HRMS (ESI) m/z: calcd for C29H46NNaO2PSi [M+Na]+, 522.2928, found 522.2926.
Di-tert-butyl(3-(2-hydroxyethyl)-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3z)

White solid (21%, 10.5 mg); mp: 138-139 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 5:1); ¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, J = 7.2 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.18 (s, 1H), 7.11 (t, J = 7.4 Hz, 1H), 3.91 (t, J = 6.0 Hz, 2H), 2.97 (t, J = 5.6 Hz, 2H), 1.95 (s, 1H), 1.34 (d, J = 14.4 Hz, 18H), 1.16 (s, 21H); ¹³C NMR (100 MHz, CDCl₃) δ 138.9, 133.6, 131.4 (d, J = 3.8 Hz), 126.2 (d, J = 7.6 Hz), 121.3, 119.0, 117.7 (d, J = 5.1 Hz), 112.7, 107.4, 95.0, 62.1, 39.2 (d, J = 67.4 Hz), 28.2, 27.1, 18.8, 11.5; ³¹P NMR (162 MHz, CDCl₃) δ 62.58-61.87 (m); IR: νmax(KBr) = 3383, 2940, 2142, 1747, 1468, 1389, 1225, 1048, 899, 806, 653, 496 cm⁻¹; HRMS (ESI) m/z: calcd for C₂₉H₄₉NO₂PSi [M+H]+, 502.3265, found 502.3271.

Di-tert-butyl(3-chloro-4-fluoro-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3aa)

Brown oil (71%, 36.1 mg); Isolation by column chromatography (petroleum ether/ethyl acetate: 20/1); ¹H NMR (400 MHz, CDCl₃) δ 7.55-7.52 (m, 1H), 7.20 (s, 1H), 6.85 (t, J = 9.0 Hz, 1H), 1.36 (d, J = 14.8 Hz, 18H), 1.15 (s, 21H); ¹³C NMR (100 MHz, CDCl₃) δ 156.0 (d, J = 252.6 Hz), 139.9 (d, J = 7.5 Hz), 135.4 (d, J = 7.6 Hz), 125.0 (d, J = 3.9 Hz), 117.5 (dd, J = 16.6, 3.2 Hz), 109.3 (d, J = 4.5 Hz), 109.2 (dd, J = 5.6, 1.9 Hz), 108.4 (d, J = 18.6 Hz), 105.9, 95.3, 39.4 (d, J = 65.8 Hz), 27.1, 18.8, 11.5; ¹⁹F NMR (376 MHz, CDCl₃) δ -123.95 (dd, J = 9.6, 5.6 Hz); ³¹P NMR (162 MHz, CDCl₃) δ 65.17-64.44 (m); IR: νmax(KBr) = 2943, 2144, 1764, 1597, 1478, 1358, 1240, 1070, 895, 802, 669, 498 cm⁻¹; HRMS (ESI) m/z: calcd for C₂₇H₄₃ClFNOPSi [M+H]+, 510.2519, found 510.2514.

Di-tert-butyl(3-chloro-5-methyl-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3ab)

Brown solid (76%, 38.3 mg); mp: 81-82 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 20/1); ¹H NMR (400 MHz, CDCl₃) δ 7.43 (s, 1H), 7.35 (s, 1H), 7.23 (s, 1H), 2.42 (s, 3H), 1.34 (d, J = 14.8 Hz, 18H), 1.16 (s, 21H); ¹³C NMR (100 MHz, CDCl₃) δ 136.0, 135.8, 131.7, 129.2 (d, J = 3.3 Hz), 124.3 (d, J = 4.7 Hz), 118.8, 112.4, 111.5 (d, J = 5.7 Hz), 106.8, 95.2, 39.2 (d, J = 66.6 Hz), 27.1, 20.7, 18.8, 11.5; ³¹P NMR (162 MHz, CDCl₃) δ 63.43-62.71 (m); IR: νmax(KBr) = 2942, 2145, 1762, 1654, 1466, 1376, 1244, 1010, 841, 655, 498 cm⁻¹; HRMS (ESI) m/z: calcd for C₂₈H₄₆ClNOPSi [M+H]+, 506.2769, found 506.2772.

