Supporting Information

Cu/Pd cooperatively catalyzed tandem C–N and C-P bond formation: access to phosphorated 2H-indazoles

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1. General Information

Reagents and Solvents: All solvents were purified and dried according to standard methods. PE refers to petroleum ether (b.p. 60–90 °C) and EA refers to ethyl acetate. 2-Alkynyl azobenzenes derivatives were synthesized following the literature procedure.\textsuperscript{1,2,3} P(O)H compounds 2b-2f, 2i, 2l were commercially available and were used without further purification, and the other P(O)H compounds were synthesized following the literature procedure.\textsuperscript{4,5}

Chromatography: Flash column chromatography was carried out using commercially available 200-300 mesh under pressure unless otherwise indicated. Gradient flash chromatography was conducted eluting with PE/EA, they are listed as volume/volume ratios.

Data collection: \textsuperscript{1}H and \textsuperscript{13}C NMR spectra were collected on BRUKER AV-300 (300 MHz) spectrometer using CDCl\textsubscript{3} as solvent. Chemical shifts of \textsuperscript{1}H NMR were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ = 0.00 ppm) with the solvent resonance as an internal standard (CDCl\textsubscript{3}: δ = 7.26 ppm). Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, brs = broad singlet, m = multiplet), coupling constant (Hz), and integration. Chemical shifts of \textsuperscript{13}C NMR were reported in ppm with the solvent as the internal standard (CDCl\textsubscript{3}: δ = 77.0 ppm). High Resolution Mass measurement was performed on Agilent QTOF 6520 mass spectrometer with electron spray ionization (ESI) as the ion source. Melting point (m.p.) was measured on a microscopic melting point apparatus. Infrared spectra (IR) were recorded on a Thermo Scientific iS10 FT/IR spectrometer using a thin film supported on KBr disks. The wave numbers (n) of recorded IR-signals are quoted in cm\textsuperscript{-1}.
2. General procedure for preparation of 2-alkynyl azobenzenes

Substituted nitroso-benzene (1.0 equiv) was added to the substituted iodinated aniline (1.0 equiv) dissolved in AcOH (0.1 M). The solution was heated to 85 °C for 40 h. The resulting mixture was cooled to room temperature, diluted with DCM, and washed with brine and H2O. The organic layer was dried through anhydrous Na2SO4, filtered over Celite, and concentrated in vacuo. Column chromatography on silica gel gave the corresponding 2-iodoazobenzenes. Then 2-iodoazobenzene (1.0 mmol, 1.0 equiv), Pd(PPh3)2Cl2 (28.1 mg, 0.04 mmol, 0.04 equiv), CuI (15.2 mg, 0.08 mmol, 0.08 equiv) and BuNH2 (497 μL, 6.0 mmol, 6.0 equiv) were dissolved in anhydrous THF (0.1 M) under Ar. To the resulting solution terminal alkyne (1.2 mmol, 1.2 equiv) was added dropwise. The mixture was stirred at room temperature. After the reaction was completed (detected by TLC) (2-7 h), saturated NH4Cl aqueous solution was added. The organic layer was separated, and the aqueous layer was extracted twice with ethyl acetate. The combined organic layers were dried over Na2SO4 and concentrated in vacuo. The crude residue was purified by column chromatography on silica gel.

11 were synthesized according to the following procedure [1]:

The 2-iodoazobenzene (1.0 equiv), PdCl2(dpff) (0.05 equiv), CuI (0.1 equiv), and (trimethylsilyl)acetylene (1.4 equiv) were dissolved in an amine base (0.1 M solution based on diazene). The mixture was immediately degassed by three successive freeze-pump-thaw cycles, and the flask was charged with Ar. The mixture was heated to 50 °C and stirred under Ar overnight. After cooling, the mixture was filtered over a short pad of silica (CH2Cl2) and concentrated in vacuo. Column chromatography on silica gel gave the desired product 11.

1-phenyl-2-(2-(p-tolylethynyl)phenyl)diazene (1c)
51% yield (151.1 mg); red solid; m. p. 56-58 °C; 1H NMR (300 MHz, CDCl3) δ 7.93 (d, J = 7.0 Hz, 2H), 7.80-7.63 (m, 2H), 7.58-7.43 (m, 5H), 7.42-7.32 (m, 2H), 7.07 (d,
$J = 7.8 \text{ Hz}, 2\text{H}$, 2.27 (s, 3H). $^{13}\text{C NMR (75 MHz, CDCl}_3\delta 153.0, 152.9, 138.7, 133.3, 131.6, 131.3, 130.5, 129.2, 129.1, 128.7, 124.0, 123.3, 120.4, 116.2, 96.0, 86.3, 21.6.

IR (KBr): $\tilde{\nu} =$3128, 2218, 1400, 812, 772, 739, 680, 506 cm$^{-1}$; HRMS (ESI) calcd for $[\text{C}_{21}\text{H}_{16}\text{N}_2\text{H}]^+$ 297.1386, found 297.1389.

1-(2-((4-fluorophenyl)ethynyl)phenyl)-2-phenylidiazene (1e)
54% yield (162.0 mg); red solid; m. p. 65-67 °C; $^1\text{H NMR (300 MHz, CDCl}_3\delta 7.94-7.85 ($m, 2H), 7.67-7.59 ($m, 1H), 7.58-7.52 ($m, 1H), 7.48-7.34 ($m, 5H), 7.31-7.24 ($m, 2H), 6.97-6.87 ($m, 2H). $^{13}\text{C NMR (75 MHz, CDCl}_3\delta 164.3, 161.0, 153.1, 152.9, 133.6$ ($d, J = 8.4 \text{ Hz})$, 133.3, 131.4, 130.6, 129.2, 129.0, 123.3, 116.3, 115.9, 115.6, 94.6, 86.6.

IR (KBr): $\tilde{\nu} =$3127, 2360, 2336, 1400, 830, 748, 686, 553 cm$^{-1}$; HRMS (ESI) calcd for $[\text{C}_{21}\text{H}_{16}\text{N}_2\text{H}]^+$ 301.1136, found 301.1138.

1-(2-((4-bromophenyl)ethynyl)phenyl)-2-phenylidiazene (1g)
60% yield (216.2 mg); red solid; m. p. 61-63 °C; $^1\text{H NMR (300 MHz, CDCl}_3\delta 7.99$ ($d, J = 7.2 \text{ Hz}, 2\text{H}), 7.80-7.60 ($m, 2\text{H}), 7.56-7.45 ($m, 5\text{H}), 7.44-7.28 ($m, 4\text{H}). $^{13}\text{C NMR (75 MHz, CDCl}_3\delta 153.1, 152.9, 133.3, 133.0, 131.8, 131.7, 131.4, 130.5, 129.1, 123.3, 123.3, 122.7, 122.4, 116.3, 94.5, 88.0. IR (KBr): $\tilde{\nu} =$3128, 2360, 2348, 1400, 818, 765,739, 683 cm$^{-1}$; HRMS (ESI) calcd for $[\text{C}_{21}\text{H}_{16}\text{N}_2\text{H}]^+$ 361.0335, found 361.0330.

1-(5-methyl-2-(phenylethynyl)phenyl)-2-phenylidiazene(1q)
62% yield (183.5 mg); red solid; m. p. 50-52 °C; $^1\text{H NMR (300 MHz, CDCl}_3\delta 7.89$ ($d, J = 7.5 \text{ Hz}, 2\text{H}), 7.56-7.38 ($m, 4\text{H}), 7.38-7.25 ($m, 3\text{H}), 7.18 ($m, 3\text{H}), 7.07$ ($d, J = 8.2 \text{ Hz}, 1\text{H}), 2.24$ (s, 3\text{H}). $^{13}\text{C NMR (75 MHz, CDCl}_3\delta 153.0, 139.4, 133.2, 131.7, 131.6, 131.3, 129.2, 129.0, 128.4, 128.4, 123.8, 123.3, 121.1, 116.6, 95.1, 87.2, 21.6.
IR (KBr): $\tilde{\nu} = 3133, 1400,863, 804,689$ cm$^{-1}$; HRMS (ESI) calcd for [C$_{21}$H$_{16}$N$_{2}$+H]$^+$ 297.1386, found 297.1391.

1-(5-chloro-2-(phenylethynyl)phenyl)-2-phenyldiazene (1r)
58% yield (183.3 mg); red solid; m. p. 60-62°C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.10-7.91 (m, 2H), 7.75 (d, $J = 2.2$ Hz, 1H), 7.66-7.55 (m, 3H), 7.53 (d, $J = 6.7$ Hz, 3H), 7.44-7.23 (m, 4H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 153.5, 152.6, 135.1, 134.2, 131.8, 131.7, 130.4, 129.2, 128.6, 128.4, 123.4, 122.4, 116.5, 109.0, 96.6, 85.8. IR (KBr): $\tilde{\nu} = 3133, 2360, 2342, 1400, 854, 824, 754, 683$ cm$^{-1}$; HRMS (ESI) calcd for [C$_{20}$H$_{13}$ClN$_{2}$+H]$^+$ 317.0840, found 317.0843.

methyl 4-((2-(phenylethynyl)phenyl)diazenyl)benzoate (1s)
64% yield (217.6 mg); red solid; m. p. 92-94 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.14-7.97 (m, 2H), 7.88 (d, $J = 8.2$ Hz, 2H), 7.66-7.49 (m, 2H), 7.51-7.35 (m, 2H), 7.24 (m, 5H), 3.77 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 166.4, 155.3, 152.8, 133.4, 132.0, 131.7, 131.3, 130.6, 128.9, 128.6, 128.5, 124.6, 123.3, 123.0, 116.1, 96.2, 86.8, 52.3. IR (KBr): $\tilde{\nu} = 3132, 1724, 1571, 1400, 1008, 837, 754, 686, 510$ cm$^{-1}$
$^1$ HRMS (ESI) calcd for [C$_{22}$H$_{16}$N$_{2}$O$_{2}$+H]$^+$ 341.1285, found 341.1289.

