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Regio- and Stereospecific Cleavage of Stannyloxiranes with Lithium Diphenylphosphide

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Unsubstituted or *C*-substituted stannyloxiranes reacted stereospecifically with lithium diphenylphosphide to give either β-hydroxyphosphane oxides resulting from α-opening or β-phosphanyl ketones by β-opening. Furthermore, the reactivities of distannyloxiranes depend on their configurations. The *cis* isomers afforded the corresponding α,β-diphosphanyl alcohols, while the *trans* isomers were shown to be unreactive. On the other hand, the regiochemistry of the ring-opening from β-silyl-stannyloxiranes is controlled by the tin group and, depending on the nature of the silyl group, led either to stereodefined β-silylated vinylphosphane oxides or to β-stannyl silyl enol ethers. Finally, the *gem*-silyl-stannyloxiranes underwent β-opening to give mixtures of β-phosphanyl acylsilanes and silyl enol ethers. All compounds are interesting synthons of great versatility in organic chemistry.

Introduction

Whereas the behaviour of epoxysilanes toward nucleophilic reagents has been widely studied,[1] there are few references relating to the reactivity of stannyloxiranes. We have only found reports of their conversion into ketones[2] by cleavage with formic acid and subsequent treatment with lithium hydroxide in aqueous THF, their transformation into olefins[3] by reductive alkylation with alkyllithium reagents, ring-opening with metal hydrides[4] or organocuprates[5] and transmetallation with an organolithium species.[6]

In a previous paper we described the regio- and stereospecific cleavage of stannyloxiranes with lithium phenylsulfide,[7] which showed behaviour different from that observed in the cleavage of silylepoxides with this same reagent.[8] Moreover, we have also reported[9] the reaction behaviour of differently substituted silyl- and disilylepoxides toward lithium diphenylphosphide. Using unsubstituted or α- and β-C-substituted silylepoxides, we have synthesised vinylphosphonium iodides or vinylphosphane oxides by α-opening and silyl enol ethers, vinylsilanes or α-hydroxysilanes by β-opening. On the other hand, α,β- or α,α-disilylepoxides afforded β-silyl vinylphosphane oxides or α-silylated silyl enol ethers by α- and β-cleavage, respectively. In view of the different behaviour of silyl- and stannyloxiranes toward the nucleophilic attack and with the aim of increasing the synthetic possibilities of the cleavage of metallated epoxides by lithium diphenylphosphide, we have extended this methodology to stannylated epoxides.

The natures of the products obtained from the reactions of stannyloxiranes with lithium diphenylphosphide depend on the substitution type of the oxirane ring. We therefore started from unsubstituted and from C-, Si- and Sn-substituted stannyloxiranes. In general, these substrates were synthesised by epoxidation of the corresponding vinylstannanes previously obtained by tributylstannyl cupration from alkynes[10] or allenes.[11]

Results and Discussion

On treatment at 0 °C with lithium diphenylphosphide, followed by hydrolysis with saturated aqueous sodium hydrogen carbonate, the α-unsubstituted stannyloxiranes **1a**–**d** afforded the β-hydroxyphosphane oxides **2a**–**d** (Scheme 1). When the hydrolysis was carried out in an acid medium (saturated aqueous solution of ammonium chloride), however, the initially formed β-hydroxyphosphane oxides were partially dehydrated to give minor amounts of the more stable *trans*-vinylphosphane oxides **3a**–**d** (10–15%), independently of the starting stannyloxirane configuration.

The lack of stereospecificity observed in the synthesis of vinylphosphane oxides **3a**–**d** indicates that their formation was different from that described for the α-opening of the corresponding epoxysilanes[9] with the same reagent, in which the alkoxysilane intermediates afforded stereodefined vinylphosphane oxides by Peterson *syn*-elimination. In this case, the evolution of the β-stannylalkoxide intermediate **A** (Scheme 2) generated by α-opening could take place by 1,3-migration of the stannyl group from carbon to oxygen and

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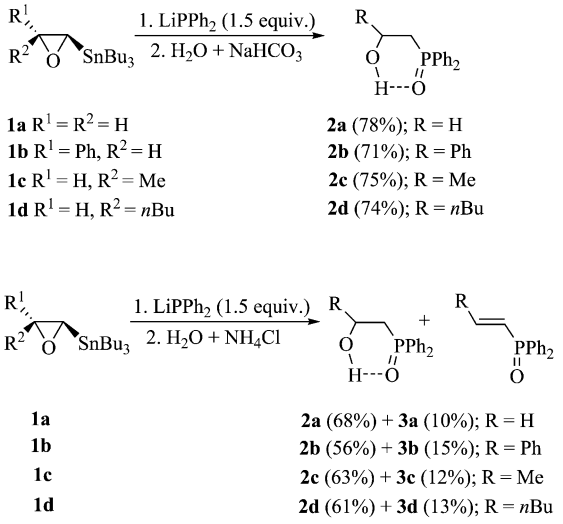
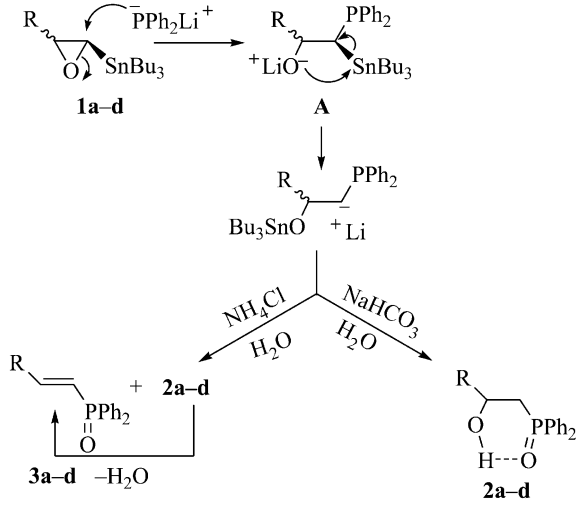


1a $R^1 = R^2 = H$ — **2a** (78%); R = H
1b R^1 = Ph, $R^2 = H$ — **2b** (71%); R = Ph
1c $R^1 = H$, R^2 = Me — **2c** (75%); R = Me
1d $R^1 = H$, R^2 = *n*Bu — **2d** (74%); R = *n*Bu

1a — **2a** (68%) + **3a** (10%); R = H
1b — **2b** (56%) + **3b** (15%); R = Ph
1c — **2c** (63%) + **3c** (12%); R = Me
1d — **2d** (61%) + **3d** (13%); R = *n*Bu

Scheme 1.

hydrolysis of the resulting stannyl ether to give the β-hydroxyphosphane oxides **2a**–**d**, which in an acidic medium could experience partial dehydration to yield *trans*-vinylphosphane oxides **3a**–**d**.

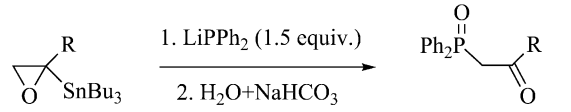


Scheme 2.

On treatment with lithium diphenylphosphide (1.5 equiv.) at room temperature, the α-*C*-substituted β-unsubstituted stannyloxiranes **1e**–**g** gave β-phosphanyl ketones **4a**–**c** (Scheme 3).

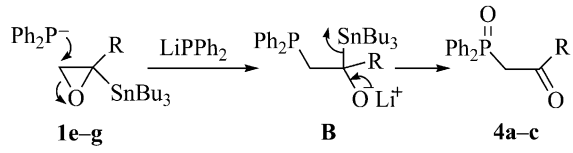
The α-*C*-substituent increases the steric impedance in this position, so the nucleophilic attack consequently takes place exclusively at β-C. This behaviour is analogous to that observed in the opening of α-*C*-substituted epoxysilanes in the presence of the same reagent,[9b] but the evolution of the intermediate resulting from the β-opening is different. In this case, the unstable β-diphenylphosphanyl-α-oxidostannane intermediate **B** (Scheme 4) is converted into a carbonyl group by elimination of the stannyl group.

These α-phosphanyl ketones, besides finding widespread application as hemilabile ligands in homogeneous catalysis,[12] could be of interest in the synthesis of heterocycles. We acylated these substrates with the goal of preparing phosphanyl-substituted isoxazoles and pyrazoles by treatment of the resulting 2-phosphanyl-substituted 1,3-diketones with hydroxylamine and methylhydrazine.