(Methylenebis(7-((triisopropylsilyl)ethynyl)-1H-indole-3,1-diyl))bis(di-tert-butylphosphine oxide (3ac)

Brown solid (48%, 44.3 mg); mp: 121-122 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 5/1); ¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, J = 7.2 Hz, 2H), 7.51 (d, J = 7.6 Hz, 2H), 7.12 (t, J = 7.6 Hz, 2H), 6.89 (s, 2H), 4.13 (s, 2H), 1.22 (d, J = 14.8 Hz, 36H), 1.16 (s, 42H); ¹³C NMR (100 MHz, CDCl₃) δ 138.9, 133.9, 131.0 (d, J = 4.2 Hz), 125.9 (d, J = 4.5 Hz), 121.3, 119.4, 118.9 (d, J = 4.9 Hz), 112.5, 107.5, 95.2, 39.0 (d, J = 67.4 Hz), 27.1, 21.0, 18.8,
Di-tert-butyl(7-((triisopropylsilyl)ethynyl)indolin-1-yl)phosphine oxide (3ad)

Brown oil (66%, 30.3 mg); Isolation by column chromatography (petroleum ether/ethyl acetate: 20/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.29 (d, \(J = 7.2\) Hz, 1H), 7.09 (d, \(J = 6.8\) Hz, 1H), 6.81 (t, \(J = 7.2\) Hz, 1H), 3.83 (q, \(J = 7.2\) Hz, 2H), 3.04 (t, \(J = 7.0\) Hz, 2H), 1.36 (d, \(J = 14.0\) Hz, 18H), 1.13 (s, 21H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 147.7, 135.1, 134.0 (d, \(J = 3.5\) Hz), 124.0, 121.8, 113.8, 107.3, 93.1, 50.1 (d, \(J = 1.5\) Hz), 38.9 (d, \(J = 69.3\) Hz), 30.9, 28.0, 18.8, 11.4; \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) 59.67-59.14 (m); IR: \(\nu_{\text{max}}(\text{KBr}) = 2941, 2142, 1705, 1454, 1214, 1048, 893, 781, 661, 486 cm\(^{-1}\)); HRMS (ESI) \(m/z\): calcld for \(\text{C}_{27}\text{H}_{32}\text{NOPSi} [\text{M}+\text{H}]^+\), 460.3159, found 460.3162.

Di-tert-butyl(1-((triisopropylsilyl)ethyl)-9H-carbazol-9-yl)phosphine oxide (3ae)

Brown solid (23%, 11.7 mg); mp: 131-132 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 10/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.96 (d, \(J = 6.4\) Hz, 1H), 7.90 (d, \(J = 7.2\) Hz, 1H), 7.86 (d, \(J = 7.2\) Hz, 1H), 7.66 (d, \(J = 7.2\) Hz, 1H), 7.37-7.30 (m, 2H), 7.26-7.21 (m, 1H), 1.35 (d, \(J = 14.8\) Hz, 18H), 1.16 (s, 21H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 143.4, 141.7 (d, \(J = 2.4\) Hz), 135.6, 128.7 (d, \(J = 2.6\) Hz), 128.6 (d, \(J = 3.4\) Hz), 125.2, 122.7, 122.2, 119.9, 119.4, 116.7, 115.4, 108.2, 94.5, 41.1 (d, \(J = 63.5\) Hz), 28.3, 18.9, 11.5; \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) 67.97-67.24 (m); IR: \(\nu_{\text{max}}(\text{KBr}) = 2938, 2141, 1653, 1465, 1388, 1209, 999, 896, 757, 661, 501 cm\(^{-1}\)); HRMS (ESI) \(m/z\): calcld for \(\text{C}_{31}\text{H}_{32}\text{NOPSi} [\text{M}+\text{H}]^+\), 508.3159, found 508.3163.

Di-tert-butyl(7-((tert-butyldimethylsilyl)ethyl)-1H-indol-1-yl)phosphine oxide (3af)

Brown oil (67%, 27.8 mg); Isolation by column chromatography (petroleum ether/ethyl acetate: 20/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.54 (d, \(J = 6.2\) Hz, 2H), 7.30 (d, \(J = 1.6\) Hz, 1H), 7.11 (t, \(J = 7.6\) Hz, 1H), 6.69 (s, 1H), 1.35 (d, \(J = 14.8\) Hz, 18H), 0.99 (s, 9H), 0.21 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 138.7, 133.0, 131.5 (d, \(J = 4.0\) Hz), 128.2 (d, \(J = 4.8\) Hz), 121.6, 121.3, 112.1, 108.1 (d, \(J = 5.0\) Hz), 106.1, 96.2, 39.3 (d, \(J = 67.3\) Hz), 27.1, 26.4, 17.0, -4.5; \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) 62.80-61.92 (m); IR: \(\nu_{\text{max}}(\text{KBr}) = 2951, 2145, 1686, 1470, 1399, 1257, 1124, 988, 818, 739, 661, 598, 525 cm\(^{-1}\)); HRMS (ESI) \(m/z\): calcld for \(\text{C}_{24}\text{H}_{29}\text{NOPSi} [\text{M}+\text{H}]^+\), 416.2533, found 416.2531.

