Regio- and Stereospecific Cleavage of Silyl- and Disilylepoxides with Lithium Diphenylphosphide

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Abstract: Unsubstituted or α- and β-C-substituted silylepoxides react stereospecifically with lithium diphenylphosphide, optionally followed by methylation, to give vinylphosphonium iodides or vinylphosphine oxides resulting from 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 vinylphosphine oxides or α-silylated silyl enol ethers by α- and β-cleavage, respectively. All compounds are interesting synthons in organic chemistry.

Keywords: cleavage reactions · enols · epoxysilanes · phosphaalkenes · silyl enol ethers

Introduction

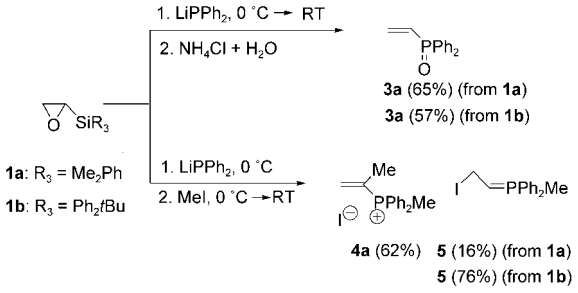
In a preliminary communication[1] we reported the regio- and stereospecific synthesis of vinylphosphonium iodides by α-cleavage of unsubstituted or *trans*-β-alkyl substituted dimethylphenylsilyl- or *tert*-butyldiphenylsilylepoxides with lithium diphenylphosphide followed by reaction with methyl iodide. Under the same conditions, the *trans*-β-phenyl-α-*tert*-butyldiphenylsilylepoxide led to the corresponding (*Z*)-silyl enol ether resulting from β-opening.

With the aim of exploring the scope of this procedure, we have extended this methodology to silylepoxides with various substitution patterns, such as α-C and *cis*-β-C substitution, α- or β-silyl substitution by different silyl groups and tri-substitution. These substrates have been synthesised by epoxidation of vinylsilanes obtained previously by dimethylphenyl- and *tert*-butyldiphenylsilyl cupration starting from alkynes[2,3] or allenes.[4,5]

In this paper, we describe the results obtained in the cleavage of silylepoxides **1** and disilylepoxides **2** by lithium diphenylphosphide, optionally followed by methylation.

Results and Discussion

Unsubstituted or *cis*- and *trans*-β-alkyldimethylphenylsilyl- and *tert*-butyldiphenylsilylepoxides **1a**–**h** undergo α-nucleophilic attack of lithium diphenylphosphide giving stereospecifically vinylphosphines resulting from Peterson elimination,[6,7] which were spontaneously oxidised to the corresponding oxides in the final hydrolysis or converted to vinylphosphonium iodides by subsequent treatment with methyl iodide (Schemes 1 and 2).



Scheme 1.

Under the latter conditions, the initially formed unsubstituted vinylphosphonium iodide—resulting from the α-cleavage of **1a** and **1b**—was transformed to the 1-methylvinylphosphonium iodide **4a** and to the iodoalkylidenephosphorane **5**, respectively. Compound **5** appears to be formed by 1,4-addition of an iodide ion and **4a** through α-methylation of **5** followed by E_2 elimination of HI by the action of the dimethylphenylsiloxide ion (Scheme 3).

β-Phenylsilylepoxides experience α- or β-opening depending on the nature of the silyl group[8] and the configuration. The *cis*-β-phenyl-α-*tert*-butyldiphenylsilylepoxide (**1i**) and the *trans*-β-phenyl-α-dimethylphenylsilylepoxide (**1j**) were opened by nucleophilic α-attack giving the corresponding vinylphosphine oxides **3f** and **3g** or the vinylphosphonium

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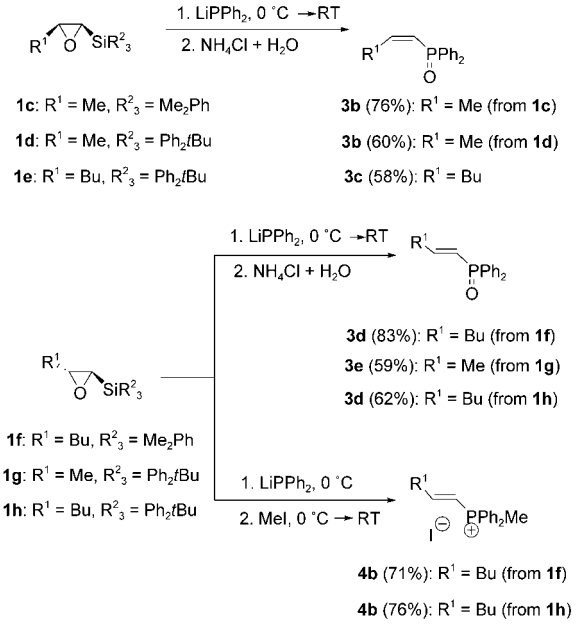
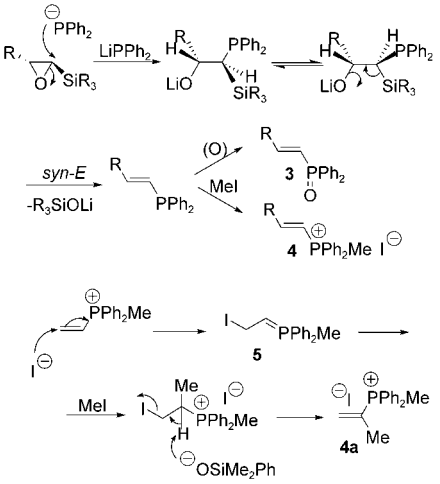


