Stereoselective inverse conjugate addition of nitrogen and carbon nucleophiles to allenyl phosphine oxide. Synthesis of α,β-unsaturated phosphine oxides

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Dedicated to Professor Paweł Kafarski to honor the achievements within his career

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Abstract

The reactivity of new three carbon synthon, generated *in situ* from the reaction of electron-deficient allenes with an appropriate phosphine as the catalyst, toward pronucleophilic reagents is described. Triphenylphosphine-catalyzed reaction of allenes derived from phosphine oxides with nitrogen- or carbonucleophiles gave the γ-addition product as a mixture of *cis* and *trans* isomers.

Keywords: Allenyl phosphine oxide, phosphine catalysis, pronucleophiles, umpolung addition, α,β-unsaturated phosphine oxides

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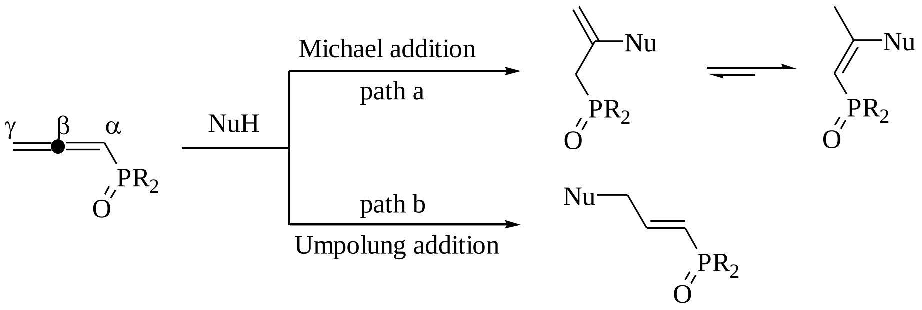
Introduction

In recent years, electron-deficient allenes have emerged as attractive electrophiles for various synthetic purposes.[1] Normally, addition of nucleophiles to electron-deficient allenes occurs at the electrophilic α,β-carbon–carbon double bond to give Michael-type adducts[2] (path a in Scheme 1). However, inverse conjugate addition (umpolung reaction) can be achieved in the presence of phosphines, taking place at the relatively electron-rich nucleophilic β,γ-carbon–carbon double bond (path b in Scheme 1).



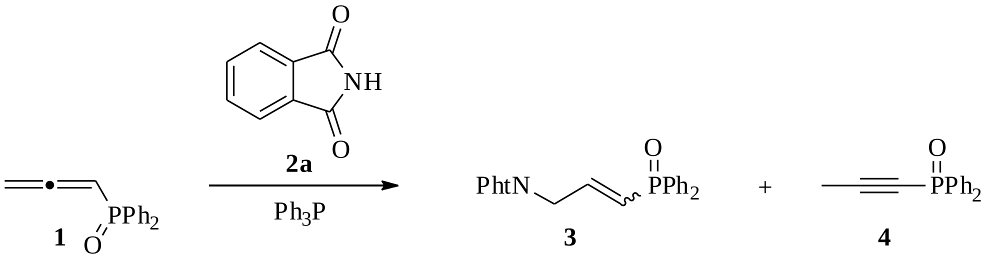
Scheme 1. Reactivity pattern of allenes.

Cristau *et al*.[3] first demonstrated the γ-umpolung addition of nucleophiles to activated allenes by multistep transformations and since the first report by Trost *et al.* on phosphine-catalyzed γ-addition of nucleophiles to 2-alkynoates,[4] there has been increasing interest in phosphine-catalyzed γ-umpolung additions of pronucleophiles to electron-deficient alkynes and allenes,[5] and has proven to be a powerful tool in organic synthesis, which can provide easy access to acyclic, carbocycles and heterocycles. With regard to asymmetric catalysis of the γ-addition of pronucleophiles to 2,3-butadienoates using chiral phosphines as catalysts for the generation of a γ-stereocenter, only a few successes have been reported.[6,7]

Taking into account our interest in the synthesis of allenes and their use as building blocks in organic synthesis,[8] we have recently describe the first approach for the construction of tertiary and quaternary stereocenters *via* stereoselective γ-addition of carbonucleophiles to allenes bearing a chiral auxiliary.[9] However, as far as we know no examples of phosphine-catalyzed reaction of phosphorated allenes have been reported. Therefore, in connection with our interest in the reactivity of phosphorated allenes as intermediates in organic synthesis, here, we wish to report our recent results of the reaction of allenes bearing a phosphine oxide group in the phosphine-catalyzed reaction leading to functionalized α,β-unsaturated phosphine oxides.

