

## Supporting Information

### Silver-Mediated Radical Phosphorylation/Cyclization of *N*-Allylbenzamides to Access Phosphoryl-Substituted Dihydroisoquinolones

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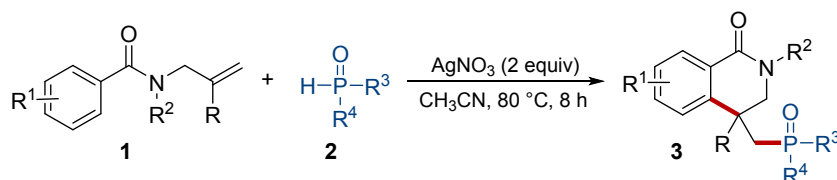
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## 1. General information

All reagents were purchased and used without further purification. All reactions were monitored by thin layer chromatography (TLC), and column chromatography was performed on 200–300 mesh of silica gel purchased from Qing Dao Hai Yang Chemical Industry Co.  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  spectra were recorded on a Bruker Avance 400 MHz spectrometer operating at 400 MHz, 101 MHz, and 162 MHz, respectively. All NMR spectra were recorded in  $\text{CDCl}_3$  at room temperature ( $20 \pm 2^\circ\text{C}$ ). Proton chemical shifts  $\delta$  were given in ppm relative to tetramethylsilane (0.00 ppm) in  $\text{CDCl}_3$ . High resolution mass spectra (HRMS) were obtained with a Waters Micromass Q-ToF Micro instrument using the ESI technique.

## Experiment procedure

### General experimental procedures for phosphoryl-substituted dihydroisoquinolones (**3**)



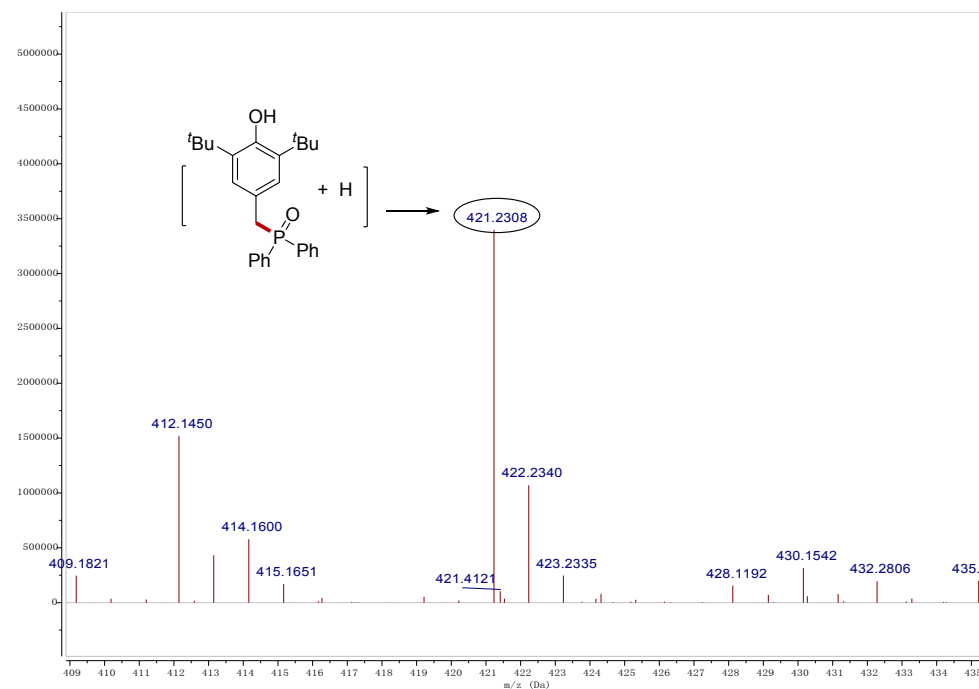
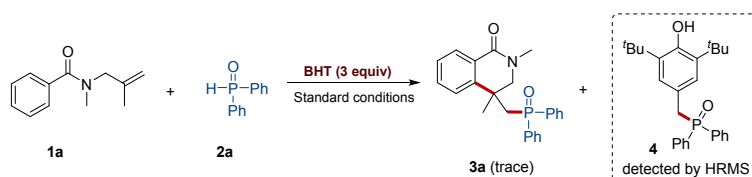
A mixture of *N*-methyl-*N*-(2-methylallyl)benzamides (**1**, 0.5 mmol, 1 equiv), phosphine oxides (1 mmol, 2 equiv),  $\text{AgNO}_3$  (2 equiv) were sequentially added in a 10-mL reaction vial. Then,  $\text{CH}_3\text{CN}$  (3 mL) was added into this reaction system. The reaction vial was sealed and stirred at  $80^\circ\text{C}$  until TLC (petroleum ether: ethyl acetate = 1:1) revealed that conversion of the starting material **1** was completed. Next, the solvent was quenched with water (10 mL), extracted with ethyl acetate ( $3 \times 10$  mL). The combined organic layers were washed with brine (25 mL) and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After filtration, the solvent was evaporated in vacuo. The crude product was purified by silica gel chromatography (petroleum ether: ethyl acetate = 1:1) to give the desired products.

**Table S1**

| entry | $\text{AgNO}_3$ (mol%) | [O] (3 equiv)                    | Yield (%) |
|-------|------------------------|----------------------------------|-----------|
| 1     | $\text{AgNO}_3$ (20)   | BPO                              | trace     |
| 2     | $\text{AgNO}_3$ (20)   | $\text{Mg}(\text{NO}_3)_2$       | 27        |
| 3     | $\text{AgNO}_3$ (20)   | $\text{Zn}(\text{NO}_3)_2$       | 25        |
| 4     | $\text{AgNO}_3$ (20)   | $\text{K}_2\text{S}_2\text{O}_8$ | trace     |

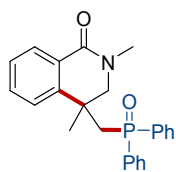
<sup>a</sup> Reaction conditions: **1a** (0.5 mmol), **2a** (1 mmol),  $\text{AgNO}_3$  (20 mol%), oxidant (3 equiv),  $\text{CH}_3\text{CN}$  (3 mL) under  $80^\circ\text{C}$  for 8 h. BPO = benzoyl peroxide. Yields were determined by  $^{31}\text{P}$  NMR using triethylphosphine oxide as internal standard

