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Highly enantioselective phosphination and hydrophosphonylation of azomethine imines: using chiral squaramide as a hydrogen bonding organocatalyst†

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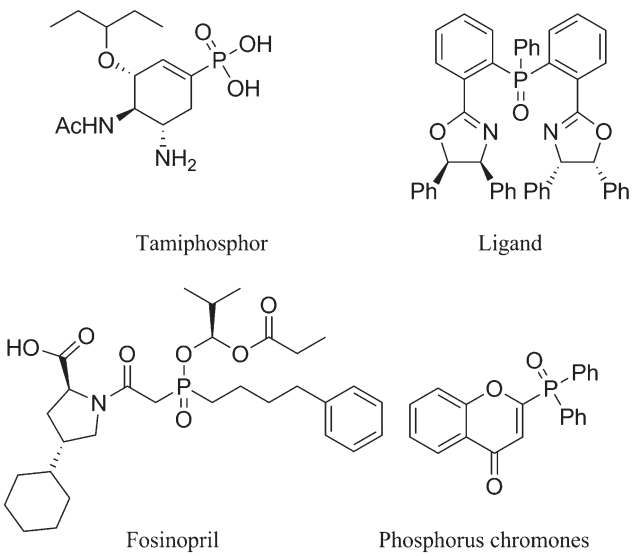
Enantioselective phosphination and hydrophosphonylation reactions between azomethine imines and diarylphosphine oxides or dialkyl phosphites were respectively developed by the use of a chiral squaramide as the hydrogen bonding organocatalyst, which afforded two types of phosphorus containing product in high yields with good to excellent enantioselectivities.

Introduction

Optically active α-amino phosphonic acid derivatives, which have found widespread uses as bioactive substances, play an important role in industrial, agricultural and pharmaceutical chemistry, and they have utility as valuable building blocks in natural product synthesis (Scheme 1).[1,2] Besides numerous reports of resolution and auxiliary-based approaches,[3] both chiral metallic complex catalysis[4] and chiral organocatalysis[4b,5] have been rapidly developed for enantioselective synthesis of optically active functionalized organophosphorus compounds. In particular, organocatalytic asymmetric carbon–phosphorus bond-forming processes have attracted considerable attention over the last few years.[6] Among them, the organocatalyzed asymmetrical conjugate additions and 1,2-addition between electron-deficient olefins,[6,7] imines[8] and phosphorus reagents have been the most straightforward and efficient methods, which have furnished enantiomerically enriched organophosphorus compounds with α- or β-functional groups.

Although azomethine imines are employed in asymmetric cycloaddition reactions as one type of 1,3-dipole,[9] they have seldom been reported as an acceptor of the nucleophilic addition. Early in 2009, enantioselective trifluoromethylation and arylation of azomethine imines were respectively reported by the Shibata[10a] and Hayashi[10b] groups. Our group recently reported an enantioselective Strecker-type reaction between azomethine imines and trimethylsilyl cyanide.[11] However, the nucleophilic addition reactions of azomethine imines with organophosphorus reagents have not been reported. Herein, we describe asymmetric phosphination and hydrophosphonylation reactions between azomethine imine and diarylphosphine oxide or dialkyl phosphite by the use of a chiral squaramide as a hydrogen bonding organocatalyst, in which the desired products were provided in high yields with good to excellent enantioselectivities.



Scheme 1 Some organophosphorus compounds.

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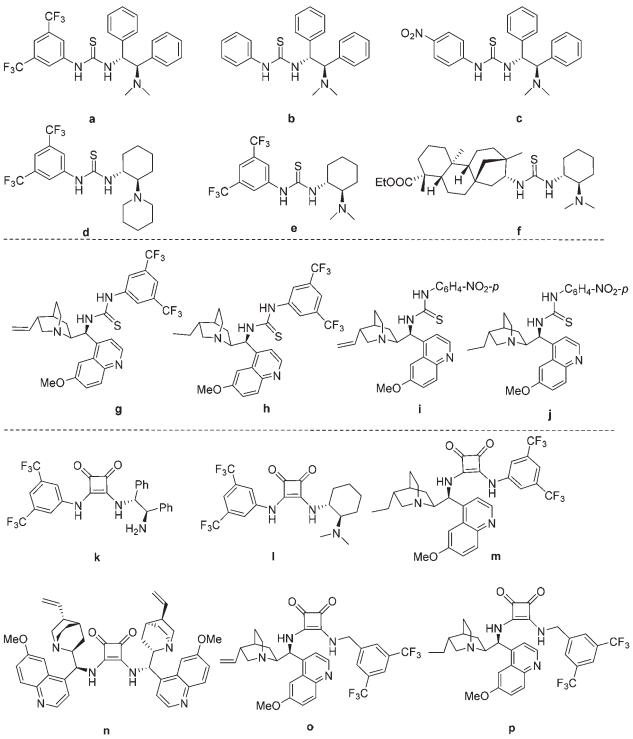
Results and discussion

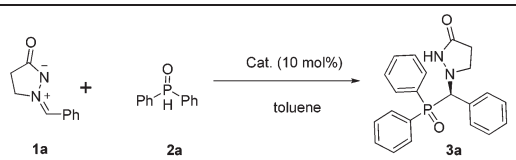
The utilization of hydrogen bonding as an activation force is widespread in organocatalysis. Chiral thioureas[12] and, more recently, chiral squaramides[13] are good hydrogen-bonding donor organocatalysts. Accordingly, our initial studies were focused on the asymmetric phosphination of azomethine imine **1a** with diphenylphosphine oxide **2a**. Preliminary screening was conducted in the presence of 10 mol% of thioureas **a–c** derived from (*R*,*R*)-1,2-diphenylethylenediamine (DPEN) in toluene at 12 °C, and only trace products were observed for all cases (Table 1, entries 1–3). Subsequently, thioureas **d–f** derived from (*R*,*R*)-1,2-cyclohexanediamine (CHDA) were tested for this transformation. The reaction smoothly gave the desired adduct **3a** in 95–99% yields with 84–90% enantioselectivities. Encouraged by these promising results, the quinine and dihydroquinine derived thioureas **g–j** were examined under otherwise identical conditions. To our delight, all the reactions provided the desired products in quantitative yields with over 90% ees (Table 1, entries 7–10). Notably, dihydroquinine derived thioureas **h** and **j** were found to be more effective catalysts, and the corresponding reactions were fully completed within four hours in both cases.

In order to compare the catalytic efficiency of chiral squaramides with that of chiral thioureas, several corresponding chiral squaramide catalysts were investigated for this transformation (Scheme 2). In comparison with squaramides **k** and **l** derived from optically pure DPEN and CHDA, the cinchona alkaloid derived squaramides **m–o** have been proven to be more effective for this reaction, which provided the desired product **3a** at over 95% yields with 80–96% ees (Table 1, entries 13–15 *vs.* entries 11–12). Gratefully, the squaramide **p** derived from dihydroquinine, the desired products **3a** was obtained in 99% yield with 95% ee in 4 hours of reaction time (Table 1, entry 16). In consideration of both the reactivity and enantioselectivity, **p** was chosen as the potent catalyst for further optimization of reaction conditions.



Scheme 2 Screened catalysts.

Table 1 Optimization of reaction catalyst



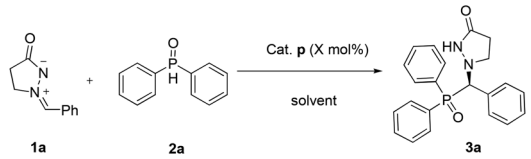
Entry[a]	Catalyst	Time (h)	Yield[b] (%)	ee[c] (%)
1	**a**	44	<10	nd[d]
2	**b**	44	<10	nd[d]
3	**c**	44	<10	nd[d]
4	**d**	40	99	−90
5	**e**	21	99	−84
6	**f**	44	95	88
7	**g**	9	99	92
8	**h**	4	99	92
9	**i**	15	99	91
10	**j**	4	99	92
11	**k**	44	80	11
12	**l**	15	99	−45
13	**m**	12	99	80
14	**n**	44	95	94
15	**o**	15	99	96
16	**p**	4	99	95

[a] Unless noted, the reaction was performed in 0.1 mmol scale and the ratio of **2a**/**1a** was 1 : 1 (temperature of 12 °C). [b] Isolated yield. [c] Determined by HPLC (AD-H). [d] Not determined.

By the use of 10 mol% of chiral squaramide **p**, the other reaction parameters, such as solvent, catalyst loading, reaction temperature and concentration, were further optimized, and the results are summarized in Table 2. Except with the highly polar and protic solvent EtOH, the addition of diphenylphosphine oxide **2a** to azomethine imine **1a** proceeded smoothly in some common solvents, such as CH_3CN, DCM, $CHCl_3$, toluene, xylene, mesitylene, Et_2O, MTBE, and THF, which furnished the desired products in over 95% yields with over 93% ees (Table 2, entry 1 *vs.* entries 2–10). After investigating the effects of reaction temperature, catalyst loading and substrate concentration, the best catalytic results (99% yield and 99% ee) were obtained in the presence of 10 mol% catalyst loading with the substrate concentration of 0.2 M at room temperature within 30 minutes of reaction time (Table 2, entry 17 *vs.* entries 11–16, 18, and 19).

Having established the optimized reaction conditions, a diverse range of azomethine imine substrates were employed to evaluate the scope of the chiral squaramide **p** catalyzed phosphination reaction. As shown in Table 3, all the reactions proceeded smoothly under the optimized conditions, affording the desired products in high chemical yields with good to excellent enantioselectivities. For the substrates **1b–1l**

Table 2 Condition optimization for the reaction of azomethine imine **1a** with diphenylphosphine oxide **2a**



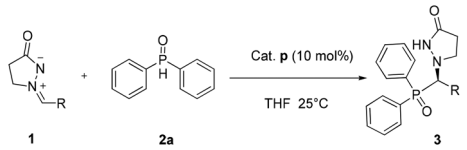
Entry[a]	Catalyst (*X* mol%)	Solvent	Time (h)	Yield[b] (%)	ee[c] (%)
1	10	EtOH	5	95	79
2	10	CH_3CN	1	99	94
3	10	DCM	5	96	94
4	10	$CHCl_3$	5	97	93
5	10	Toluene	4	99	95
6	10	Xylene	2	99	95
7	10	Mesitylene	2	98	93
8	10	Et_2O	3	97	94
9	10	MTBE	2	98	97
10	10	THF	2	99	99
11	5	THF	3	96	98
12	2.5	THF	10	94	67
13[d]	10	THF	0.75	98	98
14[e]	10	THF	0.75	97	97
15[d]	5	THF	1.5	94	62
16[e]	5	THF	1.5	90	52
17[d,f]	10	THF	0.5	99	99
18[d,g]	10	THF	0.75	99	98
19[d,h]	10	THF	1	96	96

[a] Unless noted, the reaction was performed in 0.1 mmol scale and the ratio of **2a**/**1a** was 1 : 1 in corresponding solvents (0.1 M) (temperature of 11 °C). Catalyst loading was 10 mol%. [b] Isolated yield. [c] Determined by HPLC (AD-H). [d] At 25 °C. [e] At 35 °C. [f] THF 0.2 M. [g] THF 0.067 M. [h] THF 0.05 M.

bearing halogen substituents (–F, –Cl, –Br) or strong electron-withdrawing groups ($-CF_3$, $-NO_3$), the corresponding products **3b–3l** were obtained in high yields (92–99%) with excellent enantioselectivities (96–>99% ee) (Table 3, entries 2–12). The substrates **1m–1t** that bear electron-donating substituents (–Me, –iPr, $-N(CH_3)_2$, –OMe and $-OCH_2O-$) on the phenyl rings had somewhat of an influence on the reactivity and enantioselectivity of the corresponding reactions (Table 3, entries 13–20). The substrates **1u–1y** containing fused aromatic or heteroaromatic rings were also suitable substrates for this reaction, affording the corresponding products **3u–3y** in 92–96% yields with 97–98% ees, with the exception of **3y** with 82% ee (Table 3, entries 21–25). In addition, the phosphination reaction of azomethine imines **1z** and **1aa** derived from cinnamaldehyde and aliphatic cyclohexanecarboxaldehyde also gave the desired products **3z** and **3aa** in 95% and 99% yields with 85% ee and 92% ee, respectively (Table 3, entries 26 and 27). The relative and absolute configurations of the product **3g** were determined by X-ray diffraction analysis (Fig. 1). The configurations of other products were assigned analogously.[14]

In order to probe the electronic and steric effects of the phosphine oxides, bis(*p*-tolyl)phosphine oxide **2b** and bis(3,5-dimethylphenyl)phosphineoxide **2c** were employed for this reaction under the identical reaction conditions, and the

Table 3 Substrate scope of azomethine imines in the asymmetric phosphination reaction with diphenylphosphine oxide **2a**



Entry[a]	Substrate (R)	Time (h)	Product	Yield[b] (%)	ee[c] (%)
1	Ph (**1a**)	0.5	**3a**	99	99
2	2-FC_6H_4 (**1b**)	2	**3b**	96	>99
3	4-FC_6H_4 (**1c**)	2	**3c**	95	99
4	2-ClC_6H_4 (**1d**)	0.5	**3d**	92	99
5	3-ClC_6H_4 (**1e**)	1	**3e**	99	99
6	4-ClC_6H_4 (**1f**)	1	**3f**	93	99
7	2-BrC_6H_4 (**1g**)	1	**3g**	95	98[d]
8	3-BrC_6H_4 (**1h**)	3	**3h**	94	99
9	4-BrC_6H_4 (**1i**)	1.5	**3i**	94	99
10	2,4-$Cl_2C_6H_3$ (**1j**)	1.5	**3j**	99	98
11	4-$CF_3C_6H_4$ (**1k**)	0.5	**3k**	99	99
12	3-$NO_2C_6H_4$ (**1l**)	2	**3l**	96	96
13	3-$CH_3C_6H_4$ (**1m**)	1	**3m**	94	98
14	4-iPrC_6H_4 (**1n**)	0.5	**3n**	99	98
15	4-$(CH_3)_2NC_6H_4$ (**1o**)	3	**3o**	94	95
16	2-$MeOC_6H_4$ (**1p**)	2	**3p**	92	98
17	4-$MeOC_6H_4$ (**1q**)	2	**3q**	99	93
18	3,5-$(MeO)_2C_6H_3$ (**1r**)	1.5	**3r**	90	99
19	2,4-$(MeO)_2C_6H_3$ (**1s**)	3	**3s**	91	>99
20	 (**1t**)	2.5	**3t**	88	>99
21	1-Naphthyl (**1u**)	0.75	**3u**	93	98
22	2-Naphthyl (**1v**)	2.5	**3v**	95	98
23	2-Furyl (**1w**)	2.5	**3w**	92	97
24	2-Thienyl (**1x**)	2.3	**3x**	96	98
25	2-Pyridyl (**1y**)	2.5	**3y**	94	82
26	*E*-$C_6H_5CH{=}CH$ (**1z**)	1	**3z**	95	85
27	Cyclohexyl (**1aa**)	0.5	**3aa**	99	92

[a] Unless noted, the reaction was performed in 0.1 mmol scale and the ratio of **2a**/**1** was 1 : 1 and the organocatalyst **p** (10 mol%) in the indicated solvent (0.2 M) at 25 °C. [b] Isolated yield. [c] Determined by HPLC (AD-H). [d] The absolute configuration of **3g** was determined by X-ray analysis.

