Supporting Information

A scalable electrochemical dehydrogenative cross-coupling of P(O)H compounds with RSH/ROH

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1. General information

Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Reactions were monitored by thin layer chromatography (TLC) using silica gel 60 F-254 plates. The instrument for electrolysis was dual display potentiostat (M8801) (made in China) or ElectraSyn 2.0. Cyclic voltammograms were obtained on a CHI 600E potentiostat. Gas chromatographic analyses were performed on SICT GC-2000II gas chromatography instrument with a FID detector. The anode electrode was graphite rod (φ 6 mm) and cathodic electrode was platinum plate (15 mm×10 mm×0.1 mm) or the anode electrode and cathode electrode all were platinum electrodes (15 mm×10 mm×0.1 mm). Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (bp. 60-90 °C). NMR spectra were measured on a Bruker avance III HD400 ( 1H at 400 MHz, 13C at 101 MHz, 31P at 162 MHz) magnetic resonance spectrometer. Chemical shifts (δ) are reported in ppm using tetramethylsilane as internal standard (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, ddd = triplet of doublets, m = multiplet), and coupling constants (J) were reported in Hertz (Hz). ESI-HRMS spectra were recorded on a UPLC of Thermo Q Exactive Focus.

Abbreviations used: GC = graphite rod; RVC = Reticulated Vitreous Carbon; DABCO = 1,4-Diaza[2.2.2]bicyclooctane; NMO = 4-methylmorpholin4-oxide; NHPI = N-Hydroxyphthalimide; Et3N = Triethylamine; DMF = N,N-Dimethylformamide; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene; TEMPO = 2,2,6,6-Tetramethyl-1-piperidyloxy.

2. Equipment and experiments pictures

(a) electrodes  (b) power supply
(c) reaction cell
(d) gram scale beaker
(e) flow microreactor
(f) Electrochemical flow setup

**Figure S1** Electrolysis setup
3. Experimental procedure

3.1 General procedure for coupling with thiols

Method A: In an oven-dried undivided three-necked bottle (10 mL) equipped with a stir bar, diphenylphosphine oxide (0.3 mmol), thiol (0.9 mmol), \( \text{Bu}_4\text{BF}_4 \) (0.9 mmol) were dissolved in MeCN (5 mL). The bottle was equipped with platinum plate (15 mm×10 mm×0.1 mm) as the anode and cathode. The resulting mixture was electrolyzed at a constant current mode with a constant current density of 3.3 mA/cm² under ambient temperature for corresponding time. When the reaction was finished, the solvent was removed with a rotary evaporator. The residue was purified by column chromatography on silica gel (petroleum : ethyl ether = 5 : 1 - 3 : 1) to afford the desired product.

Method B: In an oven-dried undivided three-necked bottle (10 mL) equipped with a stir bar, diphenylphosphine oxide (0.3 mmol), thiol (0.9 mmol), \( \text{Bu}_4\text{BF}_4 \) (0.9 mmol) were dissolved in DMF (5 mL). The bottle was equipped with platinum plate (15 mm×10 mm×0.1 mm) as the anode and cathode. The resulting mixture was electrolyzed at a constant current mode with a constant current density of 3.3 mA/cm² under ambient temperature for corresponding time. When the reaction was finished, the solution was extracted with EtOAc (3 × 12 mL) and brine (2 × 12 mL). The combined organic layer was dried with Na₂SO₄, filtered the solvent was removed with a rotary evaporator. The residue was purified by column chromatography on silica gel (petroleum : ethyl ether = 5 : 1 - 3 : 1) to afford the desired product.

Method C: In an exemplary procedure for the electrolysis with an ElectraSyn 2.0. diphenylphosphine oxide (0.3 mmol), thiol (0.9 mmol), \( \text{Bu}_4\text{BF}_4 \) (0.9 mmol) were added in sequence to a 5 mL ElectraSyn vial with a stirring bar. The screw thread area of the vial was covered with a piece of Parafilm and screwed to finger-tight with the ElectraSyn vial cap equipped with a Pt electrode (anode) and a Pt electrode (cathode). The undivided cell was adapted to the ElectraSyn 2.0 vial holder and electrolysed under a constant current density of 3.3 mA/cm² for 4 h. When the reaction was finished, the solvent was removed with a rotary evaporator. The residue was purified by column chromatography on silica gel (petroleum : ethyl ether = 5 : 1 - 3 : 1) to afford the desired product.
**Procedure for gram scale synthesis:**

\[
\begin{align*}
1 & \quad \text{Ph-PH} \quad \text{Ph} \\
\text{8 mmol} & \quad 3 \text{ equiv} \\
2 & \quad \text{SH} \\
& \quad \text{Ph-PH} \\
3 & \quad \text{Ph-S-Ph} \\
& \quad \text{2.2 g, 85% yield}
\end{align*}
\]

Diphenylphosphine oxide (8 mmol, 1.61 g), thiol (24 mmol, 2.98 g), \(^{n}\text{Bu}_4\text{BF}_4\) (24 mmol, 7.90 g) were placed in an beaker (250 mL). The beaker was equipped with a stir bar, followed by MeCN (135 mL). Two platinum plate (50 mm×50 mm×0.1 mm) were set up in the beaker. The resulting mixture was electrolyzed at a constant current mode with a constant current density of 1.2 mA/cm\(^2\) under ambient temperature for 22 h. When the reaction was finished, the solvent was removed with a rotary evaporator. The residue was purified by column chromatography on silica gel (petroleum : ethyl ether = 3 : 1) to afford the desired product.

**Flow chemistry:**

FEP (fluorinated ethylene propylene) with channel 3 mm width; thickness: 0.5 mm; total length of the pipeline of 30.1 cm; volume: 450 µL; exposed electrode surface: 9.57 cm\(^2\). (Figure S1e) The device comprises a micro-flow electrochemical reactor made out of two bodies (75x75x25 mm, Figure S1), which can be polymer. The bodies have a square space in the centre (50x50 mm\(^2\)), where the two-platinum plate (thickness 0.1 mm) electrodes are placed and FEP was sandwiched between two platinum electrodes. The housing of the reactor has a hole in the middle that allows an easy connection of the electrodes to the power supply by a copper wire. This plate also has 2 holes, one for the inlet and one for the outlet of the reaction solution.

The 1 (5 mmol, 1.04g), 2 (15 mmol, 1.86 g) and \(^{n}\text{Bu}_4\text{BF}_4\) (15 mmol, 4.92 g) were dissolved in MeCN (84 mL) and flowed through the electrochemical microreactor (volume = 450 µL) in a flow rate of 0.2 mL/min (Figure S1). A constant current density of 2.7 mA/cm\(^2\) was employed. The solution was concentrated under reduced pressure on a rotary evaporator. The residue was chromatographed through silica gel eluting with petroleum/ethyl ether to give the product.
Table S1 Optimization of the reaction conditions\textsuperscript{[a]}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Deviation from standard conditions</th>
<th>Yield\textsuperscript{[b]} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>84</td>
</tr>
<tr>
<td>2\textsuperscript{[c]}</td>
<td>1 equiv thiol</td>
<td>49</td>
</tr>
<tr>
<td>3\textsuperscript{[c]}</td>
<td>2 equiv thiol</td>
<td>69</td>
</tr>
<tr>
<td>4\textsuperscript{[c]}</td>
<td>3 equiv thiol</td>
<td>76</td>
</tr>
<tr>
<td>5</td>
<td>LiClO\textsubscript{4} instead of \textsuperscript{4}Bu\textsubscript{4}NBF\textsubscript{4}</td>
<td>62</td>
</tr>
<tr>
<td>6</td>
<td>\textsuperscript{4}Bu\textsubscript{4}NPF\textsubscript{6} instead of \textsuperscript{4}Bu\textsubscript{4}NBF\textsubscript{4}</td>
<td>71</td>
</tr>
<tr>
<td>7</td>
<td>MeCN = 4 mL</td>
<td>62</td>
</tr>
<tr>
<td>8</td>
<td>MeCN = 7 mL</td>
<td>56</td>
</tr>
<tr>
<td>9</td>
<td>DMF instead of MeCN</td>
<td>83</td>
</tr>
<tr>
<td>10</td>
<td>MeOH instead of MeCN</td>
<td>49</td>
</tr>
<tr>
<td>11</td>
<td>GC (+)</td>
<td>Pt (-) instead of Pt (+)</td>
</tr>
<tr>
<td>12</td>
<td>RVC (+)</td>
<td>Pt (-) instead of Pt (+)</td>
</tr>
<tr>
<td>13</td>
<td>$j = 2.7 \text{ mA/cm}^2$ instead of $j = 3.3 \text{ mA/cm}^2$</td>
<td>64</td>
</tr>
<tr>
<td>14</td>
<td>$j = 4.7 \text{ mA/cm}^2$ instead of $j = 3.3 \text{ mA/cm}^2$</td>
<td>56</td>
</tr>
<tr>
<td>15</td>
<td>10 mol % Cp\textsubscript{2}Fe as additive</td>
<td>58</td>
</tr>
<tr>
<td>16</td>
<td>10 mol % \textsuperscript{4}Bu\textsubscript{4}NBr as additive</td>
<td>81</td>
</tr>
<tr>
<td>17</td>
<td>without current</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

