Supporting Information

Photoelectrochemical cell for P-H/C-H cross-coupling with hydrogen evolution

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1. Materials and methods

$^1$H NMR spectra were recorded using a Bruker Avance DPX 400 MHz instrument with tetramethylsilane (TMS) as an internal standard. $^{13}$C NMR spectra were obtained at 101 MHz and referenced to the internal solvent signals. Multiplicities are indicated, s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), coupling constants (J) are in Hertz (Hz). High-resolution mass spectra (HRMS-ESI) were recorded on a Q-TOF mass spectrometer. Commercially available reagents and solvents were used without further purification. Cyclic voltammograms were obtained on a CHI 660E potentiostat. Photoelectrochemical was carried out with blue LEDs ($\lambda = 450$ nm). The instrument for electrolysis is dual display potentiostat (DJS-292B) (made in China). The anode electrode is reticulated vitreous carbon (RVC) electrodes (500 PPI, 1.0 cm $\times$ 1.0 cm $\times$ 0.5 cm) and the cathode electrode is platinum plate electrodes (0.5 cm $\times$ 1.0 cm). The reticulated vitreous carbon electrodes can be available at Alfa Aesar (CAS No. 7440-44-0). Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum ether.

Figure S1. The picture of the home-made BiVO$_4$ electrode and the photoelectrochemical cell.
2. General experimental procedures

2.1 Preparation of the BiVO\textsubscript{4}

The BiVO\textsubscript{4} electrode was prepared by electro-deposition. First, Bi(NO\textsubscript{3})\textsubscript{3}·5H\textsubscript{2}O (0.04 M) and KI (0.4 M) were dissolved in 50 mL distilled water to form a clear solution. Then, HNO\textsubscript{3} was added to adjust the pH to 1.7. Next, 0.23 M p-benzoquinone ethanol solution (20 mL) was added to above mixed solution and stirred vigorously for 20 min. The electrodeposition was carried out in three-electrode cell using a constant potential of -0.1 V \textit{vs} Ag/AgCl for 10 min at room temperature. (FTO as working electrode, Pt plate as the counter electrode and Ag/AgCl as the reference electrode). After being taken out and washed with distilled water, the dried BiOI film was covered by dipping 200 µL containing vanadyl acetylacetonate (0.2 M) DMSO solution. BiVO\textsubscript{4} film was formed by heating in a muffle furnace at 450 °C for 1 hour. After being cooled down to room temperature, the electrode was soaked in 1.0 M NaOH solution for 30 min to remove excess V\textsubscript{2}O\textsubscript{5}. Finally, the BiVO\textsubscript{4} electrode was rinsed with distilled water.

2.2 General procedure for the C-H/P-H Cross-coupling:

\textbf{Method A: Photoelectrochemical}

\begin{equation}
\begin{array}{c}
\text{R}^1\text{H} & \text{O} & \text{R}^2\text{H} \\
\text{Ar} & \text{P} & \text{Ar} \\
\text{R}^1 & \text{R}^2 & \text{O} & \text{N} & \text{Ar} & \text{P} & \text{R}^2 & \text{O} & \text{H} \\
1 & 2 & 3
\end{array}
\end{equation}

The PEC experiments were carried out in an undivided cell equipped with BiVO\textsubscript{4} as the working electrode (1.0 cm × 2.0 cm), Pt plate as the counter electrode (0.5 cm × 1.0 cm) and Ag/AgCl as the reference electrode. N-phenyl tetrahydroisoquinoline 1a (0.2 mmol), diphenylphosphine oxide 2a (0.2 mmol), NHPI (0.2 equiv) and 2,6-Lutidine (1.5 equiv) were dissolved in 5 mL acetonitrile with tBu\textsubscript{n}NBF\textsubscript{4} (0.1 M) as an electrolyte. The reaction mixture was stirred for 1 minutes. Then the PEC cell was sealed using a rubber septum and flushed with nitrogen gas. After piercing the septum with a nitrogen-filled balloon to sustain nitrogen atmosphere, photoelectrochemical electrolysis was performed at a constant potential of +0.1 V \textit{vs}. Ag/AgCl for 12 h. When the reaction was finished, the entire reaction mixture was then transferred to a silica gel column and eluted with a mixture of petrol ether and ethyl acetate to give the corresponding products.
Method B: Electrochemical

\[
\begin{array}{c}
\text{R}^1 \quad \text{Ar} \quad \text{R}^1 \quad \text{Ar} \\
\text{1} \\
\text{MeCN, RT} \\
10 \text{ mA/2 h} \\
\text{RVC} \\
\text{Pt} \\
\end{array}
\]

The electrolysis was carried out in an undivided cell, with a RVC anode (500 PPI, 1.0 cm × 1.0 cm × 0.5 cm) and a platinum cathode (0.5 cm × 1.0 cm). N-phenyl tetrahydroisoquinoline 1a (0.2 mmol) and diphenylphosphine oxide 2a (0.2 mmol) were dissolved in 5 mL acetonitrile with \(^4\text{Bu}_4\text{NBF}_4\) (0.1 M) as an electrolyte. The reaction mixture was then stirred for 1 minutes. Then the EC cell was sealed using a rubber septum and flushed with nitrogen gas. After piercing the septum with a nitrogen-filled balloon to sustain nitrogen atmosphere, electrolysis was performed at a constant current of 10 mA for 2 h. When the reaction was finished, the entire reaction mixture was then transferred to a silica gel column and eluted with a mixture of petrol ether and ethyl acetate to give the corresponding products.

2.3 Control Experiments:

\[
\begin{array}{c}
\text{Ph} \\
1a \\
\text{MeCN, RT} \\
\text{GC} \\
\text{Pt} \\
\end{array}
\]

Figure S2. The comparison of PEC and EC. The NHPI-mediated P-H/C-H cross-coupling in a PEC cell (red) is cathodically shifted by 1.4 V compared to an EC cell (black).
The control experiments were carried out in an undivided cell equipped with glassy carbon electrode as the working electrode (1.0 cm × 2.0 cm × 0.3 cm), Pt plate as the counter electrode (0.5 cm × 1.0 cm) and Ag/AgCl as the reference electrode. N-phenyl tetrahydropyroloquinoline 1a (0.2 mmol), diphenylphosphine oxide 2a (0.2 mmol), NHPI (0.2 equiv) and 2,6-Lutidine (1.5 equiv) were dissolved in 5 mL acetonitrile with nBu₄NBF₄ (0.1 M) as an electrolyte. The reaction mixture was stirred for 1 minutes. Then the EC cell was sealed using a rubber septum and flushed with nitrogen gas. After piercing the septum with a nitrogen-filled balloon to sustain nitrogen atmosphere, electrolysis was performed at a constant potential of +1.5 V vs. Ag/AgCl for 12 h. When the reaction was finished, the entire reaction mixture was then transferred to a silica gel column and eluted with a mixture of petrol ether and ethyl acetate to give the corresponding products.
3. Cyclic voltammograms experiments

The cyclic voltammograms were recorded in an electrolyte of $n$Bu$_4$NBF$_4$ (0.1 M) in MeCN using a glassy carbon disk working electrode (diameter, 3 mm), a Pt wire auxiliary electrode and a Ag/AgCl reference electrode. The scan rate was 100 mV/s.

**Figure S3.** CVs obtained in MeCN (6 mL) with 0.1 M $n$Bu$_4$NBF$_4$: black line, $1a$ (5 mM); red line, $2a$ (5 mM).

**Figure S4.** CVs obtained in MeCN (6 mL) with 0.1 M $n$Bu$_4$NBF$_4$: 5 mM NHPI (black); 5 mM NHPI solution containing 10 mM 2,6-Lutidine (red); 5 mM NHPI solution containing 10 mM 2,6-Lutidine and 5 mM $1a$ (blue).
4. Characterization data for all products

**diphenyl(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphine oxide (3aa)**

Reaction was proceeded according to General Method A with 0.1 V vs. Ag/AgCl constant potential electrolysis. The reaction mixture was purified by silica gel column chromatography to afford the product 3aa. (white solid, mp 197.7–200.1 °C, yield: 90%).