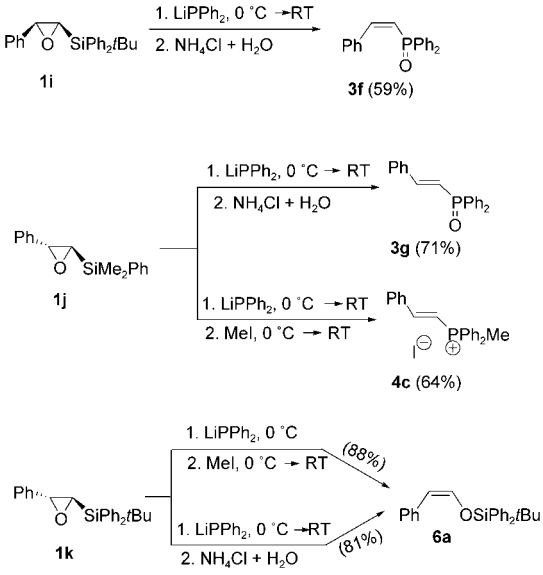
Scheme 2.



Scheme 3.

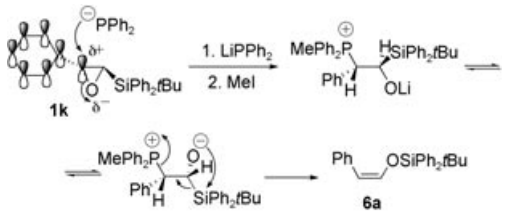
iodide **4c**. On the other hand, the *trans*-β-phenyl-α-*tert*-butyldiphenylsilylepoxide (**1k**) underwent nucleophilic attack at β-carbon followed by Brook rearrangement[9] with simultaneous elimination of a good leaving group (methyldiphenylphosphine) to give the (*Z*)-silyl enol ether **6a**. Even when the methylation was omitted, the elimination of diphenylphosphide also took place, but the yield of the silyl enol ether **6a** was slightly lower (Scheme 4).

Probably, this behaviour is due to a combination of electronic (benzylic β-carbon) and steric effects. The hindered *tert*-butyldiphenylsilyl group favours the β-opening, especially when the β-carbocation to the silicon can also be stabilised by the phenyl group. Perhaps, this is only possible in the *trans*-β-phenyl-α-*tert*-butyldiphenylsilylepoxide (**1k**) because in the *cis*-isomer **1i** the bulky *tert*-butyldiphenylsilyl group prevents the co-planarity and conjugation of the β-



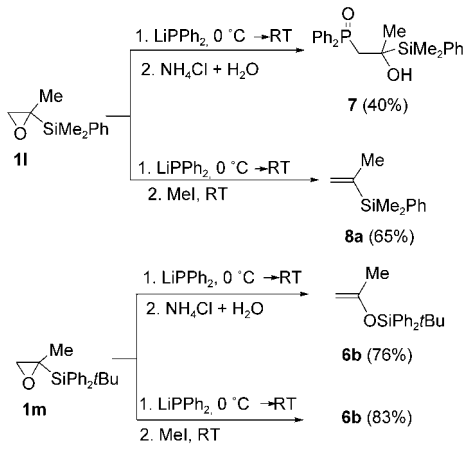
Scheme 4.

phenyl group with the incipient carbocation resulting from β-opening (Scheme 5).

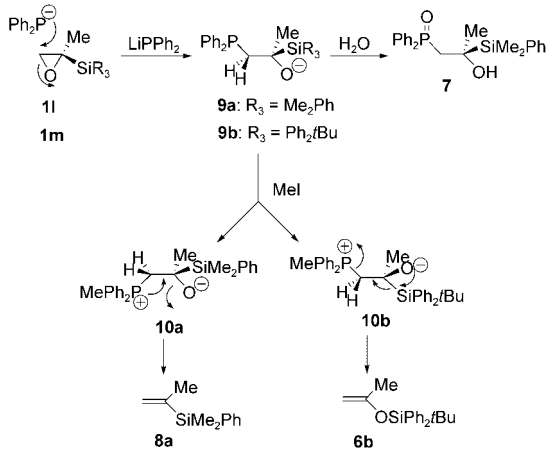


Scheme 5.

The *gem*-methyl substituted silylepoxides **1l** and **1m** undergo β-opening to give β-diphenylphosphino-α-oxidosilane intermediate **9a** and **9b**, which evolve in a different way; this depends on the nature of the silyl group (Schemes 6 and 7).



Scheme 6.

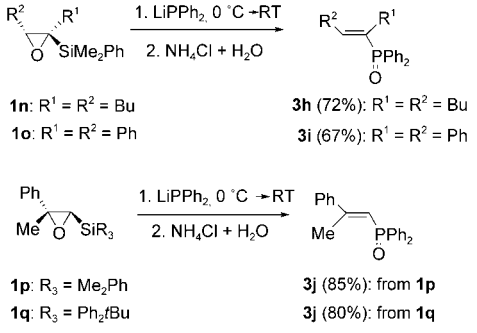


Scheme 7.