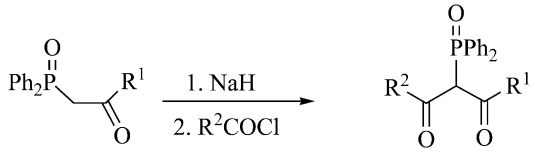
1e R = Me — **4a** (63%); R = Me
1f R = *n*Bu — **4b** (65%); R = *n*Bu
1g R = Ph — **4c** (70%); R = Ph

Scheme 3.



Scheme 4.

The irreversible condensation of the β-phosphanyl ketones **4a** and **4c** with acetyl and benzoyl chloride in the presence of NaH afforded the necessary 2-phosphanyl-substituted 1,3-diketones **5a**–**c** in good yields (Scheme 5).



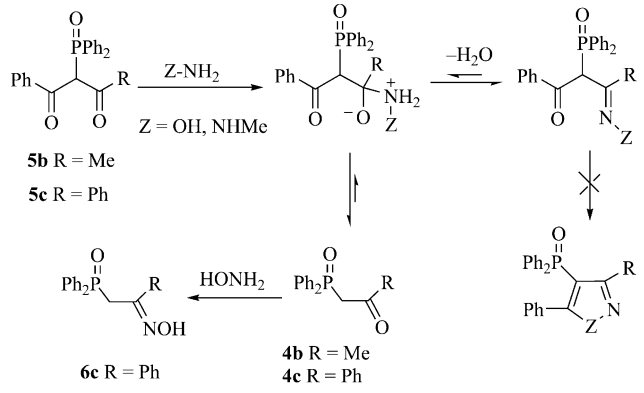
4a R^1 = Me — **5a** (92%); $R^1 = R^2$ = Me
4a — **5b** (82%); R^1 = Me, R^2 = Ph
4c R^1 = Ph — **5b** (85%); R^1 = Ph, R^2 = Me
4c — **5c** (89%); $R^1 = R^2$ = Ph

Scheme 5.

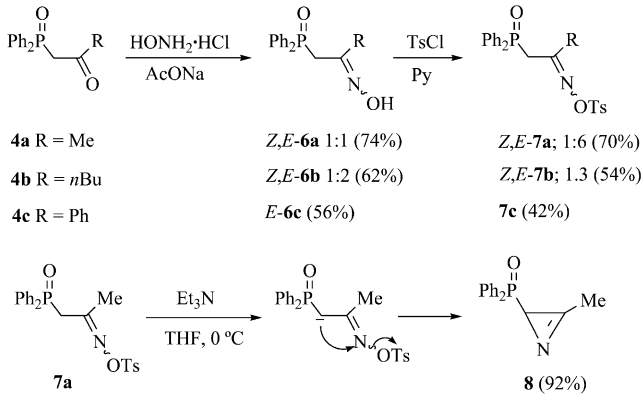
Unfortunately, the synthesis of phosphanyl-substituted isoxazoles and pyrazoles did not take place. When we treated **5a**–**c** with hydroxylamine or methyl hydrazine the α-phosphanyl ketones **4a** and **4c** resulting from retroaldolisation were obtained. In the reactions with hydroxylamine, together with the ketone **4c**, the corresponding oxime **6c** was isolated (Scheme 6).

In contrast, we were able to synthesise 2-phosphanyl-2*H*-azirines from the tosyloximes **7a**–**c** – derived from phosphorylated ketones **4a**–**c** – by cyclisation in a basic medium (Neber reaction). Treatment of the tosyloxime **7a** with triethylamine at 0 °C led in good yield to 2-(diphenylphosphanyl)-3-methyl-2*H*-azirine (**8**, Scheme 7).

These highly strained heterocycles are very useful intermediates in organic synthesis because of their versatile thermal and photochemical behaviour,[13,14] as well as their high reactivities toward nucleophilic and electrophilic rea-



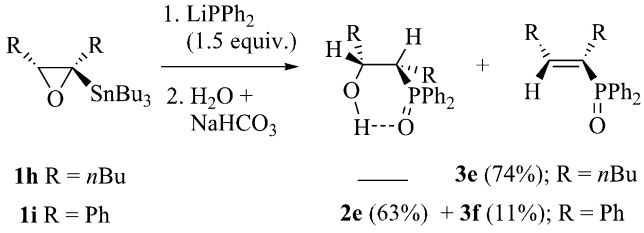
Scheme 6.



Scheme 7.

gents.[15] 2-Functionalised 2*H*-azirines are also established as building blocks for the synthesis of a range of heterocyclic compounds.[16]

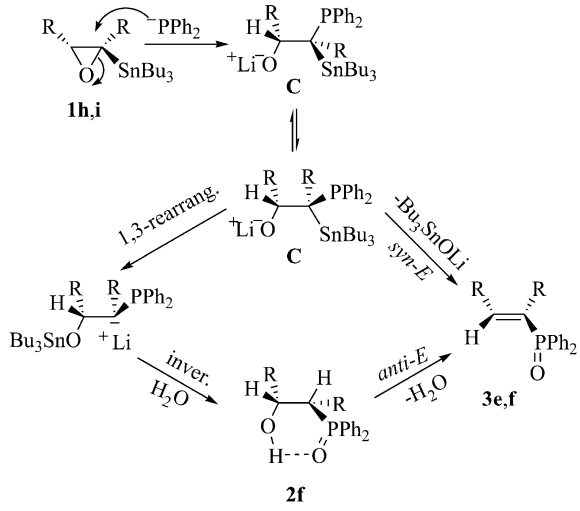
On the other hand, the α- and β-alkyl- or -phenyl-substituted stannyloxiranes **1h** and **1i** underwent α-opening to give the β-hydroxyphosphane oxide **2e** and/or the vinylphosphane oxides **3e** and **3f** stereospecifically (Scheme 8).



Scheme 8.

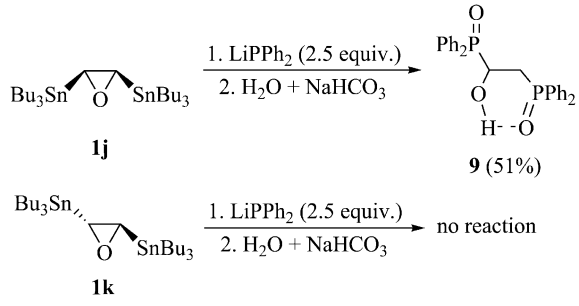
Compound **2e**, which was isolated as one diastereoisomer (a single signal appears in the ^{31}P NMR spectrum), is stabilised by intramolecular hydrogen bonds between the hydroxy and phosphanyl groups[17] and has an *anti* configuration.[18]

The substitution at α and β once again determined that the stannyl group controlled the regiochemistry. The α-opening should afford a β-oxidostannane intermediate **C**, which on Bu_3SnOLi *syn*-elimination would stereospecifically give the vinylphosphane oxides **3e** and **3f**. On the other hand, the formation of *anti*-**2e** should take place through inversion in the configuration of the carbanion resulting from the tin migration from carbon to oxygen in the cited intermediate **C**. Likewise, the formation of the vinylphosphane oxides **3e** and **3f** could occur by *anti*-elimination of water from the previously obtained alcohols (Scheme 9).



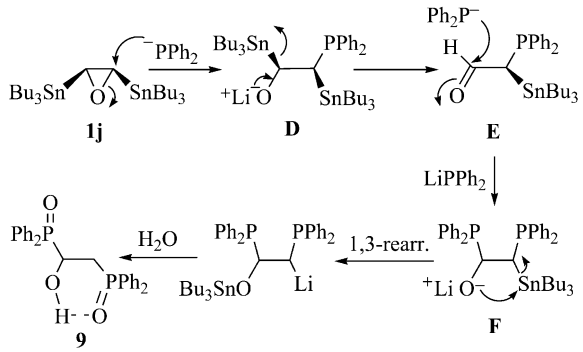
Scheme 9.

The *cis*- and *trans*-2,3-distannyloxiranes **1j** and **1k** showed very different reactivities toward lithium diphenylphosphide. The *cis*-2,3-bis(tributylstannyl)oxirane **1j** reacted at 0 °C with lithium diphenylphosphide (2.5 equiv.) to give the 1,2-bis(diphenylphosphanyl)ethanol **9** (Scheme 10), a useful tridentate ligand, whereas under the same conditions the *trans*-2,3-bis(tributylstannyl)oxirane **1k** was recovered.



Scheme 10.