1-(4-bromophenyl)-2-(2-(phenylethynyl)phenyl)diazene (1t)
72% yield (259.2 mg); red solid; m. p. 81-83 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.93 – 7.82 (m, 2H), 7.76-7.61 (m, 2H), 7.67-7.60 (m, 2H), 7.60-7.52 (m, 2H), 7.47-7.38 (m, 2H), 7.37-7.30 (m, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 152.8, 151.6, 133.4, 132.4, 131.6, 130.9, 128.9, 128.6, 128.4, 125.8, 124.7, 124.0, 123.4, 116.1, 95.9, 86.8. IR (KBr): $\tilde{\nu} = 3128, 2216, 1571, 1400, 1008, 837, 754, 686, 510$ cm$^{-1}$; HRMS (ESI) calcd for [C$_{20}$H$_{13}$BrN$_{2}$+H]$^+$ 361.0335, found 361.0336.
3. General procedure for synthesis and characterization of compounds

To a solution of the 2-alkynyl azobenzenes (0.2 mmol, 1.0 equiv), Pd(CH$_3$CN)$_2$Cl$_2$ (5.18mg, 0.02mmol, 10 mol%), Cu(CH$_3$CN)$_4$PF$_6$ (14.8mg, 0.04mmol, 20 mol%) and DIPEA (0.3 mmol, 1.5 equiv) in 2.0 mL anhydrous THF, the appropriate P(O)H compounds (0.24 mmol, 1.2 equiv) was added under Ar and the resulting mixture was stirred at 40 °C for 24 h. After the reaction was completed (detected by TLC), the solvent was removed under reduced pressure and the residue was purified by column chromatography to afford the pure product (PE:EA= 2:1).

- **diethyl (phenyl(2-phenyl-2H-indazol-3-yl)methyl)phosphonate (3aa)**
  - 94% yield (80.1 mg); colorless oil; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.46 (d, $J$ = 8.7, 1H), 7.74 (d, $J$ = 8.8 Hz, 1H), 7.57-7.48 (m, 3H), 7.46-7.38 (m, 4H), 7.19 (dd, $J$ = 8.6, 6.6 Hz, 1H), 4.94 (d, $J$ = 28.3 Hz, 1H), 4.02-3.65 (m, 4H), 1.09 (t, $J$ = 7.1 Hz, 3H), 1.00 (t, $J$ = 7.0 Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 148.9 (d, $J$ = 2.1 Hz), 139.3, 134.1 (d, $J$ = 5.1 Hz), 130.5, 129.6, 129.3, 129.2 (d, $J$ = 6.3 Hz), 128.8 (d, $J$ = 2.1 Hz), 127.6 (d, $J$ = 2.7 Hz), 126.8, 126.7, 122.8 (d, $J$ = 1.3 Hz), 122.3, 121.2 (d, $J$ = 3.0 Hz), 117.6, 63.3 (d, $J$ = 7.1 Hz), 63.0 (d, $J$ = 7.1 Hz), 43.9 (d, $J$ = 143.2 Hz), 16.3 (d, $J$ = 2.3 Hz), 16.2 (d, $J$ = 2.3 Hz); $^{31}$P NMR (CDCl$_3$, 202 MHz): $\delta$ 22.1. IR (KBr): $\bar{\nu}$ =3128, 1596, 1498, 1400, 1245, 1056, 1026, 759, 698 cm$^{-1}$; HRMS (ESI) calcd for [C$_{24}$H$_{25}$N$_2$O$_3$P+H]$^+$ 421.1676, found 421.1681.

- **diethyl (phenyl(2-phenyl-2H-indazol-3-yl)methyl)phosphonate (3ba)**
  - 68% yield (61.2 mg); yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.45 (d, $J$ = 8.7 Hz, 1H), 7.73 (d, $J$ = 8.8 Hz, 1H), 7.52 (m, 3H), 7.39 (m, 2H), 7.36-7.25 (m, 3H), 7.18 (dd,
$\delta = 8.6, 6.6$ Hz, 1H), 6.82 (d, $J = 8.7$ Hz, 2H), 4.87 (d, $J = 28.2$ Hz, 1H), 4.03-3.62 (m, 7H), 1.11 (t, $J = 7.1$ Hz, 3H), 1.01 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 158.9, 148.9, 139.4, 130.8, 130.3, 130.3, 129.5, 129.3, 126.8, 126.7, 126.0, 122.8, 122.2, 121.1, 117.6, 114.2 (d, $J = 1.9$ Hz), 63.3 (d, $J = 7.1$ Hz), 63.0 (d, $J = 7.1$ Hz), 55.2, 43.0 (d, $J = 143$ Hz), 16.3 (t, $J = 5.1$ Hz). $^{31}$P NMR (CDCl$_3$, 202 MHz): $\delta$ 22.4. IR (KBr): $\tilde{\nu} = 3134, 2360, 1508, 1400, 1252, 1051, 1026, 972, 674, 544$ cm$^{-1}$. HRMS (ESI) calcd for [C$_{25}$H$_{27}$N$_2$O$_3$P+H]$^+$ 451.1781, found 451.1785.

**diethyl ((2-phenyl-2H-indazol-3-yl)(p-toly)methyl)phosphonate(3ca)**

76% yield (66.0 mg); yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.45 (m, 1H), 7.73 (d, $J = 8.7$ Hz, 1H), 7.51 (m, 3H), 7.45-7.37 (m, 2H), 7.37-7.26 (m, 3H), 7.18 (dd, $J = 8.7, 6.6$ Hz, 1H), 7.09 (d, $J = 7.9$ Hz, 2H), 4.90 (d, $J = 28.3$ Hz, 1H), 4.03-3.62 (m, 4H), 2.29 (s, 3H), 1.11 (t, $J = 7.1$ Hz, 3H), 1.00 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 149.0, 139.4, 137.3 (d, $J = 2.9$ Hz), 131.0 (d, $J = 5.0$ Hz), 130.7, 129.5, 129.5, 129.3, 129.0 (d, $J = 6.3$ Hz), 126.8, 126.7, 122.9 (d, $J = 1.4$ Hz), 122.2, 121.2, (d, $J = 2.9$ Hz), 117.6, 63.1 (d, $J = 7.1$ Hz), 63.0 (d, $J = 7.1$ Hz), 43.5 (d, $J = 143$ Hz), 21.0, 16.3 (d, $J = 4.2$ Hz), 16.2 (d, $J = 4.4$ Hz). $^{31}$P NMR (CDCl$_3$, 202 MHz): $\delta$ 22.3. IR (KBr): $\tilde{\nu} = 3132, 1641, 1400, 1257, 1163, 1057, 853, 539$ cm$^{-1}$; HRMS (ESI) calcd for [C$_{25}$H$_{27}$N$_2$O$_3$P+H]$^+$ 435.1832, found 435.1384.

**diethyl ((1,1'-biphenyl)-4-yl)(2-phenyl-2H-indazol-3-yl)methyl)phosphonate(3da)**

85% yield (84.2 mg); white solid; m. p. 57-59 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.49 (d, $J = 8.6$ Hz, 1H), 7.76 (d, $J = 8.7$ Hz, 1H), 7.61-7.47 (m, 9H), 7.47-7.41 (m, 2H), 7.42-7.13 (m, 5H), 5.00 (d, $J = 28.3$ Hz, 1H), 4.07-3.67 (m, 4H), 1.13 (t, $J = 7.1$ Hz, 3H), 1.02 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 149.0 (d, $J = 2.2$ Hz), 140.4 (d, $J = 2.9$ Hz), 140.3, 139.4, 133.2 (d, $J = 5.1$ Hz), 130.4, 129.6, 129.6 (d, $J = 2.9$ Hz), 129.4, 128.8, 127.5, 127.4, 127.0, 126.8, 126.7, 122.8, 122.3, 121.2 (d, $J = 2.9$ Hz), 121.1, 117.6, 114.2 (d, $J = 1.9$ Hz), 63.3 (d, $J = 7.1$ Hz), 63.0 (d, $J = 7.1$ Hz), 55.2, 43.0 (d, $J = 143$ Hz), 16.3 (t, $J = 5.1$ Hz).
Hz), 118, 63.3 (d, J = 7.1 Hz), 63.0 (d, J = 7.1 Hz), 43.7 (d, J = 143.1 Hz), 16.3(d, J = 4.6 Hz), 16.2 (d, J = 4.1 Hz). \(^{31}\)P NMR (CDCl\(_3\), 202 MHz): \(\delta\) 22.0, 63.3 (d, J = 7.1 Hz), 63.0 (d, J = 7.1 Hz), 43.7 (d, J = 143.1 Hz), 16.3 (d, J = 4.6 Hz), 16.2 (d, J = 4.1 Hz). IR(KBr): \(\tilde{\nu}\) =3128, 1599, 1400, 1253, 1160, 1049, 1022, 966, 767, 697, 562 cm\(^{-1}\); HRMS (ESI) calcd for [C\(_{30}\)H\(_{29}\)N\(_{2}\)O\(_{3}\)P+H]\(^+\) 497.1989, found 497.1993.