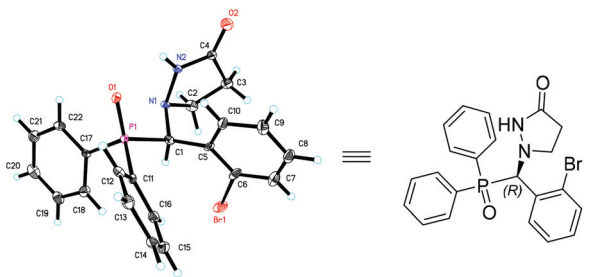
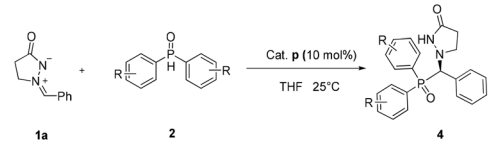
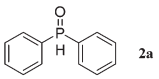
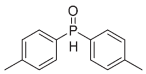
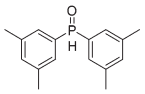


Fig. 1 X-ray crystal structure of product (*R*)-**3g**.

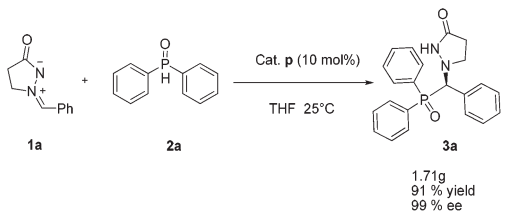
results are shown in Table 4. It turned out that both reactivity and enantioselectivity were evidently reduced in comparison with that of diphenylphosphine oxide **2a** (Table 4, entries 1 *vs.* entries 2 and 3). A gram-scale reaction was performed in THF at room temperature in the presence of 10 mol% catalyst

Table 4 Substrate scope of diarylphosphoryl oxygen



Entry[a]	Substrates	Time (h)	Product	Yield[b] (%)	ee[c] (%)
1	 2a	0.5	**3a**	99	99
2	 2b	60	**4b**	80	96
3	 2c	12	**4c**	83	82

[a] Unless noted, the reaction was performed in 0.1 mmol scale and the ratio of **2**/**1a** was 1 : 1 and the organocatalyst (10 mol%) in the indicated solvent (0.2 M) at 25 °C. [b] Isolated yield. [c] Determined by HPLC (AD-H).

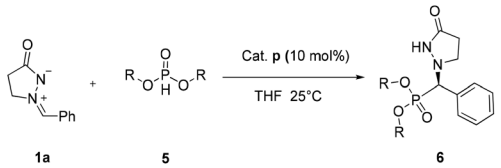


Scheme 3 Catalytic asymmetric phosphination reaction of **1a** with **2a** in gram-scale.

loading of **p**. Optically pure product **3a** (1.71 g) was smoothly obtained by filtration in 91% yield with 99% ee (Scheme 3).

Subsequently, we turned our attention to the asymmetric hydrophosphonylation reaction of azomethine imine **1a** with phosphites **5**. At the very start, several phosphites **5a–5d** were

Table 5 Condition optimization for the asymmetric hydrophosphonylation reaction of azomethine imine **1a** with phosphites **5**



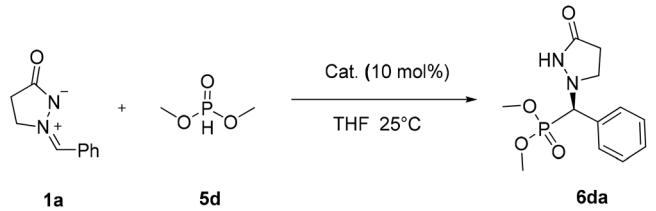
Entry[a]	Substrate (R)	Time (h)	Product	Yield[b] (%)	ee[c] (%)
1	Ph (**5a**)	4	**6aa**	90	Racemic
2	iPr (**5b**)	48	**6ba**	Trace	nd[d]
3	Et (**5c**)	15	**6ca**	70	89
4	Me (**5d**)	6	**6da**	85	88

[a] Unless noted, the reaction was performed in 0.1 mmol scale and the molar ratio of **5**/**1a** was 1.2 : 1. [b] Isolated yield. [c] Determined by HPLC (AD-H). [d] Not determined.

employed for the asymmetric hydrophosphonylation reaction with 10 mol% catalyst loading of **p** under the 1.2 : 1 molar ratio of **5**/**1a** in THF at room temperature. As illustrated in Table 5, the reaction of diphenyl phosphite **5a** proceeded smoothly to provide the desired product **6aa** in 90% yield but with racemic form (Table 5, entry 1). For substrate diisopropyl phosphite **5b**, almost no product was observed (Table 5, entry 2). Fortunately, it was found that diethyl phosphite **5c** and dimethyl phosphite **5d** were suitable substrates for the reaction, which afforded adducts **6ca** and **6da** in 70% and 85% yields with 89% ee and 88% ee enantioselectivities, respectively (Table 5, entries 3 and 4).

Accordingly, the reaction conditions were further optimized by adjusting several reaction parameters, including catalyst, solvent, substrate molar ratio, additive, and concentration. The results are summarized in Table 6. Preliminarily, several bifunctional catalysts derived from quinine **g**, **i**, **j** and **n**, **o**, **p** were reinvestigated for the asymmetric hydrophosphonylation reaction of azomethine imine **1a** with dimethyl phosphite **5d** in THF at room temperature. Catalyst **p** was proven to be the optimal catalyst in terms of both reactivity and enantioselectivity (Table 6, entry 6 *vs.* entries 1–5). A survey of solvents revealed that MTBE was the optimal reaction medium for this transformation, in which the desired product **6da** was obtained in 98% yield with 89% ee (Table 6, entries 6–9). After

Table 6 Condition optimization for the asymmetric hydrophosphonylation reaction of azomethine imine **1a** with dimethyl phosphite **5d**



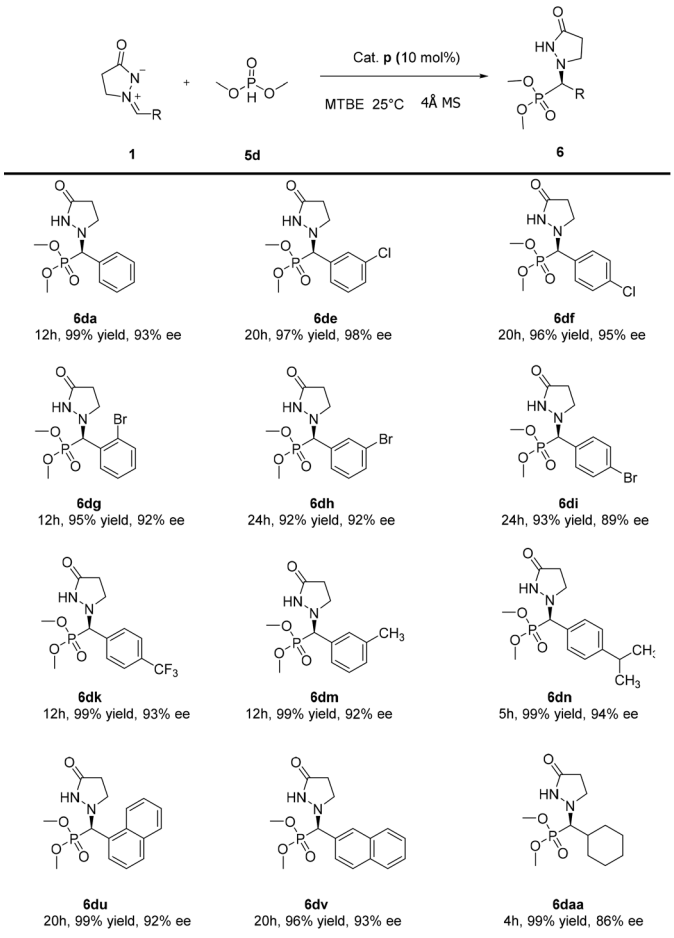
Entry[a]	Cat.	**5d** (equiv.)	Solv.	Conc. (M)	*T* (h)	Yield[b] (%)	ee[c] (%)
1	**g**	1.2	THF	0.1	48	55	83
2	**i**	1.2	THF	0.1	48	58	81
3	**j**	1.2	THF	0.1	48	70	83
4	**n**	1.2	THF	0.1	48	80	85
5	**o**	1.2	THF	0.1	48	70	84
6	**p**	1.2	THF	0.1	6	85	88
7	**p**	1.2	MTBE	0.1	7	98	89
8	**p**	1.2	DCM	0.1	7	89	85
9	**p**	1.2	Xylene	0.1	7	88	86
10	**p**	1.5	MTBE	0.1	5	96	90
11	**p**	2.0	MTBE	0.1	4	97	90
12	**p**	3.0	MTBE	0.1	4	95	88
13[d]	**p**	2.0	MTBE	0.1	3	96	91
14[d]	**p**	2.0	MTBE	0.067	10	98	91
15[d]	**p**	2.0	MTBE	0.05	12	99	93
16[d]	**p**	2.0	MTBE	0.033	24	78	90

[a] Unless noted, the reaction was performed in 0.1 mmol scale and the molar ratio of **5d**/**1a** was 1.2 : 1 in corresponding solvents (0.1 M) (temperature of 25 °C). Catalyst loading was 10 mol%. [b] Isolated yield. [c] Determined by HPLC (AD-H). [d] Under nitrogen protection, 60 mg of 4 Å MS was used.

delicately adjusting substrate molar ratio, additive, and substrate concentration, the optimized reaction conditions for the hydrophosphonylation reaction between azomethine imine **1a** with dimethyl phosphite **5d** were finally established as the reaction being performed in MTBE with 4 Å MS as additive under a 1 : 2 molar ratio of **1a** to **5d** at ambient temperature, as well as a substrate concentration of 0.05 M in the presence of 10 mol% catalyst **p** (Table 6, entry 15 *vs.* entries 10–14 and 16).

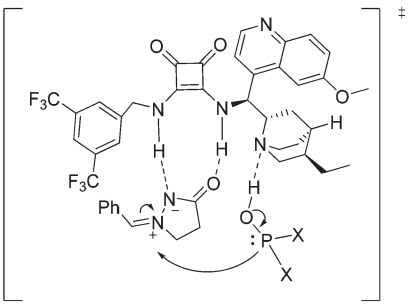
Having established the optimal reaction conditions, we explored the substrate scope and limitations of this protocol for the asymmetric hydrophosphonylation reaction of azomethine imines **1** with dimethyl phosphite **5d** and the results are summarized in Table 7. For the azomethine imine substrates, both electron-withdrawing (3-Cl, 4-Cl, 2-Br, 3-Br, 4-Br, 4-CF_3) and electron-donating (3-Me, 4-iPr) substituents on phenyl groups were tolerated for this transformation, and the desired products were obtained in high yields (92–99%) with good enantioselectivities (89–98% ee, Table 7). Among them, azomethine imine **1f** bearing *meta*-Cl on the phenyl ring furnished the desired product **6de** with the highest ee of 98%. Furthermore, the reactions for polyaromatic azomethine imines **1u** and **1v** performed very well to afford the desired products **6du** and **6dv** in 99% and 96% yields with 92% and 93% ees, respectively. In addition, the reaction of azomethine imine **1aa** bearing an aliphatic cyclohexyl group also smoothly proceeded to provide the desired product **6daa** in 99% yield with 86% ee (Table 7).

Table 7 Substrate scope examination[a]



[a] Unless noted, the reaction was performed in 0.1 mmol scale and the molar ratio of **5d**/**1** was 2 : 1 in corresponding MTBE (0.05 M) at 25 °C. Under nitrogen protection, 60 mg of 4 Å MS was used. Catalyst loading 10 mol%. Isolated yield, determined by HPLC (AD-H).

Fig. 2 Equilibrium between phosphonate form and phosphite form.



Scheme 4 Proposed transition state for the phosphination and hydrophosphonylation.

Based on the stereochemical outcome of the reaction, we proposed a ternary complex model to understand how the catalyst controls the stereochemistry (Fig. 2). Firstly, it is envisaged that the basic tertiary amine in the catalyst quinuclidine backbone may shift the phosphonate–phosphite equilibrium toward the phosphite form as the authentic nucleophile,[2c,4c] which is activated and orientated by hydrogen bonding through the interaction between the quinine nitrogen atom and the hydrogen on the phosphite. Secondly, the azomethine imine is activated by the squaramide moiety through double hydrogen bonding from the interaction between the –NH groups of the catalyst and the carbonyl and nitrogen groups on it. Thus, a preferential *Re*-face attack of organophosphorus nucleophiles to azomethine imines results in the observed major *R* enantiomer (Scheme 4).

Conclusions

In conclusion, we have reported highly enantioselective asymmetric phosphination and hydrophosphonylation reactions of azomethine imine by the use of a chiral squaramide derived from dihydroquinine as a catalyst. The reactions were performed with good to high reactivity and produced α-amino phosphorus derivatives in good yield with high enantioselectivities. Further application and biological evaluation of these chiral α-amino phosphorus compounds are in progress in our laboratory.

