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Ring-Closing Olefin Metathesis for the Synthesis of Phosphorus Containing Heterocycles

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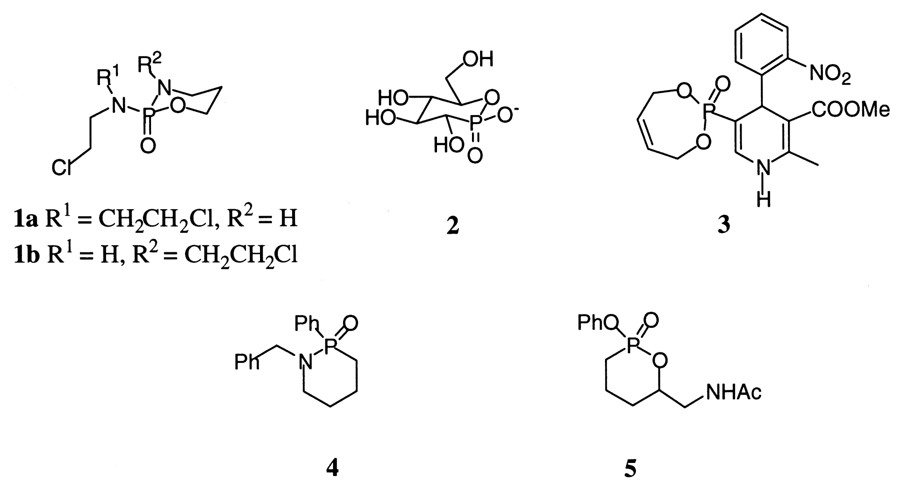
Abstract—A series of cyclic phosphorus containing heterocycles **9a–k** was prepared in a one-step procedure by ring closing metathesis of dienes **7a–k**. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

Heterocyclic systems that include a phosphorus linked to an oxygen or nitrogen atom are common to a diverse array of important biological molecules, e.g. **1–5** (Scheme 1).

These include cyclophosphamide **1a**, an anti-tumor alkylating agent which together with its structural isomer ifosfamide **1b** act as prodrugs relying on metabolism for their action.[1] In another group of compounds, cyclic phosphonates as exemplified by compound **2** are hexapyranose analogs modified at the anomeric carbon.[2] As a result, these analogs can regulate key steps in carbohydrate linked biological processes, e.g. cellular recognition.[3] 1,4-Dihydropyridine-5-cyclic phosphonate derivatives such as compound **3** are analogs of 1,4-dihydropyridine-3,5-dicarboxylate calcium antagonists and are therefore anti-hypertensive agents.[4] 1,2-Azaphosphorine such as compound **4** were developed in the search for biodegradable insecticides.[5] More recently, cyclic organophosphorus compounds have been employed for the generation of novel biocatalysts.[6] The cyclic phosphonate **5** has been successfully used to generate antibodies that catalyse the enantioselective aminolysis of lactones.[7]

We were recently attracted by the versatility and synthetic applicability of the ring-closing metathesis reaction (RCM)[8] using the well-defined transition metal catalysts **6a**,**b**[9] and **6c**[10] in the construction of functionalised carbocycles and heterocycles (Scheme 2).



1a $R^1 = CH_2CH_2Cl$, $R^2 = H$
1b $R^1 = H$, $R^2 = CH_2CH_2Cl$

2

3

4

5

Scheme 1.

Keywords: ring closing metathesis; phosphorus heterocycles.

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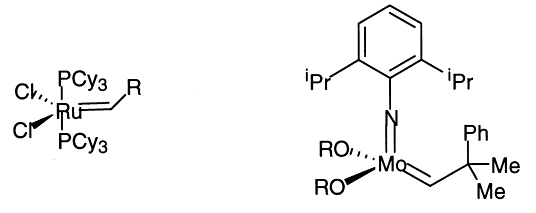


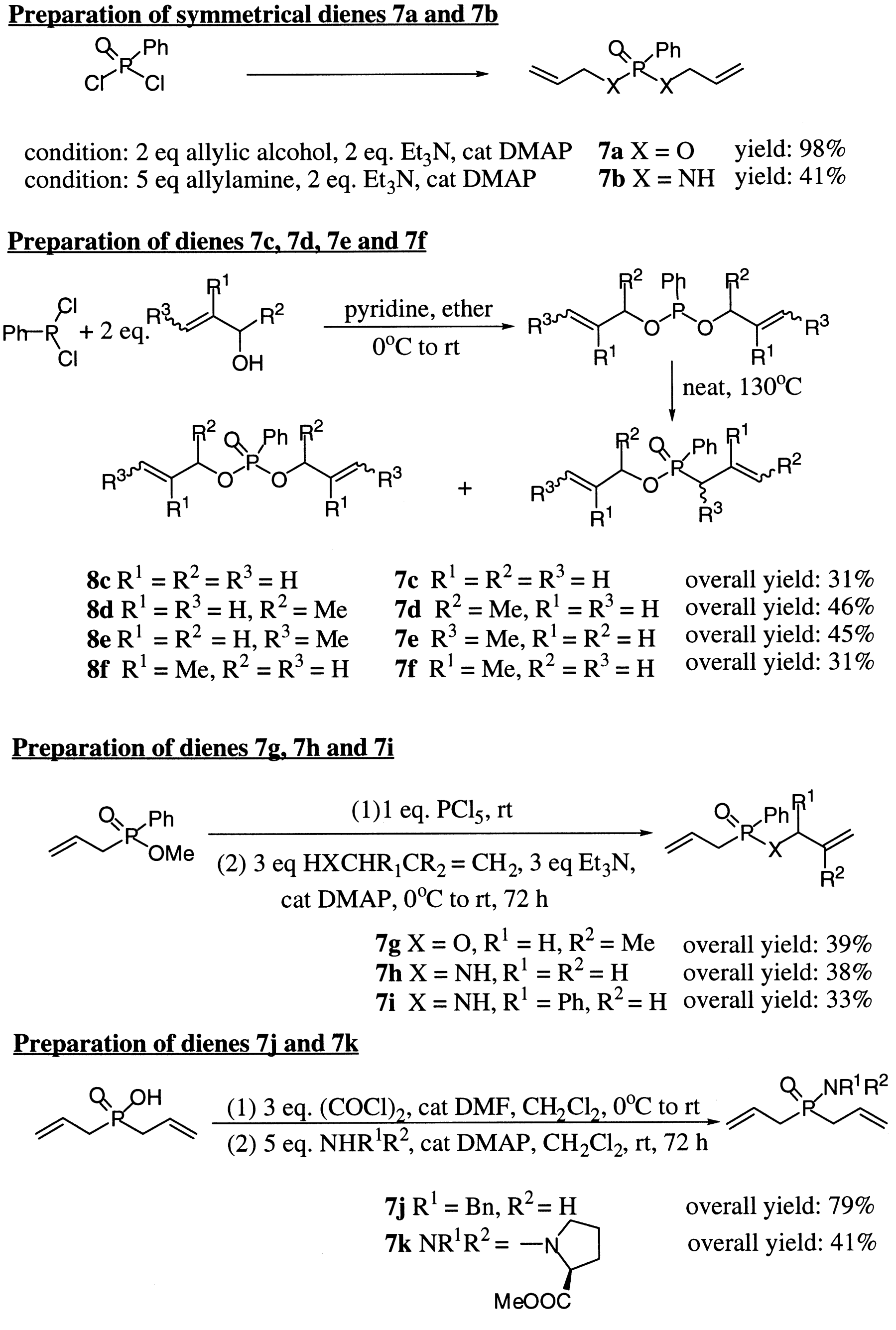
6a R = Ph
6b R = $CHCPh_2$
6c R = $CMe(CF_3)_2$

Scheme 2.

