Supporting Information

Manganese(III)-mediated Selective Phosphorylation of Direct Synthesis of β-Phosphoryl Enamides

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1. General Methods

$^1$H NMR (400 or 300 MHz) and $^{13}$C NMR (101 or 75 MHz) spectra were determined with CDCl$_3$ or DMSO-$d_6$ as solvent and tetramethylsilane (TMS) as internal standard or 85% H$_3$PO$_4$ as external standard for $^{31}$P NMR (162 MHz). Chemical shifts were reported in ppm from internal TMS ($\delta$), all coupling constants ($J$ values) were reported in Hertz (Hz). High resolution mass spectra were recorded on a TOF machine (ESI). Column chromatography was performed with 300-400 mesh silica gel using flash column techniques. All of the reagents were used directly as obtained commercially unless otherwise noted.

2. Optimization of the reaction conditions

Table S1. Phosphorus-centered radical initiating system screening results

<table>
<thead>
<tr>
<th>Entry</th>
<th>Additive (equiv)</th>
<th>Solvent</th>
<th>T (°C)</th>
<th>Time (h)</th>
<th>Yield (%)$^b$</th>
<th>($E/Z$)$^c$</th>
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<tbody>
<tr>
<td>1</td>
<td>Mn(OAc)$_2$2H$_2$O (2.5)</td>
<td>CH$_3$CN</td>
<td>80</td>
<td>6</td>
<td>40 (55:45)</td>
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</tr>
<tr>
<td>2</td>
<td>Mn(OAc)$_2$2H$_2$O (3)</td>
<td>CH$_3$CN</td>
<td>80</td>
<td>6</td>
<td>39 (53:47)</td>
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</tr>
<tr>
<td>3</td>
<td>Cu(OAc)$_2$ (0.25), K$_2$S$_2$O$_8$ (3)</td>
<td>CH$_3$CN</td>
<td>80</td>
<td>6</td>
<td>30 (34:66)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>AgNO$_3$ (0.05), K$_2$S$_2$O$_8$ (3)</td>
<td>CH$_3$CN</td>
<td>80</td>
<td>6</td>
<td>23 (22:78)</td>
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<tr>
<td>5</td>
<td>CuBr$_2$ (0.1), TBHP (3)</td>
<td>CH$_3$CN</td>
<td>80</td>
<td>6</td>
<td>15 (45:55)</td>
<td></td>
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<tr>
<td>6</td>
<td>CuBr$_2$ (0.1), TBHP (5)</td>
<td>CH$_3$CN</td>
<td>80</td>
<td>6</td>
<td>20 (45:55)</td>
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<tr>
<td>7</td>
<td>CuBr$_2$ (0.1), TBHP (5)</td>
<td>CH$_3$CN</td>
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<td>24 (46:54)</td>
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<td>8</td>
<td>Mn(OAc)$_2$2H$_2$O (0.1), MnO$_2$ (3)</td>
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<td>6</td>
<td>25 (32:68)</td>
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$^a$ Reaction conditions: 1a (1.0 mmol), 2a (2.0 mmol), additive in solvent (10 mL), in air. $^b$ Yield of isolated products. $^c$ Ratio of $E/Z$ determined by isolated yield.

Table S2. Optimization of reaction conditions

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Time (h)</th>
<th>Yield (%)$^b$</th>
<th>($E/Z$)$^c$</th>
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<tbody>
<tr>
<td>1</td>
<td>CH$_3$CN</td>
<td>80</td>
<td>6</td>
<td>40 (55:45)</td>
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</tr>
<tr>
<td>2</td>
<td>CH$_3$CN</td>
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<td>41 (55:45)</td>
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<td>CH$_3$CN</td>
<td>60</td>
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<td>45 (56:44)</td>
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<tr>
<td>4</td>
<td>CH$_3$OH</td>
<td>80</td>
<td>6</td>
<td>35 (60:40)</td>
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<tr>
<td>5</td>
<td>CH$_3$OH</td>
<td>60</td>
<td>6</td>
<td>39 (60:40)</td>
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<tr>
<td>6</td>
<td>CH$_3$OH</td>
<td>60</td>
<td>0.5</td>
<td>53 (68:32)</td>
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<tr>
<td>7</td>
<td>HAc</td>
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<td>6</td>
<td>13 (0:100)</td>
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</tr>
<tr>
<td>8</td>
<td>HAc</td>
<td>60</td>
<td>6</td>
<td>25 (0:100)</td>
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</tr>
<tr>
<td>9</td>
<td>HAc</td>
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<td>10</td>
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<td>80</td>
<td>6</td>
<td>25 (65:35)</td>
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<tr>
<td>11</td>
<td>NMP</td>
<td>60</td>
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<td>35 (60:40)</td>
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<tr>
<td>12</td>
<td>NMP</td>
<td>60</td>
<td>0.5</td>
<td>45 (62:38)</td>
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a) Reaction conditions: 1a (1.0 mmol), 2a (2.0 mmol), Mn(OAc)₃·2H₂O (2.5 equiv), solvent (10 mL) in air. b) Yield of isolated products. c) Ratio of E:Z determined by isolated yield.

Table S3. Base screening results

<table>
<thead>
<tr>
<th>Entry</th>
<th>Additive (equiv)</th>
<th>Temp (°C)</th>
<th>Yield (%)⁵</th>
<th>E:Z</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>Mn(OAc)₃·2H₂O</td>
<td>60</td>
<td>53</td>
<td>(66:34)</td>
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<tr>
<td>2</td>
<td>Mn(OAc)₃·2H₂O, K₂CO₃</td>
<td>60</td>
<td>62</td>
<td>(64:36)</td>
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<tr>
<td>3</td>
<td>Mn(OAc)₃·2H₂O, K₂HPO₄</td>
<td>60</td>
<td>54</td>
<td>(63:37)</td>
</tr>
<tr>
<td>4</td>
<td>Mn(OAc)₃·2H₂O, DMEDA</td>
<td>60</td>
<td>35</td>
<td>(66:34)</td>
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<tr>
<td>5</td>
<td>Mn(OAc)₃·2H₂O, t-BuOK</td>
<td>60</td>
<td>50</td>
<td>(70:30)</td>
</tr>
<tr>
<td>6</td>
<td>Mn(OAc)₃·2H₂O, K₂CO₃</td>
<td>40</td>
<td>68</td>
<td>(67:33)</td>
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<tr>
<td>7</td>
<td>Mn(OAc)₃·2H₂O, K₂CO₃</td>
<td>rt</td>
<td>77</td>
<td>(71:29)</td>
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<tr>
<td>8</td>
<td>Mn(OAc)₃·2H₂O, K₂CO₃</td>
<td>rt</td>
<td>15</td>
<td>(67:33)</td>
</tr>
<tr>
<td>9</td>
<td>Mn(OAc)₃·2H₂O, K₂CO₃</td>
<td>rt</td>
<td>73</td>
<td>(73:27)</td>
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<tr>
<td>10</td>
<td>Mn(OAc)₃·2H₂O, K₂CO₃</td>
<td>rt</td>
<td>20⁶</td>
<td>(69:31)</td>
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<tr>
<td>11</td>
<td>Mn(OAc)₃·2H₂O, K₂CO₃</td>
<td>rt</td>
<td>71⁷</td>
<td>(70:30)</td>
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<tr>
<td>12</td>
<td>Mn(OAc)₃·2H₂O, K₂CO₃</td>
<td>rt</td>
<td>70</td>
<td>(73:27)</td>
</tr>
</tbody>
</table>

a) Reaction conditions: 1a (1.0 mmol), 2a (2.0 mmol), Mn(OAc)₃·2H₂O, MeOH (10 mL) stirring for 0.5 h under air. b) Yield of isolated products. c) Ratio of E:Z determined by isolated yield. d) 1.0 equiv of 2a was used. e) 3.0 equiv of 2a was used.

3. Typical procedure for the synthesis of (E)-N-styrylbenzamide (1a)

An oven-dried 25 mL resealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with (E)-(2-bromovinyl)benzene (900 mg, 4.92 mmol, 1.0 equiv), benzamide (714 mg, 5.90 mmol, 1.2 equiv), CuI (93.7 mg, 0.492 mmol, 10 mol%), and K₂CO₃ (1.36 g, 9.84 mmol, 2.0 equiv). The tube was then evacuated and backfilled with argon (this sequence was repeated a total of three times). N,N′-dimetheylethylenediamine (DMEDA) (212 μL, 1.97 mmol, 40 mol%) were added into the tube followed by anhydrous THF (10.0 mL) via syringe. The sealed tube was placed in a preheated oil bath (80 °C). After stirring at the same temperature for 18 h, the reaction mixture was allowed to cool to room temperature. The reaction mixture was then extracted with ethyl acetate (EtOAc) (20 mL) and deionized water (100 mL) in a separation funnel. The aqueous fraction was further extracted with EtOAc (10 mL × 2). The combined organic fractions were then dried over Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified by flash chromatography on
silica gel (EtOAc/n-Hexane = 1:7, then 1:4) to afford the desired product 1a. Other enamides 1 were prepared according to the reported procedures.¹

4. Typical procedure for the preparation of N-(2-(diphenylphosphoryl)-2-phenylvinyl)benzamide (3a-Z) and (3a-E)

To a solution of CH₃OH (10 mL), (E)-N-styrylbzamide (1a) (0.2231 g, 1.0 mmol), K₂CO₃ (0.2758 g, 2.0 mmol) and diphenylphosphate oxide (2a) (0.4041 g, 2.0 mmol) was added Mn(OAc)₃·2H₂O (0.6700 g, 2.5 mmol) for three times in 10 minutes in air at room temperature, then the mixture was stirred for 20 minutes under same conditions. After completion of the reaction, the solvent was removed under vacuum. To the residue was added water (20 mL) and extracted with ethyl acetate (10 mL × 3). The combined organic fractions were dried over anhydrous Na₂SO₄ and concentrated under vacuum to yield the crude product, which was purified by column chromatography (silica gel, ethyl acetate/petroleum ether (1:8) and CH₃OH/CH₂Cl₂ (1:100) to give pure (Z)-N-(2-(diphenylphosphoryl)-2-phenylvinyl)benzamide (3a-Z) in 22% yield first, then (E)-N-(2-(diphenylphosphoryl)-2-phenylvinyl)benzamide (3a-E) in 55% yield.

