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The Synthesis of Novel Oxazolinylphosphinic Esters and Amides and Application to the Cyanosilylation of Aldehydes

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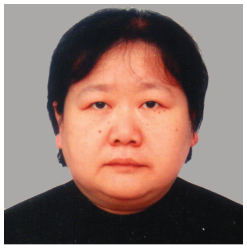

Mei Luo

Abstract: A new class of modular functionalized oxazolines are synthesized using a simple, novel one-pot method under inert moisture-free conditions. Then the oxazolines can be further elaborated to phosphine-containing oxazolines. The first step is to synthesize intermediates *via* the reaction of 2 - hydroxybenzonitrile or 2-aminobenzonitrile with chiral amino alcohols, subsequent reactions with phosphine chlorides, providing products in moderate yields. Product structures are fully characterized by NMR, IR, MS and X-Ray analyses. These compounds are found to be highly active catalysts for the cyanosilylation of prochiral benzaldehyde (20-96% yield).

Keywords: Functionalized oxazolines, chiral organometallic complexes, 2-hydroxybenzonitrile, 2-aminobenzonitrile, chiral amino alcohols, phosphine chlorides.

INTRODUCTION

Oxazolines are widely used in fields such as photography, agriculture, and they can be employed as surface coatings, plasticizers, surface active agents, additives for pharmaceuticals, additives for gasoline and lube oil additives, corrosion inhibitor, antiform agents, textile chemicals, pharmaceuticals, stabilizers for chlorinated hydrocarbons and for aqueous formaldehydes solutions, protective films in polish formulations, and foam stabilizers [1a]. In asymmetric catalysis, oxazoline structures have received much attention as "privileged" ligands for a broad wide variety of metals [1, 2]. For example, compounds containing these ligands have shown good catalytic activity in Diels-Alder reactions [3], allylic alkylations reactions [4], cyclopropanation reactions [5], aldol reactions [6], Henry reactions [7], and Michael reactions [8]. Additionally, catalysts containing chiral phosphine-substituted oxazolines have been reported to induce high enantioselectivity in asymmetric hydrogenation [8], cyanosilylation [9], allylic substitution [10], Heck reaction [11], Diels-Alder reaction [12] and hydrosilylation reactions [13].

Many methods for the synthesis of oxazolines have already been developed, but they are most commonly prepared by the condensation of amino alcohols with imidate hydrochlorides [14], carboxylic acids [15a-15b], dicarbonates [15c], ortho esters [16], imino ether hydrochlorides [17], or nitriles [18].

Encouraged by the previous pioneering work, we also report the synthesis of a new class of modular functionalized oxazolinylphosphine esters and amides using a simple, novel two-step method. Generally, the synthetic procedures for compounds involving phosphine involve multi-steps, low temperatures (-20∽-78°C), and the use of n-butyl lithium [19, 20]. In our method, n-butyl lithium is replaced with triethylamine, leading to fewer side reactions and making this synthetic method both practical and effective.

RESULTS AND DISCUSSION

Oxazolines **5(a-d)~8(a-d)** were obtained in moderate yields (40-60%) by reacting 2 – hydroxy or 2-amino substituted benzonitriles respectively with enantiomeric 2-aminoalcohols in chloro benzene under dry, anaerobic conditions. Dry zinc Chloride was used as a catalytic Lewis acid for this reaction [21-24] (Scheme **1**).

Moisture and oxygen-free conditions were also used in the second step. Compounds **5(a-d) ~8(a-d)** reacted with diphenylphosphinic chloride or phenyl phenylphosphonic dichloride to provide the target compounds in good yields. (Tables **1** and **2**) Instead of using n-butyllithium, triethylamine was employed as a proton scavenger to neutralize hydrogen chloride formed in this reaction. The excess base may also accelerate the reaction and prevent the decomposition of the oxazolines.

To drive the formation of P-N and P-O bonds, toluene was used as a high boiling point solvent so that the reactions could be conducted at higher temperatures. Compounds **9, 10** and **11** were formed when **5 and 6** reacted with diphenylphosphinic chloride or phenylphosphonic dichloride in a 1:1 ratio or 2:1 ratio. The identities of compounds **9a, 10c and 11c** were confirmed by their crystal structures.

The formation of **10 and 11** was not expected. It appears that when the attack of either the phenolic OH^- or imino nitrogen displaces the first chloride from phosphorous, this chloride attacks the carbon next to the oxygen, either prior to or concerted with the cyclization step. Compounds **12, 13 and 14** were obtained by reacting **7 and 8** with diphenylphosphinic chloride or phenylphosphonic dichloride in a 1:1 ratio or 2:1 ratio. The identities of compounds **12a and 13b** were also confirmed by their crystal structures.

Crystal of compounds **9a, 10c, 11c, 12a** and **13b** were obtained by slow evaporation of the solvent after isolation of the compound with column chromatography using CH_2Cl_2 / petroleum ether (9:1) as the eluent. (Figs **1-5**).

Interestingly, in the process of synthesizing the oxazolinyphosphine esters and amides, diphenylphosphinic acid and phenylphosphonic acid were always recovered as the side products in the last fraction collected during column purification of compounds using solvent CH_2Cl_2 / petroleum ether (9:1). The crystal structures of compounds **15 and 16** have confirmed the identity of these byproducts. (Figs **6** and **7**).

To evaluate the catalytic efficiency of the novel compounds, 20mol% of the oxazolines were used as catalysts for the cyanosilylation of prochiral benzaldehyde. The results are recorded in Table **3**.

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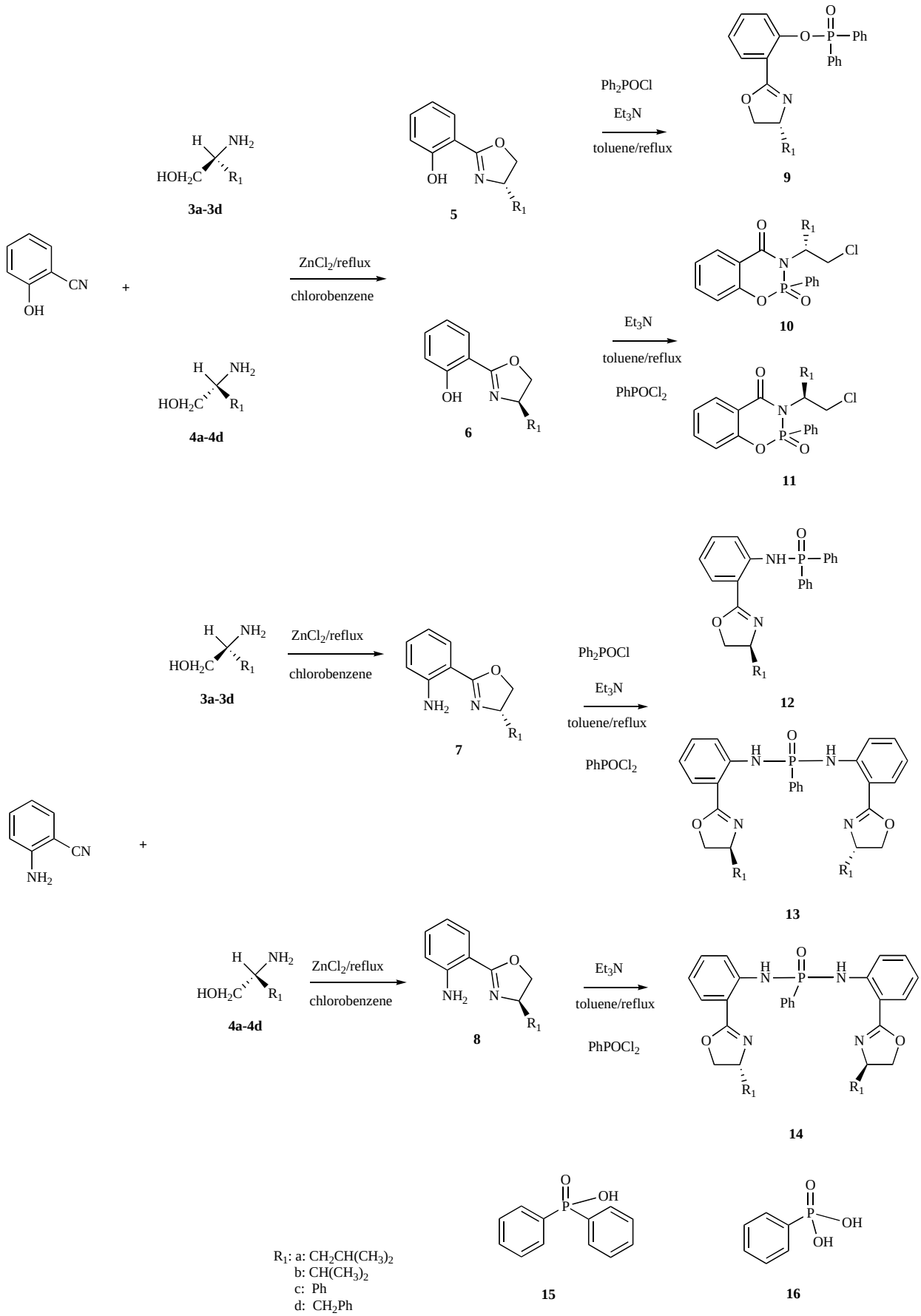


Scheme 1. The Synthetic Routes to the Compounds **9-16**.

Table 1. Synthesis of 9-11 from the Intermediate 5-6.

Entry	Reagent Ratio	Solvent	Yield (%)[d]	Time (h)
1→5[a]	1:1.43 (compound 1:3)	chlorobenzene		72
1a→5a			71	
1b→5b			65	
1c→5c			76	
1d→5d			64	
1→6[a]	1:1.43 (compound 1:4)	chlorobenzene		72
1a→6a			80	
1b→6b			85	
1c→6c			78	
5→9[b]	1.08:1(compound 5: Ph_2POCl)	toluene+ Et_3N		48
5a→9a			69	
5b→9b			64	
5c→9c			59	
5d→9d			58	
5→10[c]	2.04:1(compound 6: $PhPOCl_2$)	toluene+ Et_3N		48
5a→10a			46	
5b→10b			59	
5c→10c			62	
5d→10d			51	
6→11[c]	2.04:1(compound 4: $PhPOCl_2$)	toluene+ Et_3N		48
6a→11a			65	
6c→11c			48	
6d→11d			55	

[a]: Reaction conditions: A mixture of compound 1 (42.0mmol) 3a - 3d (60.0mmol) , 4a-4d (60.0mmol) and catalyst $ZnCl_2$ (7.8mmol) in chlorobenzene (50mL) was stirred at reflux under dry, anaerobic conditions. [b]: A mixture of compound 5 (9.17mmol), diphenylphosphinic chloride (8.50mmol) in toluene (20mL) and Et_3N (20mL) was stirred at reflux under dry, anaerobic conditions. [c]: A mixture of compound 7(6.42mmol) or 8(12.84mmol), phenylphosphonic dichloride (3.00mmol) and (4.99mmol) in toluene (20mL) and Et_3N (20mL) was stirred at reflux under dry, anaerobic conditions. [d]isolated yield.