To date, the literature contains only a few examples of RCM reactions on phosphorus containing compounds. These include a phosphine,[11] phosphinate,[12] phosphinate[13] or phosphine oxide[14] functionality. However, there exist no comprehensive study that explores the scope and limitation of the RCM reaction to generate such phosphorus containing compounds. As part of a study to prepare new transition state analogs for antibody catalysis, we extended this methodology to the preparation of new phosphorus/oxygen heterocycles with a focus on 3,6-dihydro-1,2-oxaphosphinine 2-oxide and to the synthesis of phosphorus/nitrogen heterocycles.

Results and Discussion

To establish the feasibility of this strategy, a series of representative dienes were synthesised using three different procedures (Scheme 3).



Preparation of symmetrical dienes 7a and 7b

condition: 2 eq allylic alcohol, 2 eq. Et_3N, cat DMAP **7a** X = O yield: 98%
condition: 5 eq allylamine, 2 eq. Et_3N, cat DMAP **7b** X = NH yield: 41%

Preparation of dienes 7c, 7d, 7e and 7f

8c $R^1 = R^2 = R^3 = H$ **7c** $R^1 = R^2 = R^3 = H$ overall yield: 31%
8d $R^1 = R^3 = H, R^2 = Me$ **7d** $R^2 = Me, R^1 = R^3 = H$ overall yield: 46%
8e $R^1 = R^2 = H, R^3 = Me$ **7e** $R^3 = Me, R^1 = R^2 = H$ overall yield: 45%
8f $R^1 = Me, R^2 = R^3 = H$ **7f** $R^1 = Me, R^2 = R^3 = H$ overall yield: 31%

Preparation of dienes 7g, 7h and 7i

(1)1 eq. PCl_5, rt
(2) 3 eq $HXCHR_1CR_2 = CH_2$, 3 eq Et_3N, cat DMAP, 0°C to rt, 72 h

7g X = O, $R^1 = H, R^2 = Me$ overall yield: 39%
7h X = NH, $R^1 = R^2 = H$ overall yield: 38%
7i X = NH, $R^1 = Ph, R^2 = H$ overall yield: 33%

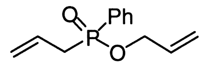
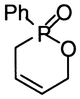
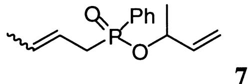
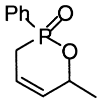
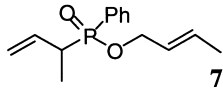
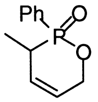
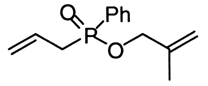
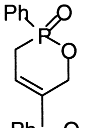
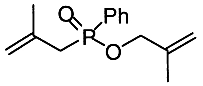
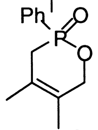
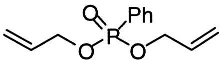
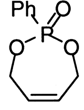
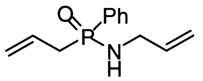
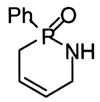
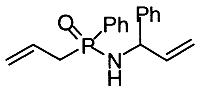
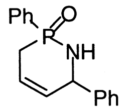
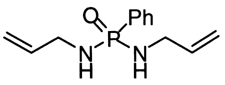
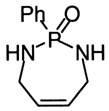
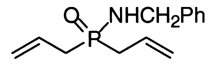
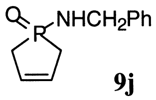
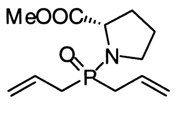
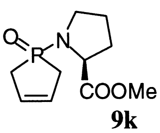
Preparation of dienes 7j and 7k

(1) 3 eq. $(COCl)_2$, cat DMF, CH_2Cl_2, 0°C to rt
(2) 5 eq. NHR^1R^2, cat DMAP, CH_2Cl_2, rt, 72 h

7j $R^1 = Bn, R^2 = H$ overall yield: 79%
7k $NR^1R^2 =$ overall yield: 41%

Scheme 3.

Table 1. RCM of dienes **7a–k** in the presence of the Ru-catalyst **6a** in CH_2Cl_2 (reflux, 0.02 M)

Entry	Substrate	Product	Condition	Yield[a]
1	 **7c**	 **9c**	4% **6a**, 16 h	92%
2	 **7d**	 **9d**	8% **6a**, 21 h	84%[b]
3	 **7e**	 **9e**	8% **6a**, 3 d	95%[b]
4	 **7g**	 **9g**	10% **6a**, 3 d	31%
5	 **7f**	 **9f**	6% **6a**, 5 d	no RCM[c]
6	 **7a**	 **9a**	16% **6a**, 5 d	34%
7	 **7h**	 **9h**	3% **6a**, 18 h	85%
8	 **7i**	 **9i**	8% **6a**, 24 h	63%[b]
9	 **7b**	 **9b**	6% **6a**, 3 d	36%
10	 **7j**	 **9j**	6% **6a**, 2 d	43%
11	 **7k**	 **9k**	6% **6a**, 2 d	80%

[a] Isolated yields.
[b] Mixture of diastereomers.
[c] 100% recovered starting material.

The symmetrical diene **7a** was prepared by the addition of two equivalents of allylic alcohol to phenylphosphonic dichloride in the presence of two equivalents of triethylamine and a catalytic amount of DMAP in 98% yield. Similarly, diene **7b** was prepared in 41% yield using an excess of allylamine. Dienes **7c**, **7d**, **7e** and **7f** were prepared in two steps from phenyldichlorophosphine according to a procedure described in the literature.[15] Addition of two equivalents of the corresponding allylic alcohol in the presence of pyridine followed by a [2,3] sigmatropic Arbusov rearrangement at 130°C of the intermediate phosphonites afforded the expected dienes with non optimised overall yields ranging from 31% to 46%. The major problem of this route is the concomitant formation of the phosphonates **8c–f** resulting from the oxidation of the intermediate diallyl phenyl phosphonites. However, the desired dienes **7c**–**f** could be obtained analytically pure by column chromatography. Dienes **7g**, **7h** and **7i** were prepared from allylphenylphosphinic methyl ester[16] by treatment with PCl_5 followed by addition of the corresponding allylic alcohol or amine in the presence of a catalytic amount of DMAP in dichloromethane. Finally, dienes **7j** and **7k** were prepared from diallylphosphinic acid [17] and the corresponding amines via the activated phosphinic acid chloride.

