

## Electronic Supporting Information

# Blue light-promoted [2 + 4] cycloaddition of phosphenes and *N*-acylimines: Highly diastereoselective access to 3,4-dihydro-1,5,2-oxazaphosphinine 2-oxides

Mengyao Zhang, Chongjie Su, Hongguang Du, and Jiayi Xu\*

State Key Laboratory of Chemical Resource Engineering, Department of Organic Chemistry, College of Chemistry, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China. E-mail: [jxxu@mail.buct.edu.cn](mailto:jxxu@mail.buct.edu.cn)

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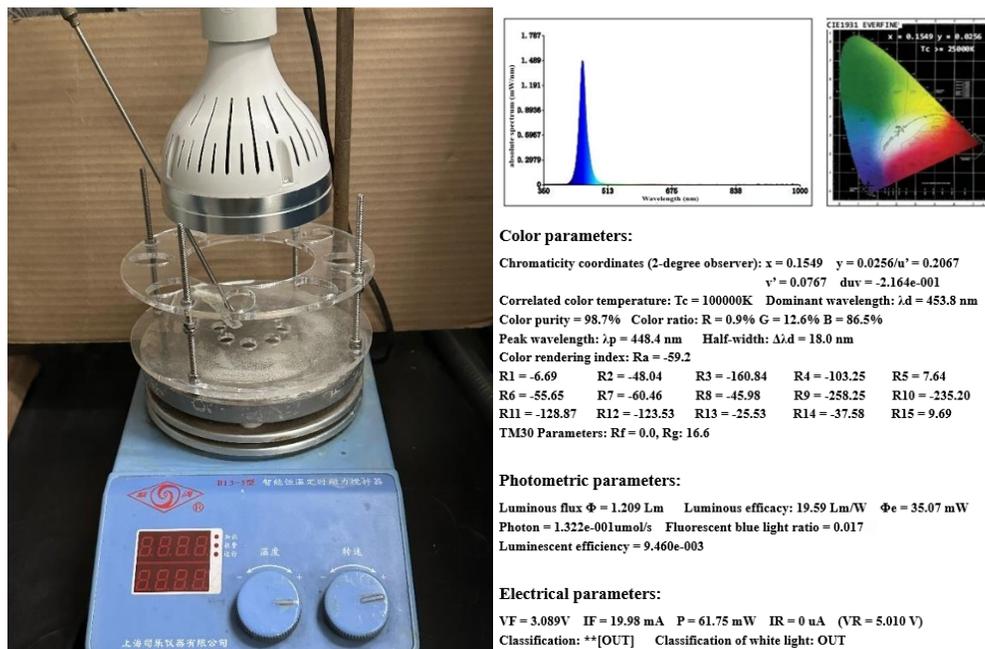
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# 1. Experimental

## 1.1. General information

Unless otherwise noted, all starting materials were purchased from commercial suppliers. MeCN, DCE, PhCl, and DCM were refluxed over CaH<sub>2</sub> and freshly distilled prior to use. THF and toluene were refluxed over sodium with benzophenone as an indicator and freshly distilled prior to use. Column chromatography was performed using silica gel (normal phase, 200–300 mesh) from Branch of Anhui Liangchen Silicon Material Co. Ltd. with petroleum ether (60–90°C fraction) (PE) and ethyl acetate (EA) as eluents. <sup>1</sup>H (400 MHz), <sup>13</sup>C{<sup>1</sup>H} (101 MHz), <sup>31</sup>P{<sup>1</sup>H} (162 MHz), and <sup>19</sup>F{<sup>1</sup>H} (376 MHz) NMR spectra were recorded on a Bruker 400 MHz spectrometer in CDCl<sub>3</sub> with TMS as an internal standard for <sup>1</sup>H NMR, the middle peak of CDCl<sub>3</sub> as an internal standard (77.00) for <sup>13</sup>C{<sup>1</sup>H} NMR in CDCl<sub>3</sub> solution, CF<sub>3</sub>CO<sub>2</sub>H as an external standard (−76.55) for <sup>19</sup>F{<sup>1</sup>H} NMR, and 85% H<sub>3</sub>PO<sub>4</sub> as an external standard (0.0) for <sup>31</sup>P{<sup>1</sup>H} NMR. The chemical shifts (δ) are reported in parts per million (ppm), and multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), dd (double doublet), tt (triple triplet), dq (double quartet), dt (double triplet), m (multiplet). HRMS measurements were carried out on an LC/MSD TOF mass spectrometer. Melting points were obtained on a melting point apparatus and are uncorrected. Crystal structure was determined on a Gemin E single crystal diffractometer. All small scaled thermal reactions were heated in a heating mantle under stirring, while large scale thermal reactions were heated in an oil bath under stirring. Microwave reactions were performed using a commercial CEMSP microwave reactor with an external IR sensor and in a closed reaction vessel. All photo-promoted reactions were set up on the bench top while subjected to irradiation from blue LEDs (440–450 nm, 10 W), with the distance of 8 cm between the light source and the irradiated vessel (Figure S1).

All aryl(diazo)methyl(diaryl)phosphine oxides **1a–1d** and diazo(phenyl)methyl(ethyl(phenyl)phosphine oxide (**1e**) were prepared according to our previous method.<sup>1</sup>

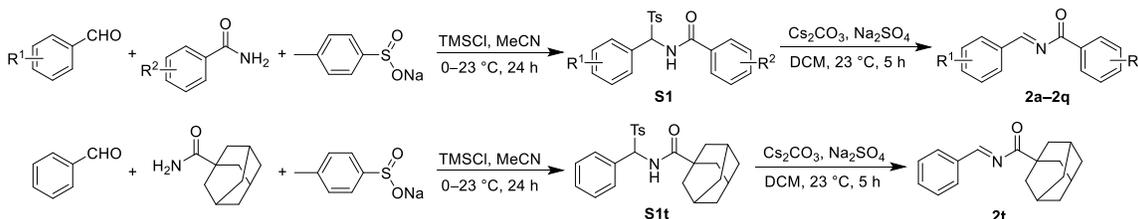


**Figure S1.** Photoreaction equipment: commercial blue LEDs (10 W,  $\lambda = 440–450$  nm) with parameters and electromagnetic stirrer

**Caution!** Although diazo compounds are potential explosives, diazomethylphosphine oxides used in this investigation are safe and their explosion never happens.

## 1.2. Synthesis of *N*-acyl imines **2**<sup>2</sup>

### A. General procedure for the synthesis of *N*-benzoyl imines **2a–2q** and **2t**

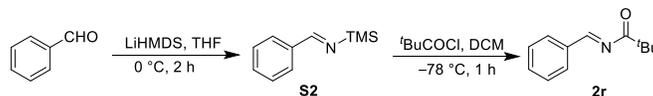


**Scheme S1.** Synthesis of *N*-benzoyl imines **2a–2q** and **2t**

**Step 1:** To a mixture of an aldehyde (5.0 mmol, 1.0 equiv.), sodium *p*-toluenesulfonate (1.34 g, 7.5 mmol, 1.5 equiv.), and an amide (7.5 mmol, 1.5 equiv.) in MeCN (60 mL) at 0 °C was added TMSCl (1.27 mL, 10.0 mmol, 2 equiv.) dropwise. Upon completion of addition the reaction was allowed to warm to room temperature and stirred for 24 hours. Then, water (60 mL) was added and the reaction was stirred for 30 minutes. The resulting precipitate was isolated by filtration, washed with water (3 × 30 mL), and dried under vacuum at 50 °C for 16 hours to yield the corresponding  $\alpha$ -amido sulfone **S1** as colorless crystals.

**Step 2:** To a 50 mL round bottom flask equipped with a magnetic stir bar was added Cs<sub>2</sub>CO<sub>3</sub> (1.65 g, 5 mmol) and Na<sub>2</sub>SO<sub>4</sub> (0.7 g, 10 mmol). The solids were flame-dried under high vacuum and allowed to cool. CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was added. The resulting slurry was vigorously stirred under N<sub>2</sub> and the requisite  $\alpha$ -amido sulfone **S1** (1 mmol, 1.0 equiv.) was added in one portion. After stirring at 23 °C for 5 h, hexane (15 mL) was added and the mixture was filtered through celite. The celite was rinsed with hexane (2 × 10 mL) and the resulting filtrate was concentrated under reduced pressure. This concentrated material was dissolved in hexane and filtered through a cotton plug. Removal of the filtrate in vacuo provided *N*-benzoyl imine (**2a–2q** or **2t**).

### B. General procedure for the synthesis of *N*-benzylidenepivalamide (**2r**)

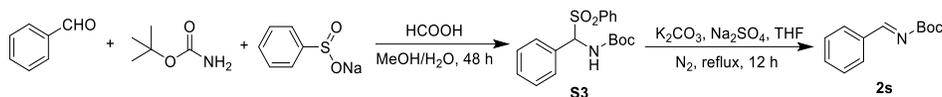


**Scheme S2.** Synthesis of *N*-benzylidenepivalamide (**2r**)

**Step 1:** To an ice-bath cooled solution of benzaldehyde (0.51 mL, 5 mmol) in THF (2.5 mL) was added a solution of LiHMDS (0.84 g, 5 mmol) in THF (20 mL) over a period of 10 min under argon. Direct fractional distillation at 45–46°C/1 mmHg of the resulting suspension gave *N*-(trimethylsilyl)benzaldimine (**S2**) as a light yellow liquid, which was stored under argon at 0 °C.

**Step 2:** To a solution of *N*-trimethylsilylbenzaldimine (**S2**) (354 mg, 2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was added pivaloyl chloride (0.25 mL, 2 mmol) dropwise at –78 °C. After stirring for 1 h at room temperature, the solvent and TMSCl were removed under reduced pressure to obtain *N*-benzylidenepivalamide (**2r**) as colorless crystals.

C. General procedure for the synthesis of *tert*-butyl benzylidenecarbamate (**2s**)



**Scheme S3.** Synthesis of *tert*-butyl benzylidenecarbamate (**2s**)

**Step 1:** A mixture of benzaldehyde (1.53 mL, 15.0 mmol, 1.5 equiv.), *tert*-butyl carbamate (1.17 g, 10.0 mmol, 1.0 equiv.), sodium *p*-toluenesulfonate (3.28 g, 20.0 mmol, 2.0 equiv.), and formic acid (0.76 mL, 20.0 mmol, 2.0 equiv.) in methanol (10 mL) and water (20 mL) was stirred at room temperature for 48 h. The resulting precipitate was filtered and washed with water and diethyl ether. After drying under vacuum, the sulfonyl amine product **S3** was obtained as colorless crystals.

**Step 2:** A 50 mL round bottom flask containing potassium carbonate (1.66 g, 12.0 mmol, 6.0 equiv.) was flame dried. After the flask was cooled to room temperature under N<sub>2</sub>, sulfonyl amine **S3** (694 mg, 2.0 mmol, 1.0 equiv.) and sodium sulfate (1.99 g, 14.0 mmol, 7.0 equiv.) were added along with dry THF (15 mL). The mixture was refluxed under N<sub>2</sub> for 12 h. Then, the reaction was allowed to cool to room temperature, filtered through Celite, and the filtrate was concentrated to obtain *tert*-butyl benzylidenecarbamate (**2s**).

**Caution:** Compounds **2** were prepared in 70–90% yields. Most of them are unstable and used directly after preparation.

**(E)-N-Benzylideneadamantane-1-carboxamide (2t)**

Colorless crystals, 172 mg, yield 13%. m.p. = 79–81 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.39 (s, 1H), 7.86–7.75 (m, 2H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.47 (dd, *J* = 8.3, 6.7 Hz, 2H), 2.08–2.00 (m, 3H), 1.98–1.92 (m, 6H), 1.78–1.70 (m, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 160.8, 134.6, 132.7, 129.5, 128.8, 43.0, 38.7, 36.5, 28.0. HRMS (ESI) *m/z*: Calcd for C<sub>18</sub>H<sub>22</sub>NO<sup>+</sup>, [M + H]<sup>+</sup>: 268.1696; Found 268.1702.

**1.3. General procedure for the reaction of diazomethylphosphine oxides **1** and *N*-acylimines **2****

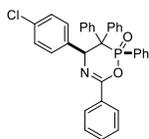
**2**



**Scheme S4.** Reaction of diazomethylphosphine oxides **1** and *N*-acylimines **2**

To a 10 mL glass reaction tube were added diazomethylphosphine oxide **1** (0.6 mmol, 3 equiv.), *N*-acylimine **2** (0.2 mmol, 1 equiv.), and dry DCM (3 mL) at room temperature, then the reaction mixture was stirred at room temperature for 4 h under blue light LED irradiation. After completion of the reaction, the mixture was concentrated under reduced pressure and the residue was subjected to silica gel column chromatography with a mixture of petroleum ether (PE) and ethyl acetate (EA) (PE:EA 8:1 to 4:1, *v/v*) as eluent to give product **3**.

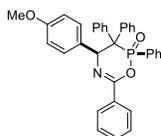
***trans*-4-(4-Chlorophenyl)-2,3,3,6-tetraphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3aa)**



Colorless crystals, 94 mg, yield 88%, 93:7 dr. m.p. = 140–142 °C,  $R_f$  = 0.37 (PE: EA = 4:1, v/v).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.19–8.01 (m, 2H), 7.69 (dt,  $J$  = 8.7, 1.5 Hz, 2H), 7.57–7.35 (m, 6H), 7.30–7.25 (m, 3H), 7.24–7.19 (m, 2H), 7.11–7.00 (m, 5H), 6.92 (t,  $J$  = 7.8 Hz, 2H), 6.88–6.83 (m, 2H), 6.24 (d,  $J$  = 6.5 Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  149.6 (d,  $J$  = 6.7 Hz), 138.7 (d,  $J$  = 2.0 Hz), 136.8 (d,  $J$  = 9.3 Hz), 135.0 (d,  $J$  = 1.0 Hz), 133.4 (d,  $J$  = 9.5 Hz), 133.2 (d,  $J$  = 2.0 Hz), 132.9, 131.9 (d,  $J$  = 6.6 Hz), 131.82, 131.76, 131.75, 131.68, 128.4, 128.04, 128.02 (d,  $J$  = 13.6 Hz), 127.74, 127.68, 127.5 (d,  $J$  = 3.1 Hz), 127.2, 127.1, 125.7 (d,  $J$  = 135.4 Hz), 65.1 (d,  $J$  = 6.4 Hz), 57.4 (d,  $J$  = 77.1 Hz).  $^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta$  37.8. HRMS (ESI)  $m/z$ : Calcd for  $\text{C}_{33}\text{H}_{26}\text{ClNO}_2\text{P}^+$ ,  $[\text{M} + \text{H}]^+$ : 534.1384; Found 534.1382.

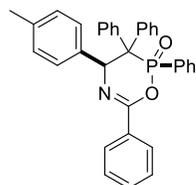
***trans*-4-(4-Methoxyphenyl)-2,3,3,6-tetraphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3ab)**



Colorless crystals, 70 mg, yield 66%, 90:10 dr. m.p. = 169–171 °C,  $R_f$  = 0.28 (PE: EA = 4:1, v/v).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 (d,  $J$  = 7.4 Hz, 2H), 7.68 (d,  $J$  = 7.6 Hz, 2H), 7.56–7.34 (m, 6H), 7.30–7.25 (m, 2H), 7.24–7.16 (m, 3H), 7.08 (dt,  $J$  = 10.7, 5.3 Hz, 3H), 6.91 (t,  $J$  = 7.7 Hz, 2H), 6.85 (d,  $J$  = 8.4 Hz, 2H), 6.60 (d,  $J$  = 8.5 Hz, 2H), 6.22 (d,  $J$  = 6.4 Hz, 1H), 3.70 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.5, 149.1 (d,  $J$  = 6.7 Hz), 139.1 (d,  $J$  = 1.9 Hz), 135.4 (d,  $J$  = 1.4 Hz), 133.3 (d,  $J$  = 9.5 Hz), 133.0 (d,  $J$  = 1.9 Hz), 132.1 (d,  $J$  = 4.7 Hz), 132.0 (d,  $J$  = 5.7 Hz), 131.8 (d,  $J$  = 6.6 Hz), 131.6, 130.4 (d,  $J$  = 9.2 Hz), 128.3, 128.1, 128.0, 127.9, 127.5, 127.3 (d,  $J$  = 2.5 Hz), 127.1, 127.0, 126.1 (d,  $J$  = 134.9 Hz), 112.4, 65.1 (d,  $J$  = 6.4 Hz), 57.6 (d,  $J$  = 76.9 Hz), 55.1.  $^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta$  38.0. HRMS (ESI)  $m/z$ : Calcd for  $\text{C}_{34}\text{H}_{29}\text{NO}_3\text{P}^+$ ,  $[\text{M} + \text{H}]^+$ : 530.1880; Found 530.1883.

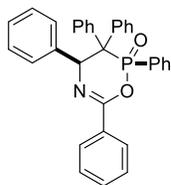
***trans*-2,3,3,6-Tetraphenyl-4-(4-tolyl)-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3ac)**



Colorless crystals, 89 mg, yield 87%, 90:10 dr. m.p. = 139–141 °C,  $R_f$  = 0.41 (PE: EA = 4:1, v/v).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 (d,  $J$  = 7.6 Hz, 2H), 7.69 (d,  $J$  = 7.6 Hz, 2H), 7.54–7.36 (m, 6H), 7.28–7.15 (m, 5H), 7.07 (dd,  $J$  = 17.6, 7.8 Hz, 3H), 6.87 (dt,  $J$  = 25.3, 7.8 Hz, 6H), 6.23 (d,  $J$  = 6.4 Hz, 1H), 2.22 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  149.1 (d,  $J$  = 6.9 Hz), 139.0, 136.5, 135.4 (d,  $J$  = 1.0 Hz), 135.2 (d,  $J$  = 9.3 Hz), 133.3 (d,  $J$  = 9.4 Hz), 133.0 (d,  $J$  = 2.0 Hz), 132.1 (d,  $J$  = 4.5 Hz), 132.0 (d,  $J$  = 6.2 Hz), 131.8 (d,  $J$  = 6.6 Hz), 131.5, 130.4, 128.3, 128.0, 127.9 (d,  $J$  = 13.2 Hz), 127.7, 127.5, 127.4, 127.3 (d,  $J$  = 2.0 Hz), 127.0, 126.0 (d,  $J$  = 134.9 Hz), 65.4 (d,  $J$  = 6.3 Hz), 57.5 (d,  $J$  = 77.2 Hz), 20.9.  $^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta$  38.0. HRMS (ESI)  $m/z$ : Calcd for  $\text{C}_{34}\text{H}_{29}\text{NO}_2\text{P}^+$ ,  $[\text{M} + \text{H}]^+$ : 514.1930; Found 514.1933.

***trans*-2,3,3,4,6-Pentaphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3ad)**

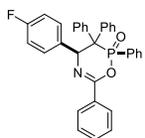


Colorless crystals, 88 mg, yield 88%, 93:7 dr. m.p. = 192–193 °C,  $R_f$  = 0.39 (PE: EA = 4:1, v/v).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.20–8.06 (m, 2H), 7.73–7.61 (m, 2H), 7.56–7.50 (m, 1H), 7.50–7.34 (m, 5H), 7.29–7.23 (m, 3H), 7.19 (t,  $J$  = 7.5 Hz, 2H), 7.12–7.00 (m, 6H), 6.99–6.80 (m, 4H), 6.27 (d,  $J$  = 6.6 Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  149.3 (d,  $J$  = 6.7 Hz), 139.0 (d,  $J$  = 2.0 Hz), 138.3 (d,  $J$  = 9.3 Hz), 135.4 (d,  $J$  = 2.0 Hz), 133.4 (d,  $J$  = 9.4 Hz), 133.0 (d,  $J$  = 2.0 Hz), 132.1 (d,  $J$  = 5.3 Hz), 132.0 (d,  $J$  = 5.9 Hz), 131.8 (d,  $J$  = 6.5 Hz), 131.6, 130.5, 128.3, 128.1, 128.0, 127.9, 127.6, 127.5, 127.3 (d,  $J$  = 2.0 Hz), 127.0, 127.0, 126.0 (d,  $J$  = 135.2 Hz), 65.6 (d,  $J$  = 6.6 Hz), 57.6 (d,  $J$  = 77.3

H<sub>z</sub>). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 38.0. HRMS (ESI) *m/z*: Calcd for C<sub>33</sub>H<sub>27</sub>NO<sub>2</sub>P<sup>+</sup>, [M + H]<sup>+</sup>: 500.1774; Found 500.1780.

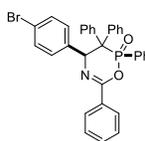
***trans*-4-(4-Fluorophenyl)-2,3,3,6-tetraphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3ae)**



Colorless crystals, 67 mg, yield 65%, 93:7 dr. m.p. = 174–175 °C, R<sub>f</sub> = 0.43 (PE: EA = 4:1, v/v).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.14–8.07 (m, 2H), 7.70–7.64 (m, 2H), 7.57–7.35 (m, 6H), 7.28 (dt, *J* = 8.2, 3.9 Hz, 3H), 7.21 (t, *J* = 7.5 Hz, 2H), 7.08 (ddd, *J* = 9.9, 7.9, 2.0 Hz, 3H), 6.98–6.83 (m, 4H), 6.74 (t, *J* = 8.7 Hz, 2H), 6.25 (d, *J* = 6.5 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 161.8 (d, *J* = 246.2 Hz), 149.6 (d, *J* = 6.8 Hz), 138.8 (d, *J* = 2.0 Hz), 135.2 (d, *J* = 1.0 Hz), 134.1 (dd, *J* = 9.2, 2.3 Hz), 133.4 (d, *J* = 9.5 Hz), 133.1 (d, *J* = 2.8 Hz), 132.04, 131.97 (d, *J* = 7.2 Hz), 131.96, 131.8 (d, *J* = 10.9 Hz), 131.72, 131.71, 128.2 (d, *J* = 31.2 Hz), 128.1, 127.8 (d, *J* = 33.8 Hz), 127.7, 127.4 (d, *J* = 3.1 Hz), 127.2 (d, *J* = 1.6 Hz), 125.8 (d, *J* = 135.2 Hz), 113.9 (d, *J* = 21.3 Hz), 65.0 (d, *J* = 6.5 Hz), 57.5 (d, *J* = 77.0 Hz). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 37.9. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ –115.7. HRMS (ESI) *m/z*: Calcd for C<sub>33</sub>H<sub>26</sub>FNO<sub>2</sub>P<sup>+</sup>, [M + H]<sup>+</sup>: 518.1680; Found 516.1683.

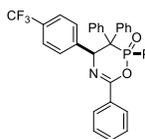
***trans*-4-(4-Bromophenyl)-2,3,3,6-tetraphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3af)**



Colorless crystals, 93 mg, yield 80%, 91:9 dr. m.p. = 151–153 °C, R<sub>f</sub> = 0.49 (PE: EA = 4:1, v/v).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.18–8.04 (m, 2H), 7.69 (d, *J* = 7.6 Hz, 2H), 7.56–7.34 (m, 6H), 7.28 (dd, *J* = 7.9, 3.8 Hz, 2H), 7.27–7.14 (m, 5H), 7.12–7.01 (m, 3H), 6.91 (t, *J* = 7.7 Hz, 2H), 6.80 (d, *J* = 8.2 Hz, 2H), 6.23 (d, *J* = 6.5 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 149.6 (d, *J* = 6.9 Hz), 138.7 (d, *J* = 2.0 Hz), 137.3 (d, *J* = 9.3 Hz), 134.9 (d, *J* = 1.0 Hz), 133.3 (d, *J* = 9.5 Hz), 132.1, 131.9 (d, *J* = 11.9 Hz), 131.8, 131.74, 131.70 (d, *J* = 7.0 Hz), 130.1, 128.4, 128.02, 128.01 (d, *J* = 13.5 Hz), 127.8, 127.7, 127.5 (d, *J* = 2.0 Hz), 127.17, 127.16, 125.7 (d, *J* = 135.5 Hz), 121.2, 65.1 (d, *J* = 6.8 Hz), 57.3 (d, *J* = 77.3 Hz). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 37.8. HRMS (ESI) *m/z*: Calcd for C<sub>33</sub>H<sub>26</sub>BrNO<sub>2</sub>P<sup>+</sup>, [M + H]<sup>+</sup>: 578.0879; Found 578.0883.

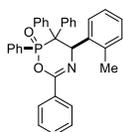
***trans*-2,3,3,6-Tetraphenyl-4-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3ag)**



Colorless crystals, 51 mg, yield 45%, 90:10 dr. m.p. = 169–171 °C, R<sub>f</sub> = 0.42 (PE: EA = 4:1, v/v).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.14 (d, *J* = 7.7 Hz, 2H), 7.68 (d, *J* = 7.7 Hz, 2H), 7.58–7.44 (m, 4H), 7.44–7.36 (m, 2H), 7.33–7.27 (m, 4H), 7.27–7.19 (m, 3H), 7.14–7.02 (m, 5H), 6.93 (t, *J* = 7.7 Hz, 2H), 6.32 (d, *J* = 6.6 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 149.9 (d, *J* = 6.7 Hz), 142.4 (d, *J* = 9.7 Hz), 138.5 (d, *J* = 1.0 Hz), 134.9 (d, *J* = 1.0 Hz), 133.5, 133.4, 133.3 (d, *J* = 8.1 Hz), 131.9, 131.8, 131.72, 131.71 (d, *J* = 11.6 Hz), 130.8, 129.1 (q, *J* = 32.4 Hz), 128.5, 128.08 (d, *J* = 13.5 Hz), 128.07, 127.8, 127.6 (d, *J* = 2.0 Hz), 127.3, 125.6 (d, *J* = 135.7 Hz), 124.1 (q, *J* = 272.3 Hz), 123.9 (q, *J* = 4.3 Hz), 65.3 (d, *J* = 6.6 Hz), 57.4 (d, *J* = 77.4 Hz). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 37.7. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ –62.5. HRMS (ESI) *m/z*: Calcd for C<sub>34</sub>H<sub>26</sub>F<sub>3</sub>NO<sub>2</sub>P<sup>+</sup>, [M + H]<sup>+</sup>: 568.1648; Found 568.1646.

***trans*-2,3,3,6-Tetraphenyl-4-(2-tolyl)-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3ah)**

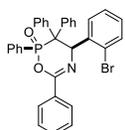


Colorless crystals, 83 mg, yield 81%, 91:9 dr. m.p. = 199–201 °C, R<sub>f</sub> = 0.45 (PE: EA = 4:1, v/v).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.13–8.06 (m, 2H), 7.86–7.76 (m, 1H), 7.61–7.55 (m, 2H), 7.53–7.48 (m, 1H), 7.47–7.38 (m, 3H), 7.34–7.27 (m, 2H), 7.24–7.10 (m, 5H), 7.10–7.03 (m, 5H), 6.92

(t,  $J = 7.8$  Hz, 2H), 6.88 (dd,  $J = 5.5, 3.6$  Hz, 1H), 6.45 (d,  $J = 7.6$  Hz, 1H), 1.63 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  149.8 (d,  $J = 7.3$  Hz), 138.9, 138.7, 137.9 (d,  $J = 9.4$  Hz), 137.0 (d,  $J = 3.5$  Hz), 133.2 (d,  $J = 9.5$  Hz), 132.9 (d,  $J = 3.1$  Hz), 132.4 (d,  $J = 5.2$  Hz), 132.0 (d,  $J = 5.1$  Hz), 131.7 (d,  $J = 7.7$  Hz), 131.5, 130.4, 129.9, 128.3, 128.1, 127.9 (d,  $J = 13.4$  Hz), 127.4, 127.3, 127.21, 127.18, 127.15, 125.9 (d,  $J = 135.1$  Hz), 125.5, 61.0 (d,  $J = 6.4$  Hz), 57.8 (d,  $J = 77.0$  Hz), 19.2.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  38.8. HRMS (ESI)  $m/z$ : Calcd for  $\text{C}_{34}\text{H}_{29}\text{NO}_2\text{P}^+$ ,  $[\text{M} + \text{H}]^+$ : 514.1930; Found 514.1931.

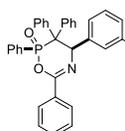
***trans*-4-(2-Bromophenyl)-2,3,3,6-tetraphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3ai)**



Colorless crystals, 61 mg, yield 53%, 87:13 dr. m.p. = 236–237 °C,  $R_f = 0.49$  (PE: EA = 4:1,  $v/v$ ).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14–8.06 (m, 2H), 7.90 (dd,  $J = 7.9, 1.6$  Hz, 1H), 7.57 (d,  $J = 7.9$  Hz, 2H), 7.52 (t,  $J = 7.3$  Hz, 1H), 7.50–7.38 (m, 3H), 7.36–7.26 (m, 3H), 7.26–7.10 (m, 6H), 7.13–6.97 (m, 4H), 6.94 (t,  $J = 7.8$  Hz, 2H), 6.86 (d,  $J = 7.9$  Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  150.2 (d,  $J = 7.3$  Hz), 139.0 (d,  $J = 10.3$  Hz), 138.1, 136.9 (d,  $J = 3.1$  Hz), 133.3 (d,  $J = 9.7$  Hz), 133.0, 132.9, 132.3, 132.2, 131.9, 131.8, 131.7, 128.9, 128.4, 128.1, 127.9 (d,  $J = 13.4$  Hz), 127.8, 127.5, 127.4, 127.3 (d,  $J = 3.3$  Hz), 127.2, 127.0, 125.8 (d,  $J = 135.7$  Hz), 64.0 (d,  $J = 6.0$  Hz), 57.8 (d,  $J = 76.9$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  38.6. HRMS (ESI)  $m/z$ : Calcd for  $\text{C}_{33}\text{H}_{26}\text{BrNO}_2\text{P}^+$ ,  $[\text{M} + \text{H}]^+$ : 578.0879; Found 578.0874.

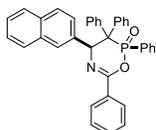
***trans*-4-(3-Bromophenyl)-2,3,3,6-tetraphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3aj)**



Colorless crystals, 74 mg, yield 64%, 92:8 dr. m.p. = 240–242 °C,  $R_f = 0.32$  (PE: EA = 4:1,  $v/v$ ).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.17–8.07 (m, 2H), 7.72–7.65 (m, 2H), 7.58–7.43 (m, 4H), 7.46–7.35 (m, 2H), 7.32–7.19 (m, 6H), 7.11–7.01 (m, 3H), 6.97–6.87 (m, 5H), 6.23 (d,  $J = 6.5$  Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  150.2 (d,  $J = 7.3$  Hz), 139.0 (d,  $J = 10.3$  Hz), 138.1, 136.9 (d,  $J = 3.1$  Hz), 133.3 (d,  $J = 9.7$  Hz), 132.9 (d,  $J = 2.1$  Hz), 132.4, 132.3 (d,  $J = 3.0$  Hz), 131.9, 131.8, 131.7, 128.9, 128.4, 128.1, 128.0, 127.9, 127.8, 127.5, 127.4, 127.3 (d,  $J = 3.3$  Hz), 127.2, 127.0, 125.8 (d,  $J = 135.7$  Hz), 64.0 (d,  $J = 6.0$  Hz), 57.8 (d,  $J = 76.9$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  37.8. HRMS (ESI)  $m/z$ : Calcd for  $\text{C}_{33}\text{H}_{26}\text{BrNO}_2\text{P}^+$ ,  $[\text{M} + \text{H}]^+$ : 578.0879; Found 578.0876.

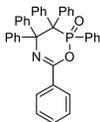
***trans*-4-(Naphthalen-2-yl)-2,3,3,6-tetraphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3ak)**



Colorless crystals, 70 mg, yield 64%, 91:9 dr. m.p. = 153–155 °C,  $R_f = 0.39$  (PE: EA = 4:1,  $v/v$ ).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.23–8.14 (m, 2H), 7.69 (t,  $J = 6.7$  Hz, 3H), 7.56–7.50 (m, 3H), 7.50–7.39 (m, 5H), 7.39–7.33 (m, 2H), 7.32–7.22 (m, 4H), 7.18 (t,  $J = 7.7$  Hz, 2H), 7.17–7.05 (m, 3H), 7.09–7.00 (m, 1H), 6.89 (t,  $J = 7.7$  Hz, 2H), 6.44 (d,  $J = 6.4$  Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  149.4 (d,  $J = 6.9$  Hz), 139.0, 135.6 (d,  $J = 9.3$  Hz), 135.2, 133.4 (d,  $J = 9.5$  Hz), 133.1 (d,  $J = 2.0$  Hz), 132.33, 132.29, 132.1 (d,  $J = 4.7$  Hz), 132.02, 131.96, 131.8 (d,  $J = 6.4$  Hz), 131.7, 129.9, 128.4, 128.09, 128.06, 127.9, 127.6, 127.5, 127.3 (d,  $J = 2.0$  Hz), 127.2, 127.1, 126.2, 125.9 (d,  $J = 135.0$  Hz), 125.7, 125.5, 65.8 (d,  $J = 6.4$  Hz), 57.7 (d,  $J = 77.1$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  38.0. HRMS (ESI)  $m/z$ : Calcd for  $\text{C}_{37}\text{H}_{29}\text{NO}_2\text{P}^+$ ,  $[\text{M} + \text{H}]^+$ : 550.1930; Found 550.1931.

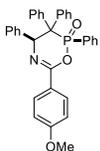
**2,3,3,4,4,6-Hexaphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3al)**



Colorless crystals, 70 mg, yield 61%. m.p. = 168–170 °C,  $R_f$  = 0.35 (PE: EA = 10:1, v/v).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.32–8.22 (m, 2H), 7.97 (d,  $J$  = 7.9 Hz, 2H), 7.86 (dd,  $J$  = 7.3, 1.9 Hz, 2H), 7.58–7.52 (m, 1H), 7.48 (dd,  $J$  = 8.2, 6.5 Hz, 2H), 7.41–7.30 (m, 1H), 7.19 (t,  $J$  = 7.3 Hz, 1H), 7.15–7.07 (m, 6H), 7.07–6.98 (m, 7H), 6.94 (t,  $J$  = 7.7 Hz, 2H), 6.86–6.73 (m, 4H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.2 (d,  $J$  = 7.3 Hz), 146.2 (d,  $J$  = 5.5 Hz), 136.3, 135.3 (d,  $J$  = 5.8 Hz), 134.50, 134.46, 134.3 (d,  $J$  = 7.6 Hz), 133.0 (d,  $J$  = 8.7 Hz), 132.6 (d,  $J$  = 3.3 Hz), 132.4, 131.7, 131.3, 130.2, 128.4, 127.8 (d,  $J$  = 139.6 Hz), 127.7, 127.5, 127.3, 127.0 (d,  $J$  = 3.5 Hz), 126.91, 126.85, 126.3, 126.2 (d,  $J$  = 2.0 Hz), 125.9, 125.6, 75.3 (d,  $J$  = 4.6 Hz), 61.9 (d,  $J$  = 76.7 Hz).  $^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta$  35.7. **HRMS** (ESI)  $m/z$ : Calcd for  $\text{C}_{39}\text{H}_{31}\text{NO}_2\text{P}^+$ ,  $[\text{M} + \text{H}]^+$ : 576.2087; Found 576.2084.

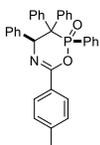
**trans-6-(4-Methoxyphenyl)-2,3,3,4-tetraphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3am)**



Colorless crystals, 80 mg, yield 76%, 90:10 dr. m.p. = 170–172 °C,  $R_f$  = 0.26 (PE: EA = 4:1, v/v).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (dd,  $J$  = 8.9, 2.5 Hz, 2H), 7.67 (d,  $J$  = 7.7 Hz, 2H), 7.47 (t,  $J$  = 7.5 Hz, 1H), 7.38 (dd,  $J$  = 11.6, 7.6 Hz, 2H), 7.31–7.22 (m, 3H), 7.18 (t,  $J$  = 7.5 Hz, 2H), 7.14–7.00 (m, 6H), 6.98–6.86 (m, 6H), 6.23 (d,  $J$  = 6.6 Hz, 1H), 3.86 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.4, 149.1 (d,  $J$  = 6.6 Hz), 139.1, 138.5 (d,  $J$  = 9.2 Hz), 135.5, 133.3 (d,  $J$  = 9.4 Hz), 133.0, 132.9, 132.1 (d,  $J$  = 5.7 Hz), 131.8 (d,  $J$  = 6.6 Hz), 130.5, 129.8, 127.9 (d,  $J$  = 13.3 Hz), 127.5, 127.4, 127.2 (d,  $J$  = 2.0 Hz), 127.0, 126.9, 126.1 (d,  $J$  = 135.2 Hz), 124.6 (d,  $J$  = 4.5 Hz), 113.7, 65.5 (d,  $J$  = 6.5 Hz), 57.5 (d,  $J$  = 77.2 Hz), 55.4.  $^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta$  37.8. **HRMS** (ESI)  $m/z$ : Calcd for  $\text{C}_{34}\text{H}_{29}\text{NO}_3\text{P}^+$ ,  $[\text{M} + \text{H}]^+$ : 530.1880; Found 530.1882.

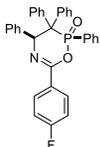
**trans-2,3,3,4-Tetraphenyl-6-(4-tolyl)-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3an)**



Colorless crystals, 89 mg, yield 87%, 94:6 dr. m.p. = 231–233 °C,  $R_f$  = 0.45 (PE: EA = 4:1, v/v).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07–8.00 (m, 2H), 7.67 (dt,  $J$  = 8.7, 1.5 Hz, 2H), 7.47 (td,  $J$  = 7.4, 1.5 Hz, 1H), 7.44–7.32 (m, 2H), 7.29–7.25 (m, 3H), 7.23 (d,  $J$  = 4.1 Hz, 2H), 7.19 (t,  $J$  = 7.5 Hz, 2H), 7.14–7.00 (m, 6H), 6.98–6.84 (m, 4H), 6.25 (d,  $J$  = 6.6 Hz, 1H), 2.42 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  149.4 (d,  $J$  = 7.1 Hz), 142.1, 139.0, 138.4 (d,  $J$  = 9.3 Hz), 135.4 (d,  $J$  = 1.0 Hz), 133.4 (d,  $J$  = 9.5 Hz), 133.0 (d,  $J$  = 2.0 Hz), 132.0 (d,  $J$  = 5.6 Hz), 131.8 (d,  $J$  = 6.6 Hz), 130.5, 129.4 (d,  $J$  = 4.8 Hz), 129.1, 128.1, 128.0, 127.9, 127.5, 127.4, 127.3 (d,  $J$  = 3.1 Hz), 127.0, 126.9, 126.1 (d,  $J$  = 135.0 Hz), 65.6 (d,  $J$  = 6.6 Hz), 57.6 (d,  $J$  = 77.3 Hz), 21.6.  $^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta$  37.8. **HRMS** (ESI)  $m/z$ : Calcd for  $\text{C}_{34}\text{H}_{29}\text{NO}_2\text{P}^+$ ,  $[\text{M} + \text{H}]^+$ : 514.1930; Found 514.1924.

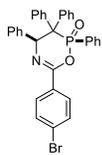
**trans-6-(4-Fluorophenyl)-2,3,3,4-tetraphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3ao)**



Colorless crystals, 79 mg, yield 77%, 91:9 dr. m.p. = 170–172 °C,  $R_f$  = 0.26 (PE: EA = 4:1, v/v).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.21–8.04 (m, 2H), 7.66 (dt,  $J$  = 8.9, 1.4 Hz, 2H), 7.53–7.44 (m, 1H), 7.38 (ddd,  $J$  = 11.6, 8.2, 1.4 Hz, 2H), 7.32–7.21 (m, 3H), 7.19 (t,  $J$  = 7.5 Hz, 2H), 7.16–7.02 (m, 8H), 6.96–6.88 (m, 4H), 6.24 (d,  $J$  = 6.6 Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.0 (d,  $J$  = 252.2 Hz), 148.5 (d,  $J$  = 6.8 Hz), 138.8 (d,  $J$  = 1.8 Hz), 138.2 (d,  $J$  = 9.2 Hz), 135.3 (d,  $J$  = 2.0 Hz), 133.4 (d,  $J$  = 9.6 Hz), 133.1 (d,  $J$  = 2.7 Hz), 132.0 (d,  $J$  = 5.7 Hz), 131.7 (d,  $J$  = 6.7 Hz), 130.5, 130.3 (d,  $J$  = 8.9 Hz), 128.3 (dd,  $J$  = 3.5, 3.5 Hz), 128.0 (d,  $J$  = 13.3 Hz), 127.6, 127.5, 127.4 (d,  $J$  = 3.2 Hz), 127.10, 127.07, 127.0, 125.8 (d,  $J$  = 135.0 Hz), 115.5 (d,  $J$  = 21.9 Hz), 65.6 (d,  $J$  = 6.6 Hz), 57.6 (d,  $J$  = 77.1 Hz).  $^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta$  38.2.  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -108.0. **HRMS** (ESI)  $m/z$ : Calcd for  $\text{C}_{33}\text{H}_{26}\text{FNO}_2\text{P}^+$ ,  $[\text{M} + \text{H}]^+$ : 518.1680; Found 516.1684.

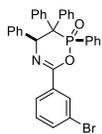
**trans-6-(4-Bromophenyl)-2,3,3,4-tetraphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3ap)**



Colorless crystals, 71 mg, yield 62%, 91:9 dr. m.p. = 219–221 °C,  $R_f$  = 0.42 (PE: EA = 4:1, v/v).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (d,  $J$  = 8.6 Hz, 2H), 7.72–7.62 (m, 2H), 7.58 (dd,  $J$  = 8.9, 2.3 Hz, 2H), 7.48 (dt,  $J$  = 7.4, 4.5 Hz, 1H), 7.42–7.32 (m, 2H), 7.32–7.21 (m, 3H), 7.19 (t,  $J$  = 7.5 Hz, 2H), 7.13–7.01 (m, 6H), 6.96–6.87 (m, 4H), 6.24 (d,  $J$  = 6.6 Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  148.7 (d,  $J$  = 6.9 Hz), 138.7, 138.0 (d,  $J$  = 9.3 Hz), 135.2, 133.3 (d,  $J$  = 9.6 Hz), 133.2, 133.1, 131.9 (d,  $J$  = 5.7 Hz), 131.8, 131.7, 131.6, 131.0 (d,  $J$  = 4.7 Hz), 130.4, 129.6, 128.0 (d,  $J$  = 13.3 Hz), 127.6, 127.5, 127.4, 127.1, 127.0, 125.7 (d,  $J$  = 135.0 Hz), 65.7 (d,  $J$  = 6.4 Hz), 57.6 (d,  $J$  = 77.2 Hz).  $^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta$  38.3. HRMS (ESI)  $m/z$ : Calcd for  $\text{C}_{33}\text{H}_{26}\text{BrNO}_2\text{P}^+$ ,  $[\text{M} + \text{H}]^+$ : 578.0879; Found 578.0883.

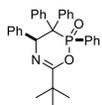
**trans-6-(3-Bromophenyl)-2,3,3,4-tetraphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3aq)**



Colorless crystals, 82 mg, yield 71%, 90:10 dr. m.p. = 151–152 °C,  $R_f$  = 0.39 (PE: EA = 4:1, v/v).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.28 (t,  $J$  = 1.8 Hz, 1H), 8.06 (d,  $J$  = 7.8 Hz, 1H), 7.74–7.60 (m, 3H), 7.50 (t,  $J$  = 7.2 Hz, 1H), 7.42–7.34 (m, 2H), 7.33–7.23 (m, 4H), 7.19 (t,  $J$  = 7.6 Hz, 2H), 7.14–7.01 (m, 6H), 6.97–6.87 (m, 4H), 6.25 (d,  $J$  = 6.5 Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  148.1 (d,  $J$  = 6.7 Hz), 138.7 (d,  $J$  = 1.0 Hz), 138.0 (d,  $J$  = 9.2 Hz), 135.2 (d,  $J$  = 2.0 Hz), 134.6, 134.0 (d,  $J$  = 4.6 Hz), 133.4 (d,  $J$  = 9.5 Hz), 133.21, 133.20, 131.9 (d,  $J$  = 5.7 Hz), 131.7 (d,  $J$  = 6.8 Hz), 131.0, 130.5, 129.9, 128.1 (d,  $J$  = 13.5 Hz), 127.62, 127.57, 127.5, 127.13, 127.09 (d,  $J$  = 8.3 Hz), 126.7, 125.6 (d,  $J$  = 135.0 Hz), 122.6, 65.8 (d,  $J$  = 6.6 Hz), 57.7 (d,  $J$  = 77.1 Hz).  $^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta$  38.4. HRMS (ESI)  $m/z$ : Calcd for  $\text{C}_{33}\text{H}_{26}\text{BrNO}_2\text{P}^+$ ,  $[\text{M} + \text{H}]^+$ : 578.0879; Found 578.0884.

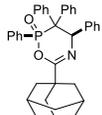
**trans-6-(tert-Butyl)-2,3,3,4-tetraphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3ar)**



Colorless crystals, 81 mg, yield 84%, > 99:1 dr. m.p. = 199–201 °C,  $R_f$  = 0.42 (PE: EA = 4:1, v/v).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (dt,  $J$  = 8.8, 1.5 Hz, 2H), 7.45 (td,  $J$  = 7.3, 1.5 Hz, 1H), 7.35–7.25 (m, 2H), 7.28–7.18 (m, 3H), 7.21–7.13 (m, 2H), 7.15–7.06 (m, 1H), 7.05–6.98 (m, 5H), 6.95 (t,  $J$  = 7.7 Hz, 2H), 6.85 (d,  $J$  = 7.3 Hz, 2H), 6.03 (d,  $J$  = 6.4 Hz, 1H), 1.35 (s, 9H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.2 (d,  $J$  = 8.2 Hz), 139.3 (d,  $J$  = 2.0 Hz), 138.2 (d,  $J$  = 9.3 Hz), 135.3, 133.2 (d,  $J$  = 9.3 Hz), 132.9, 132.2 (d,  $J$  = 5.7 Hz), 131.7 (d,  $J$  = 6.6 Hz), 130.4, 127.9 (d,  $J$  = 13.2 Hz), 127.4, 127.3, 126.9, 126.72, 126.69, 126.68, 126.4 (d,  $J$  = 135.2 Hz), 65.0 (d,  $J$  = 6.7 Hz), 57.2 (d,  $J$  = 77.1 Hz), 38.7, 27.4.  $^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta$  36.7. HRMS (ESI)  $m/z$ : Calcd for  $\text{C}_{31}\text{H}_{31}\text{NO}_2\text{P}^+$ ,  $[\text{M} + \text{H}]^+$ : 480.2087; Found 480.2089.