\textsuperscript{[a]} Standard conditions: Pt anode, Pt cathode, 1 (0.3 mmol), 2 (0.9 mmol), \textsuperscript{4}Bu\textsubscript{4}NBF\textsubscript{4} (0.18 M), MeCN (5.0 mL), rt, constant current = 5 mA ($j = 3.3 \text{ mA/cm}^2$), 4 h. \textsuperscript{[b]} Isolated yield. \textsuperscript{[c]} 0.12 M \textsuperscript{4}Bu\textsubscript{4}NBF\textsubscript{4}
3.2 General procedure for diphenylphosphine oxide with phenol

Method A: In an oven-dried undivided three-necked bottle (10 mL) equipped with a stir bar, diphenylphosphine oxide (0.3 mmol), phenol (0.9 mmol), KI (0.6 mmol), DABCO (0.15 mmol) were dissolved in MeCN (5 mL) and stir for 10 minutes. The bottle was equipped with graphite rod (φ 6 mm, about 8 mm immersion depth in solution) as the anode and platinum plate (15 mm×10 mm×0.1 mm) as the cathode. The resulting mixture was electrolyzed at a constant current mode with a constant current density of 3.3 mA/cm² under ambient temperature for corresponding time. When the reaction was finished, the solvent was removed with a rotary evaporator. The residue was purified by column chromatography on silica gel (petroleum : ethyl ether = 5 : 1 - 1 : 1) to afford the desired product.

Method B: In an exemplary procedure for the electrolysis with an ElectraSyn 2.0. diphenylphosphine oxide (0.3 mmol), phenol (0.9 mmol), KI (0.6 mmol), DABCO (0.15 mmol) were added in sequence to a 5 mL ElectraSyn vial with a stirring bar. The screw thread area of the vial was covered with a piece of Parafilm and screwed to finger-tight with the ElectraSyn vial cap equipped with a graphite electrode (anode) and a Pt electrode (cathode). The undivided cell was adapted to the ElectraSyn 2.0 vial holder and electrolysed under a constant current density of 3.3 mA/cm² for 3.5 h. When the reaction was finished, the solvent was removed with a rotary evaporator. The residue was purified by column chromatography on silica gel (petroleum : ethyl ether = 5 : 1 - 1 : 1) to afford the desired product.

Procedure for gram scale synthesis:

Diphenylphosphine oxide (8 mmol, 1.61 g), phenol (24 mmol, 2.98 g), KI (16 mmol, 2.66 g), DABCO (4 mmol, 450 mg) were placed in an beaker (250 mL). The beaker was equipped with a stir bar, followed by MeCN (135 mL) and stir for 20 minutes. Two platinum plate (50 mm×50 mm×0.1 mm) were set up in the beaker. The resulting mixture was electrolyzed at a constant current mode with a constant current density of 1.2 mA/cm² under ambient temperature for 10 h. When the reaction was finished, the solvent was removed with a rotary evaporator. The residue was purified by column chromatography on silica gel (petroleum : ethyl ether = 3 : 1) to afford the desired product.
Flow chemistry:
FEP (fluorinated ethylene propylene) with channel 3 mm width; thickness: 0.5 mm, total length of the pipeline of 30.1 cm; volume: 450 µL; exposed electrode surface: 9.57 cm². (Figure S1e)
The device comprises a micro-flow electrochemical reactor made out of two bodies (75x75x25 mm, Figure S1), which can be polymer. The bodies have a square space in the centre (50x50 mm²), where the two-platinum plate (thickness 0.1 mm) electrodes are placed and FEP was sandwiched between two platinum electrodes. The housing of the reactor has a hole in the middle that allows an easy connection of the electrodes to the power supply by a copper wire. This plate also has 2 holes, one for the inlet and one for the outlet of the reaction solution.

The 1 (50 mmol, 10.4 g) and KI (100 mmol, 16.7 g) was dissolved in MeCN/MeOH (4:1, 0.84 L) and flowed through the electrochemical microreactor (volume = 450 µL) in a flow rate of 0.2 mL/min (Figure S1). A constant current density of 3.8 mA/cm² was employed. The solution was concentrated under reduced pressure on a rotary evaporator. The residue was chromatographed through silica gel eluting with petroleum/ethyl ether to give the product.
Table S2 Optimization of the reaction conditions\(^{[a]}\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Deviation from standard conditions</th>
<th>Yield(^{[b]}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>78</td>
</tr>
<tr>
<td>2(^{[c]})</td>
<td>No DABCO</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>0.25 equiv DABCO</td>
<td>72</td>
</tr>
<tr>
<td>4</td>
<td>1.0 equiv DABCO</td>
<td>68</td>
</tr>
<tr>
<td>5</td>
<td>1.5 equiv DABCO</td>
<td>69</td>
</tr>
<tr>
<td>6</td>
<td>quinoline instead of DABCO</td>
<td>65</td>
</tr>
<tr>
<td>7</td>
<td>NMO instead of DABCO</td>
<td>47</td>
</tr>
<tr>
<td>8</td>
<td>NHPI instead of DABCO</td>
<td>n.d.</td>
</tr>
<tr>
<td>9(^{[c]})</td>
<td>Et(_3)N instead of DABCO</td>
<td>n.d.</td>
</tr>
<tr>
<td>10(^{[c]})</td>
<td>DBU instead of DABCO</td>
<td>n.d.</td>
</tr>
<tr>
<td>11</td>
<td>&quot;Bu₄NI instead of KI</td>
<td>68</td>
</tr>
<tr>
<td>12</td>
<td>NaI instead of KI</td>
<td>77</td>
</tr>
<tr>
<td>13</td>
<td>NH₄I instead of KI</td>
<td>n.d.</td>
</tr>
<tr>
<td>14</td>
<td>LiBr instead of KI</td>
<td>n.d.</td>
</tr>
<tr>
<td>15</td>
<td>&quot;Bu₄NBF₄ instead of KI</td>
<td>trace</td>
</tr>
<tr>
<td>16</td>
<td>Pt (+)</td>
<td>Pt (-) instead of GC (+)</td>
</tr>
<tr>
<td>17</td>
<td>C (+)</td>
<td>Pt (-) instead of GC (+)</td>
</tr>
<tr>
<td>18</td>
<td>GC (+)</td>
<td>GC (-) instead of GC (+)</td>
</tr>
<tr>
<td>19</td>
<td>(j = 2.0 \text{ mA/cm}^2) instead of (j = 3.3 \text{ mA/cm}^2), 4 h</td>
<td>50</td>
</tr>
<tr>
<td>20</td>
<td>(j = 4.7 \text{ mA/cm}^2) instead of (j = 3.3 \text{ mA/cm}^2), 2 h 30 min</td>
<td>67</td>
</tr>
<tr>
<td>21</td>
<td>2.5 V instead of (j = 3.3 \text{ mA/cm}^2), 2 h 10 min</td>
<td>66</td>
</tr>
<tr>
<td>22</td>
<td>without current</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

\(^{[a]}\) Standard conditions: GC anode, Pt cathode, \(1\) (0.3 mmol), \(58\) (0.9 mmol), DABCO (50 mol%), KI (0.12 M), MeCN (5.0 mL), rt, constant current = 5 mA (\(j = 3.3 \text{ mA/cm}^2\)), 3 h. \(^{[b]}\) Isolated yield. \(^{[c]}\) 5 equiv \(58\). n.d. = not detected
4. General procedure for cyclic voltammetry (CV)

Cyclic voltammetry was performed in a three-electrode cell connected to a schlenk line at room temperature. The working electrode was a platinum disk electrode, the counter electrode a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution, and separated from reaction by a salt bridge. 10 mL of MeCN containing 0.1 M $^n$Bu$_4$NBF$_4$ were poured into the electrochemical cell in all experiments. Concentration: 0.03 M. The scan rate is 0.1 V/s, ranging from 0 V to 2.5 V. The peak potentials vs. Ag/AgCl for used. The obvious oxidation peaks of 4-methylbenzenethiol and 4-methoxyphenol were observed 1.859V, 1.511V respectively.