The RCM of dienes **7a**–**k** were carried out in dichloromethane under reflux in the presence of 2–16% (added portionwise, 2 mol%) of the Ru-catalyst **6a** and at a concentration of 0.02 M to give the corresponding cyclised products with moderate to excellent yields (Table 1). Under these conditions, RCM of the diene **7c** proceeded smoothly to give the phenyl-substituted six-membered oxaphosphinine oxide **9c** in excellent yield (entry 1). The cyclic products **9d** and **9e** possessing a methyl group respectively on position 6 and 3 could also be prepared conveniently and in very high yields (entries 2 and 3). However, the formation of the structural isomer **9g** possessing the methyl group on the olefin, was less favourable. Indeed, only 31% of product **9g** was isolated after three days in the presence of 10% alkylidene **6a** (entry 4). The tetrasubstituted cyclic olefin **9f** could not be obtained using this procedure. Indeed, the alkylidene **6a** showed no reaction with the disubstituted diene **7f** over five days supporting the hypothesis that steric effects are unfavourable for promoting ring closure (entry 5).[18] The cyclisation of the diene **7a** including a phosphonate group was surprisingly sluggish and gave only 34% of the seven-membered adduct **9a** after five days in the presence of 16% of catalyst. ^{1}H NMR and mass analysis of the crude mixture showed only unreacted starting material and no trace of dimer (entry 6).

Having established that the formation of differently substituted oxaphosphinine oxides (entries 1 to 4) was feasible, attention was turned towards the compatibility of RCM for the preparation of the corresponding nitrogen containing heterocycles. It was presumed that RCM of dienes including free allylic phosphinamide or phosphonamide NH groups might be problematic as it was previously observed by other groups that cyclisation of subtrates containing free allylic amide NH group could be difficult.[19] Interestingly, the reaction of the diene **7h** required only 3% of catalyst **6a** for 85% yield of product **9h** after 18 h (entry 7). Exposure of the phenyl-substituted diene **7i** to the same alkylidene **6a** showed lower reactivity in converting this substrate to **9i**. Indeed, after 48 h in the presence of 8% of alkylidene **6a**, 63% of the expected cyclic product **9i** was isolated (entry 8). When the phosphonamide **7b** was subjected to RCM condition, only 36% of the desired product **9b** could be isolated after three days in the presence of 6% of the Ru-catalyst **6a** (entry 9). For this reaction, the NMR and mass spectrum of the crude mixture show only unreacted starting material with no trace of a dimer or other side products. The lower reactivity of substrate **7b** supports the observation that the formation of a seven-membered ring combined with the presence of free allylic NH groups is not favourable to the RCM reaction. Finally, we examined the reactivity of phosphinamides **7j** and **7k**. These dienes with alkylidene **6a** afforded the expected 5-membered ring products in 43% and 80% yield, respectively (entries 10 and 11). The reaction of the tertiary phosphinamide **7k** was more favourable, supporting once more the hypothesis that, in some cases, the catalyst might be inhibited by the complex-forming properties of the phosphinamide NH group.

Conclusion

In summary, the work presented here has established a general strategy based on the RCM reaction for the synthesis of various phosphorus containing five-, six- and seven-membered heterocycles. During the course of this study, it was reported by Hanson et al. that 6-membered allylphosphonamides, five-membered vinylphosphonamides and various five-, six- and seven-membered phosphonates could be prepared by RCM of the corresponding dienes.[20] His results are consistent with our observations as he also found that the reactions with substrates including free NH groups might be sluggish and required prolonged reaction time and higher amount of the catalyst. Both papers are complementary and show that the RCM is a valuable synthetic route for a wide range of differently substituted phosphorus containing heterocycles. Application of this methodology to new transition state analogs is in progress in this laboratory.

Experimental

General methods

Allylphenylphosphinic methyl ester,[16] diallylphenylphosphinic acid[17] and ammonium phosphinate[21] were prepared as described in the literature. The ruthenium alkylidene **6a** was purchased from Strem. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker DPX-400 and Bruker AM-500 spectrometers. ^{31}P NMR spectra were recorded on a Bruker AM-500 spectrometer at 202 MHz and were referenced externally to phosphoric acid (δ_P=0 ppm). Infrared spectra were recorded using a Perkin–Elmer Paragon 1000 FT-IR spectrometer. Mass spectra (*m/z*) were recorded on a Micromass Platform-I APCI spectrometer. HRMS were performed on a Micromass Autospec 5000 OATof. Thin layer chromatography was performed using Merck aluminium foil backed sheets pre-coated with Kieselgel 60 F_{254}. Plates were visualised using UV light or $KMnO_4$. Column chromatography was performed using Sorbsil™ C_{60} H (40–60) silica gel.

Phenylphosphonic acid diallyl ester 7a.[22] To a solution of phenylphosphonic dichloride (0.3 ml, 2.12 mmol), a catalytic amount of DMAP and Et_3N (0.65 ml, 4.7 mmol) in CH_2Cl_2 (10 ml) at 0°C was added allylic alcohol (0.32 ml, 4.71 mmol). The mixture was allowed to warm to room temperature and was stirred overnight. The solvent was removed under reduced pressure and the residue was treated with pentane (10 ml). After filtration of the salts, the residue was purified by column chromatography; yield: 0.5 g (98%); R_f=0.2 (hexane:EtOAc, 3:2); δ_H ($CDCl_3$, 400 MHz) 7.86–7.80 (m, 2H), 7.59–7.54 (m, 1H), 7.50–7.45 (m, 2H), 5.98–5.89 (m, 2H), 5.34 (d, 2H, J=17.1 Hz), 5.22 (d, 2H, J=10.4 Hz), 4.64–4.49 (m, 4H); δ_C ($CDCl_3$, 101 MHz) 132.8 (d, J=6.8 Hz), 132.6 (d, J=2.8 Hz), 131.8 (d, J=10.1 Hz), 128.5 (d, J=15.0 Hz), 127.8 (d, J=189.5 Hz), 118.0, 66.5 (d, J=5.3 Hz); δ_P ($CDCl_3$, 202 MHz) 20.9; ν_{max} (neat, cm^{-1}) 1650, 1249, 1012; *m/z* (CI^+, NH_3) 239.0 ($M+H^+$).