Reaction was proceeded according to General Method B with 10 mA constant current electrolysis. The reaction mixture was purified by silica gel column chromatography to afford the product 3aa. (white solid, mp 197.7–200.1 °C, yield: 85%).

$^1$H NMR (400 MHz, Chloroform-d) δ 7.85 – 7.76 (m, 2H), 7.74 – 7.66 (m, 2H), 7.59 – 7.49 (m, 1H), 7.49 – 7.39 (m, 3H), 7.35 - 7.30 (m, 2H), 7.17 – 7.04 (m, 4H), 6.93 (t, $J = 7.5$ Hz, 1H), 6.84 – 6.73 (m, 3H), 6.65 (d, $J = 7.8$ Hz, 1H), 5.56 (d, $J = 10.6$ Hz, 1H), 4.10 – 3.96 (m, 1H), 3.67 – 3.43 (m, 1H), 2.90 – 2.76 (m, 1H), 2.73 – 2.62 (m, 1H). $^{13}$C NMR (101 MHz, Chloroform-d) δ 150.00 (d, $J_{C-P} = 9.3$ Hz), 136.89 (d, $J_{C-P} = 4.5$ Hz), 132.28 (d, $J_{C-P} = 90.6$ Hz), 132.26 (d, $J_{C-P} = 8.5$ Hz), 131.92 (d, $J_{C-P} = 2.9$ Hz), 131.71 (d, $J_{C-P} = 9.25$ Hz), 131.37 (d, $J_{C-P} = 84.3$ Hz), 131.68, 129.94, 129.24 (d, $J_{C-P} = 4.3$ Hz), 129.13, 128.44 (d, $J_{C-P} = 11.1$ Hz), 128.27 (d, $J_{C-P} = 11.38$ Hz), 127.79 (d, $J_{C-P} = 3.6$ Hz), 127.41 (d, $J_{C-P} = 3.4$ Hz), 125.52 (d, $J_{C-P} = 3.0$ Hz), 119.55, 116.79, 61.98 (d, $J_{C-P} = 79.7$ Hz), 45.17, 25.63. $^{31}$P NMR (162 MHz, Chloroform-d) δ 32.34. HRMS (ESI) calcd. for C$_{27}$H$_{26}$NNaOP [M+Na]$^+$: 432.1488. Found: 432.1486.

**2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)diphenylphosphine oxide (3ba)**

Reaction was proceeded according to General Method A with 0.1 V vs. Ag/AgCl constant...
potential electrolysis. The reaction mixture was purified by silica gel column chromatography to afford the product **3ba**. (white solid, mp 175.3–176.9 °C, yield: 88%).

Reaction was proceeded according to General Method B with 10 mA constant current electrolysis. The reaction mixture was purified by silica gel column chromatography to afford the product **3ba**. (white solid, mp 175.3–176.9 °C, yield: 80%).

$^1$H NMR (400 MHz, Chloroform-d) δ 7.82 – 7.64 (m, 4H), 7.55 – 7.49 (m, 1H), 7.48 – 7.40 (m, 3H), 7.37 – 7.32 (m, 2H), 7.19 – 7.11 (m, 1H), 7.07 (d, J = 7.6 Hz, 1H), 6.93 (t, J = 7.5 Hz, 1H), 6.78 – 6.68 (m, 4H), 6.62 (d, J = 7.8 Hz, 1H), 5.36 (d, J = 11.8 Hz, 1H), 4.06 – 3.88 (m, 1H), 3.72 (s, 3H), 3.47 – 3.33 (m, 1H), 2.81 – 2.68 (m, 1H), 2.60 – 2.50 (m, 1H). $^{13}$C NMR (101 MHz, Chloroform-d) δ 154.08, 144.65 (d, $J_{C,P} = 10.2$ Hz), 137.04 (d, $J_{C,P} = 4.8$ Hz), 132.49 (d, $J_{C,P} = 96.43$ Hz), 132.18 (d, $J_{C,P} = 8.7$ Hz), 131.93 (d, $J_{C,P} = 92.43$ Hz), 131.80 (d, $J_{C,P} = 9.2$ Hz), 131.79 (d, $J_{C,P} = 2.9$ Hz), 131.54 (d, $J_{C,P} = 3.1$ Hz), 129.75, 129.36 (d, $J_{C,P} = 2.5$ Hz), 128.39 (d, $J_{C,P} = 11.2$ Hz), 128.22 (d, $J_{C,P} = 11.4$ Hz), 127.80 (d, $J_{C,P} = 3.6$ Hz), 127.23 (d, $J_{C,P} = 3.4$ Hz), 125.46 (d, $J_{C,P} = 3.0$ Hz), 120.38, 114.47, 62.18 (d, $J_{C,P} = 81.5$ Hz), 55.53, 46.81, 24.82. $^{31}$P NMR (162 MHz, Chloroform-d) δ 32.64. HRMS (ESI) calcd. for C$_{28}$H$_{26}$NNaO$_2$P [M+Na]$^+$: 462.1593. Found: 462.1577.

diphenyl(2-(p-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphine oxide (3ca)

Reaction was proceeded according to General Method A with 0.1 V vs. Ag/AgCl constant potential electrolysis. The reaction mixture was purified by silica gel column chromatography to afford the product **3ca**. (white solid, mp 184.6–186.3 °C, yield: 90%).

Reaction was proceeded according to General Method B with 10 mA constant current electrolysis. The reaction mixture was purified by silica gel column chromatography to afford the product **3ca**. (white solid, mp 184.6–186.3 °C, yield: 87%).

$^1$H NMR (400 MHz, Chloroform-d) δ 7.83 – 7.75 (m, 2H), 7.74 – 7.65 (m, 2H), 7.55 – 7.51 (m,
1H), 7.48 – 7.41 (m, 3H), 7.38 – 7.30 (m, 2H), 7.13 (t, J = 7.5 Hz, 1H), 7.06 (d, J = 7.6 Hz, 1H),
6.96 -6.90 (m, 3H), 6.71 (d, J = 8.1 Hz, 2H), 6.64 (d, J = 7.8 Hz, 1H), 5.47 (d, J = 11.4 Hz, 1H),
4.14 – 3.83 (m, 1H), 3.62 – 3.45 (m, 1H), 2.93 – 2.70 (m, 1H), 2.66 – 2.52 (m, 1H), 2.22 (s, 3H).^13^C NMR (101 MHz, Chloroform-d) δ 148.01 (d, J\(_{C-P}\) = 9.3 Hz), 136.93 (d, J\(_{C-P}\) = 4.5 Hz),
132.43 (d, J\(_{C-P}\) = 95.8 Hz), 132.24 (d, J\(_{C-P}\) = 8.6 Hz), 131.83 (d, J\(_{C-P}\) = 3.0 Hz), 131.82 (d, J\(_{C-P}\) =
110.2 Hz), 131.75 (d, J\(_{C-P}\) = 8.8 Hz), 131.57 (d, J\(_{C-P}\) = 3.2 Hz), 129.86, 129.68, 129.31 (d, J\(_{C-P}\) =
2.5 Hz), 128.41 (d, J\(_{C-P}\) = 11.1 Hz), 128.24 (d, J\(_{C-P}\) = 11.4 Hz), 127.82 (d, J\(_{C-P}\) = 3.6 Hz), 127.28
(d, J\(_{C-P}\) = 3.4 Hz), 125.44 (d, J\(_{C-P}\) = 3.1 Hz), 117.69, 61.98 (d, J\(_{C-P}\) = 80.6 Hz), 45.71, 25.14,
20.42.\(^{31}\)P NMR (162 MHz, Chloroform-d) δ 32.45. HRMS (ESI) calcd. for C\(_{28}\)H\(_{26}\)NNaOP

diphenyl(2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphine oxide
(3da)

Reaction was proceeded according to General Method A with 0.1 V vs. Ag/AgCl constant
potential electrolysis . The reaction mixture was purified by silica gel column chromatography to
afford the product 3da. (white solid, mp 204.7–206.5 °C, yield: 85%).