diethyl ((4-fluorophenyl)(2-phenyl-2\(H\)-indazol-3-yl)methyl)phosphonate (3ea)

77% yield (67.5 mg); yellow oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.42 (d, J = 8.6 Hz, 1H), 7.74 (d, J = 8.7 Hz, 1H), 7.53 (m, 3H), 7.45-7.25 (m, 5H), 7.19 (dd, J = 8.7, 6.6 Hz, 1H), 6.98 (t, J = 8.6 Hz, 2H), 4.90 (d, J = 28.3 Hz, 1H), 4.07-3.63 (m, 4H), 1.12 (t, J = 7.1 Hz, 3H), 1.01 (t, J = 7.1 Hz, 3H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 162.1 (d, J = 247.6 Hz), 149.0, 139.3, 130.8 (dd, J = 8.1, 6.2 Hz), 130.2, 130.1 (m), 129.6, 129.4, 126.8, 122.5, 122.4, 121.0 (d, J = 2.8 Hz), 117.7, 115.9 (d, J = 2.1 Hz), 115.6 (d, J = 2.1 Hz), 63.37 (d, J = 7.1 Hz), 62.97 (d, J = 7.2 Hz), 43.1 (d, J = 144.2 Hz), 16.3 (d, J = 3.8 Hz), 16.2 (d, J = 3.8 Hz). \(^{31}\)P NMR (CDCl\(_3\), 202 MHz): \(\delta\) 21.8. IR (KBr): \(\tilde{\nu}\) =3127, 1400, 1254, 1160, 1048, 1025, 969, 748, 571 cm\(^{-1}\); HRMS (ESI) calcd for [C\(_{24}\)H\(_{24}\)F\(_{2}\)N\(_{2}\)O\(_{3}\)P+H]\(^+\) 439.1581, found 439.1584.

diethyl ((4-chlorophenyl)(2-phenyl-2\(H\)-indazol-3-yl)methyl)phosphonate (3fa)

73% yield (66.3 mg); yellow oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.65 (d, J = 8.6 Hz, 1H), 8.08-7.97 (m, 1H), 7.73 (d, J = 8.7 Hz, 1H), 7.52 (m, 3H), 7.47-7.38 (m, 2H), 7.35 (m, 1H), 7.29-7.12 (m, 4H), 5.59 (d, J = 27.6 Hz, 1H), 4.14-3.69 (m, 4H), 1.12 (t, J = 7.1 Hz, 3H), 1.05 (t, J = 7.1 Hz, 3H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 149.0, 139.6, 133.8 (d, J = 9.0 Hz), 132.4 (d, J = 3.9 Hz), 132.0 (d, J = 4.4 Hz), 130.3, 129.6 (d, J = 1.8 Hz), 129.4 (d, J = 5.7 Hz), 128.90 (d, J = 2.6 Hz), 127.2 (d, J = 2.7 Hz), 127.0, 126.5, 122.6 (d, J = 10.3 Hz), 121.3 (d, J = 2.6 Hz), 117.8, 63.3, 63.2, 39.8 (d, J = 146 Hz), 16.2, 16.1. \(^{31}\)P NMR (CDCl\(_3\), 202 MHz): \(\delta\) 21.7. IR (KBr): \(\tilde{\nu}\) =3133, 2360, 2336, 1400, 1253, 1065, 1045, 1022, 969, 750, 692, 553 cm\(^{-1}\); HRMS (ESI) calcd for
diethyl ((4-bromophenyl)(2-phenyl-2H-indazol-3-yl)methyl)phosphonate (3ga)
86% yield (85.7 mg); colorless oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.38 (d, \(J = 8.5\) Hz, 1H), 7.74 (d, \(J = 8.7\) Hz, 1H), 7.59-7.47 (m, 3H), 7.46-7.31 (m, 5H), 7.32-7.24 (m, 2H), 7.19 (m, 1H), 4.88 (d, \(J = 28.4\) Hz, 1H), 4.01-3.56 (m, 4H), 1.13 (t, \(J = 7.1\) Hz, 3H), 1.00 (t, \(J = 7.0\) Hz, 3H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 148.9, 139.2, 133.28 (d, \(J = 5.1\) Hz), 131.93 (d, \(J = 3.1\) Hz), 130.79 (d, \(J = 6.2\) Hz), 129.8, 129.7, 129.4, 126.8, 126.7, 122.5, 122.4, 121.84 (d, \(J = 3.5\) Hz), 121.08 (d, \(J = 2.8\) Hz), 117.8, 63.5 (d, \(J = 7.1\) Hz), 43.3 (d, \(J = 44\) Hz), 16.3 (t, \(J = 5.4\) Hz). \(^{31}\)P NMR (CDCl\(_3\), 202 MHz): \(\delta\) 21.4. IR (KBr): \(\bar{\nu}\) = 3133, 2354, 2336, 1400, 1252, 1022, 966, 742, 553 cm\(^{-1}\); HRMS (ESI) calcd for [C\(_{24}\)H\(_{24}\)ClN\(_2\)O\(_3\)P]+ 499.0781, found 497.0788.

methyl 4-(((diethoxyphosphoryl)(2-phenyl-2H-indazol-3-yl)methyl)benzoate (3ha)
78% yield (74.6 mg); yellow solid; m. p. 166-168 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.33 (d, \(J = 8.7\) Hz, 1H), 7.89 (d, \(J = 8.2\) Hz, 2H), 7.67 (d, \(J = 8.7\) Hz, 1H), 7.48-7.39 (m, 5H), 7.33-7.19 (m, 3H), 7.12 (dd, \(J = 8.7, 6.6\) Hz, 1H), 4.90 (d, \(J = 28.6\) Hz, 1H), 3.95-3.58 (m, 7H), 1.03 (t, \(J = 7.1\) Hz, 3H), 0.92 (t, \(J = 7.1\) Hz, 3H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 166.6, 149.0 (d, \(J = 2.3\) Hz), 139.3 (d, \(J = 5.0\) Hz), 139.2, 130.0 (d, \(J = 2.1\) Hz), 129.7, 129.6, 129.4, 129.2, 129.2, 126.8, 126.7, 122.6, 122.4, 121.2 (d, \(J = 2.9\) Hz), 117.8, 63.5 (d, \(J = 7.1\) Hz), 63.1 (d, \(J = 7.1\) Hz), 52.2, 44.0 (d, \(J = 143\) Hz), 16.3 (d, \(J = 3.5\) Hz), 16.2 (d, \(J = 3.4\) Hz). \(^{31}\)P NMR (CDCl\(_3\), 202 MHz): \(\delta\) 21.1. IR (KBr): \(\bar{\nu}\) = 3127, 1716, 1400, 1282, 1253, 1017, 745, 701, 559 cm\(^{-1}\); HRMS (ESI) calcd for [C\(_{26}\)H\(_{27}\)N\(_2\)O\(_5\)P]+ 479.1730, found 479.1731.
diethyl ((2-chlorophenyl)(2-phenyl-2H-indazol-3-yl)methyl)phosphonate (3ia)

62% yield (56.3 mg); yellow oil; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.66 (d, $J = 8.5$ Hz, 1H), 8.07-8.00 (m, 1H), 7.74 (d, $J = 8.9$ Hz, 1H), 7.60-7.47 (m, 3H), 7.48-7.39 (m, 2H), 7.38-7.32 (m, 1H), 7.30-7.09 (m, 4H), 5.61 (d, $J = 27.6$ Hz, 1H), 4.12-3.74 (m, 4H), 1.13 (t, $J = 7.1$ Hz, 3H), 1.06 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 149.0, 139.6, 132.4, 132.0, 132.0, 130.3, 129.6 (d, $J = 1.7$ Hz), 129.4, 129.3, 128.9 (d, $J = 2.7$ Hz), 127.2 (d, $J = 2.7$ Hz), 127.0, 126.5, 122.6, 122.5, 121.2, 117.8, 63.3, 63.2, 39.8 (d, $J = 145.7$ Hz), 16.2, 16.1. $^{31}$P NMR (CDCl$_3$, 202 MHz): $\delta$ 21.7. IR (KBr): $\tilde{\nu} =$3128, 2363, 1400, 1257, 1024, 967, 743, 551 cm$^{-1}$; HRMS (ESI) calcd for [C$_{24}$H$_{24}$ClN$_2$O$_3$P+H]$^+$ 455.1286, found 455.1287.