Experimental section

General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Molecular sieves were flame-dried under high vacuum before use. The first part reactions were carried out in air and using undistilled solvent, without any precautions to exclude moisture unless otherwise noted; the second part reactions were carried out under nitrogen protection. Organic solutions were concentrated under reduced pressure on an EYELA N-1001 rotary evaporator. Reactions were monitored by thin-layer chromatography (TLC) on silica gel precoated glass plates (0.2 ± 0.03 mm thickness, GF-254, particle size 0.01–0.04 mm) from Yantai Chemical Industry Research Institute, P. R. China. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm. Flash column chromatography was performed using silica gel (particle size 0.04–0.05 mm) from Yantai Chemical Industry Research Institute, P. R. China. ^{1}H, ^{13}C NMR and ^{31}P NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on a Varian Inova (400 MHz, 101 MHz and 162 MHz, respectively) spectrometer. Chemical shifts (δ ppm) are relative to the resonance of the deuterated solvent as the internal standard ($CDCl_3$, δ 7.26 ppm for proton NMR, δ 77.23 ppm for carbon NMR; DMSO-d_6, δ 2.50 ppm for proton NMR, δ 39.52 ppm for carbon NMR) and external 85% H_3PO_4 (^{31}P NMR). ^{1}H NMR data are reported as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br. s = broad singlet, dd = double-doublet, td = triple-doublet, ddd = double-double-doublet), coupling constants (J) and assignment. Data for ^{13}C NMR are reported in terms of coupling constants (J) and chemical shift (δ, ppm). Data for ^{31}P NMR are reported in terms of chemical shift (δ, ppm). IR spectra were recorded on a Thermo Fisher Nicolet 6700. Melting points were performed electrothermally. High-resolution mass spectra were recorded on a commercial apparatus (CI or ESI source). High-performance liquid chromatography (HPLC) was performed on an Agilent 1200 Series chromatographs using Daicel Chiralpak OD-H or AD-H column (0.46 cm × 25 cm). X-ray data were recorded on a Rigaku Mercury CCD/AFC diffractometer. Optical rotations are reported as follows: $[\alpha]_D^{20}$ (c in g per 100 mL, solvent).

General procedure for the preparation of racemic compounds 3 and 4

Racemic compounds described in this paper were prepared by the phosphination reaction of the azomethine imines with phosphoryl oxides: the azomethine imines (0.2 mmol), phosphoryl oxides (0.2 mmol), DBU as base, were combined in a vessel, 2 mL THF was added *via* syringe and the system was stirred at room temperature until the reaction was complete (detected by TLC). The solvents were evaporated under reduced pressure and the residue was purified by column chromatography on silica (AcOEt–DCM = 3/2) to give compounds **3** and **4** as solids.

General procedure for the preparation of racemic compounds 6

Racemic compounds described in this paper were prepared by the hydrophosphonylation reaction of the azomethine imines with phosphoryl oxides: azomethine imines (0.2 mmol), dimethyl phosphite (0.2 mmol), DBU as base, were combined in a vessel, 2 mL MTBE was added *via* syringe and the system was stirred at room temperature until the reaction was complete (detected by TLC). The solvents were evaporated under reduced pressure and the residue was purified by column chromatography on silica (AcOEt–DCM = 1/2, then AcOEt–DCM–MeOH = 4/1/0.2 to give compounds **6** as semi-solids.

General procedure for the asymmetric phosphination reaction of azomethine imine 1 with phosphoryl oxides 2

Phosphoryl oxides **2** (0.1 mmol) and the catalyst **p** (0.01 mmol, 10 mol%) were added, stirred at 25 °C in THF (0.5 mL) for 5 min, then to this vessel was carefully added azomethine imines **1** (0.1 mmol) The system was stirred at the same temperature until the reaction was detected to be complete by TLC. Then the phosphination reaction products were obtained after purification by flash chromatography on silica (AcOEt–DCM = 3/2) to give chiral compounds **3** and **4** as solids.

General procedure for the asymmetric hydrophosphonylation reaction of azomethine imine 1 with dimethyl phosphite 5

Dimethyl phosphite **5** (0.1 mmol), 4 Å MS (60 mg) and the catalyst **p** (0.01 mmol, 10 mol%) were added, carried out under nitrogen protection stirred at 25 °C in MTBE (2 mL) for 5 min, then to this vessel was carefully added azomethine imines **1** (0.1 mmol). The system was stirred at the same temperature until the reaction was detected to be complete by TLC. Then the hydrophosphonylation reaction products were obtained after purification by flash chromatography on silica (AcOEt–DCM = 1/2, then AcOEt–DCM–MeOH = 4/1/0.2) to give chiral compounds **6** as semi-solids.

(*R*)-1-((Diphenylphosphoryl)(phenyl)methyl)pyrazolidin-3-one (3a). The title compound was isolated by column chromatography (AcOEt–DCM = 3/2) in 99% yield. White solid, mp 224–226 °C; 99% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 70/30, flow rate: 1.0 mL min^{-1}, λ = 210.8 nm, t (major) = 8.855, t (minor) = 12.358; $[\alpha]_D^{20}$ = −33.00 (c 0.515, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 1H), 7.85–7.76 (m, 2H), 7.60–7.45 (m, 5H), 7.42–7.32 (m, 3H), 7.32–7.27 (m, 2H), 7.23–7.18 (m, 3H), 4.50 (d, J = 9.1 Hz, 1H), 3.47–3.30 (m, 1H), 3.30–3.20 (m, 1H), 2.10–1.97 (m, 1H), 1.85–1.76 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.40, 132.30 (d, J = 2.8 Hz), 132.06 (d, J = 2.8 Hz), 131.74 (d, J = 14.3 Hz), 131.70 (d, J = 14.3 Hz), 131.23 (d, J = 6.5 Hz), 130.82, 129.65 (d, J = 99.1 Hz), 129.01 (d, J = 1.3 Hz), 128.69, 128.67 (d, J = 11.7 Hz), 128.31 (d, J = 11.8 Hz), 71.16 (d, J = 86.9 Hz), 51.89 (d, J = 11.7 Hz), 30.19; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.50; IR: 3306.9, 3049.5, 2912.2, 1683.8, 1436.5, 1174.7, 1118.2, 759.8, 710.4 cm^{-1}; HRMS-CI (m/z): calcd for $C_{22}H_{21}N_2O_2P$: 376.1341; found: 376.1346.

(*R*)-1-((Diphenylphosphoryl)(2-fluorophenyl)methyl)pyrazolidin-3-one (3b). The title compound was isolated by column

chromatography (AcOEt–DCM = 3/2) in 96% yield. White solid, mp 208–210 °C; >99% ee [Daicel Chiralcel OD-H], hexanes–iPrOH = 70/30, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 7.850, t (minor) = 10.599; $[\alpha]_D^{20}$ = −41.28 (*c* 0.625, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.84–7.79 (m, 3H), 7.54–7.39 (m, 5H), 7.29 (td, *J* = 7.4, 1.1 Hz, 1H), 7.25–7.19 (m, 2H), 7.14 (dd, *J* = 13.9, 6.7 Hz, 1H), 700–6.85 (m, 2H), 5.02 (d, *J* = 10.3 Hz, 1H), 3.51 (dd, *J* = 19.9, 9.0 Hz, 1H), 3.09 (td, *J* = 10.0, 6.6 Hz, 1H), 2.05–1.97 (m, 1H), 1.76–1.68 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.54, 160.88 (dd, *J* = 244.5, 8.1 Hz), 132.95 (d, *J* = 6.1 Hz), 132.94, 132.35 (d, *J* = 2.7 Hz), 132.14 (d, *J* = 2.8 Hz), 131.76 (d, *J* = 101.4 Hz), 131.44 (d, *J* = 9.1 Hz), 130.90 (d, *J* = 8.9 Hz), 130.88 (d, *J* = 8.4 Hz), 129.71 (d, *J* = 99.7 Hz), 128.80 (d, *J* = 11.9 Hz), 128.52 (d, *J* = 11.9 Hz), 124.67 (d, *J* = 2.5 Hz), 118.23 (dd, *J* = 14.7, 3.0 Hz), 114.97 (d, *J* = 23.3 Hz), 60.17 (d, *J* = 89.9 Hz), 51.97 (d, *J* = 12.5 Hz), 30.18; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.75 (d, *J* = 3.6 Hz); IR: 3190.5, 3116.9, 3078.6, 2890.2, 1695.1, 1483.2, 1439.1, 1286.1, 1188.8, 1118.2, 815.0, 712.1, 685.5 cm^{-1}; HRMS-CI (*m*/*z*): calcd for $C_{22}H_{20}FN_2O_2P$: 394.1246; found: 394.1252.

(*R*)-1-((Diphenylphosphoryl)(4-fluorophenyl)methyl)pyrazolidin-3-one (3c). The title compound was isolated by column chromatography (AcOEt–DCM = 3/2) in 95% yield. White solid, mp 201–203 °C; 99% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 70/30, flow rate: 1.0 mL min^{-1}, λ = 210.8 nm, t (major) = 7.657, t (minor) = 15.051; $[\alpha]_D^{20}$ = −28.00 (*c* 0.525, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.80–7.71 (m, 2H), 7.53–7.37 (m, 5H), 7.36–7.27 (m, 3H), 7.26–7.18 (m, 2H), 6.84 (t, *J* = 8.5 Hz, 2H), 4.45 (d, *J* = 9.4 Hz, 1H), 3.39 (dd, *J* = 19.7, 9.1 Hz, 1H), 3.23–3.07 (m, 1H), 2.00–1.93 (m, 1H), 1.78–1.69 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.51, 163.05 (d, *J* = 250.7 Hz), 132.99 (d, *J* = 1.2 Hz), 132.99 (d, *J* = 14.7 Hz) 132.38 (d, *J* = 2.7 Hz), 132.17 (d, *J* = 2.7 Hz), 131.64 (d, *J* = 8.9 Hz), 131.51 (d, *J* = 8.9 Hz), 130.68, 129.57 (d, *J* = 99.2 Hz), 128.73 (d, *J* = 11.8 Hz), 128.44 (d, *J* = 11.8 Hz), 115.81 (d, *J* = 21.4 Hz), 69.76 (d, *J* = 86.8 Hz), 51.66 (d, *J* = 11.3 Hz), 30.18; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.43 (d, *J* = 1.3 Hz); IR: 3169.9, 3111.1, 3081.6, 2893.2, 1677.5, 1503.8, 1442.1, 1227.1, 1159.4, 1112.3, 723.8, 688.5 cm^{-1}; HRMS-CI (*m*/*z*): calcd for $C_{22}H_{20}FN_2O_2P$: 394.1246; found: 394.1245.

(*R*)-1-((2-Chlorophenyl)(diphenylphosphoryl)methyl)pyrazolidin-3-one (3d). The title compound was isolated by column chromatography (AcOEt–DCM = 3/2) in 92% yield. White solid, mp 110–112 °C; 99% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 70/30, flow rate: 1.0 mL min^{-1}, λ = 210.8 nm, t (major) = 14.356, t (minor) = 18.492; $[\alpha]_D^{20}$ = −18.00 (*c* 0.60, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.89–7.79 (m, 3H), 7.53–7.41 (m, 5H), 7.31–7.24 (m, 1H), 7.24–7.17 (m, 3H), 7.11–7.05 (m, 2H), 5.33 (d, *J* = 10.5 Hz, 1H), 3.52–3.43 (m, 1H), 3.25–3.13 (m, 1H), 2.05–1.97 (m, 1H), 1.72–1.63 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.69, 134.99 (d, *J* = 9.3 Hz), 133.13 (d, *J* = 3.7 Hz), 132.34 (d, *J* = 2.7 Hz), 132.12 (d, *J* = 2.8 Hz), 131.40 (d, *J* = 9.1 Hz), 130.84 (d, *J* = 9.0 Hz), 130.29 (d, *J* = 1.0 Hz), 129.72 (d, *J* = 100.2 Hz), 129.49, 129.05 (d, *J* = 3.7 Hz), 128.84 (d, *J* = 11.9 Hz), 128.46 (d, *J* = 11.9 Hz), 127.37 (d, *J* = 1.1 Hz), 63.88 (d, *J* = 88.7 Hz), 51.80 (d, *J* = 12.5 Hz), 30.30; ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.13; IR: 3161.1, 3071.1, 2926.3, 2808.9, 1689.2, 1439.9, 1180.2, 1120.5, 1029.8, 910.5, 924.2, 696.5 cm^{-1}; HRMS-CI (*m*/*z*): calcd for $C_{22}H_{20}ClN_2O_2P$: 410.0951 and 412.0921 for ^{35}Cl and ^{37}Cl isotopic pattern; found: 410.0956 and 412.0936.

(*R*)-1-((3-Chlorophenyl)(diphenylphosphoryl)methyl)pyrazolidin-3-one (3e). The title compound was isolated by column chromatography (AcOEt–DCM = 3/2) in 99% yield. White solid, mp 171–173 °C; 99% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 70/30, flow rate: 1.0 mL min^{-1}, λ = 210.8 nm, t (major) = 7.740, t (minor) = 9.585; $[\alpha]_D^{20}$ = −26.54 (*c* 0.54, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), δ 7.80–7.68 (m, 2H), 7.55–7.38 (m, 5H), 7.35 (td, *J* = 7.5, 1.1 Hz, 1H), 7.30–7.21 (m, 3H), 7.21–7.13 (m, 2H), 7.08 (t, *J* = 7.8 Hz, 1H), 4.40 (d, *J* = 8.9 Hz, 1H), 3.32 (dd, *J* = 19.4, 9.1 Hz, 1H), 3.21–3.11 (m, 1H), 2.09–2.01 (m, 1H), 1.89–1.80 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.34, 134.51, 132.96, 132.53 (d, *J* = 2.7 Hz), 132.35 (d, *J* = 2.7 Hz), 131.72 (d, *J* = 8.9 Hz), 131.67 (d, *J* = 8.9 Hz), 131.09 (d, *J* = 7.1 Hz), 130.83 ((d, *J* = 100.8 Hz), 129.93, 129.35 (d, *J* = 5.7 Hz), 129.20 (d, *J* = 1.3 Hz), 129.17 (d, *J* = 99.9 Hz), 128.79 (d, *J* = 11.8 Hz), 128.49 (d, *J* = 11.9 Hz), 70.52 (d, *J* = 85.2 Hz), 51.90 (d, *J* = 11.5 Hz), 30.22; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.35; IR: 3181.3, 3053.4, 2919.9, 1666.8, 1590.1, 1436.7, 1175.2, 1115.6, 1101.4, 999.1, 692.2 cm^{-1}; HRMS-CI (*m*/*z*): calcd for $C_{22}H_{20}ClN_2O_2P$: 410.0951 and 412.0921 for ^{35}Cl and ^{37}Cl isotopic pattern; found: 410.0945 and 412.0915.

