Supporting Information

B(C₆F₅)₃-catalyzed O–H insertion reactions of diazoalkanes with phosphinic acids

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1. General Information

All the reactions were monitored by thin layer chromatography (TLC), carried out on 0.25 mm silica gel plates using UV light as visualizing agent. Column chromatography was carried out on silica gel (particle size 300-400 mesh). Unless stated otherwise, all the yields refer to isolated products after flash column chromatography. The solvent mixtures employed in flash column chromatography purifications are reported as volume by volume and in percentages. LEDs used in this manuscript were purchased from Taobao. Jia lamp, SF, 25W, 460-470nm. NMR spectra were recorded with BrukerAvance III HD500 spectrometer at 500 MHz. All $^1$H, $^{19}$F, $^{31}$P and $^{13}$C NMR spectra were recorded using CDCl$_3$ or DMSO-d$_6$ as solvent. Tetramethylsilane (TMS) signals or residual solvent signals were used [TMS $\delta = 0.00$ (1H NMR), CDCl$_3$ $\delta = 7.26$ ppm (1H NMR ), 77.16 ppm (13C NMR ), DMSO-d6 $\delta = 2.50$ ppm (1H NMR), 39.52 ppm (13C NMR)] as internal standards. Coupling constants ($J$) are reported in Hz. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, dd = double doublet, t = triplet, q = quartet, m = multiplet, td = triplet doublet, qd = quartet doublet. HRMS (ESI) Mass spectra were recorded on Thermo Fisher Scientific LTQ FT Ultra. The relative configuration of 3a was determined by NMR Data and molecular weight compared with literature data.$^1$

2. Experiment Section

2.1 General procedure for synthesis of aryl diazoacetates$^{2-3}$

![Chemical Reaction Diagram]

To a 100 mL round bottom flask was charged with 6 mL methanol. At 0 ℃ thionyl chloride of 1.6 mL was added dropwise and the solution in an ice bath was stirred for 30 min. Then the corresponding aryl acetic acid (1.54 g, 10 mmol) solution in 15.4 mL methanol was added dropwise and the solution in an ice bath was stirred for 30 min. The reaction mixture was stirred under 60 ℃ and monitored by TLC. After completion of the reaction, the product was extracted with ethyl acetate, washed with aqueous NaHCO$_3$, water and brine, dried over anhydrous Na$_2$SO$_4$, crude methyl arylacetate which were used to next step without further purification.

Methyl arylacetate (10 mmol), $p$-cetamidobenzenesulfonyl azide ($p$-ABSA) (3.6 g, 15 mmol) and acetonitrile (15 mL) were added to a dried flask. The mixture was
cooled with an ice-bath and a solution of 1,8-diaza[5.4.0]undec-7-ene (DBU) (2.3 mL, 2.4 g, 15 mmol) in acetonitrile (5 mL) was added dropwise. Then the ice-bath was removed and the mixture was stirred at room temperature overnight. The reaction was then quenched with saturated aqueous NH₄Cl and the mixture was extracted with diethyl ether (3 × 25 mL). The organic phases were combined, dried over anhydrous Na₂SO₄, and evaporated under reduced pressure. The filtrate was evaporated and purified by silica gel chromatography (petroleum ether/ethyl acetate =100:1~50:1) to provide product α-diazoester (red-brown oil).

2.2 Synthesis of (1-diazo-2,2,2-trifluoroethyl)benzene

![Chemical reaction diagram]

To a round bottom flask equipped with a reflux condenser was added tosylhydrazide (1.0 equiv.) and the minimum quantity of solvent (either methanol or toluene according to individual substrates) needed to dissolve the hydrazide at reflux (approximately 1.5 M). Subsequently the reaction was cooled to room temperature and trifluoroacetophenone (1.0 equiv.) was added in one portion. The reaction mixture was then stirred at 65 °C (Toluene) over 4-16 h (monitored by TLC). The solution was cooled to room temperature or 0 °C, at which point the product precipitated out of solution (precipitation can be induced by addition of pentane). The precipitate was collected by vacuum filtration and washed with pentane, in which case it was used without further purification. If no precipitation occurred, the solvent was removed under reduced pressure and the residue used in the next step without further purification.

In a round bottom flask was added tosyl hydrazone (1.0 equiv.) and a solution of KOH (2.0 equiv.) in MeOH (0.4 M). A condenser was attached and the reaction mixture refluxed for 1 h or until the colour of the solution no longer intensified. The reaction was cooled to room temperature and diluted with water. The crude product was extracted with DCM, washed with a saturated solution of NaHCO₃, brine, dried with MgSO₄, concentrated under reduced pressure, and purified by silica gel chromatography.
2.3 Synthesis of 2-substituted tert-butyldiazoacetates

A 100 mL round bottom flask fitted with a rubber septum was charged with NaH (60%, dispersion in mineral oil, 1.56 g, 39 mmol) in 30 mL of freshly distilled THF. At 0 °C tert-butyl acetoacetate (30 mmol) was added dropwise and the solution was stirred for 10 min. The reaction mixture was moved to ambient temperature then benzyl bromide (33 mmol) was added to the mixture in one portion. The resulting solution was refluxed and monitored by TLC. After completion of the reaction, the reaction mixture was quenched with sat. aq. NH₄Cl solution (20 mL) and H₂O (2 mL). The product was extracted with DCM (3 × 15 mL) and dried with Na₂SO₄. The volatiles were evaporated and the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 9:1) to give 2-substituted tert-butyl acetoacetates clear colorless liquid.

To a stirred solution of 2-substituted tert-butyl acetoacetate (10 mmol) in acetonitrile (30 mL) were added a 4-acetamidobenzenesulfonyl azide (2.88 g, 12 mmol) and DBU (2.24 mL, 15 mmol) at 0 °C. The reaction mixture was stirred under ambient temperature and monitored by TLC. After completion of the reaction, the reaction mixture was quenched with sat. aq. NH₄Cl solution (10 mL). The product was extracted with ethyl acetate (3 × 30 mL) and dried with Na₂SO₄. The volatiles were evaporated and the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to give corresponding 2-substituted tert-butyldiazoacetateas clear yellow liquid.

2.4 Synthesis of 2-diazo-1-phenylethanone

To a solution of 1,3-diphenylylpropane-1,3-dione (1 mmol, 224 mg) and TsN₃ (1 mmol, 197 mg) in EtOH (1 mL) was added MeNH₂ (40% aqueous solution, 1.2 mmol, 93 mg). After the mixture was stirred at room temperature for 25 min (monitored by TLC), the solvent was removed. The residue was purified by silica gel column.
chromatography (petroleum ether/ethyl acetate = 20:1) to give product as a yellow solid.

2.5 Preparation for synthesis of phosphinic acids\textsuperscript{7,8}

\[
\begin{align*}
& \text{MgBr} \quad (\text{EtO})_2P(O)H \\
& \text{THF} \quad \text{MeOH/H}_2\text{O, r.t.} \quad \text{MeOH/H}_2\text{O, r.t.} \\
& \quad \text{Oxone}\textsuperscript{®} (3 \text{ equiv.})
\end{align*}
\]

To a solution of arylmagnesium bromide (0.1 mol) in THF (100 mL), diethyl phosphate (4.1 g, 0.03 mol) in THF (20 mL) was added dropwise with vigorous stirring under the cooling of ice-water bath. Then the resulting mixture stirred at r.t. for 2 h. After the reaction, the resulting reaction mixture was cooled to 0 °C, and sat. aq. NH\textsubscript{4}Cl solution was added slowly upon stirring. The solution was then evaporated under reduced pressure. The residue was extracted with ethyl acetate (150 mL). The organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) to give the product H-phosphine oxide as a white solid.

The H-phosphine oxide (3.0 mmol, 1 equiv.) was dissolved in MeOH (12 mL) and charged into a 100 mL flask under air atmosphere. Oxone\textsuperscript{®} (5.5 g, 7.5 mmol, 3 equiv.) was dissolved in H\textsubscript{2}O (12 mL) and poured into the MeOH solution containing the secondary phosphine oxide, resulting in a slurry. The mixture was stirred at r.t. for 24 h and diluted with H\textsubscript{2}O (50 mL). The aqueous phase was extracted with CHCl\textsubscript{3} (3 x 75 mL) and the combined organic fractions washed with brine (100 mL). The organic fractions were then extracted with 1 M aq. NaOH solution (3 x 100 mL). The combined aqueous fractions were acidified with conc. HCl and extracted with CHCl\textsubscript{3} (3 x 150 mL). The combined organic fractions were dried over MgSO\textsubscript{4} and concentrated in vacuo to afford the target compound phosphinic acids as a white solid.

2.6 Preparation for synthesis of butyl(phenyl)phosphinic acid\textsuperscript{8,9}

\[
\begin{align*}
& \text{Cl} \quad \text{Cl} \quad \text{Pyridine (1.5 equiv.)} \\
& \text{Toluene, r.t} \quad \text{MeOH/H}_2\text{O, r.t.} \quad \text{MeOH/H}_2\text{O, r.t.}
\end{align*}
\]

The phenylphosphinate was made from dichlorophenylphosphine and the appropriate alcohol. For example, in the synthesis of ethyl phenylphosphinate, a solution of ethanol (22.1 mL, 540 mmol) and pyridine (26.2 mL, 325 mmol) in toluene (36 mL) was added dropwise over 30 min to a solution of dichlorophenylphosphine (34 mL, 250 mmol) in toluene (175 mL). The mixture was
stirred for 1.5 h and allowed to sit without stirring for 1 day. The solution and resulting white solid were washed with saturated sodium bicarbonate (80 mL), and the aqueous layer was back-extracted with DCM (70 mL). The combined organic fractions dried over magnesium sulfate, filtered, and then concentrated down to give ethyl phenylphosphinate.

**Synthesis of butyl(phenyl)phosphine oxide**

![Chemical structure](image)

The crude ethyl phenylphosphinate dissolved in freshly distilled THF (12 mL) under a nitrogen atmosphere. A flame-dried flask was charged with commercially available *n*-BuLi Solution (9.2 mL, 22 mmol, 2.4 M in hexanes) under nitrogen atmosphere and cooled to -78 °C. The ethyl phenylphosphinate solution was added dropwise over 30 min and the resulting mixture stirred at room temperature for 2 h. The reaction was then quenched with sat. aq. NH₄Cl solution and subsequently diluted with H₂O (100 mL). The aqueous phase was extracted with CHCl₃ (3 x 150 mL) and the combined organic fractions dried over MgSO₄, concentrated and dried in vacuo. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 1:1) to give the product *n*-butyl(phenyl)phosphine oxide.