5. Scope of substrates: Preparation and reaction of alkyl enamide and N-alkenyl benzamide such as (E)-N-styrylacacetamide (I), (E)-N-(prop-1-en-1-yl)benzamide (II) and (Z)-N-(prop-1-en-1-yl)acetamide (III)

5.1 Procedure for the synthesis of (E)-N-styrylacacetamide (I), (E)-N-(prop-1-en-1-yl)benzamide (II) and (Z)-N-(prop-1-en-1-yl)acetamide (III)

*Synthesis of (E)-N-styrylacacetamide (I)*

```
\[ \text{Br} \quad \text{NH₂} \quad \text{CuI, DMEDA, K₂CO₃} \quad \text{THF, 80 °C} \rightarrow \text{N} \quad \text{CH₃OH} \]
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An oven-dried 25 mL resealable screw-cap test tube equipped with a Teflon-coated magnetic stir bar was charged with (E)-(2-bromovinyl)benzene (900 mg, 4.92 mmol, 1.0 equiv), acetamide (348 mg, 5.90 mmol, 1.2 equiv), CuI (93.7 mg, 0.492 mmol, 10 mol %), and K₂CO₃ (1.36 g, 9.84 mmol, 2.0 equiv). The tube was then evacuated and backfilled with argon (this sequence was repeated a total of three times). N,N’-dimethylethlenediamine (DMEDA) (212 µL, 1.97 mmol, 40 mol %) were added into the tube followed by anhydrous THF (10.0 mL) via syringe. The sealed tube was placed in a
preheated oil bath (80 °C). After stirring at the same temperature for 18 h, the reaction mixture was allowed to cool to room temperature. The reaction mixture was then extracted with ethyl acetate (EtOAc) (20 mL) and deionized water (100 mL) in a separation funnel. The aqueous fraction was further extracted with EtOAc (10 mL × 2). The combined organic fractions were then dried over Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (EtOAc/n-Hexane = 1:7, then 1:4) to afford the desired product I. White solid, 55% yield (400 mg), m.p 116–119 °C. 

\[ ^1H \text{NMR (400 MHz, CDCl}_3\text{): } \delta 7.56–7.48 \text{ (m, 1H), } 7.35–7.23 \text{ (m, 5H), } 7.19–7.14 \text{ (m, 1H), } 6.11 \text{ (d, } J = 14.6 \text{ Hz, 1H), } 2.12 \text{ (s, 3H).} \]

\[ ^{13}C \text{NMR (101 MHz, CDCl}_3\text{): } \delta 168.14, 136.10, 128.70, 126.68, 125.58, 122.76, 112.93, 23.28. \]

**Synthesis of (E)-N-(prop-1-en-1-yl)benzamide (II)**

(E)-N-(prop-1-en-1-yl)benzamide (II) was prepared as the synthetic procedure of compound I. Compound II, white solid, 58% yield (460 mg), m.p 111–113 °C. 

\[ ^1H \text{NMR (400 MHz, CDCl}_3\text{): } \delta 7.88–7.73 \text{ (m, 2H), } 7.64 \text{ (s, 1H), } 7.54–7.49 \text{ (m, 1H), } 7.47–7.41 \text{ (m, 2H), } 7.01–6.93 \text{ (m, 1H), } 5.36–5.27 \text{ (m, 1H), } 1.77–1.71 \text{ (m, 3H).} \]

\[ ^{13}C \text{NMR (101 MHz, CDCl}_3\text{): } \delta 164.35, 133.87, 131.75, 128.63, 127.05, 123.65, 108.96, 14.99. \]

**Synthesis of (Z)-N-(prop-1-en-1-yl)acetamide (III)**

(Z)-N-(prop-1-en-1-yl)acetamide (III) was prepared as the synthetic procedure of compound I. Compound III, white solid, 41% yield (200 mg), m.p 68–70 °C. 

\[ ^1H \text{NMR (400 MHz, CDCl}_3\text{): } \delta 7.09 \text{ (s, 1H), } 6.73–6.65 \text{ (m, 1H), } 4.82–4.72 \text{ (m, 1H), } 2.07 \text{ (s, 3H), } 1.62–1.58 \text{ (m, 3H).} \]

\[ ^{13}C \text{NMR (101 MHz, CDCl}_3\text{): } \delta 167.90, 121.91, 105.48, 23.10, 10.90. \]

5.2 Reaction of (E)-N-styrylacetamide (I), (E)-N-(prop-1-en-1-yl)benzamide (II) and (Z)-N-(prop-1-en-1-yl)acetamide (III) with diphenyl phosphine oxide (2a)

The reactions of I and II with diphenyl phosphine oxide (2a) under the standard reaction conditions gave the trace of amount of the desired products I-P and II-P, respectively, which could be detected with \(^1H\) NMR. No desired product III-P was detected for the reaction of III with diphenyl phosphine oxide (Scheme S1)
Scheme S1. The reaction of (E)-N-styrylacetamide (I), (E)-N-(prop-1-en-1-yl)benzamide (II) and (Z)-N-(prop-1-en-1-yl)acetamide (III) with diphenyl phosphine oxide (2a)

6. Typical procedure for the synthesis of dimethyl (2-benzamido-1-phenylethyl)phosphonate (5)

A solution of dimethyl (2-benzamido-1-phenylvinyl)phosphonate (3k, 3.3 g, 10 mmol) in 200 mL of MeOH was hydrogenated over Raney-Ni (660 mg, 20 mol %) at 40 °C at a pressure of 10 atm for 24 h. After removal of the catalyst by filtration, the solvent was evaporated to give dimethyl (2-benzamido-1-phenylethyl)phosphonate (5) (3.1 g, 95% yield).

7. Typical procedure for the synthesis of β-amino-1-phenylethyl phosphonic acid (6)

A mixture of the dimethyl (2-benzamido-1-phenylethyl)phosphonate (5) (0.133 g, 0.4 mmol) and 8 M hydrochloric acid (20 mL) was refluxed for 12 h. The reaction mixture was then cooled to room temperature, washed with dichloromethane (20 mL × 3) and concentrated under vacuo. To the residue was added MeOH (10 mL), then the mixture was stirred for a few minutes, filtered to remove the undissolved solid. To the filtrate was added propylene oxide (100 μL), then stirred at 0 °C for 30 minutes, filtered to collect formed solid, dried to give β-amino-1-phenylethyl phosphonic acid (6) (65 mg, 81% yield).
8. Structure characterization of compounds 3-8

(Z)-N-(2-(Diphenylphosphoryl)-2-phenylvinyl)benzamide (3a-Z)

White solid, mp 210–211 °C, 22% yield (93 mg). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 12.77 (d, $J = 10.4$ Hz, 1H), 8.14–8.01 (m, 3H), 7.64 (dd, $J = 12.1, 7.5$ Hz, 4H), 7.55 (t, $J = 7.3$ Hz, 3H), 7.49 (t, $J = 7.4$ Hz, 2H), 7.43 (td, $J = 7.6, 2.7$ Hz, 4H), 7.22–7.16 (m, 1H), 7.13 (t, $J = 7.4$ Hz, 2H), 6.87 (d, $J = 7.7$ Hz, 2H).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 163.96, 141.15 (d, $J = 1.0$ Hz), 136.10 (d, $J = 9.7$ Hz), 132.03, 131.86, 131.82 (d, $J = 6.8$ Hz), 130.45, 129.63 (d, $J = 3.9$ Hz), 128.34, 128.05 (d, $J = 12.3$ Hz), 127.81, 127.36, 126.99 (d, $J = 1.3$ Hz), 109.08 (d, $J = 96.0$ Hz).

$^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 35.44. HRMS (ESI-TOF) m/z: (M+H)$^+$ Calcd for C$_{27}$H$_{23}$NO$_2$P 424.1466, found 424.1467.

(E)-N-(2-(Diphenylphosphoryl)-2-phenylvinyl)benzamide (3a-E)

White solid, mp 229–230 °C, 55% yield (232.6 mg). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.09 (d, $J = 11.2$ Hz, 1H), 7.77 (dd, $J = 11.0, 7.9$ Hz, 4H), 7.56–7.62 (m, 1H), 7.53–7.41 (m, 7H), 7.41–7.28 (m, 7H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 163.46, 133.89 (d, $J = 21.9$ Hz), 132.41 (d, $J = 6.8$ Hz), 132.26, 131.86, 131.65 (d, $J = 9.6$ Hz), 131.47 (d, $J = 2.7$ Hz), 130.91 (d, $J = 105.9$ Hz), 129.41 (d, $J = 4.1$ Hz), 129.01, 128.44, 128.07, 127.94, 126.67, 115.64 (d, $J = 106.9$ Hz). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 28.44. HRMS (ESI-TOF) m/z: (M+Na)$^+$ Calcd for C$_{27}$H$_{22}$NO$_2$PNa 446.1286, found 446.1272.