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diethyl ((3-chlorophenyl)(2-phenyl-2H-indazol-3-yl)methyl)phosphonate (3ja)

55% yield (50.1 mg); colorless oil; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.45-8.35 (m, 1H), 7.75 (d, $J = 8.8$ Hz, 1H), 7.61-7.46 (m, 3H), 7.45-7.34 (m, 4H), 7.34-7.30 (m, 1H), 7.28-7.14 (m, 3H), 4.90 (d, $J = 28.4$ Hz, 1H), 4.09-3.64 (m, 4H), 1.14 (t, $J = 7.1$ Hz, 3H), 1.00 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 149.0, 139.2, 136.2 (d, $J = 4.6$ Hz), 134.5, 130.04 (d, $J = 2.1$ Hz), 129.7, 129.6, 129.4, 129.2 (d, $J = 6.4$ Hz), 127.9 (d, $J = 2.6$ Hz), 127.4 (d, $J = 6.1$ Hz), 126.8, 126.7, 122.6, 122.4 (d, $J = 1.3$ Hz), 121.2 (d, $J = 2.9$ Hz), 117.7, 63.5 (d, $J = 7.0$ Hz), 63.1 (d, $J = 7.2$ Hz), 43.5 (d, $J = 143.6$ Hz), 16.3 (d, $J = 3.9$ Hz), 16.2 (d, $J = 3.9$ Hz). $^{31}$P NMR (CDCl$_3$, 202 MHz): $\delta$ 21.3. IR (KBr): $\tilde{\nu} =$3128, 2354, 1400, 1163, 1054, 857, 750, 550 cm$^{-1}$; HRMS (ESI) calcd for [C$_{24}$H$_{24}$ClN$_2$O$_3$P+H]$^+$ 455.1286, found 455.1287.
diethyl ((2-phenyl-2H-indazol-3-yl)(thiophen-3-yl)methyl)phosphonate (3ka)

83% yield (70.7 mg); colorless oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.16-8.07 (m, 1H), 7.65 (d, \(J = 8.8\) Hz, 1H), 7.50-7.43 (m, 3H), 7.43-7.36 (m, 2H), 7.31 – 7.22 (m, 1H), 7.22-7.12 (m, 2H), 7.10-6.97 (m, 2H), 4.98 (d, \(J = 27.9\) Hz, 1H), 3.96-3.77 (m, 3H), 3.75-3.59 (m, 1H), 1.07 (t, \(J = 7.1\) Hz, 3H), 0.94 (t, \(J = 7.1\) Hz, 3H). \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 149.0, 139.3, 133.5 (d, \(J = 4.9\) Hz), 130.2, 129.5, 129.4, 128.2 (d, \(J = 5.4\) Hz), 126.7, 126.7, 126.1, 123.9 (d, \(J = 8.2\) Hz), 122.5 (d, \(J = 1.5\) Hz), 122.0, 120.9 (d, \(J = 3.0\) Hz), 117.7, 63.4 (d, \(J = 7.1\) Hz), 62.9 (d, \(J = 7.2\) Hz), 39.4 (d, \(J = 145.3\) Hz), 16.3 (t, \(J = 5.5\) Hz). \(^31\)P NMR (CDCl\(_3\), 202 MHz): \(\delta\) 21.8 ppm. IR (KBr): \(v = 3126, 1496, 1400, 1257, 1048, 1019, 966, 754, 544\) cm\(^{-1}\); HRMS (ESI) calcd for \([\text{C}_{22}\text{H}_{23}\text{N}_2\text{O}_3\text{PS} + \text{H}]^+\) 427.1240, found 427.1236.

diethyl ((2-phenyl-2H-indazol-3-yl)methyl)phosphonate (3la)

81% yield (55.7 mg); colorless oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.73 (d, \(J = 8.5\) Hz, 1H), 7.69-7.56 (m, 3H), 7.54-7.37 (m, 3H), 7.30-7.18 (m, 1H), 7.07-7.01 (m, 1H), 4.02 – 3.78 (m, 4H), 3.53 (d, \(J = 21.6\) Hz, 2H), 1.13 (t, \(J = 7.1\) Hz, 6H) ppm. \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 148.7 (d, \(J = 3.4\) Hz), 139.4, 129.3, 129.1, 126.9, 126.5, 126.1 (d, \(J = 9.4\) Hz), 121.8, 121.7 (d, \(J = 2.0\) Hz), 120.8 (d, \(J = 2.3\) Hz), 117.7, 62.5 (d, \(J = 6.9\) Hz), 24.8 (d, \(J = 145.4\) Hz), 16.4 (d, \(J = 6.0\) Hz) ppm. \(^31\)P NMR (CDCl\(_3\), 202 MHz): \(\delta\) 22.1 ppm. IR (KBr): \(\tilde{\nu} = 3127, 1593, 1503, 1399, 1254, 1050, 1025, 969, 527\) cm\(^{-1}\); HRMS (ESI) calcd for \([\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}_3\text{P} + \text{H}]^+\) 345.1363, found 345.1368.

diethyl (1-(2-phenyl-2H-indazol-3-yl)butyl)phosphonate (3ma)

47% yield (36.3 mg); colorless oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.03 (d, \(J = 8.6\) Hz, 1H), 7.78-7.68 (m, 1H), 7.65-7.58 (m, 2H), 7.58-7.47 (m, 3H), 7.41-7.23 (m, 1H), 7.15-7.06 (m, 1H), 4.17-3.93 (m, 3H), 3.93-3.75 (m, 1H), 3.67-3.49 (m, 1H), 2.45-2.21 (m,
1H), 2.14-1.96 (m, 1H), 1.29 (t, J = 7.1 Hz, 3H), 1.12 (t, J = 7.1 Hz, 3H), 1.09-0.91 (m, 2H), 0.71 (t, J = 7.3 Hz, 3H) ppm. 13C NMR (75 MHz, CDCl3) δ 148.9 (d, J = 3.0 Hz), 139.6, 131.1 (d, J = 5.1 Hz), 129.3, 129.2, 127.1, 126.6, 121.8, 121.4 (d, J = 1.8 Hz), 120.3, 117.7, 62.8 (d, J = 7.1 Hz), 62.2 (d, J = 7.4 Hz), 37.30 (d, J = 144.5 Hz), 31.0, 21.0 (d, J = 14.9 Hz), 16.5 (d, J = 5.8 Hz), 16.3 (d, J = 5.6 Hz), 13.5. 31P NMR (CDCl3, 202 MHz): δ 25.9.

IR (KBr): ν = 3417, 2926, 1597, 1379, 1250, 1024, 964, 748, 553 cm⁻¹; HRMS (ESI) calcd for [C24H24F2N2O3P+H]+ 387.1832, found 387.1844.

diethyl ((5-fluoro-2-phenyl-2H-indazol-3-yl)(phenyl)methyl)phosphonate (3na)
90% yield (78.9 mg); colorless oil; 1H NMR (300 MHz, CDCl3) δ 8.09 (dd, J = 10.2, 2.4 Hz, 1H), 7.71 (dd, J = 9.4, 4.7 Hz, 1H), 7.59-7.45 (m, 3H), 7.43-7.34 (m, 4H), 7.32-7.20 (m, 3H), 7.20-7.10 (m, 1H), 6.89 (d, J = 28.4 Hz, 1H), 4.05-3.71 (m, 4H), 1.07 (t, J = 13.9, 7.1 Hz, 6H). 13C NMR (75 MHz, CDCl3) δ 158.4 (d, J = 240.2 Hz), 153.0, 139.2, 134.0 (d, J = 4.9 Hz), 130.9, 129.7, 129.4, 129.1 (d, J = 6.3 Hz), 128.9 (d, J = 2.1 Hz), 127.1 (d, J = 2.7 Hz), 126.7, 120.5 (dd, J = 2.9, 2.8 Hz), 119.7 (d, J = 9.7 Hz), 118.5 (d, J = 29.1 Hz), 105.2 (d, J = 25.6 Hz), 63.28 (d, J = 7.1 Hz), 63.09 (d, J = 7.1 Hz), 43.69 (d, J = 143.3 Hz) 16.3, 16.2. 31P NMR (CDCl3, 202 MHz): δ 22.0. IR (KBr): ν = 3127, 1517, 1400, 1249, 1178, 1048, 1023, 963, 768, 698, 553 cm⁻¹; HRMS (ESI) calcd for [C24H24F2N2O3P+H]+ 439.1581, found 439.1587.