***N*,*N*′-Diallyl-*p*-phenylphosphonic diamide 7b.** Same procedure as for **7a** with 0.3 ml (2.12 mmol) of phenyl phosphonic dichloride a catalytic amount of DMAP and 3 ml Et_3N (21.2 mmol), 1.6 ml allylamine (21.2 mmol). yield: 0.2 g (41%); R_f=0.2 (1% MeOH in EtOAc); δ_H ($CDCl_3$, 500 MHz) 7.87–7.83 (m, 2H), 7.54–7.51 (m, 1H), 7.48–7.44 (m, 2H), 5.91–5.84 (m, 2H), 5.27 (dd, 2H, J=16.8, 1.3 Hz), 5.13 (dd, 2H, J=10.5, 1.5 Hz), 3.64–3.58 (m, 4H), 2.56 (br s, 2H); δ_C ($CDCl_3$, 101 MHz) 136.5 (d, J=6.5 Hz), 131.7 (d, J=2.5 Hz), 131.5 (d, J=9.2 Hz), 124.9 (d, J=184.0 Hz), 115.4, 43.2; δ_P ($CDCl_3$, 202 MHz) 22.0; ν_{max} (neat, cm^{-1}) 3216, 1644, 1189; *m/z* (CI^+, NH_3) 237.2 ($M+H^+$); HRMS calcd for $C_{12}H_{18}$ N_2OP ($M+H^+$) 237.1157, found 237.1156.

Allylphenylphosphinic acid allyl ester 7c.[15] To a solution of allylic alcohol (1.1 ml, 16.1 mmol) and pyridine (1.3 ml, 16.1 mmol) in Et_2O (30 ml) at 0°C was added a solution of dichlorophenylphosphine (1 ml, 7.4 mmol) in Et_2O (1 ml). The mixture was allowed to warm to room temperature and then refluxed for 1 h. Salts were filtered off and the solvent was removed under reduced pressure. The residue was heated neat to 130°C overnight. The crude mixture was purified by column chromatography; yield: 0.5 g (31%); R_f=0.3 (EtOAc); δ_H ($CDCl_3$, 500 MHz) 7.78–7.76 (m, 2H), 7.57–7.54 (m, 1H), 7.50–7.46 (m, 2H), 5.95–5.88 (m, 1H), 5.81–5.71 (m, 1H), 5.33 (dd, 1H, J=17.1, 2.0 Hz), 5.21 (dd, 1H, J=10.4, 1.5 Hz), 5.15 (dd, 1H, J=10.1, 4.0 Hz), 5.08 (dd, 1H, J=17.1, 5.1 Hz), 4.56 (m, 1H, J=13.5, 5.5 Hz), 4.32 (dd, 1H, J=13.0, 5.5 Hz), 2.86–2.77 (m, 2H); δ_C ($CDCl_3$, 126 MHz) 133.0 (d, J=7.0 Hz), 132.0, 131.8 (d, J=9.4 Hz), 130.0 (d, J=124.9 Hz), 128.5 (d, J=12.5 Hz), 127.0 (d, J=9.3 Hz), 120.5 (d, J=13.4 Hz), 117.7, 65.0 (d, J=5.5 Hz), 36.0 (d, J=97.0 Hz); δ_P ($CDCl_3$, 202 MHz) 42.4; ν_{max} (neat, cm^{-1}) 1638, 1233, 1018; *m/z* (CI^+, NH_3) 223.1 ($M+H^+$).

But-2-enylphenylphosphinic acid 1-(methyl)allyl ester 7d. Same procedure as for **7c** with 1.41 ml (16.3 mmol) of 1-buten-3-ol, 1.31 ml (16.3 mmol) pyridine, 30 ml Et_2O, 1 ml (7.4 mmol) dichlorophenylphosphine; two diastereomers A and B (1:1 ratio); yield: 0.8 g (46%); R_f=0.3 (EtOAc: Hexane, 2:1); δ_H ($CDCl_3$, 400 MHz) (mixture of diastereomers) 7.79–7.71 (m, 2H), 7.53–7.40 (m, 3H), 5.99–5.91 (m, 1H, A or B), 5.79–5.71 (m, 1H, A or B), 5.48–4.98 (m, 4H), 4.98–4.91 (m, 1H, A or B), 4.82–4.77 (m, 1H, A or B), 2.68 (dd, 2H, J=6.4, 17.1 Hz), 1.63–1.59 (m, 3H), 1.44 (d, 3H, J=6.8 Hz, A or B), 1.25 (d, 3H, J=6.0, A or B); δ_C ($CDCl_3$, 101 MHz) (mixture of diastereomers) 139.0 (d, J=3.9 Hz, A or B), 138.6 (d, J=5.5, A or B), 132.0 (d, J=18.9 Hz), 131.6 (d, J=9.6 Hz), 131.5 (d, J=125.3 Hz), 131.1 (d, J=13.3 Hz), 128.2 (d, J=12.5 Hz), 119.3, 115.4, 73.0 (d, J=6.5 Hz, A or B), 72.5 (d, J=6.3 Hz, A or B), 35.0 (d, J=97.9 Hz), 22.8 (A or B), 22.2 (A or B), 18.0; δ_P ($CDCl_3$, 202 MHz) 42.1 (A or B), 41.5 (A or B) ν_{max} (neat, cm^{-1}) 1646, 1592, 1227, 1007; *m/z* (CI^+, NH_3) 251.1 ($M+H^+$); HRMS calcd for $C_{14}H_{21}O_2P$ ($M+H^+$) 251.1201, found 251.1204.

2-(Methyl)allylphenylphosphinic acid but-2-enyl ester (mixture of Z and E isomers) 7e. Same procedure as for **7c** with 1.88 ml (22 mmol) of but-2-en-ol, 1.8 ml (22 mmol) of pyridine, 32 ml Et_2O, 1.36 ml (10 mmol) of dichlorophenylphosphine; yield: 1.13 g (45%); R_f=0.5 (hexane: EtOAc, 1:1); δ_H ($CDCl_3$, 400 MHz) (*minor isomer) 7.72–7.66 (m,2H), 7.5–7.46 (m,1H), 7.42–7.38 (m,2H), 5.77–5.64 (m,2H), 5.53 (m,1H), 5.11–4.87 (m,2H), 4.47–4.41 (m,1H), 4.24–4.19 (m,1H), 2.78–2.69 (m,1H), 1.63 (dd, J=6.4, 1.0 Hz, 3H), 1.22 (ddd, J=7.6, 17.2, 1.2 Hz, 3H) (*1.15 (ddd, J=17.6, 1.2 Hz); δ_C ($CDCl_3$, 101 MHz) (*minor isomer) 134.2 (d, J=6.7 Hz) (*134 (d, J=8.7 Hz)), 132.4 (d, J=8.5 Hz) (*132.3 (d, J=8.5 Hz)), 132.1 (d, J=2.3 Hz), 130.6 (*130.5), 130.4 (d, J=139.5 Hz), 128.1 (d, J=11.7 Hz) (*128.3 (d, J=11.4 Hz)), 126.17 (d, J=7.1 Hz) (*126.14 (d, J=6.9 Hz)), 117.4 (d, J=11.9 Hz) (*117.6 (d, J=11.6 Hz)), 65.2 (d, J=6.5 Hz), 39.2 (d, J=97.7 Hz) (*39.5 (d, J=96.5 Hz)), 17.6, 12.1 (d, J=3.7 Hz) (*12.6 (d, J=3.7 Hz)); δ_P ($CDCl_3$, 202 MHz) (*minor isomer) 45.6 (*45.5); ν_{max} (neat, cm^{-1}) 1228; *m/z* (CI^+, NH_3) 251.2 ($M+H^+$); HRMS calcd for $C_{14}H_{21}O_2P$ ($M+H^+$) 251.1201, found 251.1205.