Results and Discussion

Initially, the effect of solvent and temperature on the umpolung reaction of allenyl phosphine oxide **1** with nitrogen nucleophiles was studied. It has been previously observed that the selection of the appropriated temperature, solvent and phosphine stoichiometry is important to optimize this umpolung reaction.[6b] Therefore, the γ-addition of phthalimide **2a** to allene **1** leading to compound **3** was carried out under different reaction conditions (Scheme 2, Table 1, entries 1–5). First, the reaction of allene **1** with phthalimide **2a** was conducted in the presence of Ph_3P and CH_2Cl_2 as solvent at room temperature (entry 1). Under these conditions no reaction was observed and compound **4**, corresponding to the isomerized starting material was recovered. Similar results have been detected in this reaction, using the same catalyst in toluene as solvent at room temperature (Table 1, entry 2). However, the umpolung addition using PPh_3 as the catalyst in toluene at 85 ºC, produced the desired γ-addition product **3** in moderate yield (56%) as a mixture of *cis* and *trans* isomers, accompanied by the minor product alkyne **4** (23%), corresponding to the isomerized starting allene **1**, in a **3**:**4** ratio of 2.4/1. Interestingly, higher temperatures and nucleophile loading provided a mixture of **3**:**4** ratio of 4.4/1, or the functionalized alkene **3** as the major product in 72% yield along with 13% of alkyne **4** in a **3**:**4** ratio of 5.5/1(Table 1, entries 4 and 5, respectively).



Scheme 2. Phthalimide **2a** in umpolung addition to phosphorated allene **1**.

Compound **3** was characterized on the basis of its spectroscopic data, which indicate that it is isolated as a mixture of *cis* and *trans* substituted alkenes for the triphenylphosphine-catalyzed reaction. Thus, the ^{31}P NMR spectrum for **3** showed two different absorptions at δ_P 23.0 and 23.5 ppm, in which the high-field chemical shift corresponds to the *cis* isomer of **3**. Both *cis* and *trans* isomers of compound **3** could be assigned based on vicinal carbon-phosphorus coupling constant ($^3J_{PC}$). Therefore, the ^{13}C NMR spectrum shows an absorption at δ_C 40.0 ppm as a doublet with coupling constant ($^3J_{PC}$ = 19 Hz) assignable to the methylene group directly bonded to the nitrogen atom of *trans*-**3**. This coupling constant indicate that the methylene group and the phosphorus atom are related *trans*.[2a,10] Conversely, in the ^{13}C NMR spectrum of *cis*-**3** the absorption of the methylene group is shifted to higher field (δ_C 37.6 ppm) with a lower value of coupling constant ($^3J_{PC}$ = 7.6 Hz)[2a,10] relative to those of *cis* isomer.

Table 1. γ-Addition of phthalimide **2a** to allenyl phosphine oxide **1**

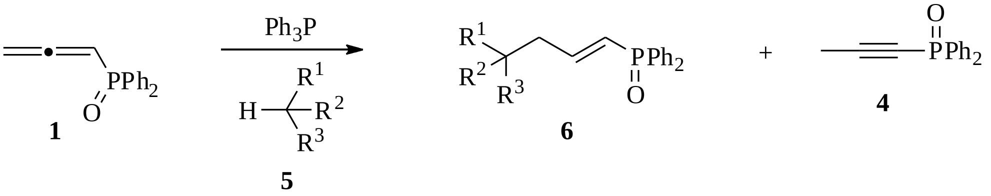
Entry	NuH equiv	Conditions	Product	**3/4** Ratio[a]
1	1	Ph_3P (10 mol%), CH_2Cl_2, rt, 72 h	**4**	n.r.
2	1	Ph_3P (10 mol%), toluene, rt, 72 h	**4**	n.r.
3	1	Ph_3P (10 mol%), toluene, 85 ºC, 48 h	**3***Z* + **3***E*	2.4/1
4	1.5	Ph_3P (10 mol%), toluene, 110 ºC, 48 h	**3***Z* + **3***E*	4.4/1
5	3	Ph_3P (10 mol%), toluene, 110 ºC, 48 h	**3***Z* + **3***E*	5.5/1