**Synthesis of butyl(phenyl)phosphinic acid**

![Chemical structure](image)

The butyl(phenyl)phosphine oxide (455.5 mg, 2.5 mmol, 1 equiv.) was dissolved in MeOH (10 mL) and charged into a 100 mL flask under air atmosphere. Oxone® (4.6 g, 7.5 mmol, 3 eq.) was dissolved in H₂O (10 mL) and poured into the MeOH solution containing the secondary phosphine oxide, resulting in a slurry. The mixture was stirred at r.t. for 24 h and diluted with H₂O (50 mL). The aqueous phase was extracted with CHCl₃ (3 x 75 mL) and the combined organic fractions washed with brine (100 mL). The organic fractions were then extracted with 1 M aq. NaOH solution (3 x 100 mL). The combined aqueous fractions were acidified with conc. HCl and extracted with CHCl₃ (3 x 150 mL). The combined organic fractions were dried over MgSO₄ and concentrated in vacuo to afford the title compound butyl(phenyl)phosphinic acid (382 mg, 1.9 mmol, 77%) as a colorless oil.
2.7 Preparation for synthesis of ethyl hydrogen phenylphosphonate\textsuperscript{10}

\[
\begin{array}{c}
\text{O} \quad \text{Et} \\
\text{P} \quad \text{Et}
\end{array}
\xrightarrow{\text{aq. NaOH, H}_2\text{O}}
\begin{array}{c}
\text{O} \quad \text{Et} \\
\text{P} \quad \text{OH}
\end{array}
\]

The corresponding diethyl phosphonate (3.0 mmol), NaOH (6.0 mmol) and H\textsubscript{2}O (15.0 mL) were stirred at 80 °C for 6-12 hours. The reaction solution was evaporated in vacuo to remove the ethanol and diluted with H\textsubscript{2}O (10 mL). The solution was neutralized with cooled concentrated hydrochloric acid and extracted with ethyl acetate. The extracts were evaporated under reduced pressure to give the title compound ethyl hydrogen phenylphosphonate (281 mg, 1.5 mmol, 50%) as a colorless oil.

3. Screening the Optimum Reaction Conditions for the Synthesis of 3aa

\[
\begin{array}{c}
\text{O} \\
\text{P} \quad \text{Ph}
\end{array}
\xrightarrow{\text{catalyst, solvent, temp}}
\begin{array}{c}
\text{O} \\
\text{P} \quad \text{Ph}
\end{array}
\]

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<th>Catalyst</th>
<th>Solvent</th>
<th>Temp. (°C)</th>
<th>Time (hour)</th>
<th>Yield(%)\textsuperscript{b}</th>
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<td>1\textsuperscript{c}</td>
<td>Rh\textsubscript{2}(OCT)\textsubscript{4}</td>
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<td>2\textsuperscript{c}</td>
<td>Cu(OAc)\textsubscript{2}</td>
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<td>RT</td>
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<tr>
<td>4\textsuperscript{c}</td>
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<td>76</td>
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<tr>
<td>5\textsuperscript{c}</td>
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<td>RT</td>
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<td>74</td>
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<tr>
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<td>Blue LEDs</td>
<td>DCM</td>
<td>RT</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>7\textsuperscript{c}</td>
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<td>36</td>
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Table S2. Screening the optimum conditions for the synthesis of 3aa
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<tr>
<td>24</td>
<td>-</td>
<td>DMC</td>
<td>50</td>
<td>168</td>
</tr>
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</table>

*a* Reaction conduction: 1a (0.15 mmol, 1.5 equiv.), 2a (0.1 mmol, 1.0 equiv.), catalyst (10 mol%), solvent (1 mL), 50 °C. *b* Isolated yield. *c* catalyst (5 mol%) *d* catalyst (20 mol%). DCM = Dichloromethane. EA = Ethyl Acetate. DMSO = Dimethyl Sulfoxide. DEC = Diethyl Carbonate. DMC = Dimethyl Carbonate. N.R. = No Reaction. symbol “-” means no catalyst. Blue LEDs: 460-470 nm light (25 W).

### 4. Typical Procedure for O-H Insertion of Phosphoric Acid

![Reaction diagram](image)

A typical procedure for the synthesis of 3aa: To the test tube was charged with diphenylphosphinic acid 2a (0.1 mmol, 21.8 mg), catalyst B(C₆F₅)₃ (5.12 mg, 10 mol%), and dimethyl carbonate (0.5 mL). Then the diazoalkane 1a (0.15 mmol, 26.4 mg) solution in dimethyl carbonate (0.5 mL) was added dropwise. The reaction mixture was reacted at 50 °C for 1.5 h until the diazoalkane 1a was completely consumed. After the reaction, the solution was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give the product 3aa (36 mg, 98%) as a colorless oil.
5. A Gram-scale Experiment

Gram-scale experiment for the synthesis of 3aa: To a 100 mL round bottom flask was charged with diphenylphosphinic acid 2a (5 mmol, 1.09 g), catalyst B(C₆F₅)₃ (256 mg, 10 mol%), and dimethyl carbonate of (25 mL). Then the 2-diazo-2-phenylacetate 1a (15 mmol, 1.32 g) solution in dimethyl carbonate of 25 mL was added dropwise. The reaction mixture was reacted at 50 °C for 1 h until the diazoalkane 1a was completely consumed. After the reaction, the solution was concentrated in vacuo and purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give the product 3aa (1.81 g, 99%) as a colorless oil.

6. Deuterium Labelling Experiments

A dried test tube was loaded with B(C₆F₅)₃ (5.12 mg, 10 mol%) and diphenylphosphinic acid 2a (0.1 mmol, 21.8 mg) and dry dimethyl carbonate (0.5 mL) and D₂O (n equiv.). The test tube was flushed and refilled with N₂ for three times. Than methyl 2-diazo-2-phenylacetate 1a (0.15 mmol, 26.4 mg) dissolved in 0.5 mL dry dimethyl carbonate was added dropwise at once. The reaction mixture was stirred at 50 °C for 1.5 h until the orange color of the diazoalkane disappeared. Purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give the product d-3aa (36 mg, 98%). Deuterium is not incorporated in the reaction product. H:D = 96:4
7. Evaluation of Green metrics of the process.

Atom economy defined as “how much of the reactants remain in the final desired product”

\[
\text{Atom economy (AE)} = \frac{\text{Molecular mass of desired product}}{\text{Molecular mass of all reactants}} \times 100
\]

Reaction mass efficiency (RME) defined as “the percentage of the mass of the reactants that remain in the product”

\[
\text{Reaction mass efficiency (RME)} = \frac{\text{mass of desired product}}{\text{mass of all reactants}} \times 100
\]

Evaluation of Green metrics for the current process

Reaction Scheme

```
1a, 1.32 g + \overset{\text{Ph-PO\textsubscript{2}OH}}{\text{Ph-PO\textsubscript{2}OH}} \xrightarrow{\text{B(C\textsubscript{8}F\textsubscript{5})\textsubscript{3}}} 3\text{aa}, 1.81 g
```

Chemical Formula: \(\text{C}_9\text{H}_3\text{N}_2\text{O}_2\)
Molecular Weight: 176.18

Chemical Formula: \(\text{C}_{12}\text{H}_{11}\text{O}_2\text{P}\)
Molecular Weight: 218.19

Chemical Formula: \(\text{C}_2\text{H}_9\text{O}_2\text{P}\)
Molecular Weight: 366.35

Total = 176.18 + 218.19 = 394.37

Product Yield: 99%
| Reactant 1 | Methyl 2-diazo-2-phenylacetate | 1.32 g | 0.007492 mol | FW 176.18 |
| Reactant 2 | Diphenylphosphinic acid | 1.09 g | 0.004996 mol | FW 218.19 |
| Catalyst | Tris(pentafluorophenyl)borane | 0.256 g | 0.0005 mol | FW 511.98 |
| Solvent | Dimethyl carbonate | 51.25 g (50 mL) | | |
| Auxiliary | | | | |
| Product | Methyl 2-(((diphenylphosphoryl)oxy)-2-phenylacetate | 1.81 g | 0.004941 mol | FW 366.35 |

E-factor = \[
\frac{1.32 \text{ g} + 1.09 \text{ g} + 0.256 \text{ g} + 51.25 \text{ g} - 1.81 \text{ g}}{1.81 \text{ g}} = 28.79 \text{ kg waste/kg product}
\]

Atom economy = \[
\frac{366.35}{394.37} \times 100 = 92.89\%
\]

Atom efficiency = \[
\frac{99 \times 92.89}{100} = 91.96\%
\]

Carbon efficiency = \[
\frac{9 + 12}{21} = 100\%
\]

Reaction mass efficiency = \[
\frac{1.81 \text{ g}}{1.32 \text{ g} + 1.09 \text{ g}} \times 100 = 75.10\%
\]

E-factor of the synthesis method is 28.79 kg waste per kg product, with 92.89% atom economy, 91.96% atom efficiency, 75.10% reaction mass efficiency and 100% carbon efficiency.
8. References

9. Characterization data for compounds

Methyl 2-((diphenylphosphoryl)oxy)-2-phenylacetate (3aa). Colorless oil, 35.9 mg, 98% yield. \(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta 7.91 - 7.87\) (m, 2H), 7.74 - 7.70 (m, 2H), 7.54 - 7.51 (m, 1H), 7.47 - 7.41 (m, 5H), 7.36 - 7.32 (m, 2H), 7.31 - 7.29 (m, 3H), 5.84 (d, \(J = 10.0\) Hz, 1H), 3.64 (s, 3H). \(^13\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta 169.47\) (d, \(J = 4.2\) Hz), 135.22 (d, \(J = 4.9\) Hz), 132.39 (d, \(J = 2.8\) Hz), 131.75 (d, \(J = 3.2\) Hz), 131.67 (d, \(J = 3.2\) Hz), 131.50 (d, \(J = 32.9\) Hz), 129.07, 128.64, 128.46 (d, \(J = 9.7\) Hz), 128.35 (d, \(J = 9.5\) Hz), 127.22, 74.12 (d, \(J = 5.0\) Hz), 52.52. \(^31\)P NMR (202 MHz, Chloroform-\(d\)) \(\delta 34.21\). HRMS (ESI) m/z calcd for C\(_{21}\)H\(_{20}\)O\(_4\)P [M+H]\(^+\): 367.1094, found: 367.1093.