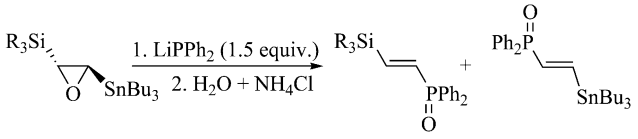
The reaction product **9** could be explained by supposing initial nucleophilic attack at one of the heterocyclic carbons and the formation of the intermediate **D** (Scheme 11), which would evolve into aldehyde **E** through elimination of the stannyl group. Nucleophilic addition of the diphenylphosphide to this aldehyde would give rise to the β-oxidostannane **F**, which would experience a 1,3-migration of the tin group from carbon to oxygen to afford, after hydrolysis, the diphosphanyl alcohol **9**.



Scheme 11.

We also studied the behaviour of silylated stannyloxiranes in the presence of lithium diphenylphosphide with the aim of establishing which of the two metallated groups would control the regiochemistry of the ring opening. We started from different silylated *cis*- and *trans*-2-silyl-3-stannyloxiranes and 2-silyl-2-stannyloxiranes and established that their reactivities depend on the nature of the silyl group and the relative position and configuration of both metallated groups.

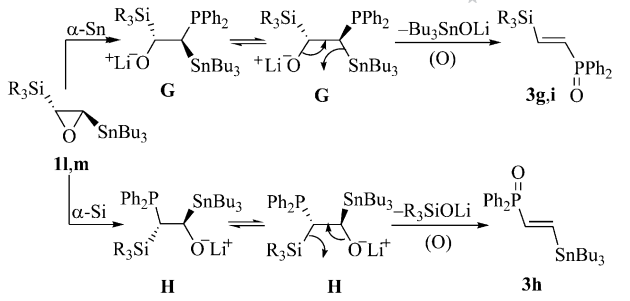
The *trans*-(tributylstannyl)-silyloxiranes **1l** and **1m** reacted with lithium diphenylphosphide to give mixtures of the corresponding β-silyl- and β-stannyl-substituted vinylphosphane oxides **3g**–**i** (Scheme 12).



1l $R_3 = Me_3$	**3g** (43%); $R_3 = Me_3$	**3h** (32%)
1m $R_3 = Me_2$, Ph	**3i** (57%); $R_3 = Me_2$, Ph	**3h** (21%)

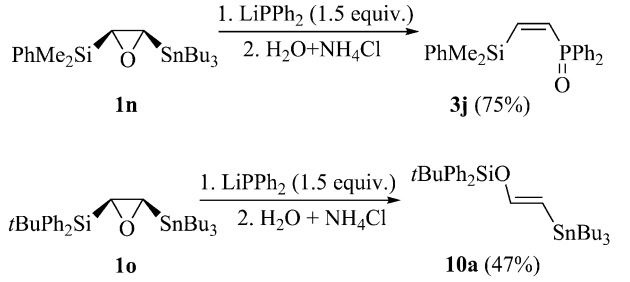
Scheme 12.

It can be postulated that the stereospecific formation of the *trans*-β-silylvinylphosphanes **3g** and **3i** takes place through nucleophilic attack at α-C to the stannyl group to give the β-silyl-β-oxidostannane intermediate **G** (Scheme 13), followed by *syn*-elimination of Bu_3SnOLi. The different behaviour shown by the intermediate **G** with respect to the β-oxidostannanes **A**, **C** and **F**, which experienced 1,3-migration of the tin group from carbon to oxygen, could be due to the presence of the silyl group, which would destabilise the hypothetical β-carbanion. On the other hand, the nucleophilic attack at α-C to the silyl group afforded the β-stannyl-β-oxidosilane **H**, which underwent Peterson *syn*-elimination to give the *trans*-β-stannylvinylphosphane **3h** (Scheme 13). The preference for α-opening with respect to the tributyltin group is increased when the silyl group is bulkier.



Scheme 13.

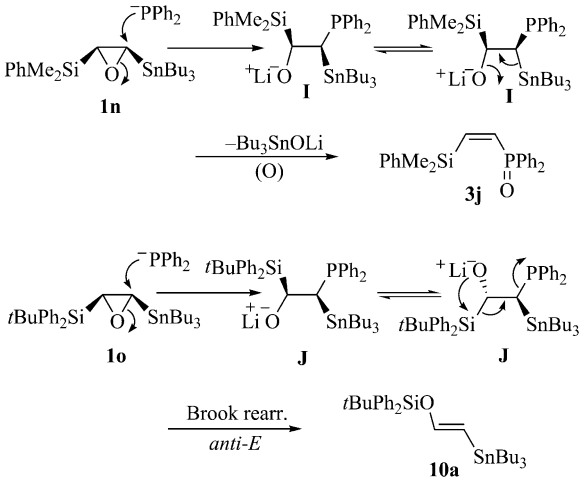
The behaviour of the *cis*-2-silyl-3-stannyloxiranes **1n** and **1o** is different from that indicated for their *trans* analogues. In this case, the reactions were regiospecific. Although in both silylstannyloxiranes **1n** and **1o** the attack of the lithium diphenylphosphide occurred exclusively at α-C to the stannyl group, the evolution of the resulting intermediate was different, depending on the nature of the silyl group. The (dimethylphenylsilyl)-stannyloxirane **1n** gave the *cis*-β-(dimethylphenylsilyl)-substituted vinylphosphane oxide **3j**, whereas the (*tert*-butyldiphenylsilyl)-stannyloxirane **1o** afforded the *trans*-β-tributylstannyl *tert*-butyldiphenylsilyl enol ether **10a** (Scheme 14).



Scheme 14.

The exclusive attack of the diphenylphosphide anion at α-C to the tin group and β to the silyl group in the case of the *cis*-(*tert*-butyldiphenylsilyl)oxirane **1o** is predictable in view of the preference previously described for these ring openings in the *trans*-silyl-stannyloxiranes **1l** and **1m**. In this case, this difference is increased by the presence of the bulky *tert*-butyldiphenylsilyl group, which guides the β-opening process.[9] However, the different behaviour of the *cis*- and *trans*-(dimethylphenylsilyl)oxiranes **1m** and **1n** is less evident. Probably, the exclusive nucleophilic attack at α-C to the stannyl group in the *cis*-epoxide **1n**, followed by Bu_3SnOLi *syn*-elimination in the intermediate **I** to give the vinylphosphane oxide **3j**, would be due to steric requirements (the tributylstannyl and diphenylphosphanyl groups were eclipsed) of the necessary conformation for the Peterson elimination in the intermediate resulting from the α-opening with respect to the silicon. When the silyl group was the bulky *tert*-butyldiphenyl system, the intermediate **J** resulting from α-opening to the tin group of the silyl-stannyloxirane **1o** underwent Brook rearrangement and *anti*-eli-

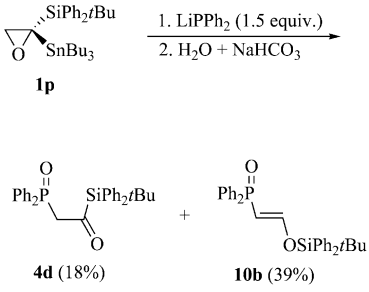
mination of diphenylphosphide to give the β-stannyl silyl enol ether **10a**, with *E* configuration, stereospecifically (Scheme 15).



Scheme 15.

The different behaviour of the intermediates **I** and **J** could depend on two factors: a) higher migratory aptitude of the *tert*-butyldiphenylsilyl group than its dimethylphenylsilyl counterpart (phenyl groups on silicon have been shown[19] to accelerate the Brook rearrangement), and b) instability of the necessary conformation for the Bu_3SnOLi *syn*-elimination in the intermediate **J** in which the bulky diphenylphosphanyl and *tert*-butyldiphenylsilyl groups should be eclipsed, whereas in the conformation for Brook rearrangement and *anti*-elimination the *tert*-butyldiphenylsilyl and stannyl groups are staggered.

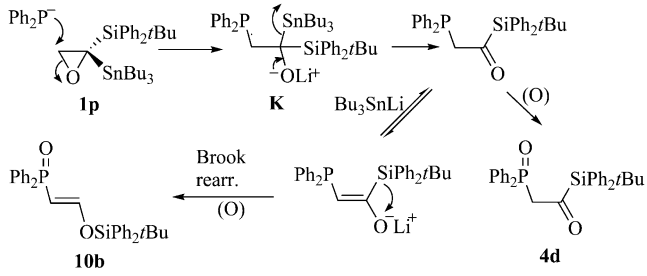
The synthesis of *gem*-silyl-stannyloxiranes from unsubstituted silyloxiranes by deprotonation at low temperature and trapping with chlorostannanes was examined, but only the oxiranyl anion resulting from deprotonation of the (*tert*-butyldiphenylsilyl)-epoxyethane was sufficiently stable to be trapped at –60 °C by the tributylstannyl chloride. We were therefore only able to obtain 2-(tributylstannyl)-2-(*tert*-butyldiphenylsilyl)oxirane (**1p**) (Scheme 16).