Reaction was proceeded according to General Method B with 10 mA constant current electrolysis .
The reaction mixture was purified by silica gel column chromatography to afford the product 3da.
(white solid, mp 204.7–206.5 °C, yield: 95%).

\(^1\)H NMR (400 MHz, Chloroform-d) δ 7.80 – 7.65 (m, 4H), 7.58 -7.54 (m, 1H), 7.50 – 7.41 (m,
3H), 7.37 – 7.31 (m, 4H), 7.17 (t, J = 7.5 Hz, 1H), 7.10 (d, J = 7.6 Hz, 1H), 6.96 (t, J = 7.5 Hz,
1H), 6.80 (d, J = 8.5 Hz, 2H), 6.66 (d, J = 7.8 Hz, 1H), 5.65 (d, J = 8.6 Hz, 1H), 4.12 – 4.00 (m,
1H), 3.66 – 3.55 (m, 1H), 2.96 – 2.74 (m, 2H). \(^{13}\)C NMR (101 MHz, Chloroform-d) δ 151.77 (d,
J\(_{C-P}\) = 5.0 Hz), 136.50 (d, J\(_{C-P}\) = 4.0 Hz), 132.27 (d, J\(_{C-P}\) = 8.7 Hz), 132.21 (d, J\(_{C-P}\) = 4.0 Hz),
131.99 (d, J\(_{C-P}\) = 2.8 Hz), 131.56 (d, J\(_{C-P}\) = 9.0 Hz), 129.82, 129.04 (d, J\(_{C-P}\) = 2.4 Hz), 128.53 (d,
J\(_{C-P}\) = 11.0 Hz), 128.47, 128.42 (d, J\(_{C-P}\) = 11.2 Hz), 127.85 (d, J\(_{C-P}\) = 3.0 Hz), 127.72 (d, J\(_{C-P}\) = 3.4
Hz), 126.33 (d, $J_{C,P} = 3.7$ Hz), 125.82 (d, $J_{C,P} = 2.4$ Hz), 123.33, 124.67 (d, $J_{C,F} = 271.6$ Hz), 114.24, 62.23 (d, $J_{C,P} = 76.9$ Hz), 44.29, 26.53. $^{31}$P NMR (162 MHz, Chloroform-d) $\delta$ 31.83. $^{19}$F NMR (377 MHz, Chloroform-d) $\delta$ -61.35. HRMS (ESI) calcd. for C$_{28}$H$_{26}$F$_{3}$NNaOP [M+Na]$^+$: 500.1362. Found: 500.1342.

(2-(2-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)diphenylphosphate oxide (3ea)

Reaction was proceeded according to General Method A with 0.1 V vs. Ag/AgCl constant potential electrolysis. The reaction mixture was purified by silica gel column chromatography to afford the product 3ea. (white solid, mp 188.5–190.6 °C, yield: 91%).

Reaction was proceeded according to General Method B with 10 mA constant current electrolysis. The reaction mixture was purified by silica gel column chromatography to afford the product 3ea. (white solid, mp 188.5–190.6 °C, yield: 84%).

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.89 – 7.82 (m, 2H), 7.77 – 7.70 (m, 2H), 7.52 – 7.46 (m, 1H), 7.44 – 7.35 (m, 3H), 7.33 – 7.26 (m, 2H), 7.20 – 7.13 (m, 1H), 7.07 (d, $J = 7.7$ Hz, 1H), 7.00 (t, $J = 7.6$ Hz, 1H), 6.96 – 6.85 (m, 2H), 6.79 (d, $J = 8.1$ Hz, 1H), 6.74 – 6.64 (m, 2H), 5.42 (d, $J = 12.4$ Hz, 1H), 3.73 – 3.60 (m, 4H), 3.43 – 3.32 (m, 1H), 2.77 – 2.62 (m, 1H), 2.62 – 2.50 (m, 1H).

$^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 153.86, 141.16 (d, $J_{C,P} = 8.9$ Hz), 137.61 (d, $J_{C,P} = 4.6$ Hz), 133.70, 132.82 (d, $J_{C,P} = 4.6$ Hz), 132.74 (d, $J_{C,P} = 4.6$ Hz), 132.09 (d, $J_{C,P} = 2.8$ Hz), 131.87 (d, $J_{C,P} = 2.7$ Hz), 131.12, 129.79 (d, $J_{C,P} = 2.2$ Hz), 128.76 (d, $J_{C,P} = 11.1$ Hz), 128.53 (d, $J_{C,P} = 11.4$ Hz), 128.56, 127.62 (d, $J_{C,P} = 3.1$ Hz), 125.97 (d, $J_{C,P} = 2.8$ Hz), 124.36, 123.47, 121.71, 113.08, 63.52 (d, $J_{C,P} = 80.9$ Hz), 56.17, 46.32, 26.37. $^{31}$P NMR (162 MHz, Chloroform-d) $\delta$ 31.82. HRMS (ESI) calcd. for C$_{28}$H$_{26}$NNaO$_2$P [M+Na]$^+$: 462.1593. Found: 462.1574.
(2-(3-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)diphenylphosphine oxide (3fa)

Reaction was proceeded according to General Method A with 0.1 V vs. Ag/AgCl constant potential electrolysis. The reaction mixture was purified by silica gel column chromatography to afford the product 3fa. (white solid, mp 176.1–178.5 °C, yield: 86%).

Reaction was proceeded according to General Method B with 10 mA constant current electrolysis. The reaction mixture was purified by silica gel column chromatography to afford the product 3fa. (white solid, mp 176.1–178.5 °C, yield: 99%).

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.83 – 7.76 (m, 2H), 7.74 – 7.67 (m, 2H), 7.57 – 7.50 (m, 1H), 7.48 – 7.39 (m, 3H), 7.37 – 7.28 (m, 2H), 7.17 – 7.09 (m, 1H), 7.09 – 7.00 (m, 2H), 6.92 (t, $J$ = 7.5 Hz, 1H), 6.62 (d, $J$ = 7.7 Hz, 1H), 6.44 – 6.39 (m, 1H), 6.35 – 6.29 (m, 2H), 5.55 (d, $J$ = 10.4 Hz, 1H), 4.10 – 3.98 (m, 1H), 3.68 (s, 3H), 3.62 – 3.52 (m, 1H), 2.93 – 2.76 (m, 1H), 2.74 – 2.61 (m, 1H).$^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 160.71, 151.47 (d, $J_{C-P}$ = 7.5 Hz), 136.91 (d, $J_{C-P}$ = 4.2 Hz), 132.52 (d, $J_{C-P}$ = 83.0 Hz), 132.34 (d, $J_{C-P}$ = 8.3 Hz), 131.96 (d, $J_{C-P}$ = 2.9 Hz), 131.79 (d, $J_{C-P}$ = 8.7 Hz), 131.71 (d, $J_{C-P}$ = 3.2 Hz), 131.66 (d, $J_{C-P}$ = 91.2 Hz), 130.10, 129.87, 129.28 (d, $J_{C-P}$ = 2.2 Hz), 128.51 (d, $J_{C-P}$ = 11.0 Hz), 128.34 (d, $J_{C-P}$ = 11.3 Hz), 127.89 (d, $J_{C-P}$ = 3.4 Hz), 127.50 (d, $J_{C-P}$ = 3.0 Hz), 125.57 (d, $J_{C-P}$ = 2.7 Hz), 109.49, 104.44, 103.35, 62.28 (d, $J_{C-P}$ = 78.9 Hz), 55.21, 45.15, 25.91. $^{31}$P NMR (162 MHz, Chloroform-d) $\delta$ 32.23. HRMS (ESI) calcd. for C$_{28}$H$_{26}$NNaO$_2$P [M+Na]$^+$: 462.1593. Found: 462.1576.