Ethyl 2-((diphenylphosphoryl)oxy)-2-phenylacetate (3ba). Colorless oil, 33.1 mg, 87% yield. \(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta 7.92 - 7.87\) (m, 2H), 7.75 - 7.71 (m, 2H), 7.54 - 7.51 (m, 1H), 7.47 - 7.42 (m, 5H), 7.37-7.33 (m, 2H), 7.31 - 7.29 (m, 3H), 5.82 (d, \(J = 10.0\) Hz, 1H), 4.17 - 4.05 (m, 2H), 1.14 (t, \(J = 7.1\) Hz, 3H). \(^13\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta 169.05\) (d, \(J = 4.3\) Hz), 135.37 (d, \(J = 4.8\) Hz), 132.37 (d, \(J = 2.8\) Hz), 132.29 (d, \(J = 2.8\) Hz), 131.81 (d, \(J = 2.8\) Hz), 131.72 (d, \(J = 2.6\) Hz), 131.58 (d, \(J = 29.9\) Hz), 130.50 (d, \(J = 29.9\) Hz), 129.00, 128.61, 128.47 (d, \(J = 9.2\) Hz), 128.36 (d, \(J = 9.1\) Hz), 127.24, 74.23 (d, \(J = 5.1\) Hz), 61.70, 13.91. \(^31\)P NMR (202 MHz, Chloroform-\(d\)) \(\delta 34.09\). HRMS (ESI) m/z calcd for C\(_{22}\)H\(_{22}\)O\(_4\)P [M+H]\(^+\): 381.1250, found: 381.1263.

Benzyl 2-((diphenylphosphoryl)oxy)-2-phenylacetate (3ca). White solid, 42.9 mg, 97% yield. \(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta 7.88 - 7.83\) (m, 2H), 7.74 - 7.70 (m, 2H), 7.51 - 7.48 (m, 1H), 7.46 - 7.44 (m, 1H), 7.43 - 7.38 (m, 4H), 7.35 - 7.31 (m, 2H), 7.29 - 7.26 (m, 6H), 7.16 - 7.13 (m, 2H), 5.88 (d, \(J = 10.1\) Hz, 1H), 5.09 (d, \(J = 2.7\) Hz, 2H). \(^13\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta 168.88\) (d, \(J = 4.4\) Hz), 135.16 (d, \(J = 4.7\) Hz), 135.05, 132.37 (d, \(J = 2.8\) Hz), 132.29 (d, \(J = 2.8\) Hz), 131.74 (d, \(J = 10.6\) Hz), 131.47 (d, \(J = 20.1\) Hz), 130.38 (d, \(J = 20.0\) Hz), 129.05, 128.61, 128.45 (d, \(J = 10.4\) Hz), 128.42, 128.39, 128.27 (d, \(J = 10.6\) Hz), 127.93, 127.28, 74.21 (d, \(J = 5.0\) Hz), 67.19. \(^31\)P NMR (202
MHz, Chloroform-$d$) $\delta$ 34.22. **HRMS** (ESI) m/z calcd for C$_{24}$H$_{24}$O$_4$P [M+H]$^+$: 443.1407, found: 443.1410.

**Tert-butyl 2-((diphenylphosphoryl)oxy)-2-phenylacetate (3da).** Colorless oil, 20.9 mg, 51% yield. $^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 7.93 – 7.88 (m, 2H), 7.77 – 7.73 (m, 2H), 7.54 – 7.51 (m, 1H), 7.47 – 7.41 (m, 5H), 7.37 – 7.33 (m, 2H), 7.32 – 7.28 (m, 3H), 5.71 (d, $J = 10.2$ Hz, 1H), 1.33 (s, 9H). $^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 168.01 (d, $J = 4.4$ Hz), 135.82 (d, $J = 4.7$ Hz), 132.28 (d, $J = 8.1$ Hz, 2H), 7.48 – 7.44 (m, 3H), 7.37 – 7.34 (m, 2H), 7.30 (d, $J = 8.1$ Hz, 2H), 7.12 (d, $J = 7.9$ Hz, 2H), 5.79 (d, $J = 9.9$ Hz, 1H), 3.64 (s, 3H), 2.32 (s, 3H). $^{31}$P NMR (202 MHz, Chloroform-$d$) $\delta$ 33.46. **HRMS** (ESI) m/z calcd for C$_{24}$H$_{26}$O$_4$P [M+H]$^+$: 409.1563, found: 409.1572.

**Methyl 2-((diphenylphosphoryl)oxy)-2-(p-tolyl)acetate (3ea).** Colorless oil, 28.9 mg, 76% yield. $^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 7.90 – 7.86 (m, 2H), 7.74 – 7.70 (m, 2H), 7.54 – 7.51 (m, 1H), 7.48 – 7.44 (m, 3H), 7.37 – 7.34 (m, 2H), 7.30 (d, $J = 8.1$ Hz, 2H), 7.12 (d, $J = 7.9$ Hz, 2H), 5.79 (d, $J = 9.9$ Hz, 1H), 3.64 (s, 3H), 2.32 (s, 3H). $^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 169.69 (d, $J = 4.3$ Hz), 139.06, 132.36 (d, $J = 3.0$ Hz), 132.30, 132.25 (d, $J = 2.8$ Hz), 131.82 (d, $J = 6.2$ Hz), 131.73 (d, $J = 6.3$ Hz), 131.61 (d, $J = 32.7$ Hz), 130.52 (d, $J = 31.4$ Hz), 129.36, 128.46 (d, $J = 10.4$ Hz), 128.35 (d, $J = 10.3$ Hz), 127.28, 74.10 (d, $J = 5.1$ Hz), 52.54, 21.21. $^{31}$P NMR (202 MHz, Chloroform-$d$) $\delta$ 34.06. **HRMS** (ESI) m/z calcd for C$_{24}$H$_{26}$O$_4$P [M+H]$^+$: 381.1250, found: 381.1254.

**Methyl 2-(4-(tert-butyl)phenyl)-2-((diphenylphosphoryl)oxy)acetate (3fa).** Colorless oil, 40.1 mg, 95% yield. $^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 7.90 – 7.86 (m, 2H), 7.73 – 7.69 (m, 2H), 7.54 – 7.50 (m, 1H), 7.47 – 7.43 (m, 3H), 7.34 – 7.29 (m, 6H), 5.81 (d, $J = 9.7$ Hz, 1H), 3.65 (s, 3H), 1.28 (s, 9H). $^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 169.66 (d, $J = 4.6$ Hz), 152.10, 132.34 (d, $J = 2.9$ Hz), 132.20 (d, $J = 2.8$ Hz), 132.13 (d, $J = 4.8$ Hz), 131.76 (t, $J = 10.2$ Hz), 131.60 (d, $J = 35.7$ Hz), 130.51 (d, $J =
34.5 Hz), 128.44 (d, J = 13.5 Hz), 128.31 (d, J = 13.4 Hz), 127.08, 125.59, 74.07 (d, J = 5.0 Hz), 52.50, 34.60, 31.21. $^3$P NMR (202 MHz, Chloroform-d) δ 33.86. HRMS (ESI) m/z calcd for C$_2$sH$_{28}$O$_4$P [M+H]$^+$: 423.1720, found: 423.1728.

Methyl 2-[(1,1'-biphenyl)-4-yl]-2-((diphenylphosphoryl)oxy)acetate (3ga). Colorless oil, 42.0 mg, 95% yield. $^1$H NMR (500 MHz, Chloroform-d) δ 7.93 – 7.89 (m, 2H), 7.76 – 7.72 (m, 2H), 7.54 – 7.51 (m, 5H), 7.49 – 7.40 (m, 7H), 7.36 – 7.32 (m, 3H), 5.89 (d, J = 9.8 Hz, 1H), 3.67 (s, 3H). $^{13}$C NMR (126 MHz, Chloroform-d) δ 169.49 (d, J = 4.6 Hz), 142.01, 134.15 (d, J = 4.7 Hz), 132.29 (d, J = 2.8 Hz), 131.80 (d, J = 4.5 Hz), 131.72 (d, J = 4.7 Hz), 131.52 (d, J = 28.5 Hz), 130.43 (d, J = 27.4 Hz), 128.79, 128.49 (d, J = 12.1 Hz), 128.38 (d, J = 12.1 Hz), 127.76, 127.58, 127.39, 127.08, 73.97 (d, J = 5.0 Hz), 52.50. $^{31}$P NMR (202 MHz, Chloroform-d) δ 34.25. HRMS (ESI) m/z calcd for C$_{27}$H$_{24}$O$_4$P [M+H]$^+$: 443.1407, found: 443.1414.

Methyl 2-((diphenylphosphoryl)oxy)-2-(4-methoxyphenyl)acetate (3ha). White solid, 38.1 mg, 96% yield. $^1$H NMR (500 MHz, Chloroform-d) δ 7.89 – 7.85 (m, 2H), 7.73 – 7.69 (m, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.47 – 7.43 (m, 3H), 7.37 – 7.32 (m, 4H), 6.82 (d, J = 8.7 Hz, 2H), 5.79 (d, J = 9.8 Hz, 1H), 3.76 (s, 3H), 3.64 (s, 3H). $^{13}$C NMR (126 MHz, Chloroform-d) δ 169.72 (d, J = 4.6 Hz), 160.18, 132.35 (d, J = 2.8 Hz), 132.24 (d, J = 2.8 Hz), 131.78 (d, J = 8.3 Hz), 131.70 (d, J = 8.5 Hz), 131.51 (d, J = 29.4 Hz), 130.54 (d, J = 29.0 Hz), 128.84, 128.45 (d, J = 11.6 Hz), 128.35 (d, J = 11.4 Hz), 127.38 (d, J = 4.8 Hz), 114.07, 73.88 (d, J = 5.1 Hz), 55.26, 52.50. $^{31}$P NMR (202 MHz, Chloroform-d) δ 33.90. HRMS (ESI) m/z calcd for C$_{27}$H$_{22}$O$_5$P [M+H]$^+$: 397.1199, found: 397.1205.