![Cyclic voltammetry experiment of reactants](image)

**Figure S2** Cyclic voltammetry experiment of reactants
5. Detection of H₂ by GC

(a) standard hydrogen sample

(b) P(O)H-SH

(c) P(O)H-OH
6. EPR experiments

EPR spectra were recorded at room temperature on a Bruker ESP-300E: Receiver Gain = 1.78 e\(^{1004}\); Phase = 0 deg; Harmoni = 1; Mod. Frequency = 100.000 KHz; Mod. Amplitude = 6.00 G; Center Field = 3360.00 G; Sweep width 90.000 G; Resolution = 2048 points; Conversion Time = 40.00 ms; Time const. = 20.48 ms; Sweep time = 81.92 s; Power = 60.39 mw.

EPR study of reaction a:
Under constant current conditions, a ElectraSyn 2.0 equipped with a stir bar was loaded with KI (0.6 mmol) and PBN (0.30 mmol) in 5.0 mL MeCN was stirred at rt. After 10 mins, the solution sample was taken out into a small tube and analyzed by EPR.

EPR study of reaction b:
Under constant current conditions, a ElectraSyn 2.0 equipped with a stir bar was loaded with 1 (0.30 mmol), KI (0.6 mmol) and PBN (0.30 mmol) in 5.0 mL MeCN was stirred at rt. After 10 mins, the solution sample was taken out into a small tube and analyzed by EPR.

EPR study of reaction c:
Under constant current conditions, a ElectraSyn 2.0 equipped with a stir bar was loaded with 1 (0.30 mmol), DABCO (0.15 mmol), KI (0.6 mmol) and PBN (0.30 mmol) in 5.0 mL MeCN was stirred at rt. After 10 mins, the solution sample was taken out into a small tube and analyzed by EPR.

EPR study of reaction d:
Under constant current conditions, a ElectraSyn 2.0 equipped with a stir bar was loaded with 1 (0.30 mmol), 58 (0.90 mmol), DABCO (0.15 mmol), KI (0.6 mmol) and PBN (0.30 mmol) in 5.0 mL MeCN was stirred at rt. After 10 mins, the solution sample was taken out into a small tube and analyzed by EPR.

EPR study of reaction e:
Under constant current conditions, a ElectraSyn 2.0 equipped with a stir bar was loaded with 1 (0.30 mmol), "Bu\(_4\)NBF\(_4\) (0.9 mmol) and PBN (0.30 mmol) in 5.0 mL MeCN was stirred at rt. After 10 mins, the solution sample was taken out into a small tube and analyzed by EPR.

EPR study of reaction f:
Under constant current conditions, a ElectraSyn 2.0 equipped with a stir bar was loaded with 1 (0.30 mmol), 2 (0.90 mmol), Bu$_4$NBF$_4$ (0.9 mmol) and PBN (0.30 mmol) in 5.0 mL MeCN was stirred at rt. After 10 mins, the solution sample was taken out into a small tube and analyzed by EPR.

Figure S3  EPR experiments pictures
7. X-Ray crystallographic data

X-Ray crystallographic data of 3:

![Crystallographic data diagram]

<table>
<thead>
<tr>
<th>Bond precision: C-C = 0.0036 Å</th>
<th>Wavelength: 0.71073</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell:</td>
<td></td>
</tr>
<tr>
<td>a=8.5391(4)</td>
<td>b=11.0667(5)</td>
</tr>
<tr>
<td>alpha=90</td>
<td>beta=90</td>
</tr>
<tr>
<td>c=16.9456(9)</td>
<td>gamma=90</td>
</tr>
<tr>
<td>Temperature: 170 K</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Volume</td>
<td>1601.35(11)</td>
</tr>
<tr>
<td>Space group</td>
<td>P 21 21 21</td>
</tr>
<tr>
<td>Hall group</td>
<td>D 2ac 2ab</td>
</tr>
<tr>
<td>Moiety formula</td>
<td>C19 H17 O P S</td>
</tr>
<tr>
<td>Sum formula</td>
<td>C19 H17 O P S</td>
</tr>
<tr>
<td>Mr</td>
<td>324.36</td>
</tr>
<tr>
<td>Ex. g cm-3</td>
<td>1.345</td>
</tr>
<tr>
<td>X</td>
<td>4</td>
</tr>
<tr>
<td>Mu (mm-1)</td>
<td>0.301</td>
</tr>
<tr>
<td>F(000)</td>
<td>680.0</td>
</tr>
<tr>
<td>F(000)'</td>
<td>681.13</td>
</tr>
<tr>
<td>h,k,lmax</td>
<td>11,14,22</td>
</tr>
<tr>
<td>Mref</td>
<td>3962</td>
</tr>
<tr>
<td>Tmin, Tmax</td>
<td>0.897, 0.743</td>
</tr>
<tr>
<td>Tmin'</td>
<td>0.867</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Correction method:</td>
<td># Reported T Limits: Tmin=0.588 Tmax=0.746</td>
</tr>
<tr>
<td></td>
<td>Absent = MULTI-SLO</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Data completeness</td>
<td>1.74/1.00</td>
</tr>
<tr>
<td>Theta(max)</td>
<td>28.296</td>
</tr>
<tr>
<td>R(reflections)</td>
<td>0.0332 (3457)</td>
</tr>
<tr>
<td>wR2(reflections)</td>
<td>0.0885 (3962)</td>
</tr>
<tr>
<td>F = 1.008</td>
<td>Npair = 200</td>
</tr>
</tbody>
</table>
X-Ray crystallographic data of 28:

![Chemical Structure Image]

**Bond precision:** C-C = 0.0075 Å  
**Wavelength:** 0.71073 Å

**Cell:**
- a = 8.9390(15) Å  
- b = 11.3093(18) Å  
- c = 9.5031(17) Å  
- alpha = 90°  
- beta = 100.362(5)°  
- gamma = 90°  
**Temperature:** 170 K

**Volume:**
- Calculated: 945.0(3) Å³  
- Reported: 945.0(3) Å³

**Space group:** P 21  
**Hall group:** D 2yb  
**MoIety formula:** C22 H23 O2 P  
**Sum formula:** C22 H23 O2 P

**Mr:** 350.37

**Dx, g cm⁻³:** 1.231

**Z:** 2

**μ (mm⁻¹):** 0.157

**F000:** 372.0

**F000':** 372.35

**h,k, max:** 11,15,12  
**Nref:** 4716 (24731)  
**Tmin, Tmax:** 0.910, 0.954  
**0.510, 0.746

**Correction method:** #  
**Reported T Limits:** Tmin=0.510 Tmax=0.746  
**AbsCorr:** MULTI-SCAN

**Data completeness:** 1.88/0.99  
**θ(α)**: 28.382°

**R(reflections):** 0.0572 (3416)  
**wR2(reflections):** 0.1624 (4654)

**S:** 1.003  
**Npar:** 229
8. Mechanistic studies

a) \( \text{Ph} - \text{Ph} + \text{Ph} - \text{Ph} \quad \text{standard condition A} \quad \text{Ph} - \text{Ph} \quad 78\% \text{ yield} \\