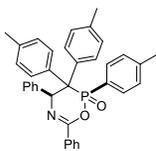
**trans-6-(adamantan-1-yl)-2,3,3,4-tetraphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3at)**



Colorless crystals, 61 mg, yield 55%, 89:11 dr. m.p. = 220–222 °C,  $R_f$  = 0.45 (PE: EA = 4:1, v/v).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68–7.59 (m, 2H), 7.49–7.40 (m, 1H), 7.35–7.25 (m, 2H), 7.27–7.19 (m, 2H), 7.17 (t,  $J$  = 7.5 Hz, 2H), 7.15–6.96 (m, 7H), 6.95 (t,  $J$  = 7.7 Hz, 2H), 6.89–6.80 (m, 2H), 6.02 (d,  $J$  = 6.4 Hz, 1H), 2.10–2.01 (m, 9H), 1.81–1.70 (m, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  157.7 (d,  $J$  = 8.6 Hz), 139.3 (d,  $J$  = 1.9 Hz), 138.3 (d,  $J$  = 9.2 Hz), 135.3, 133.3 (d,  $J$  = 9.3 Hz), 132.8 (d,  $J$  = 2.0 Hz), 132.3 (d,  $J$  = 5.6 Hz), 131.8 (d,  $J$  = 6.4 Hz), 130.4, 127.9 (d,  $J$  = 13.2 Hz), 127.5, 127.32, 127.28, 126.9, 126.74, 126.70, 126.67, 126.4 (d,  $J$  = 135.0 Hz), 64.9 (d,  $J$  = 6.7 Hz), 57.3 (d,  $J$  = 77.4 Hz), 40.5 (d,  $J$  = 3.2 Hz), 39.1, 36.6, 28.0.  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  36.5. HRMS (ESI)  $m/z$ : Calcd for  $\text{C}_{37}\text{H}_{37}\text{NO}_2\text{P}^+$ ,  $[\text{M} + \text{H}]^+$ : 558.2556; Found 558.2554.

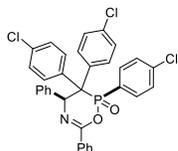
**trans-4,6-Diphenyl-2,3,3-tri-4-tolyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3bd)**



Colorless crystals, 84 mg, yield 78%, 93:7 dr. m.p. = 218–220 °C,  $R_f$  = 0.42 (PE: EA = 4:1, v/v).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.18–8.09 (m, 2H), 7.51 (td,  $J$  = 9.8, 9.0, 4.4 Hz, 3H), 7.43 (t,  $J$  = 7.5 Hz, 2H), 7.30 (dd,  $J$  = 11.4, 7.9 Hz, 2H), 7.12–7.00 (m, 5H), 7.03–6.91 (m, 6H), 6.72 (d,  $J$  = 8.1 Hz, 2H), 6.27 (d,  $J$  = 6.4 Hz, 1H), 2.33 (s, 3H), 2.32 (s, 3H), 2.18 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  149.1 (d,  $J$  = 6.9 Hz), 143.7 (d,  $J$  = 3.0 Hz), 138.6 (d,  $J$  = 9.4 Hz), 137.0, 136.9 (d,  $J$  = 2.4 Hz), 135.6 (d,  $J$  = 2.2 Hz), 133.6 (d,  $J$  = 10.0 Hz), 132.3, 131.9 (d,  $J$  = 5.9 Hz), 131.7 (d,  $J$  = 6.5 Hz), 131.4, 130.6, 128.7, 128.5, 128.3, 128.1, 128.0, 127.6, 126.9, 126.8, 122.7 (d,  $J$  = 137.3 Hz), 65.2 (d,  $J$  = 6.5 Hz), 56.7 (d,  $J$  = 78.0 Hz), 21.7, 21.0, 20.8.  $^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta$  38.4. HRMS (ESI)  $m/z$ : Calcd for  $\text{C}_{36}\text{H}_{33}\text{NO}_2\text{P}^+$ ,  $[\text{M} + \text{H}]^+$ : 542.2243; Found 542.2246.

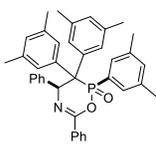
**trans-2,3,3-Tris(4-chlorophenyl)-4,6-diphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3cd)**



Colorless crystals, 84 mg, yield 70%, 93:7 dr. m.p. = 203–205 °C,  $R_f$  = 0.62 (PE: EA = 4:1, v/v).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.17–7.99 (m, 2H), 7.63–7.51 (m, 3H), 7.46 (t,  $J$  = 7.6 Hz, 2H), 7.37–7.29 (m, 4H), 7.18 (d,  $J$  = 8.6 Hz, 2H), 7.12 (dt,  $J$  = 14.5, 6.9 Hz, 3H), 7.01 (dd,  $J$  = 8.8, 2.3 Hz, 2H), 6.97–6.89 (m, 4H), 6.19 (d,  $J$  = 6.5 Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  149.2 (d,  $J$  = 6.1 Hz), 140.5 (d,  $J$  = 3.5 Hz), 137.3 (d,  $J$  = 9.3 Hz), 136.9, 134.7 (d,  $J$  = 10.4 Hz), 133.9, 133.8 (d,  $J$  = 3.2 Hz), 133.5 (d,  $J$  = 2.0 Hz), 133.1 (d,  $J$  = 5.6 Hz), 132.9 (d,  $J$  = 6.5 Hz), 132.0, 131.4 (d,  $J$  = 4.4 Hz), 130.3, 128.7, 128.6, 128.5, 128.0 (d,  $J$  = 13.8 Hz), 127.5 (d,  $J$  = 1.0 Hz), 127.4, 127.4, 123.8 (d,  $J$  = 138.2 Hz), 65.4 (d,  $J$  = 6.6 Hz), 56.7 (d,  $J$  = 78.4 Hz).  $^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta$  36.3. HRMS (ESI)  $m/z$ : Calcd for  $\text{C}_{33}\text{H}_{24}\text{Cl}_3\text{NO}_2\text{P}^+$ ,  $[\text{M} + \text{H}]^+$ : 602.0605; Found 602.0606.

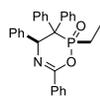
**trans-2,3,3-Tris(3,5-dimethylphenyl)-4,6-diphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3dd)**



Colorless crystals, 78 mg, yield 67%, 94:6 dr. m.p. = 225–227 °C,  $R_f$  = 0.49 (PE: EA = 4:1, v/v).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.21–8.03 (m, 2H), 7.56–7.47 (m, 1H), 7.49–7.36 (m, 2H), 7.23 (s, 2H), 7.18–7.01 (m, 4H), 7.00–6.85 (m, 5H), 6.70 (d,  $J$  = 7.0 Hz, 3H), 6.20 (d,  $J$  = 6.5 Hz, 1H), 2.21 (s, 6H), 2.19 (s, 6H), 1.93 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  149.4 (d,  $J$  = 6.5 Hz), 138.7 (d,  $J$  = 9.4 Hz), 138.6 (d,  $J$  = 2.0 Hz), 137.3, 137.2, 136.7, 136.0 (d,  $J$  = 1.0 Hz), 134.6 (d,  $J$  = 2.5 Hz), 132.5 (d,  $J$  = 4.7 Hz), 131.5 (d,  $J$  = 9.4 Hz), 131.3, 130.6, 130.2 (d,  $J$  = 5.8 Hz), 129.8 (d,  $J$  = 6.5 Hz), 128.8, 128.5 (d,  $J$  = 2.0 Hz), 128.3, 128.0, 126.8, 126.7, 125.5 (d,  $J$  = 133.7 Hz), 65.2 (d,  $J$  = 6.4 Hz), 57.4 (d,  $J$  = 76.7 Hz), 21.5, 21.2, 21.0.  $^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta$  38.8. HRMS (ESI)  $m/z$ : Calcd for  $\text{C}_{39}\text{H}_{39}\text{NO}_2\text{P}^+$ ,  $[\text{M} + \text{H}]^+$ : 584.2713; Found 584.2712.

**trans-2-Ethyl-3,3,4,6-tetraphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3ed)**



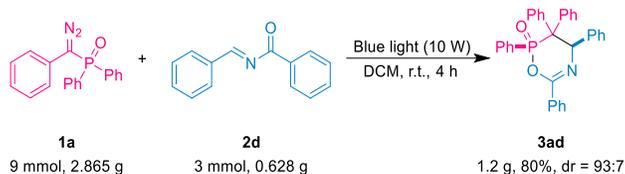
Colorless crystals, 50 mg, yield 55%, 90:10 dr. m.p. = 201–203 °C,  $R_f$  = 0.32 (PE: EA = 4:1, v/v).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.10–7.95 (m, 2H), 7.62 (dt,  $J$  = 5.9, 2.3 Hz, 2H), 7.55–7.45 (m, 1H), 7.46–7.37 (m, 2H), 7.33–7.25 (m, 3H), 7.19 (dtd,  $J$  = 6.6, 3.3, 1.5 Hz, 1H), 7.10 (d,  $J$  = 5.8 Hz, 5H), 7.03 (t,  $J$  = 7.6 Hz, 2H), 6.89 (d,  $J$  = 7.3 Hz, 2H), 6.38 (d,  $J$  = 4.9 Hz, 1H), 2.12–1.84 (m, 2H), 1.26 (dt,  $J$  = 18.2, 7.7 Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  148.1 (d,  $J$  = 6.7 Hz), 138.7 (d,  $J$  = 8.1 Hz), 137.2 (d,  $J$  = 4.0 Hz), 135.6, 132.3 (d,  $J$  = 3.6 Hz), 131.7 (d,  $J$  = 5.6 Hz), 131.43, 131.36, 130.3, 128.2, 128.0, 127.7, 127.64, 127.62,

127.5, 127.1, 127.0, 62.7 (d,  $J = 6.6$  Hz), 55.9 (d,  $J = 71.0$  Hz), 17.6 (d,  $J = 92.0$  Hz), 5.4 (d,  $J = 7.2$  Hz).  $^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta$  49.9. **HRMS** (ESI)  $m/z$ : Calcd for  $\text{C}_{29}\text{H}_{27}\text{NO}_2\text{P}^+$ ,  $[\text{M} + \text{H}]^+$ : 452.1774; Found 452.1779.

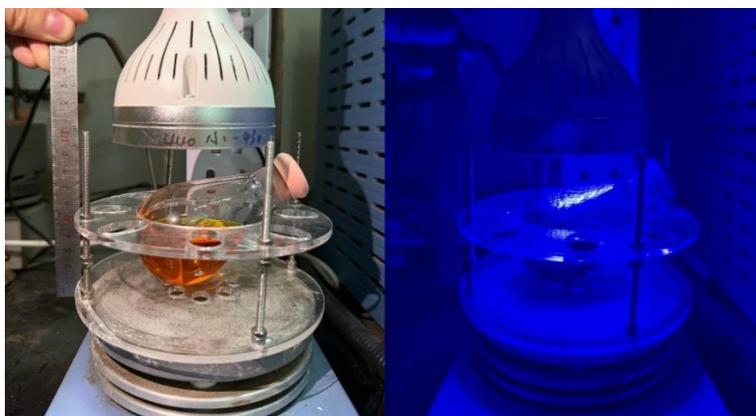
## 1.4 Gram scale synthesis and applications

### A. Gram-scale synthesis of **3ad**



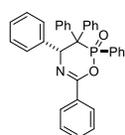
**Scheme S5.** Gram-scaled reaction of (diazo(phenyl)methyl)diphenylphosphine oxide (**1a**) and (*E*)-*N*-benzylidenebenzamide (**2d**)

To a 100 mL dry glass flask were added diazomethylphosphine oxide **1a** (2.865 g, 9 mmol), *N*-benzylidenebenzamide **2d** (0.628 g, 3 mmol), and dry DCM (45 mL) at room temperature, then the reaction mixture was stirred at room temperature for 4 h under blue light LED irradiation. After completion of the reaction, the mixture was concentrated under reduced pressure and the residue was subjected to silica gel column chromatography with a mixture of DCM and EA (DCM:EA 150:1 to 100:1,  $v/v$ ) as eluent to give product **3ad** (1.116 g) and *cis*-**3ad** (72 mg). In summary, the product was isolated as 1.2 g (2.4 mmol, 80 %). The ratio of *trans*:*cis* is 93:7.



**Figure S2.** Photoreaction equipment for the gram-scaled reaction

### *cis*-2,3,3,4,6-Pentaphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (*cis*-**3ad**)



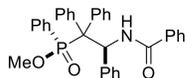
Colorless crystals, 72 mg, yield 6%. m.p. = 216–218 °C,  $R_f = 0.58$  (DCM: EA = 100:1,  $v/v$ ).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.17 (d,  $J = 7.8$  Hz, 2H), 7.54 (t,  $J = 7.4$  Hz, 1H), 7.51–7.36 (m, 3H), 7.30–7.19 (m, 6H), 7.19–7.10 (m, 4H), 7.11–6.96 (m, 7H), 6.92 (d,  $J = 7.7$  Hz, 2H), 5.98 (d,  $J = 11.3$  Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  **NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  149.6 (d,  $J = 8.0$  Hz), 137.8, 137.7 (d,  $J = 9.1$  Hz), 132.7, 132.6 (d,  $J = 9.4$  Hz), 131.8, 131.65, 131.6, 131.5 (d,  $J = 8.6$  Hz), 130.2, 128.44, 128.39, 128.3, 128.0 (d,  $J = 13.6$  Hz), 127.5, 127.41, 127.36, 127.3, 127.1, 127.0, 126.9, 66.4, 56.4 (d,  $J = 78.6$  Hz).  $^{31}\text{P NMR}$  (162 MHz,  $\text{CDCl}_3$ )  $\delta$  34.3. **HRMS** (ESI)  $m/z$ : Calcd for  $\text{C}_{33}\text{H}_{27}\text{NO}_2\text{P}^+$ ,  $[\text{M} + \text{H}]^+$ : 500.1774; Found 500.1779.

*B. Base-catalyzed ring opening reaction:*<sup>3</sup>

To a solution of **3ad** (82 mg, 0.2 mmol) in anhydrous MeOH (2 mL) was added NaOMe (1 mL, 5.4 M). The mixture was stirred at room temperature for 20 h, and aqueous saturated NH<sub>4</sub>Cl solution (2 mL) was added and then the mixture was extracted with DCM (3 × 5 mL). After drying over anhydrous sodium sulfate, the combined organic phase was concentrated and the residue was subjected to flash silica gel column chromatography (PE:EA = 2:1, v/v) to afford product **4** (76 mg, 72%).

**Methyl *rel*-(*R*)-((*S*)-2-benzamido-1,1,2-triphenylethyl)(phenyl)phosphinate (**4**)**



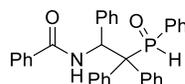
Colorless crystals, 76 mg, yield 72%. m.p. = 200–202 °C, *R<sub>f</sub>* = 0.25 (PE:EA = 2:1, v/v).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.03–7.94 (m, 2H), 7.92 (s, 1H), 7.65–7.47 (m, 2H), 7.52–7.38 (m, 5H), 7.32 (td, *J* = 7.3, 1.4 Hz, 1H), 7.27–7.17 (m, 2H), 7.19–7.07 (m, 6H), 7.07–6.93 (m, 5H), 6.87 (dd, *J* = 7.4, 4.2 Hz, 1H), 6.81–6.71 (m, 2H), 3.65 (d, *J* = 10.7 Hz, 3H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, CDCl<sub>3</sub>) δ 166.1, 139.0 (d, *J* = 7.1 Hz), 136.6 (d, *J* = 5.2 Hz), 135.8, 134.7, 132.9 (d, *J* = 8.9 Hz), 132.8 (d, *J* = 5.3 Hz), 132.4 (d, *J* = 6.8 Hz), 131.9 (d, *J* = 1.0 Hz), 131.3, 129.1, 128.6, 128.5 (d, *J* = 129.2 Hz), 127.7, 127.6, 127.55, 127.53, 127.23, 127.20, 127.13 (d, *J* = 2.0 Hz), 127.07, 62.1 (d, *J* = 87.9 Hz), 56.4, 51.9 (d, *J* = 6.9 Hz). **<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 45.5. **HRMS** (ESI) *m/z*: Calcd for C<sub>34</sub>H<sub>31</sub>NO<sub>2</sub>P<sup>+</sup>, [M + H]<sup>+</sup>: 532.2036; Found 532.2038.

*C. Procedure for the synthesis of 5*

**3ad** (82 mg, 0.2 mmol), LiAlH<sub>4</sub> (23 mg, 0.6 mmol), and 4 mL of anhydrous THF were added into a 25 mL flask under nitrogen atmosphere. The mixture was stirred at 0 °C in an ice bath for 16 h. The solvent was removed under reduced pressure and the residue was purified on silica gel column chromatography with a mixture of petroleum ether (PE) and ethyl acetate (EA) (PE:EA 1:1, v/v) as eluent to give product **5**.

***N*-(1,2,2-Triphenyl-2-(phenylhydrophosphoryl)ethyl)benzamide (**5**)**

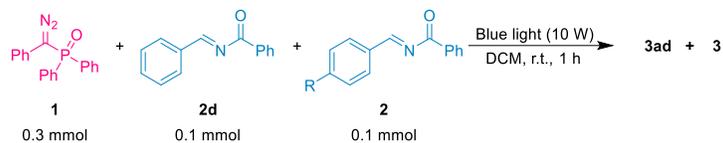


Colorless crystals, 73 mg, yield 73%. m.p. = 100–102 °C, *R<sub>f</sub>* = 0.18 (PE:EA = 2:1, v/v).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.39 (s, 1H), 7.73–7.64 (m, 2H), 7.48–7.39 (m, 1H), 7.41 – 7.27 (m, 10H), 7.28–7.18 (m, 2H), 7.21–7.09 (m, 7H), 7.06–6.95 (m, 4H), 6.90 (dd, *J* = 9.1, 6.0 Hz, 1H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (101 MHz, CDCl<sub>3</sub>) δ 166.1, 138.0 (d, *J* = 4.2 Hz), 135.9, 134.4 (d, *J* = 4.4 Hz), 134.2, 132.2, 131.9, 131.8 (d, *J* = 4.2 Hz), 131.7, 131.5, 131.2 (d, *J* = 7.5 Hz), 129.1, 128.5, 128.4, 128.1, 127.80 (d, *J* = 99.2 Hz), 127.79 (d, *J* = 12.3 Hz), 127.8, 127.5, 127.55, 126.47, 60.8 (d, *J* = 62.0 Hz), 55.4. **<sup>31</sup>P NMR** (162 MHz, CDCl<sub>3</sub>) δ 33.3 (brs). **HRMS** (ESI) *m/z*: Calcd for C<sub>33</sub>H<sub>29</sub>NO<sub>2</sub>P<sup>+</sup>, [M + H]<sup>+</sup>: 502.1930; Found 502.1932.

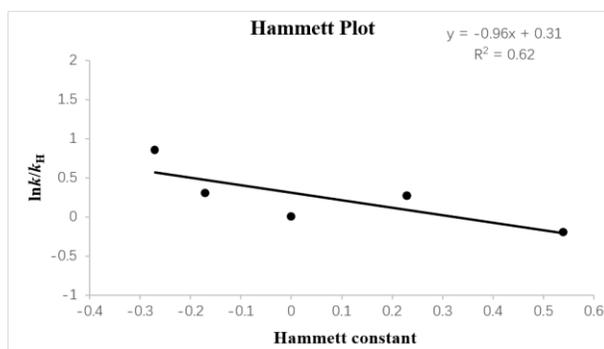
## 1.5 Competitive experiments and Hammett plot

Table S1. Competitive experiments



entry	<b>2</b>	R	relative rate ( $k/k_H$ )	$\sigma$
1	<b>2d</b>	H	1	0
2	<b>2b</b>	OMe	2.34	-0.27
3	<b>2c</b>	Me	1.35	-0.17
4	<b>2a</b>	Cl	1.30	0.23
5	<b>2g</b>	CF <sub>3</sub>	0.82	0.54

Figure S3. Hammett plot.

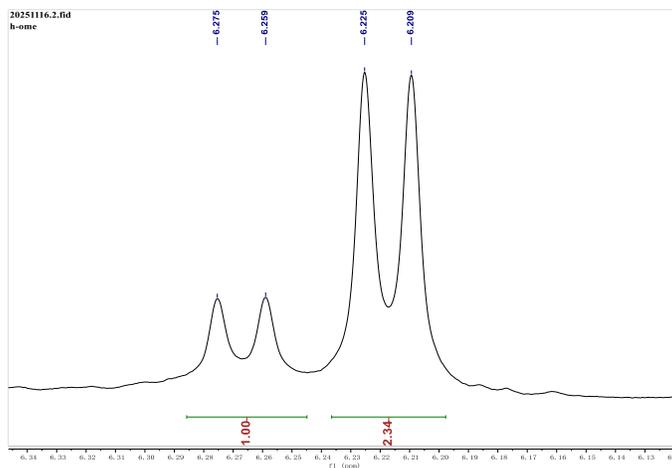


### Experimental procedure:

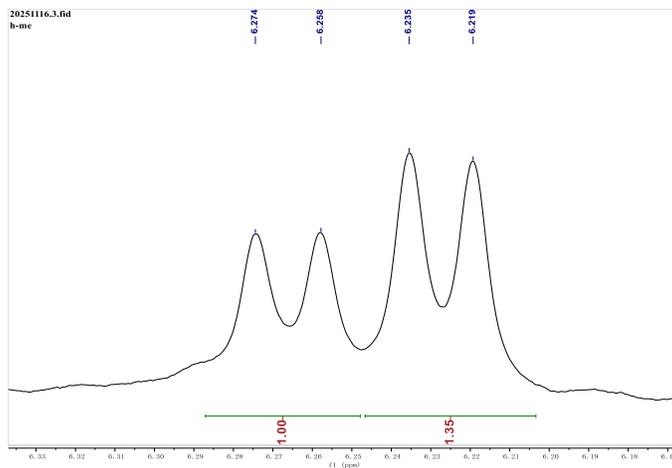
**1a** (96 mg, 0.3 mmol), **2d** (21 mg, 0.1 mmol), and **2** (0.1 mmol) in 1.5 mL of dry DCM were stirred at room temperature for 1 h under blue light LED irradiation. The reaction mixture was then moved to a dark environment. The product ratio of **3ad** and **3** was determined based on the <sup>1</sup>H NMR analysis of the reaction mixture in CDCl<sub>3</sub>.

Figure S4. Copies of NMR spectra for the reaction mixtures of **3ad** and **3**

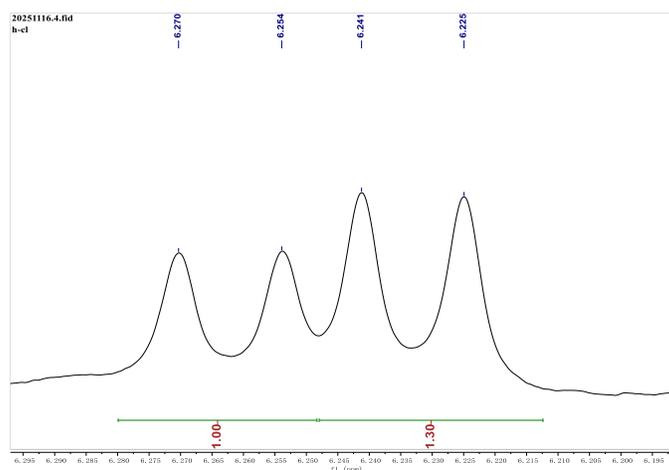
$^1\text{H}$  NMR spectrum for the reaction of **3ad** (6.267 ppm) and **3ab** (6.217 ppm) in  $\text{CDCl}_3$  (400 MHz)



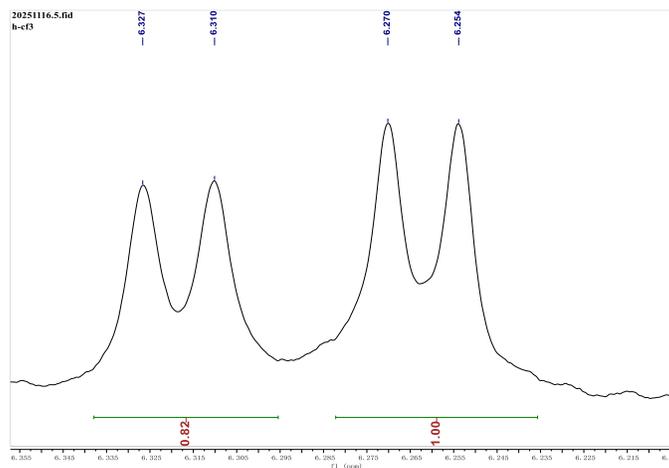
$^1\text{H}$  NMR spectrum for the reaction of **3ad** (6.266 ppm) and **3ac** (6.227 ppm) in  $\text{CDCl}_3$  (400 MHz)



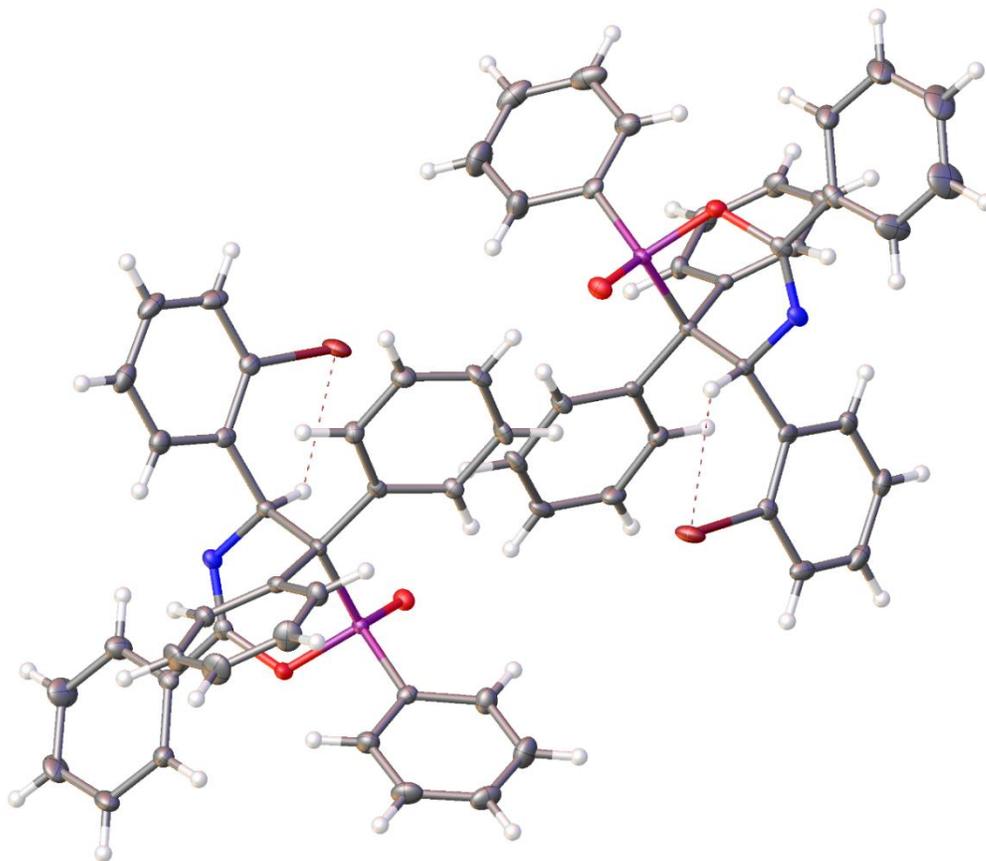
$^1\text{H}$  NMR spectrum for the reaction of **3ad** (6.262 ppm) and **3aa** (6.233 ppm) in  $\text{CDCl}_3$  (400 MHz)



$^1\text{H}$  NMR spectrum for the reaction of **3ad** (6.252 ppm) and **3ag** (6.319 ppm) in  $\text{CDCl}_3$  (400 MHz)



## 1.6 X-Ray crystallographic analysis of 3ai



CCDC: 2515767 (Displacement ellipsoids are drawn at the 50% probability level)

**Figure S5.** Stereostructure of product **3ai**

**Table S2:** Crystal data and structure refinement for compound **3ai**

Empirical formula	C <sub>33</sub> H <sub>25</sub> BrNO <sub>2</sub> P
Formula weight	578.42
Temperature / K	117.1(2)
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a / Å, b / Å, c / Å	17.5149(2), 17.46180(17), 17.58145(18)
$\alpha$ /°, $\beta$ /°, $\gamma$ /°	90.00, 90.2135(13), 90.00
Volume / Å <sup>3</sup>	5377.11(11)
Z	8
$\rho_{\text{calc}}$ / mg mm <sup>-3</sup>	1.429
$\mu$ / mm <sup>-1</sup>	2.893
F(000)	2368
Crystal size / mm <sup>3</sup>	0.33 × 0.33 × 0.29
2 $\theta$ range for data collection	6.16 to 52°
Index ranges	-20 ≤ h ≤ 19, -20 ≤ k ≤ 18, -20 ≤ l ≤ 13
Reflections collected	24252
Independent reflections	9311[R(int) = 0.0338 (inf-0.9Å)]
Data/restraints/parameters	9311/0/685
Goodness-of-fit on F <sup>2</sup>	1.034
Final R indexes [ $I > 2\sigma(I)$ i.e. $F_o > 4\sigma(F_o)$ ]	R <sub>1</sub> = 0.0324, wR <sub>2</sub> = 0.0833
Final R indexes [all data]	R <sub>1</sub> = 0.0362, wR <sub>2</sub> = 0.0856
Largest diff. peak/hole / e Å <sup>-3</sup>	0.340/-0.526
Flack Parameters	N
Completeness	0.9983

### Experimental

Single crystals of C<sub>33</sub>H<sub>25</sub>BrNO<sub>2</sub>P were recrystallized from a mixed solvent of ethyl acetate and petroleum ether. A suitable one was mounted in inert oil and transferred to the cold gas stream of the diffractometer.

### Crystal structure determination of compound **3pa**

**Crystal Data.** C<sub>33</sub>H<sub>25</sub>BrNO<sub>2</sub>P,  $M = 578.42$ , monoclinic,  $a = 17.5149(2)$  Å,  $b = 17.46180(17)$  Å,  $c = 17.58145(18)$  Å,  $\beta = 90.2135(13)^\circ$ ,  $U = 5377.11(11)$  Å<sup>3</sup>,  $T = 117.1(2)$ , space group P2<sub>1</sub>/c (no. 14),  $Z = 8$ ,  $\mu(\text{Cu K}\alpha) = 2.893$ , 24252 reflections measured, 9311 unique ( $R_{\text{int}} = 0.0338$ ) which were used in all calculations. The final  $wR(F_2)$  was 0.0856 (all data).

## 2. Computational Details

### 2.1. Details of calculation and discussion

All calculations were performed with the Gaussian 09,<sup>4</sup> and Multiwfn programs.<sup>5,6</sup> Density functional theory (DFT) calculations using the M06-2X theoretical method were used to locate all the stationary points involved.<sup>7</sup>

Structural optimizations were obtained at the M06-2X/def2-SVP level under the PCM solution model which were computed by a self-consistent reaction field (SCRF) in Gaussian 09,<sup>8,9</sup> while frequency calculations are under the same level and the substrates, intermediates, and products were characterized by no imaginary vibrational mode, but transition states characterized by only one. Intrinsic reaction coordinate (IRC) calculations for transition states were performed at the same level, helping to confirm the transition states.<sup>10</sup> The single point energies were calculated at the M06-2X/def2-tzvp level with SMD implicit solvent model to described solvation effect,

All wavefunctions analysis were calculated using the Multiwfn program. All presented structures were visualized by CYLview20 programs.<sup>11</sup>

### 2.2. DFT-Computed energies of all stationary points

Structure	$E_{\text{gas}}$	$\Delta G_{\text{correction}}$	$G_{\text{gas}}$	$\Delta G$ (kcal/mol)
A	-1149.607828	0.239888	-1149.36794	0.0
TS <sub>Sexo</sub>	-1819.6903	0.439789	-1819.250511	12.1
TS <sub>Endo</sub>	-1819.68827	0.441754	-1819.246516	14.6
TS <sub>Scis</sub>	-1819.671345	0.438657	-1819.232688	23.3
TS <sub>Strans</sub>	-1819.671534	0.439296	-1819.232238	23.6
3ad	-1819.759209	0.446363	-1819.312846	-27.0
cis-3ad	-1819.757821	0.446774	-1819.311047	-25.9
cis-6	-1819.754172	0.443183	-1819.310989	-25.8
6	-1819.749426	0.443389	-1819.306037	-22.7
2d	-670.0759714	0.174000	-669.9019714	
N <sub>2</sub>	-109.5305898	-0.012545	-109.5431348	

### 2.3 Coordinates of all stationary points

A			
P	-0.30467100	-1.40950500	0.07580900
O	-0.01594800	-2.87030300	0.19679100
C	0.79801100	-0.16934300	0.03584500
C	-2.05430400	-1.03258700	-0.05321400
C	-2.91044200	-2.02793100	0.44066900
C	-2.58606000	0.11006500	-0.67140200
C	-4.29083500	-1.86481600	0.34949700
H	-2.48583300	-2.92812500	0.88734000
C	-3.96680500	0.25759100	-0.76511700
H	-1.93229000	0.87753000	-1.08540400

C	-4.81892500	-0.72169800	-0.24948400
H	-4.95372800	-2.63606400	0.74313400
H	-4.38004700	1.14315600	-1.24912100
H	-5.89995200	-0.59528400	-0.32387800
C	2.25640100	-0.41883100	-0.00282400
C	2.80436000	-1.65224400	-0.40689200
C	3.14469000	0.60531500	0.37483900
C	4.18211400	-1.84726200	-0.42699900
H	2.14177900	-2.46654100	-0.70031000
C	4.52316300	0.40468500	0.35064300
H	2.74819300	1.56931200	0.69651700
C	5.05139700	-0.82197800	-0.05004100
H	4.58049000	-2.81181100	-0.74613100
H	5.18837200	1.21590500	0.65111800
H	6.13080800	-0.97836800	-0.06978000
C	0.29419800	1.23137300	0.09428700
C	-0.42926200	1.69801200	1.19886200
C	0.53266200	2.10599000	-0.97810400
C	-0.93720400	2.99730100	1.21794400
H	-0.60039000	1.02908800	2.04493700
C	0.03079900	3.40457700	-0.95640600
H	1.10414300	1.75082000	-1.83836900
C	-0.71384600	3.85096100	0.13884200
H	-1.50681700	3.34305100	2.08180100
H	0.21418500	4.07063800	-1.80092400
H	-1.11192400	4.86662600	0.15194300

**TSexo**

C	0.96651800	1.58765100	-1.00791600
C	-0.63172700	-1.30430100	0.14773700
C	-1.29686400	1.44243100	-1.16474400
H	-1.17812900	0.73862100	-2.00731400
C	-2.09009900	-1.49367700	0.04551300
C	-2.91538500	-1.18097100	1.14656500
C	-2.71884400	-2.03380400	-1.09852400
C	-4.28938900	-1.40643000	1.11113100
H	-2.46835300	-0.75822000	2.04763700
C	-4.09261800	-2.26071100	-1.12383200
H	-2.11192500	-2.28721600	-1.96731300
C	-4.89172900	-1.95329700	-0.02181800
H	-4.89458300	-1.15030100	1.98323500

H	-4.54280200	-2.69068100	-2.02113100
H	-5.96737600	-2.13434200	-0.04693500
C	-0.00932400	-1.09728500	1.49433900
C	0.47389700	-2.20092200	2.21313400
C	0.12882200	0.17890700	2.06110300
C	1.10350800	-2.03514400	3.44531700
H	0.36781300	-3.19766500	1.77947200
C	0.76273500	0.34832400	3.29371700
H	-0.25878700	1.04875200	1.52761500
C	1.25841700	-0.75707900	3.98495400
H	1.48161300	-2.90597700	3.98343500
H	0.87050500	1.34997200	3.71336900
H	1.75929500	-0.62411700	4.94521900
P	0.41822600	-1.38053000	-1.16409700
O	-0.01687200	-1.74011200	-2.54702800
C	2.10849700	-1.88562300	-0.77521400
C	2.89964200	-1.32287400	0.23637000
C	2.63467000	-2.88968800	-1.59535300
C	4.19860600	-1.78343200	0.43354300
H	2.51137900	-0.51998600	0.86629000
C	3.93584400	-3.34976100	-1.38857000
H	2.02045200	-3.30175400	-2.39769600
C	4.71654800	-2.79957500	-0.37392400
H	4.81235600	-1.34221300	1.22017600
H	4.33933700	-4.13661000	-2.02729900
H	5.73495600	-3.15680300	-0.21376500
C	-2.64945700	1.70053300	-0.70746500
C	-3.72307300	1.13083200	-1.40803400
C	-2.89161500	2.48317700	0.43652600
C	-5.02749600	1.33840000	-0.97040300
H	-3.52609200	0.52052200	-2.29098500
C	-4.19401700	2.68183200	0.87252700
H	-2.04523000	2.92356200	0.96553800
C	-5.26058900	2.10873800	0.16899600
H	-5.86211800	0.89036600	-1.51034900
H	-4.38780000	3.28382200	1.76094200
H	-6.28311800	2.26665300	0.51612900
N	-0.26812300	2.04176900	-0.65246900
C	2.13268200	2.42147100	-0.65253300
C	1.96414200	3.65276900	-0.00312800
C	3.42009700	1.96303600	-0.97112300

C	3.07934700	4.41857300	0.32442100
H	0.95758800	3.99153300	0.24098500
C	4.53008700	2.73111300	-0.63734500
H	3.53010100	1.00286000	-1.47719600
C	4.35964400	3.95830300	0.00946700
H	2.95201800	5.37626700	0.83022700
H	5.53179700	2.37597700	-0.88172000
H	5.23184400	4.55990500	0.27009400
O	1.15185700	0.48305600	-1.56953600

**TSendo**

C	-1.43107400	-1.59913100	-0.67864200
C	0.72975800	0.99406800	0.53999400
C	0.75277100	-1.34323500	-1.22445800
H	0.48408300	-0.47052300	-1.83605600
C	0.97382000	2.08691000	-0.43685700
C	1.86542100	3.13822200	-0.13675000
C	0.25903900	2.17254000	-1.64600200
C	2.03345700	4.21289400	-1.00343800
H	2.41221500	3.11837600	0.80730400
C	0.42263400	3.25499900	-2.51162700
H	-0.46600600	1.39724800	-1.90209500
C	1.31259700	4.27959300	-2.19931800
H	2.72431500	5.01473800	-0.73682300
H	-0.15476000	3.29324300	-3.43689900
H	1.44242800	5.12552900	-2.87568300
C	1.84061400	0.36993300	1.29178100
C	1.64483000	-0.45196500	2.42496100
C	3.17687300	0.56214700	0.87642500
C	2.72085700	-1.01619100	3.10576700
H	0.63297600	-0.64697300	2.77355400
C	4.24859300	0.00032500	1.56471900
H	3.38563100	1.15506100	-0.01317000
C	4.03386700	-0.79148500	2.69170900
H	2.52350900	-1.63888000	3.98078900
H	5.26346000	0.17724000	1.20243900
H	4.87281100	-1.23250000	3.23209600
P	-0.90314600	0.61453000	0.85297500
O	-1.30225700	-0.39009200	1.88605100
C	-2.08245500	1.97072000	0.67533200
C	-1.72012300	3.32285900	0.69507800

C	-3.43724500	1.61304100	0.69060600
C	-2.70984200	4.30487700	0.69004200
H	-0.66999600	3.61514000	0.71395500
C	-4.42154900	2.59805300	0.68442800
H	-3.71253900	0.55780500	0.72239100
C	-4.05768900	3.94545300	0.67687600
H	-2.42346000	5.35722800	0.70127200
H	-5.47445600	2.31340400	0.69164100
H	-4.82785500	4.71826900	0.67113400
C	2.15838300	-1.67530700	-1.14332700
C	2.61949800	-2.67480500	-0.26936800
C	3.06776700	-0.96351900	-1.94215300
C	3.97669900	-2.95778200	-0.20472400
H	1.89806500	-3.20797700	0.35122000
C	4.42482400	-1.26600100	-1.88878200
H	2.69920700	-0.17560300	-2.60368400
C	4.87626700	-2.25979700	-1.01874400
H	4.34323000	-3.72307500	0.48039700
H	5.13251400	-0.72330000	-2.51619200
H	5.94156000	-2.49168700	-0.96897800
N	-0.18247300	-2.09815800	-0.71835700
C	-2.56147800	-2.53032400	-0.55041600
C	-3.87080600	-2.04479600	-0.68351300
C	-2.33866900	-3.89724800	-0.32544600
C	-4.94829300	-2.91826100	-0.58330500
H	-4.02604200	-0.98406500	-0.88264600
C	-3.42068300	-4.76517500	-0.22121800
H	-1.31546600	-4.25803300	-0.22326500
C	-4.72342000	-4.27711500	-0.34880800
H	-5.96638900	-2.54269900	-0.69062400
H	-3.25058500	-5.82643500	-0.03689600
H	-5.56966900	-4.96096500	-0.26694800
O	-1.64345900	-0.34220800	-0.71721200

**TScis**

P	-0.98985500	-0.61042500	-1.30645600
C	-1.75106400	0.78321000	-0.58166700
C	0.60316300	0.17047300	0.63888500
N	0.69201700	-0.30249200	-0.59889500
O	-0.78674500	-0.85036400	-2.76698800
C	1.92135600	-0.50124700	-1.31451300

O	2.04442100	-0.12879400	-2.44789100
C	-1.40951600	-2.15659300	-0.44673700
C	-1.19431300	-3.32474200	-1.18972900
C	-1.38528700	-4.57516900	-0.60316800
C	-1.79309300	-4.66656100	0.72721300
C	-2.01502100	-3.50582700	1.47054900
C	-1.82665800	-2.25311600	0.88928200
C	-3.03897900	0.58454800	0.11852000
C	-4.07995100	-0.16627000	-0.45706400
C	-5.25088600	-0.44291800	0.24820600
C	-5.42551100	0.04584300	1.54225500
C	-4.41191000	0.80955900	2.12612600
C	-3.23420300	1.06745300	1.42875800
C	-1.23039200	2.10345300	-0.93271100
C	-0.20225600	2.27234100	-1.89749000
C	0.35442700	3.52459800	-2.15856800
C	-0.10620900	4.66737800	-1.50856200
C	-1.16122100	4.53237200	-0.60086700
C	-1.71355600	3.28820200	-0.32110200
C	1.52278500	1.10195900	1.23493300
C	1.48954600	1.26915200	2.63437300
C	2.33938800	2.18004100	3.24470800
C	3.20581700	2.95028900	2.46193700
C	3.22232900	2.81605800	1.07054800
C	2.38668700	1.89573400	0.45158400
C	2.98303100	-1.24052200	-0.56853700
C	2.68919100	-2.09792400	0.49904100
C	3.72001100	-2.78843100	1.13327300
C	5.03861600	-2.61847300	0.71010700
C	5.33128100	-1.76904900	-0.35986000
C	4.30450500	-1.08826100	-1.00562400
H	-0.22733500	-0.17495000	1.25683600
H	-0.87886000	-3.23641900	-2.23052300
H	-1.21770700	-5.47995500	-1.18900500
H	-1.94493200	-5.64467200	1.18622200
H	-2.34572300	-3.57444900	2.50769500
H	-2.03818700	-1.35729400	1.47548200
H	-3.96308000	-0.53841500	-1.47802100
H	-6.03599500	-1.03680300	-0.22316500
H	-6.34374100	-0.16418500	2.09260900
H	-4.53259300	1.19260700	3.14119300

H	-2.42968700	1.62505900	1.91410400
H	0.13853200	1.42324600	-2.49122700
H	1.14760300	3.60169500	-2.90589000
H	0.32470800	5.64612200	-1.72272600
H	-1.56580200	5.41495800	-0.10068200
H	-2.54130200	3.23094400	0.38488000
H	0.79785000	0.67047700	3.23014300
H	2.32489600	2.30234700	4.32769000
H	3.86652300	3.67401600	2.94155000
H	3.88263800	3.44076600	0.46901500
H	2.36688800	1.82428300	-0.63663300
H	1.65695200	-2.25141000	0.82075800
H	3.49204000	-3.46494800	1.95744000
H	5.84378400	-3.15519500	1.21393200
H	6.36251600	-1.64006700	-0.69020200
H	4.50967600	-0.42604500	-1.84794200

**TStrans**

P	-0.89120400	-0.09717900	-1.46415900
C	-1.75185600	1.03200600	-0.43792000
C	0.77296400	0.45003200	0.54454600
N	0.75558300	-0.07038400	-0.70272800
O	-0.74475200	0.09860500	-2.93639200
C	1.83742600	-0.75456500	-1.32556900
O	1.61838900	-1.64699600	-2.10251100
C	-1.33956800	-1.79176400	-1.00623900
C	-1.44313400	-2.22207700	0.32303700
C	-1.77302500	-3.54703500	0.59632000
C	-2.00386200	-4.44025600	-0.45349600
C	-1.89620100	-4.01214700	-1.77619400
C	-1.55741900	-2.68778100	-2.05492000
C	-2.96577400	0.54715500	0.26204600
C	-3.98109000	-0.15129000	-0.41331600
C	-5.08721000	-0.65936100	0.26765200
C	-5.21718800	-0.46339000	1.64189100
C	-4.22731700	0.24343700	2.32928300
C	-3.11610200	0.73490800	1.64923400
C	-1.40813900	2.43974700	-0.47610600
C	-0.24629000	2.92261100	-1.13963100
C	0.08996000	4.27514900	-1.14151600
C	-0.70211400	5.21017000	-0.47898600

C	-1.85840400	4.76361500	0.17101200
C	-2.20623500	3.41999200	0.17354000
C	1.48404200	-0.14183700	1.64250100
C	1.73024800	0.65159800	2.78297900
C	2.41525600	0.11874200	3.86576200
C	2.83766200	-1.21374600	3.83112800
C	2.56938800	-2.02027900	2.71878100
C	1.89635400	-1.49315000	1.62707600
C	3.21543100	-0.26140900	-1.01982000
C	4.27010200	-1.17109600	-1.15329700
C	5.57661500	-0.76139400	-0.90491800
C	5.83455200	0.56296100	-0.54419700
C	4.78667600	1.47802300	-0.43526200
C	3.47562000	1.06857800	-0.66920900
H	0.26679700	1.39837500	0.71595300
H	-1.28414800	-1.51956700	1.14522300
H	-1.85683300	-3.88347500	1.63056600
H	-2.26761400	-5.47657800	-0.23633900
H	-2.07306900	-4.71168300	-2.59434100
H	-1.45502600	-2.33508500	-3.08271100
H	-3.89693800	-0.29906200	-1.49281400
H	-5.85556200	-1.20477300	-0.28307500
H	-6.08353100	-0.85710000	2.17552700
H	-4.31503000	0.39961900	3.40602800
H	-2.33063800	1.26115300	2.19813000
H	0.38058700	2.23675600	-1.71234100
H	0.98581600	4.59614200	-1.67685100
H	-0.43467400	6.26733000	-0.47729100
H	-2.50713200	5.47966300	0.67962200
H	-3.12575800	3.11264400	0.67155300
H	1.39125400	1.68928800	2.79518400
H	2.61883700	0.73497200	4.74150300
H	3.37085100	-1.63370800	4.68526000
H	2.88092900	-3.06481300	2.71387400
H	1.65427400	-2.13234100	0.77499300
H	4.04858200	-2.19883600	-1.44497600
H	6.39713000	-1.47415200	-0.99457400
H	6.85914500	0.88523700	-0.35306800
H	4.99074500	2.51629900	-0.17188900
H	2.66267000	1.79433000	-0.59761100