Methyl 2-((diphenylphosphoryl)oxy)-2-(3,4,5-trimethoxyphenyl)acetate (3ia). White solid, 42.0 mg, 92% yield. $^1$H NMR (500 MHz, Chloroform-d) δ 7.90 – 7.85 (m, 2H), 7.72 – 7.68 (m, 2H), 7.56 – 7.53 (m, 1H), 7.49 – 7.45 (m, 3H), 7.38 – 7.34 (m, 2H), 6.59 (s, 2H), 5.79 (d, J = 9.9 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 6H), 3.70 (s, 3H). $^{13}$C NMR (126 MHz, Chloroform-d) δ 169.43 (d, J = 5.5 Hz), 153.27, 138.52,
132.47 (d, J = 2.8 Hz), 132.31 (d, J = 2.8 Hz), 131.81 (d, J = 10.5 Hz), 131.68 (d, J = 10.7 Hz), 131.56 (d, J = 11.9 Hz), 130.55 (d, J = 4.0 Hz), 130.47 (d, J = 9.4 Hz), 128.51 (d, J = 13.6 Hz), 128.28 (d, J = 13.4 Hz), 104.67, 74.24 (d, J = 4.9 Hz), 60.74, 56.12, 52.67. \(^{31}P\) NMR (202 MHz, Chloroform-\(d\)) δ 34.12. HRMS (ESI) m/z calcd for C\(_{24}\)H\(_{26}\)O\(_7\)P [M+H]\(^+\): 457.1411, found: 457.1416.

Methyl 2-(benzo[d][1,3]dioxol-5-yl)-2-((diphenylphosphoryl)oxy)acetate (3ja).

Colorless oil, 39.8 mg, 97% yield. \(^1H\) NMR (500 MHz, Chloroform-\(d\)) δ 7.89 – 7.85 (m, 2H), 7.74 – 7.70 (m, 2H), 7.54 – 7.51 (m, 1H), 7.49 – 7.43 (m, 3H), 7.39 – 7.35 (m, 2H), 6.92 (d, J = 1.7 Hz, 1H), 6.85 (dd, J = 8.0, 1.7 Hz, 1H), 6.70 (d, J = 8.0 Hz, 1H), 5.92 (s, 2H), 5.73 (d, J = 9.8 Hz, 1H), 3.65 (s, 3H). \(^{13}C\) NMR (126 MHz, Chloroform-\(d\)) δ 169.53 (d, J = 4.7 Hz), 148.33, 147.89, 132.42 (d, J = 2.8 Hz), 132.31 (d, J = 2.8 Hz), 131.79 (d, J = 8.1 Hz), 131.70 (d, J = 8.3 Hz), 131.55 (d, J = 24.3 Hz), 130.46 (d, J = 23.1 Hz), 128.94 (d, J = 4.8 Hz), 128.43 (t, J = 13.0 Hz), 121.64, 108.28, 107.66, 101.33, 73.99 (d, J = 5.0 Hz), 52.59. \(^{31}P\) NMR (202 MHz, Chloroform-\(d\)) δ 33.97. HRMS (ESI) m/z calcd for C\(_{22}\)H\(_{20}\)O\(_6\)P [M+H]\(^+\): 411.0992, found: 411.0998.

Methyl 2-((diphenylphosphoryl)oxy)-2-(4-fluorophenyl)acetate (3ka). White solid, 36.9 mg, 96% yield. \(^1H\) NMR (500 MHz, Chloroform-\(d\)) δ 7.90 – 7.86 (m, 2H), 7.73 – 7.69 (m, 2H), 7.56 – 7.52 (m, 1H), 7.49 – 7.45 (m, 3H), 7.42 – 7.35 (m, 4H), 6.99 (t, J = 8.7 Hz, 2H), 5.82 (d, J = 10.0 Hz, 1H), 3.66 (s, 3H). \(^{13}C\) NMR (126 MHz, Chloroform-\(d\)) δ 169.37 (d, J = 4.6 Hz), 163.06 (d, J = 248.4 Hz), 132.49 (d, J = 2.8 Hz), 132.40 (d, J = 2.8 Hz), 131.78 (d, J = 2.2 Hz), 131.69 (d, J = 2.0 Hz), 131.44 (d, J = 19.0 Hz), 131.24 (dd, J = 4.5, 3.4 Hz), 130.35 (d, J = 18.3 Hz), 129.27 (d, J = 8.5 Hz), 128.53 (d, J = 11.1 Hz), 128.42 (d, J = 11.1 Hz), 115.69 (d, J = 21.8 Hz), 73.43 (d, J = 4.9 Hz), 52.66. \(^{31}P\) NMR (202 MHz, Chloroform-\(d\)) δ 34.27. \(^{19}F\) NMR (471 MHz, Chloroform-\(d\)) δ -112.11. HRMS (ESI) m/z calcd for C\(_{21}\)H\(_{19}\)FO\(_4\)P [M+H]\(^+\): 385.1000, found: 385.1009.
Methyl 2-(4-chlorophenyl)-2-((diphenylphosphoryl)oxy)acetate (3la). White solid, 39.3 mg, 98% yield. $^1$H NMR (500 MHz, Chloroform-$d$) δ 7.90 – 7.86 (m, 2H), 7.74 – 7.69 (m, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.50 – 7.45 (m, 3H), 7.39 – 7.35 (m, 4H), 7.28 (d, J = 7.7 Hz, 2H), 5.81 (d, J = 10.0 Hz, 1H), 3.65 (s, 3H). $^{13}$C NMR (126 MHz, Chloroform-$d$) δ 169.16 (d, J = 4.6 Hz), 135.11, 133.82 (d, J = 4.7 Hz), 132.51 (d, J = 2.8 Hz), 132.42 (d, J = 2.9 Hz), 131.76 (d, J = 5.2 Hz), 131.68 (d, J = 5.0 Hz), 131.34 (d, J = 17.8 Hz), 130.25 (d, J = 17.2 Hz), 128.88, 128.65, 128.54 (d, J = 8.1 Hz), 128.43 (d, J = 7.9 Hz), 73.40 (d, J = 4.9 Hz), 52.70. $^{31}$P NMR (202 MHz, Chloroform-$d$) δ 34.48. HRMS (ESI) m/z calcd for C$_{21}$H$_{19}$ClO$_4$P [M+H]$^+$: 401.0704, found: 401.0709.

Methyl 2-(4-bromophenyl)-2-((diphenylphosphoryl)oxy)acetate (3ma). White solid, 43.2 mg, 97% yield. $^1$H NMR (500 MHz, Chloroform-$d$) δ 7.90 – 7.86 (m, 2H), 7.73 – 7.69 (m, 2H), 7.56 – 7.52 (m, 1H), 7.50 – 7.42 (m, 5H), 7.39 – 7.35 (m, 2H), 7.31 – 7.29 (m, 2H), 5.79 (d, J = 9.9 Hz, 1H), 3.65 (s, 3H). $^{13}$C NMR (126 MHz, Chloroform-$d$) δ 168.98 (d, J = 4.6 Hz), 134.30 (d, J = 4.8 Hz), 132.52 (d, J = 2.8 Hz), 132.43 (d, J = 2.8 Hz), 131.83, 131.73 (d, J = 5.5 Hz), 131.65 (d, J = 5.2 Hz), 131.27 (d, J = 18.0 Hz), 130.19 (d, J = 17.4 Hz), 128.91, 128.54 (d, J = 7.1 Hz), 128.43 (d, J = 6.9 Hz), 123.33, 73.45 (d, J = 4.9 Hz), 52.70. $^{31}$P NMR (202 MHz, Chloroform-$d$) δ 34.54. HRMS (ESI) m/z calcd for C$_{21}$H$_{19}$BrO$_4$P [M+H]$^+$: 445.0199, found: 445.0206.

Methyl 2-(3-bromophenyl)-2-((diphenylphosphoryl)oxy)acetate (3na). Colorless oil, 42.7 mg, 96% yield. $^1$H NMR (500 MHz, Chloroform-$d$) δ 7.90 – 7.86 (m, 2H), 7.74 – 7.70 (m, 2H), 7.57 – 7.53 (m, 2H), 7.50 – 7.46 (m, 3H), 7.44 – 7.42 (m, 1H), 7.40 – 7.35 (m, 3H), 7.17 (t, J = 7.9 Hz, 1H), 5.79 (d, J = 9.9 Hz, 1H), 3.67 (s, 3H). $^{13}$C NMR (126 MHz, Chloroform-$d$) δ 168.98 (d, J = 4.6 Hz), 137.31 (d, J = 4.6 Hz), 132.54 (d, J = 2.9 Hz), 132.50 (d, J = 2.9 Hz), 132.21, 131.77 (d, J = 1.5 Hz), 131.68 (d, J = 1.3 Hz), 131.21 (d, J = 27.1 Hz), 130.21, 130.12 (d, J = 25.6 Hz), 128.54 (d, J = 9.4 Hz), 128.43 (d, J = 9.2 Hz), 125.93, 122.62, 73.30 (d, J = 4.9 Hz), 52.77. $^{31}$P NMR (202 MHz, Chloroform-$d$) δ 34.65. HRMS (ESI) m/z calcd for C$_{21}$H$_{19}$BrO$_4$P [M+H]$^+$: 445.0199, found: 445.0208.
Methyl 2-(2-bromophenyl)-2-((diphenylphosphoryl)oxy)acetate (3oa). Colorless oil, 40.9 mg, 92% yield. $^1$H NMR (500 MHz, Chloroform-$d$) δ 7.92 – 7.88 (m, 2H), 7.71 – 7.67 (m, 2H), 7.56 – 7.52 (m, 2H), 7.48 – 7.43 (m, 4H), 7.34 – 7.29 (m, 2H), 7.28 – 7.26 (m, 1H), 7.17 – 7.13 (m, 1H), 6.24 (d, $J$ = 10.2 Hz, 1H), 3.67 (s, 3H). $^{13}$C NMR (126 MHz, Chloroform-$d$) δ 169.05 (d, $J$ = 5.2 Hz), 135.31 (d, $J$ = 4.3 Hz), 133.03, 132.39 (d, $J$ = 2.9 Hz), 131.75 (t, $J$ = 10.6 Hz), 131.42 (d, $J$ = 42.4 Hz), 129.76, 128.46 (d, $J$ = 13.5 Hz), 128.30 (d, $J$ = 13.4 Hz), 127.74, 123.28, 73.35 (d, $J$ = 4.9 Hz), 52.76. $^{31}$P NMR (202 MHz, Chloroform-$d$) δ 34.21. HRMS (ESI) m/z calcd for C$_{21}$H$_{19}$BrO$_4$P [M+H]$^+$: 445.0199, found: 445.0202.