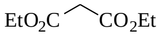
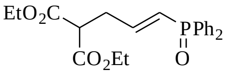
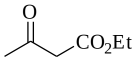
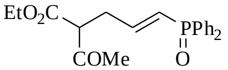
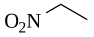
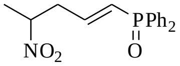
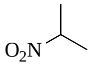
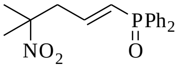
[a] **3/4** Ratio was calculated by ^{1}H NMR spectrum on the crude reaction mixture.

The umpolung reaction of allene **1** with other nitrogen nucleophiles, such as *p*-toluidine (**2b**), phenylhydrazine (**2c**), or tosylhydrazide (**2d**) was explored. Nevertheless, phosphine-catalysed γ-addition reaction of nucleophiles **2b**–**d** to allene **1** failed to give the corresponding phosphorus-substituted alkenes, and only the Michael adducts were observed. Neither the use of additives (NaOAc/AcOH) nor the increase of phosphine stoichiometry led to the γ-addition products.

We extend the study the umpolung addition reaction into phosphorated allene **1** to other nucleophiles, such as carbonucleophiles. The behaviour of allenyl phosphine oxide **1** toward carbonucleophiles such as diethyl malonate (**5a**), ethyl acetoacetate (**5b**), nitroethane (**5c**), or 2-nitropropane (**5d**) was examined (Table 2, entries 1–4). Additives play important roles in this C–C bond-forming umpolung reaction.[6b] Table 2 summaries some experimental results with **1**, the carbonucleophile and the phosphine catalyst, leading to compounds of the general structure **6** bearing a new tertiary or quaternary centre, under different reaction conditions. The γ-addition of diethyl malonate (**5a**) to allene **1** in the presence of 10 mol% of triphenylphosphine and additives (AcOH) gave the desired product **6a** as a mixture of *cis*/*trans*-isomers, accompanied by the minor product alkyne **4**, (entry 1). Surprisingly, exclusively a *trans*-selectivity was obtained when the reaction was performed with ethyl acetoacetate (**5b**) as the nucleophile in the presence of triphenylphosphine (entry 2).

Table 2. Umpolung addition of carbonucleophiles to allenyl phosphine oxide **1**



Entry	NuH	Conditions	Product	**6**/**4** Ratio[a]	Yield[b] (*cis*/*trans*)[a]
1	 **5a**	Ph_3P (10 mol%) / AcOH (20%) / toluene, Δ	 **6a**	2.6/1	50 (1.2/1)
2	 **5b**	Ph_3P (10 mol%) / AcOH (20%) / toluene, Δ	 **6b**	1.2/1	47 (*trans*)
3	 **5c**	Ph_3P (10 mol%) / AcOH (20%) / toluene, Δ	 **6c**	2.7/1	42 (2.7/1)
4	 **5d**	Ph_3P (10 mol%) / AcOH (20%) / toluene, Δ	 **6d**	1/1	51 (1.6/1)

[a]Determined by ^1H NMR spectrum on the crude reaction mixture. [b]Yield of isolated compounds after purification.

Moderate *cis* selectivity has been observed in the reaction of allene **1** using pronucleophile nitroethane (**5c**) or 2-nitropropane (**5d**) carried out in refluxing toluene in the presence of 10 mol% of triphenylphosphine. The desired γ-addition products **6c** and **6d** were obtained in moderate yield along with alkyne **4** corresponding to the isomerized starting allene **1** (see Table 2, entries 3 and 4).