(*R*)-1-((4-Chlorophenyl)(diphenylphosphoryl)methyl)pyrazolidin-3-one (3f). The title compound was isolated by column chromatography (AcOEt–DCM = 3/2) in 93% yield. White solid, mp 212–214 °C; 99% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 70/30, flow rate: 1.0 mL min^{-1}, λ = 210.8 nm, t (major) = 7.826, t (minor) = 15.342; $[\alpha]_D^{20}$ = −36.27 (*c* 0.38, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 7.78–7.71 (m, 2H), 7.52–7.39 (m, 5H), 7.34 (dd, *J* = 10.7, 4.2 Hz, 1H), 7.28–7.19 (m, 4H), 7.14 (s, 1H), 7.12 (s, 1H), 4.43 (d, *J* = 9.3 Hz, 1H), 3.37 (dd, *J* = 19.7, 9.1 Hz, 1H), 3.18–3.10 (m, 1H), 2.02–1.94 (m, 1H), 1.80–1.72 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.45, 135.25 (d, *J* = 1.6 Hz), 132.51, 132.45, 132.28 (d, *J* = 2.7 Hz), 131.64 (d, *J* = 12.7 Hz), 131.55 (d, *J* = 12.6 Hz), 130.57, 129.42 (d, *J* = 99.1 Hz), 129.40, 128.95, 128.76 (d, *J* = 11.8 Hz), 128.51 (d, *J* = 11.8 Hz), 69.96 (d, *J* = 86.3 Hz), 51.73 (d, *J* = 11.3 Hz), 30.19; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.28; IR: 3143.4, 3049.2, 2949.1, 2890.3, 1698.1, 1483.2, 1430.2, 1182.9, 1118.1, 1080.7, 1013.8, 831.8, 690.2 cm^{-1}; HRMS-CI (*m*/*z*): calcd for $C_{22}H_{20}ClN_2O_2P$: 410.0951 and 412.0921 for ^{35}Cl and ^{37}Cl isotopic pattern; found: 410.0948 and 412.0934.

(*R*)-1-((2-Bromophenyl)(diphenylphosphoryl)methyl)pyrazolidin-3-one (3g). The title compound was isolated by column chromatography (AcOEt–DCM = 3/2) in 95% yield. White solid, mp 182–184 °C; 98% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 70/30, flow rate: 1.0 mL min^{-1}, λ = 210.8 nm, t (major) = 15.363, t (minor) = 20.445; $[\alpha]_D^{20}$ = −39.02 (*c* 0.41, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.90–7.79 (m, 3H), 7.55–7.37 (m, 6H), 7.27 (dd, *J* = 10.5, 4.1 Hz, 1H), 7.23–7.18 (m, 2H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 5.35 (d, *J* = 10.5 Hz, 1H), 3.52–3.43 (m, 1H), 3.30–3.18 (m, 1H), 2.06–1.98

(m, 1H), 1.72–1.64 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.71, 133.17 (d, J = 3.6 Hz), 132.93, 132.35 (d, J = 2.8 Hz), 132.12 (d, J = 2.8 Hz), 131.38 (d, J = 9.1 Hz), 130.92 (d, J = 9.1 Hz), 130.79 (d, J = 3.8 Hz), 129.72 (d, J = 99.9 Hz), 128.87 (d, J = 11.8 Hz), 128.43 (d, J = 11.9 Hz), 127.99, 126.51 (d, J = 9.8 Hz), 66.60 (d, J = 88.2 Hz), 51.71 (d, J = 12.4 Hz), 30.32; ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.20; IR: 3152.2, 3063.9, 2928.5, 2813.7, 1683.4, 1592.1, 1433.2, 1347.8, 1297.7, 1268.3, 1185.9, 1162.3, 1112.3, 1018.1, 909.24, 723.8, 700.2 cm^{-1}; HRMS-CI (m/z): calcd for $C_{22}H_{20}BrN_2O_2P$: 454.0046 and 456.0425 for ^{79}Br and ^{81}Br isotopic pattern; found: 454.0448 and 456.0420.

(*R*)-1-((3-Bromophenyl)(diphenylphosphoryl)methyl)pyrazolidin-3-one (3h). The title compound was isolated by column chromatography (AcOEt–DCM = 3/2) in 94% yield. White solid, mp 179–181 °C; 99% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 70/30, flow rate: 1.0 mL min^{-1}, λ = 210.8 nm, t (major) = 8.161, t (minor) = 10.238; $[\alpha]_D^{20}$ = −34.56 (c 0.515, CHCl3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 7.78–7.69 (m, 2H), 7.54–7.39 (m, 5H), 7.38–7.22 (m, 6H), 7.02 (t, J = 7.8 Hz, 1H), 4.41 (d, J = 8.9 Hz, 1H), 3.31 (dd, J = 19.4, 9.1 Hz, 1H), 3.21–3.11 (m, 1H), 2.08–2.00 (m, 1H), 1.89–1.81 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.30, 133.92 (d, J = 7.1 Hz), 133.23, 132.50 (d, J = 2.7 Hz), 132.33 (d, J = 2.8 Hz), 132.07 (d, J = 1.2 Hz), 131.69 (d, J = 8.9 Hz), 131.64 (d, J = 8.9 Hz), 130.76 (d, J = 100.4 Hz), 130.14, 129.75 (d, J = 5.6 Hz), 129.12 (d, J = 99.8 Hz), 128.76 (d, J = 11.8 Hz), 128.46 (d, J = 11.9 Hz), 122.56, 70.42 (d, J = 85.8 Hz), 51.84 (d, J = 11.4 Hz), 30.20; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.37; IR: 3267.1, 3158.1, 3049.2, 2928.5, 1674.5, 1439.1, 1182.9, 1115.2, 753.2, 700.2 cm^{-1}; HRMS-CI (m/z): calcd for $C_{22}H_{20}BrN_2O_2P$: 454.0046 and 456.0425 for ^{79}Br and ^{81}Br isotopic pattern; found: 454.0458 and 456.0437.

(*R*)-1-((4-Bromophenyl)(diphenylphosphoryl)methyl)pyrazolidin-3-one (3i). The title compound was isolated by column chromatography (AcOEt–DCM = 3/2) in 94% yield. White solid, mp 221–223 °C; 99% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 70/30, flow rate: 1.0 mL min^{-1}, λ = 210.8 nm, t (major) = 8.240, t (minor) = 16.051; $[\alpha]_D^{20}$ = −43.56 (c 0.45, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.78–7.71 (m, 2H), 7.53–7.39 (m, 5H), 7.37–7.21 (m, 5H), 7.19 (d, J = 9.5 Hz, 2H), 4.40 (d, J = 9.2 Hz, 1H), 3.36 (dd, J = 19.7, 9.2 Hz, 1H), 3.18–3.08 (m, 1H), 2.03–1.96 (m, 1H), 1.82–1.73 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.38, 132.74 (d, J = 6.4 Hz), 132.47 (d, J = 2.7 Hz), 132.32 (d, J = 2.8 Hz), 131.92, 131.69 (d, J = 9.0 Hz), 131.58 (d, J = 8.9 Hz), 130.54, 129.92, 129.36 (d, J = 99.4 Hz), 128.78 (d, J = 11.8 Hz), 128.54 (d, J = 11.8 Hz), 123.55 (d, J = 1.8 Hz), 70.17 (d, J = 86.6 Hz), 51.81 (d, J = 11.5 Hz), 30.19; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.19; IR: 3140.5, 3058.1, 2893.2, 2840.2, 1677.5, 1483.2, 1430.2, 1183.0, 1121.2, 820.9, 714.9, 691.4 cm^{-1}; HRMS-CI (m/z): calcd for $C_{22}H_{20}BrN_2O_2P$: 454.0046 and 456.0425 for ^{79}Br and ^{81}Br isotopic pattern; found: 454.0443 and 456.0433.

(*R*)-1-((2,4-Dichlorophenyl)(diphenylphosphoryl)methyl)pyrazolidin-3-one (3j). The title compound was isolated by column chromatography (AcOEt–DCM = 3/2) in 95% yield. White solid, mp 135–137 °C; 98% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 70/30, flow rate: 1.0 mL min^{-1}, λ = 210.8 nm, t (major) = 12.515, t (minor) = 23.403; $[\alpha]_D^{20}$ = −37.5 (c 0.40, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.88–7.78 (m, 3H), 7.54–7.41 (m, 5H), 7.32 (td, J = 7.4, 1.0 Hz, 1H), 7.28–7.21 (m, 3H), 7.08 (dd, J = 8.5, 2.1 Hz, 1H), 5.25 (d, J = 10.5 Hz, 1H), 3.55–3.42 (m, 1H), 3.13 (ddd, J = 11.1, 9.1, 6.6 Hz, 1H), 2.05 (ddd, J = 16.0, 9.1, 6.6 Hz, 1H), 1.78–1.70 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.69, 135.73 (d, J = 1.3 Hz), 135.62 (d, J = 9.3 Hz), 133.80 (d, J = 3.5 Hz), 132.47 (d, J = 2.7 Hz), 132.37 (d, J = 2.7 Hz), 131.50 (d, J = 101.9 Hz), 131.38 (d, J = 9.2 Hz), 130.74 (d, J = 9.0 Hz), 129.41 (d, J = 100.2 Hz), 128.88 (d, J = 11.9 Hz), 128.64 (d, J = 11.9 Hz), 127.72, 127.67, 63.29 (d, J = 88.7 Hz), 51.79 (d, J = 12.3 Hz), 30.28; ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.07; IR: 3143.4, 3066.8, 2943.2, 2819.6, 1701.1, 1671.6, 1468.5, 1436.1, 1185.9, 1118.2, 720.8, 688.5 cm^{-1}; HRMS-CI (m/z): calcd for $C_{22}H_{19}Cl_2N_2O_2P$: 444.0561 and 446.0532 for ^{35}Cl and ^{37}Cl isotopic pattern; found: 444.0564 and 446.0542.

(*R*)-1-((Diphenylphosphoryl)(4-(trifluoromethyl)phenyl)methyl)-pyrazolidin-3-one (3k). The title compound was isolated by column chromatography (AcOEt–DCM = 3/2) in 99% yield. White solid, mp 214–216 °C; 99% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 70/30, flow rate: 1.0 mL min^{-1}, λ = 210.8 nm, t (major) = 6.128, t (minor) = 11.942; $[\alpha]_D^{20}$ = −48.18 (c 0.47, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 1H), 7.84 (dd, J = 10.8, 7.8 Hz, 2H), 7.63–7.44 (m, 9H), 7.40 (t, J = 7.1 Hz, 1H), 7.34–7.26 (m, 2H), 4.60 (d, J = 9.1 Hz, 1H), 3.46 (dd, J = 19.5, 9.0 Hz, 1H), 3.27–3.18 (m, 1H), 2.08 (ddd, J = 15.7, 9.0, 6.4 Hz, 1H), 1.89–1.80 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.41, 135.13 (s), 132.57 (d, J = 2.7 Hz), 132.39 (d, J = 2.7 Hz), 131.66 (d, J = 9.1 Hz), 131.49 (d, J = 9.0 Hz), 131.20 (d, J = 1.2 Hz), 130.88 (d, J = 1.1 Hz), 130.85 (d, J = 101.2 Hz), 129.17 (d, J = 99.9 Hz), 128.84 (d, J = 11.9 Hz), 128.56 (d, J = 11.9 Hz), 125.49 (q, J = 3.5 Hz), 123.79 (d, J = 272.5 Hz), 70.24 (d, J = 85.6 Hz), 51.80 (d, J = 11.2 Hz), 30.16; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.21; IR: 3172.8, 3105.1, 2969.7, 2899.1, 1677.5, 1324.3, 1165.3, 1127.1, 1068.1, 723.8, 682.6 cm^{-1}; HRMS-CI (m/z): calcd for $C_{23}H_{20}F_3N_2O_2P$: 444.1214; found: 444.1216.

(*R*)-1-((Diphenylphosphoryl)(3-nitrophenyl)methyl)pyrazolidin-3-one (3l). The title compound was isolated by column chromatography (AcOEt–DCM = 3/2) in 96% yield. Green solid, mp 172–174 °C; 96% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 70/30, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 9.590, t (minor) = 11.622; $[\alpha]_D^{20}$ = −38.54 (c 0.41, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.05 (s, 1H), 8.02–7.94 (m, 2H), 7.65–7.30 (m, 2H), 7.63–7.48 (m, 5H), 7.42–7.34 (m, 3H), 7.33–7.29 (m, 1H), 6.97 (dd, J = 5.1, 3.6 Hz, 1H), 5.61 (d, J = 11.7 Hz, 1H), 3.72–3.66 (m, 1H), 3.36 (t, J = 5.9 Hz, 1H), 1.59–1.45 (m, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 173.96, 132.95, 131.96, 131.67 (d, J = 2.1 Hz), 131.73 (d, J = 98.7 Hz), 131.58 (d, J = 2.4 Hz), 131.05 (d, J = 4.5 Hz), 130.99 (d, J = 1.8 Hz), 130.95, 130.46 (d, J = 8.8 Hz), 128.76, 128.54 (d, J = 11.7 Hz), 128.36 (d, J = 11.5 Hz), 126.81, 62.13 (d, J = 89.1 Hz), 49.94, 29.74; ^{31}P NMR (162 MHz, DMSO-d_6) δ 34.29; IR: 3161.1, 3087.5, 2955.0, 2887.3, 1680.4, 1524.4, 1439.1, 1350.7, 1174.2,

1109.4, 720.8, 685.5 cm^{-1}; HRMS-CI (*m*/*z*): calcd for $C_{22}H_{20}N_3O_4P$: 421.1191; found: 421.1193.