Methyl 2-((diphenylphosphoryl)oxy)-2-(4-(trifluoromethyl)phenyl)acetate (3pa). Colorless oil, 41.7 mg, 96% yield. $^1$H NMR (500 MHz, Chloroform-$d$) δ 7.92 – 7.87 (m, 2H), 7.74 – 7.70 (m, 2H), 7.58 – 7.55 (m, 5H), 7.50 – 7.47 (m, 3H), 7.39 – 7.35 (m, 2H), 5.90 (d, $J$ = 9.9 Hz, 1H), 3.67 (s, 3H). $^{13}$C NMR (126 MHz, Chloroform-$d$) δ 168.90 (d, $J$ = 4.7 Hz), 139.12 (d, $J$ = 4.5 Hz), 132.64 (d, $J$ = 2.9 Hz), 132.55 (d, $J$ = 2.8 Hz), 131.79 (d, $J$ = 10.8 Hz), 131.69 (d, $J$ = 10.5 Hz), 131.20 (q, $J$ = 11.3 Hz), 130.15, 130.06, 128.61 (d, $J$ = 10.0 Hz), 128.50 (d, $J$ = 9.9 Hz), 127.63, 125.66 (q, $J$ = 3.7 Hz), 123.80 (q, $J$ = 272.4 Hz), 73.45 (d, $J$ = 4.9 Hz), 52.85. $^{31}$P NMR (202 MHz, Chloroform-$d$) δ 34.80. $^{19}$F NMR (471 MHz, Chloroform-$d$) δ -62.83. HRMS (ESI) m/z calcd for C$_{22}$H$_{19}$F$_3$O$_4$P [M+H]$^+$: 435.0968, found: 435.0979.

Methyl 2-((diphenylphosphoryl)oxy)-2-(naphthalen-1-yl)acetate (3qa). White solid, 39.9 mg, 96% yield. $^1$H NMR (500 MHz, Chloroform-$d$) δ 8.21 (d, $J$ = 8.3 Hz, 1H), 7.94 – 7.90 (m, 2H), 7.80 – 7.76 (m, 2H), 7.54 – 7.49 (m, 4H), 7.48 – 7.44 (m, 4H), 7.35 (t, $J$ = 7.7 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.15 – 7.11 (m, 2H), 6.44 (d, $J$ = 10.2 Hz, 1H), 3.61 (s, 3H). $^{13}$C NMR (126 MHz, Chloroform-$d$) δ 169.93 (d, $J$ = 5.2 Hz), 133.85, 132.35 (d, $J$ = 2.8 Hz), 132.04 (d, $J$ = 2.8 Hz), 131.63 (t, $J$ = 10.4 Hz), 131.51 (d, $J$ = 86.0 Hz), 131.25 (d, $J$ = 3.9 Hz), 130.57, 130.42 (d, $J$ = 82.3 Hz), 130.00, 128.66, 128.45 (d, $J$ = 13.6 Hz), 128.01 (d, $J$ = 13.3 Hz), 127.65, 126.76, 125.92, 125.06, 123.89, 73.30 (d, $J$ = 5.1 Hz), 52.69. $^{31}$P NMR (202 MHz, Chloroform-$d$) δ 34.36. HRMS (ESI) m/z calcd for C$_{25}$H$_{22}$O$_4$P [M+H]$^+$: 417.1250, found: 417.1259.

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Methyl 2-((diphenylphosphoryl)oxy)-2-(thiophen-2-yl)acetate (3ra). Brown oil, 20.1 mg, 54% yield. $^1$H NMR (500 MHz, Chloroform-d) δ 7.89 – 7.85 (m, 2H), 7.77 – 7.73 (m, 2H), 7.55 – 7.50 (m, 1H), 7.48 – 7.44 (m, 3H), 7.40 – 7.36 (m, 2H), 7.29 (dd, $J = 5.1, 1.1$ Hz, 1H), 7.07 (d, $J = 3.5$ Hz, 1H), 6.90 (dd, $J = 5.1, 3.6$ Hz, 1H), 6.12 (d, $J = 9.7$ Hz, 1H), 3.70 (s, 3H). $^{13}$C NMR (126 MHz, Chloroform-d) δ 168.69 (d, $J = 4.3$ Hz), 137.1 (d, $J = 5.6$ Hz), 132.45 (d, $J = 2.9$ Hz), 132.38 (d, $J = 2.8$ Hz), 131.77 (d, $J = 9.6$ Hz), 131.69 (d, $J = 10.0$ Hz), 131.37 (d, $J = 32.3$ Hz), 130.29 (d, $J = 31.4$ Hz), 128.49 (d, $J = 9.1$ Hz), 128.38 (d, $J = 8.9$ Hz), 127.81, 127.25, 126.82, 69.89 (d, $J = 4.9$ Hz), 52.81. $^{31}$P NMR (202 MHz, Chloroform-d) δ 34.54. HRMS (ESI) m/z calcd for C$_{19}$H$_{18}$O$_4$PS [M+H]$^+$: 373.0658, found: 373.0663.

Tert-butyl 2-((diphenylphosphoryl)oxy)-3-phenylpropanoate (3sa). Colorless oil, 11.9 mg, 28% yield. $^1$H NMR (500 MHz, Chloroform-d) δ 7.83 – 7.79 (m, 2H), 7.63 – 7.58 (m, 2H), 7.50 – 7.45 (m, 2H), 7.43 – 7.39 (m, 2H), 7.36 – 7.32 (m, 2H), 7.25 – 7.19 (m, 5H), 4.97 – 4.93 (m, 1H), 3.25 – 3.16 (m, 2H), 1.29 (s, 9H). $^{13}$C NMR (126 MHz, Chloroform-d) δ 168.80 (d, $J = 3.4$ Hz), 135.59, 132.16 (d, $J = 2.8$ Hz), 132.04 (d, $J = 2.8$ Hz), 131.90 (d, $J = 10.6$ Hz), 131.57 (d, $J = 10.4$ Hz), 131.36 (d, $J = 135.7$ Hz), 130.29 (d, $J = 137.5$ Hz), 129.80, 128.35(d, $J = 12.4$ Hz), 128.29, 126.90, 82.21, 73.76 (d, $J = 5.8$ Hz), 39.93 (d, $J = 4.9$ Hz), 27.75. $^{31}$P NMR (202 MHz, Chloroform-d) δ 33.11. HRMS (ESI) m/z calcd for C$_{25}$H$_{28}$O$_4$P [M+H]$^+$: 423.1720, found: 423.1726.

2,2,2-trifluoro-1-phenylethyl diphenylphosphinate (3ta). Colorless oil, 6.1 mg, 16% yield. $^1$H NMR (500 MHz, Chloroform-d) δ 7.87 – 7.83 (m, 2H), 7.62 – 7.56 (m, 3H), 7.51 – 7.48 (m, 2H), 7.45 – 7.39 (m, 3H), 7.35 – 7.28 (m, 5H), 5.74 – 5.68 (m, 1H). $^{13}$C NMR (126 MHz, Chloroform-d) δ 132.69 (d, $J = 2.9$ Hz), 132.40 (d, $J = 2.9$ Hz), 131.67 (d, $J = 3.3$ Hz), 131.65, 131.59 (d, $J = 3.4$ Hz), 130.57 (d, $J = 136.3$ Hz), 130.45 (d, $J = 138.1$ Hz), 129.84, 128.61 (d, $J = 13.6$ Hz), 128.48, 128.31 (d, $J = 13.6$ Hz), 128.13, 126.58 – 119.86 (m), 73.58 (qd, $J = 33.8, 5.0$ Hz). $^{31}$P NMR (471 MHz, Chloroform-d) δ -76.48. HRMS (ESI) m/z calcd for C$_{20}$H$_{17}$F$_3$O$_2$P [M+H]$^+$: 377.0913, found: 377.0921.
2-oxo-2-phenylethyl diphenylphosphinate (3ua). Yellow oil, 30.9 mg, 92% yield. \[ \text{H NMR (500 MHz, Chloroform-}d) \delta 7.94 - 7.90 \text{ (m, 4H), 7.88 - 7.86} \text{ (m, 2H), 7.59 - 7.52 \text{ (m, 3H), 7.48 - 7.43 (m, 6H), 5.31 (d, } J = 7.5 \text{ Hz, 2H).} \text{ C NMR (126 MHz, Chloroform-}d) \delta 192.31 \text{ (d, } J = 6.8 \text{ Hz), 134.07, 133.91, 132.50 (d, } J = 2.9 \text{ Hz), 131.80 (d, } J = 10.4 \text{ Hz), 130.70 (d, } J = 137.4 \text{ Hz), 128.85, 128.64 (d, } J = 13.3 \text{ Hz), 127.74, 65.78 (d, } J = 5.6 \text{ Hz).} \text{ P NMR (202 MHz, Chloroform-}d) \delta 34.35. \text{ HRMS (ESI) m/z calcd for } C_{20}H_{18}O_3P [M+H]^+ : 337.0988, \text{ found: 337.0991.} \]