diethyl ((5-chloro-2-phenyl-2H-indazol-3-yl)(phenyl)methyl)phosphonate (3oa)
80% yield (72.7 mg); white solid; m. p. 128-129 °C; 1H NMR (300 MHz, CDCl3) δ 8.46 (d, J = 1.8 Hz, 1H), 7.68 (d, J = 9.2 Hz, 1H), 7.59-7.46 (m, 3H), 7.42-7.34 (m, 4H), 7.34-7.22 (m, 4H), 7.40 (d, J = 28.4 Hz, 1H), 4.08-3.73 (m, 4H), 1.11 (d, J = 7.3 Hz, 3H), 1.06 (d, J = 7.4 Hz, 3H). 13C NMR (75 MHz, CDCl3) δ 147.3, 139.0, 133.8 (d, J = 5.2 Hz), 130.4, 129.8, 129.4, 129.0 (d, J = 6.3 Hz), 128.9 (d, J = 2.1 Hz), 128.2, 127.9, 127.8 (d, J = 2.6 Hz), 126.7, 121.5, 121.4, 119.2, 63.3 (d, J = 7.2 Hz), 63.2 (d, J = 7.1 Hz), 43.8 (d, J = 143.2 Hz), 16.3 (d, J = 1.5 Hz), 16.2 (d, J = 1.7 Hz). 31P NMR (CDCl3, 202 MHz): δ 21.8. IR (KBr): ν = 3128, 2360, 1502, 1400, 1246, 1052, 1030, 966, 695, 553 cm⁻¹; HRMS (ESI) calcd for [C24H24ClN2O3P+H]+ 455.1286, found 455.1291.
diethyl ((5-methyl-2-phenyl-2H-indazol-3-yl)(phenyl)methyl)phosphonate (3pa)
83% yield (72.1 mg); white solid; m. p. 100-102 °C; ^1H NMR (300 MHz, CDCl3) δ 8.19 (s, 1H), 7.64 (d, J = 8.9 Hz, 1H), 7.57-7.46 (m, 3H), 7.45-7.35 (m, 4H), 7.34-7.22 (m, 3H), 7.19 (dd, J = 8.9, 1.6 Hz, 1H), 4.90 (d, J = 28.5 Hz, 1H), 4.03-3.64 (m, 4H), 2.49 (s, 3H), 1.10 (t, J = 7.1 Hz, 3H), 1.02 (t, J = 7.1 Hz, 3H). ^13C NMR (75 MHz, CDCl3) δ 148.0, 139.4, 134.2 (d, J = 5.1 Hz), 131.5, 129.7, 129.4, 129.3, 129.2, 129.1, 128.8 (d, J = 2.1 Hz), 127.56 (d, J = 2.7 Hz), 126.8, 121.5, 120.6, 117.3, 63.2 (d, J = 7.2 Hz), 62.93 (d, J = 7.1 Hz), 43.84 (d, J = 143.2 Hz), 22.2, 16.2, 16.2. ^31P NMR (CDCl3, 202 MHz): δ 22.2. IR (KBr): ν = 3128, 1596, 1496, 1400, 1251, 1022, 962, 777, 698, 556 cm⁻¹; HRMS (ESI) calcd for [C25H27N2O3P]+ 435.1832, found 435.1836.

diethyl ((6-methyl-2-phenyl-2H-indazol-3-yl)(phenyl)methyl)phosphonate (3qa)
95% yield (82.5 mg); white solid; m. p. 94-96 °C; ^1H NMR (300 MHz, CDCl3) δ 8.34 (d, J = 8.4 Hz, 1H), 7.54-7.45 (m, 4H), 7.45-7.35 (m, 4H), 7.31-7.20 (m, 3H), 7.03 (dd, J = 8.8, 1.4 Hz, 1H), 4.90 (d, J = 28.3 Hz, 1H), 3.99-3.67 (m, 4H), 2.47 (s, 3H), 1.09 (t, J = 7.1 Hz, 3H), 1.01 (t, J = 7.1 Hz, 3H). ^13C NMR (75 MHz, CDCl3) δ 149.6, 139.4, 136.6, 134.2 (d, J = 5.1 Hz), 130.2, 129.4, 129.3, 129.2 (d, J = 6.3 Hz), 128.74 (d, J = 2.2 Hz), 127.56 (d, J = 2.7 Hz), 126.8, 125.2, 122.3, 119.64 (d, J = 2.9 Hz), 115.9, 63.2 (d, J = 7.0 Hz), 62.9 (d, J = 7.1 Hz), 43.9 (d, J = 143.2 Hz), 22.1, 16.2, 16.2. ^31P NMR (CDCl3, 202 MHz): δ 22.2. IR (KBr): ν = 3128, 1596, 1496, 1400, 1251, 1022, 971, 700, 559 cm⁻¹; HRMS (ESI) calcd for [C25H27N2O3P]+ 435.1382, found 435.1380.

diethyl ((6-chloro-2-phenyl-2H-indazol-3-yl)(phenyl)methyl)phosphonate (3ra)
85% yield (77.2 mg); yellow oil; ^1H NMR (300 MHz, CDCl3) δ 8.45 (dd, J = 9.1, 0.8 Hz, 1H), 7.72 (d, J = 1.7 Hz, 1H), 7.43-7.33 (m, 3H), 7.43-7.33 (m, 4H), 7.32-7.20 (m, 3H), 7.14 (dd, J = 9.1, 1.8 Hz, 1H), 4.89 (d, J = 28.1 Hz, 1H), 4.03-3.68 (m, 4H), 1.10
(t, J = 7.1 Hz, 3H), 1.02 (t, J = 7.1 Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 149.1, 139.0, 133.8 (d, J = 5.0 Hz), 132.7, 131.3, 129.8, 129.4, 129.1 (d, J = 6.3 Hz), 128.9 (d, J = 2.1 Hz), 127.8 (d, J = 2.7 Hz), 126.7, 124.3 (d, J = 1.3 Hz), 123.8, 119.6 (d, J = 2.9 Hz), 116.5, 63.2 (t, J = 7.0 Hz), 43.8 (d, J = 143.5 Hz), 16.2 (d, J = 5.7 Hz). $^{31}$P NMR (CDCl$_3$, 202 MHz): δ 21.8. IR (KBr): $\tilde{\nu}$ = 3128, 2363, 1504, 1400, 1250, 1050, 1025, 973, 767, 684, 559 cm$^{-1}$; HRMS (ESI) calcd for [C$_{24}$H$_{24}$ClN$_2$O$_3$P+H]$^+$ 455.1286, found 455.1285.

methyl 4-((3-diethoxyphosphoryl)(phenyl)methyl)-2H-indazol-2-yl)benzoate (3s a)
86% yield (82.2 mg); yellow oil; $^1$H NMR (300 MHz, CDCl$_3$) δ 8.46 (d, J = 8.7 Hz, 1H), 8.22 (d, J = 8.2 Hz, 2H), 7.73 (d, J = 8.7 Hz, 1H), 7.52 (d, J = 8.2 Hz, 2H), 7.46-7.24 (m, 6H), 7.24-7.13 (m, 1H), 4.91 (d, J = 28.5 Hz, 1H), 4.05-3.66 (m, 7H), 1.11 (t, J = 7.1 Hz, 3H), 1.00 (t, J = 7.1 Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 165.5, 148.8, 142.5, 133.5 (d, J = 5.1 Hz), 130.5, 130.2, 130.1, 128.6 (d, J = 6.3 Hz), 128.4 (d, J = 2.1 Hz), 127.3 (d, J = 2.7 Hz), 126.6, 126.3, 122.3, 122.1, 121.0 (d, J = 3.0 Hz), 117.1, 62.8 (d, J = 7.2 Hz), 62.6 (d, J = 7.0 Hz), 52.0, 43.5 (d, J = 143.4 Hz), 15.7 (d, J = 3.2 Hz), 15.6 (d, J = 3.0 Hz). $^{31}$P NMR (CDCl$_3$, 202 MHz): δ 21.7. IR (KBr): $\tilde{\nu}$ = 3128, 2363, 1504, 1401, 1283, 1019, 969, 757, 553 cm$^{-1}$; HRMS (ESI) calcd for [C$_{26}$H$_{27}$N$_2$O$_5$P+H]$^+$ 479.1730, found 479.1735.

diethyl ((2-(4-bromophenyl)-2H-indazol-3-yl)(phenyl)methyl)phosphonate (3t a)
87% yield (86.7 mg); yellow oil; $^1$H NMR (300 MHz, CDCl$_3$) δ 8.44 (d, J = 8.8 Hz, 1H), 7.77-7.61 (m, 3H), 7.47-7.38 (m, 2H), 7.37-7.22 (m, 6H), 7.18 (dd, J = 8.8, 6.6 Hz, 1H), 4.87 (d, J = 28.4 Hz, 1H), 4.02-3.65 (m, 4H), 1.11 (t, J = 7.1 Hz, 3H), 0.99 (t, J = 7.1 Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 148.6, 137.9, δ 133.5 (d, J = 5.1 Hz), 132.0, 130.1, 128.6 (d, J = 6.3 Hz), 128.35 (d, J = 2.1 Hz), 127.9, 127.2 (d, J = 2.6 Hz), 126.4, 123.1, 122.2 (d, J = 1.5 Hz), 122.0, 120.80 (d, J = 3.0 Hz), 117.1, 62.7 (d, J = 7.0 Hz), 62.6 (d, J = 7.0 Hz), 43.5 (d, J = 143.5 Hz), 15.7 (d, J = 3.6 Hz), 15.7 (d, J = 3.7 Hz). $^{31}$P NMR (CDCl$_3$, 202 MHz): δ 21.8. IR (KBr): $\tilde{\nu}$ = 3128, 1494, 1399, 1246, 1051, 1014, 972, 835, 755, 701, 577, 549 cm$^{-1}$; HRMS (ESI) calcd for [C$_{26}$H$_{24}$BrN$_2$O$_3$P+H]$^+$ 499.0781, found 499.0787.
dimethyl (phenyl(2-phenyl-2\(H\)-indazol-3-yl)methyl)phosphonate (3ab)
85% yield (66.7 mg); yellow solid; m. p. 132-134 °C; \(^1^H\) NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.44-8.37 (m, 1H), 7.78-7.69 (m, 1H), 7.58-7.47 (m, 3H), 7.45-7.34 (m, 5H), 7.34-7.24 (m, 3H), 7.24-7.15 (m, 1H), 4.96 (d, \(J = 28.4\) Hz, 1H), 3.54 (d, \(J = 10.9\) Hz, 3H), 3.49 (d, \(J = 10.8\) Hz, 3H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 148.9, 139.2, 133.8 (d, \(J = 5.0\) Hz), 130.1, 129.6, 129.4, 129.2, 129.1, 128.92 (d, \(J = 2.0\) Hz), 127.77 (d, \(J = 2.6\) Hz), 126.8, 122.5, 121.2, 117, 53.82 (d, \(J = 7.1\) Hz), 53.54 (d, \(J = 7.1\) Hz), 43.38 (d, \(J = 143.6\) Hz).
\(^{31}\)P NMR (CDCl\(_3\), 202 MHz): \(\delta\) 24.4. IR (KBr): \(\tilde{\nu}\) = 3133, 1493, 1401, 1260, 1051, 1031, 830, 774, 748, 698, 548 cm\(^{-1}\); HRMS (ESI) calcd for \([\text{C}_{22}\text{H}_{21}\text{N}_2\text{O}_3\text{P}+\text{H}]^+\) 393.1363, found 393.1368.