(2-(4-ethylphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)diphenylphosphine oxide (3ga)

Reaction was proceeded according to General Method B with 10 mA constant current electrolysis. The reaction mixture was purified by silica gel column chromatography to afford the product 3ga. (white solid, mp 156.6–158.9 °C, yield: 84%).

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.83 – 7.76 (m, 2H), 7.75 – 7.69 (m, 2H), 7.57 – 7.50 (m, 1H), 7.47 – 7.40 (m, 3H), 7.37 – 7.30 (m, 2H), 7.13 (t, $J$ = 7.5 Hz, 1H), 7.05 (d, $J$ = 7.6 Hz, 1H), 6.92 (t, $J$ = 7.5 Hz, 1H), 6.62 (d, $J$ = 7.7 Hz, 1H), 6.44 – 6.39 (m, 1H), 6.35 – 6.29 (m, 2H), 5.55 (d, $J$ = 10.4 Hz, 1H), 4.10 – 3.98 (m, 1H), 3.68 (s, 3H), 3.62 – 3.52 (m, 1H), 2.93 – 2.76 (m, 1H), 2.74 – 2.61 (m, 1H).
7.01 – 6.90 (m, 3H), 6.74 (d, J = 8.3 Hz, 2H), 6.65 (d, J = 7.8 Hz, 1H), 5.50 (d, J = 11.2 Hz, 1H), 4.07 – 3.94 (m, 1H), 3.59 – 3.46 (m, 1H), 2.88 – 2.75 (m, 1H), 2.66 – 2.58 (m, 1H), 2.52 (q, J = 7.6 Hz, 2H), 1.17 (t, J = 7.6 Hz, 3H).

13C NMR (101 MHz, Chloroform-d) δ 148.17 (d, J_{C-P} = 8.8 Hz), 136.93 (d, J_{C-P} = 4.3 Hz), 135.75, 132.46 (d, J_{C-P} = 95.4 Hz), 132.26 (d, J_{C-P} = 8.4 Hz), 131.82 (d, J_{C-P} = 2.4 Hz), 131.77 (d, J_{C-P} = 8.6 Hz), 131.71 (d, J_{C-P} = 90.9 Hz), 131.57 (d, J_{C-P} = 2.7 Hz), 129.95, 129.29 (d, J_{C-P} = 95.4 Hz), 129.26 (d, J_{C-P} = 8.4 Hz), 128.45, 128.40 (d, J = 11.0 Hz), 128.24 (d, J = 11.2 Hz), 127.83 (d, J_{C-P} = 3.3 Hz), 127.29 (d, J_{C-P} = 2.9 Hz), 125.44 (d, J_{C-P} = 2.6 Hz), 117.57, 62.13 (d, J_{C-P} = 80.3 Hz), 45.59, 27.88, 25.28, 15.66.

31P NMR (162 MHz, Chloroform-d) δ 32.30. HRMS (ESI) calcd. for C_{29}H_{28}NNaOP [M+Na]^+: 460.1801. Found: 460.1785.

(2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)diphenylphosphine oxide (3ha)

Reaction was proceeded according to General Method B with 10 mA constant current electrolysis. The reaction mixture was purified by silica gel column chromatography to afford the product 3ha. (white solid, mp 195.3–198.1 °C, yield: 84%).

1H NMR (400 MHz, Chloroform-d) δ 7.81 – 7.65 (m, 4H), 7.56 -7.52 (m, 1H), 7.50 – 7.41 (m, 3H), 7.39 – 7.31 (m, 2H), 7.16 (t, J = 7.6 Hz, 1H), 7.08 (d, J = 7.6 Hz, 1H), 6.94 (t, J = 7.6 Hz, 1H), 6.83 (t, J = 8.5 Hz, 2H), 6.77 – 6.71 (m, 2H), 6.60 (d, J = 7.8 Hz, 1H), 5.40 (d, J = 10.9 Hz, 1H), 4.10 – 3.95 (m, 1H), 3.49 – 3.37 (m, 1H), 2.87 – 2.71 (m, 1H), 2.68 – 2.54 (m, 1H). 13C NMR (101 MHz, Chloroform-d) δ 157.15 (d, J_{C-F} = 239.3 Hz), 146.83 (dd, J = 9.0, 2.8 Hz), 136.85 (d, J_{C-P} = 4.5 Hz), 132.26 (d, J_{C-P} = 95.9 Hz), 132.20 (d, J_{C-P} = 8.7 Hz), 131.93 (d, J_{C-P} = 3.0 Hz), 131.68 (d, J_{C-P} = 9.0 Hz), 131.67 (d, J_{C-P} = 2.7 Hz), 131.42 (d, J_{C-P} = 91.2 Hz), 129.62, 129.31 (d, J_{C-P} = 2.5 Hz), 128.43 (d, J_{C-P} = 11.1 Hz), 128.28 (d, J_{C-P} = 11.3 Hz), 127.75 (d, J_{C-P} = 3.7 Hz), 127.44 (d, J_{C-P} = 3.4 Hz), 125.59 (d, J_{C-P} = 3.0 Hz), 119.24 (d, J_{C-P} = 7.8 Hz), 115.60 (d, J_{C-P} = 22.4 Hz), 62.33 (d, J_{C-P} = 80.1 Hz), 46.28, 25.28. 31P NMR (162 MHz, Chloroform-d) δ 32.40. 19F NMR (377 MHz, Chloroform-d) δ -124.09. HRMS (ESI) calcd. for C_{27}H_{23}FNNaOP
(M+Na)$^+$: 450.1394. Found: 450.1378.

\[ \text{(2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)diphenylphosphine oxide (3ia)} \]

Reaction was proceeded according to General Method B with 10 mA constant current electrolysis. The reaction mixture was purified by silica gel column chromatography to afford the product **3ia**.

(white solid, mp 180.2–181.8 °C, yield: 58%).

$^1$H NMR (400 MHz, Chloroform-d) δ 7.80 – 7.73 (m, 2H), 7.71 – 7.64 (m, 2H), 7.58 – 7.51 (m, 1H), 7.49 – 7.41 (m, 3H), 7.39 – 7.31 (m, 2H), 7.15 (t, $J$ = 7.5 Hz, 1H), 7.10 – 7.03 (m, 3H), 6.94 (t, $J$ = 7.5 Hz, 1H), 6.73 – 6.67 (m, 2H), 6.63 (d, $J$ = 7.8 Hz, 1H), 5.48 (d, $J$ = 10.1 Hz, 1H), 4.11 – 3.92 (m, 1H), 3.57 – 3.38 (m, 1H), 2.87 – 2.74 (m, 1H), 2.73 – 2.61 (m, 1H). $^{13}$C NMR (101 MHz, Chloroform-d) δ 148.56 (d, $J_{C,P}$ = 7.2 Hz), 136.68 (d, $J_{C,P}$ = 4.2 Hz), 132.23 (d, $J_{C,P}$ = 8.5 Hz), 132.06 (d, $J_{C,P}$ = 2.8 Hz), 131.87 (d, $J_{C,P}$ = 107.2 Hz), 131.82 (d, $J_{C,P}$ = 2.8 Hz), 131.63 (d, $J_{C,P}$ = 8.8 Hz), 130.95 (d, $J_{C,P}$ = 102.3 Hz), 129.63, 129.20 (d, $J_{C,P}$ = 2.3 Hz), 128.97, 128.49 (d, $J_{C,P}$ = 11.1 Hz), 128.35 (d, $J_{C,P}$ = 11.3 Hz), 127.76 (d, $J_{C,P}$ = 3.3 Hz), 127.60 (d, $J_{C,P}$ = 2.9 Hz), 125.67 (d, $J_{C,P}$ = 2.6 Hz), 124.30, 117.75, 62.17 (d, $J_{C,P}$ = 78.9 Hz), 45.25, 25.76. $^{31}$P NMR (162 MHz, Chloroform-d) δ 32.34. HRMS (ESI) calcd. for C$_{27}$H$_{23}$ClNNaOP [M+Na]$^+$: 466.1098. Found: 466.1082.