(Z)-2-Chloro-N-(2-(diphenylphosphoryl)-2-phenylvinyl)benzamide (3b-Z)

White solid, mp 185–186 °C, 16% yield (73.1 mg). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 12.19 (d, $J = 10.5$ Hz, 1H), 8.00 (dd, $J = 30.5, 10.7$ Hz, 1H), 7.71 (dd, $J = 7.3, 1.2$ Hz, 1H), 7.64–7.59 (m, 3H), 7.55 (dd, $J = 14.4, 6.9$ Hz, 3H), 7.47–7.32 (m, 7H), 7.22–7.17 (m, 1H), 7.13 (t, $J = 7.4$ Hz, 2H), 6.86 (d, $J = 7.9$ Hz, 1H).
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.43 (d, $J$ = 11.4 Hz, 1H), 7.80–7.73 (m, 5H), 7.69 (dd, $J$ = 14.1, 11.5 Hz, 1H), 7.55–7.50 (m, 2H), 7.48–7.43 (m, 4H), 7.38–7.26 (m, 8H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 162.55, 133.52 (d, $J$ = 22.0 Hz), 132.26, 132.18, 131.72, 131.62, 131.56, 131.48 (d, $J$ = 2.7 Hz), 131.32, 130.24 (d, $J$ = 7.7 Hz), 130.12, 129.72 (d, $J$ = 4.0 Hz), 128.74, 127.99 (d, $J$ = 12.2 Hz), 127.90, 126.97, 116.63 (d, $J$ = 106.1 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 28.16. HRMS (ESI-TOF) m/z: (M+H)$^+$ Calcd for C$_{27}$H$_{22}$ClNO$_2$P 458.1077, found 458.1075.

(Z)-N-(2-(Diphenylphosphoryl)-2-phenylvinyl)-2-fluorobenzamide (3c-Z)

White solid, mp 158–159 °C, 17% yield (74.9 mg). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 12.54–12.42 (m, 1H), 8.16–8.01 (m, 2H), 7.63 (dd, $J$ = 12.0, 7.3 Hz, 4H), 7.56–7.49 (m, 3H), 7.41 (td, $J$ = 7.6, 2.7 Hz, 4H), 7.26 (d, $J$ = 14.9 Hz, 1H), 7.22–7.16 (m, 2H), 7.15–7.10 (m, 2H), 6.87 (d, $J$ = 7.8 Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 161.18 (d, $J$ = 2.1 Hz), 160.56 (d, $J$ = 253.1 Hz), 140.29, 136.27 (d, $J$ = 9.5 Hz), 133.63 (d, $J$ = 9.0 Hz), 131.74, 131.65 (d, $J$ = 10.1 Hz), 131.33 (d, $J$ = 1.6 Hz), 130.55, 129.65 (d, $J$ = 3.9 Hz), 127.95 (d, $J$ = 12.3 Hz), 127.76, 126.99 (d, $J$ = 1.3 Hz), 124.13 (d, $J$ = 3.5 Hz), 120.33 (d, $J$ = 11.3 Hz), 116.16 (d, $J$ = 23.3 Hz), 110.72 (d, $J$ = 95.8 H). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 32.95. HRMS (ESI-TOF) m/z: (M+H)$^+$ Calcd for C$_{27}$H$_{22}$FNO$_2$P 442.1372, found 442.1374.
White solid, mp 232–233 °C, 67% yield (295.4 mg). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.81–8.67 (m, 1H), 8.05 (t, $J$ = 7.4 Hz, 1H), 7.77 (dd, $J$ = 11.5, 7.6 Hz, 4H), 7.73–7.64 (m, 1H), 7.55–7.42 (m, 7H), 7.38–7.32 (m, 2H), 7.32–7.26 (m, 3H), 7.21 (dd, $J$ = 17.7, 7.3 Hz, 1H), 7.01 (dd, $J$ = 12.1, 8.5 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 160.23 (d, $J$ = 248.6 Hz), 160.07 (d, $J$ = 3.3 Hz), 134.21 (d, $J$ = 9.5 Hz), 133.76 (d, $J$ = 22.1 Hz), 132.36 (d, $J$ = 6.7 Hz), 131.90, 131.67 (d, $J$ = 9.7 Hz), 131.45 (d, $J$ = 2.8 Hz), 130.43, 129.40 (d, $J$ = 4.1 Hz), 128.80, 127.98 (d, $J$ = 12.2 Hz), 127.86, 124.70 (d, $J$ = 3.1 Hz), 118.73 (d, $J$ = 10.7 Hz), 116.36 (d, $J$ = 106.4 Hz), 115.73 (d, $J$ = 24.7 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 28.36. HRMS (ESI-TOF) m/z: (M+Na)$^+$ Calcd for C$_{27}$H$_{21}$FNO$_2$PNa 464.1192, found 464.1192.

**White solid, mp 230–231 °C, 12% yield (60.1 mg).** $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 12.82 (d, $J$ = 10.4 Hz, 1H), 8.23 (s, 1H), 8.03 (dd, $J$ = 30.5, 10.5 Hz, 1H), 7.95 (d, $J$ = 7.9 Hz, 1H), 7.68 (dd, $J$ = 8.1, 0.9 Hz, 1H), 7.63 (dd, $J$ = 12.2, 7.2 Hz, 4H), 7.56 (t, $J$ = 6.9 Hz, 2H), 7.44 (t, $J$ = 7.6, 2.9 Hz, 4H), 7.36 (t, $J$ = 7.9 Hz, 1H), 7.23–7.17 (m, 1H), 7.13 (t, $J$ = 7.5 Hz, 2H), 6.86 (d, $J$ = 8.0 Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 162.55, 140.78, 135.89 (d, $J$ = 9.6 Hz), 134.96, 134.19, 131.94 (d, $J$ = 2.7 Hz), 131.62 (d, $J$ = 10.1 Hz), 131.27, 130.97, 130.24, 129.84, 129.58 (d, $J$ = 3.9 Hz), 128.08 (d, $J$ = 12.3 Hz), 127.83, 127.10 (d, $J$ = 1.3 Hz), 125.34, 122.67, 109.99 (d, $J$ = 95.3 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 35.59. HRMS (ESI-TOF) m/z: (M+Na)$^+$ Calcd for C$_{27}$H$_{21}$BrNO$_2$PNa 524.0391, found 524.0395.

**White solid, mp 192–193 °C, 55% yield (275.5 mg).** $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.05 (d, $J$ = 11.3 Hz, 1H), 7.85–7.72 (m, 5H), 7.65 (t, $J$ = 11.5 Hz, 2H), 7.57–7.51 (m, 2H), 7.50–7.44 (m, 4H), 7.39 (dd, $J$ = 13.8, 7.5 Hz, 3H), 7.29 (dt, $J$ = 18.0, 12.6 Hz, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 162.14, 135.16, 133.87, 133.53 (d, $J$ = 23.2 Hz), 132.22 (d, $J$ = 6.4 Hz), 131.64 (d, $J$ = 9.6 Hz), 131.55 (d, $J$ = 2.0 Hz), 131.27, 130.26, 129.90, 129.37 (d, $J$ = 3.5 Hz), 129.05, 128.09, 127.97, 124.82, 122.70, 116.46 (d, $J$ = 105.9 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 28.44. HRMS (ESI-TOF) m/z: (M+Na)$^+$ Calcd for C$_{27}$H$_{21}$BrNO$_2$PNa 524.0391, found 524.0378.
(Z)-4-Bromo-N-(2-(diphenylphosphoryl)-2-phenylvinyl)benzamide (3e-Z)

![Chemical structure](image)

White solid, mp 219–220 °C, 9% yield (45.1 mg). 1H NMR (400 MHz, CDCl3): δ 12.83 (d, J = 10.4 Hz, 1H), 8.03 (dd, J = 30.6, 10.5 Hz, 1H), 7.93 (d, J = 8.5 Hz, 2H), 7.69–7.59 (m, 6H), 7.56 (t, J = 7.0 Hz, 2H), 7.44 (td, J = 7.6, 2.8 Hz, 4H), 7.20 (t, J = 7.2 Hz, 1H), 7.13 (t, J = 7.5 Hz, 2H), 6.86 (d, J = 7.9 Hz, 2H). 13C NMR (101 MHz, CDCl3): δ 162.99, 140.89, 135.92 (d, J = 9.6 Hz), 131.94 (d, J = 2.7 Hz), 131.65, 131.57 (d, J = 4.2 Hz), 131.18 (d, J = 26.5 Hz), 128.92, 128.08 (d, J = 12.3 Hz), 127.84, 127.08 (d, J = 1.2 Hz), 126.98, 109.62 (d, J = 95.5 Hz). 31P NMR (162 MHz, CDCl3): δ 35.74. HRMS (ESI-TOF) m/z: (M+Na)+ Calcd for C27H21BrNO2PNa 524.0391, found 524.0389.

(E)-4-Bromo-N-(2-(diphenylphosphoryl)-2-phenylvinyl)benzamide (3e-E)

![Chemical structure](image)

White solid, mp 222–223 °C, 68% yield (340.7 mg). 1H NMR (400 MHz, CDCl3): δ 8.07 (d, J = 11.4 Hz, 1H), 7.80 (dd, J = 11.9, 7.2 Hz, 4H), 7.68 (dd, J = 13.6, 11.9 Hz, 1H), 7.62–7.54 (m, 4H), 7.54–7.44 (m, 6H), 7.44–7.39 (m, 2H), 7.35 (t, J = 7.3 Hz, 3H). 13C NMR (101 MHz, CDCl3): δ 162.58, 137.71, 133.59 (d, J = 21.9 Hz), 132.29 (d, J = 6.8 Hz), 131.74, 131.69, 131.59, 131.53, 131.51, 131.31, 130.71, 130.25, 129.37 (d, J = 4.1 Hz), 129.04, 128.18, 128.08, 127.96, 127.21, 116.23 (d, J = 106.4 Hz). 31P NMR (162 MHz, CDCl3): δ 28.31. HRMS (ESI-TOF) m/z: (M+Na)+ Calcd for C27H21BrNO2PNa 524.0391, found 524.0382.

(Z)-N-(2-(Diphenylphosphoryl)-2-phenylvinyl)-4-methoxybenzamide (3-M-Z)

![Chemical structure](image)