Conclusions

We have described the first example of umpolung reaction of nitrogen and carbonucleophiles with allenes bearing a phosphine oxide group catalysed by triphenylphosphine. This reaction started from readily available materials under mild reaction conditions to afford functionalized alkene derivatives. Triphenylphosphine-catalyzed umpolung reaction gave the γ-addition products as a mixture of *cis* and *trans* isomers, while the addition of ethyl acetoacetate (**5b**) afforded the corresponding γ-addition product stereoselectively with a *trans* stereochemistry.

Experimental Section

General. All reagents were purchased from Aldrich and used without further purification. Solvents for extraction and chromatography were of technical grade. All solvents used in reactions were freshly distilled. All other reagents were recrystallized or distilled as necessary. All reactions were performed under an atmosphere of dry nitrogen. Melting points were determined with an Electrothermal IA9100 digital apparatus and are uncorrected. Infrared (IR-FT) spectra were taken on a Nicolet FTIR Magna 550 spectrometer, and were obtained as solids in KBr or as neat oils in NaCl. Peaks are reported in cm^{-1}. Low-resolution mass spectra (MS) were obtained on a Hewlett Packard 5971 MSD Series spectrometer at 50–70 eV by electron impact (EI) or on a Hewlett Packard 1100 MSD Series spectrometer by chemical ionization (CI). Data are reported in the form *m/z* (intensity relative to base peak = 100) and high resolution mass spectra (HRMS) was measured on a MAT95S mass spectrometer by EI method.
^{1}H (300, 400 MHz), ^{13}C (75, 100 MHz) and ^{31}P NMR (120 MHz) spectra were recorded on a Varian Unity Plus 300 MHz or Bruker Avance 400 MHz spectrometers, respectively, in $CDCl_3$. All coupling constants (J) values are given in Hz. Chemical shifts (δ) are reported in parts per million (ppm), relative to $CDCl_3$, as internal standard in a broad band decoupled mode. The abbreviations used are as follows: s, singlet; d, doublet; t, triplet; q, quartet, m, multiplet. Flash-column chromatography was performed using commercial grades of silica gel finer than 230 mesh. Analytical thin layer chromatography was performed on pre-coated Merck silica gel 60 F_{254} plates, and spot visualization was accomplished by UV light (254 nm) or $KMnO_4$ solution. The starting materials such as allenyl phosphine oxide **1**, was prepared according to the literature procedures.[11]

General procedure for the preparation of γ-addition products through phosphine catalyzed umpolung reaction of allene 1 with nitrogen nucleophiles (Table 1)

To a stirred solution of phthalimide (**2a**) (1.76 g, 12 mmol) and triphenylphosphine (10 mol%) in dry toluene (5 mL) was added a solution of allene **1** (0.96 g, 4 mmol) in dry toluene (13 mL) under a N_2 atmosphere. The mixture was stirred for 48 h. under reflux. The crude reaction mixture was washed with water (3 × 15 mL) and the aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL). The organic layer was dried over anhydrous $MgSO_4$, the solvent was evaporated off and the product purified by flash chromatography (ethyl acetate/pentane).

(*Z*)-2-(3-(Diphenylphosphoryl)allyl)isoindoline-1,3-dione (*Z*-3). [M.p.: 195–197 ºC] obtained as a white solid as described in the general procedure. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.04–5.08 (m, 2H, CH_2), 6.15–6.29 (m, 1H, CH), 6.45–6.66 (m, 1H, CH), 7.26–7.86 (m, 14H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 37.6 (d, $^3J_{PC}$ = 7.6 Hz), 123.8 (d, $^1J_{PC}$ = 97.2 Hz), 128.8, 129.0, 131.3, 131.5, 132.1, 132.2, 132.4, 132.8, 134.2, 147.6, 168.0 ppm; ^{31}P NMR (120 MHz, $CDCl_3$): δ = 23.0 ppm; IR (KBr): ν_{max} = 1706, 1441, 1189, 1103, 997, 698 cm^{-1}; MS (EI) *m*/*z* 387 (M^+, 100); HRMS (EI) *m*/*z* Calcd. for $C_{23}H_{18}NO_3P$ [M^+] 387.1024, found: [M^+] 387.1023.