diisopropyl (phenyl(2-phenyl-2\(H\)-indazol-3-yl)methyl)phosphonate (3ac)
76% yield (68.1 mg); yellow solid; m. p. 105-107 °C; \(^1^H\) NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.64-8.50 (m, 1H), 7.73 (d, \(J = 8.7\) Hz, 1H), 7.59-7.47 (m, 3H), 7.46-7.33 (m, 5H), 7.33-7.24 (m, 3H), 7.19 (dd, \(J = 8.6, 6.5\) Hz, 1H), 4.86 (d, \(J = 28.5\) Hz, 1H), 4.55-4.38 (m, 2H), 1.19 (t, \(J = 6.2\) Hz, 6H), 0.93 (d, \(J = 6.2\) Hz, 3H), 0.66 (d, \(J = 6.2\) Hz, 3H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 149.0, 139.4, 134.4 (d, \(J = 5.0\) Hz), 130.9, 129.4 (d, \(J = 5.7\) Hz), 129.3, 128.7 (d, \(J = 2.2\) Hz), 127.52 (d, \(J = 2.9\) Hz), 126.8, 126.7, 123.1, 122.1, 121.2, 117.5, 72.11 (d, \(J = 7.3\) Hz), 71.72 (d, \(J = 7.4\) Hz), 23.7 (m). \(^{31}\)P NMR (CDCl\(_3\), 202 MHz): \(\delta\) 20.4. IR (KBr): \(\tilde{\nu}\) = 3128, 1496, 1400, 1252, 1008, 982, 742, 692, 550 cm\(^{-1}\); HRMS (ESI) calcd for \([\text{C}_{26}\text{H}_{29}\text{N}_2\text{O}_3\text{P}+\text{H}]^+\) 449.1989, found 479.1994.

dibutyl (phenyl(2-phenyl-2\(H\)-indazol-3-yl)methyl)phosphonate (3ad)
85% yield (80.9 mg); yellow solid; m. p. 61-63 °C; \(^1^H\) NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.48 (d, \(J = 8.6\) Hz, 1H), 7.74 (d, \(J = 8.7\) Hz, 1H), 7.60-7.46 (m, 3H), 7.46-7.36 (m, 4H),
7.35-7.23 (m, 4H), 7.21-7.14 (m, 1H), 4.94 (d, J = 28.4 Hz, 1H), 3.94-3.62 (m, 4H), 1.48-1.34 (m, 2H), 1.33-1.22 (m, 2H), 1.18-0.96 (m, 4H), 0.78 (t, J = 7.3 Hz, 3H), 0.72 (t, J = 7.3 Hz, 3H). 

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 149.0, 139.3, 134.2 (d, J = 5.1 Hz), 129.5, 129.3, 129.2, 128.8 (d, J = 2.2 Hz), 127.6 (d, J = 2.9 Hz), 126.8, 126.7, 122.8, 122.3, 121.3 (d, J = 2.6 Hz), 117.6, 66.9 (d, J = 7.3 Hz), 66.6 (d, J = 7.3 Hz), 43.9 (d, J = 143.2 Hz), 32.3 (d, J = 5.9 Hz), 32.2 (d, J = 5.9 Hz) 18.5, 18.4, 13.5, 13.4.

$^{31}$P NMR (CDCl$_3$, 202 MHz): δ 21.9. IR (KBr): $\tilde{\nu}$ = 3126, 1593, 1454, 1401, 1378, 1247, 1056, 1020, 748, 696, 589, 544 cm$^{-1}$; HRMS (ESI) calcd for [C$_{28}$H$_{33}$N$_2$O$_3$P]+ 477.2302, found 477.2307.

dibenzyl (phenyl(2-phenyl-2H-indazol-3-yl)methyl)phosphonate(3ae)

68% yield (84.0 mg); yellow solid; m. p. 100-102 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 8.50 (d, J = 8.6 Hz, 1H), 7.74 (d, J = 8.7 Hz, 1H), 7.52-7.37 (m, 5H), 7.37-7.30 (m, 1H), 7.29-7.22 (m, 6H), 7.22-7.12 (m, 6H), 7.12-6.98 (m, 2H), 6.93-6.80 (m, 2H), 4.95 (d, J = 28.6 Hz, 1H), 4.88-4.57 (m, 4H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 148.9, 139.2 (d, J = 6.0, 15.7 Hz), 133.9 (d, J = 5.1 Hz), 129.5, 129.3, 129.3, 128.9 (d, J = 2.1 Hz), 128.5, 128.4, 128.1, 127.9, 127.8 (d, J = 2.7 Hz), 126.8, 126.7, 122.8, 122.5, 121.3 (d, J = 2.9 Hz), 117.8, 68.7 (d, J = 7.0 Hz), 68.4 (d, J = 7.1 Hz), 44.2 (d, J = 143.3 Hz). $^{31}$P NMR (CDCl$_3$, 202 MHz): δ 22.9. IR (KBr): $\tilde{\nu}$ = 3126, 1593, 1454, 1401, 1378, 1247, 1056, 1020, 748, 696, 589, 544 cm$^{-1}$; HRMS (ESI) calcd for [C$_{28}$H$_{33}$N$_2$O$_3$P]+ 545.1989, found 545.1990.

diphenyl (phenyl(2-phenyl-2H-indazol-3-yl)methyl)phosphonate(3af)

88% yield (90.8 mg); yellow solid; m. p. 142-145 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 8.48 (d, J = 8.7 Hz, 1H), 7.76 (d, J = 8.8 Hz, 1H), 7.56-7.44 (m, 5H), 7.39-7.25 (m, 6H), 7.23-7.10 (m, 5H), 7.09-7.00 (m, 2H), 6.82-6.62 (m, 4H), 5.30 (d, J = 28.8 Hz, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 150.2, 150.1, 149.9, 149.0, 139.1, 133.1 (d, J = 5.6 Hz), 129.7, 129.6, 129.5, 129.4, 129.3, 129.1 (d, J = 2.3 Hz), 128.2 (d, J = 3.0 Hz), 126.8, 126.8, 125.3 (d, J = 2.3 Hz), 122.8, 122.4, 121.5, 120.3, 120.3 (d, J = 1.4 Hz), 120.3, 117.8, 43.97 (d, J = 144.1 Hz). $^{31}$P NMR (CDCl$_3$, 202 MHz): δ 14.4. IR (KBr): $\tilde{\nu}$ =
3128, 1590, 1488, 1401, 1278, 1201, 1183, 942, 698, 574, 526 cm\(^{-1}\); HRMS (ESI) calcd for [C\(_{32}\)H\(_{25}\)N\(_2\)O\(_3\)P]+ 517.1676, found 517.1674.

methyl phenyl((S)-phenyl(2-phenyl-2H-indazol-3-yl)methyl)phosphinate (3ag)