(2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)diphenylphosphine oxide (3ja)

Reaction was proceeded according to General Method B with 10 mA constant current electrolysis. The reaction mixture was purified by silica gel column chromatography to afford the product **3ja**.

(white solid, mp 197.6–200.4 °C, yield: 76%).
H NMR (400 MHz, Chloroform-d) δ 7.80 – 7.73 (m, 2H), 7.72 – 7.65 (m, 2H), 7.59 – 7.53 (m, 1H), 7.50 – 7.42 (m, 3H), 7.39 – 7.31 (m, 2H), 7.23 – 7.12 (m, 3H), 7.08 (d, J = 7.6 Hz, 1H), 6.94 (t, J = 7.5 Hz, 1H), 6.69 – 6.56 (m, 3H), 5.48 (d, J = 10.0 Hz, 1H), 4.09 – 3.97 (m, 1H), 3.56 – 3.45 (m, 1H), 2.88 – 2.76 (m, 1H), 2.74 – 2.66 (m, 1H). 13C NMR (101 MHz, Chloroform-d) δ 149.64 (d, J_C-P = 7.0 Hz), 137.27 (d, J_C-P = 4.2 Hz), 132.85 (d, J_C-P = 8.6 Hz), 132.61 (d, J_C-P = 2.8 Hz), 132.50, 132.38 (d, J_C-P = 2.8 Hz), 132.26 (d, J_C-P = 8.8 Hz), 130.37, 129.78 (d, J_C-P = 2.2 Hz), 129.08 (d, J_C-P = 11.0 Hz), 128.95 (d, J_C-P = 11.4 Hz), 128.40 (d, J_C-P = 3.5 Hz), 128.21 (d, J_C-P = 3.0 Hz), 126.26 (d, J_C-P = 2.6 Hz), 118.73, 112.17, 62.86 (d, J_C-P = 78.4 Hz), 45.75, 26.49. 31P NMR (162 MHz, Chloroform-d) δ 32.16. HRMS (ESI) calcd. for C_{27}H_{23}BrNNaOP [M+Na]^+: 510.0593. Found: 510.0578.

![Diphenyl(2-(m-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphine oxide (3ka)](image)

Reaction was proceeded according to General Method B with 10 mA constant current electrolysis. The reaction mixture was purified by silica gel column chromatography to afford the product 3ka. (white solid, mp 186.2–188.7 °C, yield: 99%).

1H NMR (400 MHz, Chloroform-d) δ 7.85 – 7.77 (m, 2H), 7.73 – 7.66 (m, 2H), 7.55 -7.51 (m, 1H), 7.49 – 7.39 (m, 3H), 7.38 – 7.29 (m, 2H), 7.18 – 7.10 (m, 1H), 7.09 – 6.99 (m, 2H), 6.94 (t, J = 7.5 Hz, 1H), 6.68 (d, J = 7.8 Hz, 1H), 6.63 – 6.53 (m, 3H), 5.55 (d, J = 10.6 Hz, 1H), 4.04 – 3.93 (m, 1H), 3.61 – 3.50 (m, 1H), 2.92 – 2.75 (m, 1H), 2.72 – 2.59 (m, 1H), 2.20 (s, 3H). 13C NMR (101 MHz, Chloroform-d) δ 150.02 (d, J_C-P = 7.6 Hz), 138.78, 136.90 (d, J_C-P = 4.2 Hz), 132.35 (d, J_C-P = 86.0 Hz), 132.28 (d, J_C-P = 8.4 Hz), 131.86 (d, J_C-P = 2.9 Hz), 131.74 (d, J_C-P = 8.8 Hz), 131.62 (d, J_C-P = 2.8 Hz), 130.04, 129.20 (d, J_C-P = 2.2 Hz), 128.90, 128.41 (d, J_C-P = 11.1 Hz), 128.23 (d, J_C-P = 11.3 Hz), 127.82 (d, J_C-P = 3.3 Hz), 127.36 (d, J_C-P = 3.0 Hz), 125.49 (d, J_C-P = 2.6 Hz), 120.44, 117.56, 113.82, 62.12 (d, J_C-P = 79.6 Hz), 45.10, 25.70, 21.75. 31P NMR (162 MHz, Chloroform-d) δ 32.16. HRMS (ESI) calcd. for C_{28}H_{26}NNaOP [M+Na]^+: 446.1644. Found: 446.1627.
(2-(3,4-dimethylphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)diphenylphosphine oxide (3la)

Reaction was proceeded according to General Method B with 10 mA constant current electrolysis. The reaction mixture was purified by silica gel column chromatography to afford the product 3la. (white solid, mp 168.9–171.7 °C, yield: 90%).

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.85 – 7.77 (m, 2H), 7.74 – 7.66 (m, 2H), 7.55 -7.51 (m, 1H), 7.48 – 7.40 (m, 3H), 7.38 – 7.29 (m, 2H), 7.13 (t, $J = 7.5$ Hz, 1H), 7.05 (d, $J = 7.6$ Hz, 1H), 6.98 – 6.86 (m, 2H), 6.67 (d, $J = 7.8$ Hz, 1H), 6.61 – 6.51 (m, 2H), 5.48 (d, $J = 11.4$ Hz, 1H), 4.05 – 3.89 (m, 1H), 3.55 – 3.47 (m, 1H), 2.89 – 2.73 (m, 1H), 2.67 – 2.53 (m, 1H), 2.12 (s, 6H).

$^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 148.34 (d, $J_{C-P} = 8.9$ Hz), 137.13, 136.92 (d, $J_{C-P} = 4.4$ Hz), 132.89, 132.42 (d, $J_{C-P} = 95.5$ Hz), 132.25 (d, $J_{C-P} = 8.3$ Hz), 131.80 (d, $J_{C-P} = 98.3$ Hz), 131.79 (d, $J_{C-P} = 2.7$ Hz), 131.78 (d, $J_{C-P} = 8.8$ Hz), 131.55 (d, $J_{C-P} = 2.8$ Hz), 130.12, 129.93, 129.28 (d, $J_{C-P} = 2.2$ Hz), 128.40 (d, $J_{C-P} = 11.1$ Hz), 128.22 (d, $J_{C-P} = 11.1$ Hz), 128.09, 127.85 (d, $J_{C-P} = 3.2$ Hz), 127.25 (d, $J_{C-P} = 2.9$ Hz), 125.41 (d, $J_{C-P} = 2.6$ Hz), 119.18, 114.96, 62.09 (d, $J_{C-P} = 80.4$ Hz), 45.58, 25.22, 20.18, 18.75. $^{31}$P NMR (162 MHz, Chloroform-d) $\delta$ 32.44. HRMS (ESI) calcd. for C$_{29}$H$_{30}$N$_2$OP [M+Na]$^+$: 460.1801. Found: 460.1785.

(2-Phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)di-p-tolylphosphine oxide (3ab)

Reaction was proceeded according to General Method A with 0.1 V vs. Ag/AgCl constant potential electrolysis. The reaction mixture was purified by silica gel column chromatography to afford the product 3ab. (white solid, mp 191.2–193.6 °C, yield: 85%).
Reaction was proceeded according to General Method B with 10 mA constant current electrolysis. The reaction mixture was purified by silica gel column chromatography to afford the product 3ab. (white solid, mp 191.2−193.6 °C, yield: 76%).