b) \begin{array}{c}
\text{Ph} - \text{Ph} + \text{Ph} - \text{Ph} \\
\text{2.0 equiv TEMPO, 72\%} \\
\text{4.0 equiv TEMPO, 31\%}
\end{array} \\
c) \text{Ph} - \text{Ph} + \text{Ph} - \text{Ph} \quad \text{standard condition A} \\
\text{2, 0.9 mmol} \\
96\% \text{ yield} \\
d) \text{Ph} - \text{Ph} + \text{Ph} - \text{Ph} \quad \text{standard condition A} \\
\text{MeOH (0.5 mL)} \\
3, 41\% \\
e) \text{Ph} - \text{Ph} + \text{Ph} - \text{Ph} \quad \text{standard conditions A} \\
\text{MeCN, rt, 4 h} \\
3, 11\% \\
f) \text{Ph} - \text{Ph} + \text{Ph} - \text{Ph} \\
1.5 equiv \\
3, 59\%
To shine light on the mechanism of this electrochemical dehydrogenative cross-coupling reaction, several control experiments were conducted. For the P-O bond formation, lower yields of the P-S coupling product 3 were obtained by adding 2.0 equiv. or 4.0 equiv. of TEMPO under the standard condition A (72% and 31% yields were obtained, respectively; equation b). The disulfide was obtained in 96% yield without substrate 1 under the standard conditions (equation c). These results suggested that thiyl radical intermediates were involved in the catalytic cycle. When disulphide was subjected to the standard conditions with adding methanol as a proton source, the coupling product...
3 was obtained in 41% yield (equation d), suggesting that the disulphide was one of the intermediates of this transformation. Furthermore, the radical trapping product 59 could react with 1 under the standard condition to afford the product 3 in 11% yield (equation e), indicating that the sulfur radical could be regenerated by the homolytic cleavage of the S-O bond of 59. To our surprise, we found that the diphenylphosphine oxide 1 could react with disulfide to give 59% yield of the product 3 without an electric current (equation f). For the P-O bond formation, the reaction worked well and the coupling product 24 was obtained in 55% yield, when using KOH instead of DABCO as base. Moreover, only trace product was obtained in absence of KI under the standard condition, indicating that the KI was essential for this reaction. Different from the previous report, only trace amount of product was obtained, when using I2 instead of KI, suggesting that the I2 was not involved in the catalytic cycle. No desired product was obtained, when the chemical oxidants such as I2, NIS, H2O2 were adding to the reaction without electricity. Based on the EPR results we have observed, we considered that the phosphorus radicals could generated from the P(O)H compounds by anode oxidation directly or by a HAT process with sulfur radicals (SI-6; experiment a-f). The signal of phosphorus radicals was observed without 4-methylbenzenethiol 2 under the standard condition, which suggested that the phosphorus radicals could generated by anode oxidation directly under electric current (SI-6; experiment e). So, according to the results we observed and previous literature reports, several alternative mechanisms were also proposed (Figure S4), such as the mechanisms including the phosphorus radicals generated from the P(O)H compounds by anode oxidation directly or DABCO working as a hydrogen atom transfer (HAT) reagent in the reaction.
9. Characterization data

![Chemical structure of S-(p-tolyl) diphenylphosphinothioate (3)](image)

**S-(p-tolyl) diphenylphosphinothioate (3)**. Yield = 84%; white solid; Mp: 117-119 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.90 – 7.79 (m, 4H), 7.54 – 7.47 (m, 2H), 7.47 – 7.39 (m, 4H), 7.32 (dd, $J = 8.1$, 1.6 Hz, 2H), 7.00 (d, $J = 8.1$ Hz, 2H), 2.24 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ = 142.92, 142.80, 139.22, 139.20, 135.40, 135.37, 133.19, 132.29, 132.26, 132.13, 131.71, 131.61, 130.00, 129.98, 128.60, 128.47, 122.27, 122.22, 21.18. $^{31}$P NMR (162 MHz, CDCl$_3$) δ = 41.39. HRMS (ESI) calcd for C$_{19}$H$_{18}$OPS (M+H)$^+$: 325.0810, found: 325.0808

![Chemical structure of S-(m-tolyl) diphenylphosphinothioate (4)](image)

**S-(m-tolyl) diphenylphosphinothioate (4)**. Yield = 66%; white solid; Mp: 96-98 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.89 – 7.80 (m, 4H), 7.52-7.48(m, 2H), 7.48 – 7.37 (m, 4H), 7.23 (dd, $J = 8.3$, 0.9 Hz, 2H), 7.12 – 7.00 (m, 2H), 2.21 (s, 3H). $^{31}$P NMR (162 MHz, CDCl$_3$) δ = 41.33. HRMS (ESI) calcd for C$_{19}$H$_{18}$OPS (M+H)$^+$: 325.0810, found: 325.0812

![Chemical structure of S-(o-tolyl) diphenylphosphinothioate (5)](image)

**S-(o-tolyl) diphenylphosphinothioate (5)**. Yield = 73%; white solid; Mp: 72-74 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.87 – 7.76 (m, 4H), 7.53 – 7.39 (m, 7H), 7.19 – 7.09 (m, 2H), 7.04 – 6.97 (m, 1H), 2.34 (s, 3H). $^{31}$P NMR (162 MHz, CDCl$_3$) δ = 41.01. HRMS (ESI) calcd for C$_{19}$H$_{18}$OPS (M+H)$^+$: 325.0810, found: 325.0815

![Chemical structure of S-(4-chlorophenyl) diphenylphosphinothioate (6)](image)

**S-(4-chlorophenyl) diphenylphosphinothioate (6)**. Yield = 80%; white solid; Mp: 108-110 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.88 – 7.79 (m, 4H), 7.57 – 7.50 (m, 2H), 7.49 – 7.42 (m, 4H), 7.38 (dd, $J = 8.5$, 1.6 Hz, 2H), 7.21 – 7.14 (m, 2H). $^{31}$P NMR (162 MHz, CDCl$_3$) δ = 41.55. HRMS (ESI) calcd for C$_{19}$H$_{15}$ClOPS (M+H)$^+$: 345.0264, found: 345.0262

![Chemical structure of S-(3-chlorophenyl) diphenylphosphinothioate (7)](image)

**S-(3-chlorophenyl) diphenylphosphinothioate (7)**. Yield = 78%; white solid; 185-187 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.90 – 7.80 (m, 4H), 7.58 – 7.51 (m, 2H), 7.48-7.44 (m, 4H), 7.39 (d, $J$
= 6.8 Hz, 2H), 7.26 – 7.19 (m, 1H), 7.14 (t, \(J = 8.2\) Hz, 1H). \({^31}P\) NMR (162 MHz, CDCl\(_3\)) \(\delta = 41.69\).

**HRMS** (ESI) calcd for C\(_{18}\)H\(_{15}\)ClOPS (M+H): 325.0264, found: 325.0269

![Structure](image)

**S-(4-fluorophenyl) diphenylphosphinothioate (8)**. Yield = 66%; white solid; Mp: 109-111 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.88 – 7.79\) (m, 4H), 7.56 – 7.49 (m, 2H), 7.49 – 7.37 (m, 6H), 6.90 (t, \(J = 8.6\) Hz, 2H). \({^31}P\) NMR (162 MHz, CDCl\(_3\)) \(\delta = 41.56\).

**HRMS** (ESI) calcd for C\(_{18}\)H\(_{15}\)FOPS (M+H): 329.0560, found: 329.0557

![Structure](image)

**S-(4-bromophenyl) diphenylphosphinothioate (9)**. Yield = 86%; white solid; Mp: 107-109 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.88 – 7.79\) (m, 4H), 7.57 – 7.50 (m, 2H), 7.50 – 7.42 (m, 4H), 7.36 – 7.28 (m, 4H). \({^31}P\) NMR (162 MHz, CDCl\(_3\)) \(\delta = 41.48\). **HRMS** (ESI) calcd for C\(_{18}\)H\(_{15}\)BrOPS (M+H): 388.9759, found: 388.9765

![Structure](image)

**S-(3-bromophenyl) diphenylphosphinothioate (10)**. Yield = 66%; white solid; Mp: 190-192 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.89 – 7.79\) (m, 4H), 7.52 -7.51 (m, 3H), 7.49-7.43 (m, 5H), 7.37 (d, \(J = 7.8\) Hz, 1H), 7.08 (t, \(J = 7.9\) Hz, 1H). \({^31}P\) NMR (162 MHz, CDCl\(_3\)) \(\delta = 41.75\). **HRMS** (ESI) calcd for C\(_{18}\)H\(_{15}\)BrOPS (M+H): 388.9759, found: 388.9759

![Structure](image)

**S-(4-methoxyphenyl) diphenylphosphinothioate (11)**. Yield = 70%; white solid; Mp: 137-139 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.90 – 7.79\) (m, 4H), 7.54 – 7.47 (m, 2H), 7.47 – 7.38 (m, 4H), 7.37 – 7.30 (m, 2H), 6.72 (d, \(J = 8.8\) Hz, 2H), 3.71 (s, 3H). \({^31}P\) NMR (162 MHz, CDCl\(_3\)) \(\delta = 41.38\). **HRMS** (ESI) calcd for C\(_{19}\)H\(_{18}\)O\(_2\)PS (M+H): 341.0760, found: 341.0762