The dimethylphenylsilyl intermediate **9a** was hydrolysed to the corresponding α-hydroxysilane **7**; on the other hand, when methylated, the vinylsilane **8a**, which resulted from Wittig elimination of the intermediate **10a**, was obtained. Nevertheless, the *tert*-butyldiphenylsilyl intermediate **9b**, or the methylated intermediate **10b**, experience a Brook rearrangement with elimination of the phosphorous leaving group to give the silyl enol ether **6b**. If the methylation is omitted, the result is the same but the yield of **6b** is lower. The different behaviour of the intermediates **10a** and **10b** may depend on two factors: a) higher migratory aptitude of the *tert*-butyldiphenylsilyl than the dimethylphenylsilyl group (phenyl groups on silicon have been shown to accelerate the Brook rearrangement[10,11]) and b) the stability of the necessary conformation for the *syn*-elimination of diphenylmethylphosphine oxide. Probably, the intermediate **10b** does not undergo Wittig elimination due to the fact that in this conformation the bulky *tert*-butyldiphenylsilyl group should be eclipsed, whereas in the conformation for Brook rearrangement and *anti*-elimination this group is staggered (Scheme 7).

The silylepoxides α,β- or β,β-disubstituted **1n–q** react with lithium diphenylphosphide to give exclusively the corresponding diphenylphosphine oxides **3h–j**, which resulted from α-opening (Scheme 8).

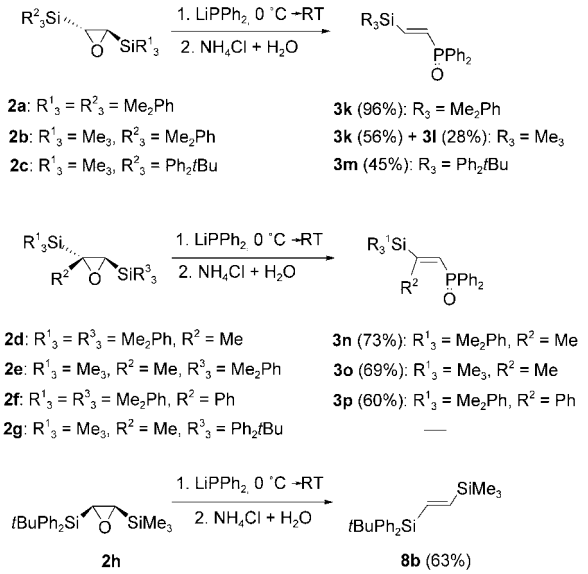
On the other hand, the behaviour of the disilylepoxides **2** toward the lithium diphenylphosphide depend on the



Scheme 8.

nature, relative position and configuration of both silyl groups.

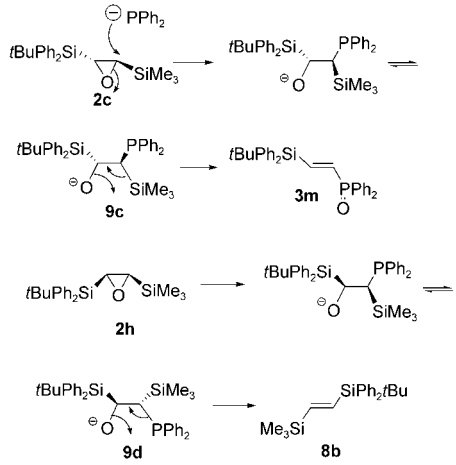
The *trans*-α,β-disilylepoxides **2a–c** are opened by nucleophilic α-attack to the less hindered silyl group followed by Peterson elimination to give the corresponding vinylphosphine oxides. When both silyl groups do not have a very different size, such as **2b** (trimethyl and dimethylphenyl), a 2:1 mixture of two possible vinylphosphine oxides **3k** and **3l** was obtained. However, if they are of drastically different size as in **2c** (trimethyl and *tert*-butyldiphenyl) the diphenylphosphide attacks only at the carbon bearing the trimethylsilyl group. In this case, the reactivity decreases, long reaction times are required (96 h) and the yield of **3m** is lower. The trisubstituted α,β-disilylepoxides **2d–f** afforded only the vinylphosphine oxide, which resulted from α-attack to the monosubstituted carbon. When this position bears the *tert*-butyldiphenylsilyl group the reaction did not take place. The epoxide **2g** was recovered even if a large excess of lithium diphenylphosphide (3.5 equiv) and long reaction times (120 h) were used (Scheme 9).



Scheme 9.

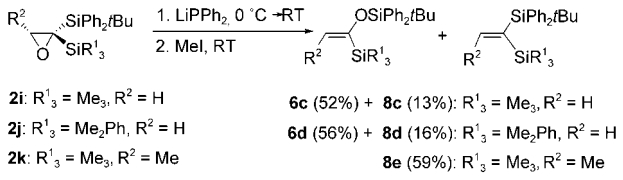
The *cis*-α,β-disilylepoxide **2h** was also opened by α-attack to the less hindered silyl group, but the intermediate now experienced Wittig elimination to afford the 1,2-disilylethylene **8b**.