(*E*)-2-(3-(Diphenylphosphoryl)allyl)isoindoline-1,3-dione (*E*-3). [M.p.: 172–175 ºC] obtained as a white solid as described in the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.50–4.53 (m, 2H, CH_2), 6.32–6.42 (m, 1H, CH), 6.62–6.73 (m, 1H, CH), 7.26–7.90 (m, 14H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 40.0 (d, $^3J_{PC}$ = 19.1 Hz), 124.6 (d, $^1J_{PC}$ = 100.8 Hz), 128.6, 128.7, 131.3, 131.4, 131.7, 131.9, 132.0, 132.8, 134.2, 144.1 (d, $^2J_{PC}$ = 3.3 Hz), 167.5 ppm; ^{31}P NMR (160 MHz, $CDCl_3$): δ = 23.5 ppm; IR (KBr): ν_{max} = 3470, 3052, 1699, 1434, 1394, 1189, 1103, 937 cm^{-1}; MS (EI) *m*/*z* 387 (M^+, 100); HRMS (EI) *m*/*z* Calcd. for $C_{23}H_{18}NO_3P$ [M^+] 387.1024, found: [M^+] 387.1049.

General procedure for the phosphine-catalyzed reaction of carbonucleophiles 5 with allene 1 (Table 2)

To a stirred solution of carbonucleophiles **5** (3 mmol), triphenylphosphine (10 mmol%) (Table 2, entries 1–4) and AcOH (20%) in dry toluene (5 mL) was added a solution of allene **1** (0.48 g, 2 mmol) in dry toluene (7 mL) under a N_2 atmosphere. The mixture was stirred under reflux. The crude reaction mixture was washed with water (3 × 15 mL) and the aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL). The organic layer was dried over anhydrous $MgSO_4$, the solvent was evaporated off.

(*E*)-Diethyl 2-(3-(diphenylphosphoryl)allyl)malonate (*E*-6a) (Table 2, entry 1). Obtained as pale yellow oil from **5a** after stirring under reflux for 40 h and purified by flash chromatography (ethyl acetate/pentane) as described in the general procedure. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.14 (t, 6H, $^3J_{HH}$ = 7.2 Hz, 2 CH_3), 2.85 (t, 2H, $^3J_{HH}$ = 6.9 Hz, CH_2), 3.50 (t, 1H, $^3J_{HH}$ = 7.5 Hz, CH), 4.02–4.2 (m, 4H, 2 OCH_2), 6.22–6.38 (m, 1H, CH), 6.56–6.70 (m, 1H, CH), 7.27–7.82 (m, 10H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.8, 33.0 (d, $^3J_{PC}$ = 17.6 Hz), 50.3, 61.5, 124.8 (d, $^1J_{PC}$ = 101.2 Hz), 128.2, 128.3, 128.4, 130.5, 130.7, 130.9, 131.1, 131.6, 131.7, 131.9, 132.1, 146.9 (d, $^2J_{PC}$ = 2.5 Hz), 168.1 ppm; ^{31}P NMR (120 MHz, $CDCl_3$): δ = 23.0 ppm; IR (NaCl): ν_{max}

= 3425, 3052, 2973, 2190, 1730, 1443, 1185, 1113, 689 cm^{-1}; MS (CI) *m*/*z* 401 (M$^+$ + 1, 100); HRMS (EI) *m*/*z* Calcd. for $C_{22}H_{25}O_5P$ [M$^+$] 400.1440, found: [M$^+$] 400.1423.