**3ad**

C	-2.02307400	-0.36937200	-0.67169000
C	0.83777100	-0.15652600	-0.12702800
C	0.13487600	-1.43170200	-0.71673400
H	0.38834700	-1.41758000	-1.79095000
C	2.34782500	-0.21413600	-0.42927300
C	3.31659600	-0.19491500	0.58478900
C	2.79501700	-0.35477200	-1.75389000
C	4.67499900	-0.30226900	0.28978900
H	3.01916600	-0.11337000	1.62956300
C	4.15391900	-0.45901100	-2.04853400
H	2.07716700	-0.36143600	-2.57254200
C	5.10348300	-0.43169600	-1.02950400
H	5.40035200	-0.28902600	1.10466200
H	4.46723600	-0.56365000	-3.08839500
H	6.16642600	-0.51487100	-1.26026900
C	0.49004500	0.15153200	1.33086100
C	1.04012200	1.28452000	1.95394300
C	-0.39371000	-0.63858500	2.08097600
C	0.71655300	1.62133000	3.26598200
H	1.74363500	1.91482000	1.40768100
C	-0.72130900	-0.30130000	3.39485200
H	-0.83237100	-1.53706400	1.64977700
C	-0.17245700	0.83069200	3.99298900
H	1.16283100	2.50828000	3.71818800
H	-1.41063100	-0.93706500	3.95218100
H	-0.43024500	1.09181600	5.02033600
P	0.02977100	1.15881000	-1.19357500
O	0.26016100	0.96083200	-2.65188500
C	0.29936700	2.83893500	-0.63299300
C	-0.51977900	3.45557700	0.32026000
C	1.37872700	3.52810600	-1.19852700
C	-0.24472100	4.76188100	0.71643500
H	-1.36004800	2.90955700	0.75207100
C	1.65423100	4.83126000	-0.78726200
H	1.99497700	3.04527600	-1.95989000
C	0.84407500	5.44446600	0.16915600
H	-0.87998300	5.24900500	1.45708400
H	2.49725500	5.37097100	-1.21990800
H	1.05872700	6.46591100	0.48693600
C	0.63160600	-2.78930400	-0.21636200

C	0.19476100	-3.91173100	-0.93326000
C	1.46936500	-2.98507500	0.88321300
C	0.58676900	-5.19552300	-0.56603700
H	-0.46878800	-3.76741600	-1.78876800
C	1.86652300	-4.27287500	1.25349200
H	1.81856700	-2.13773500	1.46966300
C	1.42905400	-5.38066200	0.53256500
H	0.23663900	-6.05483000	-1.14013400
H	2.52167000	-4.40383300	2.11608500
H	1.74100700	-6.38484800	0.82359300
N	-1.32088500	-1.41839900	-0.66532600
C	-3.50428600	-0.40265600	-0.56889300
C	-4.15107000	-1.63030300	-0.37590200
C	-4.25659500	0.77360600	-0.66029700
C	-5.53760500	-1.67818200	-0.27570500
H	-3.54791000	-2.53580800	-0.30667900
C	-5.64635100	0.72008800	-0.55877500
H	-3.75048800	1.72622400	-0.81429100
C	-6.28799500	-0.50284500	-0.36669000
H	-6.03778100	-2.63578700	-0.12504100
H	-6.22977400	1.63880500	-0.63195100
H	-7.37548400	-0.54231400	-0.28765000
O	-1.53656900	0.91308000	-0.74213000

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C	1.99099500	0.33298900	0.17326200
C	-0.74019600	-0.31014200	-0.54527300
C	-0.16566200	-0.40063100	0.90503800
H	-0.51831100	0.50202500	1.43247100
C	-2.27797900	-0.21227900	-0.52710900
C	-3.09032500	-0.93751200	-1.40977000
C	-2.91844500	0.60992100	0.41531000
C	-4.48049000	-0.83495700	-1.36305600
H	-2.64586800	-1.61674100	-2.13444300
C	-4.30735300	0.71596200	0.46034300
H	-2.34382700	1.18640700	1.14009900
C	-5.09874900	-0.00349900	-0.43229400
H	-5.08090700	-1.41891700	-2.06210100
H	-4.76856100	1.36519500	1.20595100
H	-6.18596300	0.07685200	-0.39705600
C	-0.16697000	-1.38061900	-1.48900300

C	-0.40747500	-1.31024000	-2.87260000
C	0.62501200	-2.43908000	-1.01856100
C	0.10573200	-2.26813400	-3.74417700
H	-0.99348400	-0.48548100	-3.27402400
C	1.13858800	-3.39804600	-1.89213700
H	0.85823800	-2.52839500	0.04048000
C	0.88051400	-3.32024700	-3.25827700
H	-0.10194000	-2.18547000	-4.81198200
H	1.74783800	-4.21013000	-1.49288800
H	1.28372100	-4.07050000	-3.94002400
P	-0.08369600	1.31968800	-1.19005200
O	-0.32294300	1.61894300	-2.62419700
C	-0.56888200	2.69760800	-0.13072700
C	-1.60918300	3.51255700	-0.59357900
C	0.05526300	2.97961900	1.09067000
C	-2.04606300	4.58528900	0.18005500
H	-2.07013200	3.29807000	-1.55932900
C	-0.38497700	4.05586800	1.85979600
H	0.88833900	2.36983000	1.44880200
C	-1.43828700	4.85233500	1.40790200
H	-2.86013700	5.21679600	-0.17750700
H	0.10063900	4.27607600	2.81099300
H	-1.78108400	5.69271700	2.01325600
C	-0.67176200	-1.55008500	1.78180000
C	-0.22854000	-1.56027600	3.11080600
C	-1.53847500	-2.56057700	1.35836700
C	-0.64288100	-2.55017700	3.99770300
H	0.45931100	-0.78077900	3.44504000
C	-1.95547400	-3.55500500	2.24642600
H	-1.89037600	-2.59154100	0.32844400
C	-1.51256600	-3.55375300	3.56689500
H	-0.28640400	-2.53818600	5.02888700
H	-2.63014600	-4.33717900	1.89523700
H	-1.84054800	-4.33172700	4.25792700
N	1.28489700	-0.34591900	0.97140300
C	3.47474500	0.35257100	0.24912500
C	4.22762400	1.15141500	-0.61834900
C	4.12195100	-0.44286300	1.20367200
C	5.61921100	1.15324400	-0.52948700
H	3.71999600	1.76792700	-1.35927800
C	5.51029700	-0.43673700	1.28829000

H	3.51829600	-1.06042900	1.86898300
C	6.26159400	0.36150800	0.42163300
H	6.20344300	1.77664600	-1.20755500
H	6.01122900	-1.05816600	2.03176700
H	7.35060800	0.36437800	0.48871800
O	1.51699800	1.12239100	-0.84156500

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P	-0.91698600	-0.29947400	-1.28693000
C	-0.69701700	0.87122800	0.17611900
C	0.65220600	0.09035200	0.48968100
N	0.37607400	-1.04068600	-0.42893500
O	-0.66239300	0.18850500	-2.67373100
C	1.22878400	-2.03245900	-0.87368200
O	0.97412700	-2.66176900	-1.87904900
C	-2.38688000	-1.32954100	-1.12264000
C	-2.28357900	-2.70424800	-0.89152600
C	-3.44182800	-3.46874500	-0.75575600
C	-4.69449900	-2.86025000	-0.83732700
C	-4.79645200	-1.48745800	-1.07174900
C	-3.64368000	-0.72032000	-1.22231600
C	-1.78092000	0.60116400	1.21795400
C	-2.80138700	1.53480400	1.44062700
C	-3.85265600	1.25092900	2.31265100
C	-3.90529000	0.02871700	2.97973600
C	-2.89379400	-0.90812300	2.76870800
C	-1.84444100	-0.62470200	1.89751200
C	-0.53418300	2.34659200	-0.11881600
C	-0.97656300	2.94220600	-1.30226500
C	-0.83514800	4.32009700	-1.49418500
C	-0.24958400	5.11266600	-0.51123700
C	0.19144500	4.52407000	0.67712200
C	0.04444400	3.15480300	0.87094400
C	1.94823900	0.79994000	0.17073400
C	2.86753700	1.04833300	1.19121800
C	4.07977900	1.68160000	0.91318800
C	4.37810000	2.07029100	-0.39160200
C	3.46196000	1.82246100	-1.41670100
C	2.25333700	1.18821500	-1.13992700
C	2.45885400	-2.26887600	-0.05377200
C	2.39507800	-2.40579700	1.33595600

C	3.56209100	-2.62602600	2.06491600
C	4.79221500	-2.68865500	1.40855800
C	4.85393900	-2.55969500	0.01982800
C	3.68619100	-2.36631200	-0.71489000
H	0.66483100	-0.22700400	1.54041200
H	-1.30189200	-3.17742400	-0.82657700
H	-3.36459300	-4.54248600	-0.58072000
H	-5.59859300	-3.45945000	-0.71964900
H	-5.77646500	-1.01318200	-1.13602700
H	-3.72557000	0.35513600	-1.39971100
H	-2.78097200	2.49456700	0.92341900
H	-4.63559800	1.99464900	2.46858600
H	-4.72884300	-0.19385100	3.65952800
H	-2.92250200	-1.87186300	3.27925500
H	-1.08821500	-1.39281300	1.72295100
H	-1.41503200	2.33147800	-2.09121700
H	-1.18435600	4.77045200	-2.42456400
H	-0.13671900	6.18672700	-0.66602100
H	0.64845100	5.13604400	1.45620700
H	0.38228700	2.70082100	1.80590500
H	2.63896100	0.73176700	2.21194800
H	4.79356400	1.86488200	1.71765200
H	5.32601600	2.56313400	-0.61284600
H	3.69159800	2.12443800	-2.43959100
H	1.54060800	0.99543100	-1.94707300
H	1.43205600	-2.35631700	1.84854000
H	3.51198800	-2.74550100	3.14791200
H	5.70717900	-2.84528800	1.98177000
H	5.81544300	-2.61404400	-0.49225800
H	3.71698300	-2.27084100	-1.80148600

**6**

P	-0.66673600	-0.17549700	-1.66413800
C	-0.93772700	0.85067300	-0.09501000
C	0.61774500	0.64873500	0.20549100
N	0.91701900	-0.12565800	-1.01081300
O	-0.91502700	0.45408800	-2.98974900
C	2.10107700	-0.56602400	-1.56667200
O	2.08476100	-1.36848400	-2.47791200
C	-1.32431800	-1.85211300	-1.55849700
C	-0.50919300	-2.95823900	-1.29992900

C	-1.07768700	-4.22811400	-1.20942400
C	-2.45392600	-4.39141400	-1.37164600
C	-3.26556100	-3.28858300	-1.64388000
C	-2.70195500	-2.01882500	-1.74517300
C	-1.90527700	0.30423600	0.95055300
C	-2.89901600	1.11413800	1.51755100
C	-3.76303800	0.61666600	2.49544800
C	-3.65300300	-0.70089800	2.93039800
C	-2.66637600	-1.51930900	2.37875500
C	-1.80597700	-1.02190400	1.40495100
C	-1.27326200	2.28571000	-0.48018800
C	-2.31772400	2.53687800	-1.38143400
C	-2.71447100	3.83929200	-1.67309900
C	-2.07604100	4.92144000	-1.06564200
C	-1.04278700	4.68629800	-0.16196700
C	-0.64618300	3.37929500	0.12744400
C	1.00303800	-0.00902000	1.51002400
C	0.76208000	0.69390800	2.69671000
C	1.07396700	0.13093500	3.93059500
C	1.63928300	-1.14477200	3.99419100
C	1.88968800	-1.84665800	2.81726400
C	1.57216500	-1.28131700	1.58036900
C	3.38120300	-0.04165600	-0.99283100
C	4.42028500	-0.95271700	-0.77514800
C	5.63954200	-0.50944300	-0.27003600
C	5.83365400	0.84846900	-0.00913700
C	4.81004900	1.76295400	-0.25832100
C	3.58075300	1.32008200	-0.74450800
H	1.10436800	1.62911400	0.16979800
H	0.56859700	-2.83007900	-1.18822800
H	-0.44291700	-5.09295200	-1.01298200
H	-2.89654400	-5.38540000	-1.29221500
H	-4.34019900	-3.41804400	-1.77723300
H	-3.33908400	-1.15690700	-1.95802600
H	-3.00640400	2.15154800	1.20250500
H	-4.52531600	1.27271100	2.91840000
H	-4.32775900	-1.08843800	3.69506400
H	-2.56002500	-2.55368200	2.70914700
H	-1.03890600	-1.68264400	1.00628000
H	-2.82738900	1.70246200	-1.86438900
H	-3.52706900	4.00876700	-2.38092100

H	-2.38505000	5.94221300	-1.29487800
H	-0.54019800	5.52124700	0.32818400
H	0.15180500	3.23047400	0.85677500
H	0.30313000	1.68499600	2.65509300
H	0.87317200	0.68802900	4.84673100
H	1.88427500	-1.58834300	4.96020900
H	2.33290100	-2.84266800	2.85630100
H	1.76003200	-1.85191800	0.66947500
H	4.25837400	-2.00834200	-0.99976200
H	6.44368700	-1.22274300	-0.08528500
H	6.79108500	1.19670700	0.38108000
H	4.96998500	2.82670300	-0.07857700
H	2.79344800	2.04219700	-0.96671500

**2d**

C	-1.12562200	-1.04278500	-0.35894500
C	-2.36183700	-0.24051700	-0.11422600
C	-2.32210300	1.15152100	0.02668100
C	-3.58320700	-0.91902900	-0.01528300
C	-3.49925900	1.85776800	0.26918400
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N	0.07202700	-0.29918300	-0.37140300
C	1.10969800	-0.87858100	0.09233500
H	1.03728000	-1.88895700	0.53173500
C	2.44376500	-0.26733200	0.07407200
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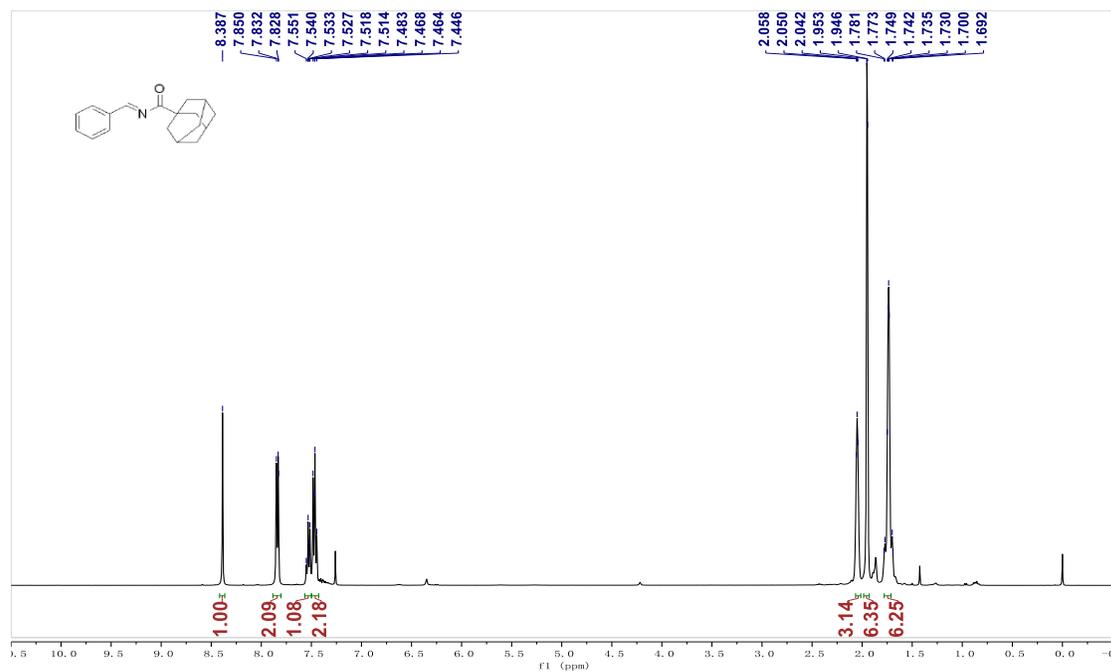
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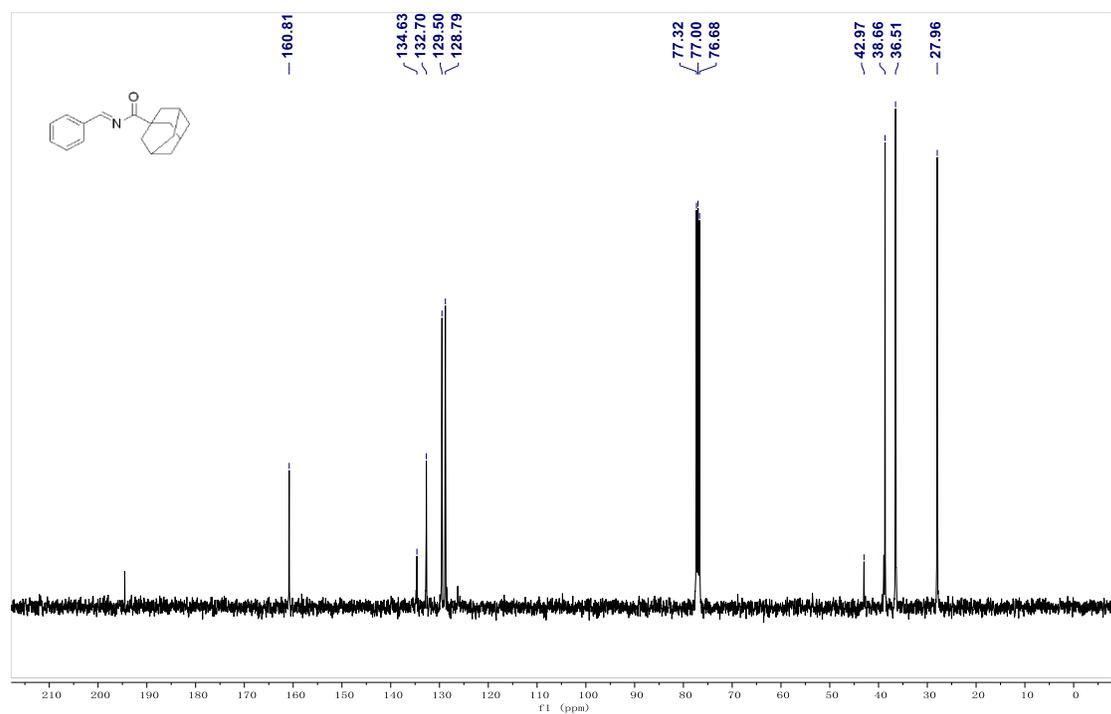
## 4. Copies of $^1\text{H}$ , $^{13}\text{C}\{^1\text{H}\}$ , $^{31}\text{P}\{^1\text{H}\}$ , $^{19}\text{F}\{^1\text{H}\}$ NMR, and HRMS Spectra of Products

### (*E*)-*N*-Benzylideneadamantane-1-carboxamide (3a)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



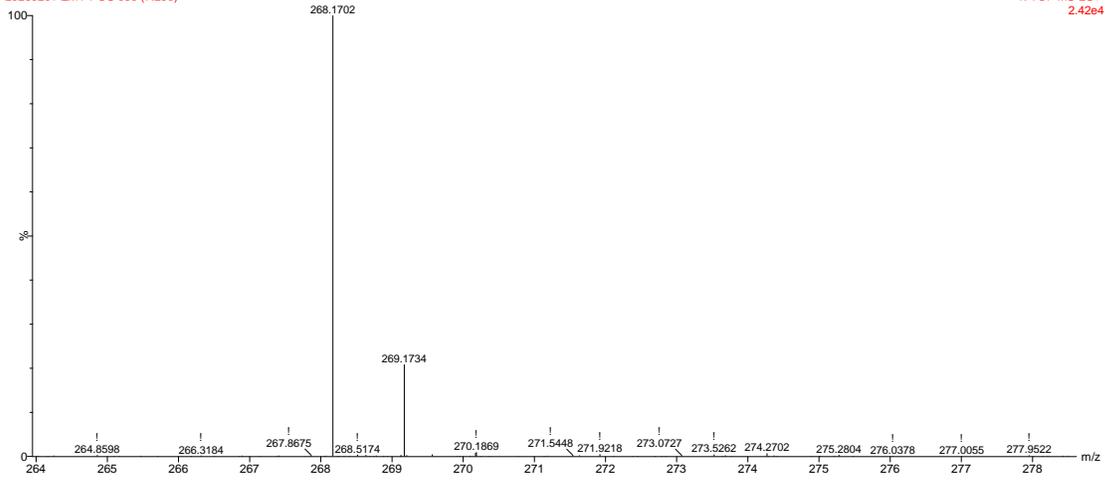
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )



# HRMS

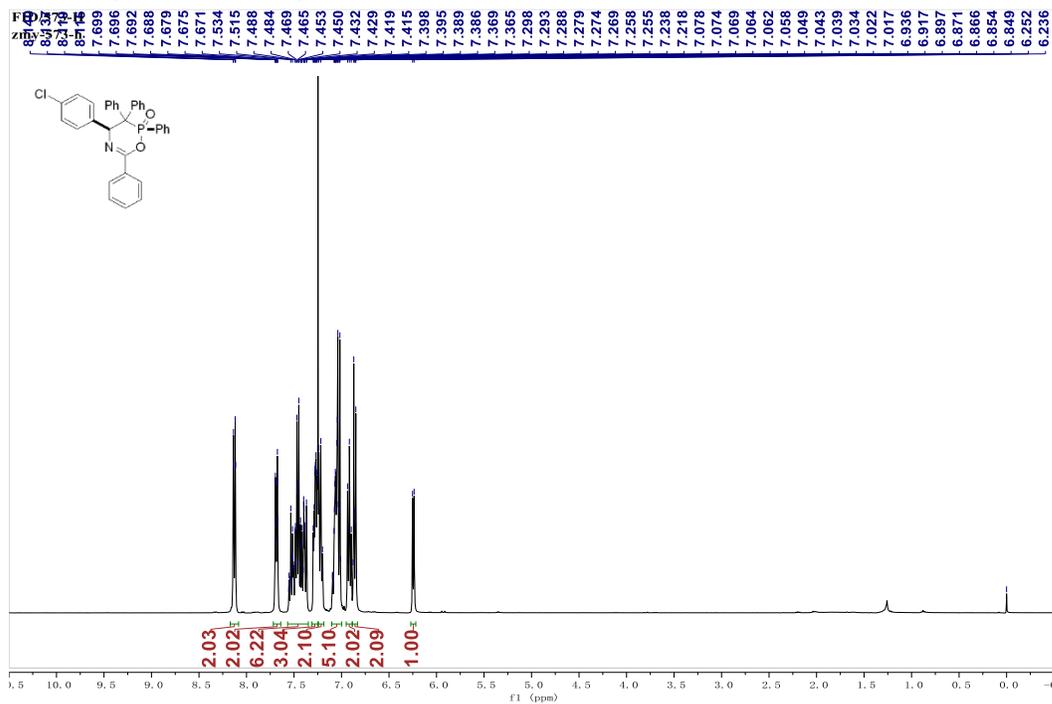
20260201-ZMY-POS 950 (7.290)

1: TOF MS ES+  
2.42e4

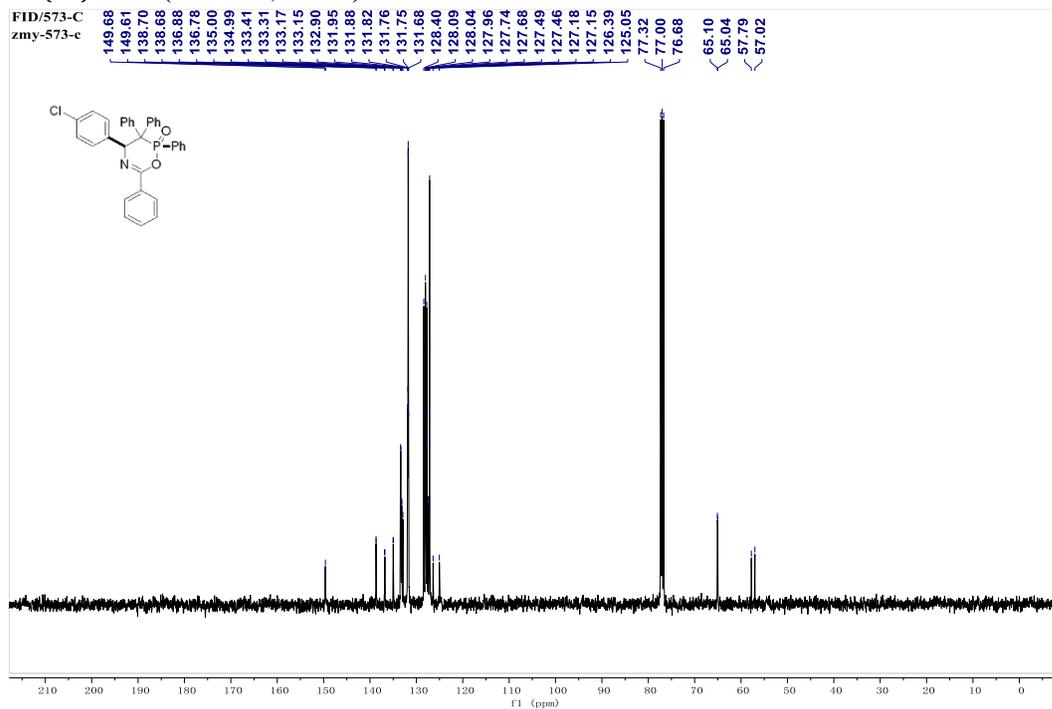


***trans*-4-(4-Chlorophenyl)-2,3,3,6-tetraphenyl-1,5,2-oxazaphosphinine 2-oxide (3aa)**

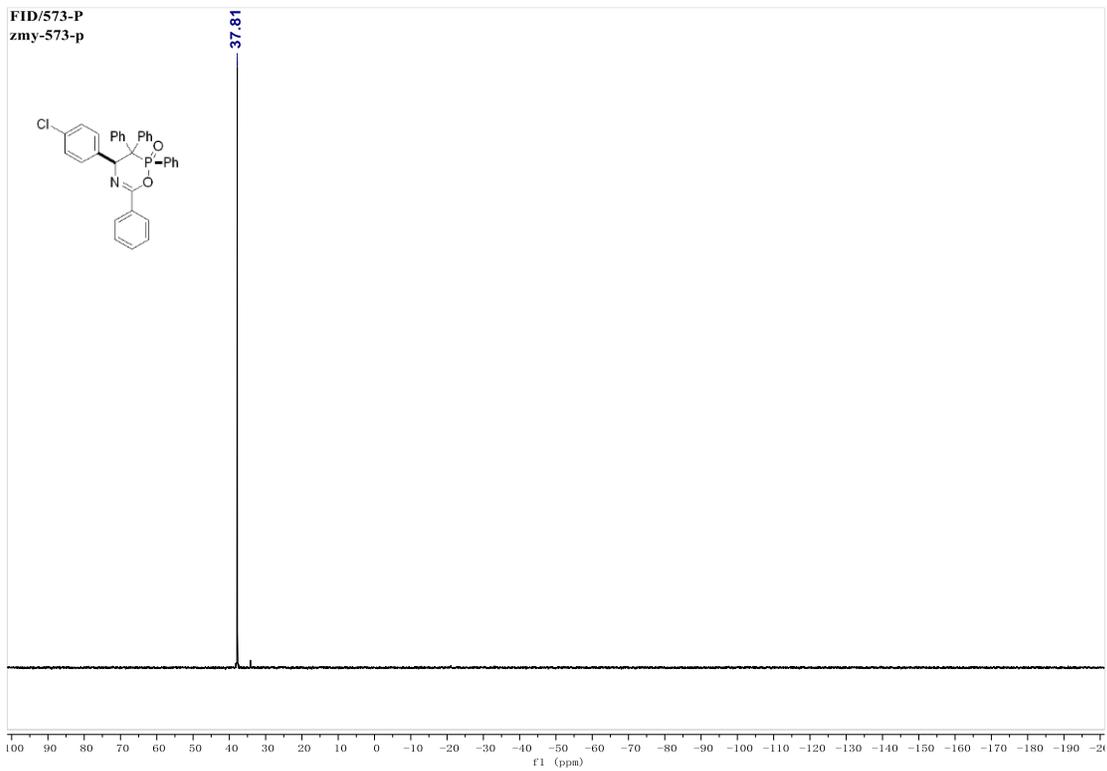
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



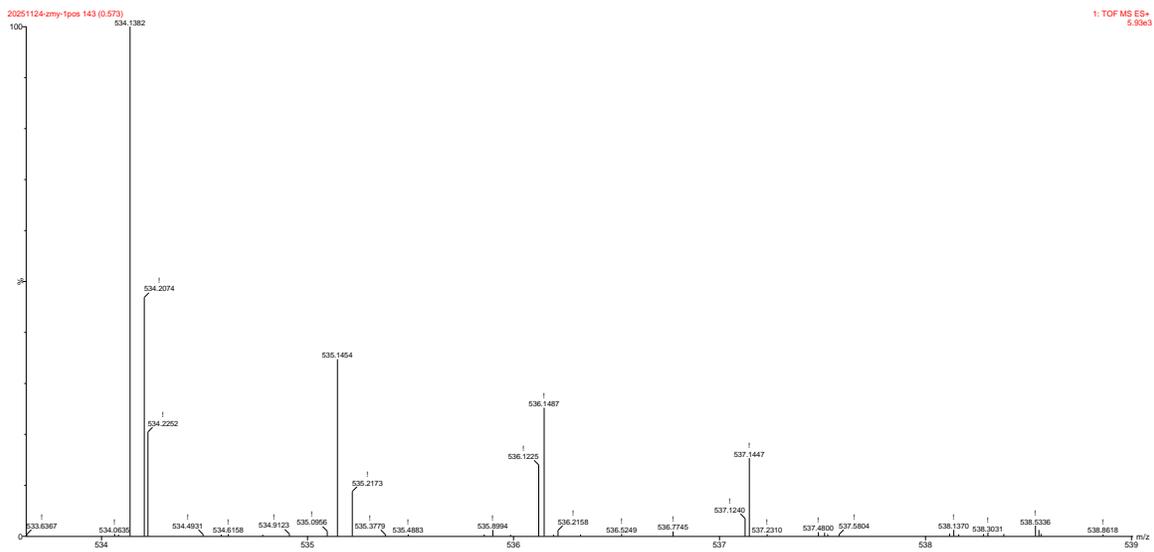
**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)**



**<sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>)**

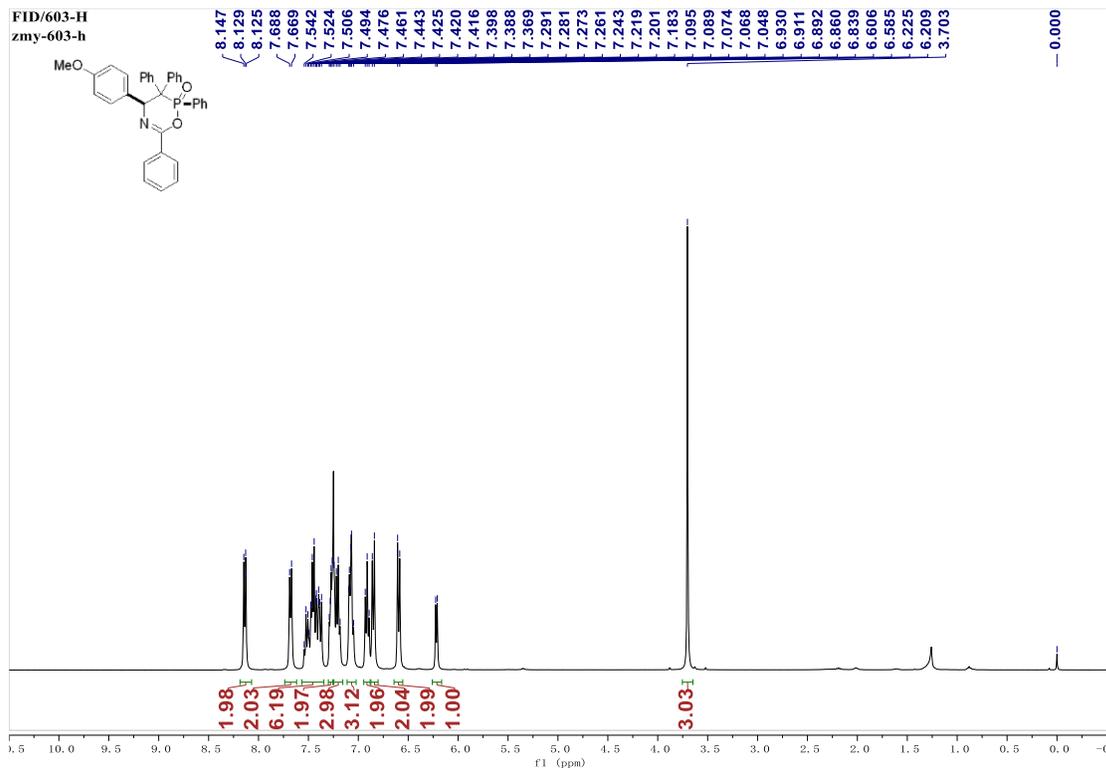


**HRMS**

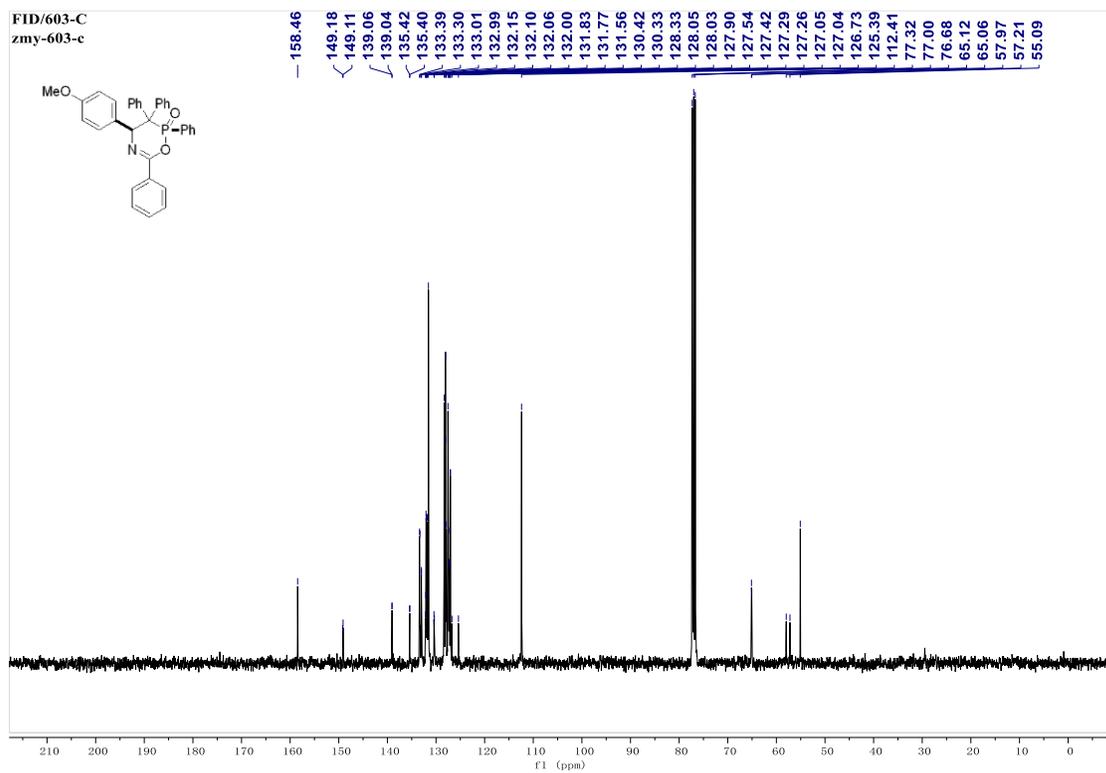


***trans*-4-(4-Methoxyphenyl)-2,3,3,6-tetraphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3ab)**

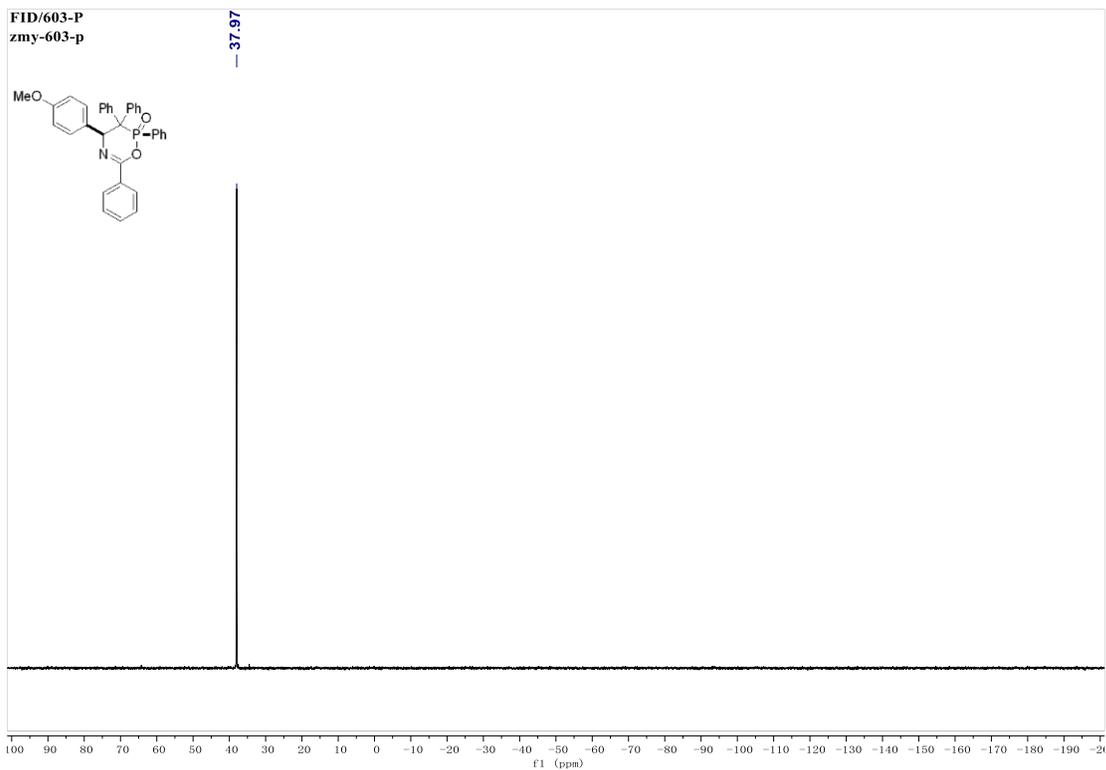
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



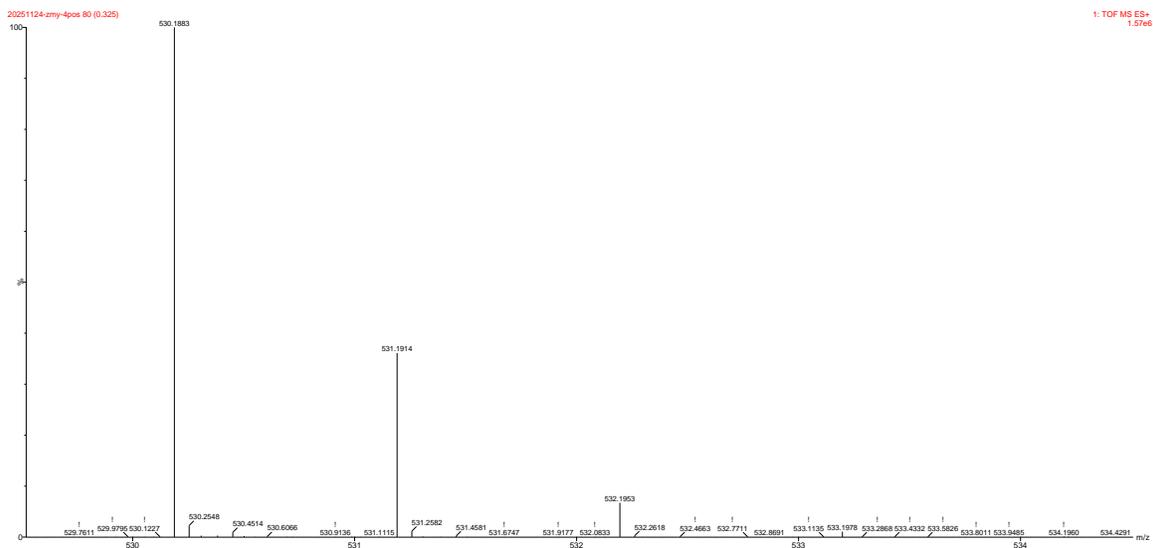
**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)**



### $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, $\text{CDCl}_3$ )

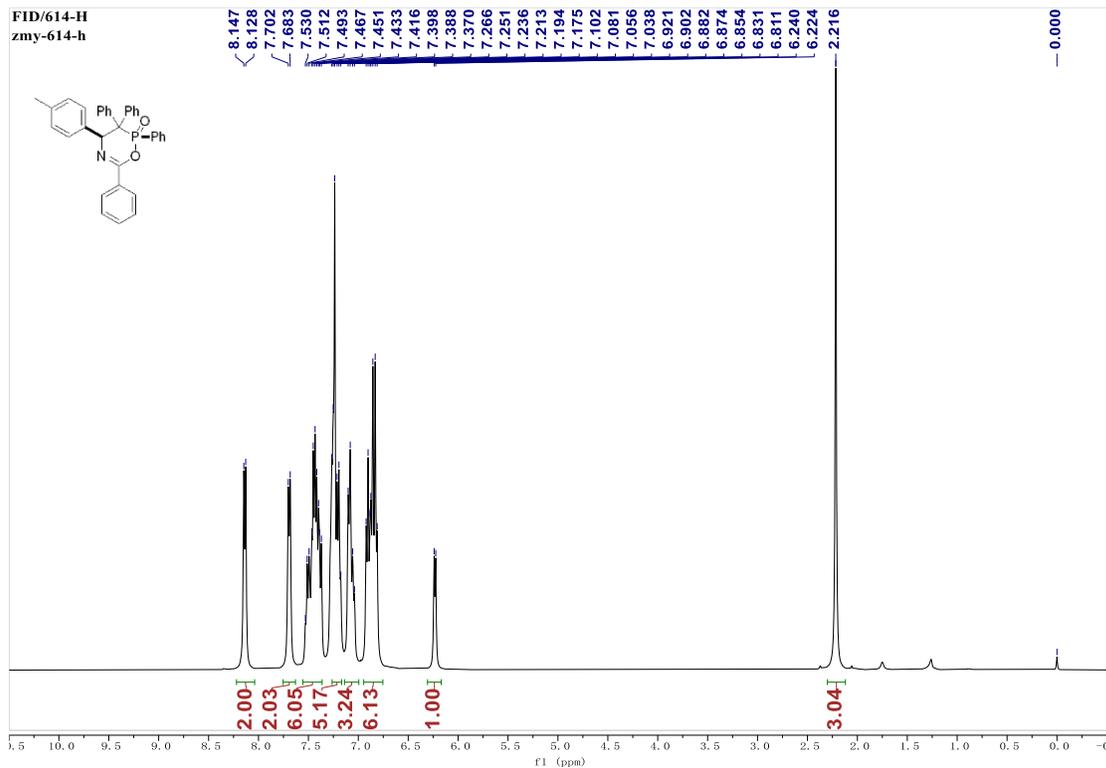


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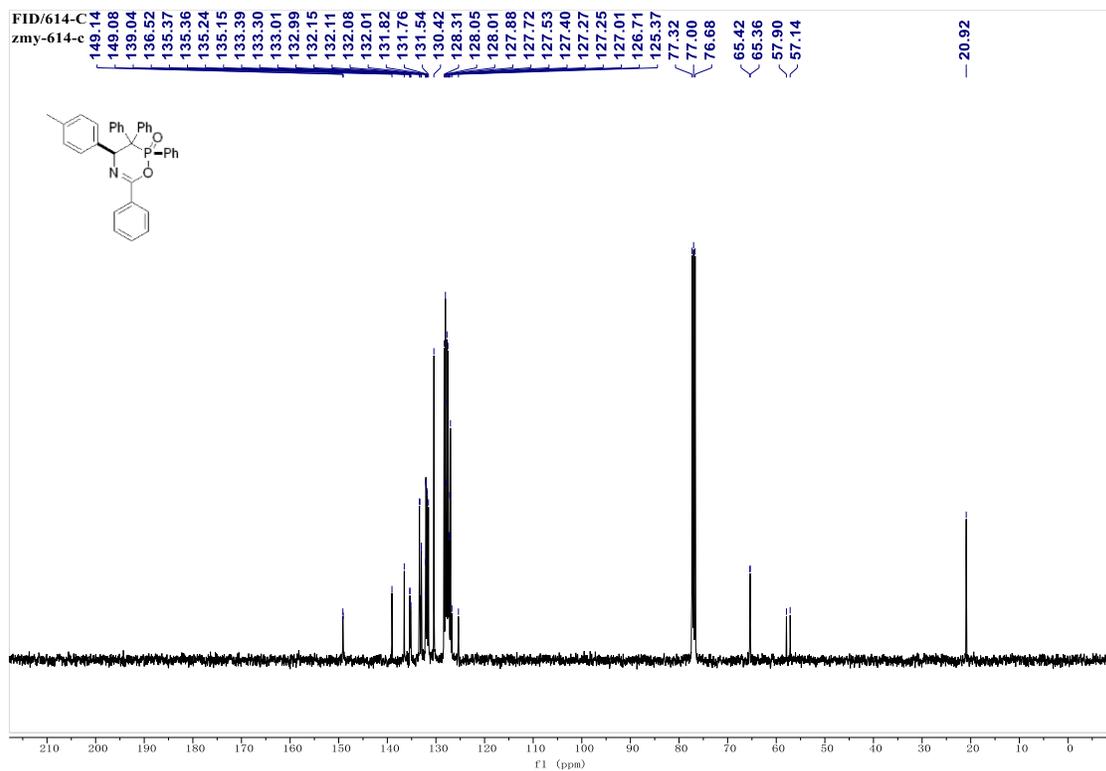


*trans*-2,3,3,6-Tetraphenyl-4-(*p*-tolyl)-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3ac)