Di-tert-butyl(7-ethynyl-1H-indol-1-yl)phosphine oxide (4a)

White solid (86%, 25.9 mg); mp: 155-156 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 5/1); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.59 (t, \(J = 7.2\) Hz, 2H), 7.34 (s, 1H), 7.14 (t, \(J = 7.6\) Hz, 1H), 6.72 (s, 1H), 3.37 (s, 1H), 1.37 (d, \(J = 14.4\) Hz)}
7-Ethynyl-1H-indole (5a)

White solid (93%, 13.1 mg); mp: 86-87 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 30/1); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.45 (s, 1H), 7.66 (d, $J = 7.6$ Hz, 1H), 7.37 (d, $J = 6.8$ Hz, 1H), 7.21 (s, 1H), 7.08 (t, $J = 7.0$ Hz, 1H), 6.57 (s, 1H), 3.37 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 136.9, 127.4, 125.9, 124.4, 122.0, 119.6, 104.8, 103.8, 81.2, 80.3; IR: $\nu_{max}$(KBr) = 3126, 2923, 1647, 1394, 1072, 793, 637 cm$^{-1}$; HRMS (ESI) m/z: calcd for C$_{10}$H$_7$NNa [M+Na]$^+$, 164.0471, found 164.0477.

Di-tert-butyl(7-(p-tolylethynyl)-1H-indol-1-yl)phosphine oxide (6a)

Brown oil (67%, 26.2 mg); Isolation by column chromatography (petroleum ether/ethyl acetate: 20/1); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.61-7.55 (m, 4H), 7.35 (s, 1H), 7.17-7.12 (m, 3H), 6.71 (s, 1H), 2.35 (s, 3H), 1.38 (d, $J = 14.8$ Hz, 18H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 139.0, 137.3, 131.5, 131.4 (d, $J = 4.1$ Hz), 128.8, 128.2 (d, $J = 5.4$ Hz), 121.9, 121.6, 120.9, 111.7, 107.8 (d, $J = 5.1$ Hz), 92.7, 90.3, 39.4 (d, $J = 67.5$ Hz), 27.1, 21.5; $^{31}$P NMR (162 MHz, CDCl$_3$) δ 62.88-62.15 (m); IR: $\nu_{max}$(KBr) = 2959, 1740, 1479, 1384, 1235, 1122, 983, 813, 726, 655, 513 cm$^{-1}$; HRMS (ESI) m/z: calcd for C$_{25}$H$_{31}$NOP [M+H]$^+$, 392.2138, found 392.2142.

7-(1-Benzyl-1H-1,2,3-triazol-5-yl)-1H-indole (7a)

White solid (65%, 17.8 mg); mp: 112-113 °C; Isolation by column chromatography (petroleum ether/ethyl acetate: 5/1); $^1$H NMR (400 MHz, CDCl$_3$) δ 10.58 (s, 1H), 7.69 (s, 1H), 7.61 (d, $J = 7.6$ Hz, 1H), 7.31 (s, 4H), 7.26-7.22 (m, 3H), 7.07 (t, $J = 7.4$ Hz, 1H), 6.57 (s, 1H), 5.45 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 148.0, 134.5, 133.0, 129.0, 128.8, 128.7, 127.9, 125.0, 120.7, 119.3, 119.2, 118.1, 113.3, 102.0, 54.1; IR: $\nu_{max}$(KBr) = 3401, 3130, 3047, 2934, 1610, 1436, 1335, 1213, 1062, 895, 799, 720, 542 cm$^{-1}$; HRMS (ESI) m/z: calcd for C$_{17}$H$_{15}$N$_4$ [M+H]$^+$, 275.1291, found 275.1287.
I. X-ray Crystallographic Analysis