White solid, mp 213–214 °C, 18% yield (81.5 mg). 1H NMR (400 MHz, CDCl3): δ 12.66 (d, J = 10.2 Hz, 1H), 8.13–7.99 (m, 3H), 7.64 (dd, J = 11.7, 7.7 Hz, 4H), 7.54 (t, J = 6.9 Hz, 2H), 7.44 (d, J = 5.1 Hz, 4H), 7.17 (d, J = 7.0 Hz, 1H), 7.12 (t, J = 7.2 Hz, 2H), 6.97 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 7.3 Hz, 2H), 3.86 (s, 3H). 13C NMR (101 MHz, CDCl3): δ 163.95, 163.03, 141.91, 136.70 (d, J = 9.8 Hz),
132.28 (d, $J = 2.7$ Hz), 132.09 (d, $J = 10.1$ Hz), 131.59 (d, $J = 104.9$ Hz), 130.12 (d, $J = 4.0$ Hz),
129.86, 128.49 (d, $J = 12.3$ Hz), 128.25, 127.36 (d, $J = 1.3$ Hz), 124.99, 114.02, 108.65 (d, $J = 96.6$ Hz),
55.46. $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 35.50. HRMS (ESI-TOF) m/z: (M+Na)$^+$ Calcd for $C_{28}H_{24}NO_3PNa$ 476.1391, found 476.1397.

**$^{(E)}$-N-$\text{(2-(Diphenylphosphoryl)-2-phenylvinyl)-4-methoxybenzamide (3f-E)}$**

![结构式]

White solid, mp 220–221 °C, 56% yield (253.7 mg). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.03 (d, $J = 10.6$
Hz, 1H), 7.87–7.70 (m, 4H), 7.63 (dd, $J = 14.3$, 11.7 Hz, 1H), 7.51 (dd, $J = 9.1$, 5.0 Hz, 4H), 7.48–7.42
(m, 4H), 7.41–7.27 (m, 5H), 6.87 (d, $J = 8.8$ Hz, 2H), 3.81 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$
162.79 (d, $J = 18.2$ Hz), 134.18 (d, $J = 22.4$ Hz), 132.57 (d, $J = 6.8$ Hz), 131.66 (d, $J = 9.6$ Hz), 131.54,
131.42 (d, $J = 2.7$ Hz), 130.49, 129.46 (d, $J = 4.1$ Hz),, 128.98, 128.69, 127.99 (d, $J = 12.1$ Hz), 127.86
(d, $J = 1.2$ Hz), 123.95, 114.83 (d, $J = 107.7$ Hz), 113.68, 55.01. $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 28.73.
HRMS (ESI-TOF) m/z: (M+Na)$^+$ Calcd for $C_{28}H_{24}NO_3PNa$ 476.1391, found 476.1397.

**$^{(Z)}$-N-$\text{(2-(Diphenylphosphoryl)-2-phenylvinyl)-4-methoxybenzamide (3f-Z)}$**

White solid, mp 190–191 °C, 13% yield (56.8 mg). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 12.74 (d, $J = 10.4$
Hz, 1H), 8.12 (dd, $J = 30.7$, 10.6 Hz, 1H), 8.01 (d, $J = 8.1$ Hz, 2H), 7.69 (dd, $J = 12.1$, 7.5 Hz, 4H),
7.60 (t, $J = 7.1$ Hz, 2H), 7.48 (td, $J = 7.6$, 2.6 Hz, 4H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.27–7.21 (m, 1H),
7.18 (t, $J = 7.4$ Hz, 2H), 6.92 (d, $J = 7.7$ Hz, 2H), 2.46 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 163.93,
141.99 (d, $J = 139.8$ Hz), 136.19 (d, $J = 9.7$ Hz), 131.81 (d, $J = 2.7$ Hz), 131.62 (d, $J = 10.1$ Hz),
131.59, 130.55, 129.64 (d, $J = 4.0$ Hz), 129.35, 129.01, 128.02 (d, $J = 12.3$ Hz),, 127.78, 127.40,
126.92 (d, $J = 11.1$ Hz), 108.63 (d, $J = 96.4$ Hz), 21.14. $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 35.37. HRMS
(ESI-TOF) m/z: (M+H)$^+$ Calcd for $C_{28}H_{25}NO_2P$ 438.1623, found 438.1614.

**$^{(E)}$-N-$\text{(2-(Diphenylphosphoryl)-2-phenylvinyl)-4-methylbenzamide (3g-E)}$**

511
White solid, mp 202–203 °C, 60% yield (262.2 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.09 (d, \(J = 11.5\) Hz, 1H), 7.83–7.75 (m, 4H), 7.66 (dd, \(J = 14.3, 11.6\) Hz, 1H), 7.56–7.51 (m, 2H), 7.50–7.43 (m, 6H), 7.41–7.30 (m, 5H), 7.20 (d, \(J = 8.0\) Hz, 2H), 2.38 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 163.86, 143.54, 134.51 (d, \(J = 22.3\) Hz), 132.97 (d, \(J = 6.7\) Hz), 132.13 (d, \(J = 9.6\) Hz), 131.92 (d, \(J = 2.7\) Hz), 131.45 (d, \(J = 105.7\) Hz), 129.92 (d, \(J = 4.1\) Hz), 129.59, 129.49, 129.46, 128.47 (d, \(J = 12.1\) Hz), 128.36 (d, \(J = 1.3\) Hz), 127.18, 115.69 (d, \(J = 107.3\) Hz), 21.54. \(^{31}\)P NMR (162 MHz, CDCl\(_3\)): \(\delta\) 28.56. HRMS (ESI-TOF) \(m/z\): (M+Na)\(^+\) Calcd for C\(_{28}\)H\(_{24}\)N\(_2\)O\(_2\)PNa 460.1442, found 460.1436.

\((Z)\)-N-(2-((Diphenylphosphoryl)-2-phenylvinyl)-4-(trifluoromethyl)benzamide (3h-Z)

White solid, mp 175–176 °C, 10% yield (49.1 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 12.97 (d, \(J = 8.9\) Hz, 1H), 8.18 (d, \(J = 7.1\) Hz, 2H), 8.04 (dd, \(J = 30.4, 10.1\) Hz, 1H), 7.75 (d, \(J = 7.2\) Hz, 2H), 7.68–7.59 (m, 4H), 7.56 (d, \(J = 6.4\) Hz, 2H), 7.45 (s, 4H), 7.20 (d, \(J = 6.6\) Hz, 1H), 7.15 (d, \(J = 6.8\) Hz, 2H), 6.87 (d, \(J = 6.5\) Hz, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 163.10, 141.11, 136.26 (d, \(J = 9.5\) Hz, 4H), 135.96, 133.95 (q, \(J = 32.3\) Hz), 132.48 (d, \(J = 2.4\) Hz), 132.08 (d, \(J = 10.1\) Hz), 131.65, 130.61, 130.04 (d, \(J = 3.8\) Hz), 128.58 (d, \(J = 12.3\) Hz), 128.31 (d, \(J = 8.0\) Hz), 127.66, 125.83 (q, \(J = 3.0\) Hz), 123.67 (q, \(J = 278.4\) Hz), 110.85 (d, \(J = 95.0\) Hz). \(^{31}\)P NMR (162 MHz, CDCl\(_3\)): \(\delta\) 35.79. HRMS (ESI-TOF) \(m/z\): (M+H)\(^+\) Calcd for C\(_{28}\)H\(_{22}\)F\(_3\)NO\(_2\)P 492.1340, found 492.1345.

\((E)\)-N-(2-((Diphenylphosphoryl)-2-phenylvinyl)-4-(trifluoromethyl)benzamide (3h-E)

White solid, mp 199–200 °C, 38% yield (186.6 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.12 (d, \(J = 11.0\) Hz, 1H), 7.81–7.73 (m, 4H), 7.72–7.62 (m, 5H), 7.53 (d, \(J = 7.1\) Hz, 2H), 7.50–7.43 (m, 4H), 7.41–7.35 (m, 2H), 7.31 (d, \(J = 7.5\) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 162.28, 135.19, 133.74 (d, \(J = 33.0\) Hz), 133.35 (d, \(J = 21.7\) Hz), 132.18 (d, \(J = 6.6\) Hz), 131.68, 131.58, 131.55, 130.69 (d, \(J = 105.9\) Hz).
(E)-N-(2-(Diphenylphosphoryl)-2-phenylvinyl)-3,4,5-trimethoxybenzamide (3i)

$$\text{MeO}\begin{array}{c} \begin{array}{c} \text{N} \to \text{PPh}_2 \\ \text{O} \\ \text{MeO} \end{array} \\ \text{Ph} \\ \text{Ph} \\ \text{O} \end{array}$$

White solid, mp 232–233 °C, 20% yield (102.6 mg). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.04 (d, $J = 11.5$ Hz, 1H), 7.77 (dd, $J = 11.9$, 7.1 Hz, 4H), 7.62 (dd, $J = 13.9$, 11.7 Hz, 1H), 7.52 (dd, $J = 10.4$, 4.2 Hz, 2H), 7.49–7.42 (m, 4H), 7.39–7.29 (m, 5H), 6.76 (s, 2H), 3.85 (s, 3H), 3.77 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 162.88, 152.79, 141.46, 134.00 (d, $J = 21.8$ Hz), 132.63 (d, $J = 6.8$ Hz), 131.63 (d, $J = 9.7$ Hz), 131.50 (d, $J = 2.7$ Hz), 130.85 (d, $J = 105.9$ Hz), 129.53 (d, $J = 4.0$ Hz), 128.90, 128.01 (d, $J = 12.2$ Hz), 127.91 (d, $J = 1.0$ Hz), 127.00, 115.56 (d, $J = 107.3$ Hz), 103.95, 60.44, 55.64. $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 28.23. HRMS (ESI-TOF) m/z: (M+Na)$^+$ Calcd for C$_{30}$H$_{21}$F$_3$NO$_2$PNa 514.1160, found 514.1164.

(Z)-N-(2-(Diphenylphosphoryl)-2-phenylvinyl)thiophene-2-carboxamide (3j-Z)

$$\text{S}$$