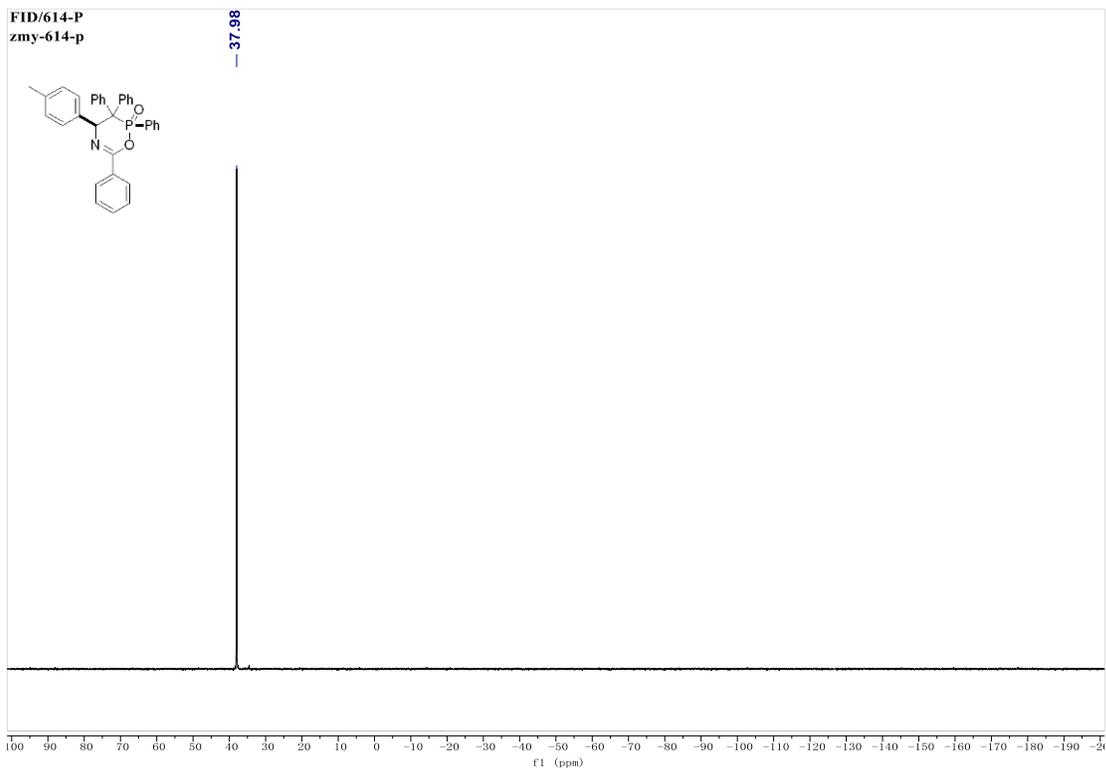
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



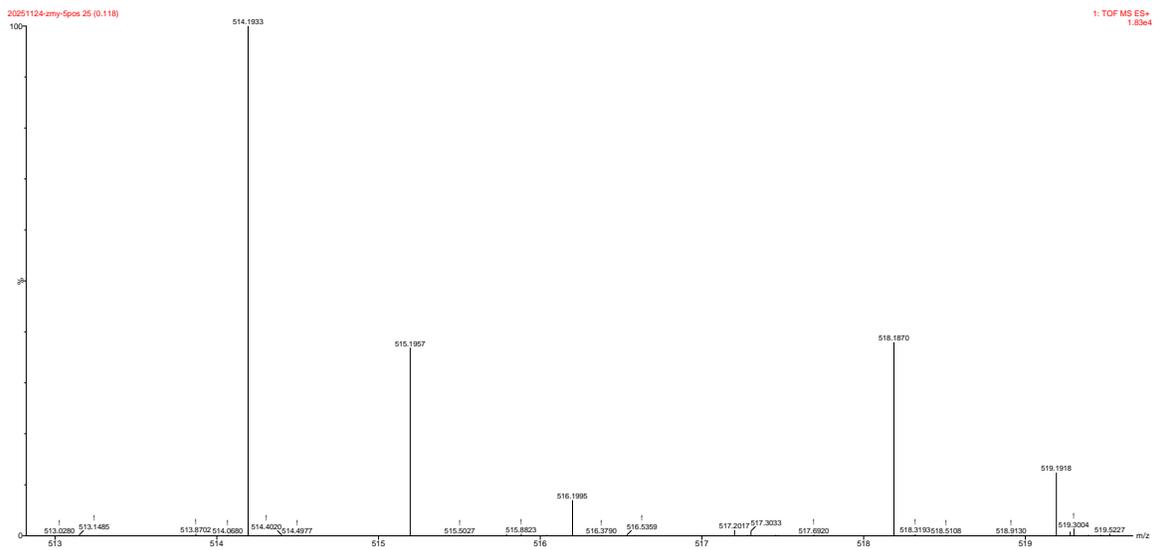
<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)



### $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, $\text{CDCl}_3$ )

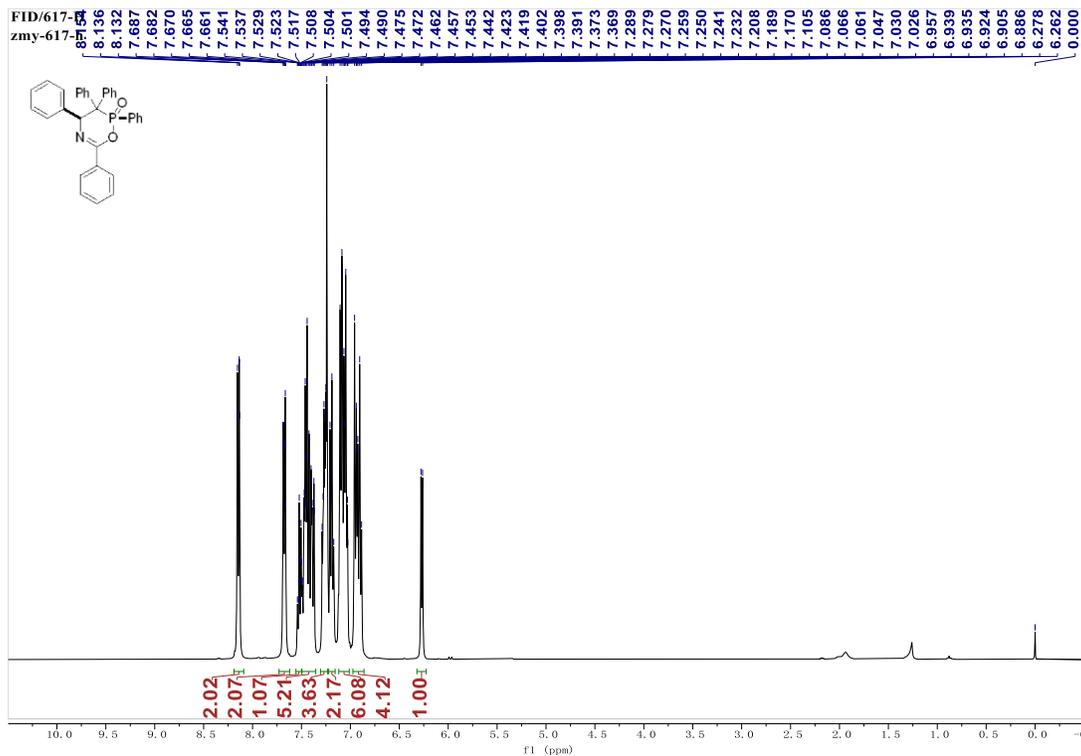


### HRMS

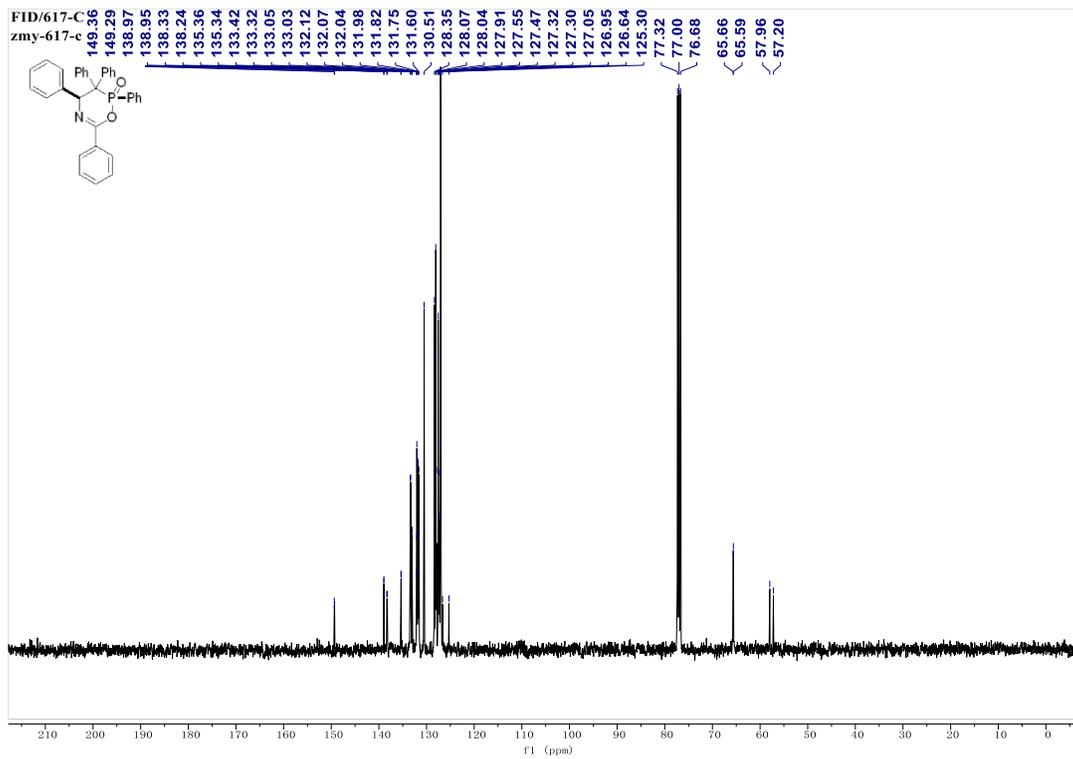


*trans*-2,3,3,4,6-Pentaphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3ad)

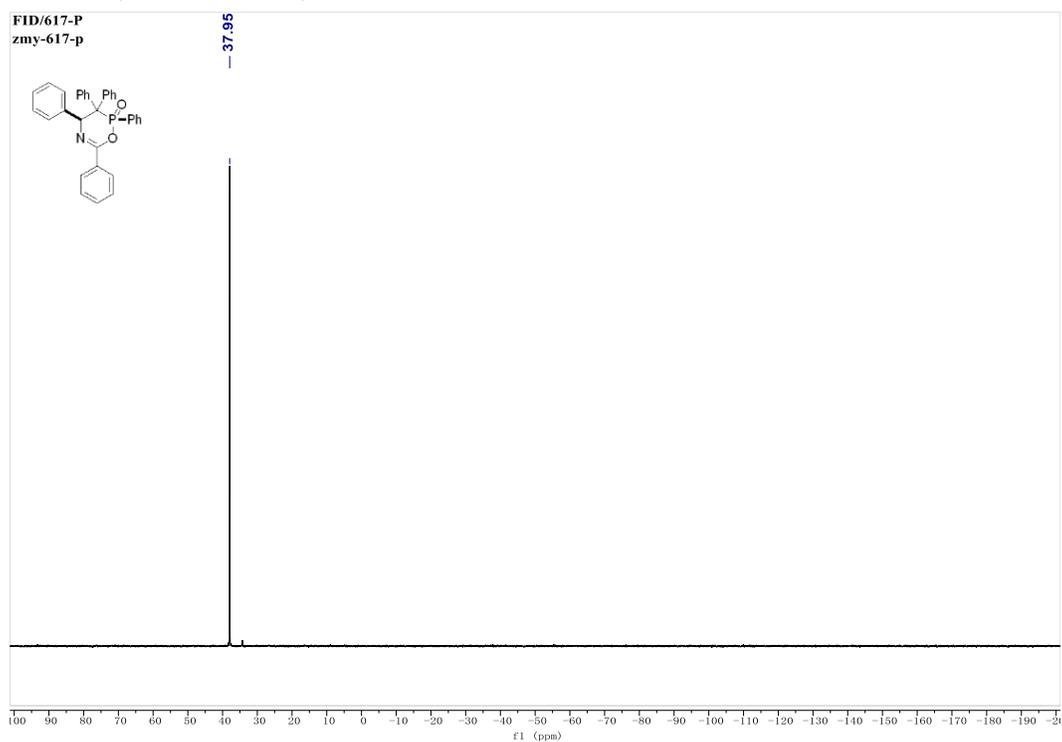
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



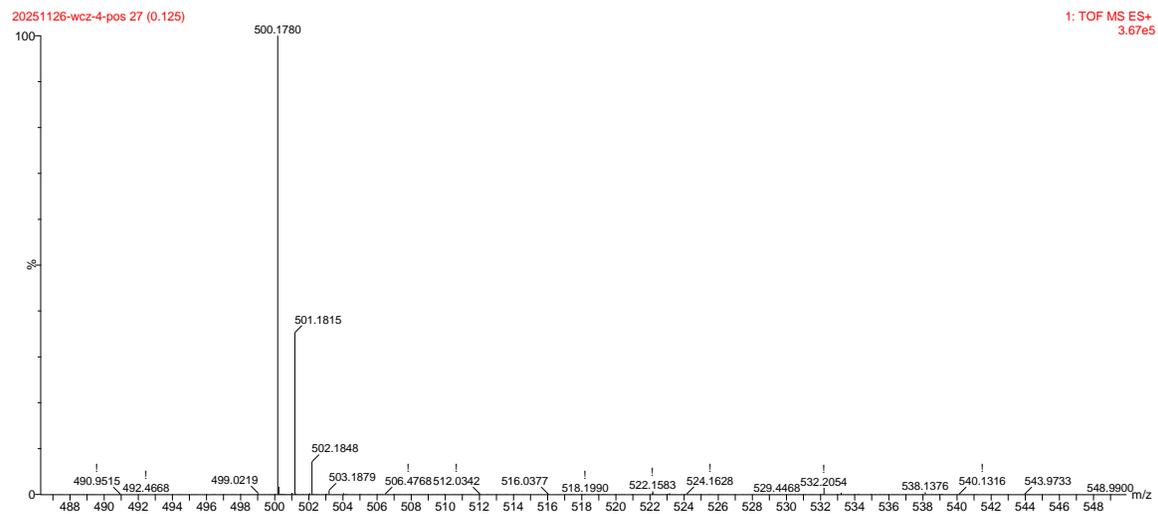
<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)



### $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, $\text{CDCl}_3$ )

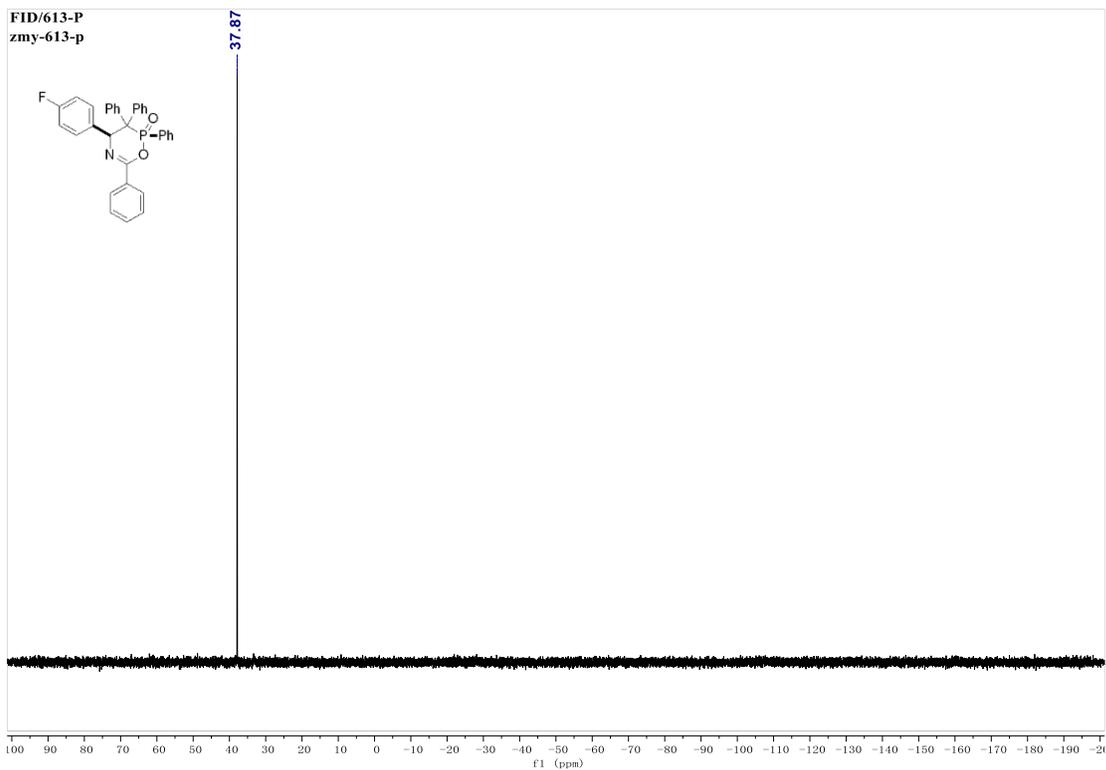


### HRMS

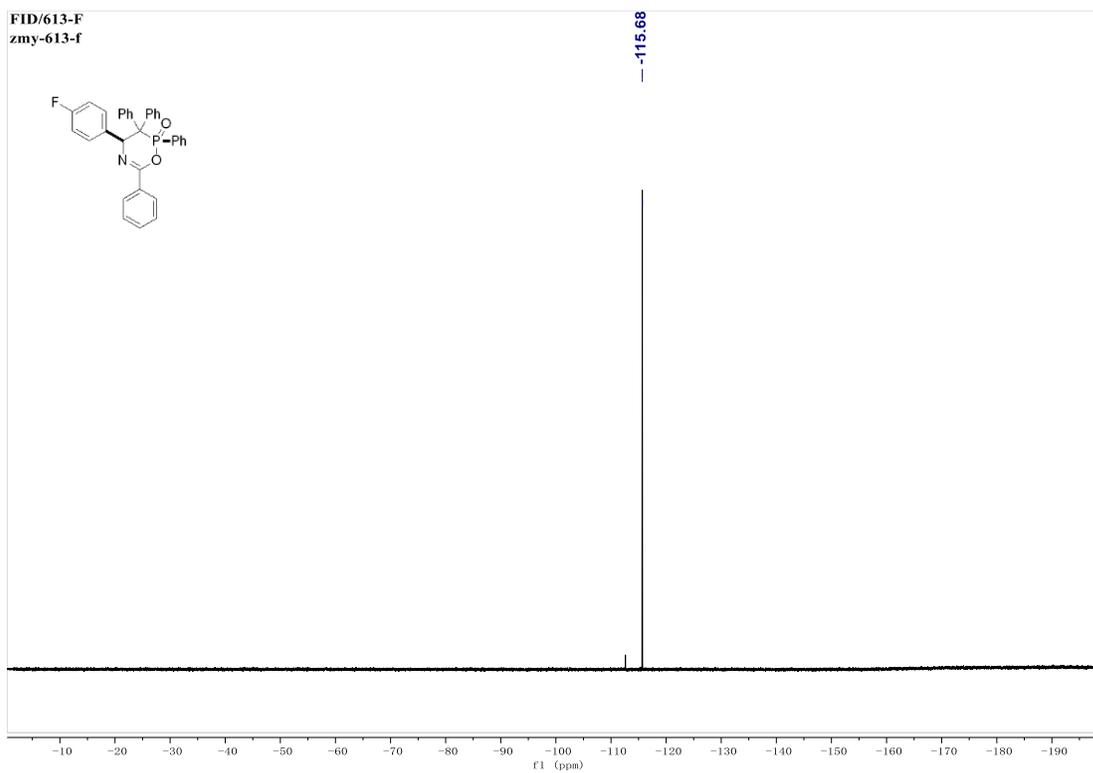




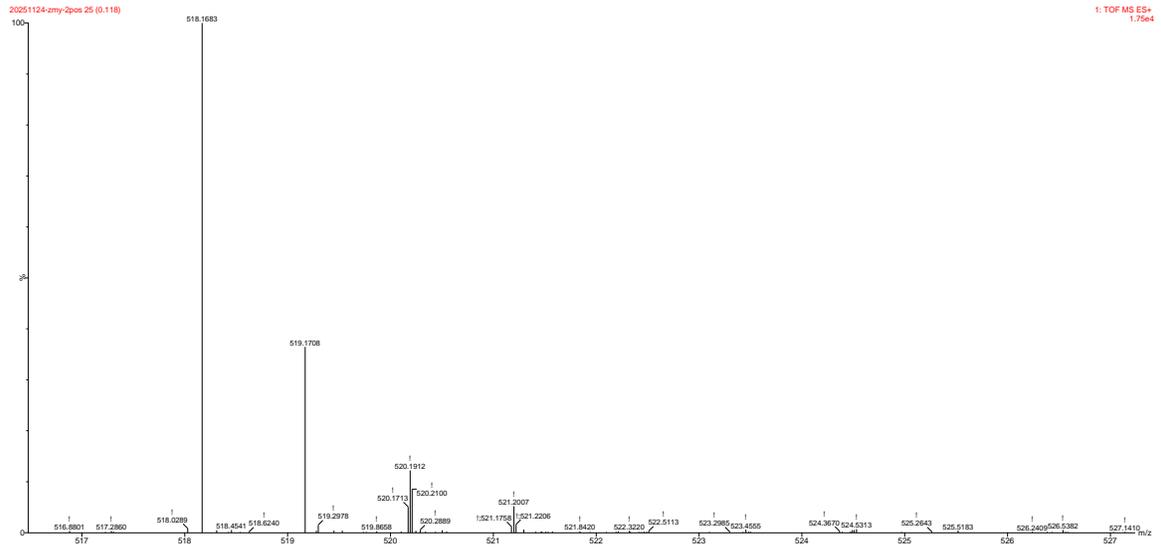
**$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ )**



**$^{19}\text{F}\{^1\text{H}\}$  NMR (376 MHz,  $\text{CDCl}_3$ )**

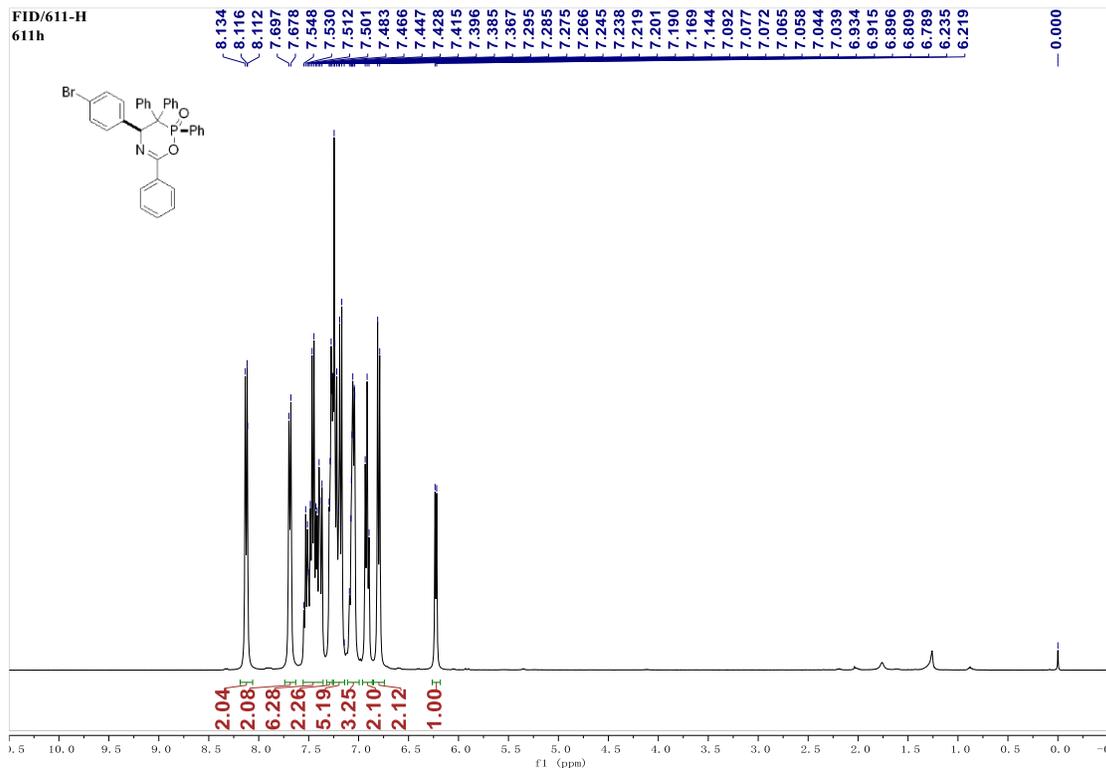


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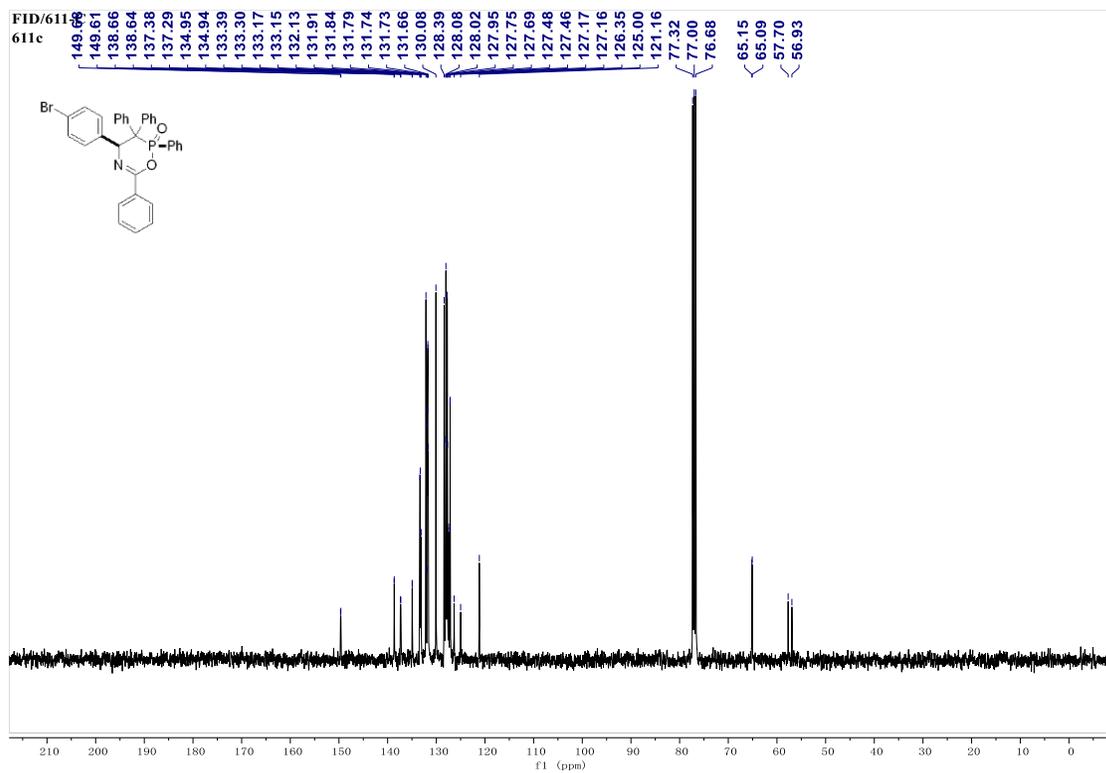


***trans*-4-(4-Bromophenyl)-2,3,3,6-tetraphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3af)**

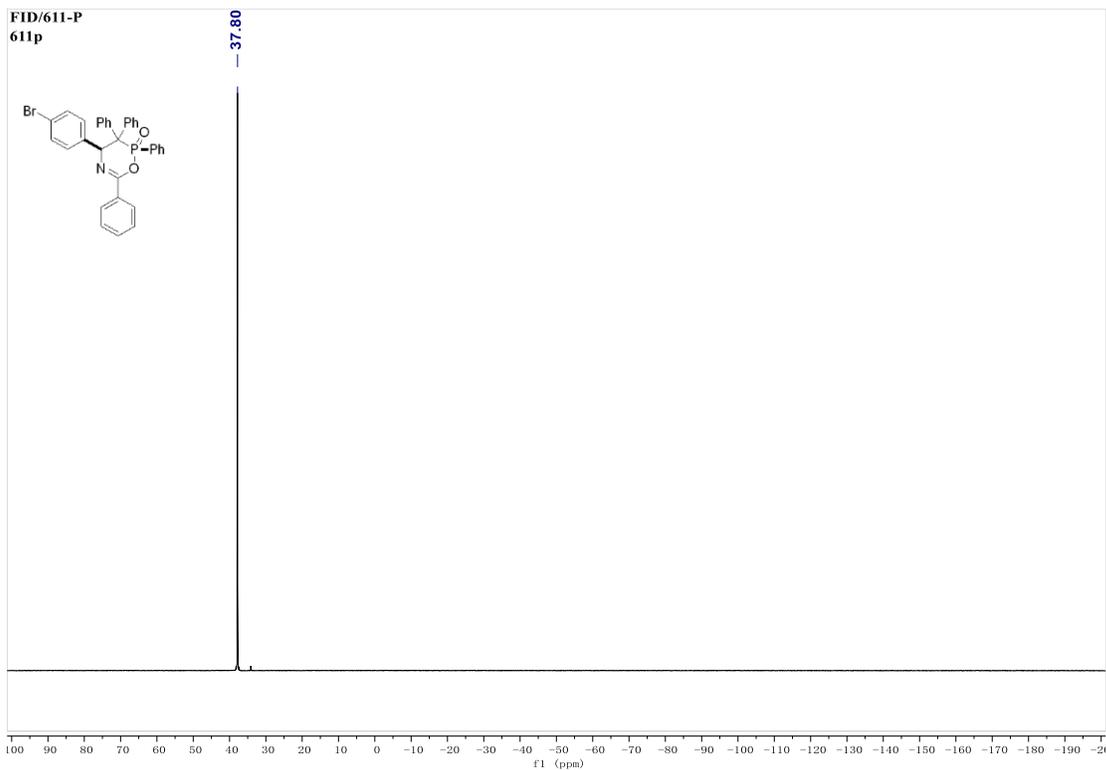
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



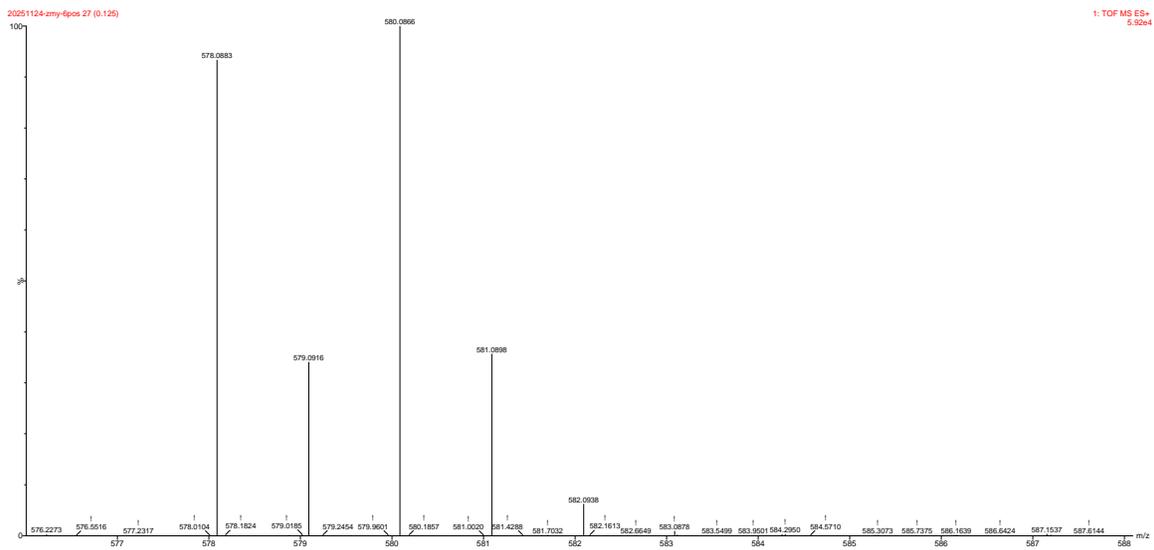
**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)**



### $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, $\text{CDCl}_3$ )

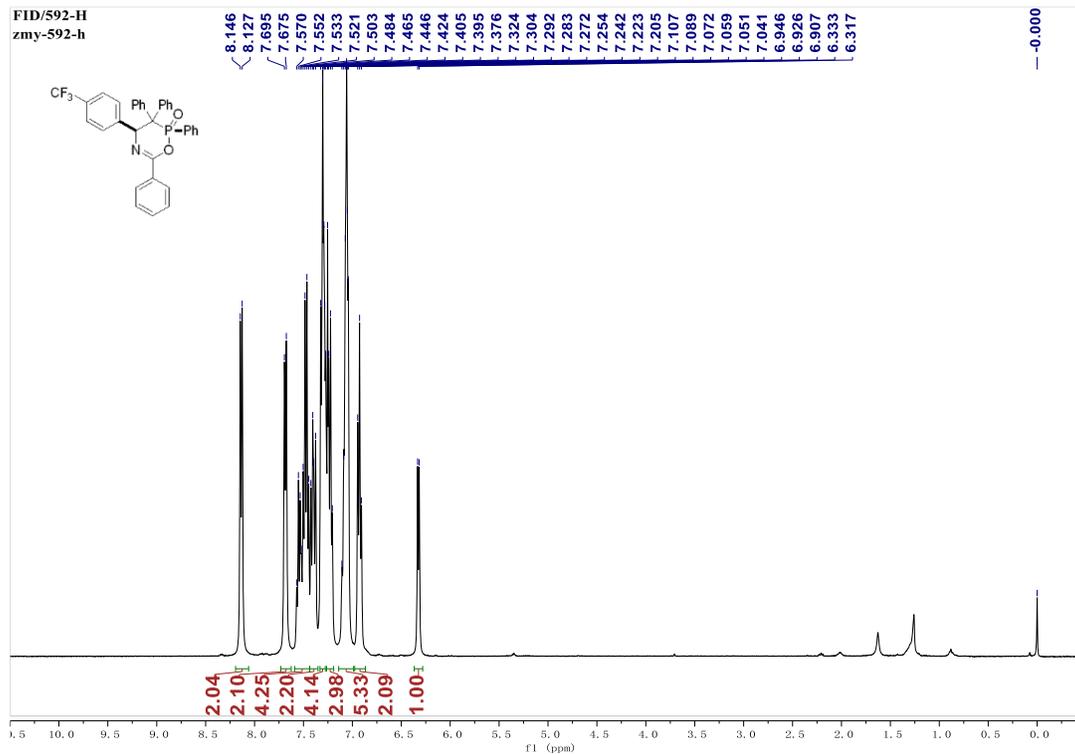


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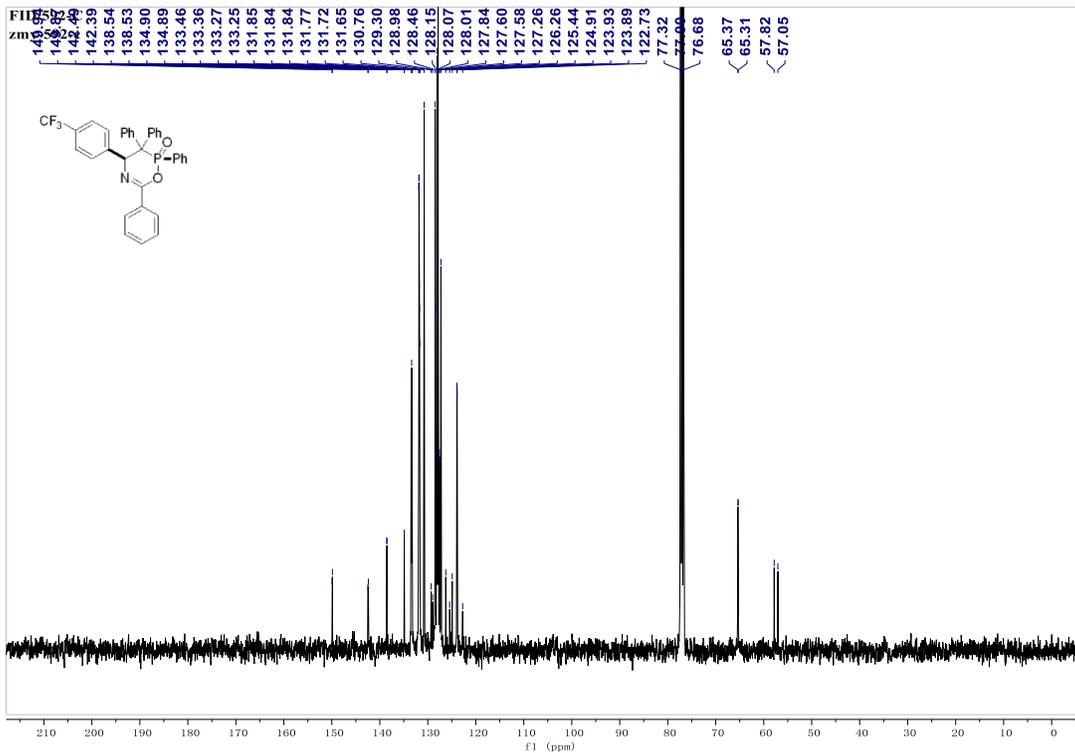


*trans*-2,3,3,6-Tetraphenyl-4-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3ag)

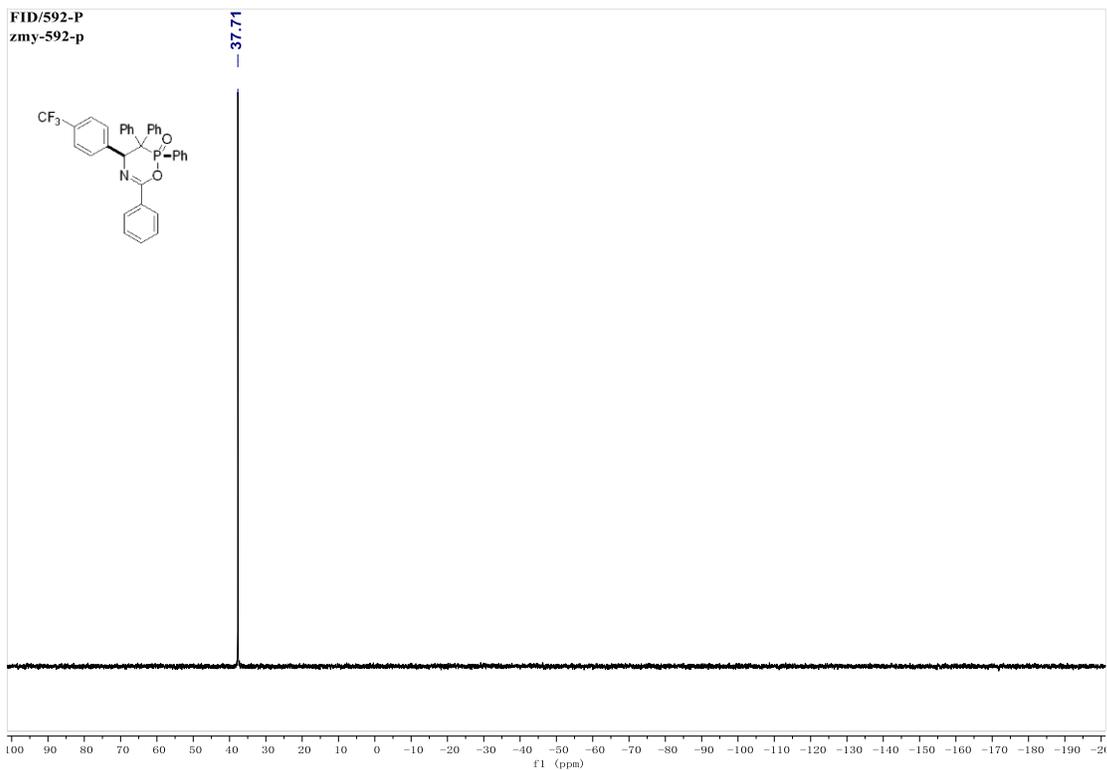
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



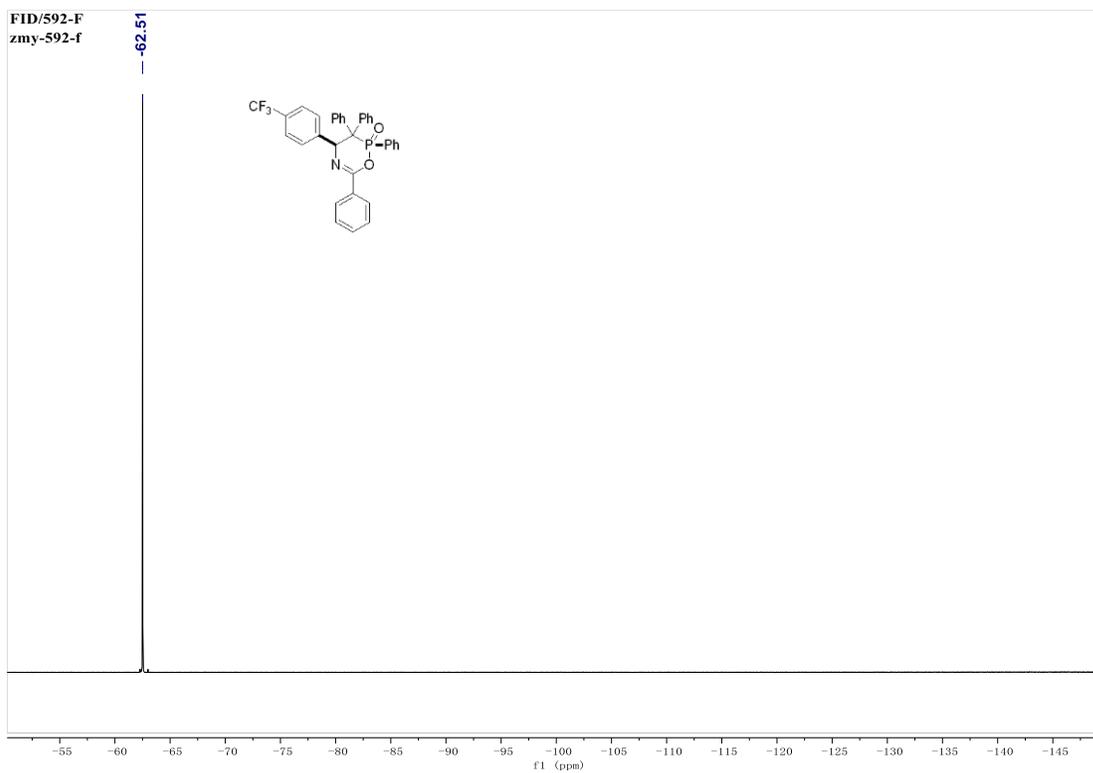
<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)



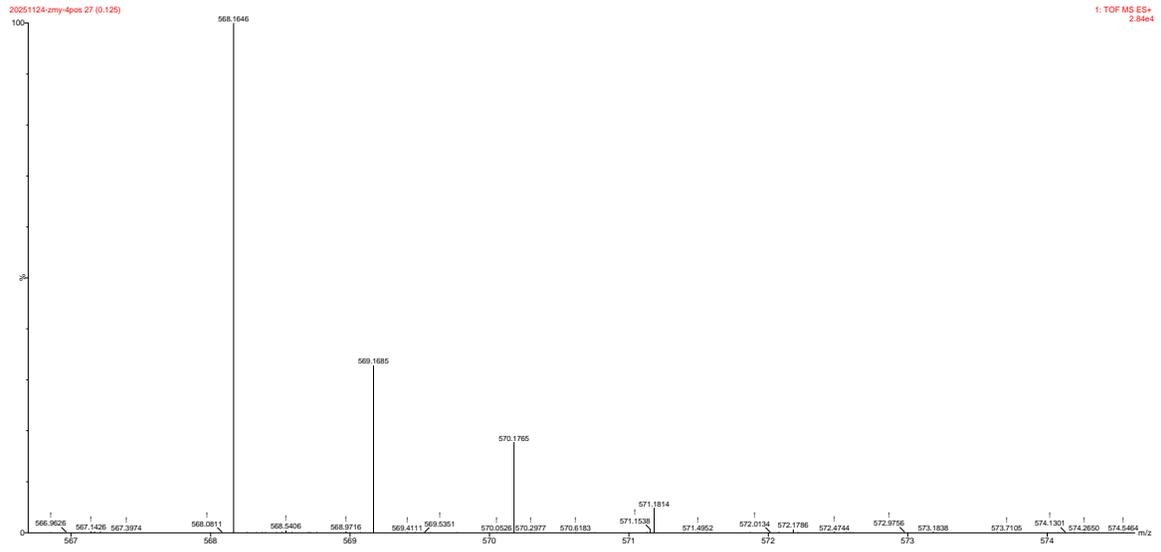
**$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ )**



**$^{19}\text{F}\{^1\text{H}\}$  NMR (376 MHz,  $\text{CDCl}_3$ )**

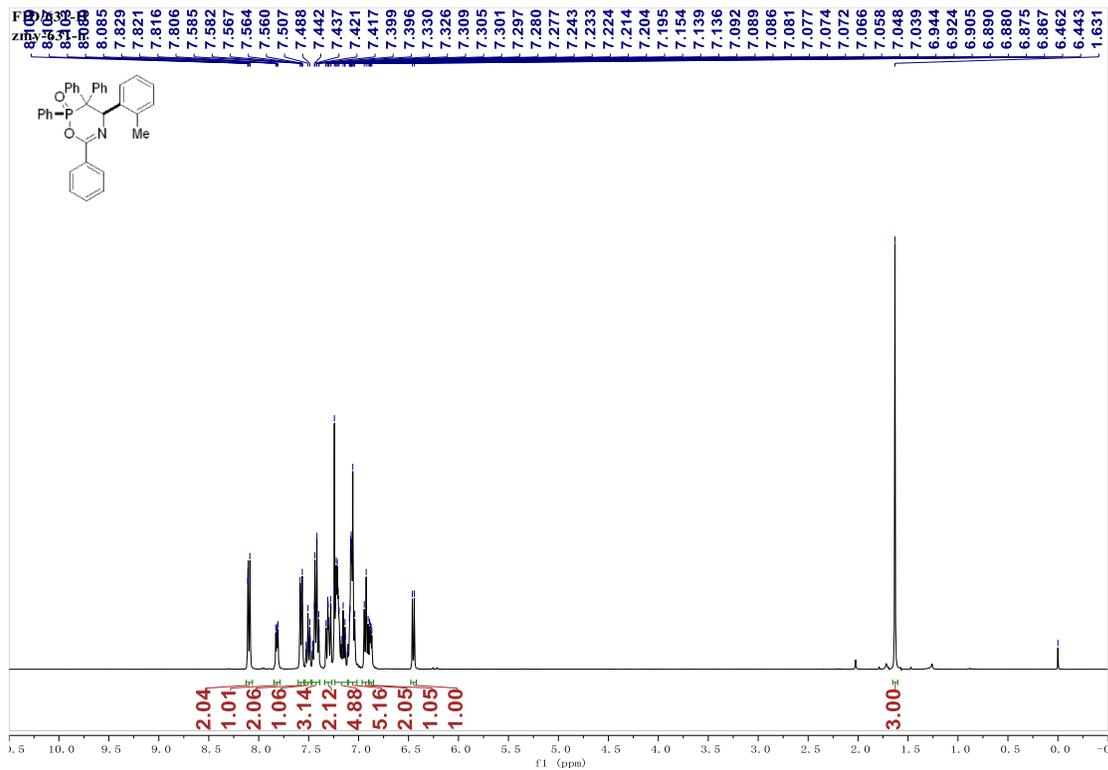


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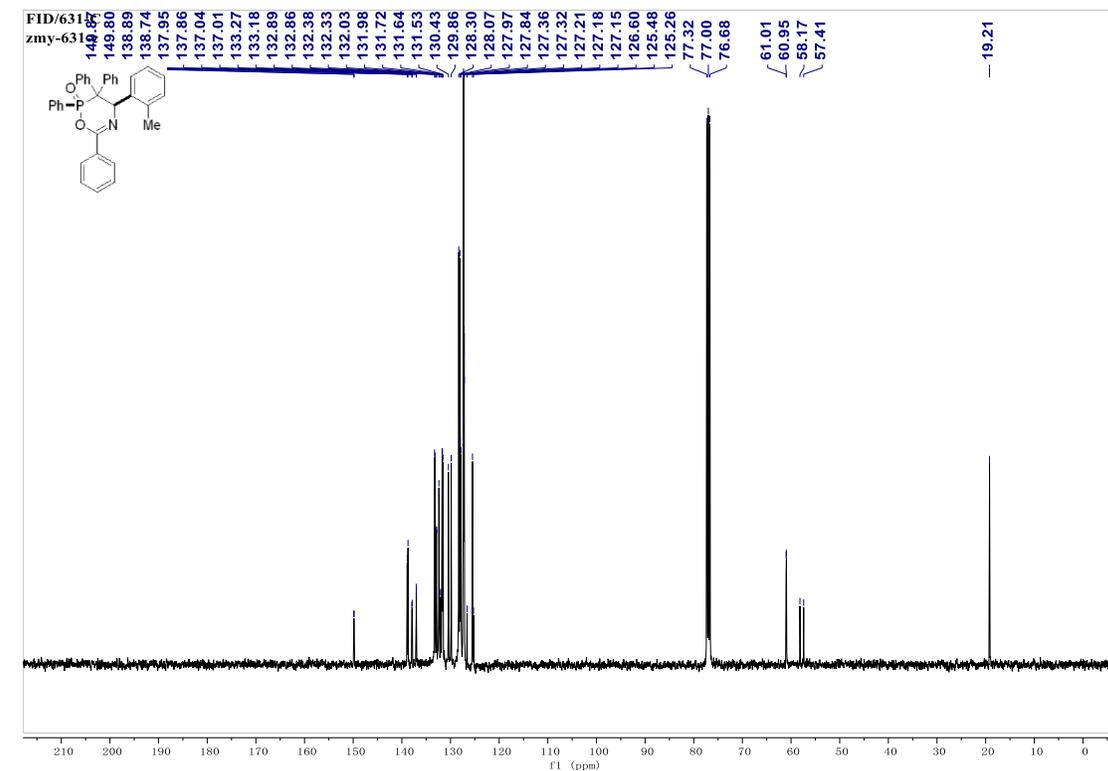