![Structure](image)

**S-(3-methoxyphenyl) diphenylphosphinothioate (12)**. Yield = 75%; colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.92 – 7.79\) (m, 4H), 7.56 – 7.47 (m, 2H), 7.48 – 7.36 (m, 4H), 7.10 (t, \(J = 7.9\) Hz, 1H), 7.04 (dd, \(J = 7.7, 1.2\) Hz, 1H), 7.00 – 6.94 (m, 1H), 6.82 – 6.75 (m, 1H), 3.66 (s, 3H). \({^31}P\) NMR
(162 MHz, CDCl₃) δ = 41.41. HRMS (ESI) calcd for C₁₉H₁₈O₂PS (M+H)⁺: 341.0760, found: 341.0762

![Ph-P-S-Ph](image1)

S-(4-(tert-butyl)phenyl) diphenylphosphinothioate (13). Yield = 75%; white solid; Mp: 124-126 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.87-7.81 (m, 4H), 7.54 – 7.47 (m, 2H), 7.43-7.41 (m, 4H), 7.35 (dd, J = 8.5, 1.7 Hz, 2H), 7.24 – 7.18 (m, 2H), 1.23 (s, 9H). ³¹P NMR (162 MHz, CDCl₃) δ = 41.58. HRMS (ESI) calcd for C₂₂H₂₄OPS (M+H)⁺: 367.1280, found: 367.1281

![Ph-P-S-(2-naphthalenyl)](image2)

S-(2-naphthalen-2-yl) diphenylphosphinothioate (14). Yield = 47%; white solid; Mp: 106-108 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.99 (s, 1H), 7.92 – 7.84 (m, 4H), 7.76 – 7.67 (m, 2H), 7.66 (d, J = 8.6 Hz, 1H), 7.52 – 7.47 (m, 3H), 7.43 (m, J = 9.8, 4.9, 1.7 Hz, 6H). ³¹P NMR (162 MHz, CDCl₃) δ = 41.59. HRMS (ESI) calcd for C₂₂H₂₀OPS (M+H)⁺: 361.0810, found: 361.0813

![Ph-P-S-(1-phenylethyl)](image3)

S-(1-phenylethyl) diphenylphosphinothioate (15). Yield = 67%; colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.88 – 7.71 (m, 4H), 7.53 – 7.47 (m, 1H), 7.47 – 7.40 (m, 3H), 7.36-7.33 (m, 2H), 7.21 – 7.10 (m, 5H), 4.50-4.46 (m, 1H), 1.73 (d, J = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ = 143.08, 143.04, 134.55, 133.49, 133.28, 132.29, 132.26, 132.22, 132.08, 132.05, 131.94, 131.83, 131.22, 131.12, 128.68, 128.55, 128.51, 128.42, 127.39, 127.02, 77.43, 77.11, 76.80, 44.49, 44.47, 24.95, 24.91. ³¹P NMR (162 MHz, CDCl₃) δ = 41.82. HRMS (ESI) calcd for C₂₀H₂₂OPS (M+H)⁺: 339.0967, found: 339.0966

![Ph-P-S-Ph](image4)

S-benzyl diphenylphosphinothioate (16). Yield = 62%; white solid; Mp: 88–90 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.91 – 7.83 (m, 4H), 7.56 – 7.49 (m, 2H), 7.49 – 7.41 (m, 4H), 7.25 – 7.13 (m, 5H), 4.02 (d, J = 9.2 Hz, 2H). ³¹P NMR (162 MHz, CDCl₃) δ = 42.81. HRMS (ESI) calcd for C₁₉H₁₈OPS (M+H)⁺: 325.0810, found: 325.0815

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S-cyclohexyl diphenylphosphinothioate (17). Yield = 90%; white solid; Mp: 87-89 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.92 – 7.83 (m, 4H), 7.57 – 7.39 (m, 6H), 3.33-3.25 (m, 1H), 1.94 (dd, $J$ = 9.7, 4.1 Hz, 2H), 1.71 – 1.58 (m, 2H), 1.60 – 1.40 (m, 3H), 1.33 – 1.20 (m, 3H). $^{31}$P NMR (162 MHz, CDCl$_3$) δ = 42.02. HRMS (ESI) calced for C$_{18}$H$_{22}$OPS (M+H)$^+$: 317.1123, found: 317.1122

S-(sec-butyl) diphenylphosphinothioate (18). Yield = 80%; colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.93 – 7.84 (m, 4H), 7.55 – 7.42 (m, 6H), 3.29-3.22 (m, 1H), 1.76 – 1.54 (m, 2H), 1.34 (d, $J$ = 6.9 Hz, 3H), 0.92 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ = 134.66, 134.41, 133.59, 133.35, 132.14, 132.12, 131.58, 131.48, 131.37, 128.63, 128.50, 77.42, 77.10, 76.79, 43.24, 43.22, 31.67, 31.62, 23.23, 23.19, 11.06. $^{31}$P NMR (162 MHz, CDCl$_3$) δ = 41.90. HRMS (ESI) calced for C$_{16}$H$_{20}$OPS (M+H)$^+$: 291.0967, found: 291.0972

S-pentyl diphenylphosphinothioate (19). Yield = 84%; colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.93 – 7.84 (m, 4H), 7.57 – 7.51 (m, 2H), 7.51 – 7.44 (m, 4H), 2.82-2.76 (m, 2H), 1.68 – 1.55 (m, 2H), 1.31 – 1.22 (m, 4H), 0.83 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ = 134.02, 132.95, 132.25, 132.22, 131.54, 131.43, 128.71, 128.58, 30.73, 30.27, 30.22, 29.28, 29.26, 22.04, 13.87. $^{31}$P NMR (162 MHz, CDCl$_3$) δ = 43.11. HRMS (ESI) calced for C$_{17}$H$_{22}$OPS (M+H)$^+$: 305.1123, found: 305.1123

methyl 2-((diphenylphosphoryl)thio)acetate (20). Yield = 84%; colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.92 – 7.84 (m, 4H), 7.60 – 7.54 (m, 2H), 7.53 – 7.46 (m, 4H), 3.62 (d, $J$ = 10.9 Hz, 2H), 3.54 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ = 169.12, 169.07, 132.80, 132.72, 132.69, 131.73, 131.64, 131.54, 128.85, 128.72, 77.44, 77.13, 76.81, 52.68, 30.09. $^{31}$P NMR (162 MHz, CDCl$_3$) δ = 42.98. HRMS (ESI) calced for C$_{15}$H$_{16}$O$_3$PS (M+H)$^+$: 307.0552, found: 307.0547
S-(p-tolyl) di-p-tolylphosphinothioate (21). Yield = 53%; white solid; Mp: 88–90 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.72 (dd, $J = 12.7, 8.1$ Hz, 4H), 7.32 (dd, $J = 8.1, 1.6$ Hz, 2H), 7.25 – 7.17 (m, 4H), 7.00 (d, $J = 8.2$ Hz, 2H), 2.37 (s, 6H), 2.25 (s, 3H). $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta = 41.88$. HRMS (ESI) calcd for C$_{21}$H$_{22}$OPS (M+H)$^+$: 353.1123, found: 353.1121

S-(p-tolyl) bis(4-fluorophenyl)phosphinothioate (22). Yield = 84%; white solid; Mp: 97–99 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.90 – 7.77 (m, 4H), 7.30 (dd, $J = 8.1, 1.7$ Hz, 2H), 7.18 – 7.10 (m, 4H), 7.03 (d, $J = 8.2$ Hz, 2H), 2.27 (s, 3H). $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta = 39.23$. HRMS (ESI) calcd for C$_{19}$H$_{16}$F$_2$OPS (M+H)$^+$: 361.0622, found: 361.0623

S-(p-tolyl) bis(3,5-dimethylphenyl)phosphinothioate (23). Yield = 80%; white solid; Mp: 141-143 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.44 (d, $J = 13.2$ Hz, 4H), 7.33 (dd, $J = 8.1, 1.5$ Hz, 2H), 7.10 (s, 2H), 7.00 (d, $J = 8.0$ Hz, 2H), 2.31 (s, 12H), 2.24 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 139.00, 138.98, 138.25, 138.12, 135.41, 135.37, 133.01, 131.96, 129.92, 129.90, 129.23, 129.12, 122.79, 122.74, 77.48, 77.16, 76.84, 21.29, 21.14. $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta = 42.56$. HRMS (ESI) calcd for C$_{23}$H$_{26}$OPS (M+H)$^+$ : 381.1436, found:381.1635