White solid, mp 185–186 °C, 16% yield (68.6 mg). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 12.70 (d, $J = 10.6$ Hz, 1H), 7.98 (dd, $J = 30.5$, 10.6 Hz, 1H), 7.82 (dd, $J = 3.8$, 1.0 Hz, 1H), 7.67–7.60 (m, 4H), 7.59–7.52 (m, 3H), 7.47–7.40 (m, 4H), 7.21–7.16 (m, 1H), 7.15–7.09 (m, 3H), 6.86 (dd, $J = 7.0$, 1.2 Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 158.80, 140.62 (d, $J = 1.2$ Hz), 137.76, 136.02 (d, $J = 9.6$ Hz), 131.86 (d, $J = 2.7$ Hz), 131.65, 131.55, 130.97 (d, $J = 105.1$ Hz), 129.61 (d, $J = 3.9$ Hz), 129.37, 128.04 (d, $J = 12.3$ Hz), 127.81, 127.57, 127.00 (d, $J = 1.3$ Hz), 108.81 (d, $J = 95.9$ Hz). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 35.40. HRMS (ESI-TOF) m/z: (M+Na)$^+$ Calcd for C$_{23}$H$_{20}$SNO$_2$PNa 452.0850, found 452.0844.

Mixture of (Z)-N-(2-(diphenylphosphoryl)-2-phenylvinyl)thiophene-2-carboxamide (3j-Z) and (E)-N-(2-(diphenylphosphoryl)-2-phenylvinyl)thiophene-2-carboxamide (3j-E)
White solid, 65% yield (278.9 mg). \(3j\)-E : \(3j\)-Z = 22 : 3, analyzed by \(^1\)H NMR spectrum. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.92 (d, \(J = 11.4\) Hz, 1H), 7.81–7.71 (m, 4H), 7.62–7.49 (m, 5H), 7.45 (t, \(J = 7.0\) Hz, 4H), 7.39–7.30 (m, 4H), 7.25–7.21 (m, 1H), 7.07–6.98 (m, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 158.44, 136.89, 133.96 (d, \(J = 22.3\) Hz), 132.80 (d, \(J = 6.7\) Hz), 132.30, 132.12 (d, \(J = 9.7\) Hz), 131.98 (d, \(J = 2.6\) Hz), 131.82, 130.77, 129.91 (d, \(J = 4.1\) Hz), 129.48, 129.34, 128.50 (d, \(J =12.1\) Hz), 128.04, 115.87 (d, \(J = 106.8\) Hz). \(^{31}\)P NMR (162 MHz, CDCl\(_3\)): \(\delta\) 35.41, 28.54. HRMS (ESI-TOF) m/z: (M+Na)^+ Calcd for C\(_{25}\)H\(_{20}\)SNO\(_2\)PNa 452.0850, found 452.0844.

**Dimethyl (Z)-(2-benzoamido-1-phenylvinyl)phosphonate (3k-Z)**

![Dimethyl (Z)-(2-benzoamido-1-phenylvinyl)phosphonate (3k-Z)](image)

White solid, mp 100–101 °C, 17% yield (56.3 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 11.85 (d, \(J = 11.0\) Hz, 1H), 8.17 (dd, \(J = 43.5, 11.1\) Hz, 1H), 8.05–8.00 (m, 2H), 7.56 (d, \(J = 7.2\) Hz, 1H), 7.50 (t, \(J = 7.4\) Hz, 2H), 7.44–7.40 (m, 2H), 7.35 (t, \(J = 7.4\) Hz, 2H), 7.32–7.27 (m, 1H), 3.76 (s, 3H), 3.73 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 163.84, 135.34 (d, \(J = 7.9\) Hz), 132.27, 131.84, 128.42, 128.22, 127.34 (d, \(J = 5.2\) Hz), 127.23, 127.00 (d, \(J = 0.9\) Hz), 105.11, 103.35, 52.09, 52.04. \(^{31}\)P NMR (162 MHz, CDCl\(_3\)): \(\delta\) 23.89. HRMS (ESI-TOF) m/z: (M+H)^+ Calcd for C\(_{17}\)H\(_{19}\)NO\(_4\)P 332.1052, found 332.1063.

**Dimethyl (E)-(2-benzoamido-1-phenylvinyl)phosphonate (3k-E)**

![Dimethyl (E)-(2-benzoamido-1-phenylvinyl)phosphonate (3k-E)](image)

White solid, mp 116–117 °C, 54% yield (178.7 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.20–8.05 (m, 2H), 7.64–7.60 (m, 2H), 7.52 (dd, \(J = 15.0, 7.5\) Hz, 3H), 7.45–7.37 (m, 5H), 3.78 (s, 3H), 3.75 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 163.49, 134.76 (d, \(J = 22.3\) Hz), 132.33, 131.89 (d, \(J = 8.8\) Hz), 129.16 (d, \(J = 1.1\) Hz), 128.70 (d, \(J = 5.1\) Hz), 128.46, 128.11 (d, \(J = 1.9\) Hz), 128.01, 126.74, 108.98 (d, \(J = 197.5\) Hz), 52.30, 52.24. \(^{31}\)P NMR (162 MHz, CDCl\(_3\)): \(\delta\) 21.01. HRMS (ESI-TOF) m/z: (M+Na)^+ Calcd for C\(_{17}\)H\(_{18}\)NO\(_4\)PNa 354.0871, found 354.0869.

*(Z)-N-(2-(Diphenylphosphoryl)-2-(methoxyphenyl)vinyl)benzamide (4a)*

![*(Z)-N-(2-(Diphenylphosphoryl)-2-(methoxyphenyl)vinyl)benzamide (4a)*](image)
White solid, mp 190–191 °C, 18% yield (81.5 mg). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 12.42 (d, $J = 10.0$ Hz, 1H), 8.05 (dd, $J = 7.7$ Hz, 2H), 7.96 (dd, $J = 31.2$, 10.6 Hz, 1H), 7.60 (dd, $J = 11.6$, 8.0 Hz, 4H), 7.48 (dd, $J = 15.8$, 8.5 Hz, 5H), 7.39 (d, $J = 7.0$ Hz, 4H), 7.18 (t, $J = 7.4$ Hz, 1H), 6.89 (d, $J = 6.8$ Hz, 1H), 6.75 (t, $J = 7.3$ Hz, 1H), 6.58 (d, $J = 8.1$ Hz, 1H), 3.18 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 164.32, 157.89 (d, $J = 3.3$ Hz), 141.38, 132.69, 132.38, 132.27 (d, $J = 15.8$ Hz), 131.95, 131.87, 131.85, 131.15, 129.44 (d, $J = 1.8$ Hz), 128.44 (d, $J = 63.9$ Hz), 127.90 (d, $J = 20.2$ Hz), 124.45 (d, $J = 8.5$ Hz), 119.99 (d, $J = 1.1$ Hz), 110.28 (d, $J = 1.0$ Hz), 106.52 (d, $J = 98.2$ Hz), 54.43.

$^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 35.00. HRMS (ESI-TOF) m/z: (M+Na)$^+$ Calcd for C$_{28}$H$_{24}$NO$_3$PNa 476.1391, found 476.1385.

(4b) $^{(Z)}$-N-(2-(Diphenylphosphoryl)-2-(o-tolyl)vinyl)benzamide

White solid, mp 146–147 °C, 11% yield (48.1 mg). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 12.65 (d, $J = 10.5$ Hz, 1H), 8.09 (dd, $J = 5.3$, 3.3 Hz, 2H), 7.90 (dd, $J = 31.7$, 10.5 Hz, 1H), 7.57–7.47 (m, 9H), 7.42–7.36 (m, 4H), 7.13 (t, $J = 7.5$ Hz, 1H), 7.01 (d, $J = 7.5$ Hz, 1H), 6.95 (t, $J = 7.5$ Hz, 1H), 6.80 (d, $J = 7.7$ Hz, 1H), 1.67 (s, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 163.89, 140.57, 138.80 (d, $J = 4.2$ Hz), 133.97 (d, $J = 8.5$ Hz), 132.18, 132.00, 131.76 (d, $J = 2.7$ Hz), 131.48, 131.38, 130.75 (d, $J = 2.9$ Hz), 129.89, 128.34, 127.89 (d, $J = 12.1$ Hz), 127.56 (d, $J = 1.9$ Hz), 127.35, 124.83 (d, $J = 1.5$ Hz), 108.04 (d, $J = 95.0$ Hz), 19.21. $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 34.23. HRMS (ESI-TOF) m/z: (M+Na)$^+$ Calcd for C$_{28}$H$_{24}$NO$_3$PNa 460.1442, found 460.1435.

(4c) $^{(Z)}$-N-(2-(Diphenylphosphoryl)-2-(2-fluorophenyl)vinyl)benzamide

White solid, mp 174–175 °C, 17% yield (74.9 mg). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 12.68 (d, $J = 10.4$ Hz, 1H), 8.18–8.02 (m, 3H), 7.69 (dd, $J = 12.1$, 7.5 Hz, 4H), 7.60 (dd, $J = 8.8$, 4.5 Hz, 3H), 7.54 (t, $J = 7.4$ Hz, 2H), 7.51–7.44 (m, 4H), 7.23 (dd, $J = 13.2$, 7.0 Hz, 1H), 6.93 (dd, $J = 15.3$, 7.8 Hz, 2H), 6.78 (t, $J = 7.6$ Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 163.9, 160.25 (dd, $J = 247.0$, 4.3 Hz), 142.39, 132.40 (t, $J = 2.0$ Hz), 132.12, 131.99, 131.88 (d, $J = 2.7$ Hz), 131.50 (d, $J = 10.1$ Hz), 130.44 (d, $J = 105.5$ Hz), 129.25 (dd, $J = 8.1$, 1.6 Hz), 128.18 (d, $J = 33.6$ Hz), 127.64 (d, $J = 50.9$ Hz), 123.22 (d, $J = 9.6$ Hz).
(Z)-N-(2-(2-Chlorophenyl)-2-(diphenylphosphoryl)vinyl)benzamide (4d)