The intermediates **9c** and **9d**, which resulted from the α-opening at the trimethylsilyl group of the *trans*- and *cis*-α-trimethyl-β-*tert*-butyldiphenylsilylepoxides **2c** and **2h**, may evolve by a different path depending on the steric requirements for the Wittig or Peterson eliminations. In case of the intermediate **9c**, the conformation required for a Peterson elimination is more stable than that necessary for Wittig elimination (the silyl and phosphino groups are eclipsed). Likewise, the differential stability of the corresponding conformations in the intermediate **9d** is the opposite (Scheme 10).



Scheme 10.

The β-unsubstituted *gem*-disilylepoxides **2i** and **2j** undergo β-opening to give the α-silylated silyl enol ethers **6c** and **6d** resulting from Brook rearrangement of the *tert*-butyldiphenylsilyl group, together with minor amounts of the *gem*-disilylalkenes **8c** and **8d** formed by Wittig elimination. On the contrary, the β-methyl *gem*-disilylepoxide **2k** afforded exclusively the *gem*-disilylalkene **8e**, which resulted from a Wittig elimination. If the methylation is omitted the results are the same, but the yields were lower (Scheme 11).



2i: $R^1_3 = Me_3$, $R^2 = H$
2j: $R^1_3 = Me_2Ph$, $R^2 = H$
2k: $R^1_3 = Me_3$, $R^2 = Me$

6c (52%) + **8c** (13%): $R^1_3 = Me_3$, $R^2 = H$
6d (56%) + **8d** (16%): $R^1_3 = Me_2Ph$, $R^2 = H$
8e (59%): $R^1_3 = Me_3$, $R^2 = Me$

Scheme 11.

Conclusion

In conclusion, the α- or β-opening of silylepoxides by lithium diphenylphosphide depends on electronic and steric factors. In general, the α-attack is preferred, except when the α-position is hindered. We have stereospecifically synthesised vinylphosphonium salts or vinylphosphonium oxides with retention of configuration by α-attack of diphenylphosphide ion to epoxysilanes, followed by Peterson elimination. These compounds are suitable reagents for the synthesis of a variety of heterocyclic, carbocyclic and chain-extended systems.[12] On the other hand, when the α-position is hindered (*gem*-disubstituted epoxysilanes or epoxides bearing the bulky *tert*-butyldiphenylsilyl group) the nucleophilic attack occurs exclusively at the β-carbon to afford vinylsilanes, which result from a Wittig elimination, or silyl enol ethers, which are formed by a Brook rearrangement and *anti*-elimination. The silyl enol ether is one of the more useful functional groups in organic synthesis[13] and few methods exist which provide them in a stereocontrolled manner.[14] Moreover, β-silyl vinylphosphine oxides and α-silylated silyl enol ethers, obtained by α- or β-cleavage of 1,2- or 1,1-disilylated epoxides, are even more versatile synthons.

Experimental Section

General: THF was distilled from sodium/benzophenone in a recycling still. All chromatographic and work-up solvents were distilled prior to use. All reactions involving organometallic reagents were carried out under nitrogen atmosphere. ^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 a pre-coated plate of silica gel 60 (nano-SIL-20, Macherey-Nagel). Flash chromatography was performed on silica gel 60 (230–400 mesh, M-N). Silylepoxides **1a–q** were prepared by epoxidation[15,3] of the corresponding vinylsilanes obtained by reaction with electrophiles of the intermediates from dimethylphenylsilyl- or *tert*-butyldiphenylsilylcupration of alkynes[2,3] (**1a–k** and **1n–q**) or allene[4,5] (**1l** and **1m**).

Synthesis of 1,2-disilylepoxides—Typical procedure: MCPBA (1.35 mmol) and $NaHCO_3$ (2 mmol) were added to a solution of 1,2-disilylalkene[3,16] (1 mmol) in CH_2Cl_2 (3 mL) (trimethylsilyl- and dimethylphenylsilylalkenes) or in $CHCl_3$ (3 mL) (*tert*-butyldiphenylsilylalkenes). The reaction mixture was stirred at room temperature in CH_2Cl_2 or under reflux in $CHCl_3$, respectively, until TLC indicated complete reaction. The mixture was washed several times with an aqueous solution of $NaHSO_3$, $NaHCO_3$, and NaCl. The organic layer was dried ($MgSO_4$), the solvent removed and the residue was purified by chromatography (silica gel, hexanes/AcOEt) to give the following products,

(*E*)-1,2-Bis(dimethylphenylsilyl)epoxyethane (2a): Yield = 90%; R_f = 0.46 (hexanes/AcOEt 20:1); ^1H NMR (300 MHz, $CDCl_3$): δ = 0.36 (s, 12H), 2.30 (s, 2H), 7.40–7.56 (m, 10H); IR (film): $\tilde{\nu}$ = 1230, 1100 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{24}OSi_2$ (312.14): C 69.17, H 7.74; found: C 69.29, H 7.65.