(*R*)-1-((Diphenylphosphoryl)(*m*-tolyl)methyl)pyrazolidin-3-one (3m). The title compound was isolated by column chromatography (AcOEt–DCM = 3/2) in 94% yield. White solid, mp 177–179 °C; 98% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 70/30, flow rate: 1.0 mL min–1, λ = 210.8 nm, t (major) = 7.862, t (minor) = 9.682; $[\alpha]_D^{20}$ = −48.68 (*c* 0.53, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (s, 1H), 7.72–7.67 (m, 2H), 7.49–7.45 (m, 3H), 7.40 (td, *J* = 7.5, 3.0 Hz, 2H), 7.36–7.29 (m, 1H), 7.26–7.18 (m, 2H), 7.05–6.95 (m, 4H), 4.36 (d, *J* = 8.7 Hz, 1H), 3.29–3.14 (m, 2H), 2.13 (s, 3H), 2.04–1.96 (m, 1H), 1.85–1.76 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.31, 138.34, 132.29 (d, *J* = 2.7 Hz), 132.07 (d, *J* = 2.8 Hz), 131.88 (d, *J* = 4.3 Hz), 131.83 (d, *J* = 2.9 Hz), 131.77, 131.64, 130.68, 129.72 (d, *J* = 1.5 Hz), 129.61 (d, *J* = 99.4 Hz), 128.61 (d, *J* = 11.7 Hz), 128.49, 128.29 (d, *J* = 6.5 Hz), 128.23 (d, *J* = 11.9 Hz), 71.54 (d, *J* = 85.0 Hz), 52.00 (d, *J* = 11.9 Hz), 30.24, 21.38; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.58; IR: 3169.9, 3110.4, 3052.1, 2916.7, 1712.8, 1662.8, 1433.2, 1374.3, 1174.1, 1118.2, 691.4, 667.8 cm^{-1}; HRMS-CI (*m*/*z*): calcd for $C_{23}H_{23}N_2O_2P$: 390.1497; found: 390.1491.

(*R*)-1-((Diphenylphosphoryl)(4-isopropylphenyl)methyl)pyrazolidin-3-one (3n). The title compound was isolated by column chromatography (AcOEt–DCM = 3/2) in 99% yield. White solid, mp 216–218 °C; 98% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 70/30, flow rate: 1.0 mL min^{-1}, λ = 210.8 nm, t (major) = 6.307, t (minor) = 11.404; $[\alpha]_D^{20}$ = −36.89 (*c* 0.52, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (s, 1H), 7.71 (dd, *J* = 10.5, 7.9 Hz, 2H), 7.50–7.35 (m, 5H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.23–7.12 (m, 4H), 6.98 (d, *J* = 8.0 Hz, 2H), 4.41 (d, *J* = 9.0 Hz, 1H), 3.30 (dd, *J* = 19.4, 9.4 Hz, 1H), 3.23–3.11 (m, 1H), 2.72 (dq, *J* = 13.7, 6.9 Hz, 1H), 1.96–1.92 (m, 1H), 1.78–1.73 (m, 1H), 1.08 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.43, 149.82 (d, *J* = 1.5 Hz), 132.19 (d, *J* = 2.7 Hz), 131.91 (d, *J* = 2.7 Hz), 131.71 (d, *J* = 8.8 Hz), 131.32 (d, *J* = 99.6 Hz), 131.10 (d, *J* = 6.4 Hz), 129.81 (d, *J* = 99.2 Hz), 128.60 (d, *J* = 11.7 Hz), 128.21 (d, *J* = 11.8 Hz), 127.92, 126.68, 70.89 (d, *J* = 86.4 Hz), 51.79 (d, *J* = 11.5 Hz), 33.72, 30.21, 23.86 (d, *J* = 4.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.66; IR: 3161.1, 3093.3, 2966.8, 2884.3, 1680.4, 1436.1, 1165.3, 1115.2, 926.9, 720.8, 691.4 cm^{-1}; HRMS-CI (*m*/*z*): calcd for $C_{25}H_{27}N_2O_2P$: 418.1810; found: 418.1800.

(*R*)-1-((4-(Dimethylamino)phenyl)(diphenylphosphoryl)methyl)-pyrazolidin-3-one (3o). The title compound was isolated by column chromatography (AcOEt–DCM = 3/2) in 94% yield. White solid, mp 219–221 °C; 95% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 70/30, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 10.320, t (minor) = 19.990; $[\alpha]_D^{20}$ = −47.76 (*c* 0.34, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 7.82–7.72 (m, 2H), 7.61–7.51 (m, 3H), 7.47 (s, 2H), 7.39 (d, *J* = 6.3 Hz, 1H), 7.31 (s, 2H), 7.13 (d, *J* = 5.0 Hz, 2H), 6.52 (d, *J* = 7.4 Hz, 2H), 4.35 (d, *J* = 8.7 Hz, 1H), 3.41–3.27 (m, 1H), 3.27–3.15 (m, 1H), 2.90 (s, 6H), 1.93–1.81 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.56, 150.67, 132.13, 132.06, 131.91 (d, *J* = 1.8 Hz), 131.84 (d, *J* = 1.3 Hz), 131.81, 130.32 (d, *J* = 98.5 Hz), 128.60 (d, *J* = 11.5 Hz), 128.31 (d, *J* = 11.6 Hz), 117.31, 114.46, 112.11, 66.60 (d, *J* = 73.5 Hz), 51.95 (d, *J* = 12.3 Hz), 40.27, 30.32; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.60; IR: 3205.2, 3072.7, 2913.8, 2887.3, 1683.4, 1609.8, 1521.5, 1436.1, 1356.6, 1168.2, 1118.2, 815.1, 714.9, 688.8 cm^{-1}; HRMS-ESI (*m*/*z*): calcd for $C_{24}H_{26}N_3O_2P[M + Na]^+$: 442.1660.1763; found: 442.1655.

(*R*)-1-((Diphenylphosphoryl)(2-methoxyphenyl)methyl)pyrazolidin-3-one (3p). The title compound was isolated by column chromatography (AcOEt–DCM = 3/2) in 92% yield. White solid, mp 172–174 °C; 98% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 70/30, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 15.618, t (minor) = 21.153; $[\alpha]_D^{20}$ = −20.8 (*c* 0.62, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.83–7.74 (m, 2H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.51–7.37 (m, 5H), 7.30–7.23 (m, 1H), 7.21–7.14 (m, 2H), 7.11 (t, *J* = 7.8 Hz, 1H), 6.75 (t, *J* = 7.5 Hz, 1H), 6.69 (d, *J* = 8.3 Hz, 1H), 5.30 (d, *J* = 10.0 Hz, 1H), 3.70 (s, 3H), 3.39 (dd, *J* = 20.1, 9.1 Hz, 1H), 3.15 (ddd, *J* = 11.1, 9.3, 5.9 Hz, 1H), 2.01–1.93 (m, 1H), 1.75–1.68 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.66, 157.20 (d, *J* = 7.5 Hz), 132.86, 132.43 (d, *J* = 3.8 Hz), 132.02 (d, *J* = 2.7 Hz), 131.82 (d, *J* = 2.8 Hz), 131.47 (d, *J* = 9.0 Hz), 130.96 (d, *J* = 8.9 Hz), 130.33 (d, *J* = 100.0 Hz), 130.18, 128.60 (d, *J* = 11.7 Hz), 128.18 (d, *J* = 11.8 Hz), 121.04 (d, *J* = 1.3 Hz), 119.43 (d, *J* = 2.4 Hz), 110.22, 60.20 (d, *J* = 89.9 Hz), 55.66, 51.80 (d, *J* = 12.7 Hz), 30.35; ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.47; IR: 3146.3, 3055.1, 2922.6, 2831.4, 1692.2, 1483.2, 1436.1, 1244.8, 1177.1, 1024.1, 717.9, 697.3 cm^{-1}; HRMS-CI (*m*/*z*): calcd for $C_{23}H_{23}N_2O_3P$: 406.1446; found: 406.1452.

(*R*)-1-((Diphenylphosphoryl)(4-methoxyphenyl)methyl)pyrazolidin-3-one (3q). The title compound was isolated by column chromatography (AcOEt–DCM = 3/2) in 99% yield. White solid, mp 131–133 °C; 93% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 70/30, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 10.288, t (minor) = 19.747; $[\alpha]_D^{20}$ = −64.86 (*c* 0.56, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.73 (dd, *J* = 10.4, 7.8 Hz, 2H), 7.47 (dd, *J* = 9.8, 8.2 Hz, 3H), 7.43–7.36 (m, 2H), 7.30 (q, *J* = 7.3 Hz, 1H), 7.26–7.17 (m, 4H), 6.67 (d, *J* = 8.6 Hz, 2H), 4.38 (d, *J* = 9.4 Hz, 1H), 3.65 (s, 3H), 3.34 (dd, *J* = 19.7, 9.5 Hz, 1H), 3.15 (ddd, *J* = 11.0, 9.3, 5.4 Hz, 1H), 1.98–1.90 (m, 1H), 1.78–1.68 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.53, 160.04, 132.46 (d, *J* = 6.6 Hz), 132.20 (d, *J* = 2.7 Hz), 132.00 (d, *J* = 2.7 Hz), 131.69 (d, *J* = 8.8 Hz), 131.63 (d, *J* = 8.7 Hz), 131.01, 130.78 (d, *J* = 11.5 Hz), 129.93 (d, *J* = 99.0 Hz), 129.00 (d, *J* = 12.9 Hz), 128.63 (d, *J* = 11.6 Hz), 128.34 (d, *J* = 11.8 Hz), 122.52, 114.12, 70.25 (d, *J* = 88.1 Hz), 55.22, 51.75 (d, *J* = 11.7 Hz), 30.21; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.55; IR: 3255.3, 3063.9, 2925.6, 2834.3, 1686.3, 1506.8, 1433.2, 1256.6, 1171.2, 1021.1, 717.9, 700.3 cm^{-1}; HRMS-CI (*m*/*z*): calcd for $C_{23}H_{23}N_2O_3P$: 406.1446; found: 406.1427.

(*R*)-1-((3,5-Dimethoxyphenyl)(diphenylphosphoryl)methyl)-pyrazolidin-3-one (3r). The title compound was isolated by column chromatography (AcOEt–DCM = 3/2) in 90% yield. White solid, mp 194–196 °C; 99% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 70/30, flow rate: 1.0 mL min^{-1}, λ =

254.4 nm, t (major) = 14.065, t (minor) = 12.113; $[\alpha]_D^{20}$ = −32.17 (*c* 0.23, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1H), 7.73–7.65 (m, 2H), 7.56–7.46 (m, 3H), 7.45–7.32 (m, 3H), 7.26 (td, *J* = 7.8, 2.7 Hz, 2H), 6.35 (s, 2H), 6.27 (s, 1H), 4.30 (d, *J* = 8.4 Hz, 1H), 3.56 (s, 6H), 3.24 (dd, *J* = 8.9, 5.5 Hz, 2H), 2.08–2.01 (m, 1H), 1.94–1.86 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.41, 160.63, 133.02, 132.39 (d, *J* = 2.7 Hz), 132.18 (d, *J* = 2.7 Hz), 131.87 (d, *J* = 8.7 Hz), 131.30, 129.64 (d, *J* = 99.3 Hz), 128.64 (d, *J* = 11.7 Hz), 128.34 (d, *J* = 11.9 Hz), 109.05 (d, *J* = 6.0 Hz), 101.32, 71.88 (d, *J* = 83.8 Hz), 55.47, 52.20 (d, *J* = 11.9 Hz), 30.27; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.60; IR: 3284.7, 3049.2, 3016.8, 2937.3, 2837.3, 1680.5, 1586.3, 1230.6, 1147.7, 1056.4, 717.9, 694.4 cm^{-1}; HRMS-CI (*m*/*z*): calcd for $C_{24}H_{25}N_2O_4P[M–Ph_2PO]^+$: 235.1083; found: 235.1075.

(*R*)-1-((2,4-Dimethoxyphenyl)(diphenylphosphoryl)methyl)-pyrazolidin-3-one (3s). The title compound was isolated by column chromatography (AcOEt–DCM = 3/2) in 91% yield. White solid, mp 152–154 °C; >99% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 70/30, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 15.070, t (minor) = 45.470; $[\alpha]_D^{20}$ = −8.6 (*c* 0.43, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.82–7.74 (m, 2H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.50–7.38 (m, 5H), 7.28 (t, *J* = 7.3 Hz, 1H), 7.23–7.16 (m, 2H), 6.31–6.25 (m, 2H), 5.19 (d, *J* = 10.4 Hz, 1H), 3.70 (s, 3H), 3.64 (s, 3H), 3.40 (dd, *J* = 20.3, 9.3 Hz, 1H), 3.13 (ddd, *J* = 11.1, 9.4, 5.5 Hz, 1H), 2.01–1.88 (m, 1H), 1.75–1.66 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.91, 161.26, 158.38 (d, *J* = 7.7 Hz), 133.31 (d, *J* = 3.8 Hz), 131.95 (d, *J* = 2.6 Hz), 131.80 (d, *J* = 2.7 Hz), 131.45 (d, *J* = 9.0 Hz), 130.91 (d, *J* = 8.9 Hz), 130.74, 130.57 (d, *J* = 99.9 Hz), 128.60 (d, *J* = 11.7 Hz), 128.26 (d, *J* = 11.7 Hz), 111.57 (d, *J* = 2.8 Hz), 104.60, 98.45, 59.90 (d, *J* = 91.1 Hz), 55.73, 55.33, 51.80 (d, *J* = 12.9 Hz), 30.39; ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.70; IR: 3143.4, 3055.1, 2937.3, 2834.3, 1680.5, 1603.9, 1297.7, 1206.5, 1171.2, 1100.5, 1021.1, 720.8, 694.4 cm^{-1}; HRMS-ESI (*m*/*z*): calcd for $C_{24}H_{25}N_2O_4P[M–Ph_2PO]^+$: 235.1083; found: 235.1090.