## 2. Mechanistic studies



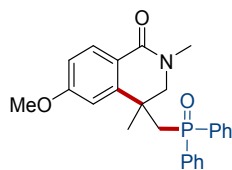
## 3. Characterization of products

### 4-((diphenylphosphoryl)methyl)-2,4-dimethyl-3,4-dihydroisoquinolin-1(2H)-one (3a)



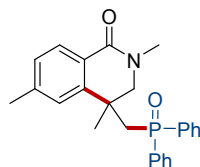
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.02 (dd,  $J$  = 7.7, 1.2 Hz, 1H), 7.69 - 7.63 (m, 4H), 7.48 - 7.39 (m, 6H), 7.35 - 7.31 (m, 1H), 7.29 - 7.24 (m, 2H), 3.80 (d,  $J$  = 12.7 Hz, 1H), 3.50 (d,  $J$  = 12.7 Hz, 1H), 3.01 (s, 3H), 2.74 - 2.67 (m, 1H), 2.58 - 2.52 (m, 1H), 1.59 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  164.6, 145.3 (d,  $J$  = 10.4 Hz), 134.8 (d,  $J$  = 98.7 Hz), 133.4 (d,  $J$  = 98.1 Hz), 132.1, 131.7 (d,  $J$  = 2.7 Hz), 131.4 (d,  $J$  = 2.8 Hz), 130.5 (d,  $J$  = 9.1 Hz), 130.2 (d,  $J$  = 9.2 Hz), 128.8 (d,  $J$  = 11.5 Hz), 128.59 (d,  $J$  = 11.5 Hz), 128.58, 127.8, 127.3, 123.9, 58.1 (d,  $J$  = 5.1 Hz), 37.9 (d,  $J$  = 67.6 Hz), 37.4 (d,  $J$  = 3.5 Hz), 34.9, 23.2 (d,  $J$  = 2.0 Hz);  $^{31}\text{P}$  NMR (162 MHz, Chloroform-*d*)  $\delta$  27.48; HRMS Calcd for  $\text{C}_{24}\text{H}_{25}\text{NO}_2\text{P}$   $[\text{M} + \text{H}]^+$ : 390.1617, found: 390.1612.

4-((diphenylphosphoryl)methyl)-6-methoxy-2,4-dimethyl-3,4-dihydroisoquinolin-1(2H)-one (**3b**)



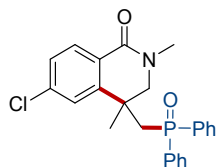
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.95 (d,  $J$  = 8.6 Hz, 1H), 7.67 - 7.59 (m, 4H), 7.48 - 7.34 (m, 6H), 6.76 (d,  $J$  = 2.5 Hz, 1H), 6.67 (dd,  $J$  = 8.7, 2.5 Hz, 1H), 3.77 (s, 3H), 3.66 (d,  $J$  = 12.7 Hz, 1H), 3.47 (d,  $J$  = 12.6 Hz, 1H), 2.98 (s, 3H), 2.66 - 2.55 (m, 2H), 1.59 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  164.6, 162.4, 147.0 (d,  $J$  = 9.6 Hz), 134.9 (d,  $J$  = 98.7 Hz), 133.2 (d,  $J$  = 98.1 Hz), 131.6 (d,  $J$  = 2.8 Hz), 131.3 (d,  $J$  = 2.8 Hz), 130.8, 130.3 (d,  $J$  = 9.1 Hz), 130.1 (d,  $J$  = 9.2 Hz), 128.7 (d,  $J$  = 11.7 Hz), 128.5 (d,  $J$  = 11.7 Hz), 120.7, 112.1, 109.9, 58.7 (d,  $J$  = 6.1 Hz), 55.3, 37.8, (d,  $J$  = 68.7 Hz), 37.5 (d,  $J$  = 3.6 Hz), 34.7, 23.1 (d,  $J$  = 1.8 Hz);  $^{31}\text{P}$  NMR (162 MHz, Chloroform-*d*)  $\delta$  27.46; HRMS Calcd for  $\text{C}_{25}\text{H}_{27}\text{NO}_3\text{P}$   $[\text{M} + \text{H}]^+$ : 420.1723, found: 420.1718.

4-((diphenylphosphoryl)methyl)-2,4,6-trimethyl-3,4-dihydroisoquinolin-1(2H)-one (**3c**)



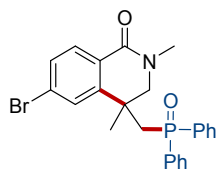
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.88 (d,  $J$  = 7.9 Hz, 1H), 7.67 - 7.60 (m, 4H), 7.47 - 7.34 (m, 6H), 7.04 - 6.97 (m, 2H), 3.68 (d,  $J$  = 12.7 Hz, 1H), 3.47 (d,  $J$  = 12.6 Hz, 1H), 2.99 (s, 3H), 2.67 - 2.55 (m, 2H), 2.25 (s, 3H), 1.60 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  164.8, 144.9 (d,  $J$  = 9.6 Hz), 142.5, 134.9 (d,  $J$  = 98.7 Hz), 133.3 (d,  $J$  = 98.0 Hz), 131.6 (d,  $J$  = 2.8 Hz), 131.3 (d,  $J$  = 2.9 Hz), 130.3 (d,  $J$  = 9.1 Hz), 130.1 (d,  $J$  = 9.2 Hz), 128.73 (d,  $J$  = 11.7 Hz), 128.67, 128.5 (d,  $J$  = 11.7 Hz), 128.1, 125.2, 124.7, 58.7 (d,  $J$  = 6.0 Hz), 37.9 (d,  $J$  = 68.1 Hz), 37.4 (d,  $J$  = 3.7 Hz), 34.8, 23.1, 21.7;  $^{31}\text{P}$  NMR (162 MHz, Chloroform-*d*)  $\delta$  27.50; HRMS Calcd for  $\text{C}_{25}\text{H}_{27}\text{NO}_2\text{P}$   $[\text{M} + \text{H}]^+$ : 404.1774, found: 404.1767.

6-chloro-4-((diphenylphosphoryl)methyl)-2,4-dimethyl-3,4-dihydroisoquinolin-1(2H)-one (**3d**)



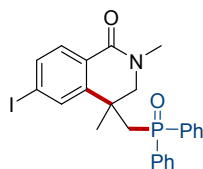
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.92 (d,  $J$  = 8.3 Hz, 1H), 7.69 - 7.64 (m, 4H), 7.51 - 7.39 (m, 6H), 7.25 (d,  $J$  = 2.0 Hz, 1H), 7.16 (dd,  $J$  = 8.3, 2.0 Hz, 1H), 3.78 (d,  $J$  = 12.0 Hz, 1H), 3.51 (d,  $J$  = 12.8 Hz, 1H), 3.04 (s, 3H), 2.68 - 2.54 (m, 2H), 1.59 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  163.8, 146.6 (d,  $J$  = 9.7 Hz), 138.3, 134.7 (d,  $J$  = 99.1 Hz), 132.9 (d,  $J$  = 98.1 Hz), 131.8 (d,  $J$  = 2.8 Hz), 131.5 (d,  $J$  = 2.8 Hz), 130.5, 130.3 (d,  $J$  = 9.7 Hz), 130.1 (d,  $J$  = 9.3 Hz), 128.8 (d,  $J$  = 11.7 Hz), 128.6 (d,  $J$  = 11.8 Hz), 127.7, 126.4, 124.6, 58.4 (d,  $J$  = 5.8 Hz), 37.7 (d,  $J$  = 68.7 Hz), 37.6 (d,  $J$  = 3.4 Hz), 34.9, 23.0 (d,  $J$  = 2.1 Hz);  $^{31}\text{P}$  NMR (162 MHz, Chloroform-*d*)  $\delta$  27.16; HRMS Calcd for  $\text{C}_{24}\text{H}_{23}\text{ClNO}_2\text{P}$   $[\text{M} + \text{H}]^+$ : 424.1228, found: 424.1224.