(*E*)-1-Dimethylphenylsilyl-2-trimethylsilylepoxyethane (2b): Yield = 85%; R_f = 0.50 (hexanes/AcOEt 20:1); ^1H NMR (300 MHz, $CDCl_3$): δ = 0.12 (s, 9H), 0.35 (s, 3H), 0.41 (s, 3H), 2.18 (d, J = 5.0 Hz, 1H), 2.31 (d, J = 5.0 Hz, 1H), 7.40–7.45 (m, 3H), 7.60–7.63 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = −5.5, −5.3, −3.8, 46.6, 47.4, 127.8, 129.4, 133.8, 136.4; IR (film): $\tilde{\nu}$ = 1250, 1120 cm^{-1}; elemental analysis calcd (%) for $C_{13}H_{22}OSi_2$ (250.12): C 62.34, H 8.85; found: C 62.51, H 8.91.

(*E*)-1-*tert*-Butyldiphenylsilyl-2-trimethylsilylepoxyethane (2c): Yield = 75%; R_f = 0.46 (hexanes/AcOEt 20:1); ^1H NMR (300 MHz, $CDCl_3$): δ = 0.83 (s, 9H), 1.23 (s, 9H), 1.99 (d, J = 4.9 Hz, 1H), 2.65 (d, J = 4.9 Hz, 1H), 7.30–7.38 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = −3.6, 18.7, 27.9, 44.3, 46.9, 127.4, 129.0, 134.8, 137.0; IR (film): $\tilde{\nu}$ = 1240, 1100 cm^{-1}; elemental analysis calcd (%) for $C_{21}H_{30}OSi_2$ (354.18): C 71.12, H 8.53; found: C 70.92, H 8.42.

(*E*)-1,2-Bis(dimethylphenylsilyl)-1,2-epoxypropane (2d): Yield = 85%; R_f = 0.46 (hexanes/AcOEt 20:1); ^1H NMR (300 MHz, $CDCl_3$): δ = 0.33 (s, 3H), 0.39 (s, 3H), 0.45 (s, 3H), 0.47 (s, 3H), 1.23 (s, 3H), 2.39 (s, 1H), 7.37–7.45 (m, 6H), 7.56–7.59 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = −5.7, −2.8, −2.1, 18.8, 52.7, 53.9, 127.8, 127.9, 129.2, 129.3, 134.0, 133.9, 136.3, 137.5; IR (film): $\tilde{\nu}$ = 1250, 1110 cm^{-1}; elemental analysis calcd (%) for $C_{19}H_{26}OSi_2$ (326.15): C 69.88, H 8.02; found: C 70.01, H 7.86.

(*E*)-1-Dimethylphenylsilyl-2-trimethylsilyl-1,2-epoxypropane (2e): Yield = 80%; R_f = 0.54 (hexanes/AcOEt 20:1) ; ^1H NMR (300 MHz, $CDCl_3$): δ = 0.07 (s, 9H), 0.44 (s, 3H), 0.46 (s, 3H), 1.23 (s, 3H), 2.31 (s, 1H), 7.39–7.41 (m, 3H), 7.58–7.61 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = −4.1, −2.8, −2.2, 18.6, 52.8, 54.3, 127.9, 129.2, 133.7, 137.7; IR (film): $\tilde{\nu}$ = 1250, 1110 cm^{-1}; elemental analysis calcd (%) for $C_{14}H_{24}OSi_2$ (264.14): C 63.57, H 9.15; found: C 63.62, H 8.97.

(*E*)-1,2-Bis(dimethylphenylsilyl)-1-phenylepoxyethane (2f): Yield = 78%; R_f = 0.44 (hexanes/AcOEt 20:1); ^1H NMR (300 MHz, $CDCl_3$): δ = −0.06 (s, 3H), −0.02 (s, 3H), 0.35 (s, 3H), 0.37 (s, 3H), 2.74 (s, 1H), 7.03–7.54 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = −5.5, −5.3, −4.9, −3.3, 54.3, 59.6, 126.2, 127.0, 127.4, 127.6, 127.7, 129.1, 129.4, 133.7, 134.3, 135.8,

137.4, 140.1; IR (film): $\tilde{\nu}$ = 1250, 1100 cm^{-1}; elemental analysis calcd (%) for $C_{24}H_{28}OSi_2$ (388.17): C 74.17, H 7.26; found: C 74.22, H 7.30.

(*E*)-1-*tert*-Butyldiphenylsilyl-2-trimethylsilyl-1,2-epoxypropane (2g): Yield = 70%; R_f = 0.54 (hexanes/AcOEt 20:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.11 (s, 9H), 0.89 (s, 3H), 1.14 (s, 9H), 2.74 (s, 1H), 7.33–7.44 (m, 6H), 7.68–7.72 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = −4.0, 17.7, 18.8, 27.7, 50.0, 54.3, 127.7, 129.4, 133.7, 136.1; IR (film): $\tilde{\nu}$ = 1250, 1110 cm^{-1}; elemental analysis calcd (%) for $C_{22}H_{32}OSi_2$ (368.20): C 71.67, H 8.75; found: C 71.59, H 8.83.