4-methoxyphenyl diphenylphosphinate (24). Yield = 78%; white solid; Mp: 100-102 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94 – 7.81 (m, 4H), 7.57 – 7.48 (m, 2H), 7.50 – 7.39 (m, 4H), 7.14 – 7.05 (m, 2H), 6.78 – 6.69 (m, 2H), 3.72 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 156.37, 144.35, 144.26, 132.43, 132.40, 131.90, 131.80, 131.68, 130.31, 128.64, 128.51, 121.68, 121.63, 114.60, 77.38, 77.06, 76.74, 55.53. $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta = 30.55$. HRMS (ESI) calcd for C$_{19}$H$_{18}$O$_3$P (M+H)$^+$ : 325.0988, found:325.0995
phenyl diphenylphosphinate (25). Yield = 54%; white solid; Mp: 134-136 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.94 – 7.84 (m, 4H), 7.55-7.51 (m, 2H), 7.48-7.43 (m, 4H), 7.27 – 7.17 (m, 4H), 7.07 (t, J = 6.9 Hz, 1H). ³¹P NMR (162 MHz, CDCl₃) δ = 30.40. HRMS (ESI) calcd for C₁₈H₁₆O₂P (M+H)+: 295.0882, found: 295.0882

p-tolyl diphenylphosphinate (26). Yield = 64%; white solid; Mp: 113-115 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.94 – 7.82 (m, 4H), 7.51 (dd, J = 10.5, 4.3 Hz, 2H), 7.46-7.41 (m, 4H), 7.08 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 8.5 Hz, 2H), 2.23 (s, 3H). ³¹P NMR (162 MHz, CDCl₃) δ = 30.27. HRMS (ESI) calcd for C₁₉H₁₈O₂P (M+H)+: 309.1039, found: 309.1044

m-tolyl diphenylphosphinate (27). Yield = 69%; white solid; Mp: 108-110 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.93 – 7.84 (m, 4H), 7.55 – 7.48 (m, 2H), 7.49 – 7.41 (m, 4H), 7.08 (dd, J = 15.6, 7.8 Hz, 2H), 6.97 (d, J = 8.2 Hz, 1H), 6.87 (d, J = 7.5 Hz, 1H), 2.25 (s, 3H). ³¹P NMR (162 MHz, CDCl₃) δ = 30.17. HRMS (ESI) calcd for C₁₉H₁₈O₂P (M+H)+: 309.1039, found: 309.1035

4-(tert-butyl)phenyl diphenylphosphinate (28). Yield = 63%; white solid; Mp: 170-172 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.95 – 7.84 (m, 4H), 7.57 – 7.48 (m, 2H), 7.50 – 7.42 (m, 4H), 7.27 – 7.20 (m, 2H), 7.09 (dd, J = 8.8, 1.1 Hz, 2H), 1.24 (s, 9H). ³¹P NMR (162 MHz, CDCl₃) δ = 30.22. HRMS (ESI) calcd for C₂₂H₂₄O₂P (M+H)+: 351.1508, found: 351.1502

4-(methylthio)phenyl diphenylphosphinate (29). Yield = 65%; white solid; Mp: 106-108 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.92 – 7.84 (m, 4H), 7.57 – 7.50 (m, 2H), 7.51 – 7.41 (m, 4H), 7.13 (s, 4H), 2.40 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ = 148.73, 148.65, 134.17, 134.16, 132.56, 132.53, 131.86, 131.76, 131.48, 130.11, 128.71, 128.58, 128.39, 121.33, 121.29, 16.56. ³¹P NMR (162 MHz, CDCl₃) δ = 30.85. HRMS (ESI) calcd for C₁₉H₁₈O₂PS (M+H)+: 341.0760, found: 341.0764
4-fluorophenyl diphenylphosphinate (30). Yield = 77%; white solid; Mp: 131 - 133 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.93 - 7.83 (m, 4H), 7.59 - 7.51 (m, 2H), 7.51 - 7.42 (m, 4H), 7.21 - 7.15 (m, 1H), 7.02 (d, \(J = 8.9\) Hz, 1H), 7.00 - 6.94 (m, 1H), 6.81 - 6.76 (m, 1H). \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) = 31.27. HRMS (ESI) calcd for C\(_{18}\)H\(_{15}\)FO\(_2\)P (M+H): 313.0788, found: 313.0786

3-fluorophenyl diphenylphosphinate (31). Yield = 81%; white solid; Mp: 130 - 132 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.98 - 7.80 (m, 4H), 7.59 - 7.51 (m, 2H), 7.51 - 7.43 (m, 4H), 7.21 - 7.16 (m, 1H), 7.05 - 6.99 (m, 1H), 6.99 - 6.93 (m, 1H), 6.81 - 6.77 (m, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) = 164.17, 161.71, 157.82, 151.82, 151.74, 151.71, 151.63, 138.00, 132.70, 132.67, 131.81, 131.71, 131.23, 130.45, 130.35, 129.86, 128.78, 128.65, 116.57, 116.54, 116.52, 116.49, 111.83, 111.63, 108.94, 108.89, 108.69, 108.64, 77.40, 77.09, 76.77. \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) = 31.28. HRMS (ESI) calcd for C\(_{18}\)H\(_{15}\)FO\(_2\)P (M+H): 313.0788, found: 313.0783

4-chlorophenyl diphenylphosphinate (32). Yield = 76%; white solid; Mp: 117 - 119 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.92 - 7.81 (m, 4H), 7.58 - 7.50 (m, 2H), 7.48 - 7.44 (m, 4H), 7.23 - 7.11 (m, 4H). \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) = 31.31. HRMS (ESI) calcd for C\(_{18}\)H\(_{15}\)ClO\(_2\)P (M+H): 329.0493, found: 329.0486

4-bromophenyl diphenylphosphinate (33). Yield = 73%; white solid; Mp: 115 - 117 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.93 - 7.81 (m, 4H), 7.58 - 7.50 (m, 2H), 7.50 - 7.43 (m, 4H), 7.36 - 7.30 (m, 2H), 7.09 (dd, \(J = 9.0, 1.2\) Hz, 2H). \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) = 31.33. HRMS (ESI) calcd for C\(_{18}\)H\(_{15}\)BrO\(_2\)P (M+H): 372.9988, found: 372.9979

2-bromophenyl diphenylphosphinate (34). Yield = 71%; white solid; Mp: 102 - 104 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.05 - 7.94 (m, 4H), 7.62 - 7.60 (m, 1H), 7.55 - 7.48 (m, 3H), 7.48 - 7.41 (m, 4H), 7.15 (ddd, \(J = 8.3, 7.6, 1.6\) Hz, 1H), 6.92 (ddd, \(J = 8.2, 7.5, 1.0\) Hz, 1H). \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) = 31.73. HRMS (ESI) calcd for C\(_{18}\)H\(_{15}\)BrO\(_2\)P (M+H): 372.9988, found: 372.9994
4-iodophenyl diphenylphosphinate (35). Yield = 75%; white solid;Mp: 140-142 °C; 1H NMR (400 MHz, CDCl3) δ 7.91 – 7.82 (m, 4H), 7.58 – 7.50 (m, 4H), 7.50 – 7.42 (m, 4H), 7.01 – 6.94 (m, 2H). 31P NMR (162 MHz, CDCl3) δ = 31.25. HRMS (ESI) calcd for C18H15IO2P (M+H)+: 420.9849, found: 420.9846

4-(methylsulfonyl)phenyl diphenylphosphinate (36). Yield = 64%; white solid;Mp: 111-113 °C; 1H NMR (400 MHz, CDCl3) δ 7.95 – 7.80 (m, 6H), 7.62 – 7.55 (m, 2H), 7.54 – 7.46 (m, 4H), 3.00 (s, 3H). 13C NMR (101 MHz, CDCl3) δ = 155.22, 155.14, 136.53, 133.04, 133.01, 131.79, 131.64, 130.69, 129.57, 129.32, 128.96, 128.82, 121.58, 121.53, 77.43, 77.11, 76.79, 44.60. 31P NMR (162 MHz, CDCl3) δ = 32.55 HRMS (ESI) calcd for C19H18O4PS (M+H)+: 373.0658, found: 373.0663

methyl 4-((diphenylphosphoryl)oxy)benzoate (37). Yield = 77%; white solid;Mp: 126-128 °C; 1H NMR (400 MHz, CDCl3) δ 7.98 – 7.84 (m, 6H), 7.58 – 7.51 (m, 2H), 7.49-7.45 (m, 4H), 7.29 (dd, J = 8.8, 1.0 Hz, 2H), 3.85 (s, 3H). 13C NMR (101 MHz, CDCl3) δ = 166.30, 154.79, 154.71, 132.76, 132.73, 131.80, 131.69, 131.52, 131.11, 129.74, 128.81, 128.67, 126.49, 120.56, 120.51, 77.42, 77.10, 76.78, 52.11. 31P NMR (162 MHz, CDCl3) δ = 31.36. HRMS (ESI) calcd for C20H18O3P (M+H)+: 353.0937, found: 353.0939