White solid, mp 180–181 °C, 15% yield (75.2 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 12.63 (d, \(J = 10.5\) Hz, 1H), 8.13–8.06 (m, 2H), 7.99 (dd, \(J = 30.7, 10.6\) Hz, 1H), 7.59 (dd, \(J = 6.6, 5.6\) Hz, 3H), 7.53 (dd, \(J = 11.0, 4.2\) Hz, 4H), 7.49 (t, \(J = 7.4\) Hz, 2H), 7.40 (td, \(J = 7.7, 3.0\) Hz, 4H), 7.22 (d, \(J = 7.8\) Hz, 1H), 7.14 (t, \(J = 7.7\) Hz, 1H), 7.01 (t, \(J = 7.5\) Hz, 1H), 6.88 (d, \(J = 7.7\) Hz, 1H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 164.40, 142.70, 136.56 (d, \(J = 4.5\) Hz), 134.10 (d, \(J = 9.1\) Hz), 132.66 (d, \(J = 2.9\) Hz), 132.61, 132.47, 132.37 (d, \(J = 2.7\) Hz), 131.95 (d, \(J = 10.0\) Hz), 130.59 (d, \(J = 105.3\) Hz), 129.85, 129.26 (d, \(J = 1.7\) Hz), 128.84, 128.44 (d, \(J = 12.3\) Hz), 127.88, 126.21 (d, \(J = 1.3\) Hz), 106.51 (d, \(J = 98.2\) Hz). \(^{31}\)P NMR (162 MHz, CDCl\(_3\)): \(\delta\) 34.70. HRMS (ESI-TOF) \(m/z\): (M+Na)\(^+\) Calcd for C\(_{27}\)H\(_{21}\)ClNO\(_2\)PNa 480.0896, found 480.0893.

Mixture of (E)-N-(2-(diphenylphosphoryl)-2-(m-tolyl)vinyl) benzamide (4e-E) and (Z)-N-(2-(diphenylphosphoryl)-2-(m-tolyl)vinyl) benzamide (4e-Z)

White solid, mp 226–227 °C, 25% yield (109.3 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 12.76 (d, \(J = 10.5\) Hz, 1H), 8.12–8.00 (m, 3H), 7.64 (dd, \(J = 12.1, 7.2\) Hz, 4H), 7.55 (t, \(J = 7.3\) Hz, 3H), 7.50 (d, \(J = 7.7\) Hz, 2H), 7.44 (td, \(J = 7.7, 2.9\) Hz, 4H), 7.05–6.95 (m, 2H), 6.67 (d, \(J = 6.2\) Hz, 1H), 6.64 (s, 1H), 2.15 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 163.95, 140.96 (d, \(J = 1.2\) Hz), 137.41, 135.92 (d, \(J = 9.6\) Hz), 132.18, 131.99, 131.81 (d, \(J = 2.7\) Hz), 131.65 (d, \(J = 10.1\) Hz), 131.12 (d, \(J = 104.9\) Hz), 130.51 (d, \(J = 4.2\) Hz), 128.32, 127.98 (d, \(J = 12.3\) Hz), 127.66 (d, \(J = 1.5\) Hz), 127.57, 127.34, 126.56 (d, \(J = 3.8\) Hz), 109.18 (d, \(J = 96.0\) Hz), 20.77. \(^{31}\)P NMR (162 MHz, CDCl\(_3\)): \(\delta\) 34.70. HRMS (ESI-TOF) \(m/z\): (M+Na)\(^+\) Calcd for C\(_{28}\)H\(_{24}\)NO\(_2\)PNa 460.1442, found 460.1429.
White solid, 60% yield (262.2 mg), **4e-E : 4e-Z = 19 : 1**, analyzed by $^1$H NMR spectrum. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.12 (d, $J = 8.3$ Hz, 1H), 7.78 (s, 4H), 7.58–7.48 (m, 6H), 7.45 (s, 4H), 7.41–7.36 (m, 2H), 7.24 (s, 1H), 7.12 (d, $J = 17.2$ Hz, 3H), 2.28 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 163.43, 138.83, 132.26, 131.99, 131.79 (d, $J = 19.3$ Hz), 131.79, 131.60, 131.52, 130.25, 128.79, 128.44, 128.06, 127.95 (d, $J = 3.2$ Hz), 127.88 (d, $J = 62.2$ Hz), 127.83 (d, $J = 98.9$ Hz), 126.70, 126.28, 21.00.

$^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 35.40, 28.68. HRMS (ESI-TOF) $m/z$: (M+H)$^+$ Calcd for C$_{28}$H$_{25}$NO$_2$P 438.1623, found 438.1608.

(Z)-N-(2-(3-Chlorophenyl)-2-(diphenylphosphoryl)vinyl)benzamide (4f-Z)

White solid, mp 245–246 °C, 20% yield (91.4 mg). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 12.77 (d, $J = 10.6$ Hz, 1H), 8.14–8.04 (m, 3H), 7.68–7.61 (m, 4H), 7.59–7.53 (m, 3H), 7.51–7.43 (m, 6H), 7.16 (dd, $J = 8.0, 0.9$ Hz, 1H), 7.06 (t, $J = 7.9$ Hz, 1H), 6.83 (d, $J = 1.3$ Hz, 1H), 6.78 (d, $J = 7.7$ Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 164.44, 142.16, 138.55 (d, $J = 9.9$ Hz), 134.05, 132.66, 132.59 (d, $J = 2.7$ Hz), 132.43, 132.05 (d, $J = 10.1$ Hz), 131.11 (d, $J = 105.4$ Hz), 130.07 (d, $J = 4.0$ Hz), 129.48, 128.85, 128.68 (d, $J = 12.3$ Hz), 128.15 (d, $J = 3.8$ Hz), 127.86, 127.57 (d, $J = 1.1$ Hz), 108.31 (d, $J = 96.3$ Hz).

$^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 35.32. HRMS (ESI-TOF) $m/z$: (M+Na)$^+$ Calcd for C$_{27}$H$_{23}$ClNO$_2$PNa 480.0896, found 480.0888.

(E)-N-(2-(3-Chlorophenyl)-2-(diphenylphosphoryl)vinyl)benzamide (4f-E)

White solid, mp 233–234 °C, 64% yield (292.5 mg). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.03 (d, $J = 11.6$ Hz, 1H), 7.77 (dd, $J = 11.6, 7.5$ Hz, 4H), 7.65–7.51 (m, 6H), 7.48 (dd, $J = 9.7, 4.4$ Hz, 4H), 7.42 (t, $J = 7.6$ Hz, 2H), 7.37–7.27 (m, 3H), 7.24 (d, $J = 6.4$ Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 163.97, 135.29, 134.88 (d, $J = 13.7$ Hz), 134.74, 132.91, 132.14, 132.05, 131.50, 130.70, 130.44, 129.93 (d, $J =$
4.0 Hz), 129.00, 128.67, 128.55, 128.12 (d, J = 4.1 Hz), 127.18, 114.81 (d, J = 106.3 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 28.50. HRMS (ESI-TOF) m/z: (M+Na)$^+$ Calcd for C$_{27}$H$_{21}$ClNO$_2$PNa 480.0896, found 480.0882.

(Z)-N-(2-(Diphenylphosphoryl)-2-(p-tolyl)vinyl)benzamide (4g-Z)

![Z](image)

White solid, mp 157–158 °C, 19% yield (83.0 mg). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 12.77 (d, J = 10.5 Hz, 1H), 8.11–7.98 (m, 3H), 7.68–7.60 (m, 4H), 7.55 (dd, J = 10.5, 4.2 Hz, 3H), 7.48 (t, J = 7.3 Hz, 2H), 7.43 (td, J = 7.6, 2.9 Hz, 4H), 6.94 (d, J = 7.9 Hz, 2H), 6.75 (d, J = 7.2 Hz, 2H), 2.26 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 163.92, 140.95, 136.78 (d, J = 1.5 Hz), 133.04 (d, J = 9.7 Hz), 132.21, 131.97, 131.81 (d, J = 2.6 Hz), 131.69, 131.59, 130.56, 129.49 (d, J = 3.9 Hz), 128.51, 128.32, 128.07, 127.95, 127.34, 108.95 (d, J = 96.1 Hz), 20.59. $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 35.38. HRMS (ESI-TOF) m/z: (M+H)$^+$ Calcd for C$_{28}$H$_{25}$NO$_2$P 438.1623, found 438.1634.

(Z)-N-(2-(2-(Diphenylphosphoryl)-2-(p-tolyl)vinyl)benzamide (4g-Z)

![E](image)

White solid, mp 223–224 °C, 60% yield (262.2 mg). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.14 (d, J = 11.3 Hz, 1H), 7.76 (dd, J = 11.5, 7.7 Hz, 4H), 7.67–7.62 (m, 1H), 7.57 (d, J = 7.6 Hz, 2H), 7.52–7.48 (m, 3H), 7.47–7.41 (m, 4H), 7.39 (t, J = 7.6 Hz, 2H), 7.18 (dd, J = 20.4, 7.8 Hz, 4H), 2.31 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 163.97, 138.28, 134.28 (d, J = 22.6 Hz), 132.69, 132.41, 132.13 (d, J = 9.6 Hz), 131.91 (d, J = 2.3 Hz), 130.90, 130.21, 129.70 (d, J = 4.1 Hz), 129.61, 128.90, 128.46 (d, J = 12.1 Hz), 127.16, 115.99 (d, J = 107.1 Hz), 21.26. $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 28.67. HRMS (ESI-TOF) m/z: (M+Na)$^+$ Calcd for C$_{28}$H$_{25}$NO$_2$PNa 460.1442, found 460.1433.

(Z)-N-(2-(Diphenylphosphoryl)-2-(4-methoxyphenyl)vinyl)benzamide (4h-Z)

![Z](image)

White solid, mp 166–167 °C, 17% yield (77.0 mg). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 12.75 (d, J = 10.5 Hz, 1H), 129.00, 128.67, 128.55, 128.12 (d, J = 4.1 Hz), 127.18, 114.81 (d, J = 106.3 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 28.50. HRMS (ESI-TOF) m/z: (M+Na)$^+$ Calcd for C$_{27}$H$_{21}$ClNO$_2$PNa 480.0896, found 480.0882.

(E)-N-(2-(Diphenylphosphoryl)-2-(p-tolyl)vinyl)benzamide (4g-E)

![E](image)