Table 2. Synthesis of 12-14 from the Intermediate 7-8.

Entry	Reagent Ratio	Solvent	Yield (%)[d]	Time (h)
2→7[a]	1:1.42 (compound 2:3)	chlorobenzene		72
2a→7a			76	
2b→7b			80	
2c→7c			79	
2d→7d			73	
2→8[a]	1:1.42 (compound 2:4)	chlorobenzene		72
2a→8a			60	
2b→8b			60	
2c→8c			58	
2d→8d			61	
7→12[b]	1.08:1 (compound 7: Ph_2POCl)	toluene+ Et_3N		48
7a→12a			80	
7b→12b			82	
7c→12c			75	
7d→12d			63	

Table 2. Contd…..

Entry	Reagent Ratio	Solvent	Yield (%)[d]	Time (h)
7→13[c]	2.14:1 (compound 7: $PhPOCl_2$)	toluene+ Et_3N		48
7a→13a			82	
7b→13b			85	
7c→13c			76	
7d→13d			70	
8→14[c]	2.57:1 (compound 8: $PhPOCl_2$)	toluene+ Et_3N		48
8a→14a			85	
8b→14b			88	
8c→14c			82	
8d→14d			80	

[a]: Reaction conditions: A mixture of compound 2 (42.3mmol), 3a-3d (60.0mmol), 4a-4d (60.0mmol) and catalyst $ZnCl_2$ (7.8mmol) in chlorobenzene (50mL) was stirred at reflux under dry, anaerobic conditions. [b]: A mixture of compound 7 (9.17mmol), diphenylphosphinic chloride (8.50mmol) in toluene (20mL) and Et_3N (20mL) was stirred at reflux under dry, anaerobic conditions. [c]: A mixture of compound 7 (6.42mmol) or 8 (12.84mmol), phenylphosphonic dichloride (3.00mmol) and (4.99mmol) in toluene (20mL) and Et_3N (20mL) was stirred at reflux under dry, anaerobic conditions; .[d]: isolated yield.

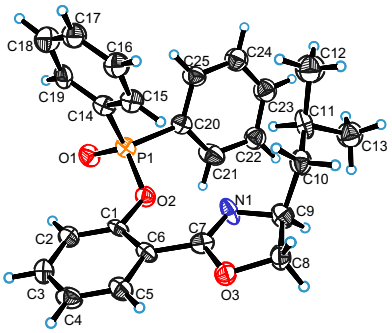


Fig. (1). The Crystal Structure of **9a**.

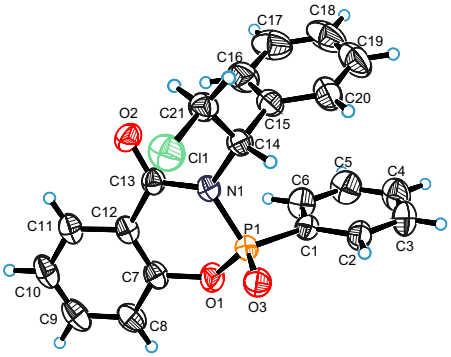


Fig. (2). The Crystal Structure of **10c**.

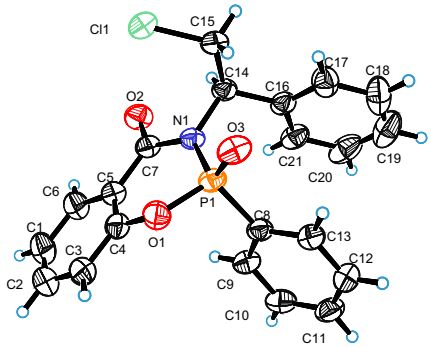


Fig. (3). The Crystal Structure of **11c**.

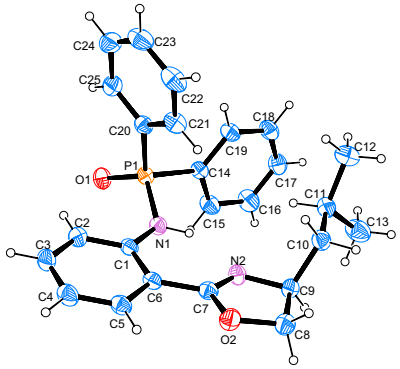


Fig. (4). The Crystal Structure of **12a**.

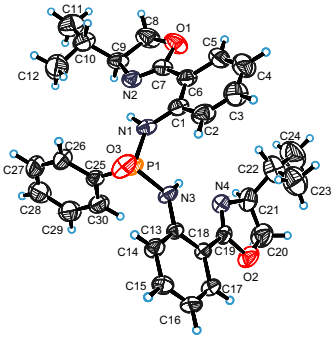


Fig. (5). The Crystal Structure of **13b**.

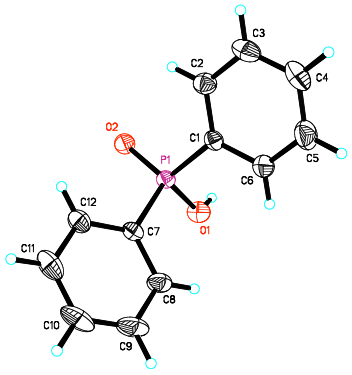


Fig. (6). The Crystal Structure of **15**.

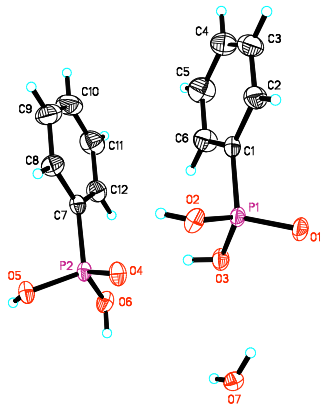


Fig. (7). The Crystal Structure of **16**.

From the data shown in Table **3**, we can conclude that our novel oxazolinylphosphinic esters and amides showed catalytic activity in the cyanosilylation of prochiral benzaldehyde. Among these catalysts **9b, 10c, 11c, 12a, 12b, 12d, 14a and 14d** showed high to excellent yields(80-96%), and catalysts **9a, 9c, 10a, 11a, 12c, 13b-13d, and 14b- 14c** afforded nearly quantitative yields(40-80%) after 6-8h or19h, but catalysts **9d-11d** showed low activity(5-40%). Although they have shown moderate to high yields, they all showed low enantiselectives (<10% ee) in this reaction.

CONCLUSION

In conclusion, we have synthesized a series of novel chiral compounds involving oxazolines which have not been reported in the literature. The next step is to determine the large-scale use of these compounds as catalysts in asymmetric application. Crystallographic information files for all compounds have been deposited with the Cambridge Crystallographic Data Center as supplementary publications CCDC 810907-810910, 853713, 853717, 1043621.

EXPERIMENTAL PART

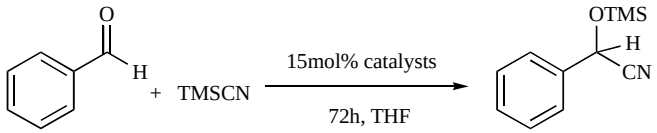
Materials and Measurements

2 - Hydroxybenzonitrile (2-cyano-phenol), 2-aminobenzonitrile, diphenylphosphinic chloride, phenylphosphonic dichloride, benzaldehyde, TMSCN and amino alcohol were purchased from Acros, Aldrich, Fluka. Flash column chromatography was performed using E. Merck silica gel (60, particle size 0.02-0.03 mm), ^{1}H and ^{13}C NMR and ^{31}PNMR spectra were obtained using Bruker AM-300, Bruker AM-400 and Bruker AM-500 spectrometers. Proton chemical shifts are reported in ppm (δ) with the solvent relative to tetramethylsilane (TMS) employed as the internal standard ($CDCl_3$, δ 7.26 ppm). The following abbreviations were used to designate chemical shift mutiplicities: s = singlet, d = doublet, t = triplet, m = multiplet. Infrared spectra were recorded on a Mattson Galaxy Series FTIR 3000 spectrometer; peaks are reported in cm-1. High resolution mass spectra (HRMS) were obtained on Micro GCT-MS equipped with an EI ion source. Optical rotations were measured on WZZ-1 automatic polarimeter with a 2 cm cell at the sodium D-line.

Structure Determination

The colorless plate crystal of the title compound **9a** of approximately 0.30x 0.20 x 0.12 mm was selected for the data collection on a "graphite" diffractometer with mirror monochromated CuK/α radiation (λ=0.71073Å). A total of 6944 reflections were collected in the range of 2.0276 < θ < 72.1972° by using "phi and omega scans" techniques at 293(2) K, $C_{25}H_{26}NO_3P$, *M* = 419.44, monoclinic, P 21, a = 8.5761(11)Å, α = 90° , b = 16.207(2) Å, β = 97.290(13) °, c = 16.011(2) Å, γ = 90° , *V* = 2207.4 Å^3, Z = 4, Dcalc. = 1.262mg/m^3, the final R factor was R_1 = 0.0501, 3508 for reflections with $I_0 > 2\sigma(I_0)$, R_ω=0.0608 for all data. The structure was solved by full-matrix least-squares on F^2 using the SHELXTL PROGREM [25, 26].

Table 3. Catalysis of Asymmetric Cyanosilylation Reactions[a].



Compound	Yield (%)[b]	Time (h)
9a	60	8
9b	94	8
9c	45	8
9d	12	8
10a	20	8
10c	85	8
10d	20	8
11a	58	8
11c	90	6
11d	22	6
12a	80	8
12b	95	8
12c	61	19
12d	95	19
13a	80	6
13b	60	6
13c	70	6
13d	45	6
14a	80	6
14b	40	6
14c	45	6
14d	80	6

[a] Reactions were carried out with 1mL PhCHO and 0.3mL TMSCN in 2 mL THF using 15mol% of catalyst at room temperature (30-40°C) for 6-8h or 19h. [b] Yield % was determined by NMR analysis.