4-(trifluoromethoxy)phenyl diphenylphosphinate (38). Yield = 70%; white solid;Mp: 58-60 °C; 1H NMR (400 MHz, CDCl3) δ 7.95 – 7.81 (m, 4H), 7.59 – 7.51 (m, 2H), 7.51 – 7.43 (m, 4H), 7.25 – 7.17 (m, 2H), 7.09 (d, J = 8.9 Hz, 2H). 31P NMR (162 MHz, CDCl3) δ = 31.59. HRMS (ESI) calcd for C19H15F3O3P (M+H)+:379.0705, found: 379.0711

4-formylphenyl diphenylphosphinate (39). Yield = 46%; white solid;Mp: 98-100 °C; 1H NMR (400 MHz, CDCl3) δ 9.89 (s, 1H), 7.94 – 7.86 (m, 4H), 7.79 (d, J = 8.6 Hz, 2H), 7.57-7.54 (m, 2H), 7.52 – 7.46 (m, 4H), 7.39 (d, J = 8.0 Hz, 2H). 31P NMR (162 MHz, CDCl3) δ = 31.77. HRMS (ESI) calcd for C19H16O3P (M+H)+: 323.0832, found:323.0829

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4-acetylphenyl diphenylphosphinate (40). Yield = 79%; white solid; Mp: 111-113 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.95 – 7.81 (m, 6H), 7.60 – 7.53 (m, 2H), 7.54 – 7.44 (m, 4H), 7.30 (dd, \(J = 8.7, 0.9\) Hz, 2H), 2.53 (s, 3H). \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) = 31.42. HRMS (ESI) calcd for C\(_{20}\)H\(_{18}\)O\(_3\)P (M+H)\(^+\) : 337.0988, found: 337.0985

3-nitrophenyl diphenylphosphinate (41). Yield = 61%; white solid; Mp: 122-124 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.01 (dd, \(J = 3.3, 2.2\) Hz, 1H), 7.99 – 7.94 (m, 1H), 7.94 – 7.87 (m, 4H), 7.64 – 7.62(m, 1H), 7.58-7.56 (m, 2H), 7.54 – 7.47 (m, 4H), 7.43 (t, \(J = 8.2\) Hz, 1H). \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) = 32.90. HRMS (ESI) calcd for C\(_{18}\)H\(_{15}\)NO\(_4\)P (M+H)\(^+\) : 340.0733, found: 340.0726

[1,1'-biphenyl]-4-yl diphenylphosphinate (42). Yield = 62%; white solid; Mp: 152-154 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.92 – 7.89 (m, 4H), 7.52 (dd, \(J = 7.3, 1.4\) Hz, 2H), 7.49 – 7.42 (m, 8H), 7.37 (t, \(J = 7.5\) Hz, 2H), 7.31 – 7.24 (m, 3H). \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) = 30.79. HRMS (ESI) calcd for C\(_{24}\)H\(_{20}\)O\(_2\)P (M+H)\(^+\) : 371.1195, found: 371.1200

4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl diphenylphosphinate (43). Yield = 41%; white solid; Mp: 117-119 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.93 – 7.83 (m, 4H), 7.69 (d, \(J = 8.4\) Hz, 2H), 7.55 – 7.49 (m, 2H), 7.48 – 7.41 (m, 4H), 7.23 (dd, \(J = 8.6, 1.1\) Hz, 2H), 1.30 (s, 12H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) = 153.60, 153.52, 136.50, 132.54, 132.51, 131.87, 131.77, 131.43, 130.05, 128.70, 128.57, 120.02, 119.97, 83.84, 24.86. \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) = 30.42. HRMS (ESI) calcd for C\(_{23}\)H\(_{37}\)BO\(_4\)P (M+H)\(^+\) : 421.1735, found: 421.1728

naphthalen-2-yl diphenylphosphinate (44). Yield = 72%; white solid; Mp: 120-122 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.97 – 7.89 (m, 4H), 7.72 (dd, \(J = 14.3, 6.3\) Hz, 4H), 7.55 – 7.48 (m, 2H), 7.48 – 7.41 (m, 5H), 7.40 – 7.34 (m, 2H). \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) = 30.75. HRMS (ESI) calcd for C\(_{22}\)H\(_{18}\)O\(_2\)P (M+H)\(^+\) : 345.1039, found: 345.1036
naphthalen-1-yl diphenylphosphinate(45). Yield = 47%; white solid; Mp: 110–112 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.26 – 8.18 (m, 1H), 8.02 – 7.89 (m, 4H), 7.79 (dd, \(J = 7.4, 1.8\) Hz, 1H), 7.58 – 7.42 (m, 10H), 7.25 (dd, \(J = 9.0, 7.0\) Hz, 1H). \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) = 30.86. HRMS (ESI) calcd for C\(_{22}\)H\(_{18}\)O\(_2\)P (M+H)\(^+\) : 345.1039, found: 345.1046

6-cyanonaphthalen-2-yl diphenylphosphinate(46). Yield = 68%; yellow oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.12 (s, 1H), 7.99 – 7.88 (m, 4H), 7.78 (dd, \(J = 10.5, 6.2\) Hz, 3H), 7.59 – 7.52 (m, 3H), 7.50 - 7.46 (m, 5H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) = 151.16, 151.07, 135.50, 133.80, 132.84, 132.81, 131.82, 131.72, 131.13, 130.49, 129.76, 129.41, 128.87, 128.74, 127.10, 122.68, 122.63, 119.10, 117.38, 117.33, 108.72, 77.42, 77.10, 76.78. HRMS (ESI) calcd for C\(_{23}\)H\(_{17}\)NO\(_2\)P (M+H)\(^+\) : 370.0991, found: 370.0991

6-bromonaphthalen-2-yl diphenylphosphinate(47). Yield = 63%; white solid; Mp: 119–121 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.98 – 7.85 (m, 5H), 7.66 (s, 1H), 7.61 (d, \(J = 8.9\) Hz, 1H), 7.57 – 7.50 (m, 3H), 7.50 – 7.42 (m, 5H), 7.36 (dd, \(J = 8.9, 1.8\) Hz, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) = 148.91, 148.83, 132.69, 132.66, 132.35, 131.87, 131.17, 131.68, 131.34, 129.96, 129.66, 129.15, 128.90, 128.80, 128.66, 121.84, 121.79, 119.13, 117.31, 117.26, 77.41, 77.10, 76.78. \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) = 31.28. HRMS (ESI) calcd for C\(_{22}\)H\(_{17}\)BrO\(_2\)P (M+H)\(^+\) : 423.0144, found: 423.0135

4-chloro-3-fluorophenyl diphenylphosphinate(48). Yield = 81%; white solid; Mp: 99–101 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.93 – 7.79 (m, 4H), 7.60 – 7.52 (m, 2H), 7.53 – 7.43 (m, 4H), 7.25 (dd, \(J = 13.6, 5.0\) Hz, 1H), 7.08-7.07 (m, 1H), 7.00-6.97 (m, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) = 159.20, 156.71, 150.09, 149.99, 149.91, 132.95, 132.92, 131.78, 131.68, 130.83, 130.71, 129.33, 128.89, 128.76, 117.48, 117.43, 117.39, 117.18, 117.01, 112.42, 110.19, 110.14, 109.95, 109.90, 104.60, 104.37, 77.43, 77.11, 76.79. \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) = 32.31. HRMS (ESI) calcd for C\(_{18}\)H\(_{13}\)ClFO\(_2\)P (M+H)\(^+\) : 347.0398, found: 347.0440
3,5-difluorophenyl diphenylphosphinate(49). Yield = 72%; white solid; Mp: 135-137 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.94 – 7.81 (m, 4H), 7.59-7.54 (m, 2H), 7.53 – 7.45 (m, 4H), 6.82-6.80 (m, 2H), 6.58-6.52 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ = 164.36, 164.21, 161.89, 161.74, 152.27, 152.19, 132.92, 132.89, 131.77, 131.66, 130.79, 129.42, 128.88, 128.75, 105.07, 105.02, 104.93, 104.86, 104.78, 104.73, 100.82, 100.57, 100.32, 77.39, 77.08, 76.76. $^{31}$P NMR (162 MHz, CDCl$_3$) δ = 32.24. HRMS (ESI) calcd for C$_{18}$H$_{14}$F$_2$O$_2$P (M+H)$^+$: 331.0694, found: 331.0692