(*Z*)-Diethyl 2-(3-(diphenylphosphoryl)allyl)malonate (*Z*-6a) (Table 2, entry 1). Obtained as pale yellow oil from **5a** after stirring under reflux for 40 h and purified by flash chromatography (ethyl acetate/pentane) as described in the general procedure. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.22 (t, 6H, $^3J_{HH}$ = 7.2 Hz, 2 CH_3), 3.24 (t, 2H, $^3J_{HH}$ = 7.3 Hz, CH_2), 3.50 (t, 1H, $^3J_{HH}$ = 7.0 Hz, CH), 4.20 (q, 4H, $^3J_{HH}$ = 7.2 Hz, 2 OCH_2), 6.15–6.28 (m, 1H), 6.60–6.82 (m, 1H), 7.31–7.87 (m, 10H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9, 28.9 (d, $^3J_{PC}$ = 8.1 Hz), 51.1, 61.4, 123.8 (d, $^1J_{PC}$ = 98.7 Hz), 128.3, 128.5, 128.6, 130.8, 131.0, 131.6, 131.7, 131.8, 131.9, 132.0, 132.1, 133.2,134.6, 149.3, 168.5 ppm; ^{31}P NMR (120 MHz, $CDCl_3$): δ = 21.5 ppm; IR (NaCl): ν_{max} = 3443, 3052, 2979, 2203, 1726, 1434, 1202, 1116, 738 cm^{-1}; MS (CI) *m*/*z* 401 (M$^+$ + 1, 100); HRMS (EI) *m*/*z* Calcd. for $C_{22}H_{25}O_5P$ [M$^+$] 400.1440, found: [M$^+$] 400.1424.

(*E*)-Ethyl 2-acetyl-5-(diphenylphosphoryl)pent-4-enoate (*E*-6b) (Table 2, entry 2). Obtained as pale yellow oil from **5b** after stirring under reflux for 72 h and purified by flash chromatography (ethyl acetate/pentane) as described in the general procedure. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.18 (t, 3H, $^3J_{HH}$ = 7.2 Hz, CH_3), 2.24 (s, 3H, CH_3), 2.83, (t, 2H, $^3J_{HH}$ = 7.0 Hz, CH_2), 3.63 (t, 1H, $^3J_{HH}$ = 7.3 Hz, CH), 4.09–4.20 (m, 2H, OCH_2), 6.26–6.40 (m, 1H, CH), 6.56–6.67 (m, 1H, CH), 7.27–7.76 (m, 10H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 29.2, 32.3 (d, $^3J_{PC}$ = 17.6 Hz), 57.9, 62.0, 125.0 (d, $^1J_{PC}$ = 101.2 Hz), 128.4, 128.6, 128.8, 130.7, 130.9, 131.0, 131.1, 131.3, 131.8, 131.9, 132.2, 147.4 (d, $^2J_{PC}$ = 2.5 Hz), 168.5, 201.2 ppm; ^{31}P NMR (120 MHz, $CDCl_3$): δ = 23.0 ppm; IR (NaCl): ν_{max} = 3417, 3059, 2979, 1713, 1434, 1182, 1123, 698 cm^{-1}; MS (CI) *m*/*z* 371 (M$^+$ + 1, 100); HRMS (EI) *m*/*z* Calcd. for $C_{21}H_{23}O_4P$ [M$^+$] 370.1334, found: [M$^+$] 370.1333.

(*E*)-4-Nitropent-1-enyl diphenylphosphine oxide (*E*-6c) (Table 2, entry 3). Obtained as pale yellow oil from **5c** after stirring under reflux for 72 h and purified by flash chromatography (ethyl acetate/pentane) as described in the general procedure. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.59 (d, 3H, $^3J_{HH}$ = 6.7 Hz, CH_3), 2.71–3.00 (m, 2H, CH_2), 4.68–4.75 (m, 1H, C$\underline{H}$-NO_2), 6.27–6.46 (m, 1H, CH), 6.55–6.69 (m, 1H, CH), 7.18–7.98 (m, 10H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.8, 39.2 (d, $^3J_{PC}$ = 17.6 Hz), 81.5, 128.4 (d, $^1J_{PC}$ = 144.0 Hz), 128.6, 128.7, 130.6, 130.7, 131.0, 131.1, 131.2, 131.8, 132.1, 132.2, 132.3, 144.0 ppm; ^{31}P NMR (120 MHz, $CDCl_3$): δ = 22.8 ppm; IR (NaCl): ν_{max} = 3430,3059, 2926, 1719, 1547, 1440, 1182, 705 cm^{-1}; MS (EI) *m*/*z* 315 (M$^+$, 100); HRMS (EI) *m*/*z* Calcd. for $C_{17}H_{18}NO_3P$ [M$^+$] 315.1024, found: [M$^+$] 315.1067.