2-(Methyl)allylphenyl-phosphinic acid 2-(methyl)allyl ester 7f. Same procedure as for **7c** with 1.36 ml (16.16 mmol) of 2-methyl-2-propen-1-ol, 1.31 ml (16.2 mmol) of pyridine, 30 ml Et_2O, 1 ml (7.4 mmol) of dichlorophenylphosphine; yield: 0.6 g (31%); R_f=0.5 (hexane:EtOAc, 2:3); δ_H ($CDCl_3$, 400 MHz) 7.77–7.72 (m, 2H), 7.53–7.49 (m, 1H), 7.46–7.41 (m, 2H), 4.98 (s, 1H), 4.87 (s, 1H), 4.83–4.81 (m, 1H), 4.64 (d, 1H, J=5.2 Hz), 4.64 (dd, 2H, J=12.4, 5.2 Hz), 4.27 (dd, 2H, J_{AB}=12.4, 6.0 Hz), 2.82–2.68 (m, 2H), 1.77 (t, 3H, J=1.4 Hz), 1.71 (s, 3H); δ_C ($CDCl_3$, 101 MHz) 141.0 (d, J=7.3 Hz), 136.3 (d, J=9.6 Hz), 132.8 (d, J=1.7 Hz), 132.4 (d, J=9.6 Hz), 130.7 (d, J=124.4 Hz), 129.0 (d, J=12.6 Hz), 116.5 (d, J=11.0 Hz), 113.3, 68.1 (d, J=6.3 Hz), 40.1 (d, J=95.6 Hz), 24.6, 19.7; δ_P ($CDCl_3$, 202 MHz) 42.1; ν_{max} (neat, cm^{-1}) 1648, 1230, 1007; *m/z* (CI^+, NH_3) 251.2 ($M+H^+$); HRMS calcd for $C_{14}H_{20}O_2P$ ($M+H^+$) 251.1201, found 251.1203.

Allylphenylphosphinic acid 2-(methyl)allyl ester 7g. To a solution of 0.5 g of allylphenylphosphinic acid in CH_2Cl_2 (5 ml) was added PCl_5 (0.53 g). The mixture was stirred at room temperature for 24 h. The solvent was removed under reduced pressure and the residue was placed at the vacuum pump for 15 min. To a solution of the crude phosphinic acid chloride (0.3 g) at 0°C in CH_2Cl_2 (10 ml) was then added dropwise a catalytic amount of DMAP, Et_3N (0.42 ml, 3 mmol) and 2-methyl allylic alcohol (0.25 ml, 3 mmol). The mixture was stirred for 72 h. The solvent was removed under reduced pressure and the crude product purified by column chromatography; yield: 80 mg (39%); R_f=0.4 (EtOAc); δ_H ($CDCl_3$, 400 MHz) 7.81–7.76 (m, 2H), 7.597.55 (m,1H), 7.51–7.46 (m, 2H), 5.83–5.71 (m,1H), 5.17–5.06 (m,2H), 5.02 (d, 1H, J=1.2 Hz), 4.92 (d, 1H, J=1.2 Hz), 4.47 (dd, 1H, J=12.6, 6.3 Hz), 4.19 (dd, 1H, J=12.6, 6.6 Hz), 2.82 (dd, J=7.6, 16.8 Hz), 1.75 (s, 3H); δ_C ($CDCl_3$, 101 MHz) 140.4 (d, J=7.2 Hz), 132.4 (d,

J=2.6 Hz), 131.8 (d, J=9.7 Hz), 129.9 (d, J=125.2 Hz), 128.5 (d, J=12.6 Hz), 127.0 (d, J=13.2 Hz), 112.7, 67.6 (d, J=6.3 Hz), 35.9 (d, J=97.1 Hz), 19.1; δ_P ($CDCl_3$, 202 MHz) 42.14; ν_{max} (neat, cm^{-1}) 1648, 1230, 1007; HRMS calcd for $C_{13}H_{18}O_2P$ ($M+H^+$) 237.1044, found 237.1045.

Allylphenylphosphinic acid allyl amide 7h. Same procedure as for **7g** with 0.5 g of allylphenylphosphinic acid, 5 ml of CH_2Cl_2, 0.53 g of PCl_5 then 1.07 ml (7.6 mmol) of Et_3N, 0.57 ml (7.65 mmol) of allylamine; yield: 232 mg (38%); R_f=0.6 (10% MeOH in EtOAc); δ_H ($CDCl_3$, 500 MHz) 7.87–7.80 (m,2H), 7.56–7.42 (m,3H), 5.93–5.77 (m,2H), 5.24–5.06 (m,4H), 3.57 (m,1H), 3.44 (m, 1H) 2.87 (br s,1H), 2.85–2.70 (m,2H); δ_C ($CDCl_3$, 126 MHz) 136.2 (d, J=8.4 Hz), 132.3 (d, J=8.6 Hz), 132.0 (d, J=3.4 Hz), 130.9 (d, J=125.1 Hz),128.5 (d, J=13.1 Hz), 128.3 (d, J=9.6 Hz), 120.1 (d, J=12.4 Hz), 115.8, 42.7, 36.6 (d, J=87.7 Hz); δ_P ($CDCl_3$, 202 MHz) 31.1; ν_{max} (neat, cm^{-1}) 3187, 1638, 1176; m/z (CI^+, NH_3) 222.1 ($M+H^+$); HRMS calcd for $C_{12}H_{17}ONP$ ($M+H^+$) 222.1048, found 222.1041.