**trans-2,3,3,6-Tetraphenyl-4-(*o*-tolyl)-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3ah)**

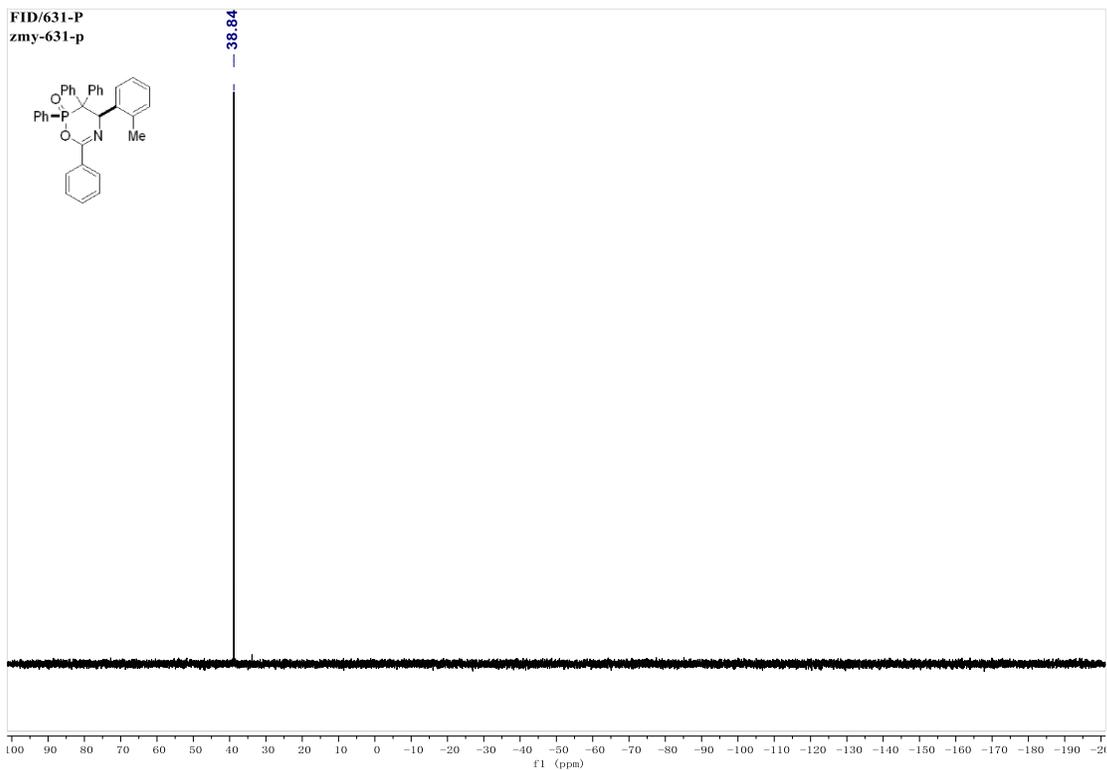
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



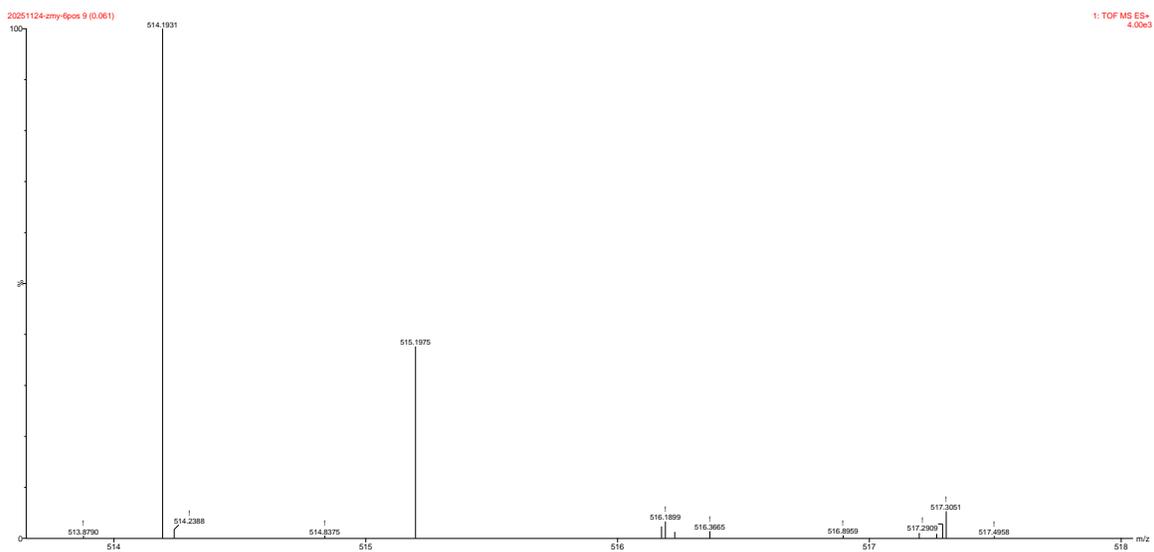
**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)**



### $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, $\text{CDCl}_3$ )

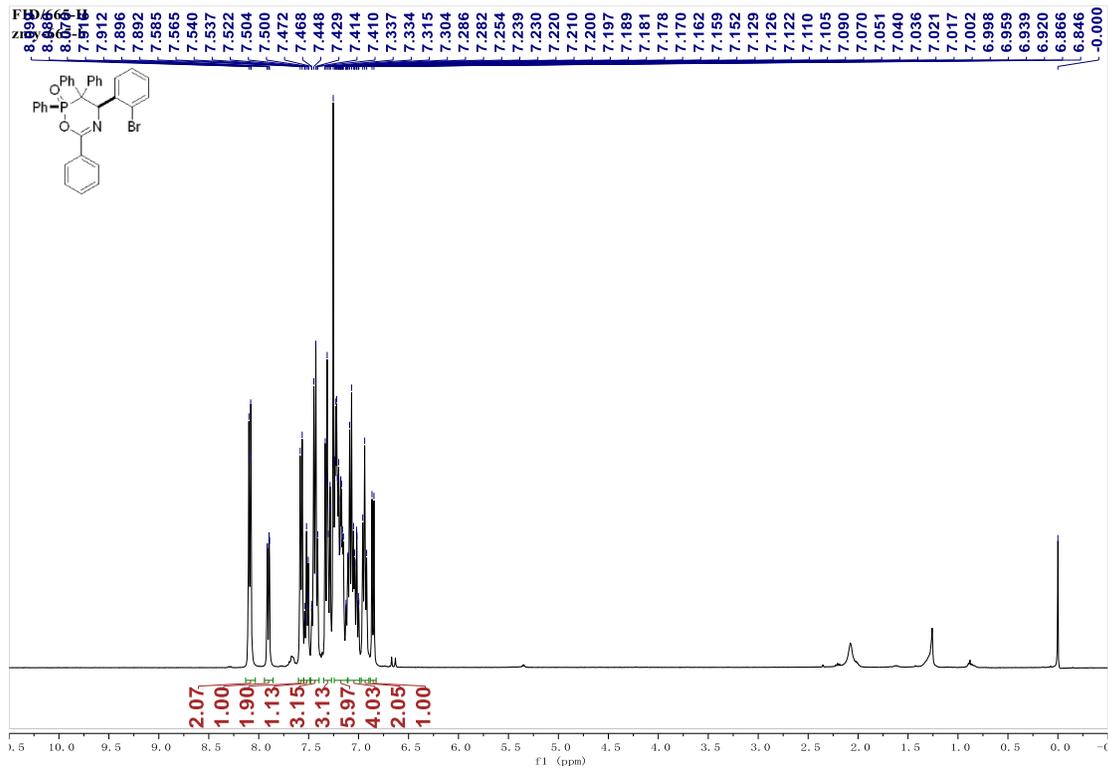


### HRMS

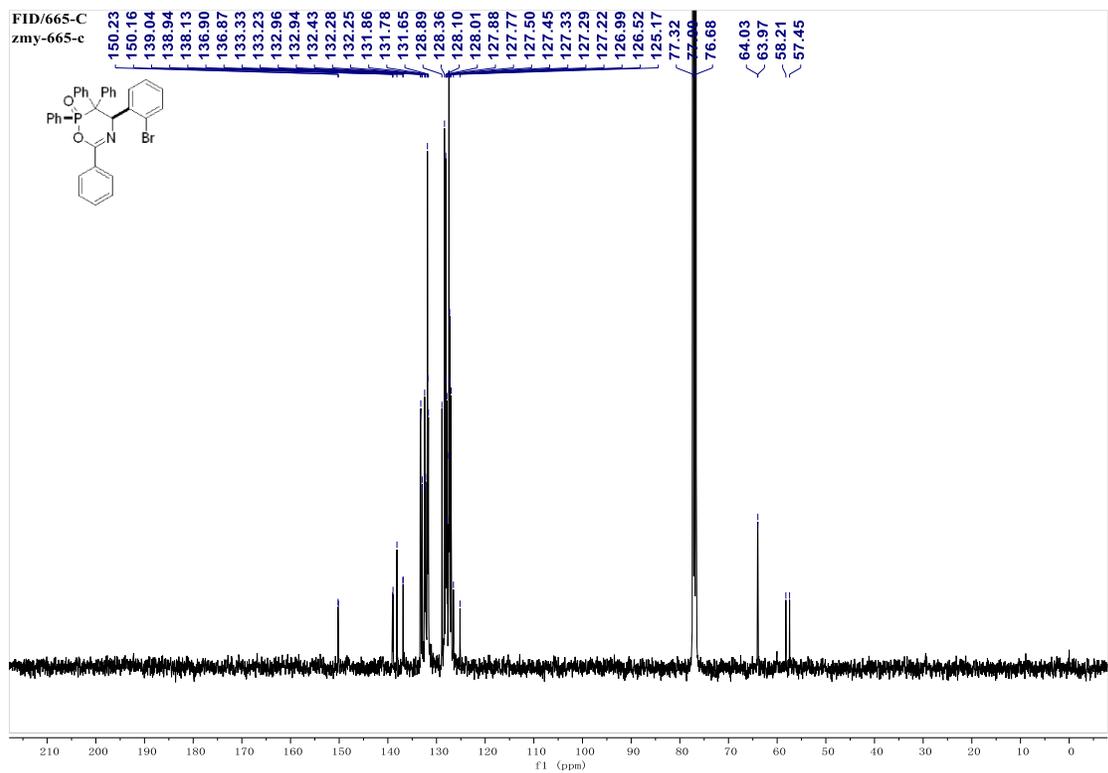


***trans*-4-(2-Bromophenyl)-2,3,3,6-tetraphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3ai)**

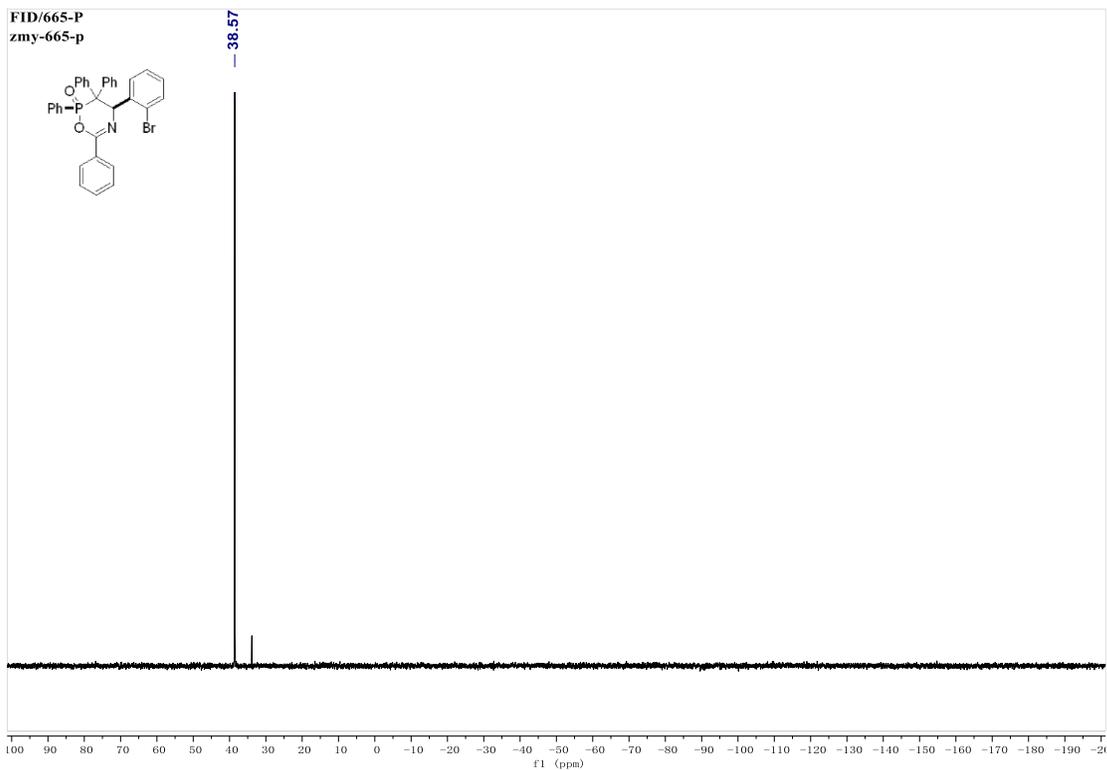
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



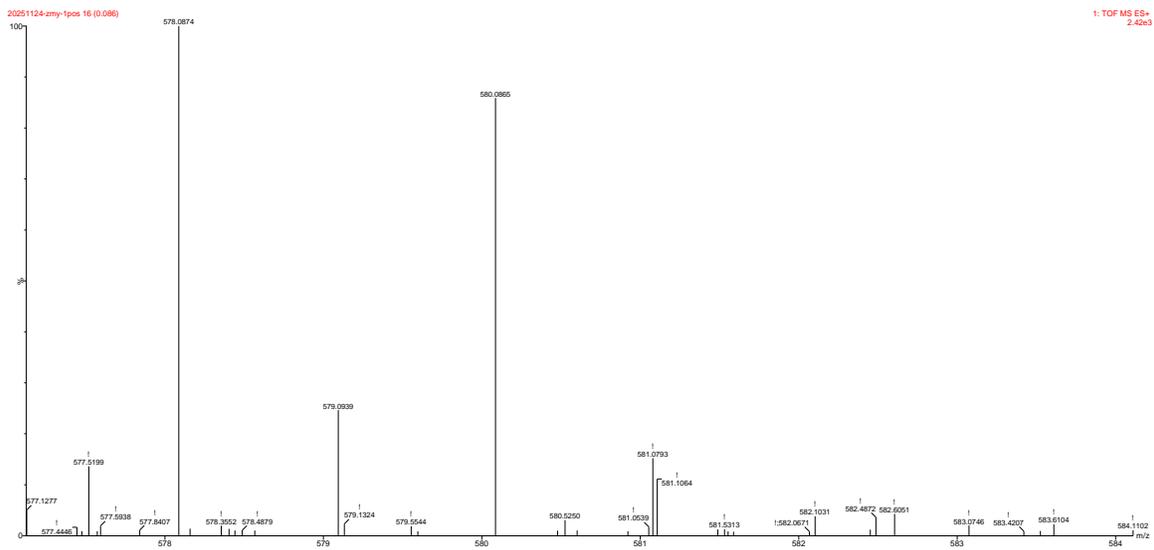
**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)**



### $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, $\text{CDCl}_3$ )

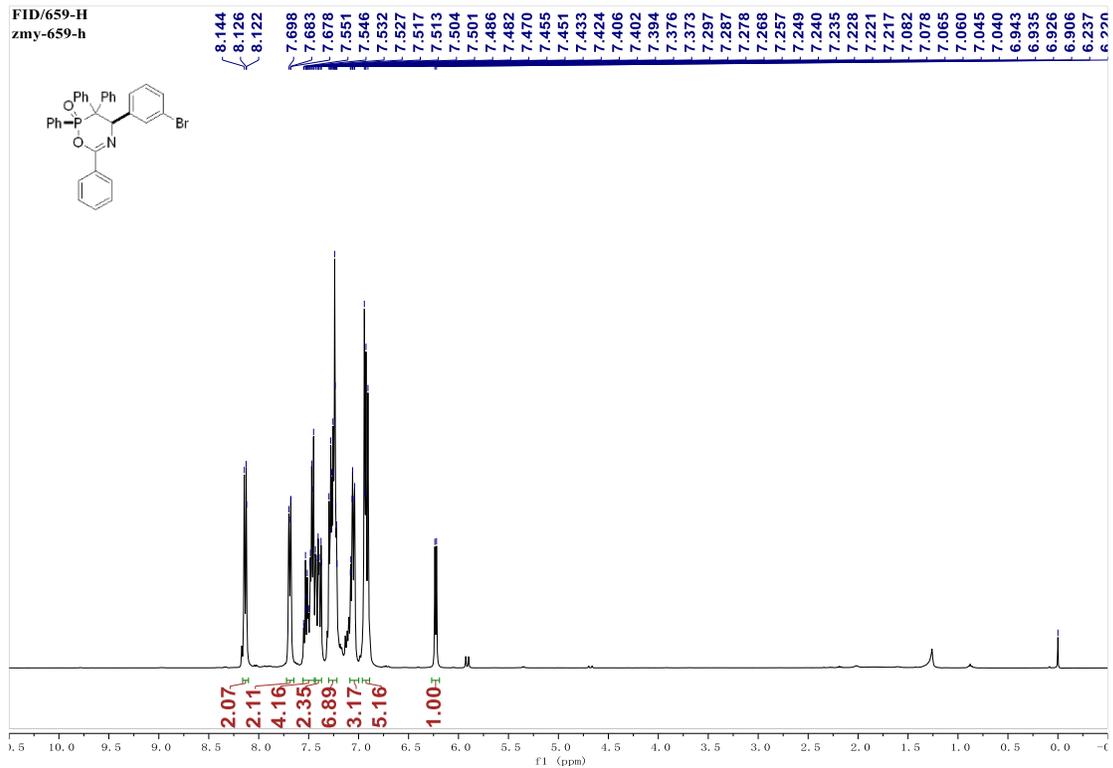


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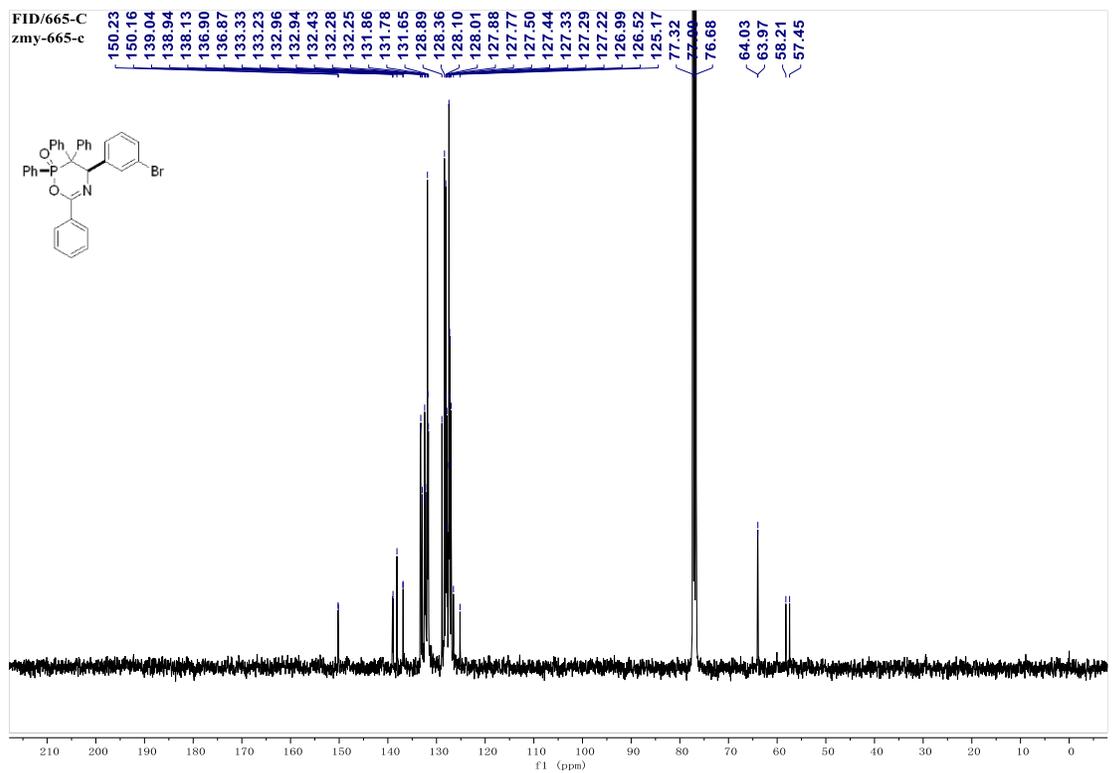


***trans*-4-(3-Bromophenyl)-2,3,3,6-tetraphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3aj)**

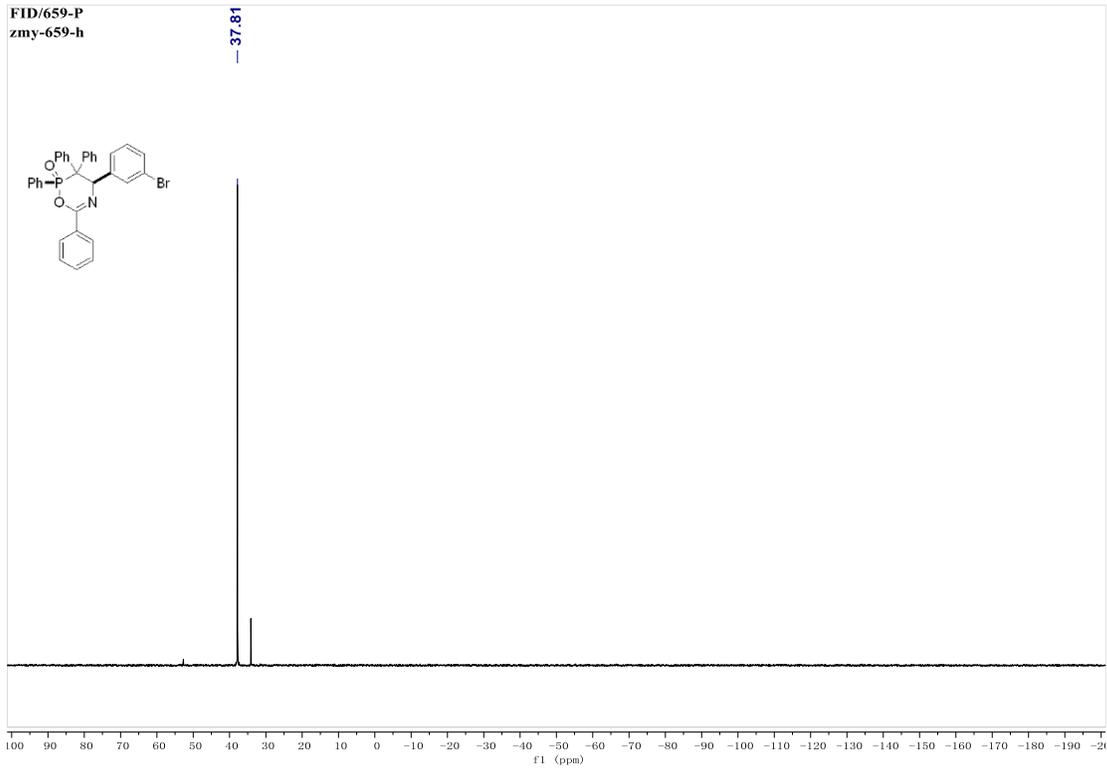
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



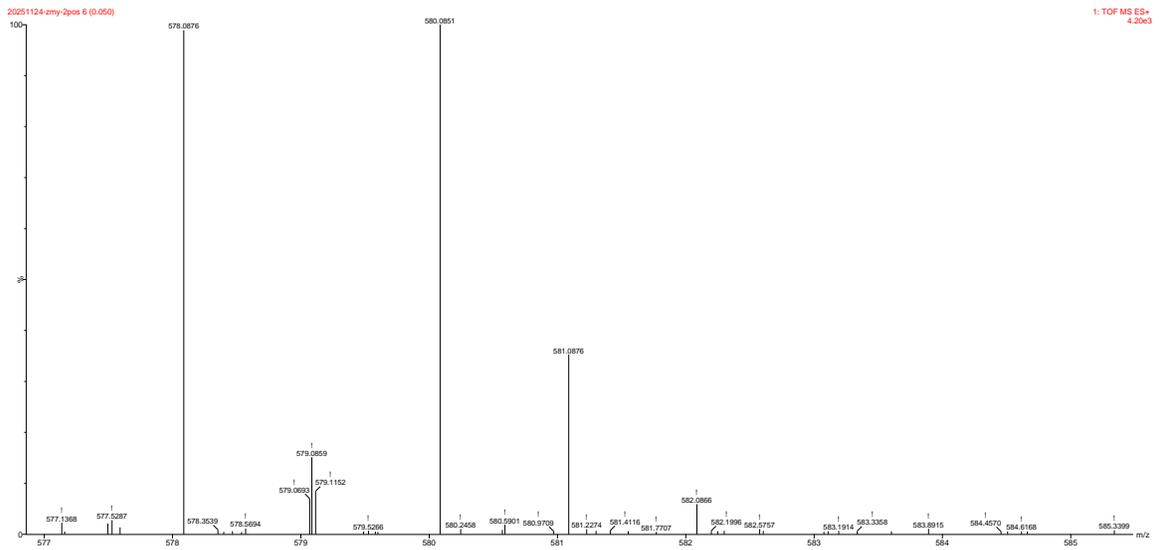
**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)**



### $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, $\text{CDCl}_3$ )

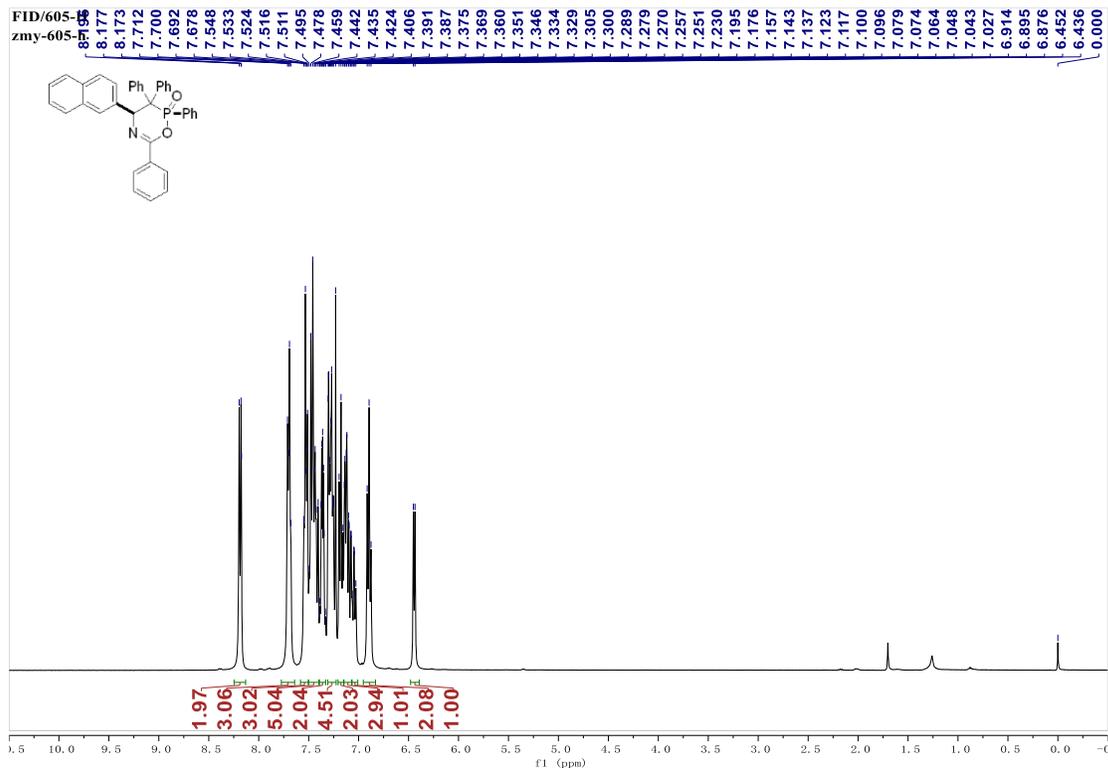


### HRMS

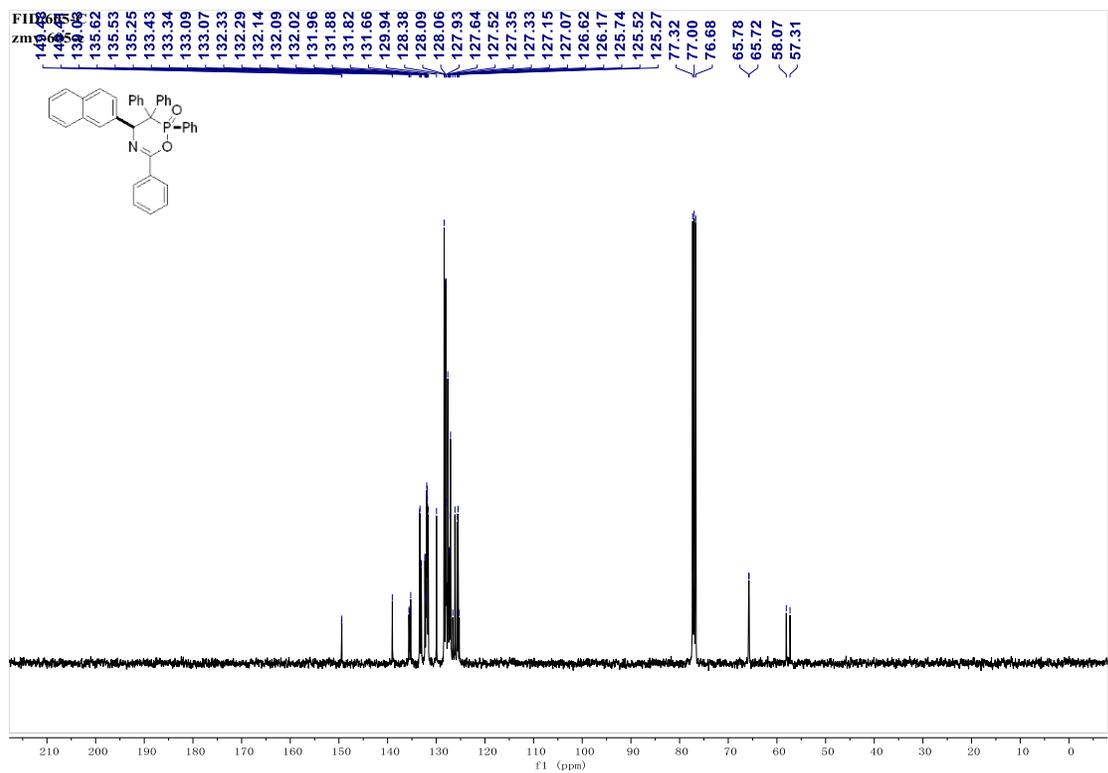


***trans*-4-(Naphthalen-2-yl)-2,3,3,6-tetraphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3ak)**

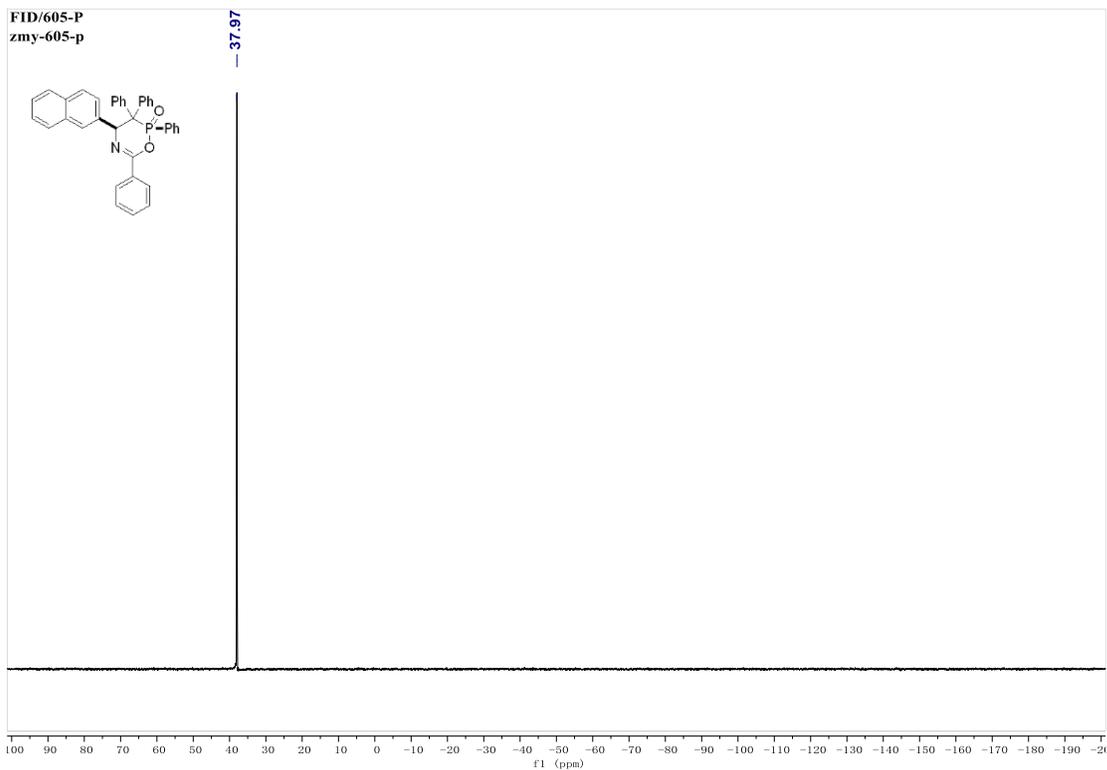
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



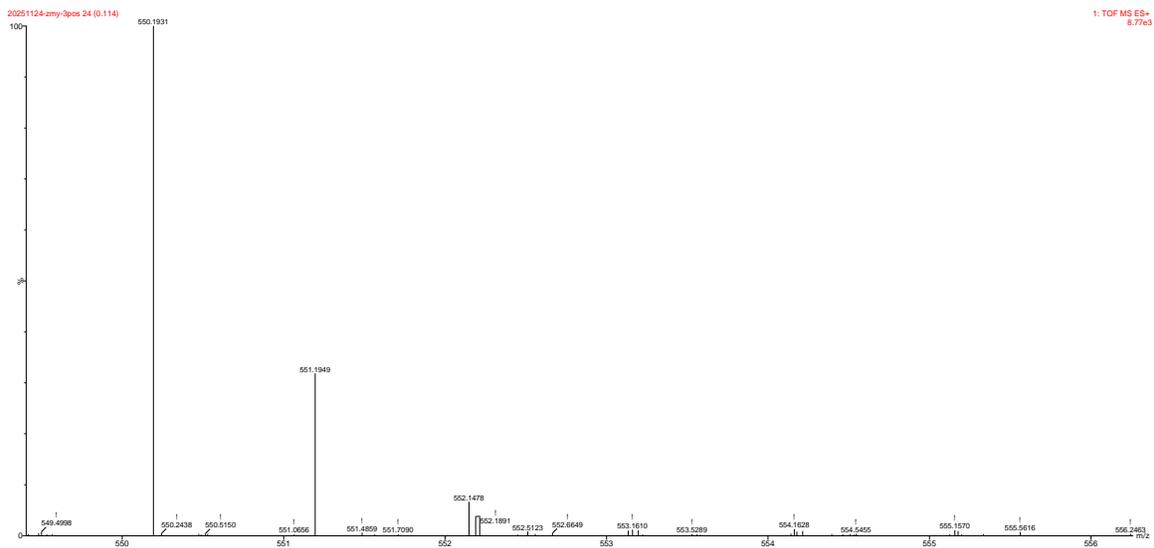
**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)**



### $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, $\text{CDCl}_3$ )

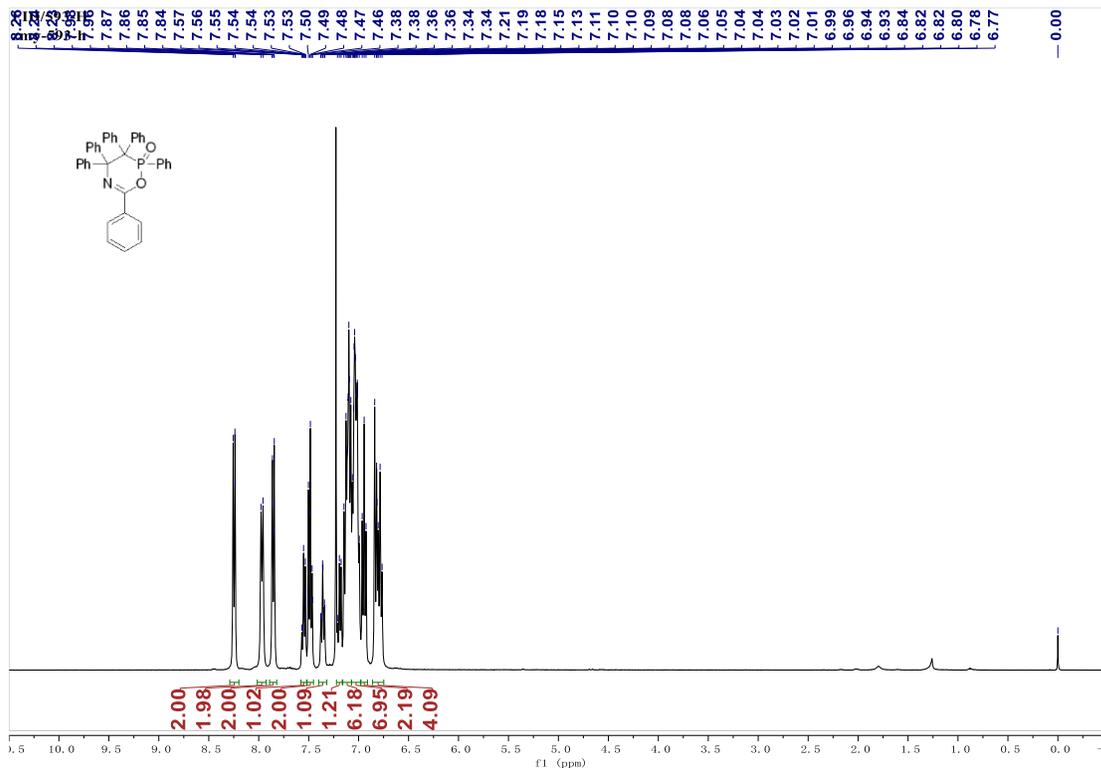


### HRMS

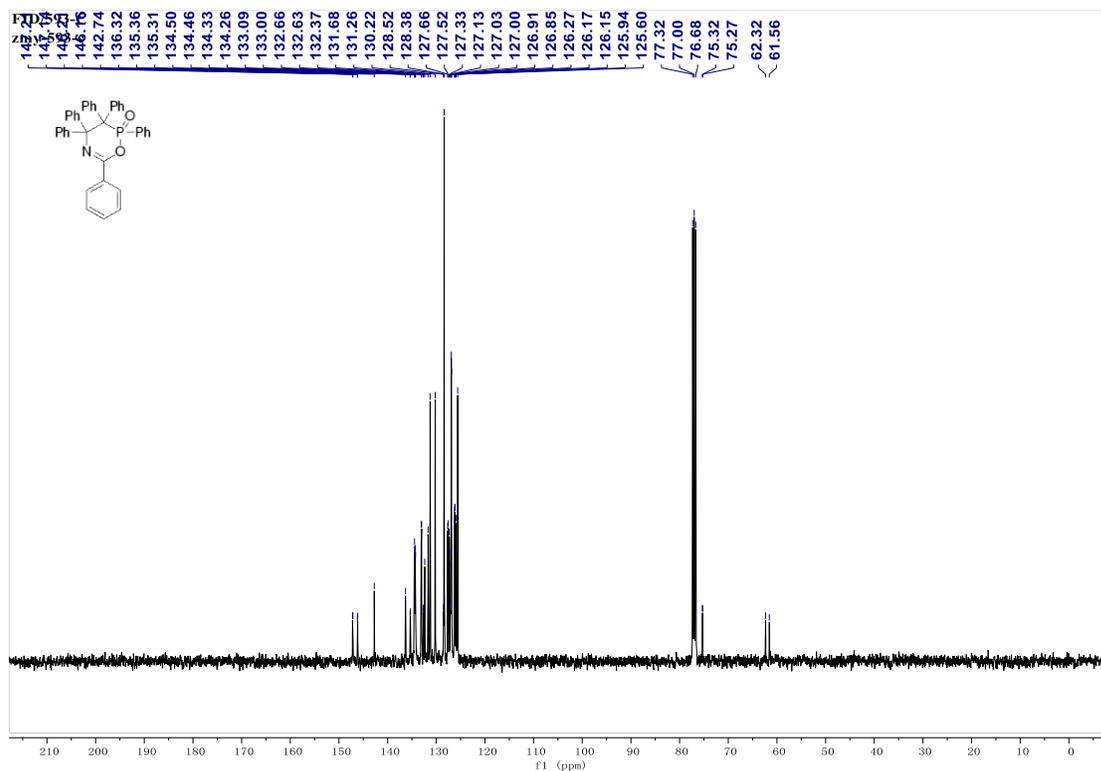


2,3,3,4,4,6-Hexaphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3a)

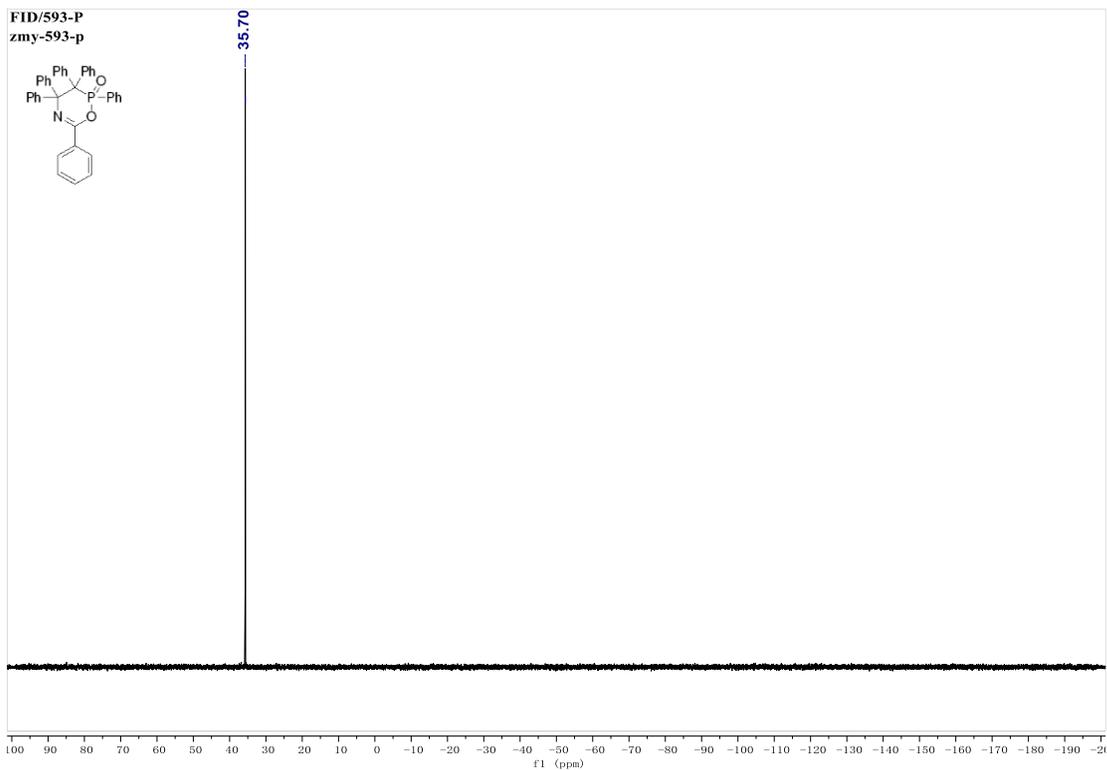
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