*6-bromo-4-((diphenylphosphoryl)methyl)-2,4-dimethyl-3,4-dihydroisoquinolin-1(2H)-one (3e)*



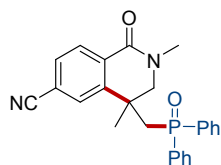
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.83 (d,  $J$  = 8.3 Hz, 1H), 7.68 - 7.63 (m, 4H), 7.49 - 7.39 (m, 7H), 7.32 (dd,  $J$  = 8.3, 1.9 Hz, 1H), 3.76 (d,  $J$  = 12.8 Hz, 1H), 3.51 (d,  $J$  = 12.8 Hz, 1H), 3.03 (s, 3H), 2.67 - 2.54 (m, 2H), 1.58 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  163.8, 146.7 (d,  $J$  = 9.7 Hz), 134.7 (d,  $J$  = 99.0 Hz), 132.8 (d,  $J$  = 98.3 Hz), 131.8 (d,  $J$  = 2.7 Hz), 131.5 (d,  $J$  = 2.8 Hz), 130.7, 130.4 (d,  $J$  = 8.9 Hz), 130.1 (d,  $J$  = 9.2 Hz), 128.8 (d,  $J$  = 11.6 Hz), 128.6 (d,  $J$  = 11.8 Hz), 127.5, 127.0, 126.8, 58.4 (d,  $J$  = 5.8 Hz), 37.7 (d,  $J$  = 67.7 Hz), 37.5 (d,  $J$  = 3.5 Hz), 34.9, 23.0 (d,  $J$  = 2.0 Hz);  $^{31}\text{P}$  NMR (162 MHz, Chloroform-*d*)  $\delta$  27.22; HRMS Calcd for  $\text{C}_{24}\text{H}_{24}\text{BrNO}_2\text{P}$  [ $\text{M} + \text{H}$ ] $^+$ : 468.0723, found: 468.0723.

*4-((diphenylphosphoryl)methyl)-6-iodo-2,4-dimethyl-3,4-dihydroisoquinolin-1(2H)-one (3f)*



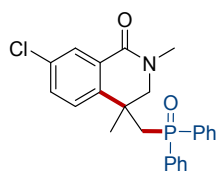
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.68 - 7.61 (m, 6H), 7.55 (dd,  $J$  = 8.2, 1.7 Hz, 1H), 7.50 - 7.39 (m, 6H), 3.73 (d,  $J$  = 12.8 Hz, 1H), 3.50 (dd,  $J$  = 12.8, 1.6 Hz, 1H), 3.03 (s, 3H), 2.65 - 2.54 (m, 2H), 1.58 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  164.0, 146.5 (d,  $J$  = 9.6 Hz), 136.7, 134.7 (d,  $J$  = 99.0 Hz), 133.5, 132.8 (d,  $J$  = 98.2 Hz), 131.7 (d,  $J$  = 2.5 Hz), 131.5 (d,  $J$  = 2.9 Hz), 130.4 (d,  $J$  = 9.1 Hz), 130.2, 130.1 (d,  $J$  = 9.2 Hz), 128.8 (d,  $J$  = 11.9 Hz), 128.7 (d,  $J$  = 11.9 Hz), 127.4, 99.9, 58.5 (d,  $J$  = 5.9 Hz), 38.1, 37.7 (d,  $J$  = 67.7 Hz), 37.4, 34.9, 23.0;  $^{31}\text{P}$  NMR (162 MHz, Chloroform-*d*)  $\delta$  27.23; HRMS Calcd for  $\text{C}_{24}\text{H}_{24}\text{INO}_2\text{P}$  [ $\text{M} + \text{H}$ ] $^+$ : 516.0584, found: 516.0588.

*4-((diphenylphosphoryl)methyl)-2,4-dimethyl-1-oxo-1,2,3,4-tetrahydroisoquinoline-6-carbonitrile (3g)*



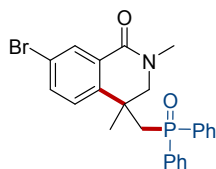
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.02 (d,  $J$  = 8.0 Hz, 1H), 7.64 - 7.55 (m, 5H), 7.47 - 7.35 (m, 7H), 3.76 (d,  $J$  = 13.0 Hz, 1H), 3.53 (dd,  $J$  = 12.9, 1.9 Hz, 1H), 3.07 (s, 3H), 2.67 - 2.54 (m, 2H), 1.60 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  162.7, 145.5 (d,  $J$  = 9.0 Hz), 134.4 (d,  $J$  = 99.7 Hz), 132.5 (d,  $J$  = 98.3 Hz), 131.9 (d,  $J$  = 2.7 Hz), 131.7 (d,  $J$  = 2.8 Hz), 131.6, 130.9, 130.4 (d,  $J$  = 9.1 Hz), 130.0 (d,  $J$  = 9.4 Hz), 129.2, 128.8 (d,  $J$  = 10.7 Hz), 128.7 (d,  $J$  = 10.3 Hz), 128.7, 118.0, 115.3, 58.5 (d,  $J$  = 6.4 Hz), 37.6 (d,  $J$  = 68.7 Hz), 37.5 (d,  $J$  = 3.5 Hz), 35.1, 23.0 (d,  $J$  = 2.1 Hz);  $^{31}\text{P}$  NMR (162 MHz, Chloroform-*d*)  $\delta$  27.10; HRMS Calcd for  $\text{C}_{25}\text{H}_{24}\text{N}_2\text{O}_2\text{P}$  [ $\text{M} + \text{H}$ ] $^+$ : 415.1570, found: 415.1568.

7-chloro-4-((diphenylphosphoryl)methyl)-2,4-dimethyl-3,4-dihydroisoquinolin-1(2H)-one (**3h**)



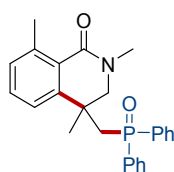
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.93 (d,  $J$  = 2.2 Hz, 1H), 7.68 - 7.56 (m, 4H), 7.52 - 7.36 (m, 6H), 7.25 - 7.19 (m, 2H), 3.69 (d,  $J$  = 12.8 Hz, 1H), 3.52 (dd,  $J$  = 12.8, 2.0 Hz, 1H), 3.06 (s, 3H), 2.65 - 2.56 (m, 2H), 1.64 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  163.3, 142.9 (d,  $J$  = 9.0 Hz), 134.7 (d,  $J$  = 99.1 Hz), 133.6, 132.7 (d,  $J$  = 98.3 Hz), 131.8, 131.7 (d,  $J$  = 2.9 Hz), 131.3 (d,  $J$  = 2.9 Hz), 130.5 (d,  $J$  = 9.1 Hz), 130.1 (d,  $J$  = 9.0 Hz), 129.5, 128.8 (d,  $J$  = 11.6 Hz), 128.6 (d,  $J$  = 11.7 Hz), 128.4, 126.1, 58.8 (d,  $J$  = 6.5 Hz), 38.0 (d,  $J$  = 68.3 Hz), 37.2 (d,  $J$  = 3.5 Hz), 35.1, 23.2;  $^{31}\text{P}$  NMR (162 MHz, Chloroform-*d*)  $\delta$  27.33; HRMS Calcd for  $\text{C}_{24}\text{H}_{24}\text{ClNO}_2\text{P}$  [ $\text{M} + \text{H}$ ] $^+$ : 424.1228, found: 424.1220.