The colorless plate crystal of the title compound **10c** of approximately 0.36x 0.30 x 0.30 mm was selected for the data collection on a "graphite" diffractometer with mirror monochromated CuK/α radiation (λ=0.71073Å). A total of 7343 reflections were collected in the range of 1.81 < θ < 27.00° by using "phi and omega scans" techniques at 293(2) K, $C_{21}H_{17}ClNO_3P$, *M* = 397.78, monoclinic, P21, a = 7.6799(1)Å, α = 90°, b = 21.7621(2) Å, β = 93.421(1) °, c = 11.3684(1) Å, γ = 90°, *V* = 1896.62 Å^3, Z = 4, Dcalc. = 1.393mg/m^3, the final R factor was R_1 = 0.0325, 7115 for reflections with $I_0 > 2\sigma(I_0)$, R_ω=0.0738 for all data. The structure was solved by full-matrix least-squares on F^2 using the SHELXTL PROGREM [25, 26].

The colorless plate crystal of the title compound **11c** of approximately 0.36x 0.30 x 0.26 mm was selected for the data collection on a "graphite" diffractometer with mirror monochromated CuKa radiation (λ=0.71073Å). A total of 2042 reflections were collected in the range of 3.18 < θ < 62.67° by using "phi and omega

scans" techniques at 293(2) K, $C_{21}H_{17}ClNO_3P$, *M* = 397.78, monoclinic, P 21, a = 11.1580(1)Å, α = 90º , b = 6.0355(3) Å, β = 100.742(4) º, c = 14.1606(6) Å, γ = 90º , *V* = 936.92 (8) Å^3, Z = 2, Dcalc. = 1.410mg/m^3, the final R factor was R_1 = 0.0308, 1810 for reflections with $I_0 > 2\sigma(I_0)$, R_ω=0.0736 for all data. The structure was solved by full-matrix least-squares on F^2 using the SHELXTL PROGREM [25, 26].

The colorless plate crystal of the title compound **12a** of approximately 0.36x 0.30 x 0.30 mm was selected for the data collection on a "graphite" diffractometer with mirror monochromated CuK/α radiation (λ=0.71073Å). A total of 6680 reflections were collected in the range of 1.81 < θ < 27.00° by using "phi and omega scans" techniques at 293(2) K, $C_{25}H_{27}N_2O_2P$, *M* = 418.46, monoclinic, P 21, a = 7.5174(1)Å, α = 90º , b = 16.2383(5) Å, β = 97.766(2) º, c = 16.0825(4) Å, γ = 90º , *V* = 2203.94 Å^3, Z = 4, Dcalc. = 1.261mg/m^3, the final R factor was R_1 = 0.0361, 5811 for reflections with $I_0 > 2\sigma(I_0)$, R_ω=0.1025 for all data. The structure was solved by full-matrix least-squares on F^2 using the SHELXTL PROGREM [25, 26].

The colorless plate crystal of the title compound **13b** of approximately 0.32x 0.30 x 0.24 mm was selected for the data collection on a "graphite" diffractometer with mirror monochromated MoK/α radiation (λ=0.71073Å). A total of 5292 reflections were collected in the range of 3.02 < θ < 72.82° by using "phi and omega scans" techniques at 293(2) K, $C_{30}H_{35}N_4O_3P$, *M* = 530.59, monoclinic, P21, a = 10.6752(5)Å, α = 90º , b = 9.2364(4) Å, β = 104.618(1) º, c = 15.1137 (6) Å, γ = 90º , *V* = 1441.98 Å^3, Z = 4, Dcalc. = 1.138mg/m^3, the final R factor was R_1 = 0.0628, 4049 for reflections with $I_0 > 2\sigma(I_0)$, R_ω=0.1618 for all data. The structure was solved by full-matrix least-squares on F^2 using the SHELXTL PROGREM [25, 26].

The prismatic brown crystal of the title compound **15** of approximately 0.465 x 0.318 x 0.227 mm was selected for the data collection on a "graphite" diffractometer with mirror monochromated MoK/α radiation (λ=0.71073Å). A total of 2343 reflections were collected in the range of 1.81 < θ < 27.00° by using "phi and omega scans" techniques at 293(2) K, $C_{12}H_{11}O_2P$, *M* = 218.18, monoclinic, P 21/c, a = 11.4280(14)Å, α = 90º , b = 6.0638(8) Å, β = 99.905(2) º, c = 15.7060(19) Å, γ = 90º , *V* = 1072.2(2) Å^3, Z = 4, Dcalc. = 1.352mg/m^3, the final R factor was R_1 = 0.0488, 2009 for reflections with $I_0 > 2\sigma(I_0)$, R_ω=0.1354 for all data. The structure was solved by full-matrix least-squares on F^2 using the SHELXTL PROGREM [25, 26].

The prismatic colorless crystal of the title compound **16** of approximately 0.169 x 0.125 x 0.097 mm was selected for the data collection on a "graphite" diffractometer with mirror monochromated MoK/α radiation (λ=0.71073Å). A total of 2901 reflections were collected in the range of 5.360 < θ < 56.360° by using "phi and omega scans" techniques at 293(2) K, $C_{12}H_{16}O_7P$, *M* = 334.19, monoclinic, P -1, a = 6.0038(18)Å, α = 96.632º , b = 7.716(2) Å, β = 97.274 (5) º, c = 16.583(5) Å, γ = 93.516º , *V* = 754.7(4) Å^3, Z = 2, Dcalc. = 1.471g/m^3, the final R factor was R_1 = 0.0435, 2447 for reflections with $I_0 > 2\sigma(I_0)$, R_ω=0.1228 for all data. The structure was solved by full-matrix least-squares on F^2 using the SHELXTL PROGREM [25, 26].

Preparation of the Intermediates 5a-5d

1.06g of dry $ZnCl_2$ (7.8mmol), 2-hydrobenzonitrile 5.0g (42.0mmol) and L-amino alcohol (60.0mmol) were added under free-water and free-oxygen conditions in a dry 100mL Schlenk flask. They were dissolved in 80mL of dry chlorobenzene; the reaction mixture was refluxed for 72h. The solvent was removed under reduced pressure and the residue was dissolved in 15mL H_2O, extracted with 10x3 mL of dichloromethane. The solvent was removed under vacuum, giving the crude red oil. Further purification was performed by silica gel. (petroleum ether/ dichlormethane 4/1).

Synthesis

Preparation of (S)-2-(4-isobutyl-4,5-dihydrooxazol-2-yl)phenol

Yield%: 71%, a colorless liquid, $[a]^{20}_D$= -48.67º (c=0.54, $CHCl_3$):

^{1}HNMR (500MHz, $CDCl_3$, 27°C), δ (ppm) = 12.30(s, 1H), 7.63(d, J= 8Hz, 1H), 7.36 (t, J=0.5Hz, 1H), 7.00(d, J=8Hz, 1H), 6.86(t, 1H), 4.47 (t, J=0.5Hz, 1H), 4.37~4.38(m, 1H), 3.95(t, J=0.5Hz, 1H), 1.84~1.87(m, 1H), 1.61~1.67(m, 1H), 1.38~1.42(m, 1H), 0.98~1.00(m, 6H).

Preparation of (S)-2-(4-isopropyl-4,5-dihydrooxazol-2-yl)phenol

Yield%: 65%, a colorless liquid, $[a]^{20}_D$= -28.6º (c=0.64, $CHCl_3$):

^{1}HNMR (500MHz, $CDCl_3$, 27°C), δ (ppm) = 12.37(s, 1H), 7.63(d, J= 7.5Hz, 1H), 7.35~7.36 (m, 1H), 7.02(d, J=8.5Hz, 1H), 6.86(t, J=0.5Hz, 1H), 4.39~4.43(m, 1H), 4.09~4.15(m, 2H), 1.78~1.82 (m, 1H), 0.94~1.02(dd, J=6.5, 6.5Hz, 6H).

Preparation of (S)-2-(4-phenyl-4,5-dihydrooxazol-2-yl)phenol

Yield%: 76%, a colorless crystals, $[a]^{20}_D$= -23.4º (c=0.35, $CHCl_3$):

^{1}HNMR (500MHz, $CDCl_3$, 27°C), δ (ppm) = 12.36 (s, 1H), 7.85~7.88(dd, J=2.5, 2.5Hz, 1H), 7.34~7.49 (m, 6H), 7.17(d, J=14Hz, 1H), 7.00(t, 1H), 5.44~5.50 (m, 1H), 4.78(t, J=2Hz, 1H), 4.26(t, 1H).

Preparation of (S)-2-(4-benzyl-4,5-dihydrooxazol-2-yl)phenol

Yield%: 64%, milk yellow paste, $[a]^{20}_D$= -3.07° (c=1.13, $CHCl_3$):

^{1}HNMR (500MHz, $CDCl_3$, 27°C), δ (ppm) = 12.22(s, 1H), 7.65(d, J= 8Hz, 1H), 7.25~7.41(m, 6H), 7.04(d, J=8Hz, 1H), 6.89(t, 1H), 4.61~4.65(m, 1H), 4.39(t, J=0.5Hz, 1H), 4.14(t, 1H), 3.10~3.14(dd, J= 6.5Hz, 6Hz, 1H), 2.81~2.85(dd, J=7.5Hz, 7.5Hz, 1H).

Preparation of 6a-6c

1.06g of dry $ZnCl_2$ (7.8mmol), 2-hydrobenzonitrile 5.0g (42.0mmol) and D-amino alcohol (60.0mmol) were added under free-water and free-oxygen conditions in a dry 100mL Schlenk flask. They were dissolved in 80mL of dry chlorobenzene; the reaction mixture was refluxed for 72h. The solvent was removed under reduced pressure and the residue was dissolved in 15mL H_2O, extracted with 10x3 mL of dichloromethane. The solvent was removed under vacuum, giving the crude red oil. Further purification was performed by silica gel. (petroleum ether/ dichlormethane 4/1).