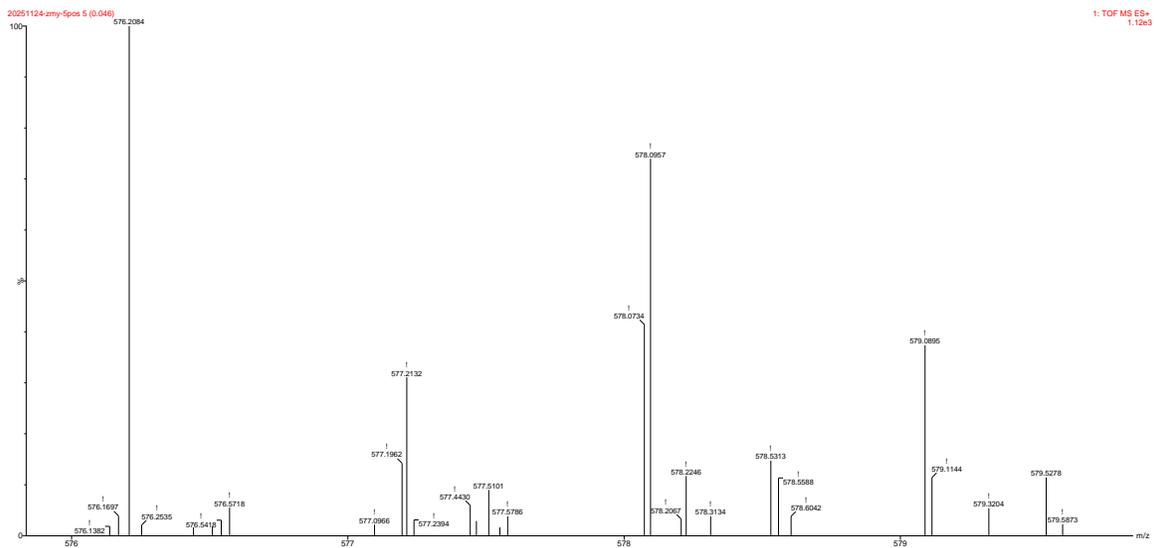
<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)



### $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, $\text{CDCl}_3$ )

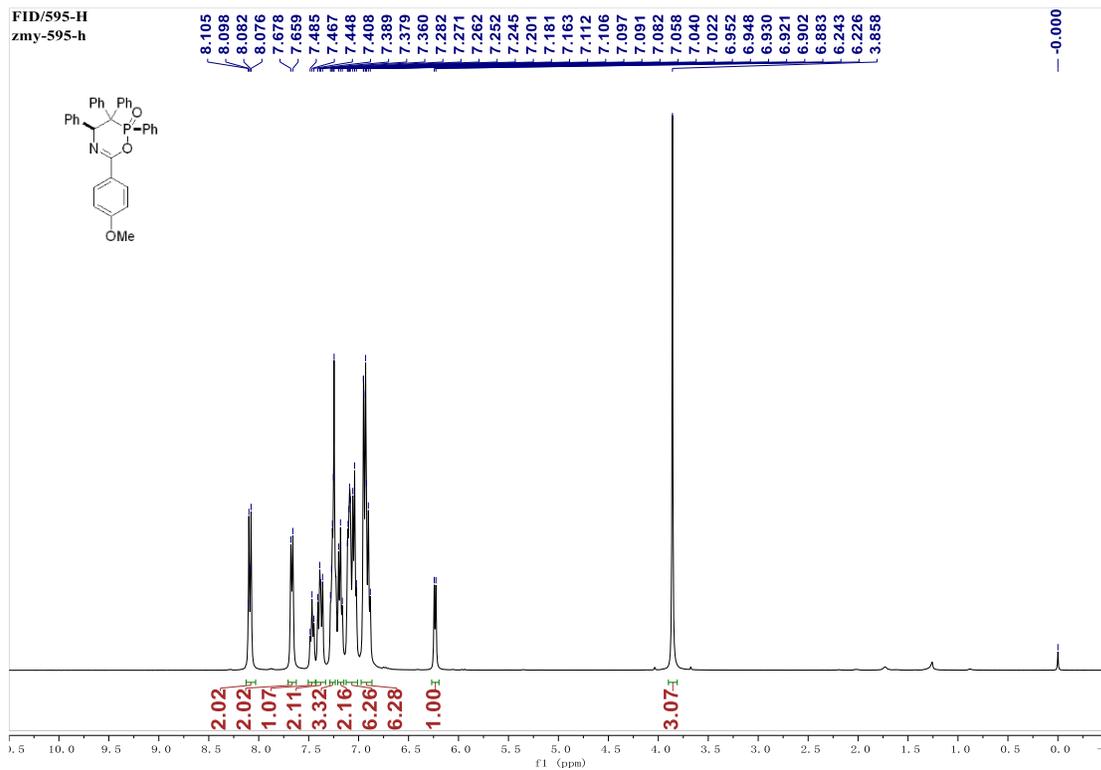


### HRMS

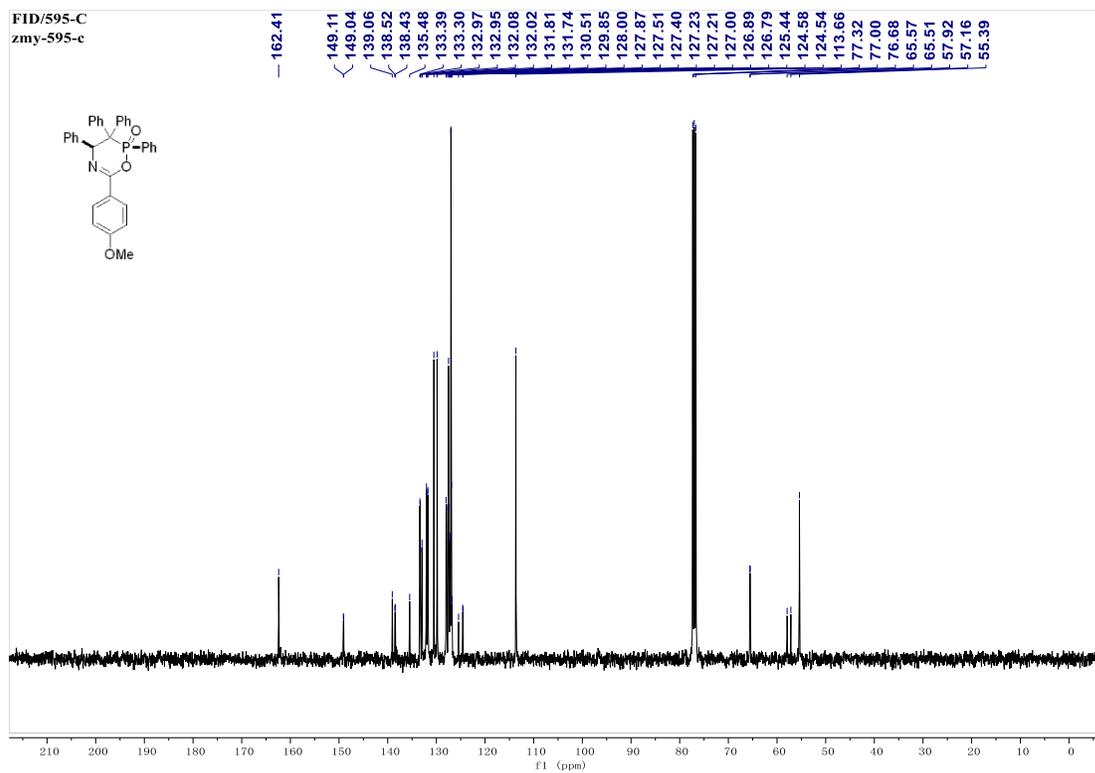


***trans*-6-(4-Methoxyphenyl)-2,3,3,4-tetraphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3am)**

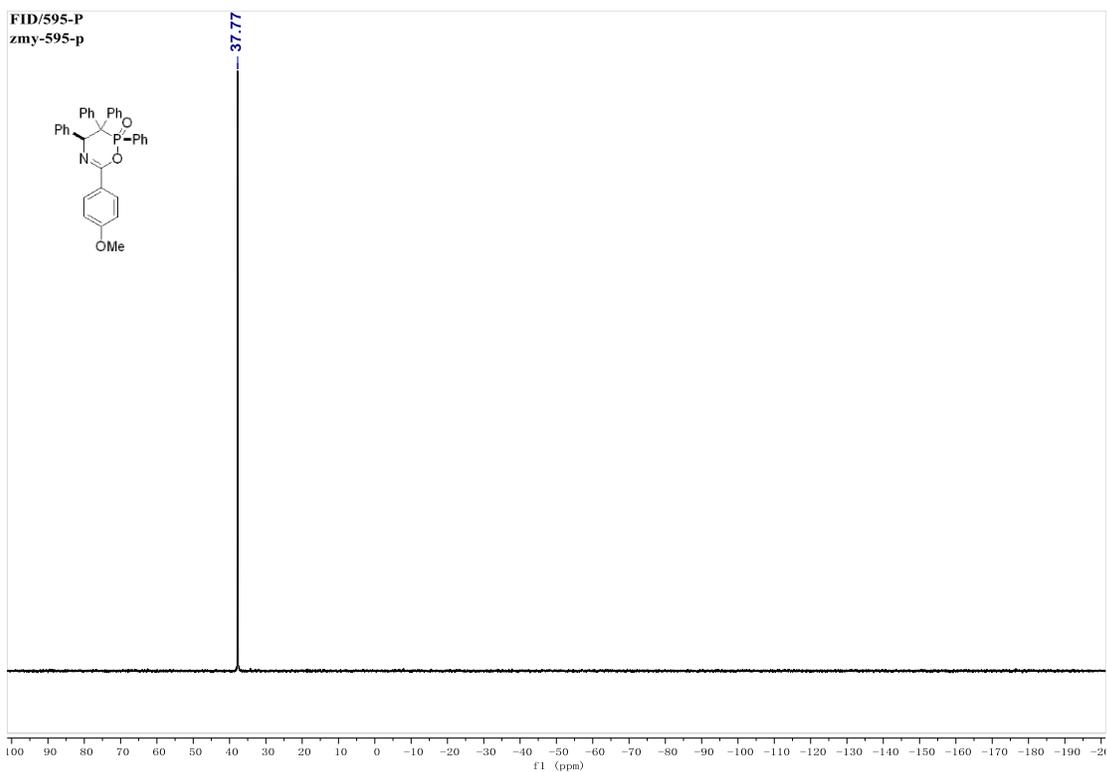
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



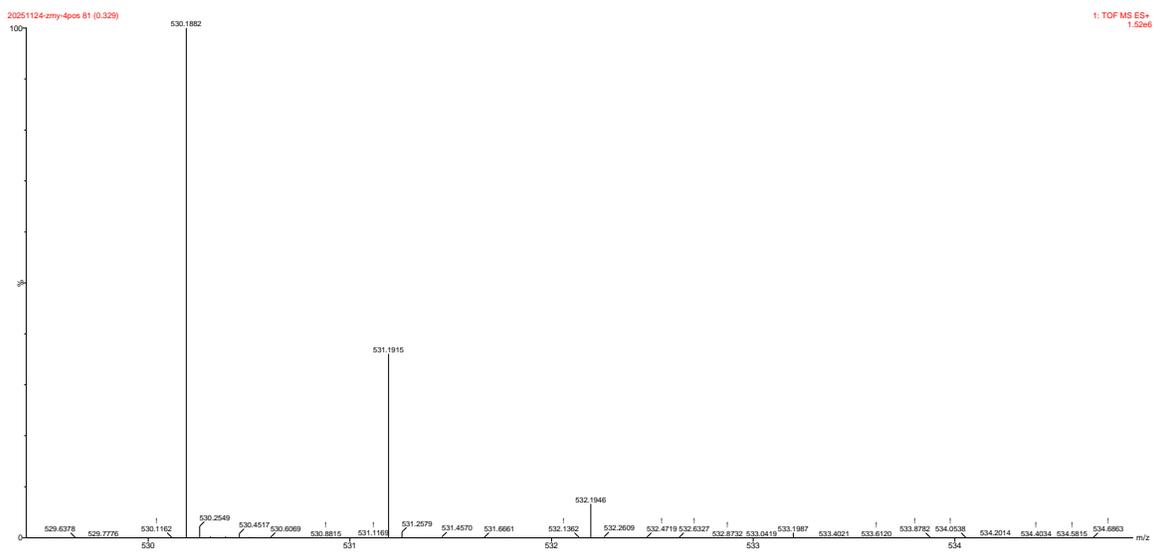
**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)**



### $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, $\text{CDCl}_3$ )

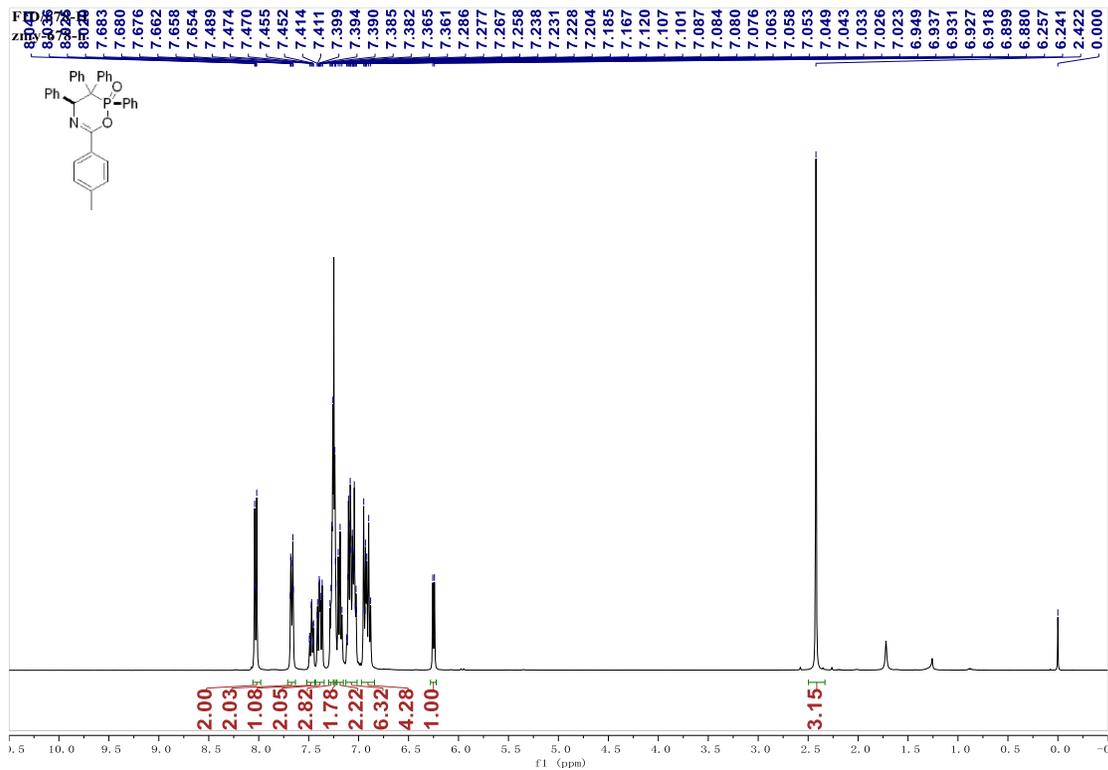


### HRMS

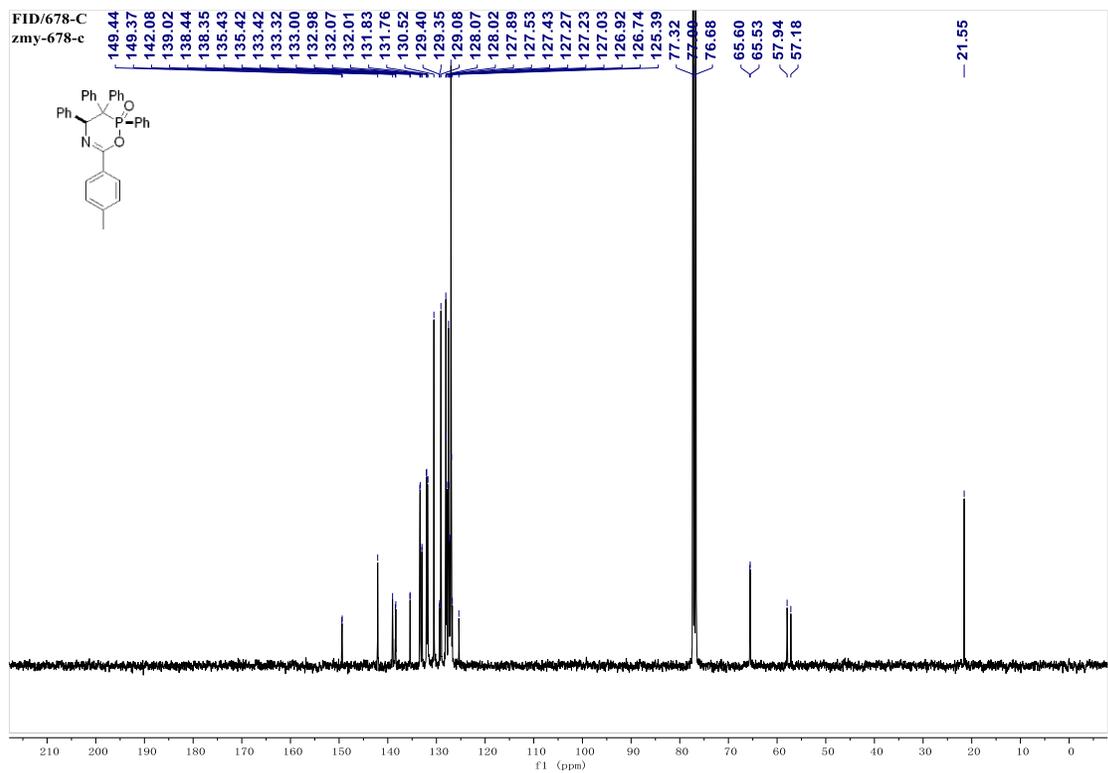


*trans*-2,3,3,4-Tetraphenyl-6-(4-tolyl)-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3an)

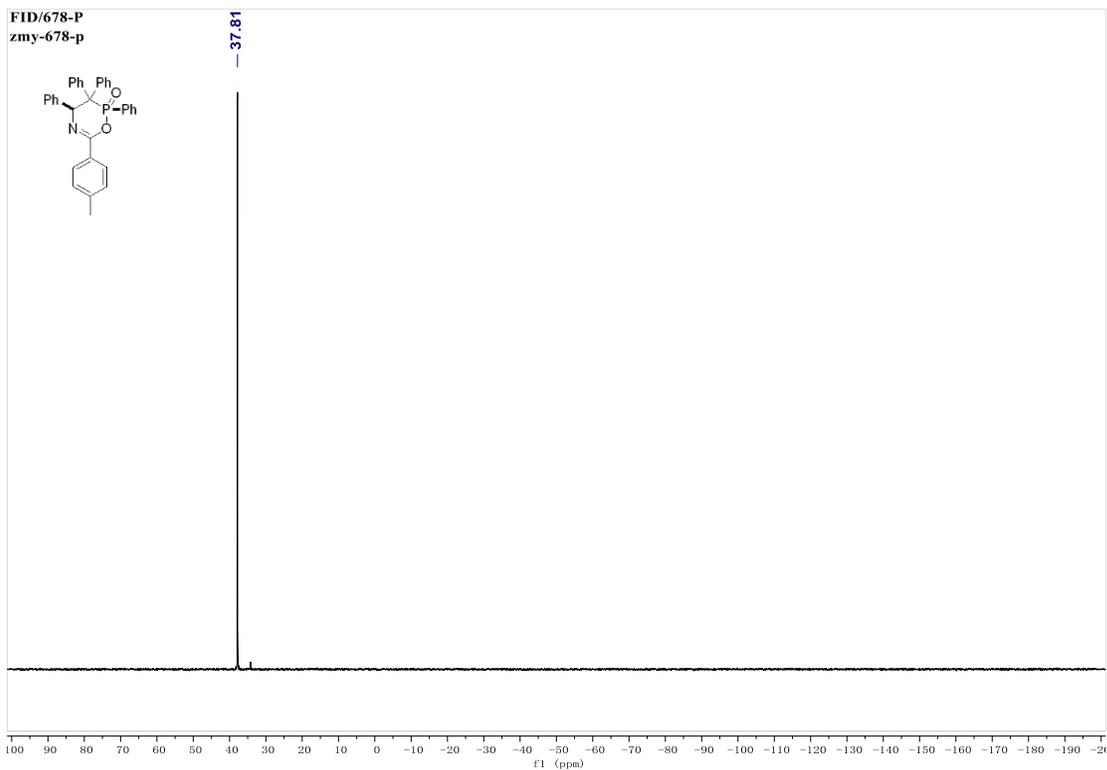
<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>)



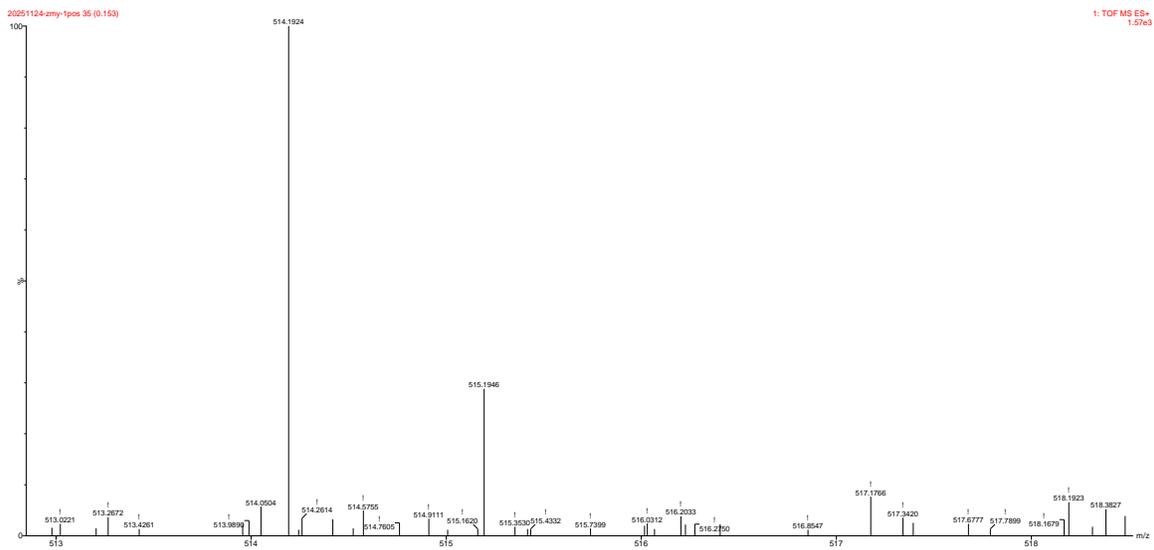
<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)



### $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, $\text{CDCl}_3$ )

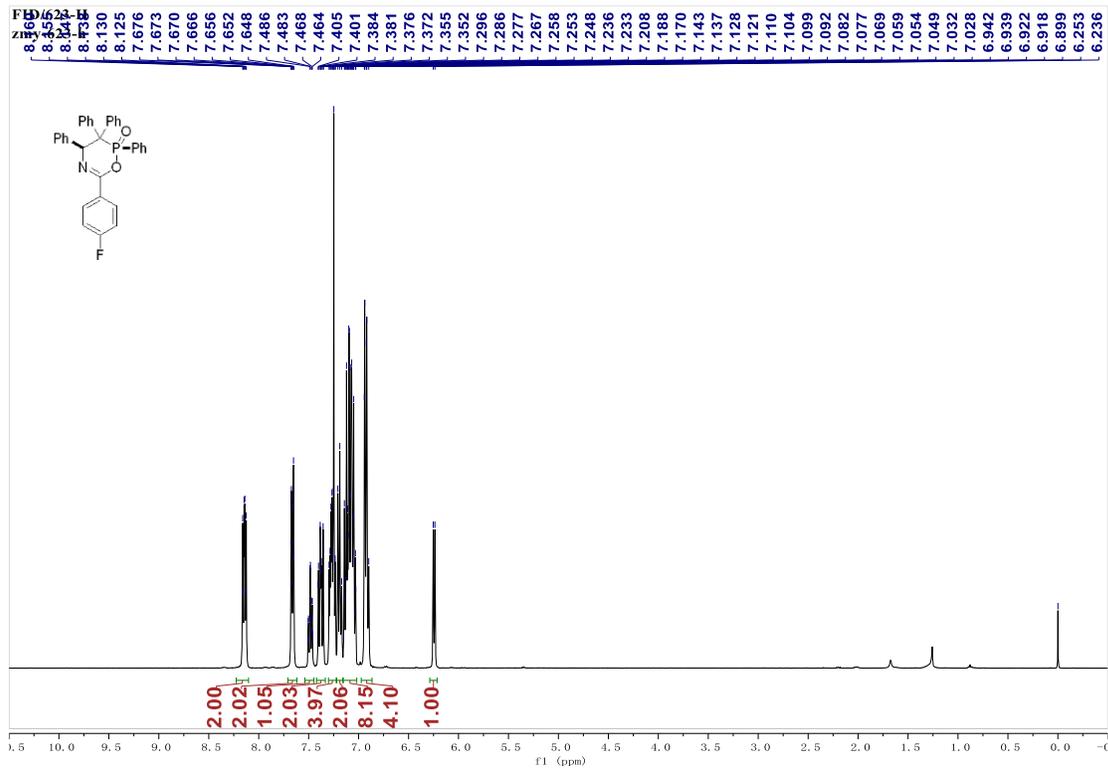


### HRMS

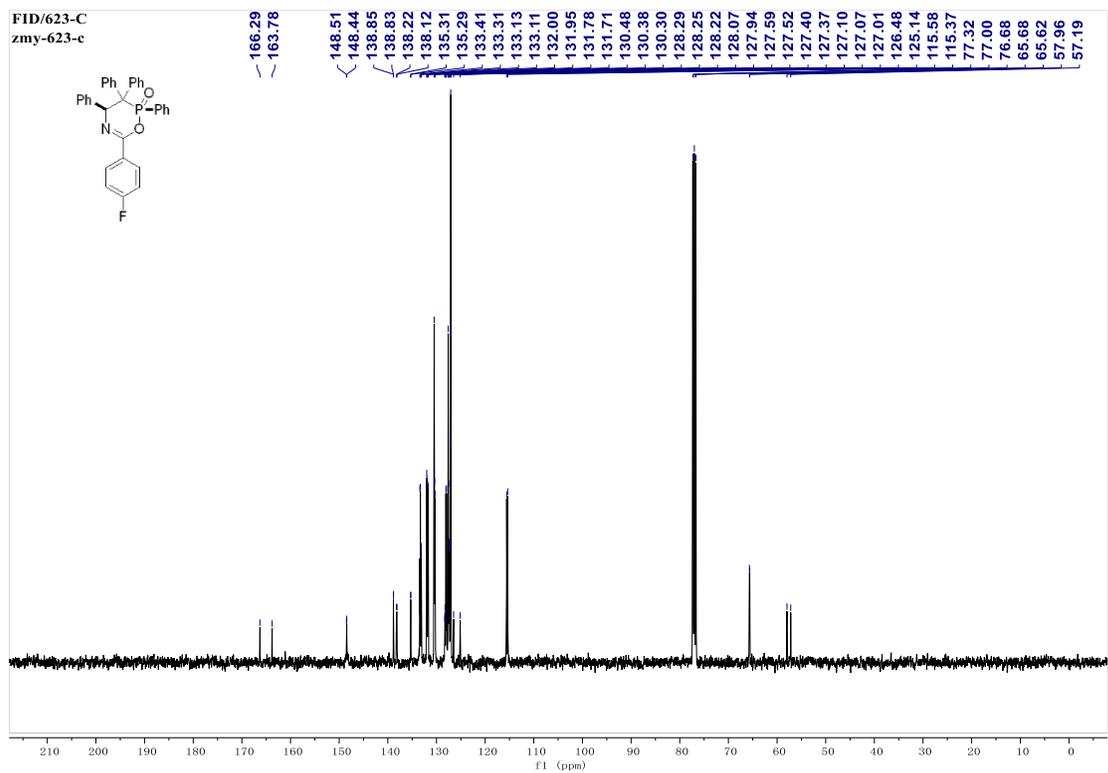


***trans*-6-(4-Fluorophenyl)-2,3,3,4-tetraphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3ao)**

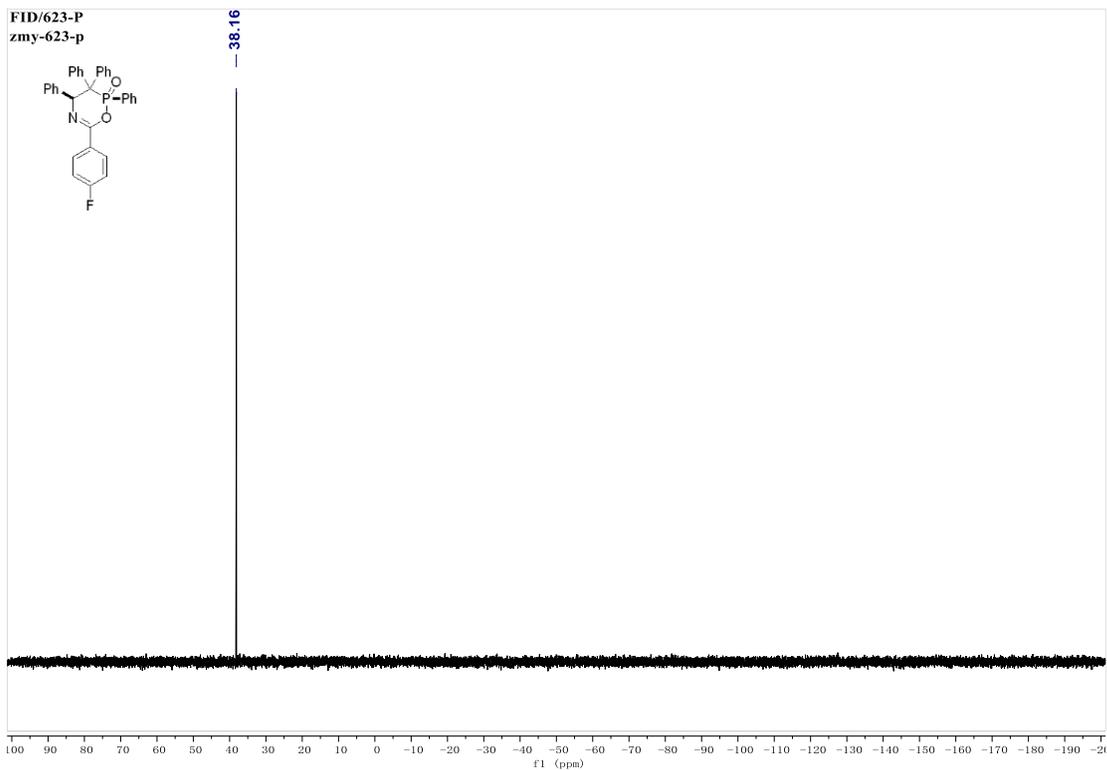
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



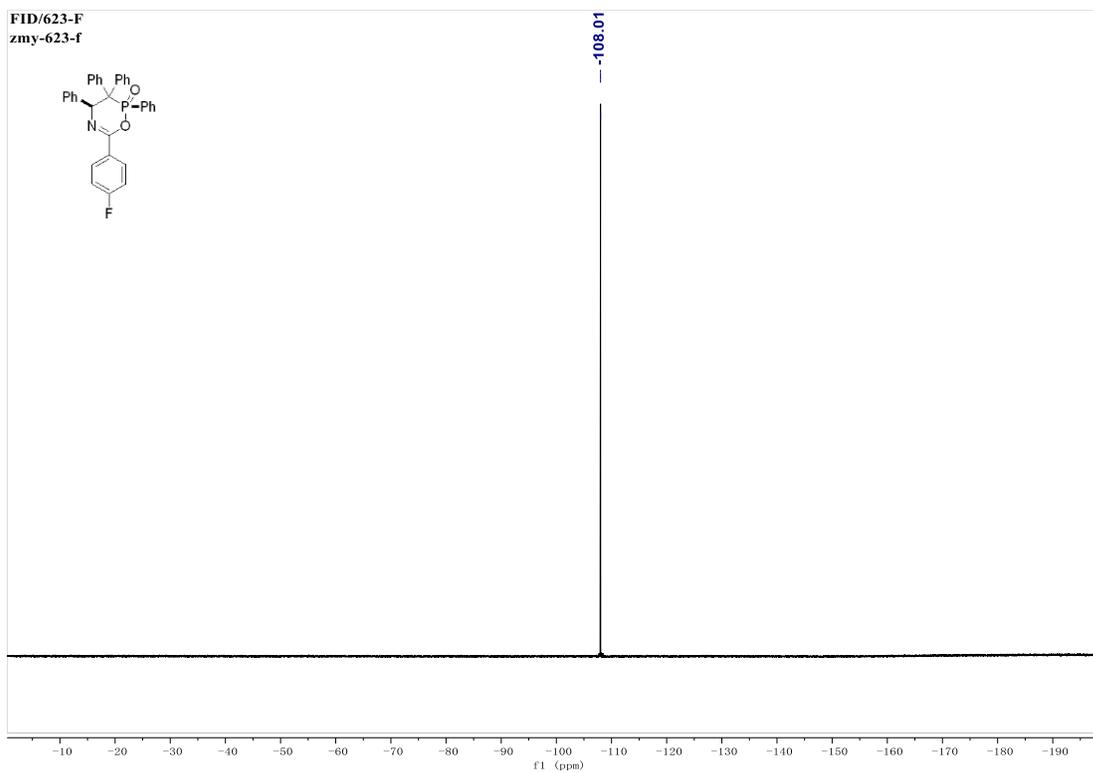
**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)**



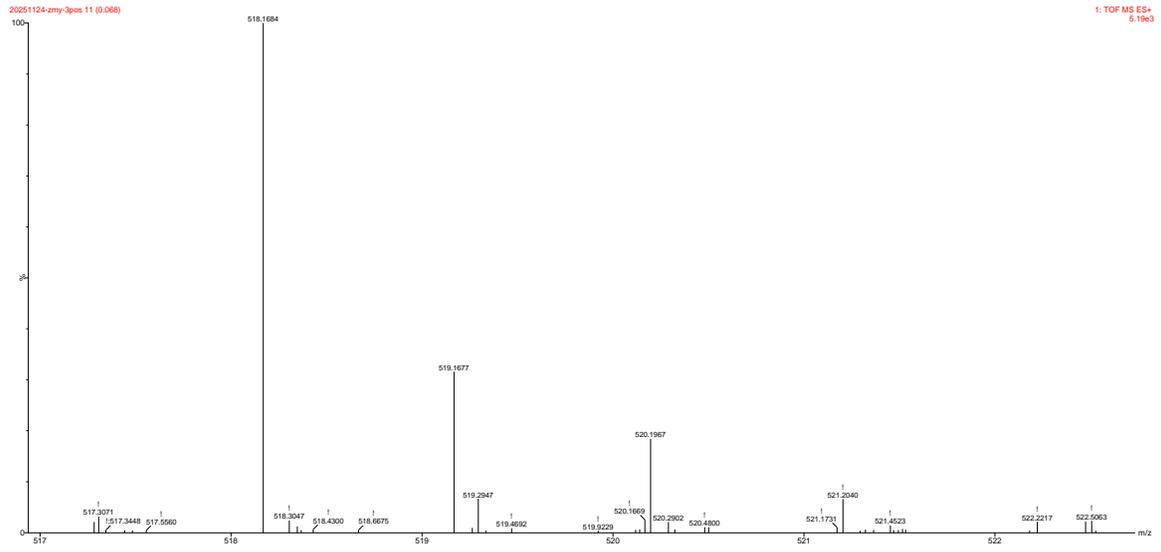
**$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ )**



**$^{19}\text{F}\{^1\text{H}\}$  NMR (376 MHz,  $\text{CDCl}_3$ )**

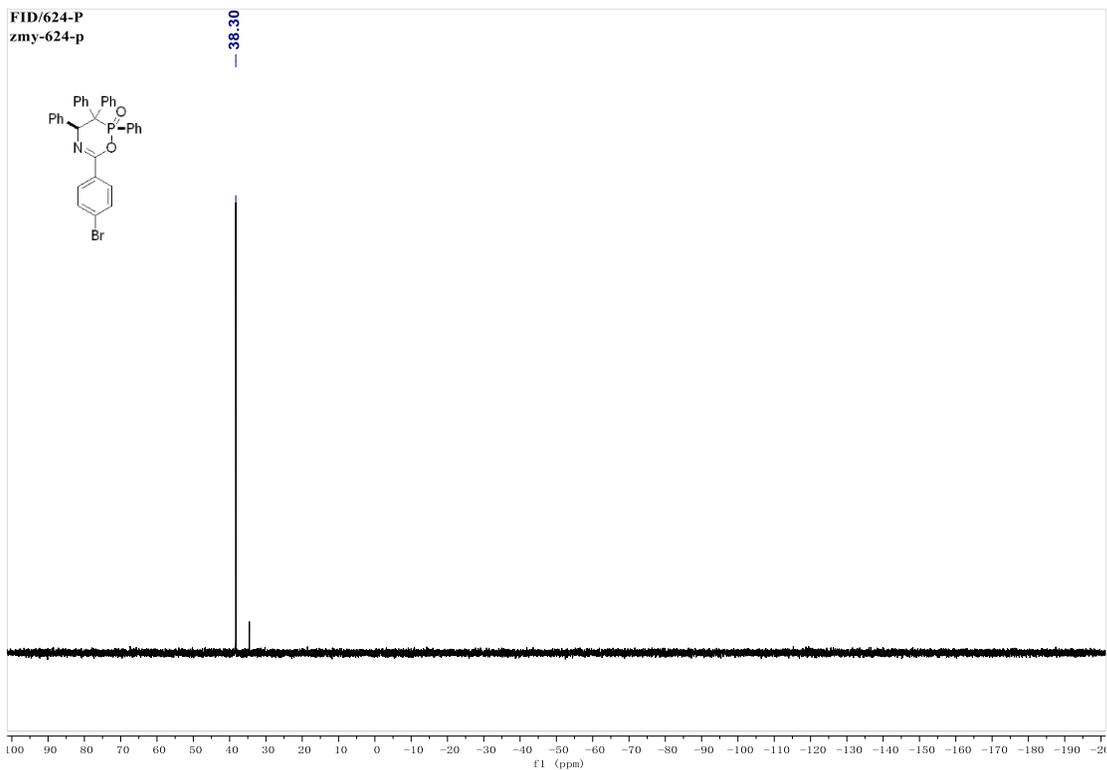


# HRMS

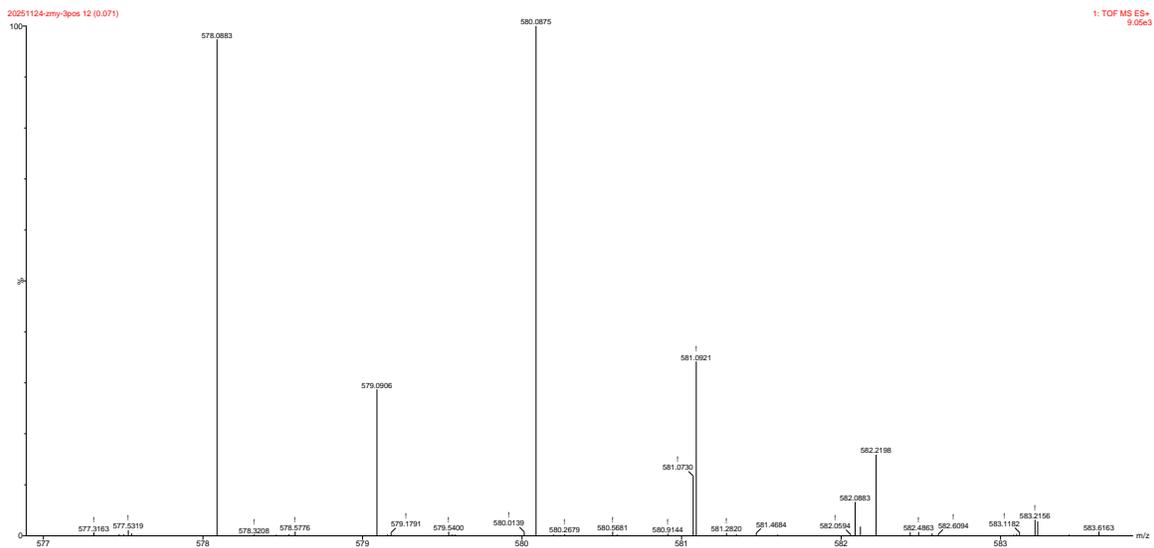




### $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, $\text{CDCl}_3$ )

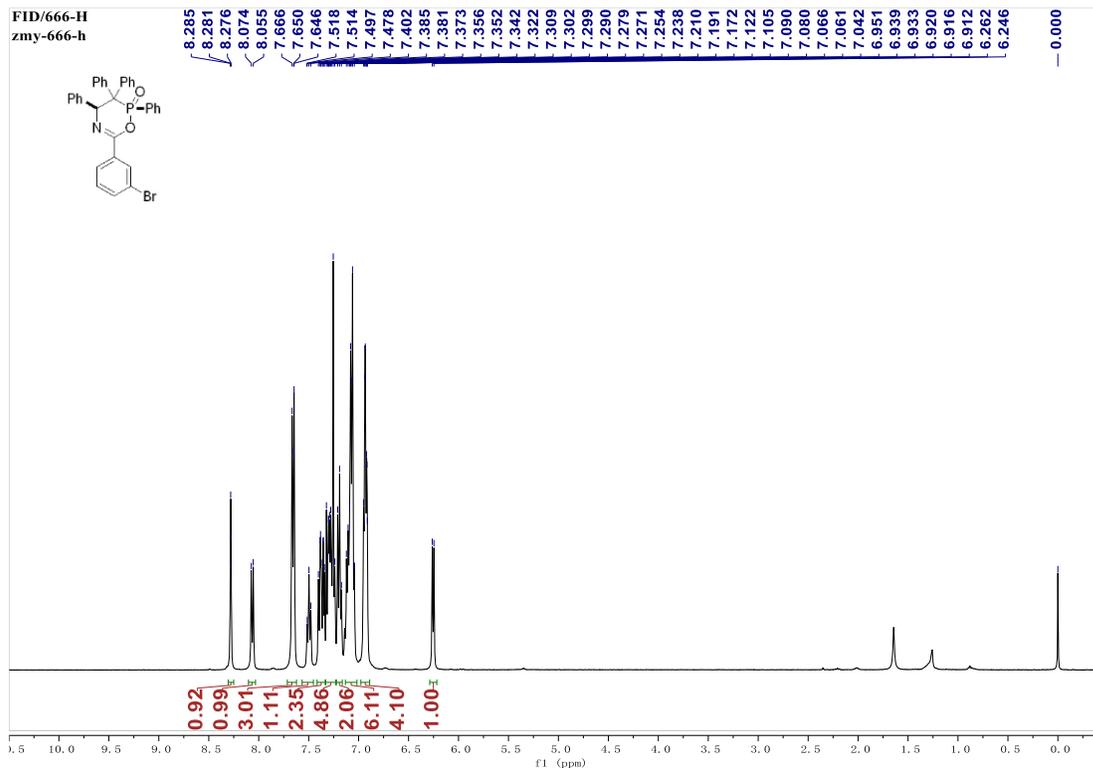


### HRMS

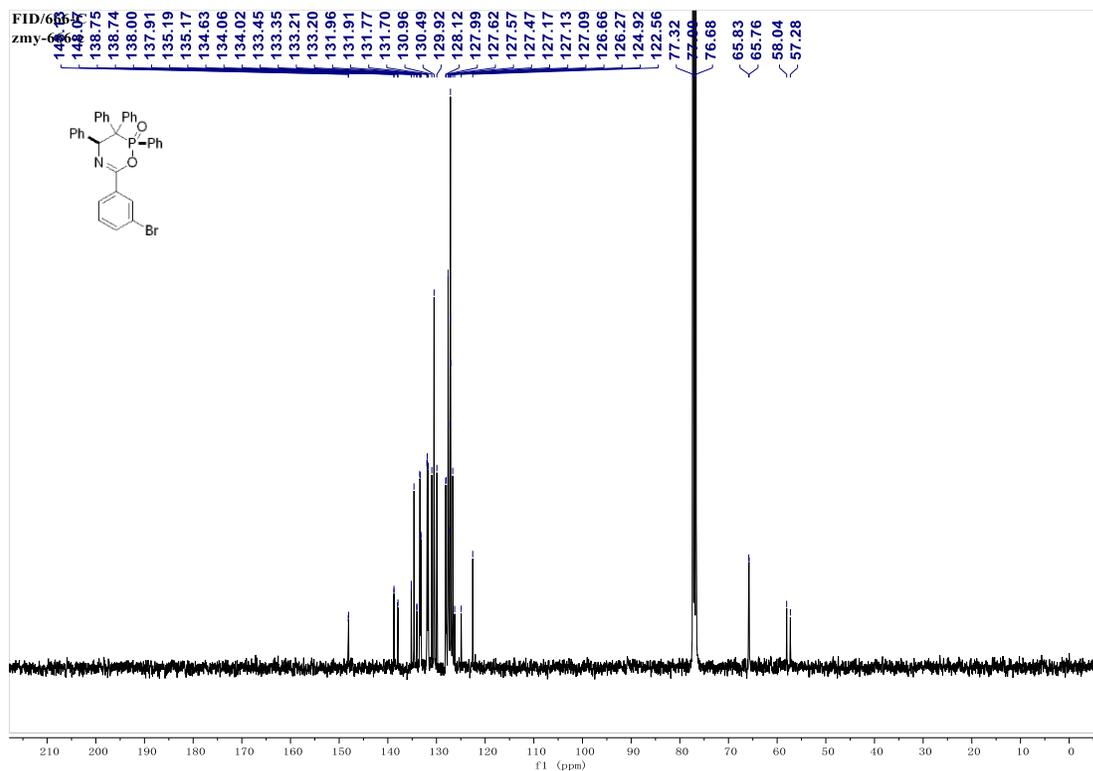


***trans*-6-(3-Bromophenyl)-2,3,3,4-tetraphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3a)**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