(*Z*)-1-*tert*-Butyldiphenylsilyl-2-trimethylsilylepoxyethane (2h): Yield = 60%; R_f = 0.54 (hexanes/AcOEt 20:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.36 (s, 9H), 1.10 (s, 9H), 2.65 (d, J = 6.5 Hz, 1H), 3.15 (d, J = 6.5 Hz, 1H), 7.30–7.46 (m, 6H), 7.60–7.73 (m, 4H); IR (film): $\tilde{\nu}$ bar = 1250, 1110 cm^{-1}; elemental analysis calcd (%) for $C_{21}H_{30}OSi_2$ (354.18): C 71.12, H 8.53; found: C 71.29, H 8.41.

Synthesis of 1,1-disilylepoxides—Typical procedure: BuLi (1.2 mmol, 1.6 M in hexane, 0.75 mL) and TMEDA (1.2 mmol) were added at −60 °C to a solution of the silylepoxides **1b** or **1d** (1 mmol) in THF (2 mL). The mixture was stirred under N_2 at −60 °C for 20 min and then chlorotrimethylsilane or chlorodimethylphenylsilane (1.65 mmol) was added and stirred at this temperature for 3 h. The mixture was hydrolysed with methanol (1 mL) and an aq. NH_4Cl solution, extracted with diethyl ether and the organic layer dried ($MgSO_4$). Chromatography of the residue obtained after evaporation of ether gave the following products.

1-*tert*-Butyldiphenylsilyl-1-trimethylsilylepoxyethane (2i): Yield = 85%; R_f = 0.49 (hexanes/AcOEt 20:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.16 (s, 9H), 1.17 (s, 9H), 3.03 (d, J = 5.7 Hz, 1H), 3.22 (d, J = 5.7 Hz, 1H), 7.36–7.46 (m, 6H), 7.66–7.84 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = −1.8, 19.3, 28.6, 44.7, 49.9, 127.6, 129.4, 133.9, 136.2; IR (film): $\tilde{\nu}$ = 1250, 1110 cm^{-1}; MS (EI, 70 eV): m/z (%): 354 (1) [M^+−*t*Bu], 297 (2), 271 (12), 255 (5), 219 (14), 193 (39), 73 (100), 57 (79); elemental analysis calcd (%) for $C_{21}H_{30}OSi_2$ (354.18): C 71.12, H 8.53; found: C 70.86, H 8.42.

1-*tert*-Butyldiphenylsilyl-1-dimethylphenylsilylepoxyethane (2j): Yield = 80%; R_f = 0.48 (hexanes/AcOEt 20:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.00 (s, 3H), 0.11 (s, 3H), 1.07 (s, 9H), 2.77 (d, J = 5.8 Hz, 1H), 3.10 (d, J = 5.8 Hz, 1H), 7.29–7.80 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = −3.4, −3.0, 19.3, 28.5, 44.4, 50.4, 127.5, 127.6, 129.1, 129.4, 133.7, 134.3, 136.2, 136.7; IR (film): $\tilde{\nu}$ = 1250, 1100 cm^{-1}; MS (EI, 70 eV): m/z (%): 359 (13) [M^+−*t*Bu], 333 (41), 317 (2), 281 (20), 255 (52), 223(4), 195 (26), 135 (100), 57 (92); elemental analysis calcd (%) for $C_{26}H_{32}OSi_2$ (416.20): C 74.94, H 7.74; found: C 75.06, H 7.79.

(*Z*)-1-*tert*-Butyldiphenylsilyl-1-trimethylsilyl-1,2-epoxypropane (2k): Yield = 75%; R_f = 0.54 (hexanes/AcOEt 20:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.21 (s, 9H), 0.98 (s, 9H), 1.57 (d, J = 5.4 Hz, 3H), 3.82 (q, J = 5.4 Hz, 1H), 7.30–7.43 (m, 6H), 7.76–7.83 (m, 2H), 7.94–7.99 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.91, 18.39, 19.51, 28.47, 52,70, 56.86, 127.55, 127.72, 129.20, 129.47, 134.69, 135.09, 136.08, 136.42; IR (film): $\tilde{\nu}$ = 1250, 1100 cm^{-1}; elemental analysis calcd (%) for $C_{22}H_{32}OSi_2$ (368.20): C 71.67, H 8.75; found: C 71.80, H 8.69.

General procedure for the cleavage of epoxysilanes with lithium diphenylphosphide: A solution of the epoxysilanes **1a–m**, **1p** or the epoxydisilanes **2a**,**b**, **2d**,**e**, **2h** (1 mmol) in THF (5 mL) was added dropwise to a stirred THF solution of lithium diphenylphosphide (1.5 mmol) [prepared from diphenylphosphine (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]. Starting from less reactive (more hindered) silylepoxides it was necessary to increase the molar ratio silylepoxide/lithium diphenylphosphide to 1:2 for **1n–o**, **2f**,**i**,**j** and 1:3.5 for **1q**, **2c**,**g**,**k**. The mixture was allowed to warm to room temperature and stirred until TLC indicated complete reaction (reaction time 2–120 h). Then, methyl iodide (2 mmol) was added, or hydrolysed with an aq. NH_4Cl solution, extracted with diethyl ether and the organic layer dried ($MgSO_4$). Ether was evaporated and the residue purified by chromatography to give the following compounds.