Scheme 16.

Treatment of **1p** with lithium diphenylphosphide (1.5 equiv.) afforded a mixture of the β-phosphorylated silyl enol ether **10b** and the acylsilane **4d**.

The steric hindrance at α-C of the *gem*-silyl-stannyloxirane **1p** induces β-opening to give exclusively an α-silyl-α-stannyloxide intermediate **K**, which, out of the different possibilities of evolution (Brook rearrangement, Wittig elimination or tin elimination), preferred conversion into the acylsilane **4d** through elimination of the tributylstannyllithium. This basic compound probably induces the isomerisation of the initially formed acylsilane into the silyl enol ether **10b** through enolisation and *tert*-butyldiphenylsilyl migration from carbon to oxygen (Scheme 17).



Scheme 17.

Conclusions

In summary, the stannyl group exercises a strong directing effect in the opening of stannyloxiranes. In general, α-opening took place except when the α-position was hindered. This regiochemistry is analogous to that described for the corresponding epoxysilanes. Nevertheless, the evolution of the resulting intermediates is very different, giving rise to other products. If the stannyloxirane bears a silyl group, the regiochemistry and evolution of the reaction is governed by the tin group. The α-attack of the diphenylphosphide anion on stannyloxiranes has allowed us to synthesise β-phosphanyl alcohols. The easy conversion of phosphane oxides into phosphanes[20] makes these compounds interesting precursors of chiral 1,2-donor bidentate ligands for transition-metal-catalysed asymmetric synthesis.[21] These hemilabile ligands have also encountered success with applications in small-molecule activation, small-molecule sensing and stabilisation of transition complexes.[22]

On the other hand, the β-phosphanyl ketones obtained by β-opening of α-substituted stannyloxiranes, besides being σ-donor/π-acceptor ligands,[12] are interesting intermediates for the synthesis of three-membered phosphanyl heterocycles with potential biological activity.[23] Moreover, the β-stannyl- and β-phosphanyl silyl enol ethers **10a** and **10b** and the β-phosphanylacylsilane **4d** resulting from opening of (*tert*-butyldiphenylsilyl)-stannyloxiranes are very versatile small synthons. The vinylstannane unit in **10a** is useful in Stille coupling,[24] as a vinyl anion equivalent[25] and in electrophilic *ipso*-substitution[7,26] or rhodium-catalysed conjugate addition processes,[27] and the phosphanyl group increases the interest of **10b**. It is known that phosphorus substituents regulate many biological functions.[28] Furthermore, compound **7**, besides being a generator of stabilised

carbanions (phosphorus ylide vs. enolate anion), has a special reactivity conferred on it by the acylsilane unit. Acylsilanes are valuable building blocks for the synthesis of complex products.[29] Among their many interesting applications, acylsilanes can be regarded as aldehyde equivalents in stereocontrolled nucleophilic acylation.[30] Finally, the presence of the β-silyl or stannyl groups in the metallated vinylphosphane oxides obtained by opening of silylstannyloxiranes should increase the versatility of these substrates. Some applications of the vinylphosphane oxides – including as Michael acceptors and as dipolarophiles in 1,3-dipolar cycloadditions – will be published as soon as possible.

Experimental Section

General: THF was distilled from sodium benzophenone ketyl in a recycling still. All chromatographic and workup solvents were distilled prior to use. All reactions involving organometallic reagents were carried out under nitrogen. ^1H, ^{13}C and ^{31}P NMR spectra were recorded at 300, 75 and 121 MHz, respectively, in $CDCl_3$ as an internal standard. Carbon multiplicities were assigned by DEPT experiments. Reactions were monitored by TLC on precoated plates (silica gel 60, nano-SIL-20, Macherey–Nagel). Flash chromatography was performed on silica gel 60 (230–400 mesh, M–N). In general, the starting stannyloxiranes were prepared by epoxidation of the corresponding vinylstannanes, obtained by treatment of the intermediates resulting from tributylstannyl cupration of alkynes[10] **1a**–**d** and **1f**–**n** or allenes[11] like **1e** with electrophiles, except for the 2,2-silyl-stannyloxirane **1o**, which was obtained by treatment of the oxiranyl anion produced from the corresponding silyl epoxide and BuLi in the presence of TMEDA with Cl*S*nBu_3.

Synthesis of Epoxystannanes

Method A. Typical Procedure: MCPBA (8.1 mmol) and $NaHCO_3$ (12 mmol) were added to a solution of stannylalkene (6 mmol) either in CH_2Cl_2 (20 mL) or, when (*tert*-butyldiphenylsilyl)-stannyl-substituted alkenes were used, in $CHCl_3$ (20 mL). The reaction mixture was stirred at room temperature in CH_2Cl_2 or at reflux in $CHCl_3$ until TLC indicated complete reaction (reaction time 0.5–5 h.). The mixture was washed with a saturated aqueous solution of $NaHSO_3$, $NaHCO_3$ and NaCl. The organic layer was dried ($MgSO_4$), the solvent was removed, and the residue was chromatographed (silica gel, hexane/AcOEt) to provide the following products.

(Tributylstannyl)epoxyethane (1a): Yield 1.5 g (72%); see ref.[5]

***trans*-1-Phenyl-2-(tributylstannyl)epoxyethane (1b):** Yield 2.1 g (85%); see ref.[31]

***cis*-1-(Tributylstannyl)-1,2-epoxypropane (1c):** Yield 1.6 g (79%). R_f = 0.39 (hexanes). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.3 Hz, 9 H), 1.00 (m, 6 H), 1.27 (d, J = 5.2 Hz, 3 H), 1.35 (m, 6 H), 1.55 (m, 6 H), 2.75 (d, J = 5.2 Hz, 1 H), 3.23 (quint, J = 5.2 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 9.5, 13.6, 19.5, 27.3, 30.0, 51.5, 53.8 ppm. MS (EI, 70 eV): m/z (%) = 291 (5) [M – Bu]$^+$, 269 (3), 177 (100), 121 (75). $C_{15}H_{32}OSn$ (348.15): calcd. C 51.90, H 9.29; found C 52.30, H 8.91.

***cis*-1-(Tributylstannyl)-1,2-epoxyhexane (1d):** Yield 1.7 g (75%). R_f = 0.40 (hexanes). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.83–0.98 (m, 18 H), 1.26–1.36 (m, 10 H), 1.39–1.58 (m, 8 H), 2.76 (d, J = 4.7 Hz, 1 H), 3.11 (dt, J = 4.7, 6.8 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 9.5, 13.6, 13.9, 22.6, 27.2, 28.9, 34.1, 53.3, 55.9 ppm. $C_{18}H_{38}OSn$ (390.19): calcd. C 55.55, H 9.84; found C 55.83, H 10.22.

2-(Tributylstannyl)-1,2-epoxypropane (1e): Yield 1.4 g (70%). R_f = 0.39 (hexanes). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.2 Hz, 9 H), 0.90 (m, 6 H), 1.31 (m, 6 H), 1.39 (s, 3 H), 1.54 (m, 6 H), 2.50 (d, J = 5.2 Hz, 1 H), 2.65 (d, J = 5.2 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.5, 13.5, 25.9, 27.3, 28.9, 51.9, 53.1 ppm. $C_{15}H_{32}OSn$ (348.15): calcd. C 51.90, H 9.29; found C 51.55, H 9.68.

2-(Tributylstannyl)-1,2-epoxyhexane (1f): Yield 1.7 g (72%). R_f = 0.40 (hexanes). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.90 (m, 18 H), 1.31 (m, 10 H), 1.54 (m, 8 H), 2.51 (d, J = 5.0 Hz, 1 H), 2.61 (d, J = 5.0 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.6, 8.9, 13.6, 13.9, 22.8, 27.3, 29.0, 40.1, 50.9, 57.8 ppm. $C_{18}H_{38}OSn$ (390.19): calcd. C 55.55, H 9.84; found C 55.17, H 9.51.

1-(Tributylstannyl)-1-phenylepoxyethane (1g): Yield 1.8 g (73%). R_f = 0.42 (hexanes). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, J = 7.2 Hz, 9 H), 0.97 (m, 6 H), 1.36 (m, 6 H), 1.56 (m, 6 H), 2.75 (d, J = 5.9 Hz, 1 H), 2.96 (d, J = 5.9 Hz, 1 H), 7.26–7.37 (m, 5 H) ppm. $C_{20}H_{34}OSn$ (410.16): calcd. C 58.70, H 8.38; found C 59.04, H 7.96.