7-bromo-4-((diphenylphosphoryl)methyl)-2,4-dimethyl-3,4-dihydroisoquinolin-1(2H)-one (**3i**)



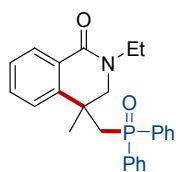
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.04 (d,  $J$  = 2.2 Hz, 1H), 7.65 - 7.61 (m, 2H), 7.58 - 7.53 (m, 2H), 7.48 - 7.31 (m, 7H), 7.15 (d,  $J$  = 8.3 Hz, 1H), 3.65 (d,  $J$  = 12.8 Hz, 1H), 3.49 (dd,  $J$  = 12.8, 2.0 Hz, 1H), 3.03 (s, 3H), 2.65 - 2.53 (m, 2H), 1.61 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  163.2, 143.3 (d,  $J$  = 9.0 Hz), 135.2, 134.67 (d,  $J$  = 100.0 Hz), 134.68, 132.6 (d,  $J$  = 98.4 Hz), 131.7 (d,  $J$  = 2.7 Hz), 131.3 (d,  $J$  = 1.9 Hz), 130.5 (d,  $J$  = 9.1 Hz), 130.1 (d,  $J$  = 9.3 Hz), 129.7, 128.8 (d,  $J$  = 11.6 Hz), 128.6 (d,  $J$  = 11.7 Hz), 126.4, 121.6, 58.7 (d,  $J$  = 6.9 Hz), 37.9 (d,  $J$  = 68.6 Hz), 37.2 (d,  $J$  = 3.5 Hz), 35.1, 23.2;  $^{31}\text{P}$  NMR (162 MHz, Chloroform-*d*)  $\delta$  27.40; HRMS Calcd for  $\text{C}_{24}\text{H}_{24}\text{BrNO}_2\text{P}$  [ $\text{M} + \text{H}$ ] $^+$ : 468.0723, found: 468.0725.

4-((diphenylphosphoryl)methyl)-2,4,8-trimethyl-3,4-dihydroisoquinolin-1(2H)-one (**3j**)



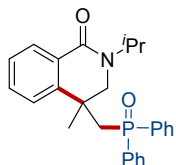
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.68 - 7.62 (m, 4H), 7.48 - 7.36 (m, 6H), 7.18 - 7.10 (m, 2H), 7.00 (d,  $J$  = 7.2 Hz, 1H), 3.75 (d,  $J$  = 12.8 Hz, 1H), 3.47 (d,  $J$  = 12.8 Hz, 1H), 3.08 (s, 3H), 2.68 - 2.51 (m, 5H), 1.53 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  165.1, 146.3 (d,  $J$  = 10.1 Hz), 141.0, 135.1 (d,  $J$  = 98.7 Hz), 133.2 (d,  $J$  = 97.9 Hz), 131.6 (d,  $J$  = 2.7 Hz), 131.3 (d,  $J$  = 2.2 Hz), 131.0, 130.5 (d,  $J$  = 9.1 Hz), 130.1 (d,  $J$  = 9.2 Hz), 128.7 (d,  $J$  = 11.6 Hz), 128.4 (d,  $J$  = 11.7 Hz), 126.5, 121.9, 57.9 (d,  $J$  = 5.1 Hz), 38.0 (d,  $J$  = 3.5 Hz), 37.2 (d,  $J$  = 67.9 Hz), 35.1, 23.4 (d,  $J$  = 1.9 Hz), 22.7;  $^{31}\text{P}$  NMR (162 MHz, Chloroform-*d*)  $\delta$  27.58; HRMS Calcd for  $\text{C}_{25}\text{H}_{27}\text{NO}_2\text{P}$  [ $\text{M} + \text{H}$ ] $^+$ : 404.1774, found: 404.1771.

4-((diphenylphosphoryl)methyl)-2-ethyl-4-methyl-3,4-dihydroisoquinolin-1(2H)-one (**3k**)



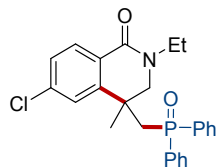
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.04 (dd,  $J = 7.7, 1.4$  Hz, 1H), 7.71 - 7.62 (m, 4H), 7.49 - 7.39 (m, 6H), 7.35 - 7.31 (m, 1H), 7.27 - 7.23 (m, 2H), 3.90 (d,  $J = 12.7$  Hz, 1H), 3.82 - 3.73 (m, 1H), 3.53 (d,  $J = 12.7$  Hz, 1H), 3.43 - 3.35 (m, 1H), 2.75 - 2.67 (m, 1H), 2.59 - 2.53 (m, 1H), 1.57 (s, 3H), 1.23 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  163.8, 145.2 (d,  $J = 10.5$  Hz), 135.1 (d,  $J = 99.0$  Hz), 133.4 (d,  $J = 97.7$  Hz), 132.0, 131.6 (d,  $J = 2.7$  Hz), 131.4 (d,  $J = 2.9$  Hz), 130.5 (d,  $J = 9.1$  Hz), 130.0 (d,  $J = 9.2$  Hz), 128.7 (d,  $J = 12.5$  Hz), 128.6 (d,  $J = 10.6$  Hz), 128.2, 127.3, 123.8, 55.6 (d,  $J = 4.8$  Hz), 42.1, 37.8, 37.42 (d,  $J = 67.7$  Hz), 37.36 (d,  $J = 3.6$  Hz), 37.1, 23.1, 12.6;  $^{31}\text{P}$  NMR (162 MHz, Chloroform-*d*)  $\delta$  27.37; HRMS Calcd for  $\text{C}_{25}\text{H}_{27}\text{NO}_2\text{P}$   $[\text{M} + \text{H}]^+$ : 404.1774, found: 404.1765.

4-((diphenylphosphoryl)methyl)-2-isopropyl-4-methyl-3,4-dihydroisoquinolin-1(2H)-one (**3l**)



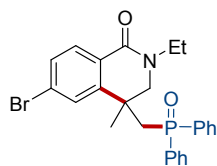
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.06 - 7.97 (m, 1H), 7.68 - 7.60 (m, 4H), 7.46 - 7.36 (m, 6H), 7.30 - 7.24 (m, 2H), 7.22 - 7.18 (m, 1H), 5.14 - 5.08 (m, 1H), 3.81 (d,  $J = 12.7$  Hz, 1H), 3.31 (dd,  $J = 12.8, 1.6$  Hz, 1H), 2.69 - 2.57 (m, 2H), 1.59 (s, 3H), 1.28 (d,  $J = 6.8$  Hz, 3H), 1.20 (d,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  163.5, 144.3 (d,  $J = 9.2$  Hz), 135.4 (d,  $J = 99.0$  Hz), 133.3 (d,  $J = 97.9$  Hz), 131.9, 131.5 (d,  $J = 2.8$  Hz), 131.3 (d,  $J = 2.9$  Hz), 130.5 (d,  $J = 8.9$  Hz), 129.9 (d,  $J = 9.1$  Hz), 128.8, 128.7 (d,  $J = 11.1$  Hz), 128.54 (d,  $J = 12.1$  Hz), 128.45, 127.3, 124.0, 50.4 (d,  $J = 5.8$  Hz), 43.9, 37.1, 37.0 (d,  $J = 3.5$  Hz), 36.7 (d,  $J = 68.7$  Hz), 36.4, 23.4, 20.0, 19.3;  $^{31}\text{P}$  NMR (162 MHz, Chloroform-*d*)  $\delta$  27.10; HRMS Calcd for  $\text{C}_{25}\text{H}_{29}\text{NO}_2\text{P}$   $[\text{M} + \text{H}]^+$ : 418.1930, found: 418.1922.