Diphenylvinylphosphine oxide (3a): Yield = 65% from **1a** and 57% from **1b**; R_f = 0.36 (AcOEt); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.30 (m, 2H), 6.70 (m, 1H), 7.44–7.57 (m, 6H), 7.67–7.74 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 128.5 (d, J = 12.1 Hz), 131.0 (d, J = 98.1 Hz), 131.3 (d, J = 9.8 Hz), 131.9 (d, J = 1.6 Hz), 132.2 (d, J = 88.8 Hz), 134.8; ^{31}P NMR (121 MHz, $CDCl_3$): δ = 24.65; IR (film): $\tilde{\nu}$ = 1180, 985, 900 cm^{-1}; elemental analysis calcd (%) for $C_{14}H_{13}OP$ (228.07): C 73.68, H 5.74; found: C 73.57, H 5.82.

(*Z*)-1-Propenyldiphenylphosphine oxide (3b): Yield = 76% from **1c** and 60% from **1d**; R_f = 0.41 (AcOEt); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.06 (ddd, J = 1.4, 2.9, 7.2 Hz, 3H), 6.09 (ddq, J = 1.4, 12.8, 25.6 Hz, 1H), 6.75 (ddq, J = 7.2, 12.8, 40.3 Hz, 1H), 7.40–7.56 (m, 6H), 7.64–7.74 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.1 (d, J = 8.9 Hz), 122.1 (d, J = 100.8 Hz), 128.4 (d, J = 12.0 Hz), 130.7 (d, J = 10.0 Hz), 131.4, 134.2 (d, J = 103.8 Hz), 149.6; ^{31}P NMR (121 MHz, $CDCl_3$): δ = 22.32; IR (film): $\tilde{\nu}$ = 1175 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_{15}OP$ (242.09): C 74.37, H 6.24; found: C 74.51, H 6.09.

(*Z*)-1-Hexenyldiphenylphosphine oxide (3c): Yield = 58%; R_f = 0.46 (AcOEt); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.78 (t, J = 7.2 Hz, 3H), 1.22 (m, 2H), 1.31 (m, 2H), 2.50 (ddt, J = 1.5, 6.1, 7.2 Hz, 2H), 6.09 (tdd, J = 1.5, 12.9, 25.7 Hz, 1H), 6.66 (tdd, J = 7.7, 12.9, 40.5 Hz, 1H), 7.30–7.76 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.7, 22.1, 30.6, 30.8, 121.1 (d, J = 100.1 Hz), 128.4 (d, J = 12.0 Hz), 130.8 (d, J = 9.81 Hz), 131.4, 134.3 (d, J = 103.9 Hz), 155.1; ^{31}P NMR (121 MHz, $CDCl_3$): δ = 21.87; IR (film): $\tilde{\nu}$ = 1177, 700 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{21}OP$ (284.13): C 76.04, H 7.44; found: C 76.41, H 7.39.

(*E*)-1-Hexenyldiphenylphosphine oxide (3d): Yield = 83% from **1f** and 62% from **1h**; R_f = 0.46 (AcOEt); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.3 Hz, 3H), 1.32 (m, 2H), 1.45 (m, 2H), 2.28 (tdd, J = 1.5, 6.5, 7.5 Hz, 2H), 6.21 (ddt, J = 1.5, 17.0, 24.7 Hz, 1H), 6.72 (ddt, J = 6.5, 17.0, 19.6 Hz, 1H), 7.40–7.52 (m, 6H), 7.64–7.71 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.7, 22.1, 29.9, 34.1 (d, J = 16.9 Hz), 121.3 (d, J = 103.5 Hz), 128.4 (d, J = 12.1 Hz), 131.2 (d, J = 9.9 Hz), 131.6, 133.0 (d, J = 104.8 Hz), 152.9; ^{31}P NMR (121 MHz, $CDCl_3$): δ = 24.50; IR (film): $\tilde{\nu}$ = 1180, 920 cm^{-1}; MS (EI, 70 eV): m/z (%): 284 (43) [M^+], 255 (27), 227 (16), 202 (100), 185 (8), 77 (44); elemental analysis calcd (%) for $C_{18}H_{21}OP$ (284.13): C 76.04, H 7.44; found: C 76.18, H 7.51.

(*E*)-1-Propenyldiphenylphosphine oxide (3e): Yield = 59%; R_f = 0.41 (AcOEt); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.98 (td, J = 1.6, 6.5 Hz, 3H), 6.26 (ddq, J = 16.9, 24.1, 1.6 Hz, 1H), 6.69 (ddq, J = 16.9, 30.0, 6.5 Hz, 1H), 7.41–7.54 (m, 6H), 7.65–7.72 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.4 (d, J = 18.6 Hz), 123.3 (d, J = 103.9 Hz), 128.4 (d, J = 12.0 Hz), 131.2 (d, J = 9.8 Hz), 131.6, 132.9 (d, J = 105.0 Hz), 133.0, 148.0; ^{31}P NMR (121 MHz, $CDCl_3$): δ = 24.19; IR (film): $\tilde{\nu}$ = 1184, 970 cm^{-1}; elemental analysis calcd (%) for $C_{15}H_{15}OP$ (242.09): C 74.37, H 6.24; found: C 74.28, H 6.41.