Preparation of (R)-2-(4-isobutyl-4,5-dihydrooxazol-2-yl)phenol

A colorless liquid, yield: 80% ; $[a]^{20}_D$=+46.29º (c=0.52, $CHCl_3$); ^{1}HNMR (500MHz, $CDCl_3$, 27°C), δ (ppm) = 12.32(s, 1H), 7.63(d, J= 7.5Hz, 1H), 7.34 (t, J=0.5Hz, 1H), 7.00(d, J=8Hz, 1H), 6.86(t, 1H), 4.47 (t, J=0.5Hz, 1H), 4.34~4.37(m, 1H), 3.94(t, J=0.5Hz, 1H), 1.84~1.87(m, 1H), 1.60~1.63(m, 1H), 1.36~1.39(m, 1H), 0.97~1.00(m, 6H). ^{13}CNMR(125MHz, $CDCl_3$, 27°C) 164.4, 159.5, 132.8, 127.6, 118.2, 116.3, 110.4, 72.0, 63.4, 45.0, 25.2, 22.6, 22.0. IR (KBr) : 3057, 2957, 2930, 2871, 2651, 1644, 1618, 1583, 1493, 1467, 1367, 1311, 1261, 1232, 1155, 1128, 1066, 1034, 968, 946, 913, 829, 765, 687, 665, 496; HRMS(EI):m/z (%): calcd for $C_{13}H_{17}NO_2$: 219.1259; found: 219.1263.

Preparation of (R)-2-(4-phenyl-4,5-dihydrooxazol-2-yl)phenol

A colorless liquid, yield: 60%; $[a]^{20}_D$=+24.5º (c=0.41, $[a]^5_D$=-65.85º (c=0.41, $CHCl_3$); ^{1}HNMR (500MHz, $CDCl_3$, 27°C), δ (ppm) = 12.36(s, 1H), 7.84(d, J=7.5Hz, 1H), 6.30~7.49 (m, 6H), 7.17(d, J=8Hz, 1H), 7.00(t, J=1Hz, 1H), 5.48 (t, J=1Hz, 1H), 4.79(t, J=1.5Hz, 1H), 4.26(t, J=0.5Hz, 1H). ^{13}CNMR(125MHz, $CDCl_3$,

27°C) 166.0, 159.9, 141.3, 133.4, 129.5,128.6, 127.6, 126.2, 118.5, 116.6, 110.3, 73.7, 68.5. IR (KBr) : 3062, 3027, 2923, 1643, 1618, 1582, 1492, 1454, 1425, 1368, 1311, 1260, 1234, 1155, 1129, 1067, 1034, 961, 922, 829, 798, 749, 757, 700, 665, 541, 496; HRMS(EI):m/z (%): calcd for $C_{15}H_{13}NO_2$: 239.0946; found:239.0948.

Preparation of (R)-2-(4-benzyl-4,5-dihydrooxazol-2-yl)phenol

A colorless liquid, yield: 78%; $[a]^{20}_D$=+4.22º (c=0.46, $CHCl_3$); ^{1}HNMR (500MHz, $CDCl_3$, 27°C), δ (ppm) = 12.26(s, 1H), 7.65(d, J= 7.5Hz, 1H), 7.27~7.41(m, 6H), 7.05(d, J=8Hz, 1H), 6.89(t, 1H), 4.62(t, J=0.5Hz, 1H), 4.39(t, J=0.5Hz, 1H), 4.13(t, J=0.5Hz, 1H), 3.09~3.13(dd, J= 6Hz, 6Hz, 1H), 2.80~2.84(dd, J=7.5Hz, 8Hz, 1H). ^{13}CNMR(125MHz, $CDCl_3$, 27°C) 165.1, 159.6, 137.2, 133.1, 129.4, 128.9, 128.3, 127.7, 126.4, 118.3, 116.4, 110.3, 70.8, 66.4, 41.5. IR (KBr): 3063, 3030, 2903, 1640, 1617, 1584, 1491, 1455, 1420, 1366, 1311, 1259, 1232, 1206, 1156, 1129, 1070, 1034, 951, 905, 831, 794, 757, 699, 685, 667, 562, 534, 513; HRMS(EI):m/z (%): calcd for $C_{16}H_{15}NO_2$: 253.1103; found: 253.1107.

Preparation of the Intermediates 7a-7d

1.06g of dry $ZnCl_2$ (7.8mmol), 2-aminobenzonitrile 5.0g(42.3mmol) and L-amino alcohol (60.0mmol) were added under free-water and free-oxygen conditions in a dry 100mL Schlenk flask. They were dissolved in 80mL of dry chlorobenzene; the reaction mixture was refluxed for 72h. The solvent was removed under reduced pressure and the residue was dissolved in 15mL H_2O, extracted with 10x3 mL of dichloromethane. The solvent was removed under vacuum, giving the crude red oil. Further purification was performed by silica gel. (petroleum ether/ dichlormethane 4/1.

Preparation of (S)-2-(4-isobutyl-4,5-dihydrooxazol-2-yl) aniline

Yellow crystals, m.p.: 34~36ºC, yield: 76% $[a]^{20}_D$= -17.26º (c= 2.17, $CHCl_3$) : ^{1}HNMR (500MHz, $CDCl_3$, 27°C), δ (ppm) = 7.73~7.76(dd, J=2Hz, 2.5Hz, 1H), 7.20~7.26 (m, 1H), 6.67~6.73(m, 2H), 6.15(s, 2H), 4.39~4.44(m, 2H), 3.89~3.94(m, 1H), 1.89~1.93(m, 1H), 1.65~1.72(m, 1H), 1.41~1.48(m, 1H), 1.02~1.05(m, 6H).

Preparation of (S)-2-(4-isopropyl-4,5-dihydrooxazol-2-yl)aniline

Colorless crystals, m.p.: 38~40°C, yield: 80% $[a]^{5}_D$= -11.88º (c=1.09, $CHCl_3$): ^{1}HNMR (500MHz, $CDCl_3$, 27°C), δ (ppm) = 7.66(d, J= 8Hz, 1H), 7.18(t, J=0.5Hz, 1H), 6.62~6.69(m, 2H), 6.12(s, 2H), 4.30(t, J=0.5Hz, 1H), 4.08~4.10(m, 1H), 3.98(m, 1H), 1.75~1.79 (m, 1H), 0.92~1.02(dd, J=7Hz, 6.5Hz, 6H).

Preparation of (S)-2-(4-phenyll-4,5-dihydrooxazol-2-yl))aniline

Colorless crystals, m.p.: 37~39ºC, yield: 79% $[a]^{20}_D$= +195.8º (c=0.25, $CHCl_3$): ^{1}HNMR (500MHz, $CDCl_3$, 27°C), δ (ppm) = 7.85(d, J= 5.5Hz, 1H), 7.29~7.43(m, 6H), 6.76(d, J=6Hz, 2H), 6.22(s, 2H), 5.51(t, 1H), 4.74(t, J=1Hz, 1H), 4.19(t, J=0.5Hz, 1H).

Preparation of (S)-2-(4-benzyl-4,5-dihydrooxazol-2-yl))aniline

Colorless crystals, m.p.: 40~42ºC, yield: 73% $[a]^{20}_D$= +25.12º (c=1.29, $CHCl_3$): ^{1}HNMR (400MHz, $CDCl_3$, 27°C), δ (ppm) =7.66~7.68 (dd, J=1.6 Hz, 1.6Hz, 1H), 7.18~7.30(m, 6H), 6.62~6.68(m, 2H), 6.08(s, 2H), 4.56~4.61 (m, 1H), 4.25(t, 1H), 3.98~4.02(m, 1H), 3.08~3.14(dd, J=6.2Hz, 6.2Hz, 1H), 2.72~2.78(dd, J=8Hz, 8Hz, 1H).

Preparation of 8a-8d

1.06g of dry $ZnCl_2$ (7.8mmol), 2-aminobenzonitrile 5.0g (42.3mmol) and D-amino alcohol (60.0mmol) were added under free-water and free-oxygen conditions in a dry 100mL Schlenk flask. They were dissolved in 80mL of dry chlorobenzene; the reaction mixture was refluxed for 72h. The solvent was removed under reduced pressure and the residue was dissolved in 15mL H_2O, extracted with 10x3 mL of dichloromethane. the solvent was removed under vacuum, giving the crude red oil. Further purification was performed by silica gel. (petroleum ether/ dichlormethane 4/1).

Preparation of (R)-2-(4-isobutyl-4,5-dihydrooxazol-2-yl))aniline

Yellow crystals, m.p.: 34~36ºC, yield: 60%; $[a]^{20}_D$=+18.01º (c= 3.04, $CHCl_3$): ^{1}HNMR (500MHz, $CDCl_3$, 27°C), δ (ppm) = 7.70(d, J=7.5Hz, 1H), 7.20(t, 1H), 6.65~6.70(m, 1H), 6.13(s, 2H), 4.38(t, J=7Hz, 2H), 3.85(s, 1H), 1.85~1.88(m, 1H), 1.63~1.68(m 1H), 1.36~1.42(m 1H), 1.36~1.42(m 1H), 0.98~1,01(m, 6H). ^{13}CNMR (125MHz, $CDCl_3$, 27°C) 163.0, 148.2, 131.5, 129.4, 128.2, 115.6, 115.3, 70.1, 64.8, 45.4, 25.3, 22.6, 22.3.

Preparation of (R)-2-(4-isopropyl-4,5-dihydrooxazol-2-yl))aniline

Colorless crystals, m.p.: 38~40ºC, yield: 60%; $[a]^{20}_D$=+12.15º (c=1.18, $CHCl_3$): ^{1}HNMR (500MHz, $CDCl_3$, 27°C), δ (ppm) = 7.66 (d, J=7.5Hz, 1H), 7.18(t, 1H), 6.63~6.69(m, 2H), 6.12(s, 2H), 4.31(t, J=0.5Hz, 1H), 4.08~4.10(m, 1H), 3.98~4.01(m, 1H), 1.75~1.79(m, 1H), 0.92~1,02 (dd, J=8.5Hz, 8.5Hz, 6H).

Preparation of (R)-2-(4-phenyl-4,5-dihydrooxazol-2-yl) aniline

Colorless crystals, m.p.: 37~39ºC, yield : 58%; $[a]^{20}_D$=-194.6º (c=0.38, $CHCl_3$)

^{1}HNMR (500MHz, $CDCl_3$, 27°C), δ (ppm) = 7.78 (d, J=9.0Hz, 1H), 7.23~7.38(m, 6H), 6.69~6.72(m, 2H), 6.16(s, 2H), 5.45(t, 1H), 4.69(t, J=5Hz, 1H), 4.13(t, 1H).

^{13}CNMR (125MHz, $CDCl_3$, 27°C) 164.6, 146.2, 142.1, 129.0 (x2), 128.4(x2), 118.1(x2), 117.8, 114.3, 74.5, 69.6.