(*R*)-1-(Benzo[*d*][1,3]dioxol-5-yl(diphenylphosphoryl)methyl)-pyrazolidin-3-one (3t). The title compound was isolated by column chromatography (AcOEt–DCM = 3/2) in 88% yield. Green solid, mp 185–187 °C; >99% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 70/30, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 13.518, t (minor) = 19.846; $[\alpha]_D^{20}$ = −46.15 (*c* 0.26, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.01 (s, 1H), 7.95 (ddd, *J* = 11.1, 7.8, 1.6 Hz, 2H), 7.66 (ddd, *J* = 10.9, 7.8, 1.5 Hz, 2H), 7.60–7.51 (m, 3H), 7.44–7.33 (m, 3H), 7.23 (s, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 5.97 (s, 2H), 5.16 (d, *J* = 10.8 Hz, 1H), 3.66–3.58 (m, 2H), 1.58–1.48 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.13, 139.01 (d, *J* = 12.0 Hz), 135.57 (d, *J* = 1.8 Hz), 132.50 (d, *J* = 5.5 Hz), 132.50, 131.97 (d, *J* = 4.9 Hz), 131.89 (d, *J* = 4.8 Hz), 130.87, 129.66 (d, *J* = 99.3 Hz), 128.97, 128.83, 128.76 (d, *J* = 8.6 Hz), 128.74, 128.64 (d, *J* = 8.7 Hz), 126.68 (d, *J* = 1.1 Hz), 118.33 (d, *J* = 1.7 Hz), 70.54 (d, *J* = 91.2 Hz), 51.65 (d, *J* = 12.0 Hz), 30.71; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.53; IR: 3155.2, 3061.0, 2931.5, 2834.3, 1680.4, 1489.1, 1436.1, 1174.2, 1024.1, 921.0, 720.8, 703.1, 685.5 cm^{-1}; HRMS-CI (*m*/*z*): calcd for $C_{23}H_{21}N_2O_4P$: 420.1239; found: 420.1232.

(*R*)-1-((Diphenylphosphoryl)(naphthalen-1-yl)methyl)pyrazolidin-3-one (3u). The title compound was isolated by column chromatography (AcOEt–DCM = 3/2) in 93% yield. White solid, mp 196–198 °C; 98% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 70/30, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 13.579, t (minor) = 19.823; $[\alpha]_D^{20}$ = +17.11 (*c* 0.42, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 7.95–7.82 (m, 2H), 7.77–7.65 (m, 4H), 7.52–7.31 (m, 7H), 7.26 (t, *J* = 7.7 Hz, 1H), 7.19 (t, *J* = 7.1 Hz, 1H), 7.14–7.00 (m, 2H), 5.46 (d, *J* = 10.6 Hz, 1H), 3.29 (dd, *J* = 19.5, 9.3 Hz, 1H), 3.11–3.05 (m, 1H), 1.90–1.86 (m, 1H), 1.50–1.41 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.43, 133.75, 132.62 (d, *J* = 7.8 Hz), 132.28 (d, *J* = 2.4 Hz), 132.15, 132.03, 131.69 (d, *J* = 8.9 Hz), 131.14 (d, *J* = 8.9 Hz), 130.54 (d, *J* = 4.6 Hz), 129.74 (d, *J* = 100.2 Hz), 129.59, 128.68 (d, *J* = 11.7 Hz), 128.26 (d, *J* = 11.8 Hz), 127.14, 126.42, 125.74, 125.43, 121.57, 63.57 (d, *J* = 86.5 Hz), 52.17 (d, *J* = 12.2 Hz), 30.22; ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.71; IR: 3287.6, 3146.4, 3055.1, 2940.3, 1674.6, 1436.1, 1344.9, 1291.9, 1191.8, 1118.2, 773.8, 720.8, 697.3 cm^{-1}; HRMS-CI (*m*/*z*): calcd for $C_{26}H_{23}N_2O_2P$: 426.1497; found: 426.1511.

(*R*)-1-((Diphenylphosphoryl)(naphthalen-2-yl)methyl)pyrazolidin-3-one (3v). The title compound was isolated by column chromatography (AcOEt–DCM = 3/2) in 95% yield. White solid, mp 230–232 °C; 98% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 70/30, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 10.739, t (minor) = 19.701; $[\alpha]_D^{20}$ = −85.11 (*c* 0.69, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.82–7.75 (m, 4H), 7.70–7.68 (m, 2H), 7.59–7.54 (m, 3H), 7.51–7.44 (m, 4H), 7.44–7.38 (m, 1H), 7.38–7.31 (m, 1H), 7.27–7.24 (m, 2H), 4.63 (d, *J* = 8.7 Hz, 1H), 3.39–3.24 (m, 2H), 2.06 (ddd, *J* = 16.3, 8.8, 5.7 Hz, 1H), 1.87–1.79 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.23, 133.15 (d, *J* = 0.6 Hz), 132.92, 132.36 (d, *J* = 2.7 Hz), 132.14 (d, *J* = 2.7 Hz), 131.81 (d, *J* = 8.8 Hz), 131.79 (d, *J* = 8.9 Hz), 131.13 (d, *J* = 99.8 Hz), 131.05 (d, *J* = 7.4 Hz), 130.80 (d, *J* = 11.5 Hz), 129.99, 129.01 (d, *J* = 12.9 Hz), 129.01, 128.68 (d, *J* = 11.7 Hz), 128.45, 128.33 (d, *J* = 11.9 Hz), 128.27 (d, *J* = 12.3 Hz), 128.13 (d, *J* = 5.8 Hz), 127.28 (d, *J* = 84.5 Hz), 126.57, 71.49 (d, *J* = 86.2 Hz), 51.99 (d, *J* = 11.7 Hz), 30.23; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.54; IR: 3175.8, 3113.9, 3061.0, 2881.4, 1689.3, 1436.1, 1171.2, 1112.3, 726.7, 691.4 cm^{-1}; HRMS-CI (*m*/*z*): calcd for $C_{26}H_{23}N_2O_2P$: 426.1497; found: 426.114861.

(*R*)-1-((Diphenylphosphoryl)(furan-3-yl)methyl)pyrazolidin-3-one (3w). The title compound was isolated by column chromatography (AcOEt–DCM = 3/2) in 92% yield. White solid, mp 191–193 °C; 97% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 70/30, flow rate: 1.0 mL min^{-1}, λ = 210.8 nm, t (major) = 10.348, t (minor) = 12.150; $[\alpha]_D^{20}$ = −50.67 (*c* 0.15, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.13 (s, 1H), 8.02–7.92 (m, 2H), 7.72–7.64 (m, 3H), 7.63–7.51 (m, 3H), 7.48–7.35 (m, 3H), 6.55 (d, *J* = 3.2 Hz, 1H), 6.39 (dd, *J* = 3.1, 1.9 Hz, 1H), 5.36 (d, *J* = 12.8 Hz, 1H), 3.81–3.69 (m, 1H), 3.37 (t, *J* = 6.0 Hz, 1H), 1.62 (ddd, *J* = 14.7, 8.5, 5.9 Hz, 1H), 1.50–1.48 (m, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 173.99, 145.91 (d, *J* = 5.1 Hz), 144.16, 132.80, 131.81 (d, *J* = 99.4 Hz), 131.77 (d, *J* = 3.4 Hz),

131.71 (d, J = 2.5 Hz), 131.09 (d, J = 9.1 Hz), 130.38 (d, J = 9.0 Hz), 128.57 (d, J = 11.9 Hz), 128.45 (d, J = 12.5 Hz), 113.41 (d, J = 3.8 Hz), 111.29, 61.14 (d, J = 88.4 Hz), 50.04, 29.15; ^{31}P NMR (162 MHz, DMSO-d_6) δ 27.52; IR: 3208.1, 3116.0, 3052.1, 2902.1, 1689.3, 1431.0, 1180.9, 1118.4, 1010.4, 922.3, 720.6, 695.1 cm^{-1}; HRMS-CI (m/z): calcd for $C_{20}H_{19}N_2O_3P$: 366.1133; found: 366.1138.

(*R*)-1-((Diphenylphosphoryl)(thiophen-2-yl)methyl)pyrazolidin-3-one (3x). The title compound was isolated by column chromatography (AcOEt–DCM = 3/2) in 96% yield. White solid, mp 195–197 °C; 98% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 70/30, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 10.342, t (minor) = 14.746; $[\alpha]_D^{20}$ = −13.11 (c 0.31, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 6.89–6.81 (m, 2H), 6.72 (d, J = 7.6 Hz, 1H), 6.66–6.57 (m, 2H), 6.38–6.24 (m, 4H), 6.21–6.12 (m, 2H), 6.05 (td, J = 7.5, 3.0 Hz, 2H), 3.43 (d, J = 9.1 Hz, 1H), 2.24 (dd, J = 19.1, 8.8 Hz, 1H), 2.03–1.90 (m, 1H), 0.95–0.87 (m, 1H), 0.69–0.60 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.40, 147.95, 137.14 (d, J = 4.6 Hz), 133.18, 132.76 (d, J = 2.6 Hz), 132.55 (d, J = 2.7 Hz), 131.63 (d, J = 9.0 Hz), 131.43 (d, J = 8.9 Hz), 130.60 (d, J = 101.3 Hz), 129.80, 128.97 (d, J = 12.0 Hz), 128.47 (d, J = 99.0 Hz), 128.72 (d, J = 11.9 Hz), 125.93 (d, J = 8.0 Hz), 123.88, 69.77 (d, J = 85.7 Hz), 51.76 (d, J = 11.2 Hz), 30.21; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.32; IR: 3181.7, 3111.0, 3075.7, 2893.2, 1671.6, 1439.1, 1165.3, 1115.3, 909.2, 714.9, 691.4 cm^{-1}; HRMS-CI (m/z): calcd for $C_{20}H_{19}N_2O_2PS$: 382.0905; found: 382.0910.

(*R*)-1-((Diphenylphosphoryl)(pyridin-2-yl)methyl)pyrazolidin-3-one (3y). The title compound was isolated by column chromatography (AcOEt–DCM = 3/2) in 94% yield. White solid, mp 177–179 °C; 82% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 70/30, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 17.646, t (minor) = 13.918; $[\alpha]_D^{20}$ = +9.75 (c 0.40, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.47 (d, J = 4.6 Hz, 1H), 7.95–7.86 (m, 2H), 7.77 (d, J = 7.8 Hz, 1H), 7.64–7.44 (m, 6H), 7.35 (t, J = 6.9 Hz, 1H), 7.31–7.24 (m, 2H), 7.17 (dd, J = 7.1, 5.3 Hz, 1H), 5.00 (d, J = 9.2 Hz, 1H), 3.67–3.55 (m, 1H), 3.44 (ddd, J = 11.2, 9.4, 5.9 Hz, 1H), 2.02 (ddd, J = 15.4, 9.1, 5.9 Hz, 1H), 1.65–1.56 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.86, 151.99 (d, J = 5.5 Hz), 149.63 (d, J = 0.5 Hz), 136.66, 132.26 (d, J = 2.8 Hz), 132.03 (d, J = 2.8 Hz), 131.72 (d, J = 102.2 Hz), 131.38 (d, J = 9.2 Hz), 131.21 (d, J = 9.1 Hz), 129.88 (d, J = 99.2 Hz), 128.77 (d, J = 12.0 Hz), 128.46 (d, J = 11.8 Hz), 126.54 (d, J = 1.8 Hz), 123.62, 71.73 (d, J = 85.2 Hz), 51.72 (d, J = 11.7 Hz), 30.05; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.70; IR: 3178.7, 3052.1, 2925.6, 2854.9, 1683.4, 1586.3, 1433.2, 1177.1, 1112.1, 994.6, 726.7, 688.5 cm^{-1}; HRMS-CI (m/z): calcd for $C_{21}H_{20}N_3O_2P$: 377.1293; found: 377.1298.

(*R*,*E*)-1-(1-(Diphenylphosphoryl)-3-phenylallyl)pyrazolidin-3-one (3z). The title compound was isolated by column chromatography (AcOEt–DCM = 3/2) in 95% yield. Yellow solid, mp 152–155 °C; 85% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 70/30, flow rate: 1.0 mL min–1, λ = 254.4 nm, t (major) = 9.166, t (minor) = 13.078; $[\alpha]_D^{20}$ = −45.53 (c 0.38, CHCl3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 7.92–7.83 (m, 2H), 7.80–7.72 (m, 2H), 7.59–7.54 (m, 1H), 7.53–7.39 (m, 6H), 7.25 (d, J = 5.7 Hz, 2H), 7.20–7.15 (m, 2H), 6.44 (dd, J = 15.9, 3.3 Hz, 1H), 6.20 (ddd, J = 15.6, 9.8, 5.4 Hz, 1H), 4.14 (dd, J = 9.9, 7.4 Hz, 1H), 3.38 (t, J = 8.2 Hz, 2H), 2.47–2.33 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.13, 139.02 (d, J = 11.9 Hz), 135.56 (d, J = 1.7 Hz), 132.44 (t, J = 2.6 Hz), 131.89 (d, J = 8.9 Hz), 131.86 (d, J = 11.8 Hz), 130.77 (d, J = 11.5 Hz), 130.41 (d, J = 99.3 Hz), 129.71 (d, J = 99.5 Hz), 128.73 (d, J = 10.8 Hz), 128.70 (d, J = 11.8 Hz), 128.56, 128.13, 126.65 (d, J = 1.0 Hz), 118.26 (d, J = 1.5 Hz), 70.39 (d, J = 86.7 Hz), 51.51 (d, J = 11.7 Hz), 30.71; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.49; IR: 3190.5, 3058.1, 2922.6, 2846.1, 1686.3, 1436.1, 1165.3, 1118.2, 965.2, 726.7, 688.5 cm^{-1}; HRMS-CI (m/z): calcd for $C_{24}H_{23}N_2O_2P$: 402.1497; found: 402.1493.