$^1$H NMR (400 MHz, Chloroform-d)  δ 7.71 – 7.50 (m, 4H), 7.28 – 7.21 (m, 2H), 7.17 – 7.11 (m, 5H), 7.06 (d, $J = 7.6$ Hz, 1H), 6.95 (t, $J = 7.5$ Hz, 1H), 6.84 – 6.73 (m, 3H), 6.69 (d, $J = 7.8$ Hz, 1H), 5.52 (d, $J = 11.1$ Hz, 1H), 4.08 – 3.91 (m, 1H), 3.68 – 3.49 (m, 1H), 2.93 – 2.76 (m, 1H), 2.69 – 2.57 (m, 1H), 2.41 (s, 3H), 2.33 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-d)  δ 150.06 (d, $J_C$=$P$ = 8.2 Hz), 142.26 (d, $J_C$=$P$ = 3.2 Hz), 141.99 (d, $J_C$=$P$ = 3.2 Hz), 136.79 (d, $J_C$=$P$ = 4.3 Hz), 132.26 (d, $J_C$=$P$ = 9.0 Hz), 131.69 (d, $J_C$=$P$ = 9.3 Hz), 130.21, 129.21, 129.17 (d, $J_C$=$P$ = 2.2 Hz), 129.09 (d, $J_C$=$P$ = 2.1 Hz), 129.07, 128.94, 127.91 (d, $J_C$=$P$ = 3.7 Hz), 127.27 (d, $J_C$=$P$ = 3.3 Hz), 125.46 (d, $J_C$=$P$ = 2.9 Hz), 119.34, 116.67, 62.05 (d, $J_C$=$P$ = 79.8 Hz), 44.96, 25.57, 21.63 (d, $J_C$=$P$ = 1.4 Hz), 21.55 (d, $J_C$=$P$ = 1.4 Hz). $^{31}$P NMR (162 MHz, Chloroform-d)  δ 32.70. HRMS (ESI) calcd. for C$_{29}$H$_{28}$NNaOP [M+Na]$^+$: 460.1801. Found: 460.1782.

Bis(4-methoxyphenyl)(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphine oxide (3ac)

Reaction was proceeded according to General Method A with 0.1 V vs. Ag/AgCl constant potential electrolysis. The reaction mixture was purified by silica gel column chromatography to afford the product 3ac. (white solid, mp 192.7−194.6 °C, yield: 80%).

Reaction was proceeded according to General Method B with 10 mA constant current electrolysis. The reaction mixture was purified by silica gel column chromatography to afford the product 3ac. (white solid, mp 192.7−194.6 °C, yield: 84%).

$^1$H NMR (400 MHz, Chloroform-d)  δ 7.75 – 7.64 (m, 2H), 7.63 – 7.48 (m, 2H), 7.17 – 7.09 (m, 3H), 7.06 (d, $J = 7.6$ Hz, 1H), 7.01 – 6.90 (m, 3H), 6.88 – 6.72 (m, 6H), 5.49 (d, $J = 11.6$ Hz, 1H),
3.98 – 3.88 (m, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 3.63 – 3.49 (m, 1H), 2.83 (m, 1H), 2.68 – 2.58 (m, 1H). $^{13}$C NMR (101 MHz, Chloroform-d) δ 162.45 (d, $J_{C,P}$ = 3.3 Hz), 162.23 (d, $J_{C,P}$ = 3.2 Hz), 150.03 (d, $J_{C,P}$ = 7.8 Hz), 136.75 (d, $J_{C,P}$ = 4.5 Hz), 134.19 (d, $J_{C,P}$ = 9.8 Hz), 133.55 (d, $J_{C,P}$ = 10.4 Hz), 130.36, 129.10, 128.03 (d, $J_{C,P}$ = 3.8 Hz), 127.29 (d, $J_{C,P}$ = 3.5 Hz), 127.05, 125.51 (d, $J_{C,P}$ = 3.1 Hz), 124.27 (d, $J_{C,P}$ = 1.8 Hz), 123.78 (d, $J_{C,P}$ = 101.5 Hz), 122.28 (d, $J_{C,P}$ = 97.9 Hz), 116.47, 114.04, 113.92, 113.80, 62.42 (d, $J_{C,P}$ = 80.8 Hz), 55.33, 55.26, 44.77, 25.71. $^{31}$P NMR (162 MHz, Chloroform-d) δ 32.15. HRMS (ESI) calcd. for C$_{29}$H$_{28}$NNaO$_3$P [M+Na]$^+$: 492.1699. Found: 492.1682.

![Structure of bis(4-fluorophenyl)(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphine oxide (3ad)](image)

**Reaction**

Reaction was proceeded according to General Method A with 0.1 V vs. Ag/AgCl constant potential electrolysis. The reaction mixture was purified by silica gel column chromatography to afford the product **3ad**. (white solid, mp 208.6–210.0 °C, yield: 72%).

Reaction was proceeded according to General Method B with 10 mA constant current electrolysis. The reaction mixture was purified by silica gel column chromatography to afford the product **3ad**. (white solid, mp 208.6–210.0 °C, yield: 78%).

$^1$H NMR (400 MHz, Chloroform-d) δ 7.84 – 7.74 (m, 2H), 7.69 – 7.58 (m, 2H), 7.21 – 7.11 (m, 5H), 7.08 (d, $J$ = 7.6 Hz, 1H), 7.06 – 6.96 (m, 3H), 6.84 – 6.76 (m, 3H), 6.73 (d, $J$ = 7.8 Hz, 1H), 5.50 (d, $J$ = 11.0 Hz, 1H), 4.01 – 3.87 (m, 1H), 3.62 – 3.51 (m, 1H), 2.90 – 2.74 (m, 1H), 2.71 – 2.58 (m, 1H). $^{13}$C NMR (101 MHz, Chloroform-d) δ 165.22 (dd, $J$ = 254.8, 3.5 Hz), 164.99 (dd, $J$ = 254.5, 3.3 Hz), 149.86 (d, $J_{C,P}$ = 7.9 Hz), 136.82 (d, $J_{C,P}$ = 4.4 Hz), 134.73 (dd, $J$ = 9.2, 9.2Hz), 134.15 (dd, $J$ = 10.1, 8.7 Hz), 129.49, 129.32 (d, $J_{C,P}$ = 2.2 Hz), 129.24, 127.95 (d, $J_{C,P}$ = 98.4 Hz), 127.78 (d, $J_{C,P}$ = 3.3 Hz), 127.65 (dd, $J$ = 13.6, 3.0 Hz), 126.99 (d, $J$ = 96.0 Hz), 125.70 (d, $J_{C,P}$ = 2.6 Hz), 120.00, 117.00, 116.00 (dd, $J$ = 21.0, 12.1 Hz), 115.67 (dd, $J$ = 21.2, 12.4 Hz), 62.19 (d,
\( J_{C,P} = 81.4 \text{ Hz} \), 45.29, 25.60. \(^{31}\)P NMR (162 MHz, Chloroform-d) \( \delta 31.05. \) \(^{19}\)F NMR (377 MHz, Chloroform-d) \( \delta -106.32, -106.62. \) HRMS (ESI) calcd. for C\(_{27}\)H\(_{22}\)F\(_2\)NNaOP \([\text{M+Na}]^+\): 468.1299. Found: 468.1282.

\[
\begin{align*}
\text{bis(3,5-dimethylphenyl)(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphine oxide (3ae)}
\end{align*}
\]

Reaction was proceeded according to General Method A with 0.1 V vs. Ag/AgCl constant potential electrolysis. The reaction mixture was purified by silica gel column chromatography to afford the product 3ae. (white solid, mp 179.9–182.2 °C, yield: 84%).

Reaction was proceeded according to General Method B with 10 mA constant current electrolysis. The reaction mixture was purified by silica gel column chromatography to afford the product 3ae. (white solid, mp 179.9–182.2 °C, yield: 92%).