![Chemical structure of 3n]

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<td>b = 10.888(2) Å, beta = 95.814(6) deg.</td>
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J. Copies of $^1$H, $^{13}$C, $^{19}$F and $^{31}$P NMR Spectra

Di-tert-butyl(7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3a)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Di-tert-butyl(4-methyl-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3b)

$^{31}$P NMR (162 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)

$^{31}$P NMR (162 MHz, CDCl$_3$)
Di-tert-butyl(4-methoxy-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3c)
(4-(Benzyloxy)-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)di-tert-butylphosphine oxide (3d)
Di-tert-butyl(4-phenyl-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3e)
2-(4-Fluoro-2-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)aniline (3f)

$^{31}$P NMR (162 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)

$^{19}$F NMR (376 MHz, CDCl$_3$)
Di-tert-butyl(4-chloro-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3g)
$^{13}$C NMR (100 MHz, CDCl$_3$)

$^{31}$P NMR (162 MHz, CDCl$_3$)
(4-Bromo-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)di-tert-butylphosphine oxide (3h)
Methyl 1-(di-tert-butylphosphoryl)-7-((triisopropylsilyl)ethynyl)-1H-indole-4-carboxylate (3i)
Di-tert-butyl(4-(trifluoromethyl)-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3j)
Di-tert-butyl(5-methyl-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3k)
Di-tert-butyl(5-methoxy-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3l)
Di-tert-butyl(5-ethoxy-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3m)
Di-tert-butyl(5-fluoro-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3n)
Di-tert-butyl(5-chloro-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3o)
(5-Bromo-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)di-tert-butylphosphine oxide (3p)
Methyl 1-(di-tert-butylphosphoryl)-7-((triisopropylsilyl)ethynyl)-1H-indole-5-carboxylate (3q)
Di-tert-butyl(6-fluoro-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3s)
Di-tert-butyl(3-methyl-7-((triisopropylsilyl)ethyl)-1H-indol-1-yl)phosphine oxide (3t)
Di-tert-butyl(3-chloro-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3u)
Ethyl 2-(1-(di-tert-butylphosphoryl)-7-((triisopropylsilyl)ethynyl)-1H-indol-3-yl)acetate (3v)
Methyl 1-(di-tert-butylphosphoryl)-7-((triisopropylsilyl)ethynyl)-1H-indole-3-carboxylate (3w)
$^{13}$C NMR (100 MHz, CDCl$_3$)

$^{31}$P NMR (162 MHz, CDCl$_3$)
1-(Di-tert-butylphosphoryl)-7-((triisopropylsilyl)ethynyl)-1H-indole-3-carbaldehyde (3x)
1-(1-(Di-tert-butylphosphoryl)-7-((triisopropylsilyl)ethynyl)-1H-indol-3-yl)ethan-1-one (3y)
Di-tert-butyl(3-(2-hydroxyethyl)-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3z)
Di-tert-butyl(3-chloro-4-fluoro-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3aa)
$^{13}$C NMR (100 MHz, CDCl$_3$)

$^{19}$F NMR (376 MHz, CDCl$_3$)
Di-tert-buty(3-chloro-5-methyl-7-((triisopropylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3ab)
(Methylenebis(7-((triisopropylsilyl)ethynyl)-1H-indole-3,1-diyl))bis(di-tert-butylphosphine oxide) (3ac)
Di-tert-butyl(7-((triisopropylsilyl)ethynyl)indolin-1-yl)phosphine oxide (3ad)

$^{31}$P NMR (102 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)

$^{31}$P NMR (162 MHz, CDCl$_3$)
Di-tert-butyl(1-((triisopropylsilyl)ethynyl)-9H-carbazol-9-yl)phosphine oxide (3ae)
Di-tert-butyl(7-((tert-butyldimethylsilyl)ethynyl)-1H-indol-1-yl)phosphine oxide (3af)
Di-tert-butyl(7-ethynyl-1H-indol-1-yl)phosphine oxide (4a)
7-Ethynyl-1H-indole (5a)

$^{31}P$ NMR (162 MHz, CDCl$_3$)

$^1H$ NMR (400 MHz, CDCl$_3$)
Di-tert-butyl(7-(p-tolylethynyl)-1H-indol-1-yl)phosphine oxide (6a)
7-(1-Benzyl-1H-1,2,3-triazol-5-yl)-1H-indole (7a)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)

S78