6-chloro-4-((diphenylphosphoryl)methyl)-2-ethyl-4-methyl-3,4-dihydroisoquinolin-1(2H)-one (**3m**)



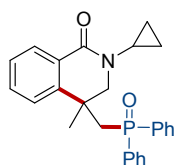
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.91 (d,  $J = 8.3$  Hz, 1H), 7.70 - 7.61 (m, 4H), 7.48-7.38 (m, 6H), 7.22 (d,  $J = 2.0$  Hz, 1H), 7.15 (dd,  $J = 8.3, 2.0$  Hz, 1H), 3.85 - 3.69 (m, 2H), 3.53 - 3.38 (m, 2H), 2.67 - 2.54 (m, 2H), 1.55 (s, 3H), 1.22 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  163.0, 146.4 (d,  $J = 9.6$  Hz), 138.2, 134.9 (d,  $J = 99.5$  Hz), 132.8 (d,  $J = 98.0$  Hz), 131.7 (d,  $J = 2.7$  Hz), 131.5 (d,  $J = 2.9$  Hz), 130.5 (d,  $J = 9.2$  Hz), 130.3, 130.0 (d,  $J = 9.2$  Hz), 128.8 (d,  $J = 12.0$  Hz), 128.6 (d,  $J = 12.1$  Hz), 127.6, 126.7, 124.5, 56.2 (d,  $J = 5.8$  Hz), 42.1, 37.5 (d,  $J = 3.4$  Hz), 37.2 (d,  $J = 67.7$  Hz), 23.0 (d,  $J = 2.1$  Hz), 12.5;  $^{31}\text{P}$  NMR (162 MHz, Chloroform-*d*)  $\delta$  27.16; HRMS Calcd for  $\text{C}_{25}\text{H}_{26}\text{ClNO}_2\text{P}$   $[\text{M} + \text{H}]^+$ : 438.1384, found: 438.1388.

6-bromo-4-((diphenylphosphoryl)methyl)-2-ethyl-4-methyl-3,4-dihydroisoquinolin-1(2H)-one (**3n**)



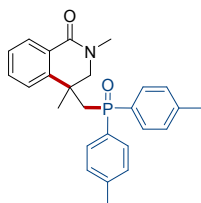
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.84 (d,  $J$  = 8.2 Hz, 1H), 7.69 - 7.61 (m, 4H), 7.48 - 7.38 (m, 7H), 7.31 (dd,  $J$  = 8.3, 1.9 Hz, 1H), 3.84 - 3.69 (m, 2H), 3.53 - 3.37 (m, 2H), 2.66 - 2.56 (m, 2H), 1.56 (s, 3H), 1.22 (t,  $J$  = 7.2 Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  163.1, 146.6 (d,  $J$  = 9.7 Hz), 134.9 (d,  $J$  = 99.6 Hz), 132.8 (d,  $J$  = 97.9 Hz), 131.7 (d,  $J$  = 2.7 Hz), 131.5 (d,  $J$  = 2.8 Hz), 130.6, 130.47 (d,  $J$  = 99.6 Hz), 130.44, 130.0 (d,  $J$  = 9.2 Hz), 128.8 (d,  $J$  = 11.1 Hz), 128.6 (d,  $J$  = 11.1 Hz), 127.5, 127.1, 127.0, 56.3 (d,  $J$  = 5.9 Hz), 42.1, 37.6, 37.4 (d,  $J$  = 3.3 Hz), 37.2 (d,  $J$  = 68.7 Hz), 36.9, 23.0 (d,  $J$  = 2.1 Hz), 12.5;  $^{31}\text{P}$  NMR (162 MHz, Chloroform-*d*)  $\delta$  27.17; HRMS Calcd for  $\text{C}_{25}\text{H}_{26}\text{BrNO}_2\text{P}$  [ $\text{M} + \text{H}$ ] $^+$ : 482.0879, found: 482.0876.

2-cyclopropyl-4-((diphenylphosphoryl)methyl)-4-methyl-3,4-dihydroisoquinolin-1(2H)-one (**3o**)



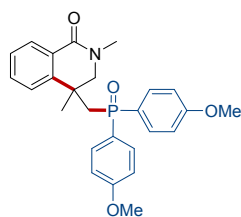
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.02 (dd,  $J$  = 7.7, 1.4 Hz, 1H), 7.69 - 7.58 (m, 4H), 7.47 - 7.37 (m, 6H), 7.32 - 7.28 (m, 1H), 7.25 - 7.19 (m, 2H), 3.90 (d,  $J$  = 12.6 Hz, 1H), 3.43 (d,  $J$  = 12.6 Hz, 1H), 2.92 - 2.87 (m, 1H), 2.64 - 2.48 (m, 2H), 1.53 (s, 3H), 1.04 - 0.75 (m, 4H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  166.0, 145.0 (d,  $J$  = 10.0 Hz), 135.2 (d,  $J$  = 99.0 Hz), 133.1 (d,  $J$  = 97.8 Hz), 132.2, 131.6 (d,  $J$  = 2.7 Hz), 131.4 (d,  $J$  = 2.7 Hz), 130.6 (d,  $J$  = 9.0 Hz), 129.9 (d,  $J$  = 9.2 Hz), 128.8, 128.7 (d,  $J$  = 2.0 Hz), 128.5 (d,  $J$  = 1.7 Hz), 128.3, 127.3, 123.9, 57.0 (d,  $J$  = 5.0 Hz), 37.5 (d,  $J$  = 3.6 Hz), 37.1 (d,  $J$  = 68.3 Hz), 30.1, 23.1 (d,  $J$  = 2.4 Hz), 7.2, 6.1;  $^{31}\text{P}$  NMR (162 MHz, Chloroform-*d*)  $\delta$  27.49; HRMS Calcd for  $\text{C}_{26}\text{H}_{27}\text{NO}_2\text{P}$  [ $\text{M} + \text{H}$ ] $^+$ : 416.1774, found: 416.1780

4-((di-*p*-tolylphosphoryl)methyl)-2,4-dimethyl-3,4-dihydroisoquinolin-1(2H)-one (**3p**)