64% yield (56.1 mg); white solid; m. p. 182-184 °C; The \(^1\)H NMR spectrum of the isolated product characterized as a 1:1 diastereomeric mixture. \(^1\)H NMR (300 MHz, CDCl\(_3\)) a mixture: \(\delta 8.67 (d, J = 8.6 \text{ Hz}, 1\text{H}), 8.37 (d, J = 8.7 \text{ Hz}, 1\text{H}), 7.73 (d, J = 8.9 \text{ Hz}, 1\text{H}), 7.61 (d, J = 8.5 \text{ Hz}, 1\text{H}), 7.56-7.48 (m, 3\text{H}), 7.48-7.38 (m, 7\text{H}), 7.38-7.29 (m, 10\text{H}), 7.28-7.25 (m, 3\text{H}), 7.25-7.15 (m, 7\text{H}), 7.11-7.01 (m, 2\text{H}), 6.96-6.80 (m, 2\text{H}), 4.99 (d, J = 20.9 Hz, 1\text{H}), 4.86 (d, J = 20.3 Hz, 1\text{H}), 3.57 (d, J = 11.0 Hz, 3\text{H}), 3.52 (d, J = 10.8 Hz, 3\text{H}). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta 148.4 \pm 2.2 \text{ Hz}), 148.4 \pm 2.6 \text{ Hz), 138.6, 138.5, 133.4, 133.3, 132.9, 132.8, 132.1 \pm 3.0 \text{ Hz), 132.0 (d, J = 2.8 \text{ Hz), 131.5 (d, J = 9.5 \text{ Hz), 131.1 (d, J = 9.6 \text{ Hz), 128.4 (d, J = 2.1 \text{ Hz), 128.2 (d, J = 1.8 \text{ Hz), 128.1, 127.9, 127.9, 127.8, 127.2 (d, J = 2.3 \text{ Hz), 127.0 (d, J = 2.5 \text{ Hz), 126.3, 126.2, 122.6, 122.4, 121.9, 121.8, 121.02 (d, J = 3.1 \text{ Hz), 120.9 (d, J = 2.8 \text{ Hz), 117.3, 117.0, 51.64 (d, J = 6.9 \text{ Hz), 51.50 (d, J = 6.7 \text{ Hz), 47.41 (d, J = 31.5 \text{ Hz), 46.13 (d, J = 30.6 Hz), 31P NMR (CDCl3, 202 MHz):} \delta 37.3. IR (KBr): v \text{cm}^{-1} \approx 3133, 1496, 1400, 1240, 1025, 748, 691, 550, 488 \text{ cm}^{-1}; \text{HRMS (ESI) calcd for [C27H23N2O2P]+ 439.1570, found 439.1570.}

ethyl phenyl((S)-phenyl(2-phenyl-2H-indazol-3-yl)methyl)phosphinate (3ah)

50% yield (45.2 mg); yellow solid; m. p. 55-57 °C; The \(^1\)H NMR spectrum of the isolated product characterized as a 1:2:1 diastereomeric mixture. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 8.73 (d, J = 8.5 \text{ Hz}, 0.45 \text{H}), 8.42 (d, J = 8.6 \text{ Hz}, 0.55 \text{H}), 7.73 (d, J = 8.7 \text{ Hz}, 0.57 \text{H}), 7.62 (d, J = 8.5 \text{ Hz}, 0.56 \text{H}), 7.57-7.49 (m, 1\text{H}), 7.50-7.35 (m, 5\text{H}), 7.35-7.27 (m, 4\text{H}), 7.27-7.11 (m, 5\text{H}), 7.10-6.82 (m, 2\text{H}), 4.99 (d, J = 20.8 \text{ Hz}, 0.54 \text{H}), 4.84 (d, J = 20.3 \text{ Hz}, 0.45 \text{H}), 4.06-3.75 (m, 2\text{H}), 1.16-1.07 (m, 3\text{H}). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta 149.0 (d, J = 2.2 \text{ Hz), 148.9 (d, J = 2.2 Hz), 139.1, 139.0, 134.0 (d, J = 7.5 \text{ Hz), 133.5 (d, J = 4.0 \text{ Hz), 132.5 (d, J = 2.8 Hz), 132.3 (d, J = 2.9 Hz), 131.9 (d, J = 9.5 Hz), 131.4
(d, J = 9.7 Hz), 130.7, 130.7, 130.6, 129.9 (d, J = 3.5 Hz), 129.7 (d, J = 5.0 Hz), 129.5 (d, J = 4.4 Hz), 129.3 (d, J = 5.7 Hz), 129.1 (d, J = 10.5 Hz), 128.8 (d, J = 2.0 Hz), 128.7 (d, J = 1.9 Hz), 128.4 (d, J = 9.6 Hz), 128.2 (d, J = 9.7 Hz), 127.6 (d, J = 2.5 Hz), 127.5 (d, J = 2.4 Hz), 126.7, 126.7, 126.6, 123.2 (d, J = 11.2 Hz), 122.2 (d, J = 15.8 Hz), 121.6 (d, J = 3.0 Hz), 121.4 (d, J = 2.8 Hz), 117.7, 117.5, 62.0 (d, J = 6.9 Hz), 61.7 (d, J = 6.6 Hz), 48.2 (d, J = 31.7 Hz), 46.9 (d, J = 31.0 Hz), 16.4 (d, J = 3.5 Hz), 16.3 (d, J = 3.1 Hz). $^{31}$P NMR (CDCl$_3$, 202 MHz): δ 37.1, 35.6. IR (KBr): $\tilde{\nu}$ =3127, 2361, 1593, 1400, 1237, 1120, 1026, 749, 696, 549 cm$^{-1}$; HRMS (ESI) calcd for [C$_{28}$H$_{35}$N$_2$O$_2$P+$\text{H}^+]^+$ 453.1726, found 453.1730.

![Diphenyl(phenyl(2-phenyl-2H-indazol-3-yl)methyl)phosphine oxide (3ai)](image)

**diphenyl(phenyl(2-phenyl-2H-indazol-3-yl)methyl)phosphine oxide (3ai)**

73% yield (70.7 mg): yellow solid; m. p. 243-244 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 8.85 (d, $J$ = 8.6 Hz, 1H), 7.60 (d, $J$ = 8.8 Hz, 1H), 7.56-7.45 (m, 4H), 7.46-7.35 (m, 4H), 7.35-7.23 (m, 7H), 7.23-7.14 (m, 5H), 7.09 (d, $J$ = 7.2 Hz, 2H), 5.13 (d, $J$ = 12.3 Hz, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 149.0, 139.3, 134.0 (d, $J$ = 4.9 Hz), 131.9, 131.9, 131.8, 131.40 (d, $J$ = 8.7 Hz), 131.9, 131.9, 131.8, 130.0 (d, $J$ = 5.0 Hz), 129.6, 129.2, 128.6 (d, $J$ = 1.1 Hz), 128.4 (dd, $J$ = 2.3, 11.6 Hz), 127.5 (d, $J$ = 1.4 Hz), 126.9, 126.7, 123.8, 122.4, 121.6 (d, $J$ = 2.5 Hz), 117.3, 47.7 (d, $J$ = 65.6 Hz). $^{31}$P NMR (CDCl$_3$, 202 MHz): δ 29.0. IR (KBr): $\tilde{\nu}$ =3133, 2360, 1588, 1493, 1401, 1207, 1117, 742, 694, 539, 517 cm$^{-1}$; HRMS (ESI) calcd for [C$_{32}$H$_{35}$N$_2$OP+$\text{H}^+]^+$ 485.1777, found 485.1774.

![Bis(4-methoxyphenyl)(phenyl(2-phenyl-2H-indazol-3-yl)methyl)phosphine oxide (3aj)](image)

**bis(4-methoxyphenyl)(phenyl(2-phenyl-2H-indazol-3-yl)methyl)phosphine oxide (3aj)**

56% yield (60.9 mg): yellow solid; m. p. 90-92 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 8.81 (d, $J$ = 8.6 Hz, 1H), 7.65-7.58 (m, 1H), 7.55-7.43 (m, 3H), 7.41-7.23 (m, 8H), 7.22-7.13 (m, 4H), 7.14-7.03 (m, 2H), 6.80 (dd, $J$ = 8.9, 2.4 Hz, 2H), 6.72 (dd, $J$ = 8.9, 2.4 Hz, 2H), 5.03 (d, $J$ = 12.6 Hz, 1H), 3.76 (s, 3H), 3.72 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$)
13C NMR (75 MHz, CDCl₃) δ 162.3, 139.3, 134.4 (d, J = 4.7 Hz), 133.2 (d, J = 10.0 Hz), 132.7 (d, J = 10.3 Hz), 131.7, 130.0 (d, J = 5.0 Hz), 129.6, 129.1, 128.6 (d, J = 1.6 Hz), 127.3 (d, J = 2.0 Hz), 127.0, 126.7, 123.9, 122.2, 121.8, 121.6 (d, J = 2.8 Hz), 117.2e, 113.9 (d, J = 12.7 Hz), 55.2, 48.10 (d, J = 66.1 Hz).

31P NMR (CDCl₃, 202 MHz): δ 29.5.

IR (KBr): ν ~ = 3139, 2360, 1400, 1172, 759, 668, 538 cm⁻¹; HRMS (ESI) calcd for [C₃₄H₂₉N₂O₃P]+ 513.2090, found 513.2093.