(*R*)-1-(Cyclohexyl(diphenylphosphoryl)methyl)pyrazolidin-3-one (3aa). The title compound was isolated by column chromatography (AcOEt–DCM = 3/2) in 99% yield. White solid, mp 199–201 °C; 92% ee [Daicel Chiralcel OD-H], hexanes–iPrOH = 70/30, flow rate: 1.0 mL min–1, λ = 254.4 nm, t (major) = 4.938, t (minor) = 6.767; $[\alpha]_D^{20}$ = +39.54 (c 0.53, CHCl3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.86–7.80 (m, 4H), 7.58–7.43 (m, 6H), 3.52–3.43 (m, 2H), 3.39 (td, J = 10.1, 6.7 Hz, 1H), 2.47 (ddd, J = 16.5, 9.7, 6.7 Hz, 1H), 2.32 (ddd, J = 16.7, 9.9, 8.2 Hz, 1H), 1.89 (ddd, J = 34.4, 24.6, 9.9 Hz, 3H), 1.66–1.63 (m, 2H), 1.53 (d, J = 12.7 Hz, 1H), 1.35 (qd, J = 12.3, 3.1 Hz, 1H), 1.18–1.05 (m, 3H), 0.93–0.87 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.98, 134.29, 132.92 (d, J = 91.4 Hz), 132.03 (d, J = 2.7 Hz), 131.68 (d, J = 2.8 Hz), 131.20 (d, J = 3.3 Hz), 131.11 (d, J = 3.0 Hz), 128.80 (d, J = 6.2 Hz), 128.69 (d, J = 6.3 Hz), 68.96 (d, J = 77.5 Hz), 51.43 (d, J = 9.8 Hz), 38.11 (d, J = 4.1 Hz), 32.54 (d, J = 2.2 Hz), 32.30 (d, J = 8.5 Hz), 31.23, 31.07, 27.00 (d, J = 5.2 Hz), 25.91; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.68; IR: 3175.8, 3102.2, 2925.6, 2843.1, 1692.2, 1439.1, 1174.2, 1150.6, 1115.3, 717.9, 694.4 cm^{-1}; HRMS-ESI (m/z): calcd for $C_{22}H_{27}N_2O_2P[M + Na]^+$: 405.1702; found: 405.1687.

(*R*)-1-((Di-*p*-tolylphosphoryl)(phenyl)methyl)pyrazolidin-3-one (4b). The title compound was isolated by column chromatography (AcOEt–DCM = 3/2) in 80% yield. White solid, mp 195–197 °C; 96% ee [Daicel Chiralcel OD-H], hexanes–iPrOH = 90/10, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 43.464, t (minor) = 55.743; $[\alpha]_D^{20}$ = −40.00 (c 0.30, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.65 (dd, J = 10.8, 8.1 Hz, 2H), 7.41 (dd, J = 11.0, 8.1 Hz, 2H), 7.33 (d, J = 7.0 Hz, 2H), 7.28 (d, J = 2.9 Hz, 1H), 7.26–7.18 (m, 4H), 7.08 (dd, J = 8.0, 2.2 Hz, 2H), 4.44 (d, J = 9.0 Hz, 1H), 3.36 (dd, J = 19.5, 9.5 Hz, 1H), 3.28–3.17 (m, 1H), 2.40 (s, 3H), 2.28 (s, 3H), 2.03 (ddd, J = 16.0, 8.9, 5.5 Hz, 1H), 1.86–1.77 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.28, 142.74 (d, J = 2.8 Hz), 142.49 (d, J = 2.8 Hz), 131.73 (d, J = 9.2 Hz), 131.22 (d, J = 6.4 Hz), 131.05, 129.35 (d, J = 12.1 Hz), 129.04 (d, J = 12.2 Hz), 128.88 (d, J = 1.2 Hz), 128.60, 128.02 (d, J = 102.2 Hz), 126.43 (d, J = 101.7 Hz), 71.36 (d, J = 85.7 Hz), 51.89 (d, J = 11.6 Hz), 30.21, 21.69 (d, J = 0.9 Hz), 21.61 (d, J = 0.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.03; IR: 3228.8, 3058.1, 2975.6, 2919.7, 1689.3, 1174.1, 1118.2, 1097.6, 800.3, 712.1, 650.2 cm^{-1}; HRMS-CI (m/z): calcd for $C_{24}H_{25}N_2O_2P$: 404.1654; found: 404.1651.

(*R*)-1-((Bis(3,5-dimethylphenyl)phosphoryl)(phenyl)methyl)-pyrazolidin-3-one (4c). The title compound was isolated by column chromatography (AcOEt–DCM = 3/2) in 83% yield. White solid, mp 173–175 °C; 82% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 70/30, flow rate: 1.0 mL min^{-1}, λ = 210.8 nm, t (major) = 4.657, t (minor) = 9.660; $[\alpha]_D^{20}$ = −18.96 (*c* 0.68, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.90 (s, 1H), 7.39 (s, 1H), 7.35 (d, *J* = 9.9 Hz, 3H), 7.27–7.20 (m, 3H), 7.17 (s, 1H), 7.10 (d, *J* = 11.5 Hz, 2H), 6.98 (s, 1H), 4.46 (d, *J* = 8.9 Hz, 1H), 3.37 (dd, *J* = 19.5, 9.5 Hz, 1H), 3.28–3.19 (m, 1H), 2.35 (s, 6H), 2.19 (s, 6H), 2.05 (ddd, *J* = 15.9, 8.9, 5.5 Hz, 1H), 1.87–1.78 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.30, 138.31 (d, *J* = 12.3 Hz), 137.84 (d, *J* = 12.5 Hz), 134.00 (d, *J* = 2.8 Hz), 133.70 (d, *J* = 2.9 Hz), 131.28 (d, *J* = 6.3 Hz), 131.18, 131.03 (d, *J* = 99.1 Hz), 129.45 (d, *J* = 98.8 Hz), 129.31 (d, *J* = 8.9 Hz), 129.19 (d, *J* = 8.8 Hz), 128.85 (d, *J* = 1.2 Hz), 128.49, 71.27 (d, *J* = 85.6 Hz), 51.96 (d, *J* = 11.7 Hz), 30.21, 21.47, 21.25; ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.03; IR: 3187.6, 2960.9, 2910.6, 2852.0, 1680.5, 1271.3, 1162.3, 1124.1, 876.8, 844.5, 694.4, 650.2 cm^{-1}; HRMS-CI (*m*/*z*): calcd for $C_{26}H_{29}N_2O_2P$: 432.1976; found: 432.1974.

Dimethyl (*R*)-((3-oxopyrazolidin-1-yl)(phenyl)methyl)phosphonate (6da). The title compound was isolated by column chromatography (AcOEt–DCM = 1/2, then AcOEt–DCM–MeOH = 4/1/0.2) in 99% yield. Semi-solid; 93% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 11.583, t (minor) = 12.938; $[\alpha]_D^{20}$ = −34.00 (*c* 0.80, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.45 (dd, *J* = 4.2, 1.3 Hz, 2H), 7.43–7.34 (m, 3H), 4.05 (d, *J* = 16.5 Hz, 1H), 3.79 (d, *J* = 10.7 Hz, 3H), 3.60 (d, *J* = 10.6 Hz, 3H), 3.35–3.28 (m, 2H), 2.26–2.18 (m, 1H), 2.09–2.01 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.64, 131.39 (d, *J* = 1.8 Hz), 130.27 (d, *J* = 7.1 Hz), 129.28 (d, *J* = 2.2 Hz), 129.01 (d, *J* = 1.1 Hz), 69.66 (d, *J* = 163.2 Hz), 54.21 (d, *J* = 6.9 Hz), 53.77 (d, *J* = 7.1 Hz), 51.88 (d, *J* = 15.4 Hz), 30.32; ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.47; IR: 3202.3, 3058.1, 2955.0, 2928.5, 2849.1, 1692.2, 1492.1, 1450.8, 1253.6, 1177.1, 1029.9, 770.9, 703.2 cm^{-1}; HRMS-CI (*m*/*z*): calcd for $C_{12}H_{17}N_2O_4P$: 284.0926; found: 284.0926.

Dimethyl (*R*)-((3-chlorophenyl)(3-oxopyrazolidin-1-yl)-methyl)phosphonate (6de). The title compound was isolated by column chromatography (AcOEt–DCM = 1/2, then AcOEt–DCM–MeOH = 4/1/0.2) in 97% yield. Semi-solid; 98% ee [Daicel Chiralcel OD-H], hexanes–iPrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 13.358, t (minor) = 15.366; $[\alpha]_D^{20}$ = +71.43 (*c* 0.70, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.43 (d, *J* = 1.6 Hz, 1H), 7.41–7.31 (m, 3H), 4.03 (d, *J* = 16.1 Hz, 1H), 3.80 (d, *J* = 10.8 Hz, 3H), 3.66 (d, *J* = 10.6 Hz, 3H), 3.33 (ddd, *J* = 10.8, 8.9, 6.0 Hz, 1H), 3.22 (d, *J* = 5.4 Hz, 1H), 2.29 (ddd, *J* = 14.6, 8.4, 6.2 Hz, 1H), 2.20–2.11 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.54, 134.86 (d, *J* = 1.3 Hz), 133.65 (d, *J* = 1.9 Hz), 130.19 (d, *J* = 1.3 Hz), 130.11, 129.43 (d, *J* = 2.3 Hz), 128.31 (d, *J* = 6.4 Hz), 69.12 (d, *J* = 164.2 Hz), 54.27 (d, *J* = 6.8 Hz), 53.88 (d, *J* = 7.1 Hz), 51.92 (d, *J* = 15.1 Hz), 30.28; ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.71; IR (KBr) ν_{max}: 3205.2, 3066.8, 2952.1, 2916.7, 2846.1, 1704.1, 1589.2, 1571.5, 1250.7, 1180.1, 1053.5, 1029.9, 829.7, 759.1, 694.4 cm^{-1}; HRMS-CI (*m*/*z*): calcd for $C_{12}H_{16}ClN_2O_4P$: 318.0536 and 320.0507 for ^{35}Cl and ^{37}Cl isotopic pattern; found: 318.0537 and 320.0509.

Dimethyl (*R*)-((4-chlorophenyl)(3-oxopyrazolidin-1-yl)-methyl)phosphonate (6df). The title compound was isolated by column chromatography (AcOEt–DCM = 1/2, then AcOEt–DCM–MeOH = 4/1/0.2) in 96% yield. Semi-solid, 95% ee [Daicel Chiralcel OD-H], hexanes–iPrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 13.364, t (minor) = 18.127; $[\alpha]_D^{20}$ = +54.00 (*c* 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.42–7.37 (m, 4H), 4.03 (d, *J* = 16.5 Hz, 1H), 3.80 (d, *J* = 10.7 Hz, 3H), 3.64 (d, *J* = 10.6 Hz, 3H), 3.34–3.28 (m, 2H), 2.29–2.21 (m, 1H), 2.14–2.05 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.64, 135.33 (d, *J* = 2.7 Hz), 131.49 (d, *J* = 7.1 Hz), 130.01 (d, *J* = 2.8 Hz), 129.18 (d, *J* = 1.1 Hz), 68.72 (d, *J* = 165.2 Hz), 54.11 (d, *J* = 6.9 Hz), 53.86 (d, *J* = 7.1 Hz), 51.76 (d, *J* = 15.0 Hz), 30.23; ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.91; IR (KBr) ν_{max}: 3199.3, 3055.1, 2952.1, 2913.8, 2486.1, 1701.1, 1492.1, 1459.8, 1250.8, 1177.3, 1086.0, 1056.7, 832.8, 762.2 cm^{-1}; ESI-MS (%): *m*/*z* = 202.1 $[M + H]^+$; HRMS-CI (*m*/*z*): calcd for $C_{12}H_{16}ClN_2O_4P$: 318.0536 and 320.0507 for ^{35}Cl and ^{37}Cl isotopic pattern; found: 318.0535 and 320.0515.

Dimethyl (*R*)-((2-bromophenyl)(3-oxopyrazolidin-1-yl)-methyl-)phosphonate (6dg). The title compound was isolated by column chromatography (AcOEt–DCM = 1/2, then AcOEt–DCM–MeOH = 4/1/0.2) in 95% yield. Semi-solid; 92% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 210.8 nm, t (major) = 13.246, t (minor) = 15.575; $[\alpha]_D^{20}$ = +13.40 (*c* 0.96, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.82–7.79 (m, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.38 (td, *J* = 7.7, 1.0 Hz, 1H), 7.28–7.21 (m, 1H), 4.91 (d, *J* = 18.6 Hz, 1H), 3.87 (d, *J* = 10.8 Hz, 3H), 3.58 (d, *J* = 10.7 Hz, 3H), 3.42–3.32 (m, 2H), 2.33–2.25 (m, 1H), 2.09–2.00 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.91, 133.46, 132.03 (d, *J* = 3.7 Hz), 131.19, 130.64 (d, *J* = 2.1 Hz), 127.95 (d, *J* = 2.2 Hz), 125.97 (d, *J* = 11.2 Hz), 66.30 (d, *J* = 165.7 Hz), 54.14 (d, *J* = 6.9 Hz), 53.96 (d, *J* = 7.1 Hz), 51.77 (d, *J* = 16.1 Hz), 30.28; ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.29; IR (KBr) ν_{max}: 3196.3, 3111.1, 3077.3, 2952.1, 2922.6, 2849.1, 1698.1, 1462.6, 1230.1, 1185.9, 1062.3, 1081.1, 800.3, 744.4, 653.1 cm^{-1}; HRMS-CI (*m*/*z*): calcd for $C_{12}H_{16}BrN_2O_4P$: 362.0031 and 364.0011 for ^{79}Br and ^{81}Br isotopic pattern; found: 362.0021 and 363.9995.