(*E*)-5-(Tributylstannyl)-5,6-epoxydecane (1h): Yield 1.9 g (71%). R_f = 0.46 (hexanes). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.80–1.00 (m, 25 H) 1.25–1.50 (m, 20 H), 2.77 (t, J = 5.9 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.6, 9.0, 13.5, 13.9, 22.6, 27.3, 29.0, 33.9, 60.8, 63.8 ppm. $C_{22}H_{46}OSn$ (446.26): calcd. C 59.34, H 10.41; found C 58.96, H 10.79.

(*E*)-1,2-Diphenyl-1-(tributylstannyl)epoxyethane (1i): Yield 2.1 g (75%). R_f = 0.51 (hexanes). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.81 (t, J = 7.1 Hz, 9 H), 1.57–1.11 (m, 18 H), 3.91 (s, 1 H), 7.18–7.43 (m, 10 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.3, 13.5, 27.2, 28.7, 64.5, 69.9, 125.3, 125.7, 126.1, 126.8, 127.3, 127.9, 128.3, 138.6, 144.7 ppm. $C_{26}H_{38}OSn$ (486.19): calcd. C 64.35, H 7.89; found C 64.71, H 8.06.

***cis*-1,2-Bis(tributylstannyl)epoxyethane (1j):** Yield 2.2 g (60%). R_f = 0.59 (hexanes). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.1 Hz, 18 H), 0.92 (m, 12 H), 1.33 (m, 12 H), 1.54 (m, 12 H), 2.60 (s, 2 H) ppm. $C_{26}H_{56}OSn_2$ (624.24): calcd. C 50.19, H 9.07; found C 49.73, H 8.67.

***trans*-1,2-Bis(tributylstannyl)epoxyethane (1k):** Yield 2.3 g (65%). R_f = 0.61 (hexanes). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, J = 7.0 Hz, 18 H), 0.93 (m, 12 H), 1.36 (m, 12 H), 1.60 (m, 12 H), 2.62 (s, 2 H) ppm. $C_{26}H_{56}OSn_2$ (624.24): calcd. C 50.19, H 9.07; found C 50.41, H 9.25.

***trans*-1-(Tributylstannyl)-2-(trimethylsilyl)epoxyethane (1l):** Yield 1.9 g (80%). R_f = 0.47 (hexanes). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.05 (s, 6 H), 0.90 (t, J = 7.3 Hz, 9 H), 0.92 (m, 6 H), 1.50 (m, 6 H), 1.53 (m, 6 H), 2.10 (d, J = 5.2 Hz, 1 H), 2.55 (d, J = 5.2 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –3.8, 8.6, 13.6, 27.3, 29.0, 47.4, 48.2 ppm. MS (EI, 70 eV): m/z (%) = 349 (5) [M – Bu]$^+$, 177 (77), 121 (65). $C_{17}H_{38}OSiSn$ (406.17): calcd. C 50.38, H 9.45; found C 50.72, H 9.81.

***trans*-1-(Tributylstannyl)-2-(dimethylphenylsilyl)epoxyethane (1m):** Yield 2.1 g (76%). R_f = 0.45 (hexanes). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.37 (s, 3 H), 0.43 (s, 3 H), 0.96 (t, J = 7.3 Hz, 9 H), 0.96 (m, 6 H), 1.39 (m, 6 H), 1.56 (m, 6 H), 2.37 (d, J = 5.2 Hz, 1 H), 2.67 (d, J = 5.2 Hz, 1 H), 7.41–7.45 (m, 3 H), 7.62–7.65 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –5.2, 8.7, 13.7, 27.3, 29.0, 46.8, 48.2, 127.8, 129.3, 133.9, 136.6 ppm. $C_{22}H_{40}OSiSn$ (468.19): calcd. C 56.54, H 8.63; found C 56.91, H 9.03.

***cis*-1-(Tributylstannyl)-2-(dimethylphenylsilyl)epoxyethane (1n):** Yield 1.8 g (67%). R_f = 0.44 (hexanes). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.35 (s, 6 H), 0.89 (t, J = 7.2 Hz, 9 H), 0.90 (m, 6 H), 1.31 (m, 6 H), 1.46 (m, 6 H), 2.70 (d, J = 6.4 Hz, 1 H), 2.98 (d, J = 6.4 Hz, 1 H), 7.37–7.40 (m, 3 H), 7.59–7.62 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –4.1, –3.6, 9.5, 13.7, 27.3, 29.0, 48.5, 51.3, 127.9, 129.4, 133.1, 136.9 ppm. $C_{22}H_{40}OSiSn$ (468.19): calcd. C 56.54, H 8.63; found C 56.16, H 8.20.

***cis*-1-(Tributylstannyl)-2-(*tert*-butyldiphenylsilyl)epoxyethane (1o):** Yield 1.7 g (63%). R_f = 0.43 (hexanes). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.80 (t, J = 7.2 Hz, 9 H), 0.98–0.86 (m, 6 H), 1.10 (s, 9 H), 1.40–1.12 (m, 12 H), 3.15 (d, J = 6.5 Hz, 1 H), 3.18 (d, J = 6.5 Hz, 1 H), 7.32–7.46 (m, 6 H), 7.74–7.81 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 9.6, 13.5, 18.9, 27.1, 27.4, 28.7, 45.7, 50.8, 127.5, 127.8, 129.5, 131.0, 133.1, 135.9, 136.4 ppm. $C_{30}H_{48}OSiSn$ (572.25): calcd. C 63.05, H 8.47; found C 63.37, H 8.45.

Method B. – Synthesis of 1-(*tert*-Butyldiphenylsilyl)-1-(tributylstannyl)epoxyethane (1p): BuLi (7.2 mmol, 1.6 M in hexane, 4.5 mL) and TMEDA (1.08 mL) were added at –60 °C under N_2 to a stirred solution of the (*tert*-butyldiphenylsilyl)epoxyethane[10c] (6 mmol) in THF (12 mL) The mixture was stirred at –60 °C for 20 min, tributylchlorostannane (10 mmol) was then added, and the system was stirred at this temperature for 3 h. The mixture was hydrolysed with methanol (1 mL) and an aq. NH_4Cl soln. and extracted with diethyl ether, and the organic layer was dried ($MgSO_4$). The residue obtained after evaporation of ether was purified by flash chromatography on silica gel with hexanes/AcOEt 20:1 as eluent to give **1p** (2.5 g, 73%); R_f = 0.44 (hexane/AcOEt, 20:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.3 Hz, 9 H), 0.98–0.86 (m, 6 H), 1.05 (s, 9 H), 1.40–1.12 (m, 12 H), 4.35 (d, J = 6.0 Hz, 1 H), 4.45 (d, J = 6.0 Hz, 1 H), 7.37–7.50 (m, 6 H), 7.67–7.84 (m, 4 H) ppm. $C_{30}H_{48}OSiSn$ (572.25): calcd. C 63.05, H 8.47; found C 62.72, H 8.69.

General Procedure for the Cleavage of Epoxystannanes with Lithium Diphenylphosphide: A solution of a stannyloxirane **1a**–**i** or **1k**–**n** (1 mmol) in THF (5 mL) was added dropwise to a stirred THF solution of lithium diphenylphosphide (1.5 mmol) [prepared from diphenylphosphane (0.258 mL, 1.5 mmol) and BuLi (0.936 mL, 1.6 M solution in hexane, 1.5 mmol) in THF (5 mL) at 0 °C under N_2 for 30 min]. When starting from distannyloxirane **1j** the stannyloxirane/lithium diphenylphosphide molar ratio was 1:2.5. The mixture was stirred at 0 °C until TLC indicated complete reaction (reaction time = 1 h–6.5 h). For the silyl-stannyloxiranes **1l** and **1o** the mixture was allowed to warm to room temperature and stirred for 12 h and 30 h, respectively. The reaction mixture was then hydrolysed with a saturated aq. $NaCO_3H$ solution and extracted with diethyl ether, and the organic layer was dried ($MgSO_4$). Ether was evaporated, and the residue was chromatographed to give the compounds characterized below.