(phenyl(2-phenyl-2H-indazol-3-yl)methyl)di-p-tolylphosphine oxide (3ak)
64% yield (65.6 mg): yellow solid; m. p. 129-131 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.89-8.82 (m, 1H), 7.60 (d, J = 8.9 Hz, 1H), 7.55-7.41 (m, 3H), 7.38-7.21 (m, 7H), 7.21-7.13 (m, 4H), 7.13-7.05 (m, 4H), 7.01 (dd, J = 8.1, 2.9 Hz, 2H), 5.08 (d, J = 12.3 Hz, 1H), 2.28 (s, 3H), 2.24 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 149.0, 142.2 (d, J = 2.7, 5.3 Hz), 139.4, 134.3 (d, J = 4.8 Hz), 131.6, 131.4 (d, J = 9.0 Hz), 130.8 (d, J = 9.3 Hz), 130.0 (d, J = 5.0 Hz), 129.6, 129.2 (d, J = 3.1 Hz), 129.0, 128.6 (d, J = 1.7 Hz), 127.4 (d, J = 2.3 Hz), 127.0, 126.7, 123.9, 122.2, 121.6, 117.2, 47.8 (d, J = 65.4 Hz), 21.5, 21.4. ³¹P NMR (CDCl₃, 202 MHz): δ 29.5. IR (KBr): ν ~ = 3139, 2360, 1400, 1172, 759, 668, 538 cm⁻¹; HRMS (ESI) calcd for [C₃₄H₂₉N₂OP]+ 513.2090, found 513.2093.

bis(3,5-dimethylphenyl)(phenyl(2-phenyl-2H-indazol-3-yl)methyl)phosphine oxide (3al)
75% yield (81.0 mg): yellow solid; m. p. 190 °C decomposed ¹H NMR (300 MHz, CDCl₃) δ 8.82-8.75 (m, 1H), 7.66-7.57 (m, 1H), 7.57-7.44 (m, 3H), 7.36-7.26 (m, 3H), 7.26-7.17 (m, 4H), 7.16-7.08 (m, 2H), 7.00 (d, J = 7.6 Hz, 2H), 6.94 (d, J = 10.6 Hz, 4H), 5.09 (d, J = 12.6 Hz, 1H), 2.18 (s, 6H), 2.13 (s, 6H); ¹³C NMR (75 MHz, CDCl₃)
δ 148.5 (d, J = 1.8 Hz), 138.8, 137.5 (d, J = 3.4 Hz), 137.3 (d, J = 3.6 Hz), 133.8 (d, J = 4.8 Hz), 133.0 (dd, J = 2.9 Hz, 8.0 Hz), 131.1, 131.0, 129.8 (d, J = 6.0 Hz), 129.5 (d, J = 4.8 Hz), 129.0, 128.7, 128.6, 128.1, 128.0, 127.9, 126.9 (d, J = 2.2 Hz), 126.5, 126.2, 123.5, 121.7, 121.3 (d, J = 2.8 Hz), 116.6, 47.6, 46.7, 20.7, 20.6. $^{31}$P NMR (CDCl$_3$, 202 MHz): δ 29.9. IR (KBr): $\tilde{\nu}$ = 3139, 1597, 1498, 1401, 1374, 1272, 1204, 1123, 877, 857, 776, 746, 695, 441 cm$^{-1}$; HRMS (ESI) calcd for [C$_{36}$H$_{33}$N$_2$OP+H]$^+$ 541.2403, found 541.2401.
4. General Procedure for the Further Transformation of 3aa

4.1 Transformation of 3aa

a) General procedure

To a solution of 3aa (0.1 mol, 1 equiv) in anhydrous THF was added slowly LDA (0.2 mmol, 2 equiv) at 0 °C under Ar atmosphere. After 10 min, paraformaldehyde (0.2 mmol, 2 equiv) was added. The reaction mixture was stirred at room temperature until the reaction was completed (detected by TLC). Then solvent was removed under reduced pressure and the residue was purified by column chromatography to afford the pure product 5aa (PE:EA = 50:1).

b) Characterization of the product

2-phenyl-3-(1-phenylvinyl)-2H-indazole (5aa)
84% yield (24.9 mg); white solid; m. p. 96-98 °C; 1H NMR (300 MHz, CDCl₃) δ 7.80 (dt, J = 8.8, 1.0 Hz, 1H), 7.57-7.43 (m, 3H), 7.40-7.33 (m, 1H), 7.32-7.21 (m, 3H), 7.20 -7.03 (m, 6H), 5.93 (d, J = 1.0 Hz, 1H), 5.52 (d, J = 1.0 Hz, 1H). 13C NMR (75 MHz, CDCl₃) δ 148.9, 140.3, 138.9, 138.5, 132.2, 128.7, 128.3, 128.2, 128.1, 126.9, 126.9, 125.3, 122.3, 120.7, 119.9, 117.7, 113.4. IR (KBr): ν =2953, 2850, 1597, 1499, 1361, 1024, 901, 831, 822, 781, 691 cm⁻¹; HRMS (ESI) calcd for [C₂₁H₁₆N₂+H]+ 297.1386, found 297.1391.

4.1 The reaction of 3aa with NFSI

a) General procedure

A THF solution (1.0 mL) of 3aa (0.1 mol, 1 equiv) was treated with LiHMDS (0.2 mmol, 2 equiv) at 0 °C for 10 min under Ar atmosphere before the addition of NFSI (0.2 mmol, 2 equiv). Then resulting solution was stirred at room temperature until a complete consumption of 3aa (detected by TLC). The solvent was removed under reduced pressure and the residue was purified by column chromatography to afford the pure product 6aa (PE:EA = 2:1).
b) Characterization of the product

![Image of the molecule]

diethyl (fluoro(phenyl)(2-phenyl-2H-indazol-3-yl)methyl)phosphonate (6aa)

65% yield (28.4 mg); colorless oil; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.35 (dd, $J = 17.2, 8.8$ Hz, 1H), 7.75 (d, $J = 8.7$ Hz, 1H), 7.41-7.31 (m, 1H), 7.30-7.24 (m, 1H), 7.24-7.10 (m, 7H), 7.04 (t, $J = 8.7$ Hz, 2H), 6.82 (t, $J = 8.5$ Hz, 1H), 4.24 - 3.73 (m, 4H), 1.24 (t, $J = 7.1$ Hz, 3H), 1.15 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 147.3, 140.2 (d, $J = 8.0$ Hz), 135.5 (d, $J = 21.7$ Hz), 128.0, 127.8, 127.7, 126.9, 126.8, 126.6 (d, $J = 2.2$ Hz), 125.7, 125.6 (d, $J = 1.6$ Hz), 125.5, 125.4, 121.7 (dd, $J = 10.0$ Hz, 69 Hz), 116.8 (d, $J = 5.4$ Hz), 114.0 (dd, $J=1.2$ Hz, 22.5Hz), 63.7 (d, $J = 7.5$ Hz), 63.5 (d, $J = 8.5$ Hz), 15.3 (d, $J = 5.7$ Hz), 15.2 (d, $J = 2.4$ Hz). $^{31}$P NMR (CDCl$_3$, 121 MHz): $\delta$ 11.76 (d, $J = 80.4$ Hz). IR (KBr): $\tilde{\nu}$ =2980, 2924, 2853, 1449, 1499, 1260, 1053, 1024, 975, 920, 791 cm$^{-1}$; HRMS (ESI) calcd for [C$_{24}$H$_{24}$F$_{2}$N$_{2}$O$_{3}$P+H]$^+$ 439.1581, found 439.1600.
5. The trapping experiments of carbene intermediates

5.1 Formation of Dimmer 7

The reaction was carried out with 1a at the absence of phosphonate 2a at standard condition. After 12h, the dimer 6 was observed by LCMS. The results indicated that the carbene complex possibly formed during the process.\(^6\)

\[
\begin{align*}
\text{N=N} & \quad \text{Pd(} \text{CH}_3 \text{CN)}_2 \text{Cl}_2 (10 \text{ mol } \%) \\
\text{Cu(} \text{CH}_3 \text{CN)}_2 \text{PF}_6 (20 \text{ mol } \%) & \quad \text{DIPEA (1.5 equiv)} \\
\text{THF, 40°C, 12 h} & \quad \text{Ph} \quad \text{N-Ph} \\
\end{align*}
\]

Exact Mass: 564.2314
5.2 Trapping of palladium carbene

Benzyl bromide was added into reaction instead of phosphonate 2a at standard condition. The product 8 was detected after 24h by LCMS and indicated that the palladium carbene may exist.\(^7\)

\[
\text{N} \quad \begin{array}{c}
\text{Ph} \\
\text{Ph}
\end{array}
\quad + \quad \begin{array}{c}
\text{Ph} \\
\text{Br}
\end{array}
\xrightarrow{\text{Pd(CH}_3\text{CN)}_2\text{Cl}_2 \ (10 \text{ mol } \%) \ \text{Cu(CH}_3\text{CN)}_2\text{PF}_6 \ (20 \text{ mol } \%) \ \text{P(2-furyl)}_3 \ (20 \text{ mol } \%)}
\text{DIPEA (1.5 equiv)}
\text{THF, 40°C, 24 h}
\text{N} \quad \begin{array}{c}
\text{Ph} \\
\text{Ph}
\end{array}
\]

Exact Mass: 372.1626
6. Reference


7. NMR Spectra
$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^1$Н ЯМР (ДДМС, CDCl$_3$)

$^1$C ЯМР (ДДМС, CDCl$_3$)
$^3$P NMR (202 MHz CDCl$_3$)

$^1$H NMR (300 MHz CDCl$_3$)

S49
$^{31}P$ NMR (202 MHz CDCl$_3$)

$^1$H NMR (300 MHz CDCl$_3$)
$^{13}$C NMR (70 MHz CDCl$_3$)

$^{31}$P NMR (202 MHz CDCl$_3$)
$^31$P NMR (203 MHz CDCl$_3$)

$^1$H NMR (200 MHz CDCl$_3$)

S64
$^{1}H$ NMR (DMSO- $d_6$; CDCl$_3$)

$^{13}C$ NMR (75MHz; CDCl$_3$)
8. X-ray crystal structure of 3oa

CCDC-1553330 (3oa) contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.