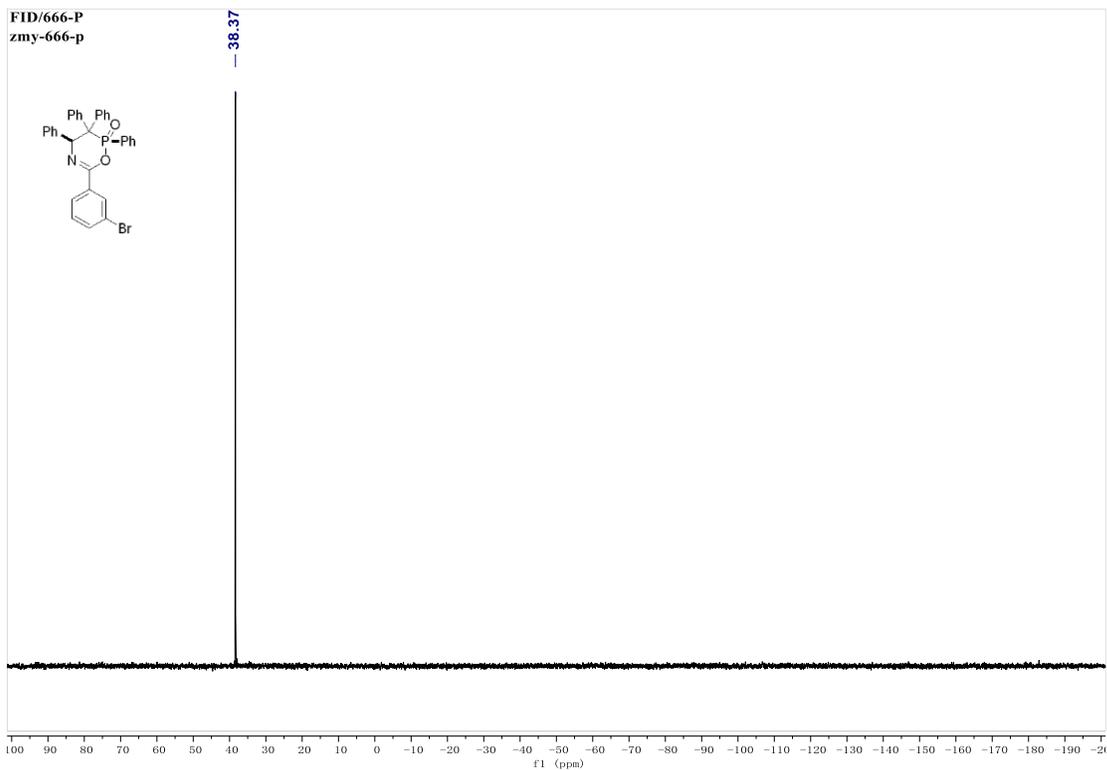


**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)**

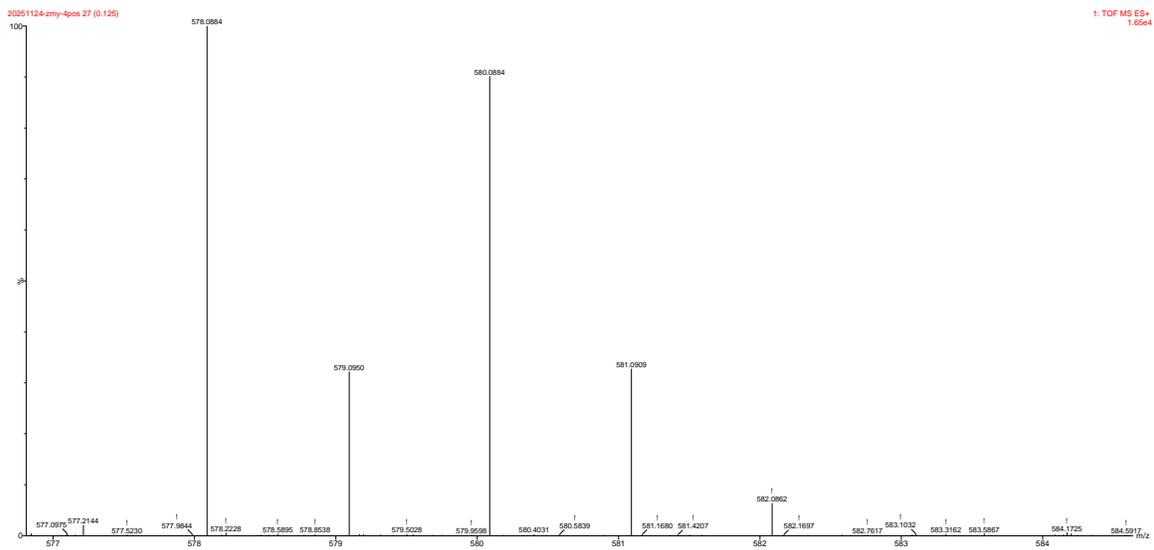


### $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, $\text{CDCl}_3$ )

FID/666-P  
zmy-666-p

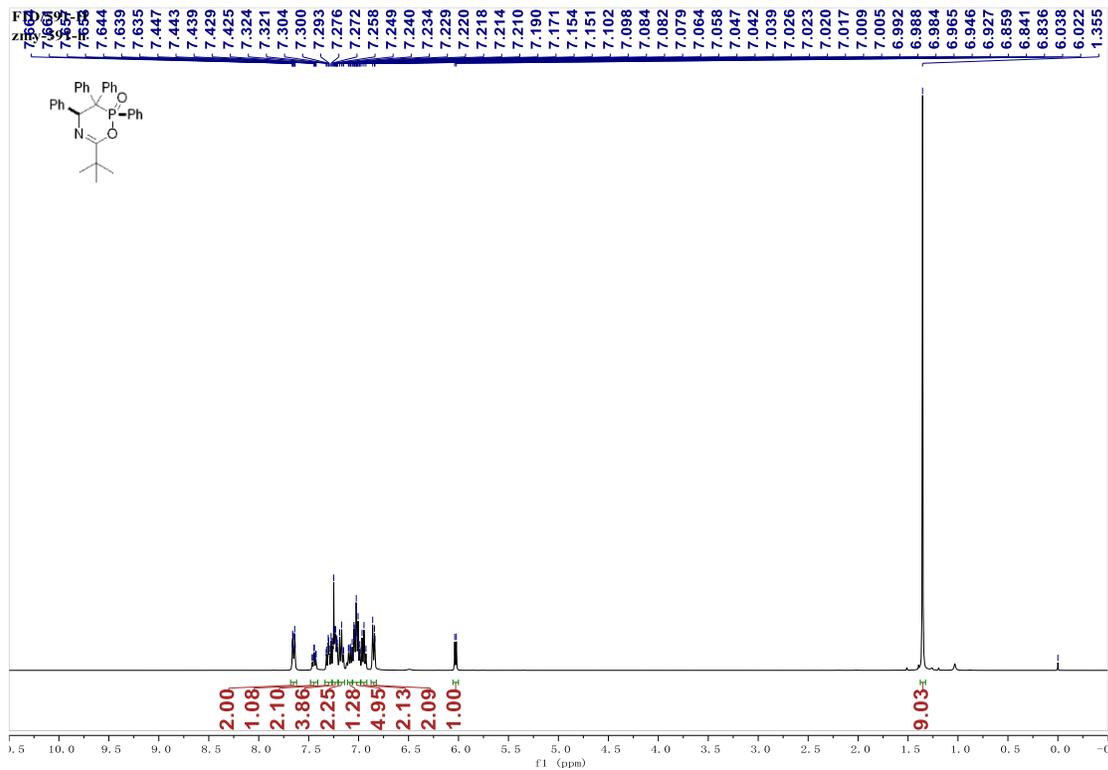


### HRMS

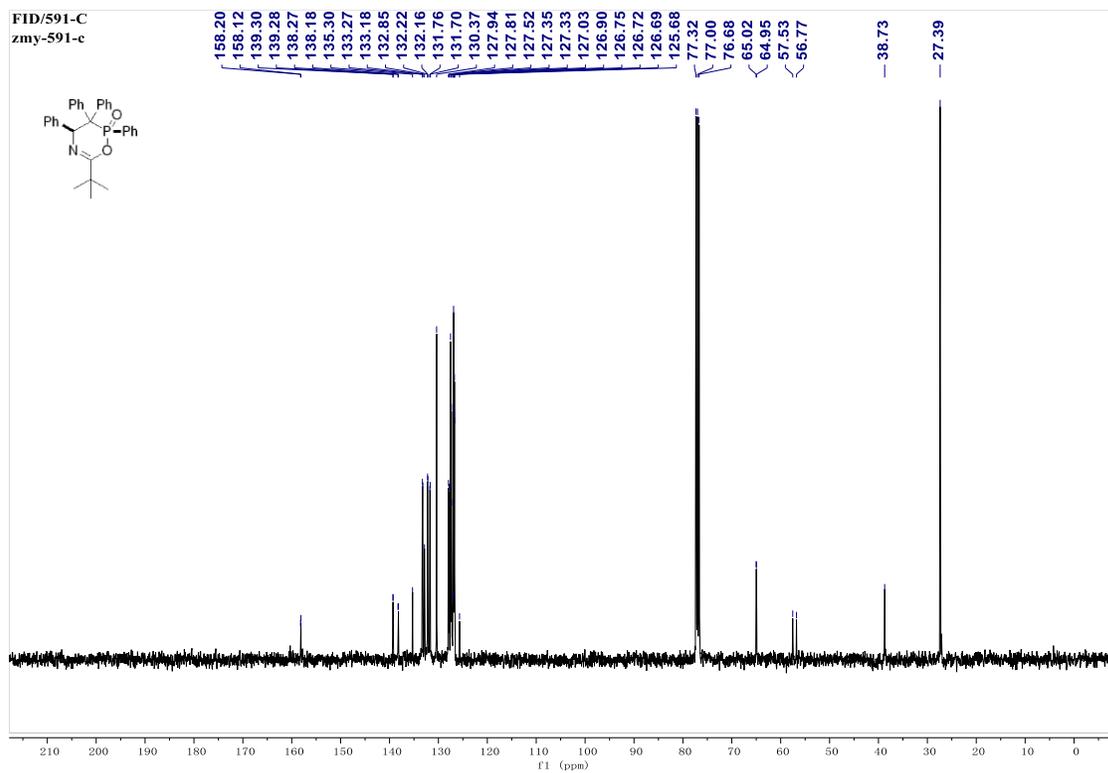


***trans*-6-(*tert*-Butyl)-2,3,3,4-tetraphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3ar)**

**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )**

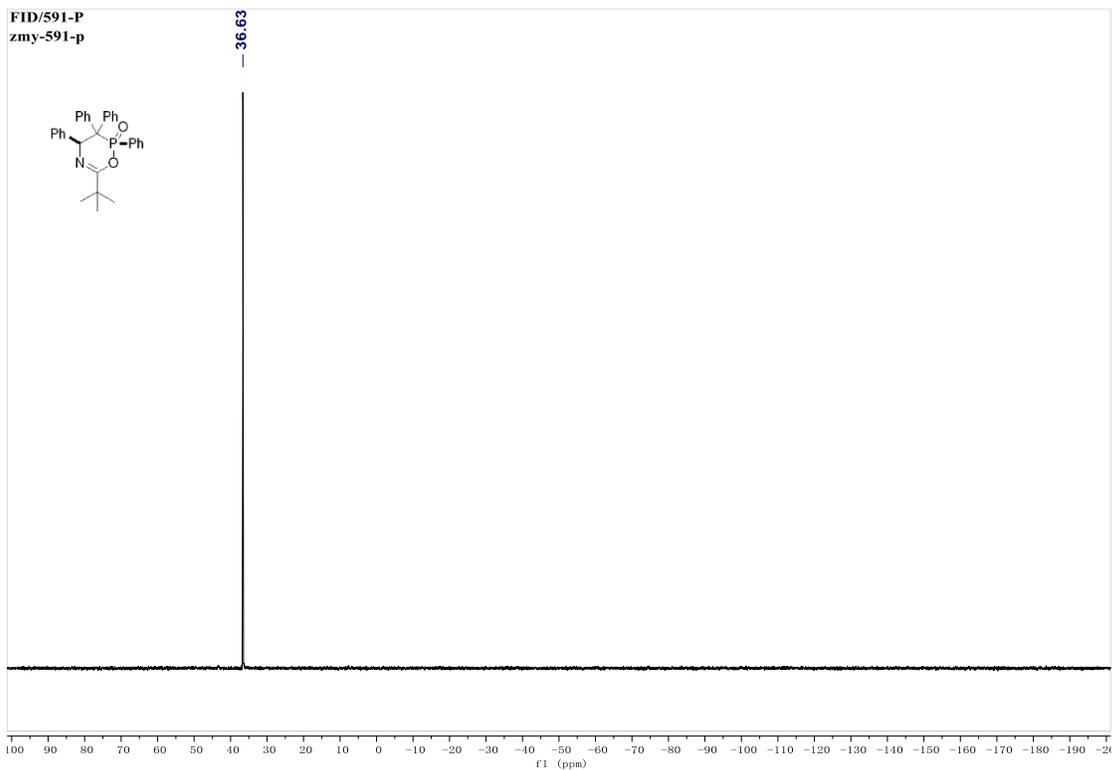


**$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )**

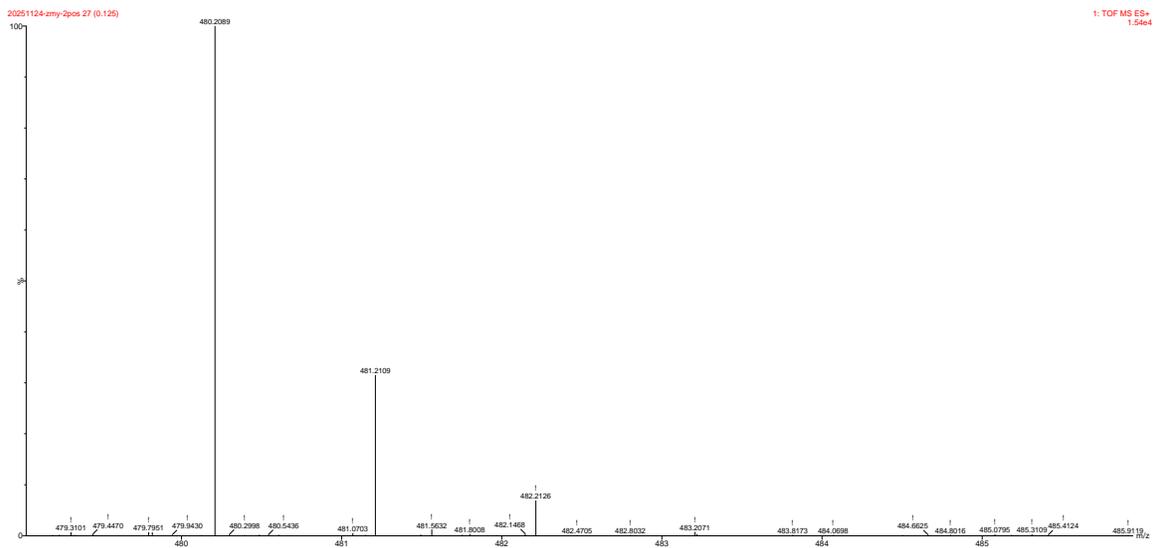


### $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, $\text{CDCl}_3$ )

FID/591-P  
zmy-591-p

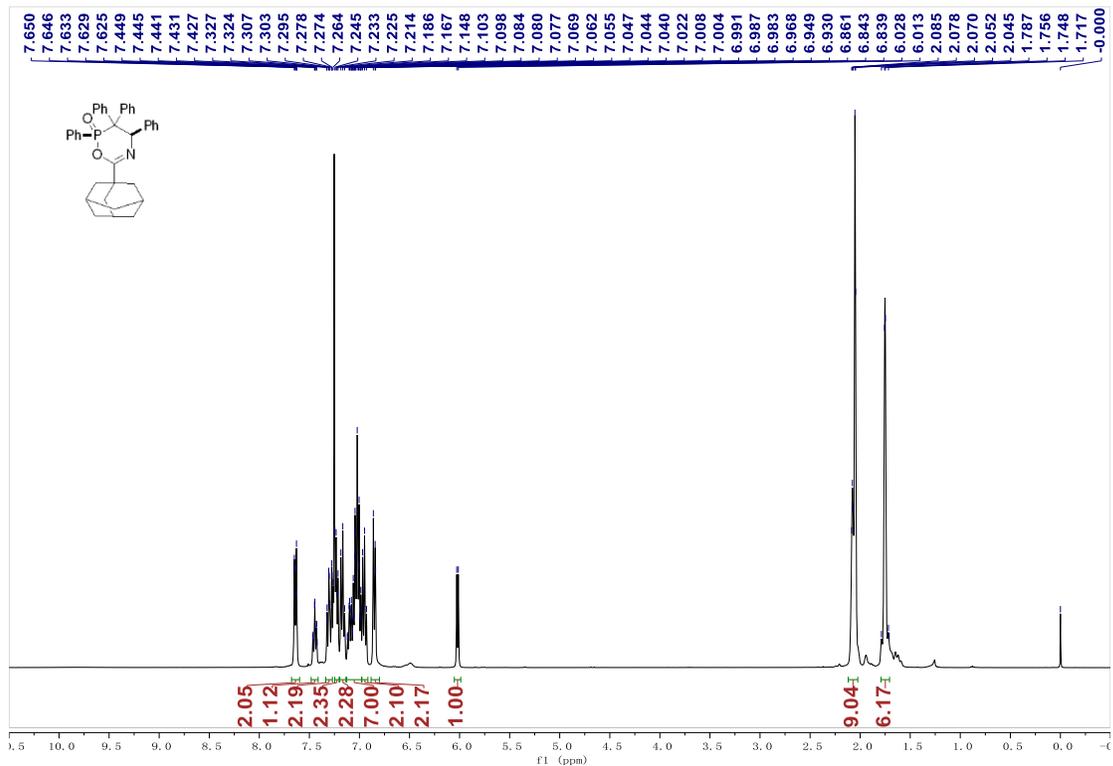


### HRMS

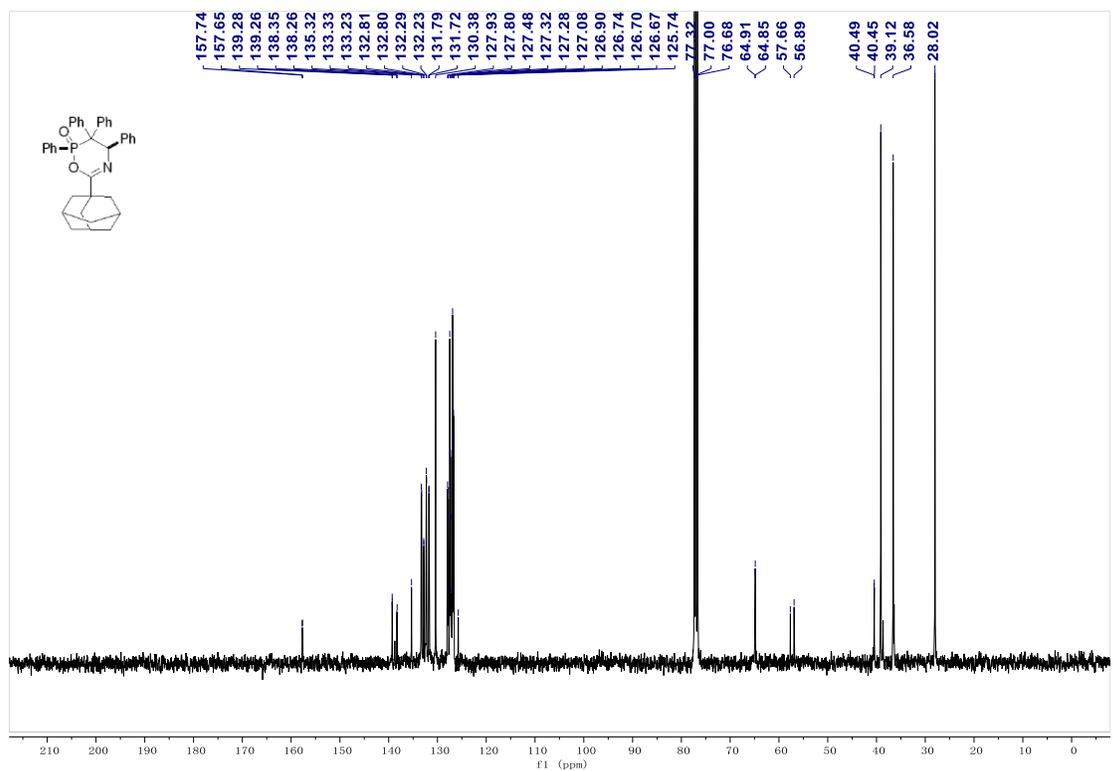


***trans*-6-(Adamantan-1-yl)-2,3,3,4-tetraphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3at)**

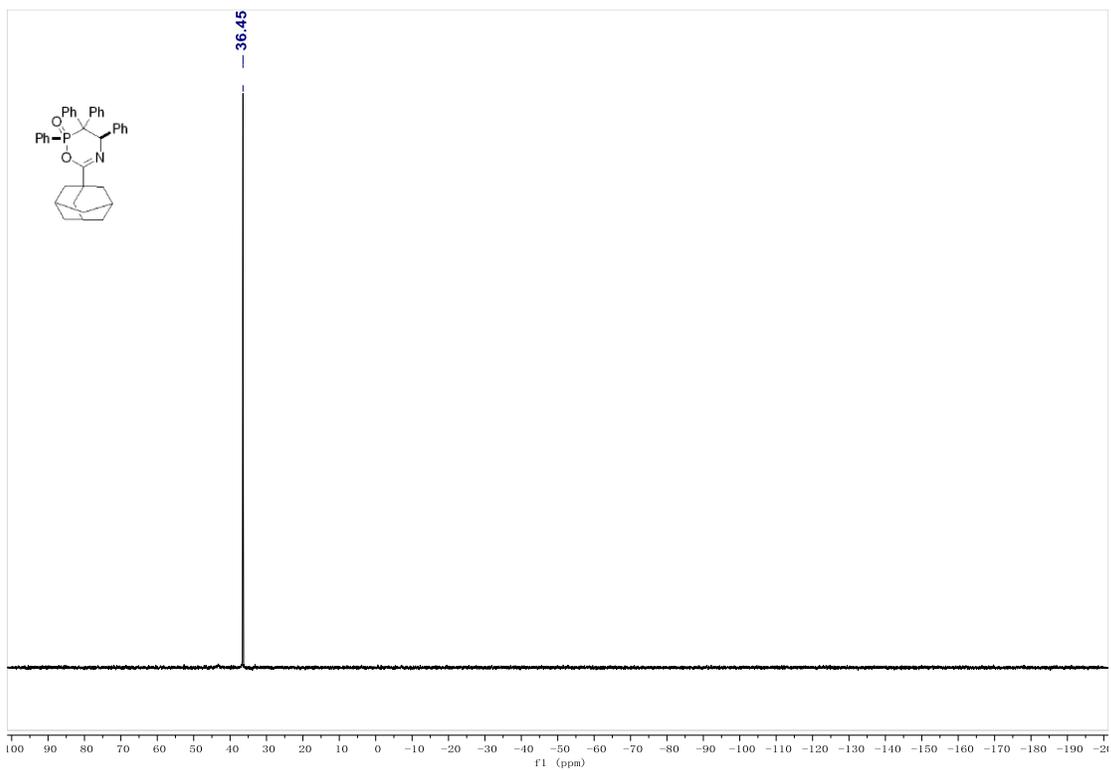
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



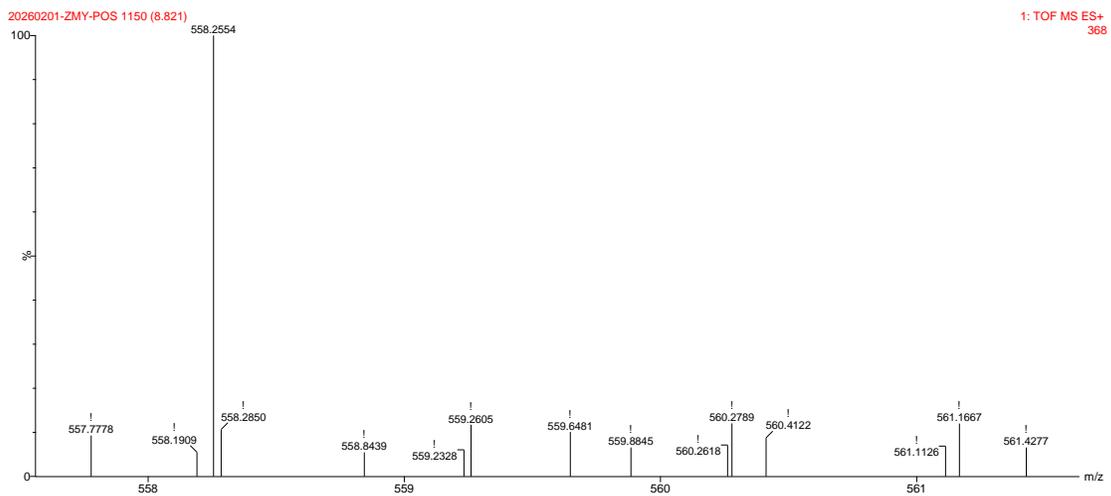
**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)**



$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ )

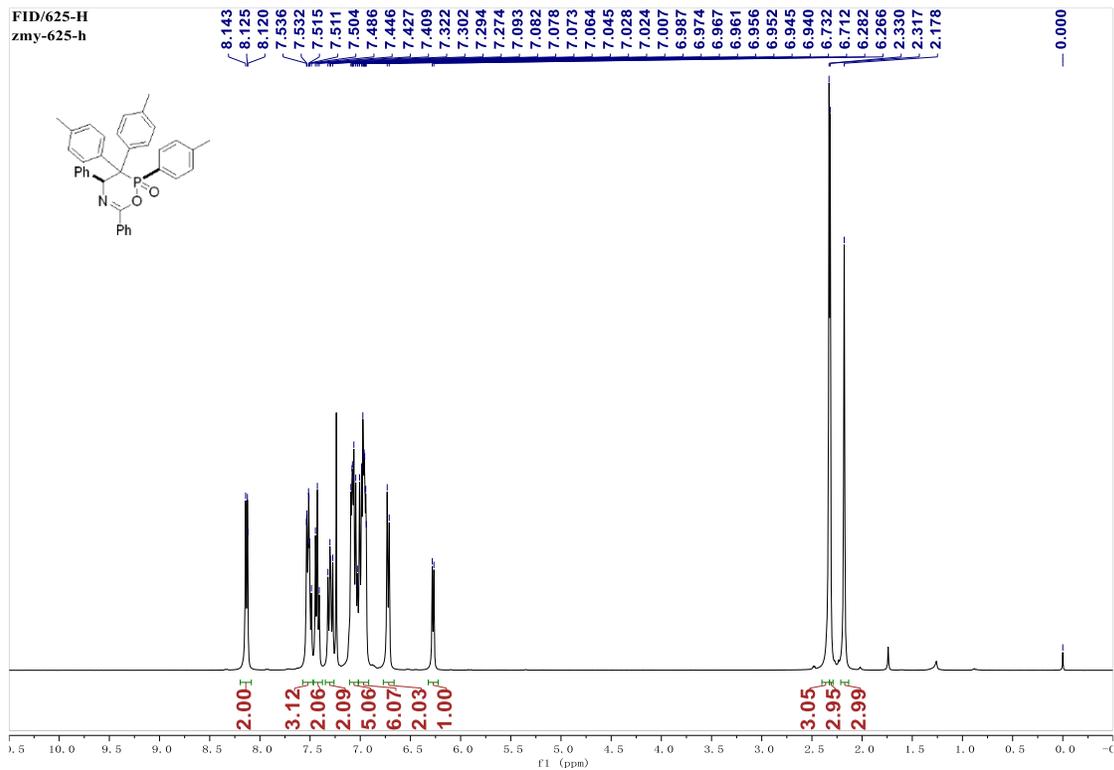


HRMS

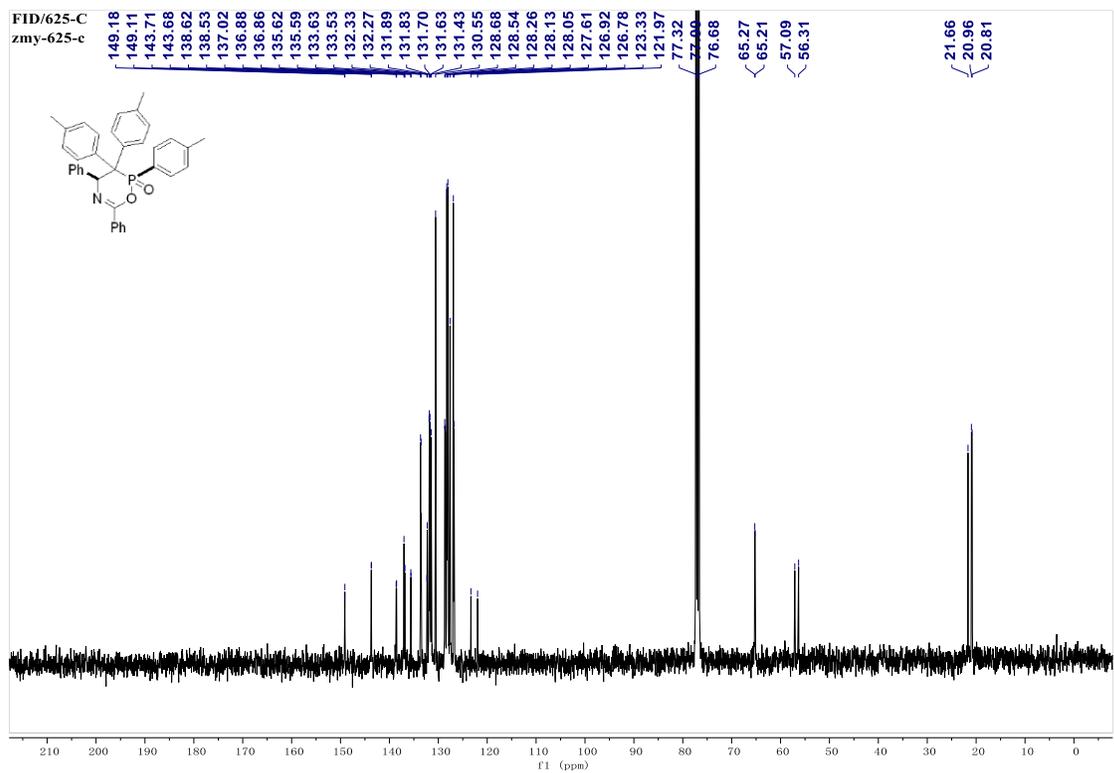


*trans*-4,6-Diphenyl-2,3,3-tri-*p*-tolyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3bd)

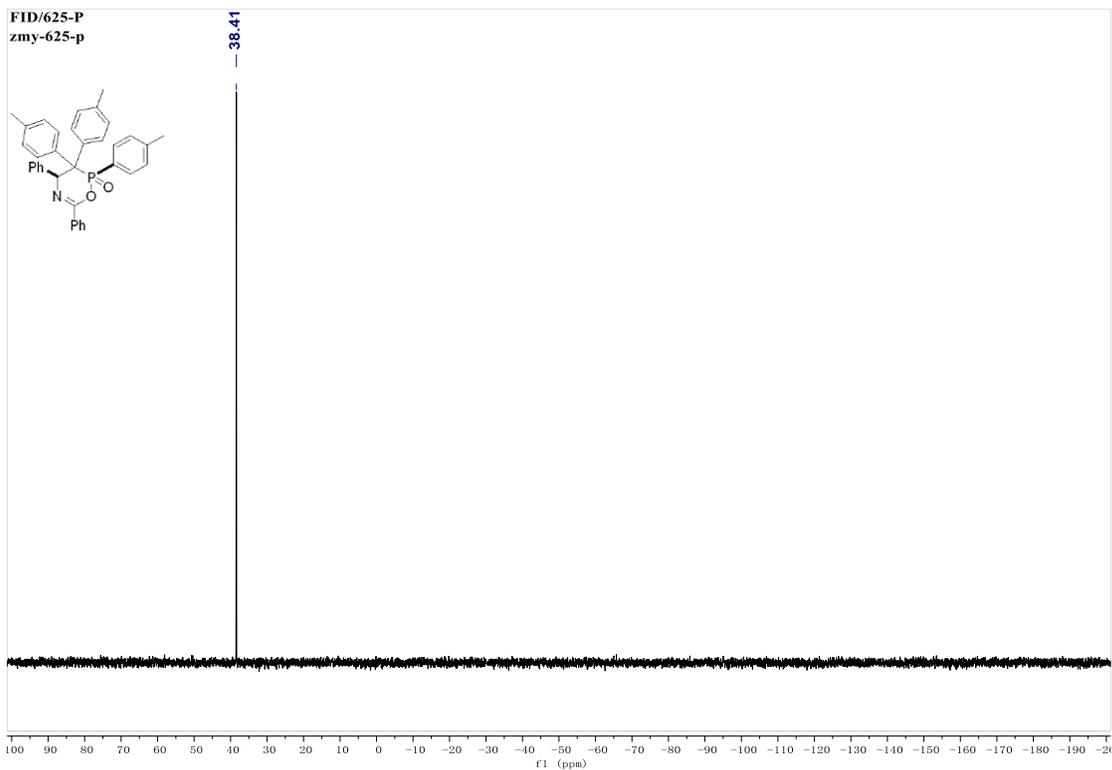
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



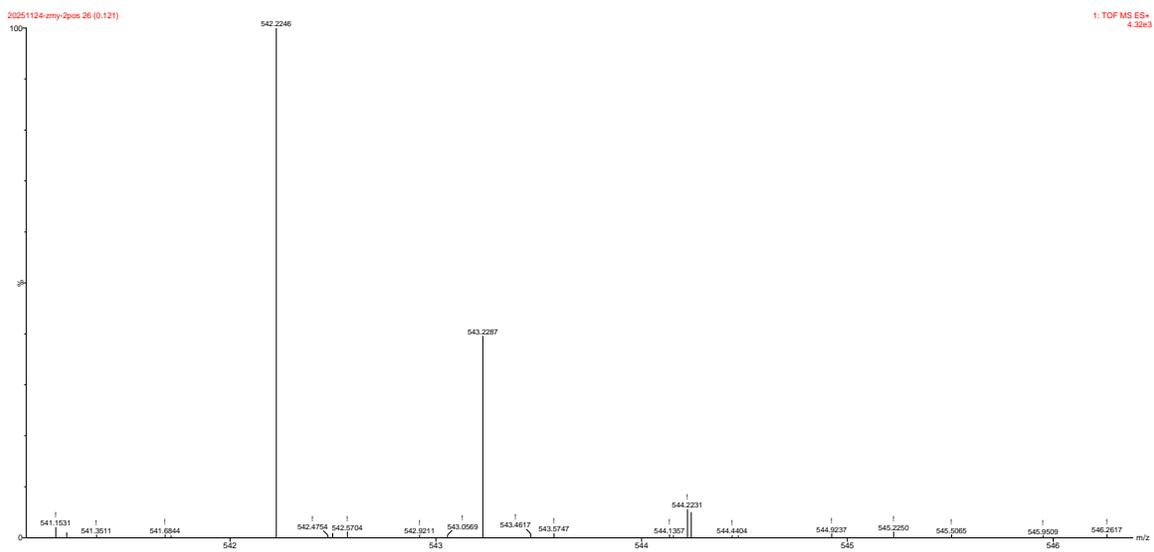
$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )



### $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, $\text{CDCl}_3$ )

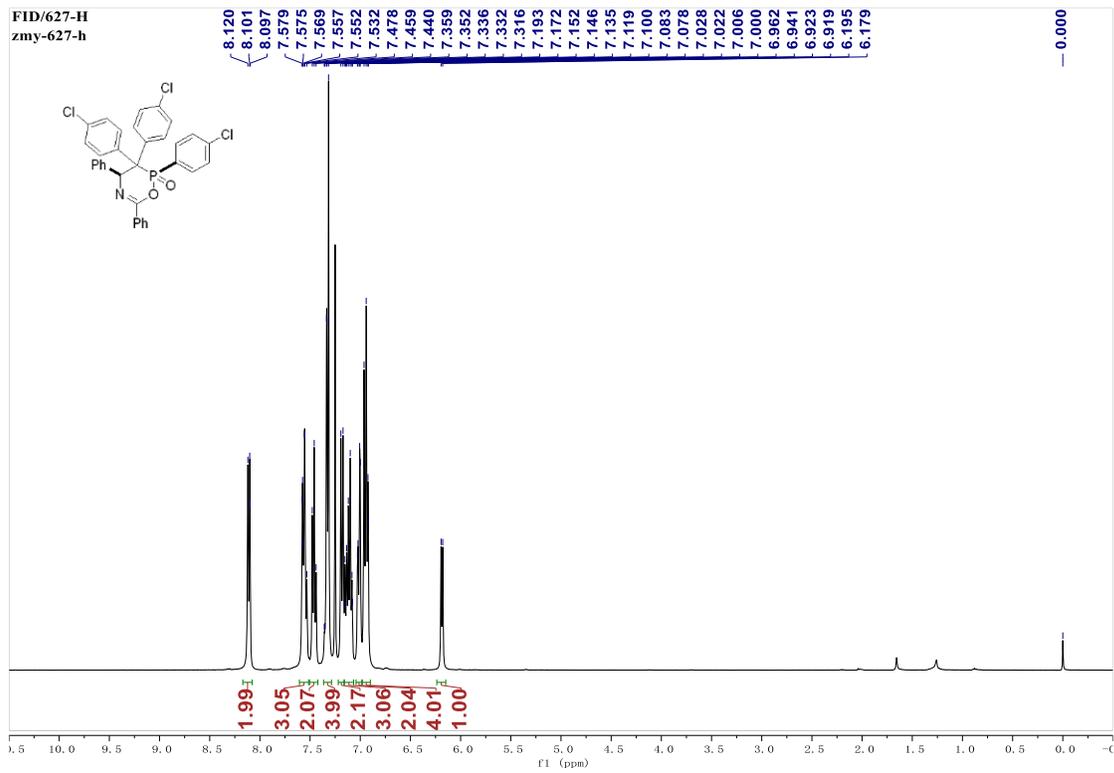


### HRMS

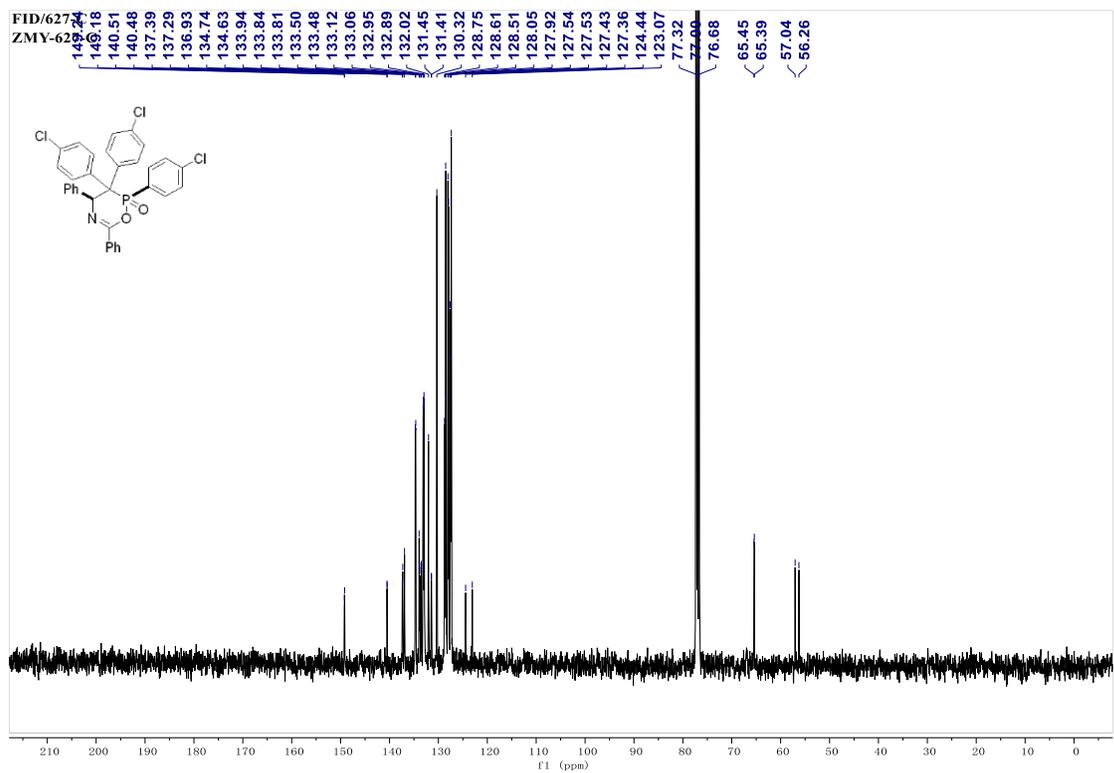


***trans*-2,3,3-Tris(4-chlorophenyl)-4,6-diphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3cd)**

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

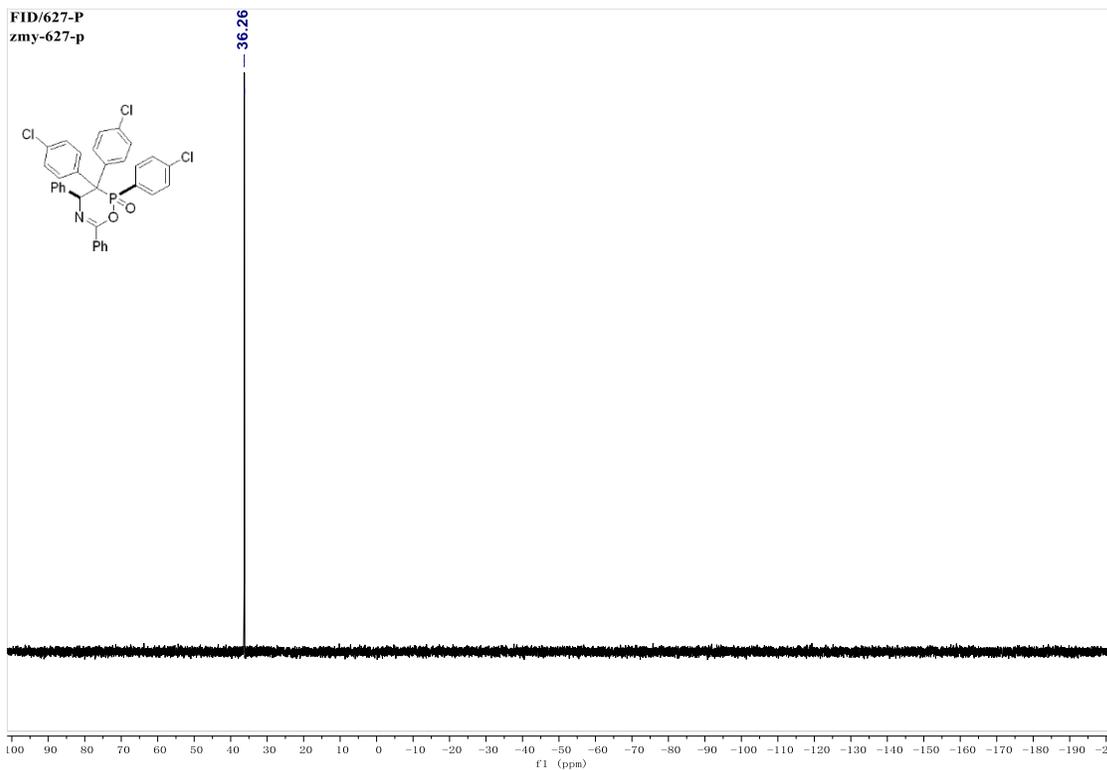


**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)**



### $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, $\text{CDCl}_3$ )

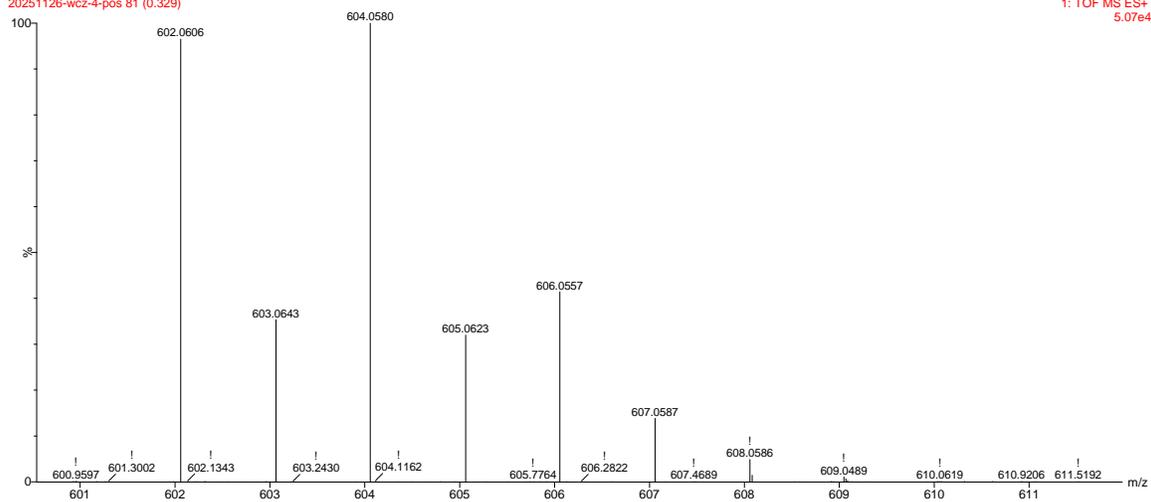
FID/627-P  
zmy-627-p



### HRMS

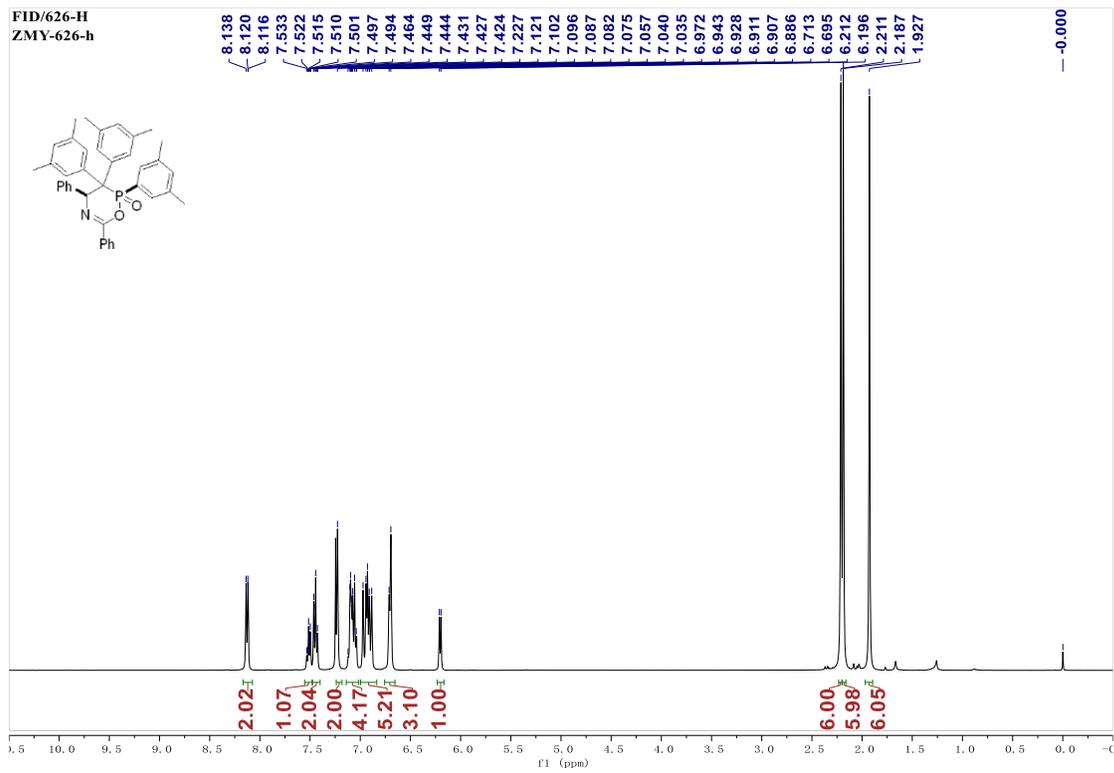
20251126-wcz-4-pos 81 (0.329)