Preparation of (R)-2-(4-benzyl-4,5-dihydrooxazol-2-yl))aniline

Colorless crystals, m.p.: 40~42ºC, yield: 61%; $[a]^{20}_D$=-26.02º (c=1.34, $CHCl_3$): ^{1}HNMR (500MHz, $CDCl_3$, 27°C), δ (ppm) = 7.67 (d, J=8.0Hz, 1H), 7.19~7.33(m, 6H), 6.64~6.71(m, 2H), 6.10(s, 2H), 4.59~4.62(m, 1H), 4.27(t, J=0.5Hz, 1H), 4.02(t, J=0.5Hz, 1H), 3.11~3.15(dd, J=6Hz, 6Hz, 1H), 2.74~2.79 (dd, J=8Hz, 8Hz, 1H).

^{13}CNMR (125MHz, $CDCl_3$, 27°C) 163.7, 148.4, 138.1, 131.8 (x2), 129.3(x2), 128.9, 128.2, 126.1, 115.7, 115.4, 108.6, 69.9, 67.8, 42.0.

Preparation of 9a-9d

Compound 5 (9.17mmol) and triethylamine 20mL were added under free-water and free-oxygen conditions in a dry 100mL Schlenk flask. They were dissolved in 30mL of dry toluene, and then diphenylphosphinic chloride (8.50mmol) was added dropwise. The reaction mixture was refluxed for 72h. The solvent was removed under reduced pressure, giving the crude red oil. Further purification was performed by silica gel. (petroleum ether/ dichlormethane 1/9).

Preparation of (S)-2-(4-isobutyl-4, 5-dihydrooxazol-2-yl)phenyl diphenylphosphinate

Colorless crystals, yield%: 69%, m.p.32~34°C; $[a]^{20}_D$= -17.68º (c=0.27, $CHCl_3$):

^{1}HNMR (500MHz, $CDCl_3$, 27°C), δ (ppm) = 8.05~8.07 (m, 4H), 7.75 (d, J=8.0Hz, 1H), 7.66(d, J=8.5Hz, 1H), 7.41~7.42(m, 6H), 7.26~7.31(m, 1H), 7.08(t, J=0.5Hz, 1H), 4.39~4.47(m, 2H), 3.90 (t, 1H), 1.87~1.90 (m, 1H), 1.73~1.76(m, 1H), 1.40~1.43(m, 1H), 0.97~1.02(dd, J=6.5Hz, 6.5Hz, 6H). ^{13}CNMR(125MHz, $CDCl_3$, 27°C) 161.0, 150.0(x2), 132.3(x2), 132.1(x2), 131.3(x2), 128.5(x2), 128.4(x2), 124.2(x2), 121.7, 120.2, 118.6, 116.7, 72.5, 65.6, 45.7, 25.5, 23.0, 22.7. ^{31}PNMR(121.5MHz, $CDCl_3$, 27°C): δ (ppm) = 27.462, IR (KBr): 2970, 2917, 2849, 2251, 1679, 1612, 1588, 1462, 1440, 1390, 1313, 1273, 1221, 1124, 1063, 1031, 789, 733, 691, 649, 621, 592, 570, 528; HRMS(EI):m/z (%): calcd for $C_{25}H_{26}NO_3P$: 419.1650; found: 419.1659.

Preparation of (S)-2-(4-isopropyl-4,5-dihydrooxazol-2-yl)phenyl diphenylphosphinate

Light yellow liquid, yield%: 64%, $[a]^{20}_D$= -20.27º (c=0.28, $CHCl_3$) :

^{1}HNMR (500MHz, $CDCl_3$, 27°C) δ (ppm) = 7.61~7.68(m, 5H), 7.24~7.36(m, 7H), 6.98(d, J=8.5, 1H), 6.84(t, 1H), 4.38~4.43(m, 1H), 4.08~4.14 (m, 2H), 1.76~1.82(m, 1H), 0.92~1.00(dd, J=7Hz, 6.5Hz, 6H). ^{13}CNMR(125MHz, $CDCl_3$, 27°C) 165.2, 160.1(x2), 133.3(x2), 131.4(x2), 131.3(x2), 128.3(x2), 128.1(x2), 128.1(x2), 118.6(x2), 116.8(x2), 71.6, 69.9, 33.1, 18.8, 18.7.. ^{31}PNMR(121.5MHz, $CDCl_3$, 27°C) δ (ppm) = 23.180. IR (KBr): 3057, 2959, 2926, 2872, 2250, 1676, 1644, 1618, 1583, 1555, 1492, 1464, 1438, 1364, 1438, 1364, 1309, 1260, 1233, 1201, 1155, 1094, 1069, 1035, 999, 959, 911, 859, 830, 800, 755, 728; HRMS(EI):m/z (%): calcd for $C_{24}H_{24}NO_3P$: 405.1494; found: 405.1502.

Preparation of (S)-2-(4-phenyl-4,5-dihydrooxazol-2-yl)phenyldi-phenylphosphinate

Light yellow liquid, yield%: 59%, $[a]^{20}_D$= +19.38º (c=0.05, $CHCl_3$):

^{1}HNMR(500MHz, $CDCl_3$, 27°C) δ (ppm) = 8.00~8.07(m, 3H), 7.88(d, J=7.5Hz, 1H), 7.72(d, J=8.5Hz, 2H), 7.24~7.46(m, 12H), 7.12(t, 1H), 5.46 (t, J=1.5Hz, 1H), 4.74~4.77 (m, 1H), 4.25(t, J=0.5Hz, 1H). ^{13}CNMR(125MHz, $CDCl_3$, 27°C) 166.4, 160.2(x2), 141.7(x2), 133.7(x2), 131.4(x2), 131.3(x2), 128.9(x2), 128.3(x2), 128.2(x2), 128.0(x2), 126.6(x2), 118.8(x2), 117.0(x2), 74.12, 69.0. ^{31}PNMR(121.5MHz, $CDCl_3$, 27°C), δ (ppm)=25.560. IR (KBr): 3064, 3033, 2956, 2924, 2854, 2250, 1684, 1643, 1612, 1590, 1537, 1495, 1479, 1461, 1440, 1378, 1304, 1274, 1249, 1221, 1138, 1156, 1126, 1070, 1030, 909,793, 754, 734, 698, 648, 626, 557, 527.; HRMS(EI):m/z (%): calcd for $C_{27}H_{22}NO_3P$: 439.1337; found: 439.1344.

Preparation of (S)-2-(4-benzyl-4,5-dihydrooxazol-2-yl)phenyldi-phenylphosphinate

Light yellow liquid, yield%: 58%, $[a]^{20}_D$= +14.04º (c=0.14, $CHCl_3$):

^{1}HNMR (500MHz, $CDCl_3$, 27°C) δ (ppm) = 7.61~7.70(m, 5H), 7.23~7.38(m, 11H), 7.02(d, J=8Hz, 1H), 6.86(t, J=0.5Hz, 2H), 4.60~4.64(m, 1H), 4.40(t, J=0.5Hz, 1H), 4.14(t, J=0.5Hz, 1H), 3.09~3.13(dd, J=6, 6.5Hz, 1H), 2.80~2.84(dd, J=7.5, 8Hz, 1H), ^{13}CNMR(125MHz, $CDCl_3$, 27°C) 165.6, 160.0(x2), 137.6(x2), 133.5(x2), 131.3(x2), 131.2(x2), 129.3(x2), 128.7(x2), 128.3(x2), 128.1(x2), 126.8(x2), 118.7(x2), 116.8(x2), 71.3, 66.8, 42.0. ^{31}PNMR (121.5MHz, $CDCl_3$, 27°C), δ (ppm)=23.205. IR (KBr): 3061, 3028, 2955, 2924, 2854, 2249, 1642, 1617, 1492, 1438, 1367, 1311, 1259, 1234, 1156, 1129, 1067, 960, 756, 727, 698; HRMS(EI): m/z (%): calcd for $C_{28}H_{24}NO_3P$: 453.1494; found: 453.149.

Preparation of 10a-10d

Compound 5 (9.17mmol) and triethylamine 20mL were added under free-water and free-oxygen conditions in a dry 100mL Schlenk flask. They were dissolved in 30mL of dry toluene, and then phenylphosphonic dichloride (4.50mmol) was added dropwise. The reaction mixture was refluxed for 72h. The solvent was removed under reduced pressure, giving the crude red oil. Further purification was performed by silica gel. (petroleum ether/ dichlormethane 1/9).

Preparation of 3-((S)-1-chloro-4-methylpentan-2-yl)-2-phenyl-3-hydrobenzo[e][1,3,2]oxazaphosphinin-4-one-oxide

Light yellow liquid, yield%: 46%, $[a]^{20}_D$= +50.7º (c=0.18, $CHCl_3$):

^{1}HNMR (500MHz, $CDCl_3$, 27°C), δ (ppm) = 8.15~8.18 (dd, J=3, 3Hz, 1H), 7.75~7.82 (m, 2H), 7.56~7.62(m, 2H), 7.43~7.50(m, 2H), 7.30~7.35(m, 1H), 7.11(d, J=13.5Hz, 1H), 4.06~4.12(m, 2H), 3.76~3.82(m, 1H), 1.55~1.94(m, 3H), 0.94(d, J=11Hz, 6H), ^{13}CNMR (125MHz, $CDCl_3$, 27°C) 163.1, 150.7, 150.6, 135.7, 134.0, 131.9, 130.3, 128.9, 128.8, 125.0, 118.7, 118.6, 118.2, 56.6, 45.8, 39.7, 25.2, 22.4, 22.3. ^{31}PNMR(121.5MHz, $CDCl_3$, 27°C): δ (ppm)=12.259, IR (KBr): 3440, 3070, 3049, 3024, 2250, 1591, 1487, 1429, 1187, 1119, 1103, 1028, 997, 741, 717, 698, 528, 510, 493; HRMS(EI):m/z (%): calcd for $C_{19}H_{21}NO_3PCl$: 377.0948; found:377.0945.

Preparation of 3-((S)-1-chloro-3-methylbutan-2-yl)-2-phenyl-3-hydrobenzo[e][1,3,2]oxazaphosphinin-4-one-2-oxide

Light yellow liquid, yield%: 59%, $[a]^{20}_D$= +28.3º (c=0.16, $CHCl_3$):

^{1}HNMR (500MHz, $CDCl_3$, 27°C) δ (ppm) = 8.13 (d, J=7Hz, 1H), 7.72~7.76 (m, 2H), 7.54~7.58(m, 2H), 7.26~7.41(m, 3H), 7.12(d, J= 8Hz, 1H), 4.28(s, 1H), 3.78~3.80(m, 2H), 2.54(s, 1H), 1.05 (m, 6H). ^{13}CNMR(125MHz, $CDCl_3$, 27°C) 163.12, 150.77, 150.70, 135.76, 133.72, 131.89, 130.26, 128.72, 128.57, 124.98(x2), 118.71, 118.62, 65.94, 44.62, 29.85, 20.82, 20.60. ^{31}PNMR(121.5MHz, $CDCl_3$, 27°C) δ (ppm)=14.066. IR (KBr): 2970, 2917, 2849, 2251, 1679, 1612, 1568, 1462, 1440, 1390, 1313, 1273, 1221, 1124, 1063, 1031, 908, 789, 733, 691, 649, 621, 570, 528; HRMS(EI): m/z (%): calcd for $C_{18}H_{19}NO_3PCl$: 363.0791; found: 363.0793.