Methyl 2-((di-p-tolylphosphoryl)oxy)-2-phenylacetate (3ab). Colorless oil, 35.1 mg, 89% yield. \[ \text{H NMR (500 MHz, Chloroform-}d) \delta 7.78 \text{ (dd, } J = 12.5, 8.1 \text{ Hz, 2H), 7.62 (dd, } J = 12.3, 8.1 \text{ Hz, 2H), 7.45 - 7.43 (m, 2H), 7.34 - 7.32 (m, 3H), 7.29 - 7.27 (m, 2H), 7.18 (dd, } J = 7.8, 3.4 \text{ Hz, 2H), 5.82 (d, } J = 10.1 \text{ Hz, 1H), 3.67 (s, 3H), 2.40 (s, 3H), 2.36 (s, 3H).} \text{ C NMR (126 MHz, Chloroform-}d) \delta 169.68 \text{ (d, } J = 4.1 \text{ Hz), 142.83 (d, } J = 3.0 \text{ Hz), 142.76 (d, } J = 2.9 \text{ Hz), 135.47 (d, } J = 5.0 \text{ Hz), 131.82 (d, } J = 2.2 \text{ Hz), 131.73 (d, } J = 2.5 \text{ Hz), 129.19 (d, } J = 7.8 \text{ Hz), 129.08 (d, } J = 7.7 \text{ Hz), 128.96, 128.62, 128.53 \text{ (d, } J = 35.4 \text{ Hz), 127.42 (d, } J = 34.8 \text{ Hz), 127.22, 74.00 \text{ (d, } J = 5.0 \text{ Hz), 52.53, 21.66 (d, } J = 1.1 \text{ Hz), 21.60 (d, } J = 1.1 \text{ Hz).} \text{ P NMR (202 MHz, Chloroform-}d) \delta 35.26. \text{ HRMS (ESI) m/z calcd for } C_{23}H_{24}O_4P [M+H]^+ : 395.1407, \text{ found: 395.1417.} \]

Methyl 2-((bis(4-methoxyphenyl)phosphoryl)oxy)-2-phenylacetate (3ac). Colorless oil, 40.9 mg, 96% yield. \[ \text{H NMR (500 MHz, Chloroform-}d) \delta 7.82 - 7.77 (m, 2H), 7.66 - 7.62 (m, 2H), 7.43 - 7.41 (m, 2H), 7.32 - 7.30 (m, 3H), 6.96 (dd, } J = 8.8, 2.8 \text{ Hz, 2H), 6.85 (dd, } J = 8.8, 2.8 \text{ Hz, 2H), 5.78 (d, } J = 10.2 \text{ Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 3.66 (s, 3H).} \text{ C NMR (126 MHz, Chloroform-}d) \delta 169.75 \text{ (d, } J = 4.1 \text{ Hz), 162.72 (d, } J = 3.1 \text{ Hz), 162.66 (d, } J = 3.1 \text{ Hz), 135.53 (d, } J = 4.9 \text{ Hz), 133.75, 133.65, 128.96, 128.63, 127.22, 123.19 \text{ (d, } J = 40.8 \text{ Hz), 122.04 (d, } J = 40.2 \text{ Hz), 113.99 (d, } J = 7.6 \text{ Hz), 113.87 (d, } J = 7.5 \text{ Hz), 73.92, 55.32, 55.29, 52.54.} \text{ P NMR (202 MHz, Chloroform-}d) \delta 35.11. \text{ HRMS (ESI) m/z calcd for } C_{23}H_{24}O_6P [M+H]^+ : 427.1305, \text{ found: 427.1318.} \]
Methyl 2-((bis(4-(trifluoromethoxy)phenyl)phosphoryl)oxy)-2-phenylacetate (3ad). Colorless oil, 52.3 mg, 98% yield. $^1$H NMR (500 MHz, Chloroform-d) $\delta$ 7.97 – 7.92 (m, 2H), 7.75 – 7.70 (m, 2H), 7.39 – 7.37 (m, 2H), 7.34 – 7.28 (m, 5H), 7.19 – 7.17 (m, 2H), 5.85 (d, $J = 9.7$ Hz, 1H), 3.68 (s, 3H). $^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 169.27 (d, $J = 5.1$ Hz), 152.47 (d, $J = 3.4$ Hz), 152.32 (d, $J = 3.4$, 1.6 Hz), 134.80 (d, $J = 4.4$ Hz), 133.92 (d, $J = 3.4$ Hz), 133.83 (d, $J = 3.1$ Hz), 129.44, 129.38 (d, $J = 141.5$ Hz), 129.21 (d, $J = 139.3$ Hz), 128.84, 127.47, 120.58 (t, $J = 15.0$ Hz), 120.29 (qd, $J = 259.0, 6.7$ Hz), 74.52 (d, $J = 5.0$ Hz), 52.76. $^{31}$P NMR (202 MHz, Chloroform-d) $\delta$ 31.00. $^{19}$F NMR (471 MHz, Chloroform-d) $\delta$ -57.64, -57.68. HRMS (ESI) m/z calcd for C$_{23}$H$_{18}$F$_{6}$O$_{6}$P [M+H]$^+$: 535.0740, found: 535.0742.

Methyl 2-((bis(4-fluorophenyl)phosphoryl)oxy)-2-phenylacetate (3ae). Colorless oil, 36.6 mg, 91% yield. $^1$H NMR (500 MHz, Chloroform-d) $\delta$ 7.92 – 7.86 (m, 2H), 7.72 – 7.66 (m, 2H), 7.41 – 7.38 (m, 2H), 7.33 – 7.30 (m, 3H), 7.17 (td, $J = 8.8$, 2.6 Hz, 2H), 7.04 (td, $J = 8.6$, 2.4 Hz, 2H), 5.82 (d, $J = 10.0$ Hz, 1H), 3.67 (s, 3H). $^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 169.39 (d, $J = 4.7$ Hz), 166.36 (dd, $J = 12.9$, 3.5 Hz), 164.34 (dd, $J = 12.9$, 3.5 Hz), 135.00 (d, $J = 4.7$ Hz), 134.40 (dd, $J = 9.1$, 2.1 Hz), 134.31 (dd, $J = 9.1$, 1.8 Hz), 129.29, 128.78, 127.48(dd, $J = 29.3$, 3.4 Hz), 127.34, 126.36 (dd, $J = 29.3$, 3.4 Hz), 116.13 – 115.96 (m), 115.90 – 115.73 (m), 74.28 (d, $J = 5.0$ Hz), 52.70. $^{31}$P NMR (202 MHz, Chloroform-d) $\delta$ -105.42 (d, $J = 1.3$ Hz), -105.53(d, $J = 1.0$ Hz). HRMS (ESI) m/z calcd for C$_{21}$H$_{18}$F$_{6}$O$_{6}$P [M+H]$^+$: 403.0905, found: 403.0911.

Methyl 2-((bis(4-chlorophenyl)phosphoryl)oxy)-2-phenylacetate (3af). Colorless oil, 41.8 mg, 96% yield. $^1$H NMR (500 MHz, Chloroform-d) $\delta$ 7.83 – 7.79 (m, 2H), 7.63 – 7.59 (m, 2H), 7.47 – 7.45 (m, 2H), 7.40 – 7.38 (m, 2H), 7.35 – 7.30 (m, 5H), 5.83 (d, $J = 9.9$ Hz, 1H), 3.68 (s, 3H). $^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 169.27 (d, $J = 4.6$ Hz), 139.28 (d, $J = 3.7$ Hz), 139.17 (d, $J = 3.6$ Hz), 134.87 (d, $J = 4.7$ Hz), 133.14 (d, $J = 3.6$ Hz), 133.05 (d, $J = 3.4$ Hz), 129.79 (d, $J = 24.4$ Hz), 129.79 (d, $J = 24.4$ Hz), 129.79 (d, $J = 24.4$ Hz), 129.79 (d, $J = 24.4$ Hz), 129.79 (d, $J = 24.4$ Hz), 129.79 (d, $J = 24.4$ Hz).
129.33, 128.92 (t, \( J = 14.1 \) Hz), 128.79, 128.68 (d, \( J = 23.1 \) Hz), 127.34, 74.37 (d, \( J = 5.0 \) Hz), 52.72. \(^{31}\)P NMR (202 MHz, Chloroform-\( d \)) \( \delta \) 32.16. HRMS (ESI) m/z calcd for C\(_{21}\)H\(_{18}\)Cl\(_2\)O\(_4\)P [M+H]\(^+\) : 435.0314, found: 435.0321.

**Methyl 2-((bis(4-bromophenyl)phosphoryl)oxy)-2-phenylacetate (3ag).** Colorless oil, 39.8 mg, 76% yield. \(^1\)H NMR (500 MHz, Chloroform-\( d \)) \( \delta \) 7.75 – 7.71 (m, 2H), 7.63 – 7.61 (m, 2H), 7.55 – 7.53 (m, 1H), 7.51 – 7.48 (m, 3H), 7.40 – 7.35 (m, 2H), 7.34 – 7.30 (m, 3H), 5.82 (d, \( J = 9.8 \) Hz, 1H), 3.68 (s, 3H). \(^{13}\)C NMR (126 MHz, Chloroform-\( d \)) \( \delta \) 169.25 (d, \( J = 4.7 \) Hz), 134.84 (d, \( J = 4.7 \) Hz), 133.21 (d, \( J = 4.0 \) Hz), 133.12 (d, \( J = 3.8 \) Hz), 131.88 (t, \( J = 14.0 \) Hz), 130.24 (d, \( J = 23.1 \) Hz), 129.34, 129.13 (d, \( J = 21.5 \) Hz), 128.80, 127.95 (d, \( J = 3.7 \) Hz), 127.84 (d, \( J = 5.0 \) Hz), 52.73. \(^{31}\)P NMR (202 MHz, Chloroform-\( d \)) \( \delta \) 32.45. HRMS (ESI) m/z calcd for C\(_{21}\)H\(_{18}\)Br\(_2\)O\(_4\)P [M+H]\(^+\) : 522.9304, found: 522.9308.

**Methyl 2-((bis(3-fluoro-4-methylphenyl)phosphoryl)oxy)-2-phenylacetate (3ah).** Colorless oil, 41.7 mg, 97% yield. \(^1\)H NMR (500 MHz, Chloroform-\( d \)) \( \delta \) 7.56 – 7.49 (m, 2H), 7.42 – 7.40 (m, 2H), 7.39 – 7.34 (m, 1H), 7.34 – 7.28 (m, 5H), 7.20 – 7.16 (m, 1H), 5.82 (d, \( J = 9.9 \) Hz, 1H), 3.68 (s, 3H), 2.31 (s, 3H), 2.26 (s, 3H). \(^{13}\)C NMR (126 MHz, Chloroform-\( d \)) \( \delta \) 169.35 (d, \( J = 4.5 \) Hz), 161.93 (dd, \( J = 19.5, 14.7 \) Hz), 159.96 (dd, \( J = 19.5, 14.9 \) Hz), 135.03 (d, \( J = 4.8 \) Hz), 132.04 (dd, \( J = 12.2, 3.7 \) Hz), 131.90 (dd, \( J = 12.0, 3.7 \) Hz), 130.83 (dd, \( J = 22.9, 6.0 \) Hz), 130.34 (dd, \( J = 12.8, 2.8 \) Hz), 130.21 (dd, \( J = 12.8, 2.8 \) Hz), 129.71 (dd, \( J = 21.6, 6.0 \) Hz), 129.25, 128.75, 127.31, 127.27 (d, \( J = 3.7 \) Hz), 127.19 (d, \( J = 3.7 \) Hz), 118.20 (dd, \( J = 11.7, 1.6 \) Hz), 118.02 (dd, \( J = 11.7, 1.5 \) Hz), 74.39 (d, \( J = 5.0 \) Hz), 52.68, 14.81 (d, \( J = 3.6 \) Hz), 14.74 (d, \( J = 3.6 \) Hz). \(^{31}\)P NMR (202 MHz, Chloroform-\( d \)) \( \delta \) -115.59 (d, \( J = 6.4 \) Hz), -115.73 (d, \( J = 6.6 \) Hz). HRMS (ESI) m/z calcd for C\(_{23}\)H\(_{22}\)F\(_2\)O\(_4\)P [M+H]\(^+\) : 431.1218, found: 431.1226.