2-(Diphenylphosphanyl)ethanol (2a): Yield 192 mg (78%). R_f = 0.20 (AcOEt). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.58 (dt, J = 10.3, 6.3 Hz, 2 H), 3.98 (dt, J = 16.5, 6.3 Hz, 2 H), 4.12 (br. s, 1 H), 7.44–7.53 (m, 6 H), 7.68–7.75 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 32.4 (d, J = 70.5 Hz), 56.4, 128. 7 (d, J = 11.9 Hz), 130.6 (d, J = 9.6 Hz), 131.9, 132.3 (d, J = 99.5 Hz) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 34.62 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3364, 1437, 1172 cm^{-1}. $C_{14}H_{15}O_2P$ (246.08): calcd. C 68.29, H 6.14; found C 68.67, H 5.85.

2-(Diphenylphosphanyl)-1-phenylethanol (2b): Yield 229 mg (71%). R_f = 0.40 (AcOEt). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.59 (ddd, J = 15.0, 7.1, 2.1 Hz, 1 H), 2.78 (ddd, J = 15.0, 10.9, 10.5 Hz, 1 H), 5.03 (br. s, 1 H), 5.16 (ddd, J = 10.9, 10.5, 2.1 Hz, 1 H), 7.20–7.82 (m, 15 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 39.1 (d, J = 68.6 Hz), 68.9 (d, J = 7.5 Hz), 125.3, 128.4, 129.8, 130.5, 131.2, 132.7, 133.9 (d, J = 95.2 Hz), 143.8 (d, J = 13.0 Hz) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 34.52 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3365, 1439, 1172 cm^{-1}. $C_{20}H_{19}O_2P$ (322.11): calcd. C 74.52, H 5.94; found C 74.81, H 6.24.

1-(Diphenylphosphanyl)propan-2-ol (2c): Yield 195 mg (75%). R_f = 0.25 (AcOEt); m.p. 200–205 °C (from hexane/AcOEt). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.28 (dd, J = 6.1, 1.5 Hz, 3 H), 2.36 (ddd, J = 14.9, 7.6, 2.4 Hz, 1 H), 2.49 (ddd, J = 14.9, 11.7, 9.8 Hz, 1 H), 4.24 (m, 1 H), 4.59 (br. s, 1 H), 7.30–7.92 (m, 10 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.8 (d, J = 14.4 Hz), 37.9 (d, J = 71.0 Hz), 63.2 (d, J = 4.7 Hz), 128.7 (d, J = 11.8 Hz), 130.9 (d, J = 9.3 Hz), 132.0, 133.1 (d, J = 99.2 Hz) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 34.71 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3383, 1437, 1170 cm^{-1}. $C_{15}H_{17}O_2P$ (260.10): calcd. C 69.22, H 6.58; found C 68.96, H 6.89.

1-(Diphenylphosphanyl)hexan-2-ol (2d): Yield 223 mg (74%). R_f = 0.31 (AcOEt). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.3 Hz, 3 H), 1.38 (m, 4 H), 1.50 (m, 2 H), 2.45 (m, 2 H), 2.85 (br. s, 1 H), 4.03 (m, 1 H), 7.35–7.52 (m, 6 H), 7.64–778 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9, 22.4, 27.3, 36.2 (d, J = 71.4 Hz), 38.3 (d, J = 13.2 Hz), 66.8 (d, J = 4.9 Hz), 127.5 (d, J = 13.1 Hz), 131.2 (d, J = 9.0 Hz) 132.7, 134.0 (d, J = 98.5 Hz) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 35.07 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3317, 1437, 1164 cm^{-1}. $C_{18}H_{23}O_2P$ (302.14): calcd. C 71.50, H 7.67; found C 71.21, H 7.32.

(1*R*,2*S*)-2-(Diphenylphosphanyl)-1,2-diphenylethanol (2e): Yield 250 mg (63%). R_f = 0.58 (AcOEt); m.p. 170–176 °C (from hexane/AcOEt). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.63 (dd, J = 8.1, 1.8 Hz, 1 H), 5.17 (br. s, 1 H), 5.50 (dd, J = 7.6, 1.8 Hz, 1 H), 6.85–8.07 (m, 20 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 53.1 (d, J = 66.2 Hz), 72.4 (d, J = 2.3 Hz), 125.8, 128.1, 129.4, 130.9, 131.7, 132.1, 133.6 (d, J = 95.2 Hz), 141.1 (d, J = 12.2 Hz) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 39.89 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3374, 1437, 1175 cm^{-1}. $C_{26}H_{22}O_2P$ (397.14): calcd. C 78.58, H 5.58; found C 78.18, H 5.22.

Diphenylvinylphosphane Oxide (3a): Yield 22.8 mg (10%); see ref.[9b]

(*E*)-(2-Phenylethenyl)diphenylphosphane Oxide (3b): Yield 45.6 mg (15%); see ref.[9b]

(*E*)-Diphenyl(prop-1-enyl)phosphane Oxide (3c): Yield 29 mg (12%); see ref.[9b]

(*E*)-(Hex-1-enyl)diphenylphosphane Oxide (3d): Yield 36.9 mg (13%); see ref.[9b]

(*E*)-(Dec-5-enyl)diphenylphosphane Oxide (3e): Yield 251 mg (74%); see ref.[9b]

(*E*)-(1,2-Diphenylethenyl)diphenylphosphane Oxide (3f): Yield 41.8 mg (11%); see ref.[9b]

(*E*)-Diphenyl[2-(trimethylsilyl)ethenyl]phosphane Oxide (3 g): Yield 129 mg (43%); see ref.[9b]

(*E*)-Diphenyl[2-(tributylstannyl)ethenyl]phosphane Oxide (3h): Yield 165 mg (32%). R_f = 0.65 (AcOEt); m.p. 155–160 °C (from hexane/AcOEt). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.84–1.02 (m, 15 H), 1.30 (m, 6 H), 1.43–1.64 (m, 6 H) 6.90 (dd, J = 33.2, 20.8 Hz, 1 H), 7.42–7.52 (m, 6 H), 7.63–7.71 (m, 4 H), 7.73 (dd, J = 30.2, 20.8 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 9.8, 13.6, 27.2 (d, J = 77.4 Hz), 28.9, 128.4 (d, J = 12.0 Hz), 131.4 (d, J = 9.7 Hz), 131.6, 131.7 (d, J = 101.5 Hz), 139.5 (d, J = 85.0 Hz), 157.3 (d, J = 8.9 Hz) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 22.42 ($J_{P,Sn^{19}}$ = 177.0, $J_{P,Sn^{17}}$ = 168.0 Hz) ppm. $C_{26}H_{39}OPSn$ (518.18): calcd. C 60.37, H 7.60; found C 60.01, H 7.96.

(*E*)-[2-(Dimethylphenylsilyl)ethenyl]diphenylphosphane Oxide (3i): Yield 206 mg (57%); see ref.[9b]

(*Z*)-[2-(Dimethylphenylsilyl)ethenyl]diphenylphosphane Oxide (3j): Yield 271 mg (75%). R_f = 0.60 (AcOEt). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.59 (s, 6 H), 7.09 (dd, J = 31.0, 17.4 Hz, 1 H), 7.23 (dd, J = 44.2, 17.4 Hz, 1 H),7.30–7.69 (m, 15 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –1.20, 127.6, 128.5 (d, J = 11.9 Hz), 128.7, 131.1 (d, J = 9.7 Hz), 131.5, 133.7 (d, J = 97.6 Hz), 133.8, 139.3, 139.6 (d, J = 100.5 Hz), 154.9 (d, J = 6.9 Hz) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 21.59 ppm. $C_{22}H_{23}OPSi$ (362.13): calcd. C 72.90, H 6.40; found C 73.38, H 6.77.

1-(Diphenylphosphanyl)propan-2-one (4a): Yield 162 mg (63%). R_f = 0.32 (AcOEt); m.p. 116–118 °C (from hexane/AcOEt). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.32 (s, 3 H), 3.60 (d, J = 14.8 Hz, 2 H), 7.45–7.58 (m, 6 H), 7.72–7.79 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 32.6, 47.9 (d, J = 56.5 Hz), 128.7 (d, J = 12.3 Hz), 130.8 (d, J = 9.9 Hz), 131.9 (d, J = 104.2 Hz), 132.3, 201.0 (d, J = 4.9 Hz) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 27.02 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1733, 1437, 1195 cm^{-1}. $C_{15}H_{15}O_2P$ (258.08): calcd. C 69.76, H 5.85; found C 70.10, H 5.55.