(*Z*)-4-Nitropent-1-enyl diphenylphosphine oxide (*Z*-6c) (Table 2, entry 3). Obtained as pale yellow oil from **5c** after stirring under reflux for 72 h and purified by flash chromatography (ethyl acetate/pentane) as described in the general procedure. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.53 (d, 3H, $^3J_{HH}$ = 6.7 Hz, CH_3), 3.20–3.37 (m, 2H, CH_2), 4.65–4.70 (m, 1H, C$\underline{H}$-NO_2), 6.22–6.35 (m, 1H, CH), 6.52–6.70 (m, 1H, CH), 7.27–7.73 (m, 10H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.3, 34.7 (d, $^3J_{PC}$ = 7.6 Hz), 83.1, 125.9 (d, $^1J_{PC}$ = 97.2 Hz), 128.7, 128.8, 128.9, 129.1, 131.1, 131.2, 131.3, 131.5, 131.6, 132.0, 132.2, 132.3, 132.4, 133.1, 146.7 ppm; ^{31}P NMR

(120 MHz, $CDCl_3$): δ = 22.0 ppm; IR (NaCl): ν_{max} = 3059, 2933, 1620, 1554, 1434, 1182, 1116, 725 cm^{-1}; MS (EI) *m/z* 315 (M^+, 100); HRMS (EI) *m/z* Calcd. for $C_{17}H_{18}NO_3P$ [M^+] 315.1024, found: [M^+] 315.1047.

(*E*)-4-Methyl-4-nitropent-1-enyl diphenylphosphine oxide (*E*-6d) (Table 2, entry 4). Obtained as pale yellow oil from **5d** after stirring under reflux for 72 h and purified by flash chromatography (ethyl acetate/pentane) as described in the general procedure. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.61 (s, 6H, 2 CH_3), 2.88 (d, 2H, $^3J_{HH}$ = 7.3 Hz, CH_2), 6.20–6.40 (m, 1H, CH), 6.46–6.70 (m, 1H, CH), 7.31–7.80 (m, 10H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.5, 44.9 (d, $^3J_{PC}$ = 17.1 Hz), 87.2, 127.5 (d, $^1J_{PC}$ = 97.7 Hz), 127.5, 128.4, 128.5, 128.7, 128.8, 130.6, 130.7, 130.9, 131.1, 131.2, 131.8, 132.1, 132.1, 132.3, 134.6, 143.6 ppm; ^{31}P NMR (120 MHz, $CDCl_3$): δ = 22.6 ppm; IR (NaCl): ν_{max} = 3410, 3059, 2986, 2913, 1699, 1533, 1428, 1348, 1188, 725 cm^{-1}; MS (EI) *m/z* 329 (M^+, 100); HRMS (EI) *m/z* Calcd. for $C_{18}H_{20}NO_3P$ [M^+] 329.1181, found: [M^+] 329.1199.

(*Z*)-4-Methyl-4-nitropent-1-enyl diphenylphosphine oxide (*Z*-6d) (Table 2, entry 4). Obtained as pale yellow oil from **5d** after stirring under reflux for 72 h and purified by flash chromatography (ethyl acetate/pentane) as described in the general procedure. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.60 (s, 6H, 2 CH_3), 3.43 (m, 2H, CH_2), 6.25–6.39 (m, 1H, CH), 6.43–6.63 (m, 1H, CH), 7.27–7.79 (m, 10H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.0, 26.1, 39.6 (d, $^3J_{PC}$ = 7.1 Hz), 87.7, 125.6(d, $^1J_{PC}$ = 97.7 Hz), 128.4, 128.6, 128.8, 130.8, 130.9, 131.1, 131.4, 131.5, 131.9, 131.9, 146.4 ppm; ^{31}P NMR (120 MHz, $CDCl_3$): δ = 22.3 ppm; IR (NaCl): ν_{max} = 3271, 2097, 1633, 1540, 1434, 1176, 1116 cm^{-1}; MS (EI) *m/z* 329 (M^+, 100); HRMS (EI) *m/z* Calcd. for $C_{18}H_{20}NO_3P$ [M^+] 329.1181, found: [M^+] 329.1199.

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