Preparation of 3-((S)-2-chloro-1-phenylethyl)-2-phenyl-3-hydrobenzo[e][1,3,2]oxazaphosphinin-4-one-2-oxide

Colorless crystals, yield%: 62%, m.p.: 38~40 ºC; $[a]^{20}_D$= -57.05º (c=0.19, $CHCl_3$):

^{1}HNMR (500MHz, $CDCl_3$, 27°C) δ (ppm) =8.10(d, J=6.5Hz, 1H), 7.53~7.65(m, 4H), 7.08~7.28(m, 9H), 5.24~5.26(m, 1H), 4.54~4.58(m, 1H), 4.34~4.38(m, 1H). ^{13}CNMR(125MHz, $CDCl_3$, 27°C) 162.8, 150.4(x2), 136.2, 135.8, 133.9, 132.3, 132.2, 130.3(x2), 129.0(x2), 128.9, 128.7, 128.5, 128.3, 125.0, 118.8, 118.7, 61.8, 43.7. ^{31}PNMR(121.5MHz, $CDCl_3$, 27°C), δ (ppm)=18.338. IR (KBr): 3064, 3033, 2956, 2924, 2854, 2250, 1684, 1643, 1612, 1590, 1537, 1495, 1479, 1461, 1440, 1378, 1304, 1274, 1249, 1221, 1138, 1156, 1126, 1070, 1030, 909,793, 754, 734, 698, 648, 626, 557, 527; HRMS(EI):m+1/z (%): calcd for $C_{21}H_{18}NO_3PCl$: 398.0713; found: 398.0710.

Preparation of 3-((S)-1-chloro-3-phenylpropan-2-yl)-2-phenyl-3-hydrobenzo[e][1,3,2]oxazaphosphinin-4-one-2-oxide

Light yellow liquid, yield%: 51%, $[a]^{20}_D$= -26.5º (c=0.053, $CHCl_3$):

^{1}HNMR (500MHz, $CDCl_3$, 27°C) δ (ppm) = 8.18~8.22(dd, J=3, 2.5Hz, 1H), 7.75~7.80(m, 2H), 7.56~7.60(m, 2H), 7.11~7.44(m, 9H), 4.42(t, J=2.5Hz, 2H), 3.60~3.64(m, 1H), 3.38~3.42 (m, 2H). ^{13}CNMR(125MHz, $CDCl_3$, 27°C) 163.1, 150.7, 150.6, 137.2, 135.7, 134.0, 132.3, 132.2, 130.2, 129.3, 129.2, 128.9, 128.8, 128.7, 127.0, 125.0, 118.8, 118.7, 59.8, 44.0, 38.1, 29.8. ^{31}PNMR(121.5MHz, $CDCl_3$, 27°C), δ (ppm)=13.076. IR (KBr): 3028, 2918, 2849, 2248, 1679, 1642, 1612, 1586, 1479, 1461, 1440, 1304, 1156, 1126, 1092, 1030, 978, 926, 844, 789, 730, 690, 648, 626, 594, 551, 480; HRMS(EI):m+1/z (%): calcd for $C_{22}H_{20}NO_3PCl$: 412.0871; found: 412.0869.

Preparation of 11a-11d

Compound 6 (10.95mmol) and triethylamine 20mL were added under free-water and free-oxygen conditions in a dry 100mL Schlenk flask. They were dissolved in 30mL of dry toluene, and then diphenylphosphonic dichloride (3.48mmol) was added dropwise. The reaction mixture was refluxed for 72h. The solvent was

removed under reduced pressure, giving the crude red oil. Further purification was performed by silica gel. (petroleum ether/ dichlormethane 1/9).

Preparation of 3-((R)-1-chloro-4-methylpentan-2-yl)-2-phenyl-3-hydrobenzo[e][1,3,2]oxazaphosphinin-4-one-2-oxide

Light yellow liquid, yield: 65%; $[a]^{20}_D$= -24.3º (c=0.21, $CHCl_3$):

^{1}HNMR (500MHz, $CDCl_3$, 27°C), δ (ppm) = 8.14~8.17 (dd, J=2.5Hz, 2.5Hz, 1H), 7.75~7.82 (m, 2H), 7.74~7.81(m, 2H), 7.56~7.62(m, 2H), 7.27~7.32 (m, 1H), 7.10(d, J=13.5Hz, 1H), 4.06~4.12(m, 2H), 3.75~3.81(m, 1H), 1.73~1.75(m, 3H), 0.94(d, J=11Hz, 6H), ^{13}CNMR(125MHz, $CDCl_3$, 27°C) 163.1, 150.6, 135.7, 134.0, 133.9, 130.3, 129.0, 128.7, 125.0, 118.7, 118.6, 118.2, 56.6, 44.6, 39.7, 29.7, 25.2, 22.4, 22.3. ^{31}PNMR(121.5MHz, $CDCl_3$, 27°C): δ (ppm)=15.421, IR (KBr): 3062, 2958, 2927, 2870, 1725, 1682, 1642, 1612, 1586,1479,1461,1439,1387, 1306, 1250, 1216, 1154, 1126, 1097, 1068, 1030, 999, 926, 790, 755, 722, 692, 620, 613, 582,556, 508. HRMS(EI):m/z (%): calcd for $C_{19}H_{21}NO_3PCl$: 377.0948; found: 377.0937.

Preparation of 3-((R)-2-chloro-1-phenylethyl)-2-phenyl-3-hydrobenzo[e][1,3,2] oxazaphosphinin-4-one-2-oxide

Colorless crystals, m.p.: 38~40 ºC, yield: 48%; $[a]^{20}_D$= -58.9º (c=0.132, $CHCl_3$):

^{1}HNMR (500MHz, $CDCl_3$, 27°C) δ (ppm) = 8.14 (d, J=7.5Hz, 1H), 7.03~7.55 (m, 13 H), 5.95(s, 1H), 4.40~4.45(m, 2H); ^{13}CNMR(125MHz, $CDCl_3$, 27°C) 162.6, 150.2(x2), 135.5(x2), 132.8(x2), 130.6(x2), 130.2(x2), 129.1(x2), 128.2, 128.1, 127.9, 124.6, 118.3, 118.2, 57.8, 43.4. ^{31}PNMR(121.5MHz, $CDCl_3$, 27°C) δ (ppm)=16.040. IR (KBr): 3063,2966,2924, 2248, 1682, 1641, 1612, 1588, 1496, 1479, 1439, 1304, 1249, 1220, 1155, 1126, 1072, 1030, 928,791, 753, 724,691, 608, 587, 575, 555, 523; HRMS(EI): m/z (%): calcd for $C_{21}H_{17}NO_3P$（M- Cl): 362.0946; found: 362.0928.

Preparation of 3-((R)-1-chloro-3-phenylpropan-2-yl)-2-phenyl-3-hydroben-zo[e] [1,3,2]oxazaphosphinin-4-one-2-oxide

Light yellow liquid, yield: 55%, $[a]^{20}_D$= +24.5º (c=0.269, $CHCl_3$):

^{1}HNMR (500MHz, $CDCl_3$, 27°C) δ (ppm) = 8.15~8.18(dd, J=2.5, 2.5Hz, 1H), 7.50~7.57(m, 3H), 7.10~7.37(m, 5H), 7.07~7.10(m, 3H), 6.83(d, J= 9.5Hz, 2H), 4.16~4.31(m, 1H), 3.90~3.96 (m, 1H). 3.33(d, J=12.5Hz, 2H); ^{13}CNMR(125MHz, $CDCl_3$, 27°C) 162.9, 150.6, 137.1, 135.7, 133.7(x2), 132.2, 132.0, 130.1, 129.2, 129.1, 129.0, 128.9, 128.7, 128.6, 126.7, 125.0, 118.7, 118.6, 60.3, 43.8, 36.8. ^{31}PNMR(121.5MHz, $CDCl_3$, 27°C), δ (ppm)=16.515,IR (KBr) : 3338, 3062, 3027, 2965, 2929, 2248, 1641, 1679, 1611,1590, 1479, 1461, 1440, 1304, 1155, 1126, 1090, 1031, 976, 930, 873, 789, 753, 691, 622, 594, 593, 553, 529, 485; HRMS(EI):m+1/z (%): calcd for $C_{22}H_{20}NO_3PCl$: 412.0871; found: 412.0869.

Preparation of 12a-12d

Compound 7 (9.17mmol) and triethylamine 20mL were added under free-water and free-oxygen conditions in a dry 100mL Schlenk flask. They were dissolved in 30mL of dry toluene, and then phenylphosphonic dichloride (8.50mmol) was added dropwise. The reaction mixture was refluxed for 72h. The solvent was removed under reduced pressure, giving the crude red oil. Further purification was performed by silica gel. (petroleum ether/ dichlormethane 1/9).

Preparation of ((S)-N-(2-(4-isobutyl-4,5-dihydrooxazol-2-yl) phenyl)-P,P-diphenylphosphinic amide

Light yellow liquid, m.p.: 68-70°C; yield: 80% $[a]^{20}_D$= +11.16º (c=0.089, $CHCl_3$):

^{1}HNMR (500MHz, $CDCl_3$, 27°C), δ (ppm) = 11.00 (d, J=21.5Hz, 1H), 7.83~7.91 (m, 4H), 7.76(d, J= 13Hz, 1H), 7.28~7.52(m, 6H), 7.11~7.16(m, 2H), 6.80~.86(m, 1H), 4.31~4.43(m, 1H), 4.21~4.22(m, 1H), 3.83(t, 1H), 1.23~1.46(m, 3H), 0.72~0.76(dd, J=6.5, 6.5Hz, 6H). ^{13}CNMR(125MHz, $CDCl_3$, 27°C) 163.9, 143.3, 132.2, 132.0(x2), 131.9, 131.8(x2), 131.7(x2), 129.4(x2), 128.8(x2), 128.6(x2), 119.9, 118.3, 118.3, 71.9, 64.7, 45.8, 25.2, 23.4, 22.0. ^{13}PNMR(121.5MHz, $CDCl_3$, 27°C): δ (ppm)=14.818, IR (KBr): 3058, 2956, 2925, 2869, 2248, 1634, 1602, 1583, 1504, 1486, 1438, 1363, 1308, 1259, 1213, 1123, 1109, 1061, 938, 752; HRMS(EI):m/z (%): calcd for $C_{25}H_{27}N_2O_2P$: 418.1810; found: 418.1806.