White solid, mp 157–158 °C, 19% yield (83.0 mg). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 12.75 (d, J = 10.5 Hz, 1H), 8.11–7.98 (m, 3H), 7.68–7.60 (m, 4H), 7.55 (dd, J = 10.5, 4.2 Hz, 3H), 7.48 (t, J = 7.3 Hz, 2H), 7.43 (td, J = 7.6, 2.9 Hz, 4H), 6.94 (d, J = 7.9 Hz, 2H), 6.75 (d, J = 7.2 Hz, 2H), 2.26 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 163.92, 140.95, 136.78 (d, J = 1.5 Hz), 133.04 (d, J = 9.7 Hz), 132.21, 131.97, 131.81 (d, J = 2.6 Hz), 131.69, 131.59, 130.56, 129.49 (d, J = 3.9 Hz), 128.51, 128.32, 128.07, 127.95, 127.34, 108.95 (d, J = 96.1 Hz), 20.59. $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 35.38. HRMS (ESI-TOF) m/z: (M+H)$^+$ Calcd for C$_{28}$H$_{25}$NO$_2$P 438.1623, found 438.1634.

(Z)-N-(2-(Diphenylphosphoryl)-2-(4-methoxyphenyl)vinyl)benzamide (4h-Z)

![Z](image)

White solid, mp 157–158 °C, 19% yield (83.0 mg). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 12.75 (d, J = 10.5 Hz, 1H), 8.11–7.98 (m, 3H), 7.68–7.60 (m, 4H), 7.55 (dd, J = 10.5, 4.2 Hz, 3H), 7.48 (t, J = 7.3 Hz, 2H), 7.43 (td, J = 7.6, 2.9 Hz, 4H), 6.94 (d, J = 7.9 Hz, 2H), 6.75 (d, J = 7.2 Hz, 2H), 2.26 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 163.92, 140.95, 136.78 (d, J = 1.5 Hz), 133.04 (d, J = 9.7 Hz), 132.21, 131.97, 131.81 (d, J = 2.6 Hz), 131.69, 131.59, 130.56, 129.49 (d, J = 3.9 Hz), 128.51, 128.32, 128.07, 127.95, 127.34, 108.95 (d, J = 96.1 Hz), 20.59. $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 35.38. HRMS (ESI-TOF) m/z: (M+H)$^+$ Calcd for C$_{28}$H$_{25}$NO$_2$P 438.1623, found 438.1634.
Hz, 1H), 8.09–7.97 (m, 3H), 7.68–7.60 (m, 4H), 7.55 (dd, J = 11.1, 4.0 Hz, 3H), 7.49 (d, J = 7.7 Hz, 2H), 7.43 (td, J = 7.6, 3.0 Hz, 4H), 6.77 (dd, J = 8.7, 1.2 Hz, 2H), 6.67 (d, J = 8.7 Hz, 2H), 3.73 (s, 3H).

\[^{13}\text{C} \text{NMR}\ (101 \text{ MHz}, \text{CDCl}_3): \delta 164.38, 159.00 \text{ (d, J = 1.4 Hz)}, 141.29 \text{ (d, J = 1.9 Hz)}, 132.68, 132.45, 132.30 \text{ (d, J = 2.7 Hz)}, 132.10 \text{ (d, J = 10.0 Hz)}, 131.98, 131.34 \text{ (d, J = 3.9 Hz)}, 130.94, 128.80, 128.51 \text{ (d, J = 12.2 Hz)}, 127.81, 113.69, 109.13 \text{ (d, J = 96.4 Hz)}, 55.19. \[^{31}\text{P} \text{NMR}\ (162 \text{ MHz}, \text{CDCl}_3): \delta 35.30. \]

**HRMS (ESI-TOF) m/z**: (M+Na)+ Calcd for C\(_{28}\)H\(_{24}\)NO\(_3\)PNa 476.1391, found 476.1383.

(E)-N-(2-(Diphenylphosphoryl)-2-(4-methoxyphenyl)vinyl)benzamide (4h-E)

![Chemical structure](image)

White solid, mp 234–235 °C, 52% yield (235.6 mg). \(^{1}\text{H} \text{NMR}\ (400 \text{ MHz}, \text{CDCl}_3): \delta 8.10 \text{ (d, J = 11.3 Hz, 1H)}, 7.76 \text{ (dd, J = 11.6, 7.4 Hz, 4H)}, 7.66–7.60 \text{ (m, 1H)}, 7.58 \text{ (d, J = 7.5 Hz, 2H)}, 7.51 \text{ (d, J = 6.0 Hz, 3H)}, 7.46 \text{ (dd, J = 9.8, 4.5 Hz, 4H)}, 7.40 \text{ (t, J = 7.6 Hz, 2H)}, 7.25 \text{ (d, J = 8.3 Hz, 1H)}, 6.89 \text{ (d, J = 8.5 Hz, 2H)}, 3.78 \text{ (s, 3H)}. \[^{13}\text{C} \text{NMR}\ (101 \text{ MHz}, \text{CDCl}_3): \delta 163.93, 159.48, 134.27 \text{ (d, J = 23.7 Hz)}, 132.71, 132.40, 132.13 \text{ (d, J = 9.6 Hz)}, 131.90, 131.17 \text{ (d, J = 3.9 Hz)}, 130.93, 128.93, 128.48 \text{ (d, J = 12.1 Hz)}, 127.16, 124.57 \text{ (d, J = 6.1 Hz)}, 115.75 \text{ (d, J = 107.5Hz)}, 114.96, 55.27. \[^{31}\text{P} \text{NMR}\ (162 \text{ MHz}, \text{CDCl}_3): \delta 28.66. \]**HRMS (ESI-TOF) m/z: (M+H)^+ Calcd for C\(_{28}\)H\(_{25}\)NO\(_3\)P 454.1572, found 454.1564.

(Z)-N-(2-(Diphenylphosphoryl)-2-(4-fluorophenyl)vinyl)benzamide (4i-Z)

![Chemical structure](image)

White solid, mp 136–137 °C, 17% yield (75.0 mg). \(^{1}\text{H} \text{NMR}\ (400 \text{ MHz}, \text{CDCl}_3): \delta 12.73 \text{ (d, J = 10.6 Hz, 1H)}, 8.09–7.97 \text{ (m, 3H)}, 7.63 \text{ (dd, J = 6.7, 5.5 Hz, 3H)}, 7.60 \text{ (d, J = 1.2 Hz, 1H)}, 7.59–7.53 \text{ (m, 3H)}, 7.52–7.42 \text{ (m, 6H)}, 6.82 \text{ (d, J = 7.1 Hz, 4H)}. \[^{13}\text{C} \text{NMR}\ (101 \text{ MHz}, \text{CDCl}_3): \delta 164.44, 163.41 \text{ (d, J = 1.6 Hz)}, 160.95 \text{ (d, J = 1.7 Hz)}, 141.78, 132.58, 132.51, 132.46 \text{ (d, J = 2.7 Hz)}, 132.11, 132.01, 131.91 \text{ (d, J = 3.8 Hz)}, 131.83 \text{ (d, J = 3.8 Hz)}, 131.65, 130.61, 128.83, 128.67, 128.55, 127.83, 115.26 \text{ (d, J = 21.3 Hz)}, 108.53 \text{ (d, J = 96.5 Hz)}. \[^{31}\text{P} \text{NMR}\ (162 \text{ MHz}, \text{CDCl}_3): \delta 35.30. \]**HRMS (ESI-TOF) m/z: (M+H)^+ Calcd for C\(_{27}\)H\(_{22}\)FNO\(_2\)P 442.1372, found 442.1370.

(E)-N-(2-(Diphenylphosphoryl)-2-(4-fluorophenyl)vinyl)benzamide (4i-E)

![Chemical structure](image)
White solid, mp 211–212 °C, 54% yield (238.1 mg). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.01 (d, $J = 11.3$ Hz, 1H), 7.76 (dd, $J = 11.9$, 7.2 Hz, 4H), 7.65–7.60 (m, 1H), 7.57 (d, $J = 7.6$ Hz, 3H), 7.53 (dd, $J = 5.3$, 1.8 Hz, 2H), 7.47 (td, $J = 7.4$, 2.7 Hz, 4H), 7.41 (t, $J = 7.7$ Hz, 2H), 7.32 (dd, $J = 7.3$, 5.5 Hz, 2H), 7.07 (t, $J = 8.6$ Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 163.50, 163.30 (d, $J = 1.4$ Hz), 160.83 (d, $J = 1.6$ Hz), 134.14 (d, $J = 22.7$ Hz), 132.39, 131.73 (d, $J = 0.6$ Hz), 131.66, 131.61 (d, $J = 2.8$ Hz), 131.57, 131.38 (d, $J = 4.1$ Hz), 131.29 (d, $J = 4.1$ Hz), 131.09, 130.04, 128.51, 128.04, 126.66, 116.16 (d, $J = 21.7$ Hz), 114.66 (d, $J = 107.5$ Hz). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 28.73. HRMS (ESI-TOF) m/z: (M+Na)$^+$ Calcd for C$_{27}$H$_{21}$FNO$_2$PNa 464.1192, found 464.1191.

$(Z)$-$N$-$\text{2-}$($\text{4-Chlorophenyl}$)-$2$-(diphenylphosphoryl)$\text{vinyl} \text{benzamide}$ (4j-Z)

White solid, mp 228–229 °C, 14% yield (64.0 mg). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 12.76 (d, $J = 10.5$ Hz, 1H), 8.11–7.98 (m, 3H), 7.64 (dd, $J = 6.7$, 5.5 Hz, 3H), 7.61 (d, $J = 1.2$ Hz, 1H), 7.59–7.53 (m, 3H), 7.52–7.42 (m, 6H), 7.11 (d, $J = 8.3$ Hz, 2H), 6.79 (dd, $J = 8.3$, 1.0 Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 164.44, 141.90 (d, $J = 0.8$ Hz), 135.18 (d, $J = 9.9$ Hz), 133.57 (d, $J = 1.8$ Hz), 132.61, 132.52 (d, $J = 2.7$ Hz), 132.46, 132.05 (d, $J = 10.1$ Hz), 131.34 (d, $J = 3.9$ Hz), 131.15 (d, $J = 105.2$ Hz), 128.84, 128.65 (d, $J = 12.3$ Hz), 128.50, 127.84, 108.37 (d, $J = 96.3$ Hz). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 35.23. HRMS (ESI-TOF) m/z: (M+H)$^+$ Calcd for C$_{27}$H$_{22}$ClNO$_2$P 458.1077, found 458.1073.

$(E)$-$N$-$\text{2-}$($\text{4-Chlorophenyl}$)-$2$-(diphenylphosphoryl)$\text{vinyl} \text{benzamide}$ (4j-E)