\(^1\)H NMR (400 MHz, Chloroform-d) \( \delta 7.35 – 7.24 \) (m, 4H), 7.19 – 7.11 (m, 4H), 7.09 – 7.03 (m, 2H), 6.94 (t, \( J = 7.5 \text{ Hz} \), 1H), 6.83 (d, \( J = 8.2 \text{ Hz} \), 2H), 6.77 (t, \( J = 7.3 \text{ Hz} \), 1H), 6.61 (d, \( J = 7.8 \text{ Hz} \), 1H), 5.53 (d, \( J = 10.6 \text{ Hz} \), 1H), 4.10 – 3.96 (m, 1H), 3.63 – 3.47 (m, 1H), 2.88 – 2.74 (m, 1H), 2.70 – 2.58 (m, 1H), 2.29 (s, 6H), 2.20 (s, 6H). \(^{13}\)C NMR (101 MHz, Chloroform-d) \( \delta 150.19 \) (d, \( J_{C,P} = 7.3 \text{ Hz} \)), 137.98 (d, \( J_{C,P} = 11.7 \text{ Hz} \)), 137.76 (d, \( J_{C,P} = 11.9 \text{ Hz} \)), 137.02 (d, \( J_{C,P} = 4.2 \text{ Hz} \)), 133.48 (d, \( J_{C,P} = 2.9 \text{ Hz} \)), 133.27 (d, \( J_{C,P} = 2.9 \text{ Hz} \)), 131.97 (d, \( J_{C,P} = 94.8 \text{ Hz} \)), 131.21 (d, \( J_{C,P} = 89.9 \text{ Hz} \)), 130.25, 129.79 (d, \( J_{C,P} = 8.5 \text{ Hz} \)), 129.37 (d, \( J_{C,P} = 8.8 \text{ Hz} \)), 129.08 (d, \( J_{C,P} = 2.3 \text{ Hz} \)), 129.02, 127.93 (d, \( J_{C,P} = 3.3 \text{ Hz} \)), 127.27 (d, \( J_{C,P} = 2.9 \text{ Hz} \)), 125.33 (d, \( J_{C,P} = 2.6 \text{ Hz} \)), 119.41, 117.00, 61.69 (d, \( J_{C,P} = 78.6 \text{ Hz} \)), 45.21, 25.84, 21.29, 21.24. \(^{31}\)P NMR (162 MHz, Chloroform-d) \( \delta 33.37. \) HRMS (ESI) calcd. for C\(_{31}\)H\(_{32}\)NNaOP \([\text{M+Na}]^+\): 488.2114. Found: 488.2097.
di(naphthalen-2-yl)(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphine oxide (3af)

Reaction was proceeded according to General Method A with 0.1 V vs. Ag/AgCl constant potential electrolysis. The reaction mixture was purified by silica gel column chromatography to afford the product 3af. (white solid, mp 197.4–200.1 °C, yield: 79%).

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.47 (d, $J = 12.6$ Hz, 1H), 8.35 (d, $J = 12.7$ Hz, 1H), 7.91 – 7.83 (m, 3H), 7.81 – 7.68 (m, 5H), 7.62 – 7.41 (m, 4H), 7.13 (t, $J = 7.7$ Hz, 3H), 7.06 (d, $J = 7.7$ Hz, 1H), 6.91 – 6.84 (m, 3H), 6.78 (t, $J = 7.3$ Hz, 1H), 6.69 (d, $J = 7.8$ Hz, 1H), 5.78 (d, $J = 11.1$ Hz, 1H), 4.17 – 4.03 (m, 1H), 3.67 – 3.53 (m, 1H), 2.90 – 2.75 (m, 1H), 2.68 – 2.58 (m, 1H). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 150.16 (d, $J_{C,P} = 8.5$ Hz), 136.89 (d, $J_{C,P} = 4.6$ Hz), 134.76, 134.69 (d, $J_{C,P} = 2.3$ Hz), 134.60 (d, $J_{C,P} = 2.7$ Hz), 133.81 (d, $J_{C,P} = 8.4$ Hz), 132.60 (d, $J_{C,P} = 10.7$ Hz), 132.47 (d, $J_{C,P} = 10.9$ Hz), 129.92, 129.76 (d, $J_{C,P} = 89.9$ Hz), 129.40 (d, $J_{C,P} = 2.5$ Hz), 129.22, 129.03 (d, $J_{C,P} = 14.8$ Hz), 128.29, 128.16 (d, $J_{C,P} = 10.8$ Hz), 128.03 (d, $J_{C,P} = 2.5$ Hz), 127.89 (d, $J_{C,P} = 4.4$ Hz), 127.77 (d, $J_{C,P} = 9.7$ Hz), 127.46 (d, $J_{C,P} = 3.3$ Hz), 126.94, 126.76 (d, $J_{C,P} = 4.1$ Hz), 126.68, 126.66 (d, $J_{C,P} = 4.7$ Hz), 125.65 (d, $J_{C,P} = 3.1$ Hz), 125.36 (d, $J_{C,P} = 91.0$ Hz), 119.90, 117.34, 61.85 (d, $J_{C,P} = 80.1$ Hz), 45.53, 25.49. $^{31}$P NMR (162 MHz, Chloroform-d) $\delta$ 32.89. HRMS (ESI) calcd. for C$_{35}$H$_{28}$NNaOP [M+Na]$^+$: 532.1801. Found: 532.1783.

Diphenyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (3ag)

Reaction was proceeded according to General Method A with 0.1 V vs. Ag/AgCl constant potential electrolysis. The reaction mixture was purified by silica gel column chromatography to
afford the product 3ag. (white solid, mp 105.6–108.3 °C, yield: 75%).

Reaction was proceeded according to General Method B with 10 mA constant current electrolysis.

The reaction mixture was purified by silica gel column chromatography to afford the product 3ag.

(white solid, mp 105.6–108.3 °C, yield: 78%).

\[ \text{1H NMR (400 MHz, Chloroform-d)} \delta 7.53-7.50 \text{ (m, 1H), 7.28-7.09 (m, 10H), 7.07-7.00 (m, 5H), 6.89-6.79 (m, 3H), 5.59 (d, } J = 19.9 \text{ Hz, 1H), 4.14-3.96 (m, 1H), 3.69-3.63 (m, 1H), 3.12-2.94 (m, 2H).} \]

\[ \text{13C NMR (101 MHz, Chloroform-d)} \delta 150.82 \text{ (d, } J_{C-P} = 10.6 \text{ Hz), 150.37 (d, } J_{C-P} = 11.5 \text{ Hz), 149.28 (d, } J_{C-P} = 7.0 \text{ Hz), 136.77 (d, } J_{C-P} = 6.2 \text{ Hz), 129.64, 129.57 (d, } J_{C-P} = 1.1 \text{ Hz), 129.45, 129.28, 129.05 (d, } J_{C-P} = 3.1 \text{ Hz), 128.43 (d, } J_{C-P} = 5.4 \text{ Hz), 127.97 (d, } J_{C-P} = 4.2 \text{ Hz), 126.24 (d, } J_{C-P} = 3.4 \text{ Hz), 125.07 (d, } J_{C-P} = 1.6 \text{ Hz), 124.86 (d, } J_{C-P} = 1.3 \text{ Hz), 120.67 (d, } J_{C-P} = 4.5 \text{ Hz), 120.41 (d, } J_{C-P} = 4.4 \text{ Hz), 119.17, 115.51, 59.19 (d, } J_{C-P} = 160.6 \text{ Hz), 44.03, 26.65.} \]

\[ \text{31P NMR (162 MHz, Chloroform-d)} \delta 16.37. \]


\[
\text{Bis(4-chlorophenyl)(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphine oxide (3ah)}
\]

Reaction was proceeded according to General Method B with 10 mA constant current electrolysis.

The reaction mixture was purified by silica gel column chromatography to afford the product 3ah.