Preparation of ((S)-N-(2-(4-isopropyl-4,5-dihydrooxazol-2-yl)phenyl)-P,P-diphenylphosphinic amide

Light yellow liquid, yield: 82% $[a]^{20}_D$= -11.8º (c=0.67, $CHCl_3$):

^{1}HNMR (500MHz, $CDCl_3$, 27°C) δ (ppm) = 11.02 (d, J = 13.5Hz, 1H), 7.73~7.89 (m, 5H), 7.10~7.46(m, 7H), 7.12(t, J= 0.5Hz, 1H), 6.80 (t, 1H), 4.29~4.32(m, 1H), 3.92~3.96 (m, 2H), 1.55~1.58(m, 1H), 0.66~0.74(dd, J=6.5Hz, 6.5Hz, 6H). ^{13}CNMR(125MHz, $CDCl_3$, 27°C) 163.9, 143.3, 133.2(x2), 132.1, 131.9(x2), 131.7(x2), 129.4(x2), 128.7(x2), 128.6(x2), 119.8(x2), 118.2(x2), 72.7, 69.4, 33.0, 18.9, 18.4. ^{31}PNMR(121.5MHz, $CDCl_3$, 27°C), δ (ppm)=14.846. IR (KBr): 3028, 2918, 2849, 2248, 1679, 1642, 1612, 1586, 1479, 1461, 1440, 1304, 1156, 1126, 1092, 1030, 978, 926, 844, 789, 730, 690, 648, 626, 594, 551, 480; HRMS(EI):m/z (%): calcd for $C_{24}H_{25}N_2O_2P$:404.1654 ; found: 404.1657.

Preparation of ((S)-P,P-diphenyl-N-(2-(4-phenyl-4,5-dihydro-oxazol-2-yl)phenyl)phosphinic amide

Light yellow liquid, yield: 75% $[a]^{20}_D$= +62.5º (c=0.14, $CHCl_3$):

^{1}HNMR (500MHz, $CDCl_3$, 27°C) δ (ppm) =11.03(d, J=13Hz, 1H), 7.70~7.82(m, 5H), 7.16~7.40(m, 13H), 6.86(t, 1H), 5.35(t, J=0.5Hz, 1H), 4.72(t, J=0.5Hz, 1H), 4.21(t, J=0.5Hz, 1H). ^{13}CNMR(125MHz, $CDCl_3$, 27°C) 165.1, 143.4, 141.8, 132.7, 131.9(x2), 131.8(x2), 131.7, 131.6, 131.5(x2), 129.6(x2), 128.8(x2), 128.7(x2), 128.6(x2), 127.8, 126.6, 120.0, 118.4, 118.3, 73.2, 69.8. ^{31}PNMR(121.5MHz, $CDCl_3$, 27℃), δ (ppm)=14.756. IR (KBr): 3404, 3059, 2957, 2924, 2853, 2250, 1632, 1601, 1583, 1501, 1455, 1438, 1361, 1304, 1267, 1212, 1163, 1123, 1108, 1064, 1046, 938, 793, 752, 698, 611, 546, 533, 522; HRMS(EI):m/z (%): calcd for $C_{27}H_{23}N_2O_2P$: 438.1497; found: 438.1494.

Preparation of ((S)-P,P-diphenyl-N-(2-(4-benzyl-4,5-dihydro-oxazol-2-yl)phenyl)phosphinic amide

Light yellow liquid, yield: 63% $[a]^{20}_D$= +45.73º (c=0.066, $CHCl_3$):

^{1}HNMR (500MHz, $CDCl_3$, 27°C) δ (ppm) = 11.01(d, J=13Hz, 1H), 7.86~7.90(m, 3H), 7.74(d, J=7.5Hz, 1H), 7.12~7.50(m, 13H), 6.86(t, 1H), 4.60(t, J=0.5Hz, 2H), 4.27~4.33(m, 1H), 4.02~4.08(m, 1H), 2.99~3.02(dd, J=5.5, 6Hz, 1H), 2.70~2.75(dd, J=8.5, 8Hz, 1H) ^{13}CNMR(125MHz, $CDCl_3$, 27°C) 164.5, 143.3(x2), 137.5(x2), 132.5, 132.0(x2), 131.8(x2), 131.7(x2), 131.6(x2), 129.5(x2), 129.2, 128.8, 128.7, 126.7(x2), 120.0(x2), 118.4, 118.3, 70.6, 67.6, 42.0. ^{31}PNMR(121.5MHz, $CDCl_3$, 27°C), δ (ppm)=14.787. IR (KBr): 3370, 3059, 3026, 2956, 2923, 2852, 2249, 1633, 1602, 1583, 1502, 1438, 1454, 1363, 1308, 1268, 1203, 1123, 1108, 1061, 941, 751, 725, 698; HRMS(EI):m/z (%): calcd for $C_{28}H_{25}N_2O_2P$:452.1654 ; found: 452.1650.

Preparation of 13a-13d

Compound 7 (6.42mmol) and triethylamine 20mL were added under free-water and free-oxygen conditions in a dry 100mL Schlenk flask. They were dissolved in 30mL of dry toluene, and

then phenyl phosphine dichloride (3.00mmol) was added dropwise. The reaction mixture was refluxed for 72h. The solvent was removed under reduced pressure, giving the crude red oil. Further purification was performed by silica gel. (petroleum ether/ dichlormethane 1/9).

Preparation of N, N'-bis[2-[(4S)-4, 5-dihydro-4-(isobutyl)-2-oxazolyl]phenyl]-P-phenyl phosphonic diamide

Light yellow liquid, yield: 82% $[a]^{20}_D$= -3.6º (c=0.208, CH_2Cl_2):

^{1}HNMR (500MHz, $CDCl_3$, 27°C), δ (ppm) = 10.90~10.98(dd, J=12, 13.5Hz, 2H), 7.96~7.99 (m, 2H), 7.64~7.72(m, 3H), 7.43~7.52(m, 4H), 7.24~7.26(m, 2H), 6.84~6.86(m, 2H), 4.21~4.37(m, 4H), 3.77~3.79(m, 2H), 1.23~1.32(m, 2H), 1.12~1.16(m, 4H), 0.66~0.72(m, 12H). ^{13}CNMR (125MHz, $CDCl_3$, 27°C) 163.6(x2), 143.4, 143.2, 132.3(x2), 132.1, 132.0(x2), 131.8, 131.7, 129.3(x2), 128.7, 128.6, 119.8, 119.69, 118.1, 118.0, 118.0, 71.8(x2), 64.6, 64.6, 45.7, 45.5, 25.2(x2), 23.4, 23.3, 21.9, 21.8. ^{31}PNMR(121.5MHz, $CDCl_3$, 27°C): δ (ppm)=4.907, IR (KBr) : 3076, 2958, 2925, 2869, 2251, 1636, 1583, 1501, 1466, 1438, 1385, 1365, 1309, 1258, 1216, 1162, 1139, 1122, 1162, 1061, 946, 905, 854, 809, 750, 694, 622, 537, 479; HRMS(EI):m/z (%): calcd for $C_{32}H_{39}N_4O_3P$: 558.2760; found: 558.2767.

Preparation of N,N'-bis[2-(4S)-4, 5-dihydro- 4-(2-isopropyl)-2-oxazolyl]phenyl]-P-phenyl phosphonic diamide

Colorless crystals, m.p.:38-40ºC; yield: 85% $[a]^{20}_D$= -11.8º (c=0.67, $CHCl_3$):

^{1}HNMR (500MHz, $CDCl_3$, 27°C) δ (ppm) = 11.00(d, J = 20.5Hz, 2H), 7.98~8.03(m, 2H), 7.69~7.76(m, 4H), 7.42~7.48(m, 3H), 7.24~7.26(m, 2H), 6.84~6.88 (m, 2H), 4.27~4.30(m, 2H), 3.90~3.95(m, 4H), 1.46~1.52(m, 2H), 0.61~0.72(m, 12H). ^{13}CNMR(125MHz, $CDCl_3$, 27°C) 163.9(x2), 143.3(x2), 132.1(x2), 131.9(x2), 131.7(x2), 129.4(x2), 128.7(x2), 128.6(x2), 119.8(x2), 118.2(x2), 72.7(x2), 69.4(x2), 33.0(x2), 18.9(x2), 18.4(x2). ^{31}PNMR(121.5MHz, $CDCl_3$, 27°C), δ (ppm)=4.884. IR (KBr) : 3075, 2960, 2904, 2250, 1634, 1583, 1500, 1437, 1360, 1305, 1156, 1269, 1254, 1217, 1122, 1064, 950, 897, 751, 729, 695, 621, 507; HRMS(EI):m/z (%): calcd for $C_{30}H_{35}N_4O_3P$:530.2447 ; found: 530.2444.

Preparation of N, N'-bis[2-[(4S)-4,5-dihydro-4-(phenyll)-2-oxazolyl]phenyl]-P-phenyl phosphonic diamide

Light yellow liquid, yield: 76% $[a]^{20}_D$=+72.3º (c=0.85, $CHCl_3$):

^{1}HNMR(500MHz, $CDCl_3$, 27°C) δ (ppm)=10.89(d, J=12Hz, 2H), 7.67~7.87(m, 6H), 6.88~7.26(m, 17H), 5.27(t, J = 0.5Hz, 1H), 5.08(t, J = 0.5Hz, 1H), 4.56~4.68(m, 2H), 4.00~4.10(m, 2H). ^{13}CNMR(125MHz, $CDCl_3$, 27°C) 165.0(x2), 143.5, 143.3, 141.9, 141.8, 132.7(x2), 132.1(x2), 131.5, 131.4, 129.6(x2), 128.8(x2), 128.7(x2), 128.6, 128.5, 127.6, 127.5, 126.5, 126.4, 120.0(x2), 119.9(x2), 118.4, 118.4, 118.1, 118.0, 73.1, 73.0, 69.6, 69.5. ^{31}PNMR(121.5MHz, $CDCl_3$, 27°C), δ (ppm)=5.474. IR (KBr): 3062, 2957, 2924, 2853, 2251, 1633, 1602, 1584, 1499, 1455, 1437, 1361, 1301, 1265, 1218, 1164, 1136, 1122, 1065, 1047, 954, 910, 752, 731, 697, 645, 621, 514, 475; HRMS(EI):m/z (%): calcd for $C_{36}H_{31}N_4O_3P$: 598.2134; found: 598.2131.