White solid, mp 221–222 °C, 52% yield (237.6 mg). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.02 (d, $J = 11.5$ Hz, 1H), 7.81–7.71 (m, 4H), 7.63–7.51 (m, 6H), 7.50–7.44 (m, 4H), 7.42 (t, $J = 7.7$ Hz, 2H), 7.35 (d, $J = 8.5$ Hz, 2H), 7.32–7.28 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 163.52, 134.11 (d, $J = 22.0$ Hz),
134.04 (d, $J = 1.7$ Hz), 132.43, 131.66, 131.56, 131.09, 130.92, 130.85, 130.83, 130.79, 130.04, 129.28, 128.53, 128.18, 128.06, 126.69, 114.52 (d, $J = 107.0$ Hz). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 28.61. HRMS (ESI-TOF) m/z: (M+Na)$^+$ Calcd for C$_{27}$H$_{21}$ClNO$_2$PNa 480.0896, found 480.0878.

(Z)-N-(2-(4-Bromophenyl)-2-(diphenylphosphoryl)vinyl)benzamide (4k-Z)

White solid, mp 175–176 °C, 19% yield (95.2 mg). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 12.77 (d, $J = 10.3$ Hz, 1H), 8.11–7.99 (m, 3H), 7.63 (dd, $J = 12.1, 7.7$ Hz, 3H), 7.56 (dd, $J = 6.3, 4.4$ Hz, 3H), 7.47 (dt, $J = 7.0, 6.2$ Hz, 7H), 7.26 (d, $J = 7.8$ Hz, 2H), 6.73 (d, $J = 7.9$ Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 163.96, 141.39, 135.21 (d, $J = 9.8$ Hz), 132.14, 132.04 (d, $J = 2.7$ Hz), 131.97, 131.57 (d, $J = 10.1$ Hz), 131.15 (d, $J = 3.9$ Hz), 130.97, 130.15, 128.36, 128.18 (d, $J = 12.3$ Hz), 127.36, 121.25 (d, $J = 2.0$ Hz), 107.89 (d, $J = 96.2$ Hz). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 35.08. HRMS (ESI-TOF) m/z: (M+H)$^+$ Calcd for C$_{27}$H$_{22}$BrNO$_2$P 502.0572, found 502.0559.

(E)-N-(2-(4-Bromophenyl)-2-(diphenylphosphoryl)vinyl)benzamide (4k-E)

White solid, mp 224–225 °C, 51% yield (255.5 mg). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.05 (d, $J = 11.0$ Hz, 1H), 7.76 (dd, $J = 11.5, 7.7$ Hz, 4H), 7.60 (t, $J = 11.6$ Hz, 3H), 7.55–7.44 (m, 9H), 7.41 (t, $J = 7.6$ Hz, 2H), 7.24 (d, $J = 7.8$ Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 164.02, 138.60, 134.57 (d, $J = 22.2$ Hz), 132.91, 132.69, 132.13, 132.03, 131.86 (d, $J = 6.7$ Hz), 131.56 (d, $J = 4.2$ Hz), 131.00 (d, $J = 106.3$ Hz), 129.00, 128.61 (d, $J = 12.2$ Hz), 127.19, 122.77 (d, $J = 1.8$ Hz), 114.96 (d, $J = 106.8$ Hz). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 28.62. HRMS (ESI-TOF) m/z: (M+Na)$^+$ Calcd for C$_{27}$H$_{22}$BrNO$_2$PNa 524.0391, found 524.0389.

Dimethyl (2-benzamido-1-phenylethyl)phosphonate (5)

White solid, mp 82–83 °C, 95% yield (3.1 g). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.72 (t, $J = 5.6$ Hz, 1H),
7.70–7.65 (m, 2H), 7.40–7.31 (m, 3H), 7.27 (t, J = 7.4 Hz, 4H), 7.24 – 7.20 (m, 1H), 4.10–3.98 (m, 1H), 3.97–3.83 (m, 1H), 3.74–3.63 (m, 4H), 3.46 (d, J = 10.6 Hz, 3H). 13C NMR (101 MHz, CDCl3): δ 167.54, 134.16, 134.00 (d, J = 6.7 Hz), 131.22, 129.14 (d, J = 6.7 Hz), 128.60 (d, J = 1.9 Hz), 128.23, 127.54 (d, J = 2.7 Hz), 126.92, 53.29 (d, J = 7.0 Hz), 52.70 (d, J = 7.2 Hz), 42.91 (d, J = 135.5 Hz), 40.45. 31P NMR (162 MHz, CDCl3): δ 28.75.

HRMS (ESI-TOF) m/z: (M+Na)+ Calcd for C17H20NO4PNa 356.1028, found 356.1028.

β-Amino-1-phenylethyl phosphonic acid (6)

![β-Amino-1-phenylethyl phosphonic acid](image)

White solid, mp 295–296 °C, 81% yield (65 mg). 1H NMR (400 MHz, D2O): δ 7.40–7.24 (m, 5H), 3.62–3.36 (m, 2H), 3.30–3.11 (m, 1H). 13C NMR (101 MHz, D2O): δ 134.66 (d, J = 6.4 Hz), 129.01, 128.85 (d, J = 4.0 Hz), 127.75, 44.73 (d, J = 127.0 Hz), 40.60. 31P NMR (162 MHz, D2O): δ 16.73.

(2,2-Diphenylvinyl)diphenylphosphine oxide (7)

![2,2-Diphenylvinyl)diphenylphosphine oxide](image)

1H NMR (400 MHz, CDCl3): δ 7.73–7.63 (m, 4H), 7.39–7.28 (m, 11H), 7.24–7.20 (m, 2H), 7.14–7.05 (m, 3H), 6.79 (d, J = 18.3 Hz, 1H). 13C NMR (101 MHz, CDCl3): δ 161.67 (d, J = 2.2 Hz), 141.36 (d, J = 16.2 Hz), 137.50 (d, J = 6.7 Hz), 133.71 (d, J = 106.2 Hz), 130.64 (d, J = 2.6 Hz), 130.40 (d, J = 9.5 Hz), 129.82, 129.08, 128.17, 127.89 (d, J = 3.2 Hz), 127.82, 127.75, 127.12, 119.86 (d, J = 103.9 Hz). 31P NMR (162 MHz, CDCl3): δ 19.21. HRMS (ESI-TOF) m/z: (M+H)+ Calcd for C26H22OP 381.1408, found 381.1395.

(3,5-Di-tert-butyl-4-hydroxybenzyl)diphenylphosphine oxide (BHT-POPh2) (8)

![3,5-Di-tert-butyl-4-hydroxybenzyl)diphenylphosphine oxide](image)

1H NMR (400 MHz, CDCl3): δ 7.71–7.62 (m, 4H), 7.53–7.48 (m, 2H), 7.47–7.40 (m, 4H), 6.73 (d, J = 2.1 Hz, 2H), 5.06 (s, 1H), 3.57 (d, J = 13.8 Hz, 2H), 1.28 (s, 18H). 13C NMR (101 MHz, CDCl3): δ 152.30 (d, J = 3.4 Hz), 135.30 (d, J = 2.6 Hz), 132.02, 131.27 (d, J = 2.6 Hz), 131.00, 130.91, 127.97,
127.86, 126.50 (d, $J = 5.0$ Hz), 120.56 (d, $J = 8.0$ Hz), 37.48 (d, $J = 67.2$ Hz), 33.65, 29.64. $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 30.91. HRMS (ESI-TOF) $m/\ell$: (M+Na)$^+$ Calcd for C$_{27}$H$_{33}$O$_2$PNa 443.2116, found 443.2124.

Reference:

9. $^1$H, $^{13}$C and $^{31}$P NMR spectra of compounds 3-8

Compound 3a-Z

![NMR spectrum image]
Compound 3a-£
Compound 3b-Z
Compound 3b-E
Compound 3c-E
Compound 3d-Z

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533
Compound 3d-\(E\)
Compound 3e-E
Compound 3f-E
Compound 3g-\textit{E}
Compound 3h-Z
Compound 3h-E
Compound 3j-Z
Mixture of 3j-E and 3j-Z
Compound 3k-Z
Compound 4a
Compound 4b
Compound 4c
Compound 4e-Z
Mixture of 4e-E and 4e-Z
Compound 4f-Z
Compound 4f-E
Compound 4g-Z
Compound 4g-E
Compound 4b-Z
Compound 4i-
Compound 4j-Z
Compound 4k-Z
Compound 4k-E
Compound 5
Compound 7
Compound 8
10. $^1$H and $^{13}$C NMR spectra of compounds I-III, and $^1$H NMR spectra of trace amount of I-P and II-P

Compound I
Compound II

**Chemical Structure:**

![Chemical Structure](image)

**NMR Spectrum:**

![NMR Spectrum](image)

**1H NMR Spectral Data:**

- δ 2.01, 3.07
- δ 1.09, 1.69
- δ 3.65, 1.05
- δ 1.03

**Mass Spectral Data:**

- m/z 108.96
- m/z 145.99
- m/z 123.05
- m/z 127.05

**Other Notations:**

- 13C NMR Spectral Data
- 1H NMR Spectral Data
Compound III
$^1$H NMR of trace amount of I-P

$^1$H NMR of trace amount of II-P
11. X-ray crystallographic data for compounds 3a-Z and 3a-E

![Chemical structure of 3a-Z]

**CCDC 1871954**

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Final R indices [I>2 sigma (I)]

R1 = 0.0269  wR2 = 0.0732

R indices (all data)

R1 = 0.0275  wR2 = 0.0738

Largest diff. peak, hole/e.Å⁻³

0.210, -0.251
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Final R indices [I>2σ(I)]
- R1 = 0.0427
- wR2 = 0.0850

R indices (all data)
- R1 = 0.0488
- wR2 = 0.0879

Largest diff. peak, hole/e.Å³
- 0.264, -0.277