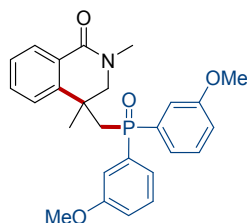
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.04 (dd,  $J$  = 8.0, 1.5 Hz, 1H), 7.57 - 7.51 (m, 4H), 7.36 - 7.32 (m, 1H), 7.29 - 7.25 (m, 2H), 7.24 - 7.20 (m, 4H), 3.85 (d,  $J$  = 12.7 Hz, 1H), 3.49 (d,  $J$  = 12.7 Hz, 1H), 3.00 (s, 3H), 2.72 - 2.65 (m, 1H), 2.50 - 2.44 (m, 1H), 2.37 (s, 3H), 2.35 (s, 3H), 1.56 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  164.6, 145.8 (d,  $J$  = 10.9 Hz), 142.1 (d,  $J$  = 2.8 Hz), 141.8 (d,  $J$  = 2.8 Hz), 132.1, 130.5 (d,  $J$  = 9.4 Hz), 130.5 (d,  $J$  = 101.0 Hz), 130.2 (d,  $J$  = 9.6 Hz), 131.7 (d,  $J$  = 102.0 Hz), 129.4 (d,  $J$  = 12.1 Hz), 129.3, 128.6, 127.8, 127.1, 123.7, 57.9 (d,  $J$  = 4.4 Hz), 38.1 (d,  $J$  = 67.4 Hz), 37.4 (d,  $J$  = 3.6 Hz), 34.8, 23.1 (d,  $J$  = 2.1 Hz), 21.5;  $^{31}\text{P}$  NMR (162 MHz, Chloroform-*d*)  $\delta$  27.80; HRMS Calcd for  $\text{C}_{26}\text{H}_{29}\text{NO}_2\text{P}$  [ $\text{M} + \text{H}$ ] $^+$ : 418.1930, found: 418.1920.

4-((bis(4-methoxyphenyl)phosphoryl)methyl)-2,4-dimethyl-3,4-dihydroisoquinolin-1(2H)-one (**3q**)



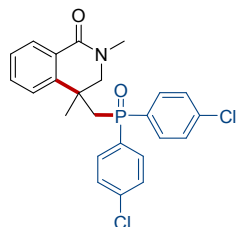
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.03 (dd,  $J$  = 8.0, 1.5 Hz, 1H), 7.58 - 7.52 (m, 4H), 7.36 - 7.32 (m, 1H), 7.27 - 7.23 (m, 2H), 6.94 - 6.89 (m, 4H), 3.85 - 3.82 (m, 4H), 3.80 (s, 3H), 3.48 (d,  $J$  = 12.7 Hz, 1H), 3.02 (s, 3H), 2.64 (m, 1H), 2.43 (m, 1H), 1.56 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  164.6, 162.2 (d,  $J$  = 2.8 Hz), 162.0 (d,  $J$  = 3.0 Hz), 145.7 (d,  $J$  = 10.7 Hz), 133.8 (d,  $J$  = 11.2 Hz), 132.3 (d,  $J$  = 10.4 Hz), 132.0 (d,  $J$  = 10.1 Hz), 128.6, 127.8, 127.2, 126.3 (d,  $J$  = 105.3 Hz), 124.8 (d,  $J$  = 104.5 Hz), 123.8, 114.3 (d,  $J$  = 9.6 Hz), 114.1 (d,  $J$  = 9.6 Hz), 58.0 (d,  $J$  = 4.6 Hz), 55.3 (d,  $J$  = 1.6 Hz), 38.3 (d,  $J$  = 68.2 Hz), 37.4 (d,  $J$  = 3.6 Hz), 34.9, 23.1;  $^{31}\text{P}$  NMR (162 MHz, Chloroform-*d*)  $\delta$  27.80; HRMS Calcd for  $\text{C}_{26}\text{H}_{29}\text{NO}_4\text{P}$   $[\text{M} + \text{H}]^+$ : 450.1829, found: 450.1826.

4-((bis(3-methoxyphenyl)phosphoryl)methyl)-2,4-dimethyl-3,4-dihydroisoquinolin-1(2H)-one (**3r**)



$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.01 (dd,  $J$  = 7.7, 1.5 Hz, 1H), 7.35 - 7.15 (m, 9H), 7.00 - 6.94 (m, 2H), 3.81 - 3.77 (m, 7H), 3.50 (d,  $J$  = 12.7 Hz, 1H), 3.03 (s, 3H), 2.70 - 2.63 (m, 1H), 2.56 - 2.51 (m, 1H), 1.59 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  164.5, 159.7 (d,  $J$  = 15.2 Hz), 159.5, (d,  $J$  = 14.1 Hz), 145.3 (d,  $J$  = 10.3 Hz), 136.1 (d,  $J$  = 97.9 Hz), 134.7 (d,  $J$  = 97.1 Hz), 132.0, 130.0 (d,  $J$  = 13.6 Hz), 129.8 (d,  $J$  = 13.8 Hz), 128.5, 127.9, 127.3, 123.9, 122.5 (d,  $J$  = 9.2 Hz), 122.1 (d,  $J$  = 9.3 Hz), 117.7 (d,  $J$  = 2.8 Hz), 117.5 (d,  $J$  = 2.7 Hz), 115.3 (d,  $J$  = 4.5 Hz), 115.2 (d,  $J$  = 4.3 Hz), 58.2 (d,  $J$  = 5.2 Hz), 55.4 (d,  $J$  = 1.8 Hz), 37.9 (d,  $J$  = 67.7 Hz), 37.4 (d,  $J$  = 3.7 Hz), 34.9, 23.1 (d,  $J$  = 2.1 Hz);  $^{31}\text{P}$  NMR (162 MHz, Chloroform-*d*)  $\delta$  27.46; HRMS Calcd for  $\text{C}_{26}\text{H}_{29}\text{NO}_4\text{P}$   $[\text{M} + \text{H}]^+$ : 450.1829, found: 450.1825.

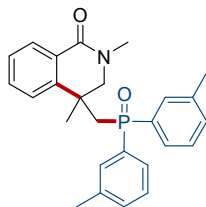
4-((bis(4-chlorophenyl)phosphoryl)methyl)-2,4-dimethyl-3,4-dihydroisoquinolin-1(2H)-one (**3s**)



$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.99 (dd,  $J$  = 7.2, 1.4 Hz, 1H), 7.56 - 7.46 (m, 4H), 7.40 (dd,  $J$  = 8.5, 2.4 Hz, 2H), 7.33 (dd,  $J$  = 8.5, 2.4 Hz, 2H), 7.28 - 7.23 (m, 3H), 3.66 (d,  $J$  = 12.7 Hz, 1H), 3.54 (dd,  $J$  = 12.8, 2.0 Hz, 1H), 3.07 (s, 3H), 2.59 (d,  $J$  = 10.5 Hz, 2H), 1.62 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  164.5, 144.2 (d,  $J$  = 9.0 Hz), 138.5 (d,  $J$  = 3.3 Hz), 138.2 (d,  $J$  = 3.5 Hz), 133.0 (d,  $J$  =

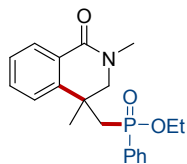
100.3 Hz), 132.1, 131.8 (d,  $J = 10.0$  Hz), 131.4 (d,  $J = 10.1$  Hz), 131.1 (d,  $J = 100.0$  Hz), 129.2 (d,  $J = 12.2$  Hz), 129.0 (d,  $J = 12.3$  Hz), 128.6, 127.9, 127.5, 124.2, 58.9 (d,  $J = 6.7$  Hz), 37.9 (d,  $J = 69.4$  Hz), 37.4 (d,  $J = 3.6$  Hz), 35.0, 23.2 (d,  $J = 2.1$  Hz);  $^{31}\text{P}$  NMR (162 MHz, Chloroform- $d$ )  $\delta$  26.64; HRMS Calcd for  $\text{C}_{24}\text{H}_{23}\text{Cl}_2\text{NO}_2\text{P}$   $[\text{M} + \text{H}]^+$ : 458.0838, found: 458.0831.