(white solid, mp 196.2–199.4 °C, yield: 48%).

\[ \text{1H NMR (400 MHz, Chloroform-d)} \delta 7.73-7.68 \text{ (m, 2H), 7.59-7.55 (m, 2H), 7.47-7.41 (m, 2H), 7.36-7.29 (m, 2H), 7.21-7.13 (m, 3H), 7.09 (d, } J = 7.6 \text{ Hz, 1H), 7.01 (t, } J = 7.5 \text{ Hz, 1H), 6.86-6.77 (m, 3H), 6.72 (d, } J = 7.7 \text{ Hz, 1H), 5.50 (d, } J = 11.0 \text{ Hz, 1H), 4.00-3.87 (m, 1H), 3.62-3.51 (m, 1H), 2.90-2.75 (m, 1H), 2.70-2.59 (m, 1H).} \]

\[ \text{13C NMR (101 MHz, Chloroform-d)} \delta 149.87 \text{ (d, } J_{C-P} = 8.5 \text{ Hz), 138.85 (d, } J_{C-P} = 3.8 \text{ Hz), 138.52 (d, } J_{C-P} = 3.7 \text{ Hz), 136.80 (d, } J_{C-P} = 4.8 \text{ Hz).} \]
Hz), 133.54 (d, $J_{C,P} = 9.4$ Hz), 133.01 (d, $J_{C,P} = 9.9$ Hz), 130.43 (d, $J_{C,P} = 96.3$ Hz), 129.64 (d, $J_{C,P} = 103.1$ Hz), 129.43 (d, $J_{C,P} = 2.7$ Hz), 129.29, 129.25, 128.93 (d, $J_{C,P} = 11.7$ Hz), 128.72 (d, $J_{C,P} = 11.9$ Hz), 127.70 (d, $J_{C,P} = 3.9$ Hz), 125.76 (d, $J_{C,P} = 3.1$ Hz), 120.22, 117.28, 61.99 (d, $J_{C,P} = 81.1$ Hz), 45.49, 25.47. 

$^{31}$P NMR (162 MHz, Chloroform-d) $\delta$ 31.22. HRMS (ESI) calcd. for C$_{27}$H$_{22}$C$_{12}$NNaOP [M+Na]$^+$: 500.0708. Found: 500.0691.

![Structure of dimethyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (3ai)](image)

**dimethyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (3ai)**

Reaction was proceeded according to General Method A with 0.1 V vs. Ag/AgCl constant potential electrolysis. The reaction mixture was purified by silica gel column chromatography to afford the product 3ai. (white solid, mp 85.9–87.9 °C, yield: 81%).

Reaction was proceeded according to General Method B with 10 mA constant current electrolysis. The reaction mixture was purified by silica gel column chromatography to afford the product 3ai. (white solid, mp 85.9–87.9 °C, yield: 89%).

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.38 – 7.32 (m, 1H), 7.29 – 7.23 (m, 2H), 7.21 – 7.12 (m, 3H), 6.97 (d, $J = 8.3$ Hz, 2H), 6.80 (t, $J = 7.3$ Hz, 1H), 5.20 (d, $J = 19.9$ Hz, 1H), 4.09 – 3.94 (m, 1H), 3.79 – 3.53 (m, 7H), 3.17 – 2.86 (m, 2H). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 149.27 (d, $J_{C,P} = 6.2$ Hz), 136.44 (d, $J_{C,P} = 5.9$ Hz), 130.43, 129.27, 128.86 (d, $J_{C,P} = 3.0$ Hz), 127.97 (d, $J_{C,P} = 4.8$ Hz), 127.57 (d, $J_{C,P} = 4.0$ Hz), 126.08 (d, $J_{C,P} = 3.2$ Hz), 118.71, 114.81, 58.78 (d, $J_{C,P} = 159.4$ Hz), 53.95 (d, $J_{C,P} = 7.4$ Hz), 52.97 (d, $J_{C,P} = 7.9$ Hz), 43.59, 26.71. $^{31}$P NMR (162 MHz, Chloroform-d) $\delta$ 26.01. HRMS (ESI) calcd. for C$_{17}$H$_{20}$NNaO$_3$P [M+Na]$^+$: 340.1073. Found: 340.1060.

![Structure of diethyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (3aj)](image)

**diethyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (3aj)**
Reaction was proceeded according to General Method A with 0.1 V vs. Ag/AgCl constant potential electrolysis. The reaction mixture was purified by silica gel column chromatography to afford the product 3aj. (white solid, mp 61.4–63.8 °C; yield: 70%).

Reaction was proceeded according to General Method B with 10 mA constant current electrolysis. The reaction mixture was purified by silica gel column chromatography to afford the product 3aj. (white solid, mp 61.4–63.8 °C; yield: 62%).

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.41 – 7.34 (m, 1H), 7.27 – 7.21 (m, 2H), 7.20 – 7.12 (m, 3H), 6.97 (d, $J$ = 8.3 Hz, 2H), 6.79 (t, $J$ = 7.2 Hz, 1H), 5.18 (d, $J$ = 20.0 Hz, 1H), 4.14 – 3.93 (m, 4H), 3.93 – 3.82 (m, 1H), 3.65-3.59 (m, 1H), 3.15 – 2.91 (m, 2H), 1.24 (t, $J$ = 7.1 Hz, 3H), 1.13 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 149.42 (d, $J_{C,P}$ = 6.1 Hz), 136.46 (d, $J_{C,P}$ = 5.8 Hz), 130.69, 129.14, 128.75 (d, $J_{C,P}$ = 3.0 Hz), 128.14 (d, $J_{C,P}$ = 5.1 Hz), 127.43 (d, $J_{C,P}$ = 3.8 Hz), 125.87 (d, $J_{C,P}$ = 2.9 Hz), 118.47, 114.81, 63.32 (d, $J_{C,P}$ = 7.7 Hz), 62.34 (d, $J_{C,P}$ = 8.1 Hz), 58.83 (d, $J_{C,P}$ = 159.2 Hz), 43.50, 26.79, 16.47 (d, $J_{C,P}$ = 5.6 Hz), 16.38 (d, $J_{C,P}$ = 6.0 Hz). $^{31}$P NMR (162 MHz, Chloroform-d) $\delta$ 23.79. HRMS (ESI) calcd. for C$_{19}$H$_{24}$NNaO$_3$P [M+Na]$^+$: 368.1386. Found: 368.1373.

![Dibutyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (3ak)](image)

Dibutyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (3ak)

Reaction was proceeded according to General Method A with 0.1 V vs. Ag/AgCl constant potential electrolysis. The reaction mixture was purified by silica gel column chromatography to afford the product 3ak. (white solid, mp 46.3–49.0 °C; yield: 64%).

Reaction was proceeded according to General Method B with 10 mA constant current electrolysis. The reaction mixture was purified by silica gel column chromatography to afford the product 3ak. (white solid, mp 46.3–49.0 °C; yield: 43%).

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.40 – 7.34 (m, 1H), 7.27 – 7.21 (m, 2H), 7.21 – 7.11 (m, 3H), 6.97 (d, $J$ = 8.3 Hz, 2H), 6.78 (t, $J$ = 7.2 Hz, 1H), 5.20 (d, $J$ = 19.9 Hz, 1H), 4.09 – 3.74 (m,
5H), 3.66-3.60 (m, 1H), 3.16 – 2.89 (m, 2H), 1.62 – 1.51 (m, 2H), 1.49 – 1.40 (m, 2H), 1.39 – 1.16 (m, 4H), 0.88 (t, J = 7.3 Hz, 3H), 0.81 (t, J = 7.4 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$
149.36 (d, $J_{C,P}$ = 5.8 Hz), 136.41 (d, $J_{C,P}$ = 5.9 Hz), 130.79, 129.12, 128.73 (d, $J_{C,P}$ = 3.0 Hz), 128.13 (d, $J_{C,P}$ = 5.0 Hz), 127.40 (d, $J_{C,P}$ = 3.9 Hz), 125.85 (d, $J_{C,P}$ = 3.3 Hz), 118.41, 114.77, 66.92 (d, $J_{C,P}$ = 7.8 Hz), 65.98 (d, $J_{C,P}$ = 8.5 Hz), 58.75 (d, $J_{C,P}$ = 158.5 Hz), 43.46, 32.58 (dd, $J_{C,P}$ = 6.2, 6.4 Hz), 26.84, 18.68 (d, $J_{C,P}$ = 6.6 Hz), 13.57 (d, $J_{C,P}$ = 4.5 Hz). $^{31}$P NMR (162 MHz, Chloroform-d) $\delta$ 23.93. HRMS (ESI) calcd. for C$_{23}$H$_{32}$NNaO$_3$P [M+Na]$^+$: 424.2012. Found: 424.1997.
5. $^1$H and $^{13}$C spectra of products