**Methyl 2-((bis(4-(trifluoromethyl)phenyl)phosphoryl)oxy)-2-phenylacetate (3ai).** Colorless oil, 48.2 mg, 96% yield. \(^1\)H NMR (500 MHz, Chloroform-\( d \)) \( \delta \) 8.04 (dd, \( J = 12.4, 8.0 \) Hz, 2H), 7.80 (dd, \( J = 12.3, 8.0 \) Hz, 2H), 7.76 (dd, \( J = 8.2, 2.9 \) Hz, 2H), 7.61 (dd, \( J = 8.2, 2.9 \) Hz, 2H), 7.40 – 7.38 (m, 2H), 7.35 – 7.29 (m,
3H), 5.89 (d, J = 9.5 Hz, 1H), 3.69 (s, 3H). 13C NMR (126 MHz, Chloroform-d) δ 169.09 (d, J = 5.0 Hz), 135.29 (d, J = 12.1 Hz), 134.62 – 134.43 (m), 134.36 – 134.17 (m), 132.27 (d, J = 6.4 Hz), 132.18 (d, J = 6.3 Hz), 129.56, 128.89, 127.48, 125.64 (q, J = 3.8 Hz), 125.57 – 125.44 (m), 125.37 (q, J = 3.7 Hz), 123.36 (q, J = 272.7 Hz), 123.44 (q, J = 272.7 Hz), 74.75 (d, J = 5.1 Hz), 52.83. 31P NMR (202 MHz, Chloroform-d) δ 30.11. 19F NMR (471 MHz, Chloroform-d) δ -63.36, -63.43. HRMS (ESI) m/z calcd for C23H18F6O4P [M+H]+: 503.0841, found: 503.0847.

Methyl 2-((bis(3-(trifluoromethyl)phenyl)phosphoryl)oxy)-2-phenylacetate (3aj).

Colorless oil, 45.2 mg, 90% yield. 1H NMR (500 MHz, Chloroform-d) δ 8.19 (d, J = 13.0 Hz, 1H), 8.09 (dd, J = 12.4, 7.7 Hz, 1H), 7.93 (d, J = 12.8 Hz, 1H), 7.89 – 7.83 (m, 2H), 7.73 (d, J = 7.9 Hz, 1H), 7.65 (td, J = 7.8, 3.4 Hz, 1H), 7.51 (td, J = 7.8, 3.3 Hz, 1H), 7.41 – 7.37 (m, 2H), 7.32 – 7.28 (m, 3H), 5.90 (d, J = 9.8 Hz, 1H), 3.70 (s, 3H).

13C NMR (126 MHz, Chloroform-d) δ 169.03 (d, J = 5.4 Hz), 135.03 (dd, J = 10.2, 7.7 Hz), 134.52 (d, J = 4.1 Hz), 132.06 (d, J = 140.2 Hz), 131.92 (d, J = 137.9 Hz), 131.80 – 131.27 (m), 131.26 – 130.73 (m), 129.61, 129.56 – 129.51 (m), 129.43 (d, J = 13.5 Hz), 129.27 (d, J = 13.4 Hz), 128.91, 128.58 (q, J = 3.9 Hz), 128.49 (q, J = 3.9 Hz), 127.53, 123.53 (qd, J = 272.7, 2.0 Hz), 123.38 (qd, J = 272.6, 1.9 Hz), 74.82 (d, J = 5.1 Hz), 52.83. 31P NMR (202 MHz, Chloroform-d) δ 29.92.

Methyl 2-((bis(2-(trifluoromethyl)phenyl)phosphoryl)oxy)-2-phenylacetate (3ak).

Colorless oil, 46.2 mg, 92% yield. 1H NMR (500 MHz, Chloroform-d) δ 8.60 (dd, J = 14.3, 7.7 Hz, 1H), 8.05 (dd, J = 14.7, 7.7 Hz, 1H), 7.79 – 7.74 (m, 2H), 7.70 (t, J = 7.4 Hz, 1H), 7.64 (t, J = 7.4 Hz, 1H), 7.56 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.41 – 7.39 (m, 2H), 7.31 – 7.27 (m, 3H), 6.00 (d, J = 8.6 Hz, 1H), 3.61 (s, 3H). 13C NMR (126 MHz, Chloroform-d) δ 169.32 (d, J = 4.2 Hz), 135.32 (d, J = 6.6 Hz), 134.96 (d, J = 8.0 Hz), 134.55 (d, J = 5.7 Hz), 132.45 (d, J = 2.7 Hz), 132.26 (d, J = 2.7 Hz), 131.88 (dd, J = 10.5, 8.5 Hz), 131.62 (dd, J = 10.6, 8.5 Hz), 131.39 (d, J = 11.7 Hz), 131.13 (d, J = 12.6 Hz), 130.73 – 129.66 (m), 130.46 – 129.37 (m), 129.20, 128.62, 127.55, 127.35 – 127.24 (m), 127.23 – 127.11 (m), 123.36 (qd, J = 274.5, 3.8 Hz), 123.16 (qd, J = 274.5, 3.7 Hz), 75.28 (d, J = 5.2 Hz), 52.59. 31P NMR (202 MHz, Chloroform-d) δ 28.77.
(471 MHz, Chloroform-\textit{d}) \( \delta \) -56.99, -57.16. \textbf{HRMS} (ESI) m/z calcd for C\textsubscript{23}H\textsubscript{18}F\textsubscript{6}O\textsubscript{4}P [M+H]\textsuperscript{+} : 503.0841, found: 503.0844.

\textbf{Methyl 2-((di(naphthalen-2-yl)phosphoryl)oxy)-2-phenylacetate (3al).} Colorless oil, 42.9 mg, 92% yield. \textit{\textsuperscript{1}H NMR} (500 MHz, Chloroform-\textit{d}) \( \delta \) 8.54 (d, \( J = 14.6 \) Hz, 1H), 8.41 (d, \( J = 14.4 \) Hz, 1H), 7.92 (t, \( J = 7.3 \) Hz, 3H), 7.85 – 7.78 (m, 4H), 7.70 (t, \( J = 9.4 \) Hz, 1H), 7.58 – 7.49 (m, 4H), 7.47 – 7.46 (m, 2H), 7.32 – 7.27 (m, 3H), 5.93 (dd, \( J = 10.0, 3.2 \) Hz, 1H), 3.64 (s, 3H).

\textit{\textsuperscript{13}C NMR} (126 MHz, Chloroform-\textit{d}) \( \delta \) 169.56 (d, \( J = 4.3 \) Hz), 135.29 (d, \( J = 4.8 \) Hz), 134.97 (d, \( J = 2.5 \) Hz), 134.87 (d, \( J = 2.5 \) Hz), 134.06 (d, \( J = 10.2 \) Hz), 133.93 (d, \( J = 10.5 \) Hz), 132.36 (d, \( J = 11.5 \) Hz), 132.24 (d, \( J = 11.4 \) Hz), 129.12, 129.07, 128.99, 128.68, 128.65 (d, \( J = 31.7 \) Hz), 128.45, 128.37 (d, \( J = 1.9 \) Hz), 128.34 (d, \( J = 1.9 \) Hz), 128.27, 127.81, 127.75, 127.55 (d, \( J = 30.7 \) Hz), 127.34, 126.88, 126.85, 126.44 (d, \( J = 4.6 \) Hz), 126.35 (d, \( J = 4.5 \) Hz), 74.33 (d, \( J = 5.0 \) Hz), 52.60. \textit{\textsuperscript{31}P NMR} (202 MHz, Chloroform-\textit{d}) \( \delta \) 34.66.

\textbf{HRMS} (ESI) m/z calcd for C\textsubscript{29}H\textsubscript{24}O\textsubscript{4}P [M+H]\textsuperscript{+} : 467.1407, found: 467.1413.

\textbf{Methyl 2-((dibenzylphosphoryl)oxy)-2-phenylacetate (3am).} Colorless oil, 35.9 mg, 91% yield. \textit{\textsuperscript{1}H NMR} (500 MHz, Chloroform-\textit{d}) \( \delta \) 7.41 – 7.39 (m, 2H), 7.36 – 7.31 (m, 5H), 7.30 – 7.26 (m, 2H), 7.24 (d, \( J = 2.1 \) Hz, 1H), 7.17 – 7.11 (m, 3H), 7.01 – 7.00 (m, 2H), 5.55 (d, \( J = 8.8 \) Hz, 1H), 3.66 (s, 3H), 3.42 – 3.26 (m, 2H), 2.99 – 2.86 (m, 2H). \textit{\textsuperscript{13}C NMR} (126 MHz, Chloroform-\textit{d}) \( \delta \) 170.17 (d, \( J = 3.2 \) Hz), 135.40 (d, \( J = 5.5 \) Hz), 131.34 (d, \( J = 7.1 \) Hz), 130.45 (d, \( J = 8.5 \) Hz), 130.13 (d, \( J = 6.0 \) Hz), 129.93 (d, \( J = 5.7 \) Hz), 129.01, 128.66 (d, \( J = 2.7 \) Hz), 128.61, 128.45 (d, \( J = 2.6 \) Hz), 127.40, 127.00 (d, \( J = 3.3 \) Hz), 126.80 (d, \( J = 3.1 \) Hz), 74.42 (d, \( J = 6.4 \) Hz), 52.60, 37.15 (d, \( J = 85.0 \) Hz), 36.03 (d, \( J = 85.3 \) Hz). \textit{\textsuperscript{31}P NMR} (202 MHz, Chloroform-\textit{d}) \( \delta \) 51.80. \textbf{HRMS} (ESI) m/z calcd for C\textsubscript{29}H\textsubscript{24}O\textsubscript{4}P [M+H]\textsuperscript{+} : 395.1407, found: 395.1410.