*4-((di-*m*-tolylphosphoryl)methyl)-2,4-dimethyl-3,4-dihydroisoquinolin-1(2H)-one (3t)*



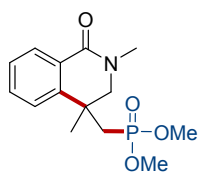
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  8.04 (dd,  $J = 7.7, 1.4$  Hz, 1H), 7.53 - 7.39 (m, 4H), 7.33 - 7.22 (m, 7H), 3.77 (d,  $J = 12.7$  Hz, 1H), 3.50 (d,  $J = 12.7$  Hz, 1H), 3.01 (s, 3H), 2.70 - 2.63 (m, 1H), 2.58 - 2.52 (m, 1H), 2.36 (s, 3H), 2.35 (s, 3H), 1.61 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  164.6, 145.3 (d,  $J = 10.1$  Hz), 138.7 (d,  $J = 11.5$  Hz), 138.4 (d,  $J = 11.5$  Hz), 134.8 (d,  $J = 98.1$  Hz), 133.4 (d,  $J = 97.6$  Hz), 132.4 (d,  $J = 2.9$  Hz), 132.2 (d,  $J = 2.8$  Hz), 132.0, 131.0 (d,  $J = 8.8$  Hz), 130.6 (d,  $J = 9.0$  Hz), 128.6 (d,  $J = 12.3$  Hz), 128.5, 128.4 (d,  $J = 13.1$  Hz), 127.9, 127.4 (d,  $J = 9.4$  Hz), 127.3, 127.2 (d,  $J = 9.5$  Hz), 123.9, 58.3 (d,  $J = 5.1$  Hz), 37.9 (d,  $J = 67.3$  Hz), 37.4 (d,  $J = 3.6$  Hz), 34.8, 23.2 (d,  $J = 2.0$  Hz), 21.4 (d,  $J = 3.1$  Hz);  $^{31}\text{P}$  NMR (162 MHz, Chloroform- $d$ )  $\delta$  27.52; HRMS Calcd for  $\text{C}_{26}\text{H}_{29}\text{NO}_2\text{P}$   $[\text{M} + \text{H}]^+$ : 418.1930, found: 418.1928.

*ethyl-((-2,4-dimethyl-1-oxo-1,2,3,4-tetrahydroisoquinolin-4-yl)methyl)(phenyl)phosphinate (3u),  $dr = 1.15:1$*



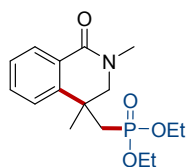
$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  8.06 (dd,  $J = 7.7, 1.5$  Hz, 1H), 7.74 - 7.68 (m, 2H), 7.56 - 7.46 (m, 4H), 7.35 - 7.29 (m, 2H), 3.98 - 3.92 (m, 1H), 3.77 (d,  $J = 12.7$  Hz, 1H), 3.71 - 3.65 (m, 1H), 3.49 (d,  $J = 12.7$  Hz, 1H), 2.99 (s, 3H), 2.48 - 2.21 (m, 2H), 1.75 (s, 3H), 1.20 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  164.50, 164.45, 146.14, 146.01, 145.58, 145.45, 132.61, 132.38, 132.35, 132.19, 132.16, 132.07, 132.02, 131.99, 131.49, 131.39, 131.36, 131.26, 130.85, 128.86, 128.73, 128.67, 128.58, 128.54, 128.51, 127.81, 127.19, 127.15, 123.63, 123.58, 60.46, 60.43, 60.39, 60.36, 57.94, 57.89, 57.51, 57.47, 39.09, 38.62, 38.12, 37.65, 36.71, 36.67, 36.31, 36.29, 35.12, 34.75, 23.11, 23.09, 22.96, 22.94, 16.47, 16.40, 16.38, 16.32;  $^{31}\text{P}$  NMR (162 MHz, Chloroform- $d$ )  $\delta$  40.54, 40.40; HRMS Calcd for  $\text{C}_{20}\text{H}_{25}\text{NO}_3\text{P}$   $[\text{M} + \text{H}]^+$ : 358.1567, found: 358.1563.

*dimethyl((2,4-dimethyl-1-oxo-1,2,3,4-tetrahydroisoquinolin-4-yl)methyl)phosphonate (3v)*



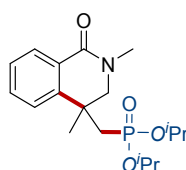
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.11 (dd,  $J = 7.7, 1.4$  Hz, 1H), 7.51 - 7.47 (m, 1H), 7.39-7.34 (m, 2H), 3.70 - 3.52 (m, 8H), 3.20 (s, 3H), 2.22 - 2.13 (m, 1H), 2.07 - 1.99 (m, 1H), 1.61 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  164.5, 145.4 (d,  $J = 14.8$  Hz), 132.1, 128.7, 128.0, 127.4, 123.7, 57.8 (d,  $J = 5.8$  Hz), 52.2 (dd,  $J = 6.8, 1.6$  Hz), 35.5 (d,  $J = 2.2$  Hz), 35.1, 34.4, 33.1, 22.9 (d,  $J = 2.4$  Hz);  $^{31}\text{P}$  NMR (162 MHz, Chloroform-*d*)  $\delta$  29.60; HRMS Calcd for  $\text{C}_{14}\text{H}_{21}\text{NO}_4\text{P}$   $[\text{M} + \text{H}]^+$ : 298.1203, found: 298.1194.

*diethyl((2,4-dimethyl-1-oxo-1,2,3,4-tetrahydroisoquinolin-4-yl)methyl)phosphonate (3w)*



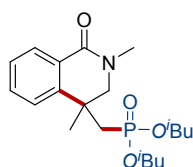
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.11 (dd,  $J = 8.2, 1.5$  Hz, 1H), 7.50 - 7.46 (m, 1H), 7.38 - 7.34 (m, 2H), 4.06 - 3.94 (m, 4H), 3.73 (d,  $J = 12.7$  Hz, 1H), 3.53 (d,  $J = 12.6$  Hz, 1H), 3.20 (s, 3H), 2.21 - 1.98 (m, 2H), 1.61 (s, 3H), 1.28 (t,  $J = 7.1$  Hz, 3H), 1.24 (t,  $J = 7.1$  Hz, 4H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  164.5, 145.6 (d,  $J = 14.9$  Hz), 132.0, 128.6, 128.0, 127.3, 123.7, 61.6 (d,  $J = 5.7$  Hz), 61.5, (d,  $J = 6.1$  Hz), 57.7 (d,  $J = 5.7$  Hz), 35.6 (d,  $J = 2.3$  Hz), 35.2 (d,  $J = 36.4$  Hz), 23.0 (d,  $J = 2.4$  Hz), 16.43 (d,  $J = 6.3$  Hz), 16.35 (d,  $J = 6.3$  Hz);  $^{31}\text{P}$  NMR (162 MHz, Chloroform-*d*)  $\delta$  27.01; HRMS Calcd for  $\text{C}_{16}\text{H}_{25}\text{NO}_4\text{P}$   $[\text{M} + \text{H}]^+$ : 326.1516, found: 326.1502.