1-(Diphenylphosphanyl)hexan-2-one (4b): Yield 195 mg (65%). R_f = 0.38 (AcOEt); m.p. 120–122 °C (from hexane/AcOEt). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.82 (t, J = 7.3 Hz, 3 H), 1.18 (m, 2 H), 1.45 (m, 2 H), 2.63 (t, J = 7.3 Hz, 2 H), 3.58 (d, J = 15.0 Hz, 2 H), 7.44–7.57 (m, 6 H), 7.71–7.79 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.6, 21.8, 25.1, 44.9, 46.8 (d, J = 56.7 Hz), 128.6 (d, J = 12.4 Hz), 130.7 (d, J = 9.8 Hz), 131.8 (d, J = 103.2 Hz), 132.0, 203.0 (d, J = 5.1 Hz) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 27.35 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1710, 1438, 1198 cm^{-1}. $C_{18}H_{21}O_2P$ (300.13): calcd. C 71.98, H 7.05; found C 72.31, H 7.34.

2-(Diphenylphosphanyl)-1-phenylethanone (4c): Yield 224 mg (70%). R_f = 0.42 (AcOEt); m.p. 140–142 °C (from hexane/AcOEt). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.14 (d, J = 15.4 Hz, 2 H), 7.36–7.56 (m, 9 H), 7.76–7.83 (m, 4 H), 7.97 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 43.3 (d, J = 58.0 Hz), 128.5, 128.6 (d, J = 12.9 Hz), 129.2, 131.0 (d, J = 9.9 Hz), 131.8 (d, J = 109.1 Hz), 133.6, 136.9, 192.7 (d, J = 5.0 Hz) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 27.48 ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 1675, 1438, 1200 cm^{-1}. $C_{20}H_{17}O_2P$ (320.10): calcd. C 74.99, H 5.35; found C 75.33, H 5.76.

1-(*tert*-Butyldiphenylsilyl)-2-(diphenylphosphanyl)ethanone (4d): Yield 86.8 mg (18%). R_f = 0.25 (hexanes/AcOEt 5:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.06 (s, 9 H), 3.77 (d, J = 12.7 Hz, 2 H), 7.31–7.71 (m, 20 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.6, 26.8, 50.5 (d, J = 60.5 Hz), 127.3, 128.2 (d, J = 11.6 Hz), 128.7, 129.8, 130.4 (d, J = 8.3 Hz), 134.3 (d, J = 101.5 Hz), 135.5, 136.3, 238.7 ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 27.91 ppm. $C_{30}H_{31}O_2PSi$ (482.18): calcd. C 74.66, H 6.47; found C 75.01, H 6.78.

1,2-Bis(diphenylphosphanyl)ethanol (9): Yield 227 mg (51%). R_f = 0.20 (AcOEt). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.47 (m, 1 H), 2.96 (m, 1 H), 4.96 (m, 1 H), 7.19–7.81 (m, 20 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 29.7 (d, J = 69.0 Hz), 66.6 (d, J = 85.6 Hz), 127.6, 128.5, 129.1, 130.6, 131.3, 132.1, 133.6, 133.8 ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 37.09 (d, $J_{P,P}$ = 50.9 Hz), 30.78 (d, $J_{P,P}$ = 50.9 Hz) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3368, 1438, 1175 cm^{-1}. $C_{26}H_{24}O_3P_2$ (446.12): calcd. C 69.95, H 5.42; found C 70.36, H 5.13.

(*E*)-1-(*tert*-Butyldiphenylsilyloxy)-2-(tributylstannyl)ethene (10a): Yield 268 mg (47%). R_f = 0.60 (hexanes). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.74–0.96 (m, 15 H), 1.10 (s, 9 H), 1.20–1.75 (m, 12 H), 5.04 (d, J = 14.8 Hz, 1 H), 6.24 (d, J = 14.8 Hz, 1 H), 7.33–7.77 (m, 10 H) ppm. IR (film): $\tilde{\nu}$ = 1100), 960 cm^{-1}. $C_{30}H_{48}OSiSn$ (562.25): calcd. C 63.05, H 8.47; found C 62.61, H 8.82.

(*E*)-2-(*tert*-Butyldiphenylsilyloxy)-1-(diphenylphosphanyl)ethene (10b): Yield 180 mg (39%). R_f = 0.23 (hexanes/AcOEt 5:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20 (s, 9 H), 4.89 (d, J = 24.5 Hz, 1 H), 7.31–7.71 (m, 21 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.4, 27.4, 99.0 (d, J = 93.7 Hz), 127.7, 128.3, 128.9, 130.3, 131.3, 132.1, 133.7 (d, J = 103.0 Hz), 135.5, 136.3 ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 36.64 ppm. $C_{30}H_{31}O_2PSi$ (482.18): calcd. C 74.66, H 6.47; found C 74.91, H 6.78.

Acylation of β-Phosphanyl Ketones. – General Procedure: A mixture of NaH (2 mmol, 48 mg) and β-phosphanyl ketone **4a** or **4c** (1 mmol) in THF (8 mL) was stirred at 0 °C under N_2 for 30 min. Acetyl or benzoyl chloride (2 mmol) was then added and the reaction mixture was stirred at room temperature (**4a**) or 78 °C (**4c**) until TLC indicated complete reaction. Quenching with aqueous ammonium chloride, aqueous workup with diethyl ether, drying ($MgSO_4$) and chromatography gave the products characterized below.

3-(Diphenylphosphanyl)pentane-2,4-dione (5a): Yield 276 mg (92%). R_f = 0.38 (AcOEt). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.31 (s, 6 H), 5.98 (d, J = 13.5 Hz, 1 H), 7.47–7.78 (m, 10 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.0, 22.2, 109.3 (d, J = 102.5 Hz), 128.4 (d, J = 12.3 Hz), 130.8 (d, J = 9.2 Hz), 131.6, 133.4 (d, J = 107.7 Hz), 163.1 (d, J = 4.6 Hz) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 19.15 ppm. IR (film): $\tilde{\nu}$ = 1705, 1437, 1170 cm^{-1}. $C_{17}H_{17}O_3P$ (300.09): calcd. C 68.00, H 5.71; found C 68.36, H 6.08.

2-(Diphenylphosphanyl)-1-phenylbutane-1,3-dione (5b): Yield 296 mg (82%) from **4a** and 307 mg (85%) from **4c**. R_f = 0.40 (AcOEt). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.96 (s, 3 H), 6.37 (d, J = 12.9 Hz, 1 H), 7.35–7.84 (m, 15 H) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 20.39 ppm. $C_{22}H_{19}O_3P$ (362.11): calcd. C 72.92, H 5.29; found C 72.50, H 4.66.

2-(Diphenylphosphanyl)-1,3-diphenylpropane-1,3-dione (5c): Yield 377 mg (89%). R_f = 0.43 (AcOEt). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.58 (d, J = 11.0 Hz, 1 H), 7.30–8.10 (m, 20 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 109.6 (d, J = 103.0 Hz), 125.7, 128.5 (d, J = 16.4 Hz), 128.8, 130.2, 131.0 (d, J = 10.0 Hz), 131.6, 133.0 (d, J = 108.4 Hz), 134.0, 161.4 (d, J = 3.3 Hz) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 21.05 ppm. IR (film): $\tilde{\nu}$ = 1703, 1437, 1178 cm^{-1}. $C_{27}H_{21}O_3P$ (424.43): calcd. C 76.41, H 4.99; found C 76.26, H 4.64.

Treatment of β-Phosphanyl Ketones with Hydroxylamine. – General Procedure: A mixture of a β-phosphanyl ketone **4a**–**c** (1 mmol), hydroxylamine hydrochloride (4 mmol) and sodium acetate (4 mmol) was heated at reflux in a water/ethanol mixture (15:1, 16 mL) for 6 h. The reaction mixture was extracted with CH_2Cl_2, the organic layer was dried ($MgSO_4$), and the solvent was evaporated under reduced pressure. The following oximes **6a**–**c** were isolated:

(*Z*,*E*)-[2-(Hydroximino)propyl]diphenylphosphane Oxide (6a): Yield 202 mg (74%). R_f = 0.26 (AcOEt); m.p. 188–190 °C (from hexane/CH_2Cl_2). *Z* Isomer: 101 mg (37%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.94 (d, J = 2.0 Hz, 3 H), 3.29 (d, J = 13.8 Hz, 2 H), 7.35–7.54 (m, 6 H), 7.72–7.75 (m, 4 H), 10.34 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.9, 37.4 (d, J = 67.5 Hz), 128.2 (d, J = 11.5 Hz), 130.4 (d, J = 9.6 Hz), 131.5, 132.7 (d, J = 100.2 Hz), 148.9 ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 29.63. *E* Isomer: 101 mg (37%) ppm. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.98 (d, J = 2.1 Hz, 3 H), 3.60 (d, J = 14.9 Hz, 2 H), 7.35–7.54 (m, 6 H), 7.72–7.75 (m, 4 H), 10.67 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.9, 30.7 (d, J = 66.1 Hz), 128.0 (d, J = 10.2 Hz), 130.4 (d, J = 9.6 Hz), 131.5, 132.4 (d, J = 99.4 Hz), 148.8 ppm. ^{31}P NMR

(121 MHz, $CDCl_3$): δ = 29.54 ppm. $C_{15}H_{16}NO_2P$ (273.09): calcd. C 65.93, H 5.90, N 5.13; found C 66.20, H 5.65, N 4.81.