Allylphenylphosphinic acid 1-(phenyl)allyl amide 7i. 0.5 g of allylphenylphosphinic acid, 5 ml CH_2Cl_2, 0.53 g of PCl_5 then 1.07 ml (7.6 mmol) of Et_3N, 1.02 g (7.66 mmol) 1-(phenyl)allylamine; yield (mixture of two diastereomers A and B, ratio 1:1): 270 mg (33%); R_f=0.6 (10% MeOH in EtOAc); δ_H ($CDCl_3$, 400MHz) (mixture of two diastereomers A and B, ratio 1:1) 7.86–7.67 (m, 2H), 7.57–7.16 (m, 8H), 6.12–6.05 (m, 1H), 6.00–5.70 (m, 1H), 5.27–5.07 (m, 4H), 4.79–4.74 (m, 1H), 3.33–3.24 (m, 1H), 2.79 (dd, 2H, J=7.6, 17.2, dia A or B), 2.73 (dd, 2H, J=7.6, 17.4, A or B); δ_C ($CDCl_3$, 101 MHz) (mixture of two diastereomers) 142.0, 141.9, 140.1, 140.1, 139.6, 132.3, 132.2, 131.9, 131.8, 130.6, 128.6, 128.5, 128.4, 128.3, 128.2, 127.4, 127.4, 127.0, 120.2 (d, J=12.3 Hz), 115.6, 56.7, 36.9 (d, J=87.6 Hz, A or B), 36.7 (d, J=88.0 Hz, A or B); δ_P ($CDCl_3$, 202 MHz) 29.9; ν_{max} ($CHCl_3$, cm^{-1}) 3019, 1222; m/z (CI^+, NH_3) 298.2 ($M+H^+$); HRMS calcd for $C_{18}H_{21}NOP$ ($M+H^+$) 298.1361, found 298.1371.

Diallyl phosphinic acid benzyl amide 7j. To a solution of diallyl phosphinic acid (0.4 g, 2.74 mmol) and a catalytic amount of DMF in CH_2Cl_2 (10 ml) at 0°C was added oxalyl chloride (0.7 ml, 8.02 mmol). After addition, the mixture was allowed to warm to room temperature and was stirred for 1 h. The solvent was removed under reduced pressure and the crude acid chloride was used without purification in the next step. To a solution of the crude phosphinic acid chloride, a catalytic amount of DMAP and Et_3N (1.9 ml, 13.6 mmol) in CH_2Cl_2 (15 ml) at 0°C was added the benzylamine (1.5 ml, 13.7 mmol). The mixture was allowed to warm to room temperature and was stirred for 72 h. The solvent was removed under reduced pressure and the residue was treated with Et_2O (10 ml). After filtration of the salts, the residue was purified by column chromatography; yield: 0.5 g (79%); R_f=0.4 (5% MeOH in EtOAc); δ_H ($CDCl_3$, 400 MHz) 7.35–7.26 (m, 5H), 5.91–5.79 (m, 2H), 5.25–4.17 (m, 4H), 4.21–4.17 (m, 2H), 2.74 (br s, 1H), 2.66 (dd, 4H, J=15.9, 7.5 Hz); δ_C ($CDCl_3$, 101 MHz) 139.7, 128.7, 128.3 (d, J=8.9 Hz), 127.5 (d, J=6.9 Hz), 120.3 (d, J=12.2 Hz), 43.8, 34.4 (d, J=83.8 Hz); δ_P ($CDCl_3$, 202 MHz) 38.1; ν_{max} (neat, cm^{-1}) 3182, 1637, 1226; m/z (CI^+, NH_3) 258.1 ($M+H^+$).

Diallyl phosphinic acid (*S*)-2-(methoxycarbonyl)pyrrolidyl amide 7k. Same procedure as for **7j** with 0.5 g (3.42 mmol) of diallyl phosphinic acid, a catalytic amount of DMF, 20 ml of CH_2Cl_2, 0.9 ml (10.32 mmol) of oxalyl chloride then a catalytic amount of DMAP, 1.43 ml (10.26 mmol) of Et_3N, 20 ml of CH_2Cl_2, 1.7 g (10.26 mmol) of the hydrochloride salt of L-proline methyl ester; yield: 0.4 g (41%); R_f=0.4 (10% MeOH in EtOAc); δ_H ($CDCl_3$, 400 MHz) 5.95–5.80 (m, 2H), 5.25–5.17 (m, 4H), 4.39–4.34 (m, 1H), 3.71 (s, 3H), 3.33–3.29 (m, 2H), 2.74–2.61 (m, 4H), 2.16–2.09 (m, 2H), 2.06–1.85 (m, 2H); δ_C ($CDCl_3$, 101 MHz) 174.6, 128.4 (d, J=8.6 Hz), 128.0 (d, J=9.1 Hz), 120.0 (d, J=10.9 Hz), 59.0, 52.1, 46.8, 34.7 (d, J=82.4 Hz), 33.3 (d, J=82.7 Hz), 31.1 (d, J=5.5 Hz), 25.2 (d, J=6.1 Hz); δ_P ($CDCl_3$, 202 MHz) 40.7; ν_{max} (neat, cm^{-1}) 1743, 1637, 1210, 920; m/z (CI^+, NH_3) 258.1 ($M+H^+$); HRMS calcd for $C_{12}H_{21}$ NO_3P ($M+H^+$) 258.1259, found 258.1256.

General procedure for ring-closing metathesis reactions

To a solution of the diene **7a–k** in dry CH_2Cl_2 (0.02 M) was added portionwise (2 mol%) the Grubbs' catalyst. The reaction was refluxed until maximum conversion as shown by TLC or ^1H NMR. The reaction was then concentrated and purified by column chromatography.

2-Phenyl-4,7-dihydro-[1,3,2]dioxaphosphepine 2-oxide 9a. 100 mg (0.4 mmol) of **7a**, 20 ml of CH_2Cl_2, catalyst (42 mg, 12%), 5 d; yield: 31 mg (34%); R_f=0.2 (hexane: EtOAc, 1:1); δ_H ($CDCl_3$, 400 MHz) 7.90–7.85 (m, 2H), 7.62–7.57 (m, 1H), 7.52–7.47 (m, 2H), 5.81 (t, 2H, J=1.8 Hz), 4.88 (dd, 2H, J_{AB}=15.8 Hz), 4.59 (dd, 2H, J_{AB}=15.5 Hz); δ_C ($CDCl_3$, 101 MHz) 132.8 (d, J=2.9 Hz), 131.6 (d, J=9.7 Hz), 128.6 (d, J=15.2 Hz) 127.5, 63.6 (d, J=6.7 Hz); δ_P ($CDCl_3$, 202 MHz) 24.5; ν_{max} (neat, cm^{-1}) 1256; m/z (CI^+, NH_3) 211.0 ($M+H^+$); HRMS calcd for $C_{10}H_{12}O_3P$ ($M+H^+$) 211.0524, found 211.0527.

2-Phenyl-1,3,4,7-tetrahydro-[1,3,2]diazaphosphepine 2-oxide 9b. 77 mg (0.3 mmol) of **7b**, 17 ml of CH_2Cl_2, catalyst (18 mg, 6%), 3 d; yield: 24 mg (36%); R_f=0.2 (5% MeOH in EtOAc); δ_H ($CDCl_3$, 500 MHz) 7.95–7.91 (m, 2H), 7.58–7.55 (m, 1H), 7.51–7.47 (m, 2H), 5.70 (t, 2H, J=2.2 Hz), 3.91 (m, 2H), 3.67 (m, 2H), 3.29 (br, 2H); δ_C ($CDCl_3$, 126 MHz) 131.8, 131.2 (d, J=9.2 Hz), 128.9, 128.5 (d, J=13.1 Hz), 39.5; δ_P ($CDCl_3$, 202 MHz) 26.0; ν_{max} ($CHCl_3$, cm^{-1}) 3019, 1520, 1210; m/z (CI^+, NH_3) 209.0 ($M+H^+$); HRMS calcd for $C_{10}H_{14}$ N_2OP ($M+H^+$) 209.0844, found 209.0839.