Preparation of N, N'-bis[2-[(4S)-4, 5-dihydro- 4-(benzyl)-2-oxazolyl]phenyl]-P-phenyl phosphonic diamide

Light yellow liquid, yield: 70% $[a]^{20}_D$= 44.63º (c=0.081, $CHCl_3$):

^{1}HNMR (500MHz, $CDCl_3$, 27°C) δ (ppm) = 10.84~10.92 (dd, J=11Hz, 12.5Hz, 2H), 7.98~8.02(m, 2H), 7.24~7.71(m, 7H), 7.04~7.21(m, 12H), 6.85~6.87(m, 2H), 4.43~4.45(m, 2H), 4.23~4.26(m, 2H), 3.97~3.98(m, 2H), 2.92~2.95(dd, J=5Hz, 5.5Hz, 1H), 2.79~2.83(dd, J=8.5Hz, 8.5Hz, 1H), 2.59~2.64(dd, J=8Hz, 8Hz, 1H), 2.47~2.52(dd, J=8.5Hz, 8.5Hz, 1H), ^{13}CNMR(125MHz, $CDCl_3$, 27°C) 164.2(x2), 143.2, 143.0, 137.7(x2), 137.5(x2), 132.5(x2), 132.3(x2), 131.6(x2), 131.5(x2), 129.4(x2), 129.1(x2), 128.7(x2), 128.6(x2), 128.6(x2), 126.6, 126.5, 120.0, 119.9, 118.1, 118.0, 70.3(x2), 67.6, 67.5, 41.6(x2).^{31}PNMR(121.5MHz, $CDCl_3$, 27°C), δ (ppm) =4.281. IR (KBr) : 3462, 3028, 2924, 2853, 2249, 1635, 1562, 1493, 1455, 1439, 1365, 1315, 1246, 1161, 1142, 1082, 1054, 971, 926, 750, 699, 540; HRMS(EI):m/z (%): calcd for $C_{38}H_{35}N_4O_3P$:626.2447 ; found: 626.2452.

Preparation of 14a-14d

Compound 8 (12.84mmol) and triethylamine 20mL were added under free-water and free-oxygen conditions in a dry 100mL Schlenk flask. They were dissolved in 40mL of dry toluene, and then phenylphosphonic dichloride 0.7mL (4.99mmol) was added dropwise. The reaction mixture was refluxed for 72h. The solvent was removed under reduced pressure, giving the crude red oil. Further purification was performed by silica gel. (petroleum ether/ dichlormethane 1/9).

Preparation of N, N'-bis[2-[(4R)-4, 5-dihydro-4-isobutyl-2-oxazolyl]phenyl]-P-phenyl phosphonic diamide

Light yellow liquid, yield: 85%; $[a]^{20}_D$= 5.10º (c=0.294, CH_2Cl_2):

^{1}HNMR (500MHz, $CDCl_3$, 27°C), δ (ppm) = 10.92~11.00(dd, J=12Hz, 13.5Hz，2H), 7.95~7.99 (m, 2H), 7.65~7.72(m, 4H), 7.41~7.52(m, 3H), 7.21~7.23(m, 2H), 6.81~6.83(m, 2H), 4.30~4.33(m, 2H), 4.10~4.19(m, 2H), 3.72~3.77(m, 2H), 1.23~1.32(m, 4H), 1.11~1.13(m, 2H), 0.63~0.70(m, 12H). ^{13}CNMR(125MHz, $CDCl_3$, 27°C) 163.3, 163.1, 142.9, 142.7, 131.8, 131.7, 131.3, 131.8, 131.3, 131.0, 129.2, 128.8, 128.1, 119.3, 119.2, 117.6, 117.4, 115.9, 112.0, 112.0, 71.3, 64.1, 64.0, 45.3, 45.2, 25.2, 24.7, 23.0, 22.8, 22.6, 22.3, 21.3. ^{31}PNMR (121.5MHz, $CDCl_3$, 27°C), δ (ppm)= 8.614, IR (KBr) : 3389, 3293, 3075, 2956, 2926, 2869, 1692, 1636, 1583, 1501, 1466, 1438, 1365, 1258, 1215, 1162, 1122, 1061, 946, 904, 854, 750, 694, 622, 538, 484; HRMS(EI):m/z (%): calcd for $C_{32}H_{39}N_4O_3P$: 558.2760; found: 558.2764.

Preparation of N, N'-bis[2-[(4R-4,5-dihydro-4-isopropyll-2-oxazolyl]phenyl]-P-phenyl phosphonic diamide

Pale yellow crystals, yield: 88%; $[a]^{20}_D$=+12.89º (c=0.0368, CH_2Cl_2):

^{1}HNMR (500MHz, $CDCl_3$, 27°C) δ (ppm) = 11.01(d, J = 13Hz, 2H), 7.97~8.01(m, 2H), 7.68~7.74(m, 4H), 7.39~7.45(m, 3H), 7.20~7.23 (m, 2H), 6.80~6.83 (m, 2H), 4.22~4.23 (m, 2H), 3.85~3.88 (m, 4H), 1.41~1.47 (m, 2H), 0.56~0.67 (m, 12H). ^{13}CNMR(125MHz, $CDCl_3$, 27°C) 163.2(x2), 142.9, 142.7, 131.9(x2), 131.9(x2), 131.3(x2), 131.2(x2), 128.8, 128.3, 128.2(x2), 119.39(x2), 117.5, 117.3, 72.1(x2), 69.1, 68.8, 32.8, 32.6, 18.6 18.3, 17.9, 17.6. ^{13}PNMR(21.5MHz, $CDCl_3$, 27°C), δ (ppm)= 8.651. IR (KBr) : 3392, 3292, 3076, 2960, 2904, 2230, 1636, 1583 1500，1437, 1360, 1305, 1156, 1269, 1251, 1217, 1122, 1064, 957, 897, 751, 730, 695, 622, 507, 475. HRMS(EI):m/z (%): calcd for $C_{30}H_{35}N_4O_3P$: 530.2447 ; found: 530.2446.

Preparation of N, N'-bis[2-[(4R)-4, 5-dihydro-4-phenyl-2-oxazolyl] phenyl]-P-phenyl phosphonic diamide

Light yellow liquid, yield: 82%; $[a]^{20}_D$=+105.73º (c=0.212, CH_2Cl_2):

^{1}HNMR(500MHz, $CDCl_3$, 27°C) δ (ppm) = 10.92(d, J= 12.5Hz, 2H), 7.69~7.89(m, 6H), 6.88~7.26(m, 17H), 5.29(t, J = 0.5Hz, 1H), 5.09 (t, J = 0.5Hz, 1H), 4.56~4.67(m, 2H), 4.00~4.10(m, 2H). ^{13}CNMR(125MHz, $CDCl_3$, 27°C) 164.5, 164.4, 143.0, 142.8, 132.2(x2), 132.0, 131.7(x2) 131.0, 131.0(x2), 130.8(x2), 129.1(x2), 128.3（x2), 128.2, 128.0, 127.1, 127.0, 126.0, 126.5, 125.9, 119.6, 119.5, 117.9, 117.5, 112.0, 112.0, 111.8, 72.7, 72.6, 69.10, 69.01.

^{13}PNMR(300MHz, $CDCl_3$, 27°C), δ (ppm)=9.299. IR (KBr) : 3466, 3393, 3292, 3061, 2917, 2233, 1813, 1634, 1582, 1499, 1454, 1438, 1363, 1307, 1256, 1216, 1163, 1135, 1122, 1059, 954, 910, 751, 730, 698, 620, 540, 490; HRMS(EI):m/z (%): calcd for $C_{36}H_{31}N_4O_3P$: 598.2134; found: 598.2132.

Preparation of N, N'- bis[2-[(4R)-4, 5-dihydro-4-benzyl-2-oxazolyl] phenyl]-P-phenyl phosphonic diamide

Light yellow liquid, yield: 80%; $[a]^{20}_D$= +53.09º (c=0.574, CH_2Cl_2):

^{1}HNMR (500MHz, $CDCl_3$, 27°C) δ (ppm) = 10.95~11.03 (dd, J=2.5Hz, 2.0Hz, 2H), 8.05~8.09(m, 2H), 7.31~7.81(m, 3H), 7.20~7.27(m, 14H), 6.67~6.73(m, 4H), 4.47~4.61(m, 2H), 4.25~4.26(m, 2H), 3.99~4.03(m, 2H), 2.54~3.16(m, 4H), ^{13}CNMR(125MHz, $CDCl_3$, 27°C) 163.8, 148.2, 142.9, 142.8, 137.9, 137.3, 137.2, 132.5, 132.4, 132.1, 131.9, 131.2, 131.1, 129.3, 129.0, 128.9, 128.8, 128.6, 128.4, 128.2, 127.9, 126.2, 126.1, 120.0, 119.6, 119.5, 117.8, 117.7, 115.8, 115.6, 112.2, 108.5, 70.0, 67.5, 67.2, 67.0, 41.8. 41.2. ^{31}PNMR (121.5MHz, $CDCl_3$, 27°C), δ (ppm)=9.200. IR(KBr) : 3466, 3395, 3297, 3062, 3030, 2965, 2899, 2244, 1633, 1562, 1498, 1455, 1438, 1362, 1302, 1266, 1212, 1163, 1123, 1064, 954, 751, 698, 606, 533. HRMS(EI):m/z (%): calcd for $C_{38}H_{35}N_4O_3P$:626.2447; found: 626.2448.

Preparation of 2-phenyl-2-((trimethylsilyl)oxy) acetonitrile

Products **9a-9d, 10a, 10c, 10d, 11a, 11c, 11d, 12(a-d)-14(a-d)** (0.15mmol) were dissolved in 2ml THF, benzaldehyde 0.12g(1 mmol) and TMSCN (25mL) at room temperature. After 6h, 8h or 19h, the reaction was quenched and the mixture was extracted with dichloromethane (3x10mL). The combined organic layers were dried over Na_2SO_4, and concentrated in vacuo. Further purification was performed by silica gel (petroleum/dichloro-methane 4/1).

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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SUPPLEMENTARY MATERIAL

Supplementary material is available on the publisher's web site along with the published article.

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