(*Z*,*E*)-[2-(Hydroximino)hexyl]diphenylphosphane Oxide (6b): Yield 195 mg (62%). R_f = 0.32 (AcOEt). *Z* isomer: 65 mg (41%). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.85 (t, *J* = 7.3 Hz, 3 H), 1.20 (m, 2 H), 1.37 (m, 2 H), 2. 38 (t, *J* = 7.6 Hz, 2 H), 3.29 (d, *J* = 14.2 Hz, 2 H), 7.33–7.45 (m, 6 H), 7.63–7.82 (m, 4 H), 10.29 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.5, 22.7, 27.3, 34.4, 36.0 (d, *J* = 67.7 Hz), 128.8 (d, *J* = 12.1 Hz), 130.1 (d, *J* = 8.9 Hz), 131.5, 132.8 (d, *J* = 100.4 Hz), 153.7 ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 29.76. *E* isomer: 130 mg (41%) ppm. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.76 (t, *J* = 7.3 Hz, 3 H), 1.22 (m, 2 H), 1.40 (m, 2 H), 2. 28 (t, *J* = 6.8 Hz, 2 H), 3.60 (d, *J* = 15.4 Hz, 2 H), 7.33–7.45 (m, 6 H), 7.63–7.82 (m, 4 H), 10.59 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.8, 22.0, 28.1, 29.9 (d, *J* = 66.0 Hz), 34.4, 128.3 (d, *J* = 12.2 Hz), 130.8 (d, *J* = 9.8 Hz), 131.8 (d, *J* = 2.1 Hz), 132.4 (d, *J* = 101.2 Hz), 151.8 (d, *J* = 7.5 Hz) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 29.58 ppm. $C_{18}H_{22}NO_2P$ (315.14): calcd. C 68.56, H 7.03, N 4.44; found C 68.81, H 7.36, N 4.71.

(*E*)-[2-(Hydroximino)-2-(phenyl)ethyl]diphenylphosphane Oxide (6c): Yield 187 mg (56%). R_f = 0.41 (AcOEt); m.p. 183–185 °C (from hexane/AcOEt). ^1H NMR (300 MHz, $CDCl_3$): δ = 4.05 (d, *J* = 15.5 Hz, 2 H), 7.20 (m, 3 H), 7.50 (m, 6 H), 7.60 (m, 2 H), 7.80 (m, 4 H), 11.51 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.9 (d, *J* = 64.4 Hz), 126.4, 128.8 (d, *J* = 11.7 Hz) 130.3, 130.9 (d, *J* = 9.3 Hz), 131.6, 132.8, 134.0 (d, *J* = 98.8 Hz), 135.8, 149.0 (d, *J* = 9.2 Hz) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 28.54 ppm. $C_{20}H_{18}NO_2P$ (335.11): calcd. C 71.63, H 5.41, N 4.18; found C 71.31, H 5.73, N 4.42.

Preparation of *N*-Tosyloximes. Typical Procedure: Tosyl chloride (1.03 mmol) was added at 0 °C to a stirred solution of an oxime **6a**–**c** (1 mmol) in dry pyridine (1 mL), and stirring was continued for 1 h. The mixture was allowed to warm to room temperature and stirred for 1 h. Quenching with ice water (13 mL) afforded a white precipitate, which was isolated by filtration in vacuo and washed with water several times. The following products were obtained.

(*Z*,*E*)-[2-(*p*-Tolylsulfonyloximino)propyl]diphenylphosphane Oxide (7a): Yield 298 mg (70%). R_f = 0.35 (AcOEt); m.p. 130–133 °C (from pyridine/water). *Z* isomer: 43 mg (10%). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.15 (d, *J* = 1.8 Hz, 3 H), 2.43 (s, 3 H), 3.58 (d, *J* = 14.7 Hz, 2 H), 7.20–7.81 (m, 14 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.2, 21.9, 34.4 (d, *J* = 64.5 Hz), 128.2, 130.4, 131.5, 132.5, 144.9, 159.8 ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 27.05. *E* isomer: 255 mg (60%) ppm. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.11 (d, *J* = 1.8 Hz, 3 H), 2.47 (s, 3 H), 3.32 (d, *J* = 13.9 Hz, 2 H), 7.20–7.81 (m, 14 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.3, 21.7, 38.0 (d, *J* = 63.3 Hz), 128.2, 130.4, 131.5, 132.5, 144.8, 161.9 ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 27.95 ppm. IR (film): $\tilde{\nu}$ = 3052, 1600, 1470, 1262, 1192 cm^{-1}. $C_{22}H_{22}NO_4PS$ (427.10): calcd. C 61.82, H 5.19, N 3.28; found C 61.55, H 5.36, N 3.47.

(*Z*,*E*)-[2-(*p*-Tolylsulfonyloximino)hexyl]diphenylphosphane Oxide (7b): Yield 253 mg (54%). R_f = 0.41 (AcOEt). *Z* isomer: 64 mg (14%). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.84 (t, *J* = 7.3 Hz, 3 H), 1.14 (m, 2 H), 1.42 (m, 2 H), 1.99 (s, 3 H), 2. 36 (t, *J* = 7.3 Hz, 2 H), 3.61 (d, *J* = 15.3 Hz, 2 H), 7.33–7.45 (m, 8 H), 7.63–7.83 (m, 6 H) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 27.70 ppm. *E* isomer: 189 mg (40%) ppm. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.78 (t, *J* = 7.2 Hz, 3 H), 1.14 (m, 2 H), 1.42 (m, 2 H), 2.00 (s, 3 H), 2. 58 (t, *J* = 7.3 Hz, 2 H), 3.58 (d, *J* = 15.1 Hz, 2 H), 7.33–7.45 (m, 8 H), 7.63–7.83 (m, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.7, 21.7, 21.8, 25.2, 44.9, 46.7 (d, *J* = 57.1 Hz), 128.2 (d, *J* = 11.4 Hz), 130.8, 131.8 (d, *J* = 8.8 Hz), 133.3, 144.4, 161.9 (d, *J* = 6.7 Hz) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 27.98 ppm. IR (film): $\tilde{\nu}$ = 3053, 1591, 1437, 1265, 1193 cm^{-1}. $C_{25}H_{28}NO_4PS$ (469.15): calcd. C 63.95, H 6.01, N 2.98; found C 64.21, H 5.86, N 2.74.

(*E*)-2-Phenyl-[2-(*p*-tolylsulfonyloximino)ethyl]diphenylphosphane Oxide (7c): Yield 205 mg (42%). R_f = 0.45 (AcOEt); m.p. 142–144 °C (from pyridine/water). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.44 (s, 3 H), 4.01 (d, *J* = 15.4 Hz, 2 H), 7.23 (m, 3 H), 7.45 (m, 6 H), 7.52–7.83 (m, 5 H) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 26.18 ppm. $C_{27}H_{24}NO_4PS$ (489.12): calcd. C 66.25, H 4.94, N 2.86; found C 65.91, H 5.14, N 4.68.

Synthesis of 2-(Diphenylphosphanyl)-3-methyl-2*H*-azirine (8): Triethylamine (2 mmol, 0.258 mL) was added to a solution of the *N*-tosyloxime **7a** (1 mmol) in dry THF (5 mL) at 0 °C. After stirring for 10 h at this temperature, the mixture was diluted with CH_2Cl_2 and washed with a solution of HCl (2 M) and with water. The organic layer was dried ($MgSO_4$), and solvents were evaporated under reduced pressure. The crude product was purified by crystallisation from hexane/CH_2Cl_2 to give **8** (234 mg, 92%) as a white solid; m.p. 98–99 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.24 (d, *J* = 36.6 Hz, 1 H), 2.43 (s, 3 H), 7.51 (m, 6 H), 7.73 (m, 4 H) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ = 30.56 ppm. $C_{15}H_{14}NOP$ (255.08): calcd. C 70.58, H 5.53, N 5.49; found C 70.82, H 5.40, N 5.75.

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