4-fluoro-3-methylphenyl diphenylphosphinate(50). Yield = 57%; white solid; Mp: 102-105 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.88-7.84 (m, 4H), 7.58 – 7.50 (m, 2H), 7.50 – 7.42 (m, 4H), 7.05 (dd, J = 6.2, 2.7 Hz, 1H), 6.96 – 6.89 (m, 1H), 6.83 (t, J = 8.9 Hz, 1H), 2.17 (d, J = 1.9 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ = 159.28, 156.89, 146.26, 146.18, 132.57, 132.54, 131.85, 131.75, 131.46, 130.08, 128.71, 128.57, 126.31, 126.11, 123.52, 123.47, 119.20, 119.16, 119.12, 119.08, 115.72, 115.48, 14.65, 14.62. $^{31}$P NMR (162 MHz, CDCl$_3$) δ = 30.91. HRMS (ESI) calcd for C$_{19}$H$_{17}$FO$_2$P (M+H)$^+$: 327.0945, found: 327.0942

3,4-dimethylphenyl diphenylphosphinate(51). Yield = 41%; white solid; Mp: 112-114 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.89-7.85 (m, 4H), 7.56 – 7.49 (m, 2H), 7.49 – 7.41 (m, 4H), 7.01 (s, 1H), 6.95 (d, J = 8.3 Hz, 1H), 6.89 (d, J = 8.3 Hz, 1H), 2.15 (d, J = 7.4 Hz, 6H). $^{31}$P NMR (162 MHz, CDCl$_3$) δ = 29.95. HRMS (ESI) calcd for C$_{20}$H$_{20}$O$_2$P (M+H)$^+$: 323.1195, found: 323.1200

methyl diphenylphosphinate(52). Yield = 91%; colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.86 – 7.77 (m, 4H), 7.57 – 7.50 (m, 2H), 7.50 – 7.42 (m, 4H), 3.77 (d, J = 11.1 Hz, 3H). $^{31}$P NMR (162 MHz, CDCl$_3$) δ = 33.26. HRMS (ESI) calcd for C$_{13}$H$_{14}$O$_2$P (M+H)$^+$: 233.0726, found: 233.0723
ethyl diphenylphosphinate. Yield = 79%; colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.82-7.79 (m, 4H), 7.55 – 7.48 (m, 2H), 7.45 -7.42(m, 4H), 4.11-4.07 (m, 2H), 1.37 (t, \(J = 7.1\) Hz, 3H). \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) = 31.39. HRMS (ESI) calcd for C\(_{14}\)H\(_{16}\)O\(_2\)P (M+H): 247.0882, found: 247.0889

isopropyl diphenylphosphinate. Yield = 40%; white solid; Mp: 101-103 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.86 – 7.77 (m, 4H), 7.50 (m, \(J = 6.4, 2.9, 1.4\) Hz, 2H), 7.44-7.41 (m, 4H), 4.71-4.63 (m, 1H), 1.35 (d, \(J = 6.2\) Hz, 6H). \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) = 29.81. HRMS (ESI) calcd for C\(_{15}\)H\(_{18}\)O\(_2\)P (M+H): 261.1039, found: 261.1039

4-methoxyphenyl bis(3,5-dimethylphenyl)phosphinate. Yield = 54%; white solid; Mp: 100-103 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.49 (d, \(J = 12.7\) Hz, 4H), 7.19 – 7.03 (m, 4H), 6.74 (d, \(J = 8.9\) Hz, 2H), 3.71 (s, 3H), 2.33 (s, 12H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) = 156.26, 144.51, 144.43, 138.30, 138.16, 134.08, 131.62, 130.19, 129.42, 129.32, 121.75, 121.70, 114.55, 77.40, 77.08, 76.76, 55.53, 21.29 \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) = 31.86. HRMS (ESI) calcd for C\(_{23}\)H\(_{26}\)O\(_3\)P (M+H): 381.1614, found: 381.1611

4-methoxyphenyl bis(4-fluorophenyl)phosphinate. Yield = 69%; colorless oil ; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.90-7.83 (m, 4H), 7.17-7.12 (m, 4H), 7.10 – 7.05 (m, 2H), 6.75 (d, \(J = 9.0\) Hz, 2H), 3.72 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) = 166.66, 166.62, 164.13, 164.09, 156.56, 144.01, 143.93, 134.51, 134.42, 134.39, 134.30, 127.51, 127.48, 126.09, 126.06, 121.59, 121.55, 116.28, 116.13, 116.06, 115.92, 114.69, 77.41, 77.09, 76.78, 55.52. \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) = 28.62. HRMS (ESI) calcd for C\(_{19}\)H\(_{16}\)F\(_2\)O\(_3\)P (M+H): 361.0800, found: 361.0795
3-fluorophenyl di-p-tolylphosphinate. Yield = 30%; colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.75 (dd, \(J = 12.4, 8.1\) Hz, 4H), 7.31 – 7.24 (m, 4H), 7.18 - 7.15 (m, 1H), 7.01 (dd, \(J = 8.3, 0.8\) Hz, 1H), 6.96 - 6.92 (m, 1H), 6.78 - 6.75 (m, 1H), 2.38 (s, 6H). \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) = 164.16, 161.70, 143.24, 143.21, 131.80, 131.69, 130.37, 130.28, 129.49, 129.35, 128.19, 126.79, 77.37, 77.05, 76.74, 21.69 \(^3\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) = 32.40 HRMS (ESI) calcd for C\(_{20}\)H\(_{19}\)FO\(_2\)P (M+H)\(^+\): 341.1101, found: 341.1096

2,2,6,6-tetramethyl-1-((p-tolylthio)oxy)piperidine. Yield = 24%; colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.58 – 7.52 (m, 2H), 7.25 (d, \(J = 7.9\) Hz, 2H), 2.39 (s, 3H), 1.75 – 1.34 (m, 15H), 0.92 (s, 3H). \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) = 147.09, 139.46, 129.27, 125.94, 77.38, 77.07, 76.75, 61.19, 58.75, 43.52, 41.41, 35.35, 32.60, 28.74, 27.96, 26.99, 21.23, 17.30. HRMS (ESI) calcd for C\(_{16}\)H\(_{26}\)NOS (M+H)\(^+\): 280.1730, found: 280.1730

2,2,6,6-tetramethylpiperidin-1-yl diphenylphosphinate. Yield = 26%; colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.91 – 7.80 (m, 4H), 7.53 – 7.37 (m, 6H), 1.31 – 0.88 (m, 18H). \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) = 134.51, 133.16, 131.68, 131.58, 131.55, 128.35, 128.23, 61.62, 61.60, 40.11, 16.89. \(^3\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) = 33.66. HRMS (ESI) calcd for C\(_{21}\)H\(_{29}\)NO\(_2\)P (M+H)\(^+\): 358.1930, found: 358.1927

1-phenyl-2-(p-tolylthio)ethan-1-ol. Yield = 78%; colorless oil; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.36 – 7.23 (m, 7H), 7.13 (d, \(J = 7.9\) Hz, 2H), 4.66 (dd, \(J = 9.6, 3.3\) Hz, 1H), 3.26 (dd, \(J = 13.8, 3.4\) Hz, 1H), 3.02 (dd, \(J = 13.8, 9.7\) Hz, 1H), 2.96 (s, 1H), 2.33 (s, 3H). \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) = 142.18, 137.18, 131.10, 130.90, 130.00, 128.57, 127.96, 125.90, 71.47, 44.85, 21.12. HRMS (ESI) calcd for C\(_{15}\)H\(_{17}\)OS (M+H)\(^+\): 245.0995, found: 245.0998
10. References

11. NMR spectra of product
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