2-Phenyl-3,6-dihydro-[1,2]oxaphosphinine 2-oxide 9c. 100 mg (0.5 mmol) of **7c**, 20 ml of CH_2Cl_2, catalyst (14 mg, 4%), 16 h; yield: 80 mg (92%); R_f=0.3 (3% MeOH in EtOAc); δ_H ($CDCl_3$, 500 MHz) 7.85–7.81 (m, 2H), 7.59–7.56 (m, 1H), 7.51–7.47 (m, 2H), 5.96–5.85 (m, 2H), 5.06–4.99 (m, 1H), 4.76–4.69 (m, 1H), 2.75–2.57 (m, 2H); δ_C ($CDCl_3$, 126 MHz) 132.6, 131.0 (d, J=135.6 Hz), 130.9 (d, J=10.6 Hz), 128.6 (d, J=13.2 Hz), 126.2 (d,

J=16.4 Hz), 120.5 (d, J=9.0 Hz), 66.1 (d, J=7.2 Hz), 25.3 (d, J=89.8 Hz); δ_P (CDCl$_3$, 202 MHz) 32.1; ν_{max} (neat, cm^{-1}) 1227, 1068; *m/z* (CI$^+$, NH$_3$) 195.0 (M+H$^+$); HRMS calcd for C$_{10}$H$_{12}$O$_2$P (M+H$^+$) 195.0575, found 195.0575.

2-Phenyl-6-methyl-3,6-dihydro-[1,2]oxaphosphinine 2-oxide 9d. 120 mg (0.5 mmol) of **7d**, 20 ml of CH$_2$Cl$_2$, catalyst (28 mg, 8%), 21 h; two diastereomers A and B (ratio 1:1); yield: 84 mg (84%); R_f=0.2 (EtOAc); δ_H (CDCl$_3$, 400 MHz) 7.83–7.73 (m, 2H), 7.55–7.49 (m, 1H), 7.46–7.41 (m, 2H), 5.89–5.72 (m, 2H), 5.25–5.14 (m, 1H, A or B), 4.88–4.81 (m, 1H, A or B), 2.67–2.41 (m, 2H), 1.51 (d, 3H, J=6.7 Hz, A or B), 1.44 (d, 3H, J=6.8, A or B); δ_C (CDCL$_3$, 101 MHz) 132.5 (d, J=2.4 Hz, A or B), 132.4 (d, J=2.4 Hz, A or B), 132.0, 131.4 (d, J=13.7 Hz, A or B), 131.2 (d, J=10.3 Hz, A or B), 130.8, 130.5 (d, J=10.1 Hz), 128.6 (d, J=6.8 Hz, A or B), 128.5 (d, J=7.1 Hz, A or B), 120.1 (d, J=9.2 Hz, A or B), 119.5 (d, J=8.3 Hz, A or B), 75.7 (d, J=8.2 Hz, A or B), 71.6 (d, J=7.1 Hz, A or B), 25.2 (d, J=90.5 Hz, A or B), 24.3 (d, J=90.2 Hz, A or B), 22.6 (d, J=3.6 Hz, A or B), 22.1 (d, J=7.2 Hz, A or B); δ_P (CDCl$_3$, 202 MHz) 32.9 (A or B), 31.1 (A or B); ν_{max} (neat, cm^{-1}) 1226; *m/z* (CI$^+$, NH$_3$) 209.1 (M+H$^+$), 417.1 (2M+H$^+$); HRMS calcd for C$_{11}$H$_{14}$O$_2$P (M+H$^+$) 209.0731, found 209.0732.

2-Phenyl-3-methyl-3,6-dihydro-[1,2]oxaphosphinine 2-oxide 9e. 100 mg (0.4 mmol) of diene **7e**, 20 ml of CH$_2$Cl$_2$, catalyst (26 mg, 8%); yield: 79 mg (95%); less polar diastereomer: R_f=0.3 (2% MeOH in AcOEt); δ_H (CDCl$_3$, 250 MHz) 7.91–7.82 (m, 2H), 7.63–7.46 (m, 3H), 5.86–5.64 (m, 2H), 5.05–4.94 (m, 1H), 4.75 (m, 1H), 2.75 (m, 1H), 1.30 (dd, J=7.45, 16.8 Hz); δ_C (CDCL$_3$, 62.9 MHz) 133.0, 131.9 (d, J=9.9 Hz), 130.4 (d, J=133.7 Hz), 128.97 (d, J=12.8 Hz), 127.96 (d, J=8.1 Hz), 125.3 (d, J=15.2 Hz), 66.1 (d, J=6.9 Hz), 29.4 (d, J=91.5 Hz), 14.4; δ_P (CDCl$_3$, 202 MHz) 36.2 ν_{max} (neat, cm^{-1}) 1226; more polar diastereomer: R_f=0.23 (2% MeOH in AcOEt); δ_H (CDCl$_3$, 250 MHz) 7.86–7.76 (m, 2H), 7.59–7.42 (m, 3H), 5.94–5.77 (m, 2H), 5.08–4.95 (m, 1H), 4.85–4.70 (m, 1H), 2.65 (m, 1H), 1.00 (dd, J=7.48, 18.9 Hz); δ_C (CDCL$_3$, 62.9 MHz) 132.8, 132.3 (d, J=9.4 Hz), 129.4 (d, J=133.0 Hz), 129.0 (d, J=13.5 Hz), 128.7 (d, J=6.2 Hz), 125.5 (d, J=15.0 Hz), 66.6 (d, J=7.3 Hz), 30.7 (d, J=89.4 Hz), 16.7; δ_P (CDCl$_3$, 202 MHz) 38.3; ν_{max} (neat, cm^{-1}) 1226; HRMS calcd for C$_{11}$H$_{14}$O$_2$P (M+H$^+$) 209.0730, found 209.0731.

2-Phenyl-4,5-dimethyl-3,6-dihydro-[1,2]oxaphosphinine 2-oxide 9f. 50 mg (0.2 mmol) of diene **7f**, 10 ml of CH$_2$Cl$_2$, catalyst (9 mg, 6%), 5 d; yield: 0% (100% recovered diene **7f**).