\textbf{Methyl 2-((butyl(phenyl)phosphoryl)oxy)-2-phenylacetate (3an).} Colorless oil, 23.1 mg, 67% yield. \textit{\textsuperscript{1}H NMR} (500 MHz, Chloroform-\textit{d}) \( \delta \) 7.91 – 7.87 (m, 2H), 7.59 – 7.56 (m, 1H), 7.52 – 7.49 (m, 4H), 7.41 – 7.35 (m, 3H), 5.79 (d, \( J = 10.4 \) Hz, 1H), 3.54 (s, 3H), 1.93 – 1.83 (m, 2H), 1.48 – 1.36 (m, 2H), 1.32 – 1.24 (m, 2H), 0.79 (t, \( J = 7.3 \) Hz, 3H). \textit{\textsuperscript{13}C NMR} (126 MHz, Chloroform-\textit{d}) \( \delta \) 169.59 (d, \( J = 4.7 \) Hz), 135.80 (d, \( J = 4.0 \) Hz), 132.41 (d, \( J =
2.7 Hz), 131.57 (d, J = 10.1 Hz), 130.72 (d, J = 123.4 Hz), 129.10, 128.75, 128.49 (d, J = 12.6 Hz), 127.23, 73.56 (d, J = 5.5 Hz), 52.39, 29.79 (d, J = 98.1 Hz), 23.67 (d, J = 16.6 Hz), 23.51 (d, J = 3.7 Hz), 13.44. \(^{31}\)P NMR (202 MHz, Chloroform-d) \(\delta 48.00\).

**HRMS (ESI) m/z calcd for C\(_{19}\)H\(_{24}\)O\(_4\)P [M+H]^+: 347.1407, found: 347.1413.**

Methyl 2-((ethoxy(phenyl)phosphoryl)oxy)-2-phenylacetate (3ao). Colorless oil, 27.1 mg, 81% yield. \(^1\)H NMR (500 MHz, Chloroform-d) \(\delta 7.93 – 7.88 (m, 2H), 7.72 – 7.68 (m, 2H), 7.58 – 7.54 (m, 1H), 7.51 – 7.46 (m, 5H), 7.41 – 7.33 (m, 7H), 7.31 – 7.28 (m, 3H), 5.93 (d, J = 9.2 Hz, 1H), 5.83 (d, J = 8.7 Hz, 1H), 4.36 – 4.24 (m, 2H), 4.03 – 3.89 (m, 2H), 3.74 (s, 3H), 3.62 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H), 1.18 (t, J = 7.1 Hz, 3H).

\(^{13}\)C NMR (126 MHz, Chloroform-d) \(\delta 169.72 (d, J = 4.1 Hz), 169.34 (d, J = 5.4 Hz), 135.41 (d, J = 4.8 Hz), 134.90 (d, J = 6.0 Hz), 132.59 (d, J = 3.1 Hz), 132.47 (d, J = 3.1 Hz), 131.76 (d, J = 10.3 Hz), 131.63 (d, J = 10.2 Hz), 129.21, 129.09, 128.76, 128.62, 128.41 (d, J = 11.8 Hz), 128.29 (d, J = 11.7 Hz), 127.92 (d, J = 192.1 Hz), 127.87 (d, J = 192.8 Hz), 127.29, 127.19, 75.41 (t, J = 4.5 Hz), 62.72 (d, J = 6.2 Hz), 62.30 (d, J = 6.1 Hz), 52.64, 52.54, 16.28 (d, J = 6.6 Hz), 16.08 (d, J = 6.6 Hz). \(^{31}\)P NMR (202 MHz, Chloroform-d) \(\delta 19.31, 19.15\).

**HRMS (ESI) m/z calcd for C\(_{17}\)H\(_{20}\)O\(_5\)P [M+H]^+: 335.1043, found: 335.1050.**

Methyl 2-((4-oxidodinaphtho[2,1-d:1’,2’-f][1,3,2]dioxaphosphepin-4-yl)oxy)-2-phenylacetate (3ap). Colorless oil, 27.8 mg, 56% yield. \(^1\)H NMR (500 MHz, Chloroform-d) \(\delta 8.07 (d, J = 8.9 Hz, 1H), 8.01 (d, J = 8.9 Hz, 1H), 7.97 (d, J = 8.2 Hz, 1H), 7.94 (d, J = 8.2 Hz, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.53 (d, J = 8.9 Hz, 1H), 7.50 – 7.46 (m, 2H), 7.40 – 7.36 (m, 4H), 7.34 – 7.28 (m, 5H), 6.07 (d, J = 7.5 Hz, 1H), 3.83 (s, 3H). \(^{13}\)C NMR (126 MHz, Chloroform-d) \(\delta 168.83 (d, J = 4.1 Hz), 146.87 (d, J = 169.1 Hz), 146.79 (d, J = 166.0 Hz), 134.09 (d, J = 7.4 Hz), 132.20 (dd, J = 7.0, 0.9 Hz), 131.85 (dd, J = 12.9, 1.1 Hz), 131.38 (d, J = 0.72 Hz), 131.12, 129.47, 128.78, 128.48, 128.87, 127.23, 127.19, 127.15, 126.72 (d, J = 15.6 Hz), 125.81 (d, J = 12.5 Hz), 120.85 (d, J = 3.0 Hz), 120.56 (d, J = 3.0 Hz), 78.49 (d, J = 4.4 Hz), 53.00. \(^{31}\)P NMR (202 MHz, Chloroform-d) \(\delta 19.31, 19.15\).

**HRMS (ESI) m/z calcd for C\(_{29}\)H\(_{22}\)O\(_8\)P [M+H]^+: 497.1149, found: 497.1155.**
10. Copies of NMR Spectra

Methyl 2-((diphenylphosphoryl)oxy)-2-phenylacetate (3aa)
Ethyl 2-((diphenylphosphoryl)oxy)-2-phenylacetate (3ba)
Benzyl 2-((diphenylphosphoryl)oxy)-2-phenylacetate (3ca)
**Tert-butyl 2-((diphenylphosphoryl)oxy)-2-phenylacetate (3da)**

![Chemical Structure of Tert-butyl 2-((diphenylphosphoryl)oxy)-2-phenylacetate (3da)](attachment:image)
Methyl 2-((diphenylphosphoryl)oxy)-2-(p-tolyl)acetate (3ea)
Methyl 2-(4-(tert-butyl)phenyl)-2-((diphenylphosphoryl)oxy)acetate (3fa)
Methyl 2-((1,1'-biphenyl)-4-yl)-2-((diphenylphosphoryl)oxy)acetate (3ga)
methyl 2-((diphenylphosphoryl)oxy)-2-(4-methoxyphenyl)acetate (3ha)
Methyl 2-((diphenylphosphoryl)oxy)-2-(3,4,5-trimethoxyphenyl)acetate (3ia)
Methyl 2-(benzo[d][1,3]dioxol-5-yl)-2-((diphenylphosphoryl)oxy)acetate (3ja)
Methyl 2-((diphenylphosphoryl)oxy)-2-(4-fluorophenyl)acetate (3ka)
Methyl 2-(4-chlorophenyl)-2-((diphenylphosphoryl)oxy)acetate (3la)
Methyl 2-(4-bromophenyl)-2-(((diphenylphosphoryl)oxy)acetate (3ma)
Methyl 2-(3-bromophenyl)-2-((diphenylphosphoryl)oxy)acetate (3na)
Methyl 2-(2-bromophenyl)-2-((diphenylphosphoryl)oxy)acetate acetate (30a)
Methyl 2-((diphenylphosphoryl)oxy)-2-(4-(trifluoromethyl)phenyl)acetate (3pa).
Methyl 2-((diphenylphosphoryl)oxy)-2-(naphthalen-1-yl)acetate (3qa).
Methyl 2-((diphenylphosphoryl)oxy)-2-(thiophen-2-yl)acetate (3ra)
Tert-butyl 2-((diphenylphosphoryl)oxy)-3-phenylpropanoate (3sa).
2,2,2-trifluoro-1-phenylethyl diphenylphosphinate (3ta)
2-oxo-2-phenylethyl diphenylphosphinate (3ua)
Methyl 2-(((di-p-tolylphosphoryl)oxy)-2-phenylacetate (3ab)
Methyl 2-(((bis(4-methoxyphenyl)phosphoryl)oxy)-2-phenylacetate (3ac)
Methyl 2-((bis(4-(trifluoromethoxy)phenyl)phosphoryl)oxy)-2-phenylacetate
(3ad)
Methyl 2-((bis(4-fluorophenyl)phosphoryl)oxy)-2-phenylacetate (3ae)
Methyl 2-((bis(4-chlorophenyl)phosphoryl)oxy)-2-phenylacetate (3af)
Methyl 2-((bis(4-bromophenyl)phosphoryl)oxy)-2-phenylacetate (3ag)
Methyl 2-((bis(3-fluoro-4-methylphenyl)phosphoryl)oxy)-2-phenylacetate (3ah)
Methyl 2-((bis(4-(trifluoromethyl)phenyl)phosphoryl)oxy)-2-phenylacetate (3ai)
Methyl 2-((bis(3-(trifluoromethyl)phenyl)phosphoryl)oxy)-2-phenylacetate (3aj)
Methyl 2-(((bis(2-(trifluoromethyl)phenyl)phosphoryl)oxy)-2-phenylacetate (3ak)
Methyl 2-((di(naphthalen-2-yl)phosphoryl)oxy)-2-phenylacetate (3a1)
Methyl 2-((dibenzylphosphoryl)oxy)-2-phenylacetate (3am)
Methyl 2-((butyl(phenyl)phosphoryl)oxy)-2-phenylacetate (3an)
Methyl 2-((ethoxy(phenyl)phosphoryl)oxy)-2-phenylacetate (3ao)
Methyl 2-((4-oxidodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yl)oxy)-2-phenylacetate (3ap)