Dimethyl (*R*)-((3-bromophenyl)(3-oxopyrazolidin-1-yl)-methyl)phosphonate (6dh). The title compound was isolated by column chromatography (AcOEt–DCM = 1/2, then AcOEt–DCM–MeOH = 4/1/0.2) in 92% yield. Semi-solid; 92% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 210.8 nm, t (major) = 10.747, t (minor) = 11.762; $[\alpha]_D^{20}$ = +18.24 (*c* 0.80, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.58 (dd, *J* = 3.3, 1.6 Hz, 1H), 7.53 (ddd, *J* = 7.9, 2.7, 1.7 Hz, 1H), 7.43 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.28 (dd, *J* = 8.3, 7.4 Hz, 1H), 4.01 (d, *J* = 16.1 Hz, 1H), 3.79 (d, *J* = 10.8 Hz, 3H), 3.66 (d, *J* = 10.6 Hz, 3H), 3.36–3.29 (m, 1H), 3.23 (t, *J* = 12.7 Hz, 1H), 2.29 (ddd, *J* = 14.7, 8.5, 6.2 Hz, 1H),

2.20–2.11 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.56, 133.93 (d, J = 3.3 Hz), 133.01 (d, J = 7.6 Hz), 132.35 (d, J = 2.3 Hz), 130.45 (d, J = 1.7 Hz), 128.75 (d, J = 6.2 Hz), 122.93 (d, J = 1.2 Hz), 69.10 (d, J = 164.7 Hz), 54.27 (d, J = 6.9 Hz), 53.88 (d, J = 7.1 Hz), 51.95 (d, J = 15.2 Hz), 30.28; ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.69; IR (KBr) ν_{max}: 3258.2, 3058.1, 2952.1, 2916.7, 2849.1, 1724.6, 1683.4, 1470.7, 1425.3, 1215.1, 1178.1, 1030.3, 888.3, 805.8, 760.4, 686.5 cm^{-1}; HRMS-CI (m/z): calcd for $C_{12}H_{16}BrN_2O_4P$: 362.0031 and 364.0011 for ^{79}Br and ^{81}Br isotopic pattern; found: 362.0020 and 364.0006.

Dimethyl (*R*)-((4-bromophenyl)(3-oxopyrazolidin-1-yl)-methyl-)phosphonate (6di). The title compound was isolated by column chromatography (AcOEt–DCM = 1/2, then AcOEt–DCM–MeOH = 4/1/0.2) in 93% yield. Semi-solid, 89% ee [Daicel Chiralcel OD-H], hexanes–iPrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 210.8 nm, t (major) = 14.050, t (minor) = 20.691; $[\alpha]_D^{20}$ = +54.14 (c 0.79, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.54 (d, J = 8.1 Hz, 2H), 7.34 (dd, J = 8.4, 1.7 Hz, 2H), 4.02 (d, J = 16.6 Hz, 1H), 3.80 (d, J = 10.7 Hz, 3H), 3.64 (d, J = 10.6 Hz, 3H), 3.31–3.27 (m, 2H), 2.29–2.21 (m, 1H), 2.11 (dd, J = 17.0, 8.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.60, 132.19 (d, J = 1.2 Hz), 131.77 (d, J = 7.0 Hz), 130.54 (d, J = 2.5 Hz), 123.60 (d, J = 2.9 Hz), 68.92 (d, J = 164.9 Hz), 54.20 (d, J = 6.9 Hz), 53.90 (d, J = 7.1 Hz), 51.87 (d, J = 15.3 Hz), 30.26; ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.78; IR (KBr) ν_{max}: 3223.5, 3059.8, 2946.8, 2845.6, 2360.7, 1718.7, 1590.1, 1482.9, 1215.2, 1180.1, 1074.1, 1030.7, 1009.3, 834.4, 760.0, 640.9 cm^{-1}; HRMS-CI (m/z): calcd for $C_{12}H_{16}BrN_2O_4P$: 362.0031 and 364.0011 for ^{79}Br and ^{81}Br isotopic pattern; found: 362.0020 and 364.0002.

Dimethyl (*R*)-((3-oxopyrazolidin-1-yl)(4-(trifluoromethyl)-phenyl)methyl)phosphonate (6dk). The title compound was isolated by column chromatography (AcOEt–DCM = 1/2, then AcOEt–DCM–MeOH = 4/1/0.2) in 99% yield. Semi-solid; 93% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 9.855, t (minor) = 8.881; $[\alpha]_D^{20}$ = +63.31 (c 0.88, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.66 (d, J = 8.2 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 4.13 (d, J = 16.1 Hz, 1H), 3.80 (d, J = 10.8 Hz, 3H), 3.65 (t, J = 10.7 Hz, 3H), 3.33 (ddd, J = 10.7, 9.0, 5.9 Hz, 1H), 3.20 (d, J = 7.8 Hz, 1H), 2.32–2.24 (m, 1H), 2.18–2.10 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.49, 135.87, 131.50 (d, J = 2.5 Hz), 131.17 (d, J = 2.3 Hz), 130.56 (d, J = 6.8 Hz), 127.94, 125.84 (dd, J = 3.7, 1.3 Hz), 123.88 (d, J = 272.6 Hz), 69.26 (d, J = 164.3 Hz), 54.22 (d, J = 6.9 Hz), 53.93 (d, J = 7.1 Hz), 51.97 (d, J = 15.2 Hz), 30.25; ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.49; IR (KBr) ν_{max}: 3211.1, 3075.7, 3013.9, 2957.9, 2849.1, 1704.1, 1618.4, 1421.4, 1324.3, 1256.6, 1171.2, 1121.2, 1068.2, 835.6, 765.0, 606.1 cm^{-1}; HRMS-CI (m/z): calcd for $C_{13}H_{16}F_3N_2O_4P$: 352.0800; found: 352.0796.

Dimethyl (*R*)-((3-oxopyrazolidin-1-yl)(m-tolyl)methyl)phosphonate (6dm). The title compound was isolated by column chromatography (AcOEt–DCM = 1/2, then AcOEt–DCM–MeOH = 4/1/0.2) in 99% yield. Semi-solid; 92% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 210.8 nm, t (major) = 8.974, t (minor) = 10.464; $[\alpha]_D^{20}$ = +96.91 (c 0.75, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.29–7.23 (m, 3H), 7.20 (d, J = 6.5 Hz, 1H), 4.01 (d, J = 16.3 Hz, 1H), 3.79 (d, J = 10.7 Hz, 3H), 3.60 (d, J = 10.6 Hz, 3H), 3.32–3.28 (m, 2H), 2.37 (s, 3H), 2.37–2.18 (m, 1H), 2.11–2.03 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.50, 138.64 (d, J = 1.3 Hz), 131.14 (d, J = 2.8 Hz), 130.77 (d, J = 7.2 Hz), 129.91 (d, J = 2.2 Hz), 128.73 (d, J = 1.3 Hz), 127.19 (d, J = 7.0 Hz), 69.49 (d, J = 164.3 Hz), 54.06 (d, J = 6.9 Hz), 53.61 (d, J = 7.1 Hz), 51.71 (d, J = 15.2 Hz), 30.24, 21.43; ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.64; IR (KBr) ν_{max}: 3217.1, 3022.7, 2952.1, 2916.7, 2843.2, 1698.1, 1456.7, 1238.9, 1177.1, 1056.4, 1032.8, 835.6, 756.1, 697.3 cm^{-1}; HRMS-CI (m/z): calcd for $C_{13}H_{19}N_2O_4P$: 298.1082; found: 298.1082.

Dimethyl (*R*)-((4-isopropylphenyl)(3-oxopyrazolidin-1-yl)-methyl)phosphonate (6dn). The title compound was isolated by column chromatography (AcOEt–DCM = 1/2, then AcOEt–DCM–MeOH = 4/1/0.2) in 99% yield. Semi-solid; 94% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 90/10, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 19.946, t (minor) = 22.517; $[\alpha]_D^{20}$ = +97.18 (c 0.82, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.36 (dd, J = 8.1, 1.5 Hz, 2H), 7.22 (dd, J = 14.7, 7.4 Hz, 2H), 4.03 (d, J = 16.5 Hz, 1H), 3.78 (d, J = 10.7 Hz, 3H), 3.60 (d, J = 10.5 Hz, 3H), 3.29 (t, J = 7.7 Hz, 2H), 2.91 (dq, J = 14.2, 7.1 Hz, 1H), 2.24–2.16 (m, 1H), 2.08–2.02 (m, 1H), 1.26 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.62, 150.09 (d, J = 2.4 Hz), 130.19 (d, J = 7.1 Hz), 128.43 (d, J = 1.9 Hz), 127.39, 127.05 (d, J = 1.1 Hz), 126.66, 69.25 (d, J = 165.4 Hz), 54.13 (d, J = 6.9 Hz), 53.71 (d, J = 7.1 Hz), 51.74 (d, J = 15.1 Hz), 33.90, 30.36, 23.97, 23.94; ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.78; IR (KBr) ν_{max}: 3217.1, 3052.2, 2955.1, 2872.6, 1733.4, 1689.3, 1509.7, 1459.7, 1418.5, 1250.7, 1224.2, 1180.5, 1056.4, 832.7, 767.9 cm^{-1}; HRMS-CI (m/z): calcd for $C_{15}H_{23}N_2O_4P$: 326.1395; found: 326.1401.

Dimethyl (*R*)-(naphthalen-1-yl(3-oxopyrazolidin-1-yl)methyl)-phosphonate (6du). The title compound was isolated by column chromatography (AcOEt–DCM = 1/2, then AcOEt–DCM–MeOH = 4/1/0.2) in 99% yield. Semi-solid; 99% yield, 92% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 14.905, t (minor) = 28.062; $[\alpha]_D^{20}$ = +50.06 (c 0.84, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.11 (s, 1H), 7.90 (dd, J = 7.6, 4.8 Hz, 3H), 7.61–7.51 (m, 3H), 5.04 (s, 1H), 3.74 (d, J = 10.7 Hz, 3H), 3.47 (d, J = 10.6 Hz, 3H), 3.31 (ddd, J = 10.8, 8.9, 6.2 Hz, 1H), 3.15 (s, 1H), 2.29 (dd, J = 17.2, 9.8 Hz, 1H), 2.02 (d, J = 3.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.68, 134.08, 132.02 (d, J = 7.4 Hz), 129.77, 129.36, 129.01, 127.07, 126.10, 125.37 (d, J = 2.8 Hz), 63.89, 54.28 (d, J = 7.0 Hz), 53.57 (d, J = 6.6 Hz), 51.91 (d, J = 15.6 Hz), 30.28; ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.11; IR (KBr) ν_{max}: 3181.1, 3096.3, 3049.2, 3008.1, 2952.1, 2852.3, 1709.9, 1680.5, 1509.7, 1280.1, 1206.5, 1177.1, 1062.3, 1006.4, 827.1, 816.9, 773.8, 656.9 cm^{-1}; HRMS-CI (m/z): calcd for $C_{16}H_{19}N_2O_4P$: 334.1082; found: 334.1090.

Dimethyl (*R*)-(naphthalen-2-yl(3-oxopyrazolidin-1-yl)methyl)-phosphonate (6dv). The title compound was isolated by column chromatography (AcOEt–DCM = 1/2, then AcOEt–DCM–MeOH = 4/1/0.2) in 96% yield. Semi-solid; 93% ee

[Daicel Chiralcel AD-H], hexanes–iPrOH = 80/20, flow rate: 1.0 mL min^{-1}, λ = 210.8, t (major) = 15.837, t (minor) = 17.719; $[\alpha]_D^{20}$ = +52.77 (*c* 0.47, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.94–7.84 (m, 4H), 7.59 (d, *J* = 8.5 Hz, 1H), 7.53 (dd, *J* = 6.2, 3.2 Hz, 2H), 4.22 (d, *J* = 15.8 Hz, 1H), 3.79 (d, *J* = 10.7 Hz, 3H), 3.61 (d, *J* = 10.6 Hz, 3H), 3.36–3.32 (m, 2H), 2.33–2.21 (m, 1H), 2.11–2.07 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.55, 133.43 (d, *J* = 1.6 Hz), 133.15 (d, *J* = 1.3 Hz), 129.95 (d, *J* = 8.6 Hz), 129.01 (d, *J* = 3.7 Hz), 128.72 (d, *J* = 0.9 Hz), 128.21, 127.83 (d, *J* = 0.6 Hz), 127.06, 127.00, 126.78, 69.82 (d, *J* = 164.1 Hz), 54.23 (d, *J* = 6.9 Hz), 53.74 (d, *J* = 7.1 Hz), 51.92 (d, *J* = 15.4 Hz), 30.32; ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.46; IR (KBr) ν_{max}: 3208.2, 3055.1, 2955.0, 2919.7, 2846.1, 1701.1, 1618.6, 1456.7, 1250.7, 1180.1, 1050.5, 1032.8, 835.6, 750.3 cm^{-1}; HRMS-CI (*m*/*z*): calcd for $C_{16}H_{19}N_2O_4P$: 334.1082; found: 334.1084.

Dimethyl (*R*)-(cyclohexyl(3-oxopyrazolidin-1-yl)methyl)phosphonate (6daa). The title compound was isolated by column chromatography (AcOEt–DCM = 1/2, then AcOEt–DCM–MeOH = 4/1/0.2) in 99% yield. Semi-solid; 86% ee [Daicel Chiralcel AD-H], hexanes–iPrOH = 90/10, flow rate: 1.0 mL min^{-1}, λ = 254.4 nm, t (major) = 12.881, t (minor) = 14.183; $[\alpha]_D^{20}$ = +29.93 (*c* 0.73, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 3.80 (d, *J* = 3.4 Hz, 3H), 3.77 (d, *J* = 3.5 Hz, 3H), 3.59–3.42 (m, 2H), 2.89 (dd, *J* = 17.9, 3.6 Hz, 1H), 2.69–2.53 (m, 2H), 1.88–1.72 (m, 5H), 1.67 (d, *J* = 11.8 Hz, 1H), 1.44–1.37 (m, 1H), 1.35–1.29 (m, 2H), 1.23–1.14 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.25, 69.02 (d, *J* = 142.0 Hz), 52.98 (d, *J* = 7.2 Hz), 52.62 (d, *J* = 7.1 Hz), 51.50 (d, *J* = 9.2 Hz), 37.71 (d, *J* = 3.4 Hz), 31.21 (d, *J* = 5.5 Hz), 31.16, 31.12 (d, *J* = 5.8 Hz), 29.79, 26.71 (d, *J* = 14.4 Hz), 26.14; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.61; IR (KBr) ν_{max}: 3187.6, 3081.6, 2952.1, 2919.7, 2852.0, 1692.3, 1450.8, 1235.9, 1177.1, 1050.5, 1024.1, 826.8, 794.4, 650.2 cm^{-1}; ESI-MS (%): *m*/*z* = 202.1 $[M + H]^+$; HRMS-CI (*m*/*z*): calcd for $C_{12}H_{23}N_2O_4P$: 290.1395; found: 290.1397.

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14 CCDC 941868 (for **3g**) contains the supplementary crystallographic data for this paper. See the ESI† for details.