2-Phenyl-5-methyl-3,6-dihydro-[1,2]oxaphosphinine 2-oxide 9g. 75 mg (0.32 mmol) of diene **7g**, 15 ml of CH$_2$Cl$_2$, catalyst (25 mg, 10%), 3 d; yield: 21 mg (31%); R_f=0.16 (AcOEt); δ_H (CDCl$_3$, 400 MHz) 7.86–7.80 (m, 2H), 7.59–7.55 (m, 1H), 7.51–7.47 (m, 2H), 5.60 (dxm, J=23.2 Hz, 2H), 4.90–4.85 (m, 1H), 4.58–4.50 (m, 1H), 2.66–2.56 (m, 2H), 1.72 (s, 3H); δ_C (CDCl$_3$, 100.6 MHz) 133.0 (d, J=15.3 Hz), 132.5, 130.9 (d, J=11.4 Hz), 130.8 (d, J=135.7 Hz), 128.6 (d, J=13.0 Hz), 114.9 (d, J=9.2 Hz), 68.7 (d, J=11.5 Hz), 25.0 (d, J=86.1 Hz), 19.3; δ_P (CDCl$_3$, 202 MHz) 32.3; ν_{max} (neat, cm^{-1}) 1227, 1068; *m/z* (CI$^+$, NH$_3$) 195.0 (M+H$^+$); HRMS calcd for C$_{11}$H$_{14}$O$_2$P (M+H$^+$) 209.0730, found 209.0731.

2-Phenyl-3,6-dihydro-1H-[1,2]azaphosphinine 2-oxide 9h. 65 mg (0.3 mmol) of diene **7h**, 15 ml of CH$_2$Cl$_2$, catalyst (7.5 mg, 3%), 18 h; yield: 46.6 mg (85%); R_f=0.3 (10% MeOH in EtOAc); δ_H (CDCl$_3$, 500 MHz) 7.86–7.80 (m, 2H), 7.55–7.51 (m, 1H), 7.48–7.43 (m, 2H), 5.86–5.76 (m, 2H), 4.15–3.82 (m, 1H), 3.89–3.82 (m, 1H), 2.99 (br, 1H), 2.72–2.52 (m, 2H); δ_C (CDCl$_3$, 126 MHz) 133.7 (d, J=123.6 Hz), 131.9 (d, J=3.3 Hz), 131.2 (d, J=9.4 Hz), 128.5 (d, J=12.4 Hz), 126.3 (d, J=16.0 Hz), 119.9 (d, J=9.4 Hz), 43.2 (d, J=3.8 Hz), 26.8 (d, J=88.9 Hz); δ_P (CDCl$_3$, 202 MHz) 21.5; ν_{max} (CHCl$_3$, cm^{-1}) 3019, 1520, 1220; *m/z* (CI$^+$, NH$_3$) 194.1 (M+H$^+$); HRMS calcd for C$_{10}$H$_{13}$NOP (M+H$^+$) 194.0735, found 194.0736.

2,6-Diphenyl-3,6-dihydro-1H-[1,2]-azaphosphinine 2-oxide 9i. 100 mg (0.3 mmol) of **7i**, 20 ml of CH$_2$Cl$_2$, catalyst (22 mg, 8%), 24 h; yield: 57 mg (63%); R_f=0.4 (EtOAc); δ_H (CDCl$_3$, 400 MHz) 7.91–7.86 (m, 2H), 7.56–7.47 (m, 4H), 7.39–7.35 (m, 2H), 7.31–7.27 (m, 2H), 5.06–5.05 (m, 1H), 3.15 (s, 1H), 2.76–2.72 (m, 2H), 5.87–5.77 (m, 2H); δ_c (CDCl$_3$, 101 MHz) 142.5, 131.9, 130.9, 130.7, 128.9, 128.5 (d, J=12.5 Hz), 128.0, 127.0, 118.7 (d, J=8.2 Hz), 59.8 (d, J=3.1 Hz), 26.4 (d, J=88.6 Hz); δ_P (CDCl$_3$, 202 MHz) 21.2; ν_{max} (CHCl$_3$, cm^{-1}) 3020, 1522, 1210; *m/z* (CI$^+$, NH$_3$) 270.1 (M+H$^+$), 539.1 (2M+H$^+$); HRMS calcd for C$_{16}$H$_{17}$NOP (M+H$^+$) 270.1048, found 270.1042.

1-Benzylamino-3-phospholene 1-oxide 9j.[23] 100 mg (0.43 mmol) of **7j**, 20 ml of CH$_2$Cl$_2$, catalyst (21 mg, 6%), 2 d; two rotamers A and B (ratio 2:1); yield: 38 mg (43%); R_f=0.1 (5% MeOH in EtOAc); δ_H (CDCl$_3$, 400 MHz) 7.36–7.27 (m, 5H), 5.92 (d, 2H, J=31.7 Hz, A), 5.78 (d, 2H, J=30.4 Hz, B), 4.18 (d, 2H, J=9.2 Hz), 3.92 (s, 2H, B), 2.45 (dAB, 4H, J=12.0 Hz, J_{AB}=17.2 and 17.9 Hz, A), 2.02 (d, 4H, J=12.7 Hz, B); δ_C (CDCl$_3$, 126 MHz) 134.1, 128.8 (d, J=8.9 Hz), 128.6 (d, J=21.9 Hz), 127.6, 127.5 (d, J=14.9 Hz), 44.4 (s, A or B), 43.0 (s, A or B), 30.8 (d, J=84.3 Hz), 29.7; δ_P (CDCl$_3$, 202 MHz) 64.2, 63.7; ν_{max} (CHCl$_3$, cm^{-1}) 3019, 1217; *m/z* (CI$^+$, NH$_3$) 208.1 (M+H$^+$).

1-[(*S*)-2-(methoxycarbonyl)pyrrolidino]-3-phospholene 1-oxide 9k. 100 mg (0.4 mmol) of diene **7k**, 20 ml of CH$_2$Cl$_2$, catalyst (21 mg, 6%), 4 d; yield: 71 mg (80%); R$_f$=0.3 (10% MeOH in EtOAc); δ_H (CDCl$_3$, 400 MHz) 6.00–5.84 (m, 2H), 4.37 (dt, 1H, J=3.2, 8.4 Hz), 3.70 (s, 3H), 3.13 (td, 2H, J=6.8, 3.2 Hz), 2.68–2.60 (m, 1H), 2.44 (d, 3H, J=12.4 Hz), 2.21–2.02 (m, 2H), 1.97–1.89 (m, 2H); δ_C (CDCl$_3$, 101 MHz) 174.6, 127.7 (d, J=14.7 Hz), 126.7 (d, J=15.0 Hz), 59.4 (d, J=2.3 Hz), 52.1, 46.4 (d, J=3.9 Hz), 30.9 (d, J=6.4 Hz), 29.7 (d, J=82.1 Hz), 29.6 (d, J=83.6 Hz), 25.1 (d, J=6.8 Hz); δ_P (CDCl$_3$, 202 MHz) 65.6; ν_{max} (neat, cm^{-1}) 1741, 1613; *m/z* (CI$^+$, NH$_3$) 230.1 (M+H$^+$); HRMS calcd for C$_{10}$H$_{16}$NO$_3$P (M+H$^+$) 230.0946, found 230.0944.

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