1: TOF MS ES+  
5.07e4

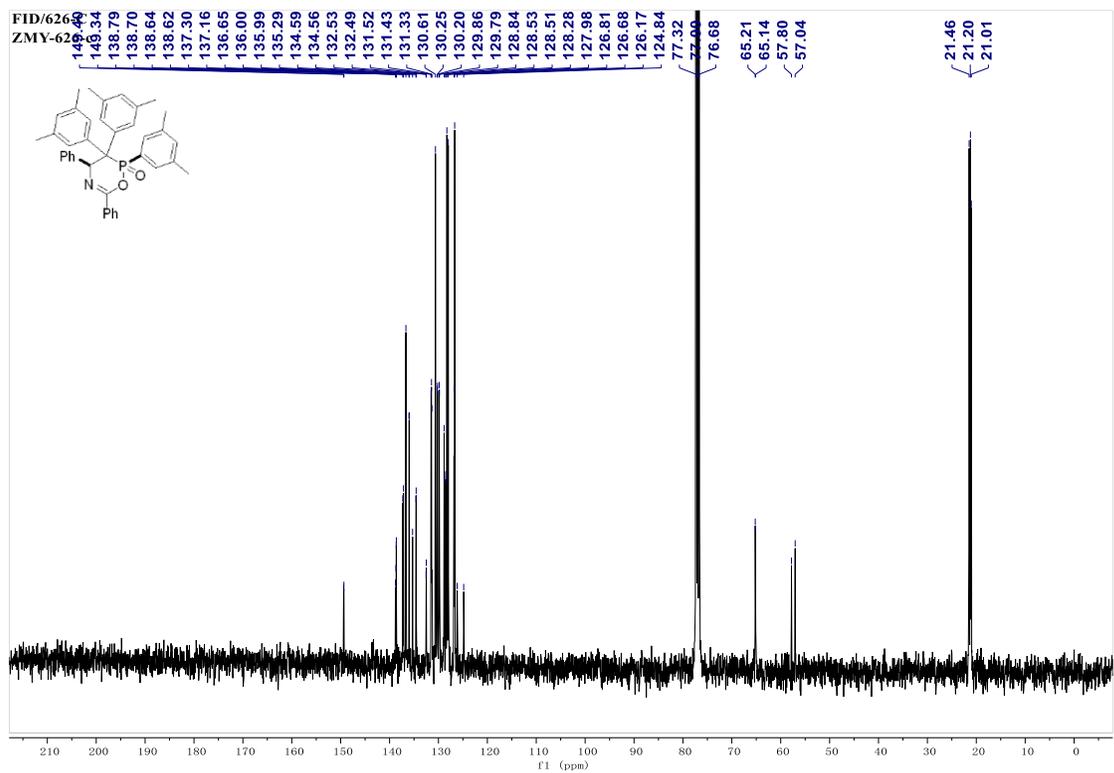


*trans*-2,3,3-Tris(3,5-dimethylphenyl)-4,6-diphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3dd)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

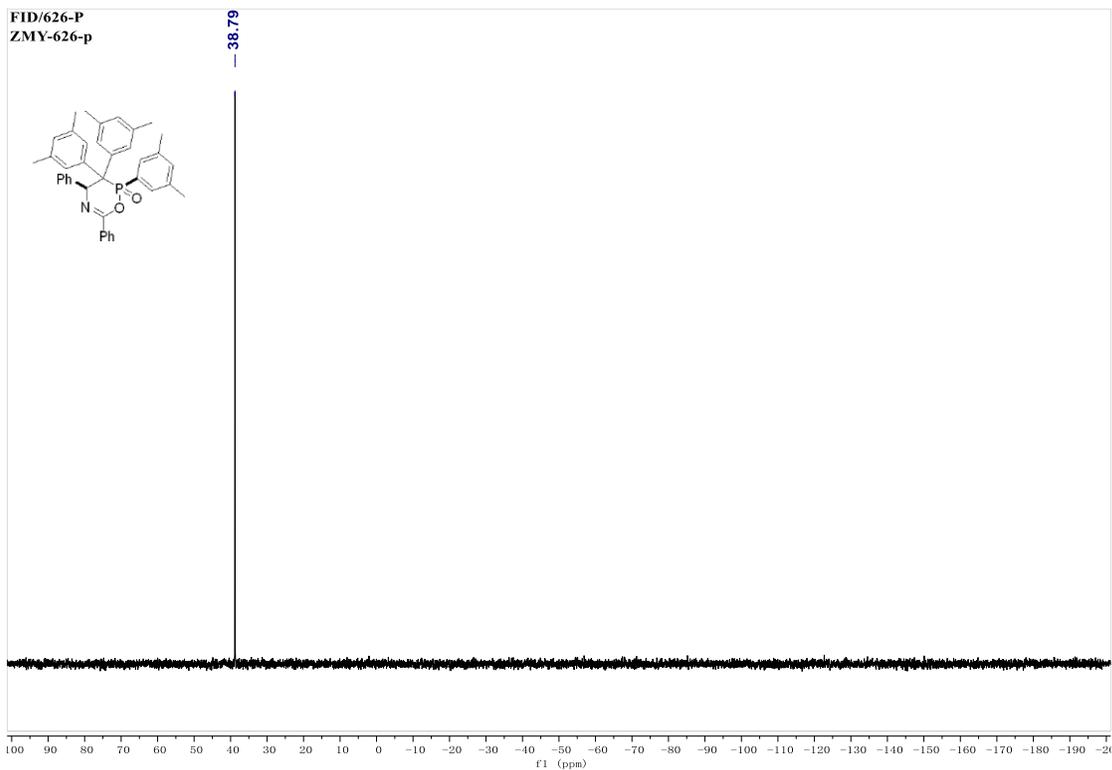


$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )

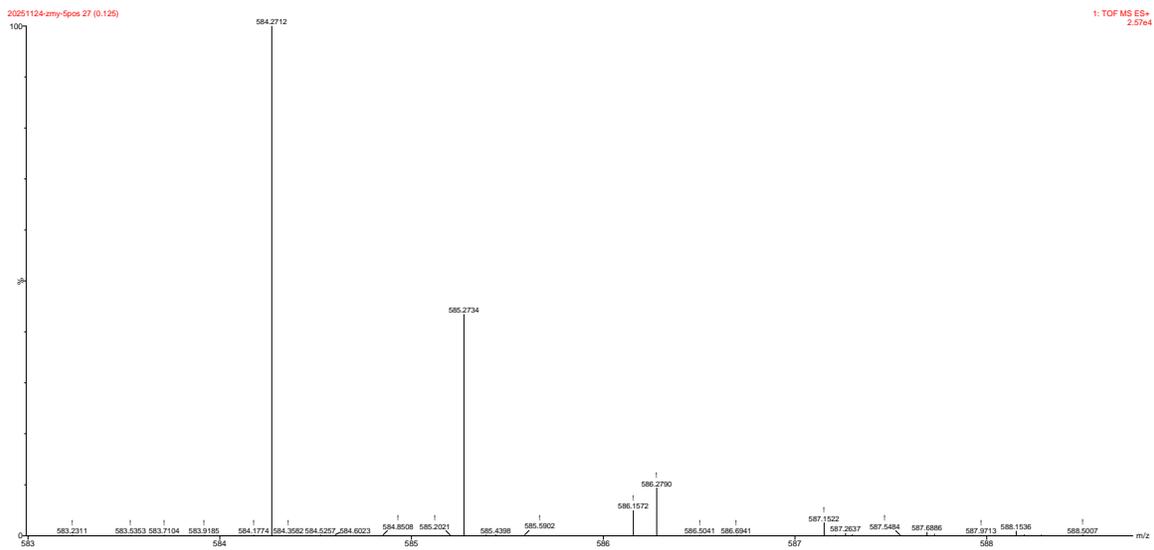


### $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, $\text{CDCl}_3$ )

FID/626-P  
ZMY-626-p

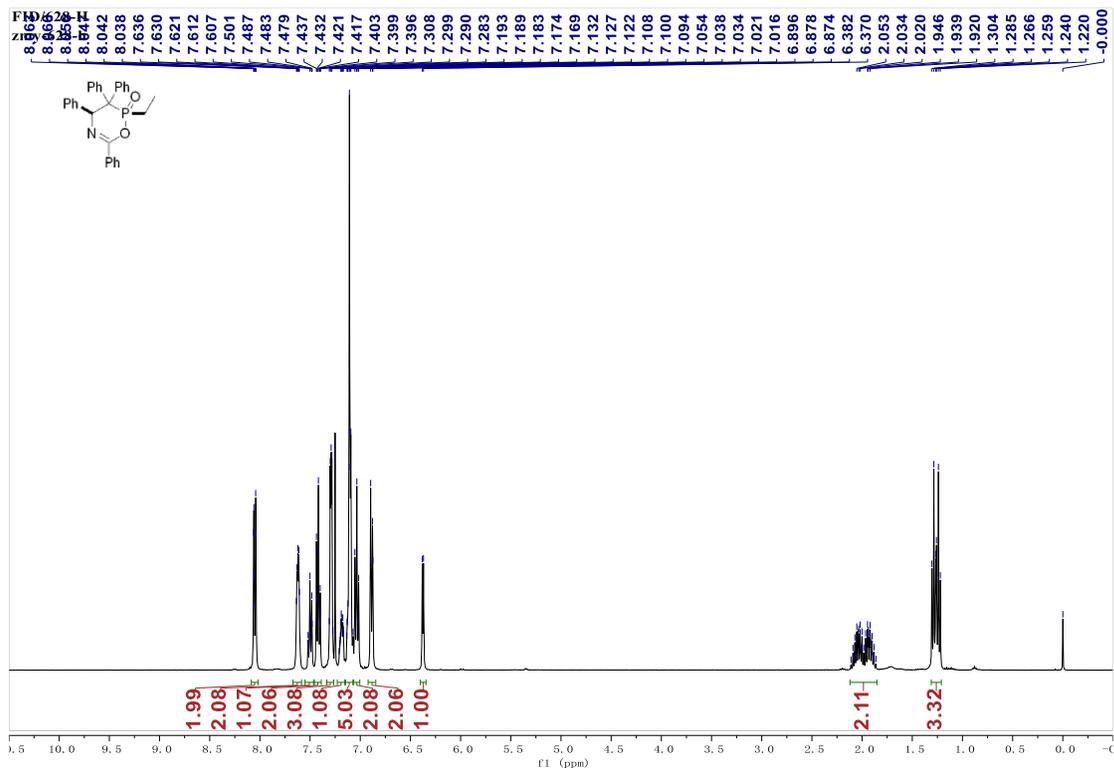


### HRMS

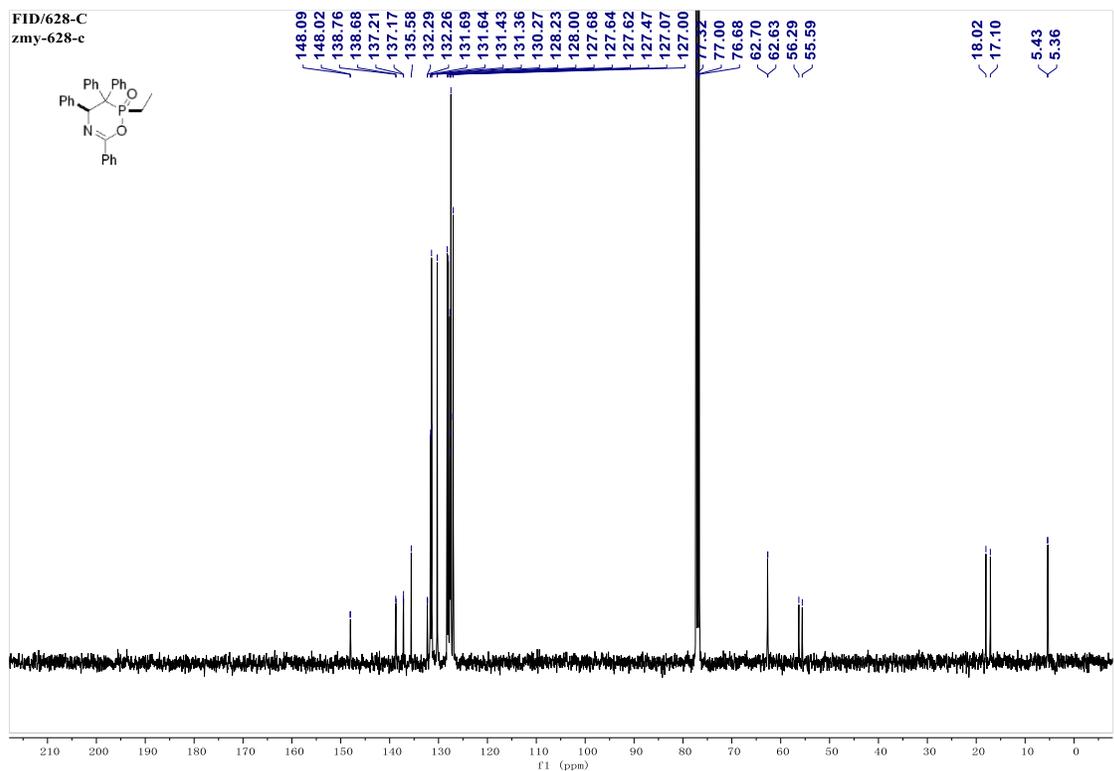


***trans*-2-Ethyl-3,3,4,6-tetraphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (3ed)**

**<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>)**

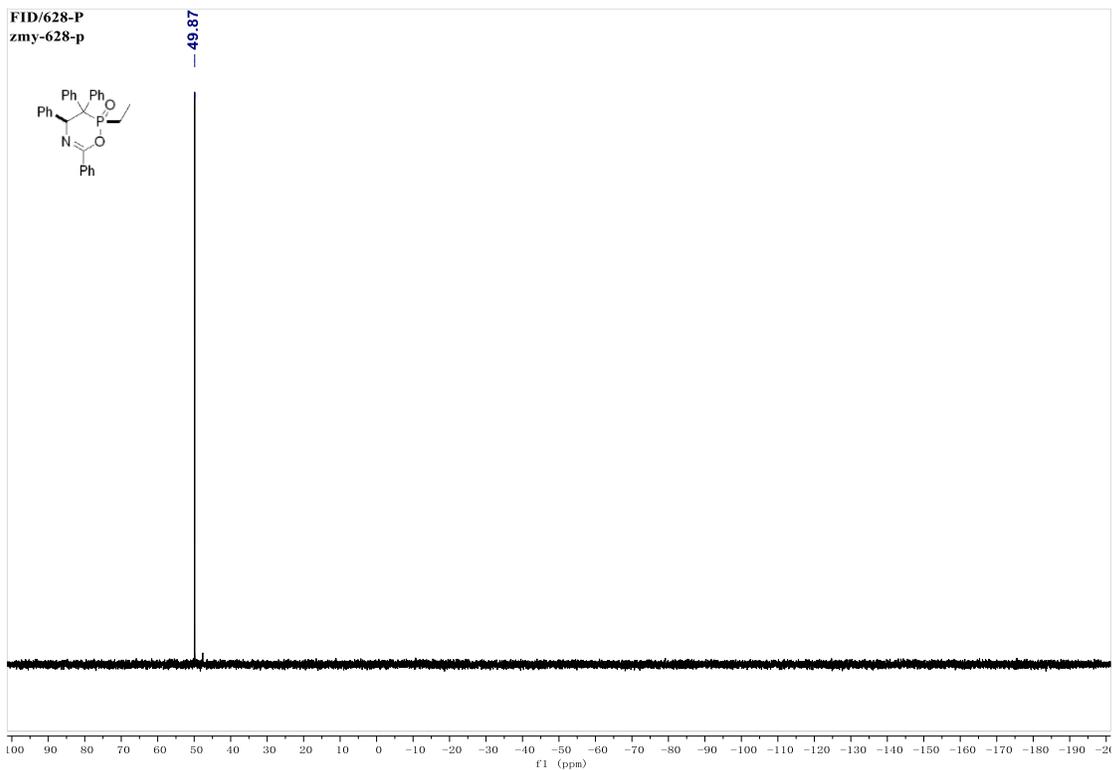


**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)**

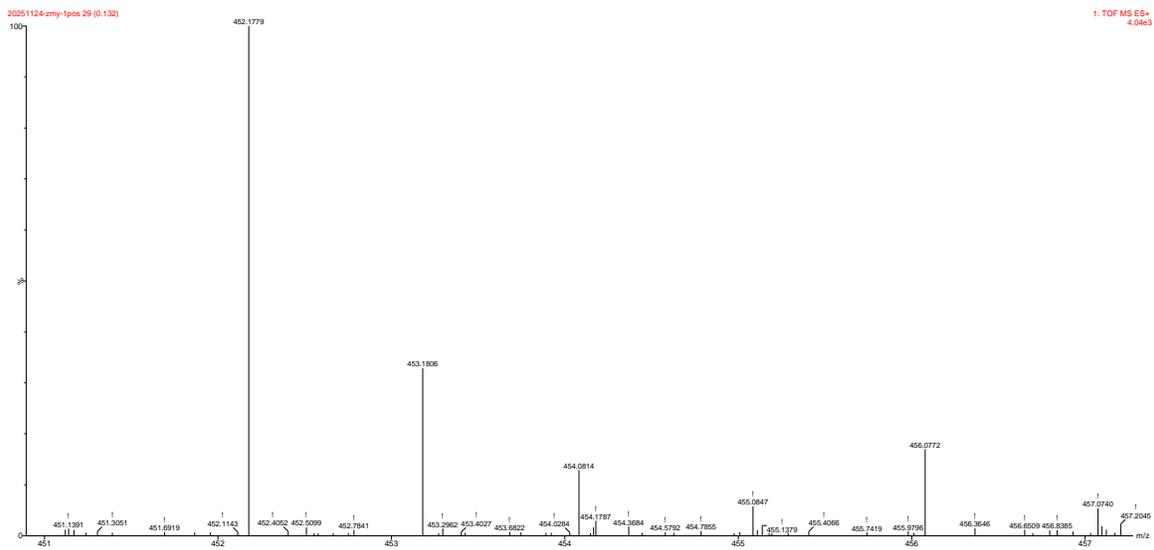


### $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, $\text{CDCl}_3$ )

FID/628-P  
zmy-628-p

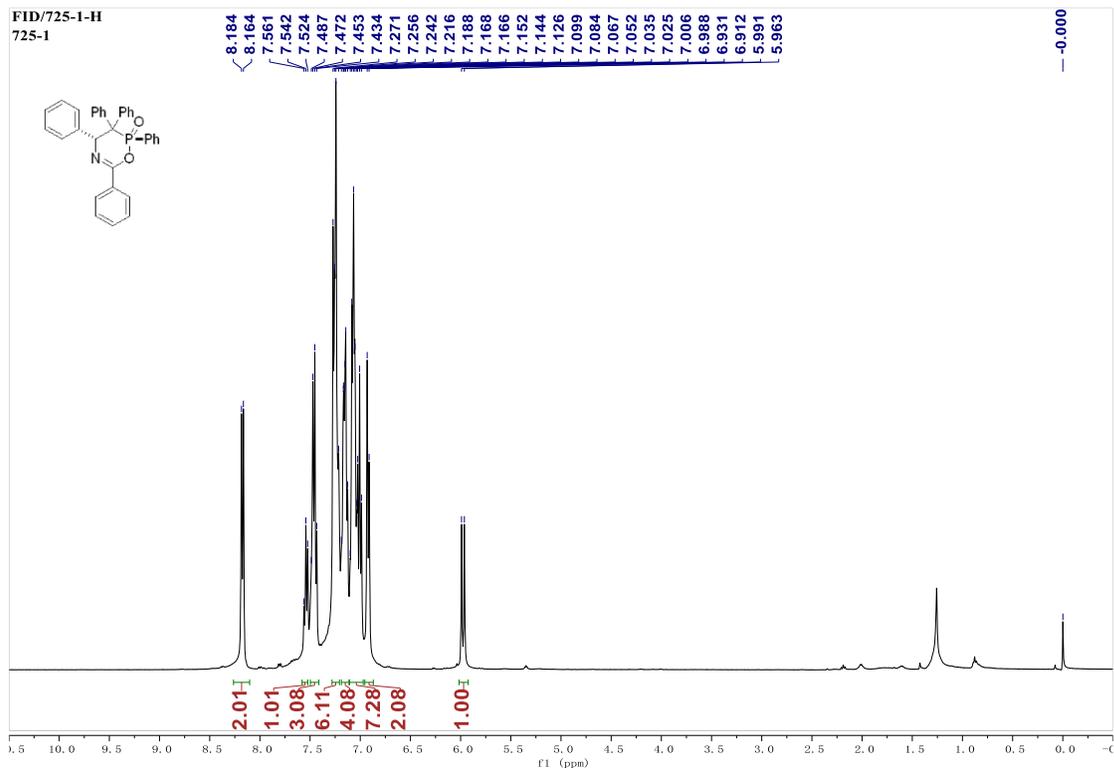


### HRMS

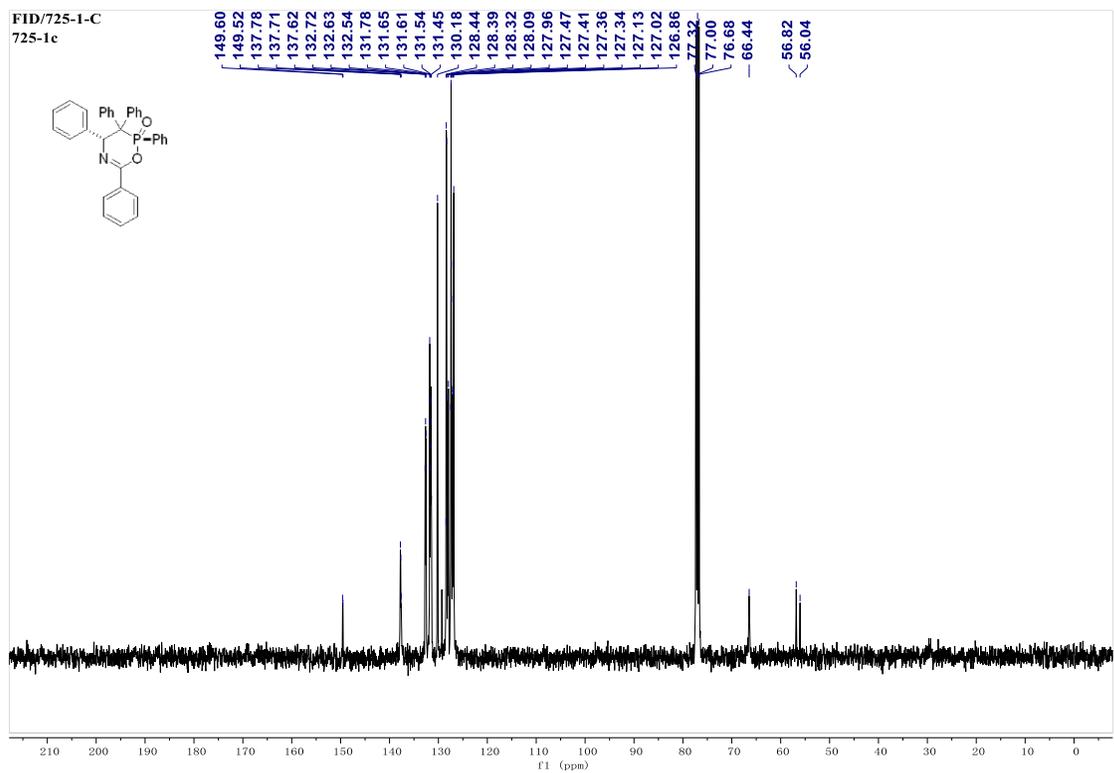


*cis*-2,3,3,4,6-Pentaphenyl-3,4-dihydro-1,5,2-oxazaphosphinine 2-oxide (*cis*-3ad)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

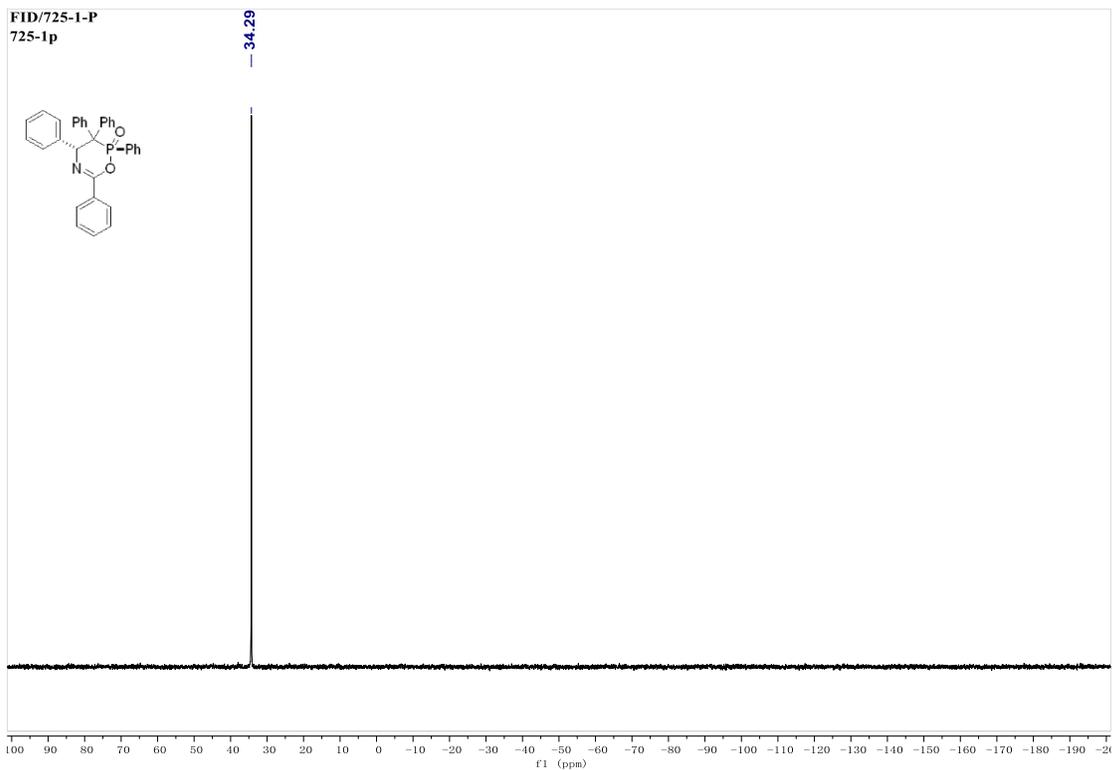


<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)

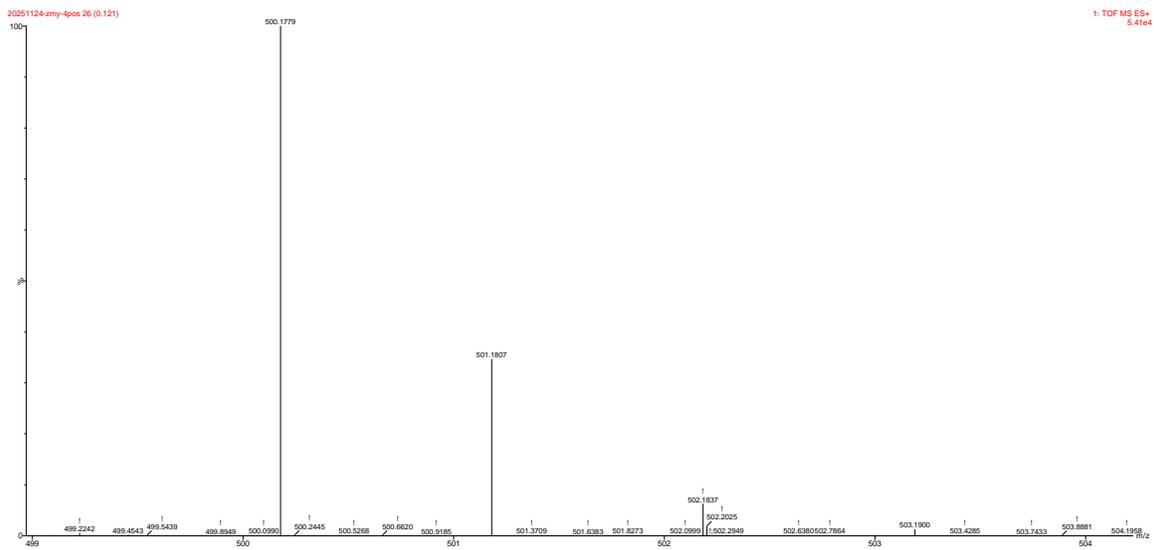


### $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, $\text{CDCl}_3$ )

FID/725-1-P  
725-1p

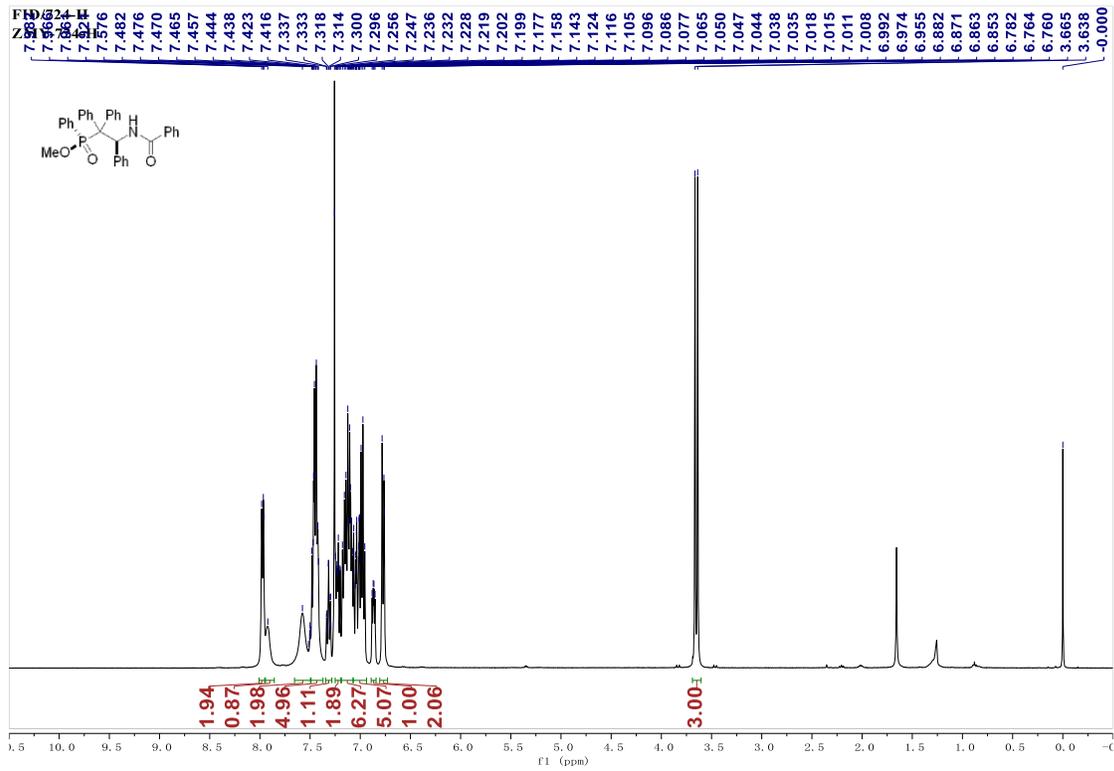


### HRMS

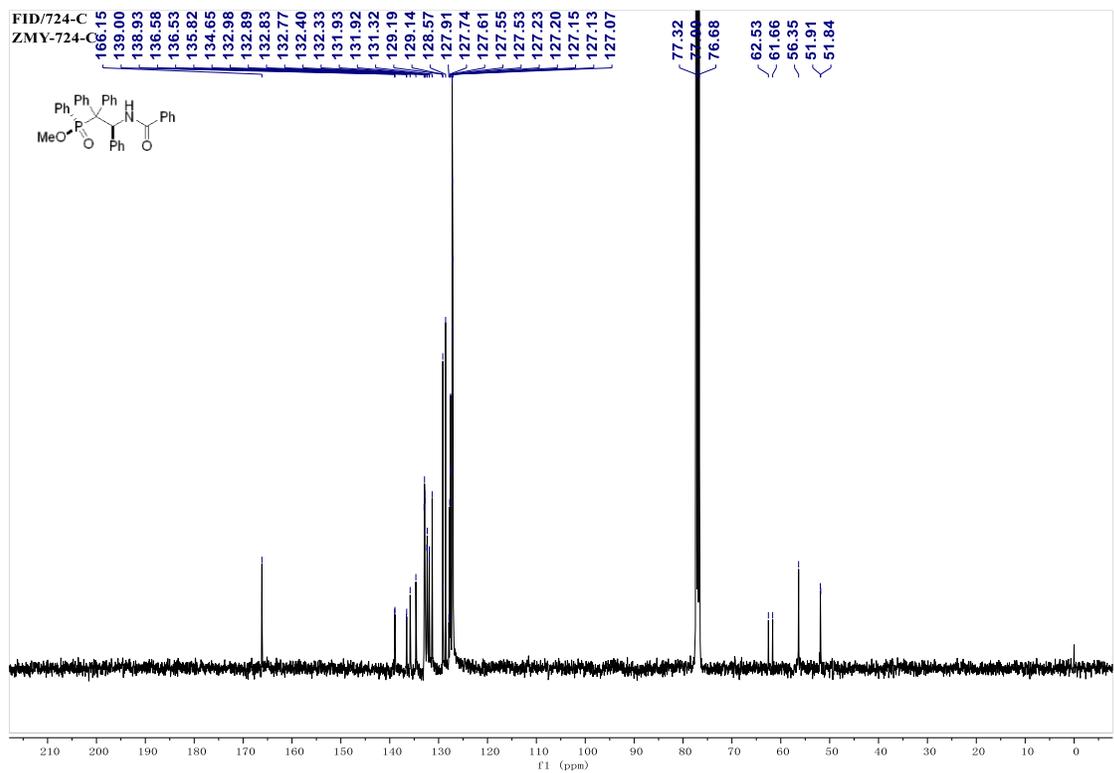


Methyl *rel*-(*R*)-(*S*)-2-benzamido-1,1,2-triphenylethyl(phenyl)phosphinate (4)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

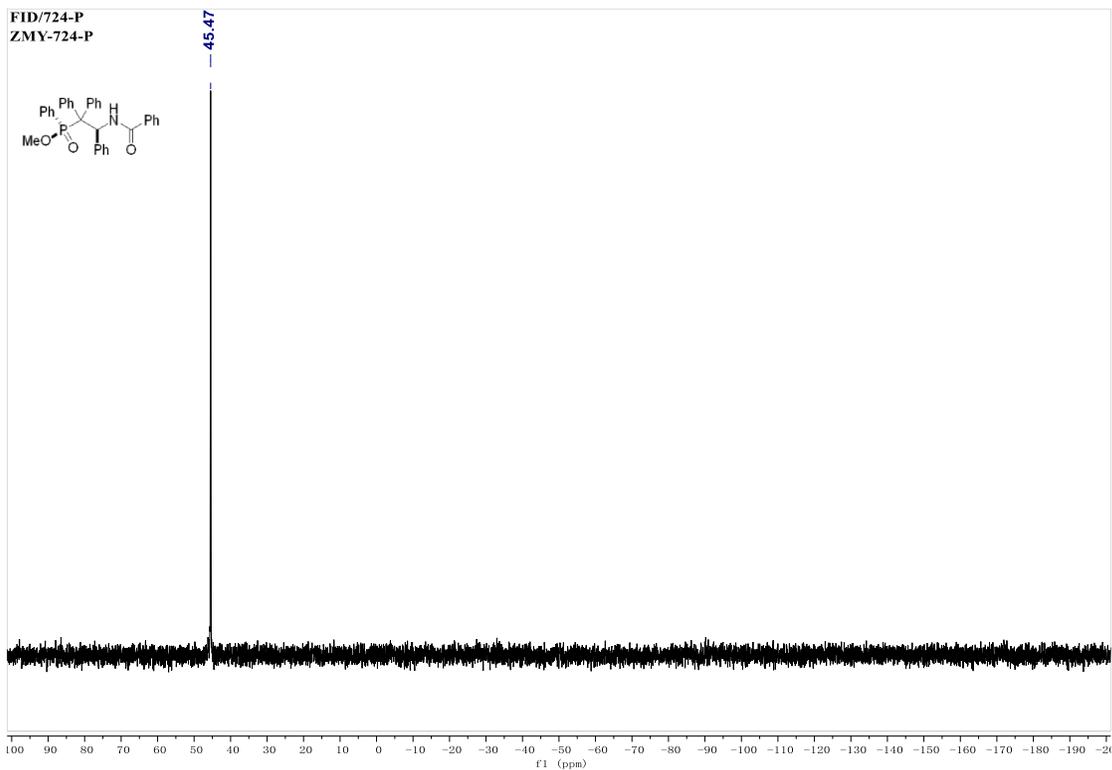


<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)

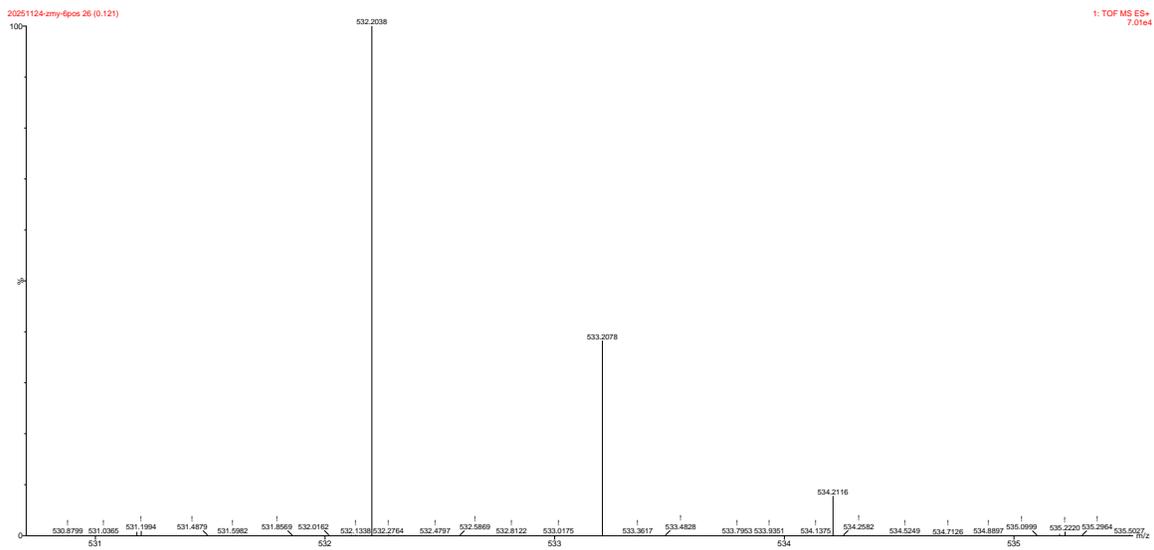


### $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, $\text{CDCl}_3$ )

FID/724-P  
ZMY-724-P

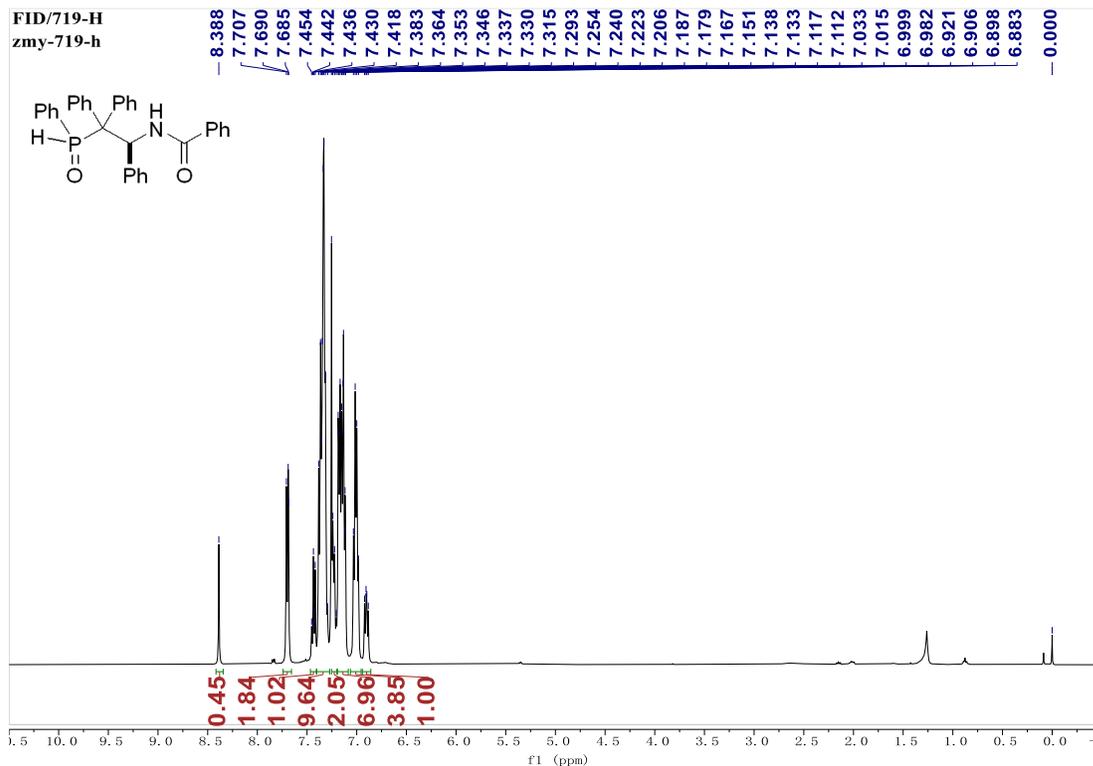


### HRMS

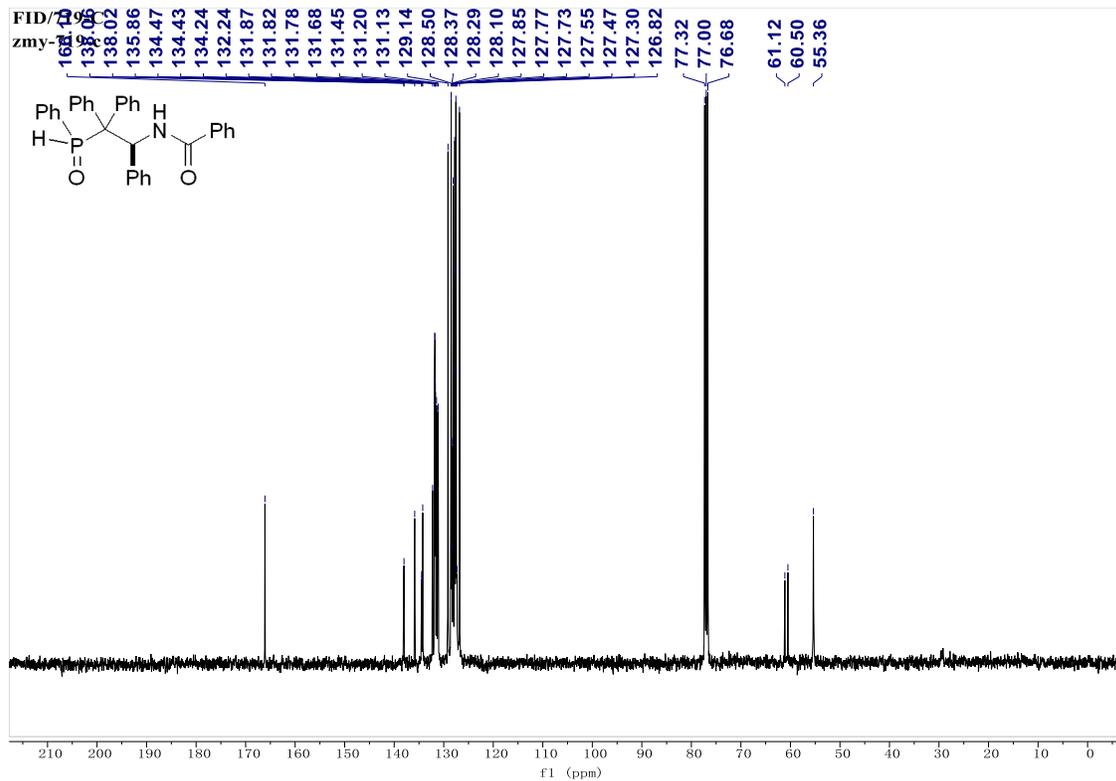


***N*-(1,2,2-Triphenyl-2-(phenylhydrophosphoryl)ethyl)benzamide (5)**

**<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>)**

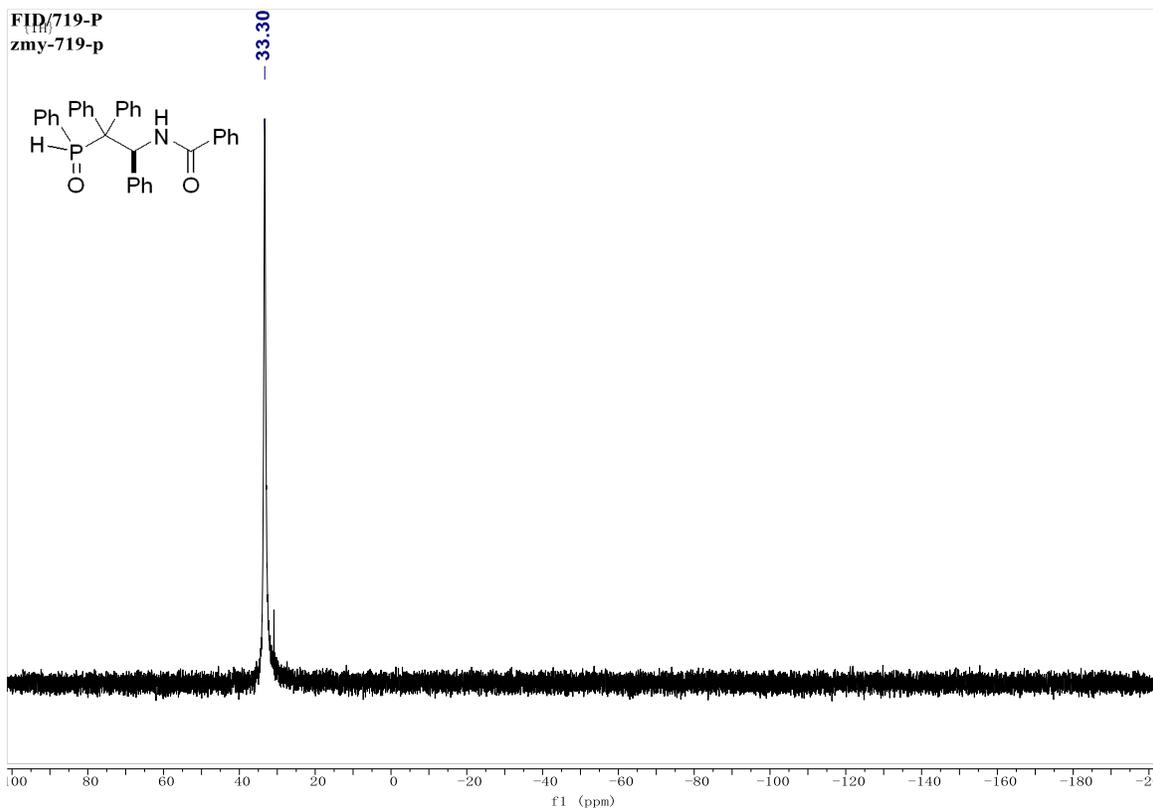


**<sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>)**



**$^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz,  $\text{CDCl}_3$ )**

FID/719-P  
zmy-719-p



**HRMS**