*diisopropyl((2,4-dimethyl-1-oxo-1,2,3,4-tetrahydroisoquinolin-4-yl)methyl)phosphonate (3x)*



$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.10 (dd,  $J = 7.7, 1.5$  Hz, 1H), 7.49 - 7.45 (m, 1H), 7.37 - 7.32 (m, 2H), 4.69 - 4.61 (m, 2H), 3.82 (d,  $J = 12.6$  Hz, 1H), 3.50 (d,  $J = 12.6$  Hz, 1H), 3.21 (s, 3H), 2.18 - 2.09 (m, 1H), 1.98 - 1.89 (m, 1H), 1.60 (s, 3H), 1.30 - 1.25 (m, 12H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  164.5, 146.1 (d,  $J = 16.0$  Hz), 132.1, 128.6, 127.9, 127.2, 123.6, 70.3 (d,  $J = 6.5$  Hz), 70.2 (d,  $J = 7.0$  Hz), 57.4 (d,  $J = 4.4$  Hz), 36.1 (d,  $J = 137.4$  Hz), 35.7 (d,  $J = 2.5$  Hz), 35.1, 24.1 (d,  $J = 4.1$  Hz), 24.1 (d,  $J = 5.2$  Hz), 23.0 (d,  $J = 2.4$  Hz);  $^{31}\text{P}$  NMR (162 MHz, Chloroform-*d*)  $\delta$  25.32; HRMS Calcd for  $\text{C}_{18}\text{H}_{29}\text{NO}_4\text{P}$   $[\text{M} + \text{H}]^+$ : 354.1829, found: 354.1830.

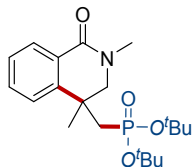
*diisobutyl((2,4-dimethyl-1-oxo-1,2,3,4-tetrahydroisoquinolin-4-yl)methyl)phosphonate (3y)*



$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.11 (dd,  $J = 8.0, 1.5$  Hz, 1H), 7.50 - 7.46 (m, 1H), 7.38 - 7.34 (m, 2H), 3.77 (d,  $J = 12.7$  Hz, 1H), 3.74 - 3.65 (m, 4H), 3.53 (d,  $J = 12.7$  Hz, 1H), 3.21 (s, 3H), 2.23 - 2.15 (m, 1H), 2.08 - 1.99 (m, 1H), 1.90 - 1.81 (m, 2H), 1.61 (s, 3H), 0.92 (d,  $J = 1.4$  Hz, 6H), 0.90 (d,  $J = 1.5$  Hz, 6H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  164.5, 145.7 (d,  $J = 15.2$  Hz), 132.1, 128.6, 127.9, 127.3, 123.7, 71.6 (d,  $J = 6.8$  Hz), 71.5 (d,  $J = 7.2$  Hz), 57.6 (d,  $J = 5.2$  Hz), 35.5 (d,  $J = 2.2$  Hz), 35.1,

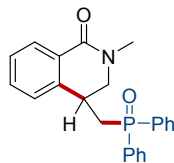
34.3 (d,  $J = 136.6$  Hz), 29.2 (d,  $J = 6.4$  Hz), 29.1, (d,  $J = 7.1$  Hz),, 23.2 (d,  $J = 2.3$  Hz), 18.80, 18.76;  $^{31}\text{P}$  NMR (162 MHz, Chloroform- $d$ )  $\delta$  27.10; HRMS Calcd for  $\text{C}_{20}\text{H}_{33}\text{NO}_4\text{P}$   $[\text{M} + \text{H}]^+$ : 382.2142, found: 382.2133.

*di-tert-butyl((2,4-dimethyl-1-oxo-1,2,3,4-tetrahydroisoquinolin-4-yl)methyl)phosphonate (3z)*



$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  8.10 (dd,  $J = 7.6, 1.5$  Hz, 1H), 7.49 - 7.45 (m, 1H), 7.36 - 7.31 (m, 2H), 3.95 (d,  $J = 12.6$  Hz, 1H), 3.47 (d,  $J = 12.5$  Hz, 1H), 3.21 (s, 3H), 2.16 - 2.08 (m, 1H), 1.91 - 1.82 (m, 1H), 1.58 (s, 3H), 1.49 (s, 9H), 1.45 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  164.6, 146.7 (d,  $J = 16.6$  Hz), 132.0, 128.5, 127.9, 127.0, 123.6, 82.6 (d,  $J = 9.5$  Hz), 82.2 (d,  $J = 8.2$  Hz), 57.0 (d,  $J = 3.7$  Hz), 38.7 (d,  $J = 141.1$  Hz), 35.9 (d,  $J = 2.9$  Hz), 35.0, 30.6 (d,  $J = 4.1$  Hz), 30.4 (d,  $J = 3.8$  Hz), 23.1 (d,  $J = 2.6$  Hz);  $^{31}\text{P}$  NMR (162 MHz, Chloroform- $d$ )  $\delta$  19.02; HRMS Calcd for  $\text{C}_{20}\text{H}_{33}\text{NO}_4\text{P}$   $[\text{M} + \text{H}]^+$ : 382.2142, found: 382.2149.

*4-((diphenylphosphoryl)methyl)-2-methyl-3,4-dihydroisoquinolin-1(2H)-one (3aa)*



$^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  8.07 - 8.04 (m, 1H), 7.78 - 7.70 (m, 4H), 7.55 - 7.45 (m, 6H), 7.34 - 7.28 (m, 2H), 7.04 - 7.02 (m, 1H), 3.76 (dd,  $J = 12.9, 4.0$  Hz, 1H), 3.59 (dd,  $J = 12.9, 2.2$  Hz, 1H), 3.52 - 3.44 (m, 1H), 2.91 (s, 3H), 2.85 - 2.73 (m, 1H), 2.46 - 2.39 (m, 1H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform- $d$ )  $\delta$  164.5, 141.7 (d,  $J = 11.6$  Hz), 133.7 (d,  $J = 98.4$  Hz), 132.5 (d,  $J = 102.0$  Hz), 132.0 (d,  $J = 2.7$  Hz), 131.9 (d,  $J = 2.9$  Hz), 130.6 (d,  $J = 9.2$  Hz), 130.4 (d,  $J = 9.5$  Hz), 128.9 (d,  $J = 8.3$  Hz), 128.8 (d,  $J = 8.2$  Hz), 128.4 (d,  $J = 2.0$  Hz), 127.6, 126.2, 51.7 (d,  $J = 3.2$  Hz), 35.1, 33.2 (d,  $J = 68.3$  Hz), 32.5 (d,  $J = 2.7$  Hz);  $^{31}\text{P}$  NMR (162 MHz, Chloroform- $d$ )  $\delta$  29.29; HRMS Calcd for  $\text{C}_{23}\text{H}_{23}\text{NO}_2\text{P}$   $[\text{M} + \text{H}]^+$ : 376.1461, found: 376.1460

#### 4. $^1\text{H}$ , $^{13}\text{C}$ and $^{31}\text{P}$ NMR spectra