(*Z*)-(2-Phenylethenyl)diphenylphosphine oxide (3f): Yield = 59%; R_f = 0.47 (AcOEt); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.31 (dd, J = 14.1, 19.4 Hz, 1H), 7.12–7.16 (m, 3H), 7.29–7.46 (m, 11H), 7.52 (dd, J = 14.1, 40.4 Hz, 1H), 7.66–7.76 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 121.6 (d, J = 98.2 Hz), 127.9, 128.5 (d, J = 12.1 Hz), 129.2, 130.1, 130.8 (d, J = 9.7 Hz), 131.3, 133.7 (d, J = 105.5 Hz), 134.7 (d, J = 7.2 Hz), 150.0; ^{31}P NMR (121 MHz, $CDCl_3$): δ = 20.84; IR (film): $\tilde{\nu}$ = 1175, 710 cm^{-1}; elemental analysis calcd (%) for $C_{20}H_{17}OP$ (304.10): C 78.93, H 5.63; found: C 79.18, H 5.75.

(*E*)-(2-Phenylethenyl)diphenylphosphine oxide (3g): Yield = 71%; R_f = 0.47 (AcOEt); m.p. 166–168 °C (from ethanol/H_2O); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.84 (dd, J = 17.4, 22.4 Hz, 1H), 7.35–7.78 (m, 16H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 119.0 (d, J = 104.4 Hz), 127.6, 128.5 (d, J = 12.1 Hz), 128.7, 130.0, 131.3 (d, J = 9.9 Hz), 131.8 (d, J = 1.4 Hz), 132.7 (d, J = 106.0 Hz), 134.9 (d, J = 18.0 Hz), 147.4 (d, J = 2.8 Hz); ^{31}P NMR (121 MHz, $CDCl_3$): δ = 25.46; IR (CH_2Cl_2): $\tilde{\nu}$ = 1175, 1000 cm^{-1}; elemental analysis calcd (%) for $C_{20}H_{17}OP$ (304.10): C 78.93, H 5.63; found: C 79.03, H 5.49.

(*E*)-5-Decenyldiphenylphosphine oxide (3h): Yield = 72%; R_f = 0.48 (AcOEt); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.73 (t, J = 7.0 Hz, 3H), 0.89 (t, J = 7.1 Hz, 3H), 1.13–1.40 (m, 8H), 2.19–2.31 (m, 4H), 6.15 (dt, J = 7.2, 21.6 Hz, 1H), 7.40–7.53 (m, 6H), 7.63–7.70 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.5, 13.8, 22.4, 22.8, 27.5, 28.7, 30.9, 31.7, 128.2 (d, J = 11.6 Hz), 131.5, 131.9 (d, J = 9.4 Hz), 132.2 (d, J = 1.3.9 Hz), 132.3 (d, J = 96.6 Hz), 147.1 (d, J = 9.9 Hz); ^{31}P NMR (121 MHz, $CDCl_3$): δ = 33.32; IR (film): $\tilde{\nu}$ = 1178, 815 cm^{-1}; elemental analysis calcd (%) for $C_{22}H_{29}OP$ (340.20): C 77.62, H 8.59; found: C 77.54, H 8.66.

(*E*)-(1,2-Diphenylethenyl)diphenylphosphine oxide (3i): Yield = 67%; R_f = 0.49 (AcOEt); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.92–7.70 (m, 21H);

^{13}C NMR (75 MHz, $CDCl_3$): δ = 127.71, 128.2 (d, J = 11.8 Hz), 128.7, 128.9, 129.8, 129.9, 130.2, 130.8 (d, J = 103.2 Hz), 131.8, 132.3 (d, J = 9.5 Hz), 134.7 (d, J = 17.4 Hz), 135.2 (d, J = 94.1 Hz), 135.4 (d, J = 8.9 Hz), 143.1 (d, J = 9.7 Hz); ^{31}P NMR (121 MHz, $CDCl_3$): δ = 29.51; IR (CH_2Cl_2): $\tilde{\nu}$ = 1179, 825 cm^{-1}; elemental analysis calcd (%) for $C_{26}H_{21}OP$ (380.13): C 82.09, H 5.56; found: C 81.94, H 5.68.

(*E*)-2-Phenyl-1-propenyldiphenylphosphine oxide (3j): Yield: 85% from **1p** and 80% from **1q**; R_f = 0.48 (AcOEt); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.43 (d, J = 1.7 Hz, 3H), 6.35 (d, J = 23.6 Hz, 1H), 7.27–7.78 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.3 d, J = 7.6 Hz), 117.9 (d, J = 104.7 Hz), 127.9, 128.6 (d, J = 13.7 Hz), 128.7, 130.2, 130.6 (d, J = 9.8 Hz), 131.2, 134.0 (d, J = 104.7 Hz), 141.5 (d, J = 17.0 Hz), 159.0; ^{31}P NMR (121 MHz, $CDCl_3$): δ = 22.06; IR (film): $\tilde{\nu}$ = 1178, 815 cm^{-1}; elemental analysis calcd (%) for $C_{21}H_{19}OP$ (318.12): C 79.23, H 6.02; found: C 79.04, H 5.91.

(*E*)-(2-Dimethylphenylsilylethenyl)diphenylphosphine oxide (3k): Yield = 96% from **2a** and 56% from **2b**; R_f = 0.53 (AcOEt); m.p. 122–124 °C (from CH_2Cl_2/hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.43 (s, 6H), 6.91 (dd, J = 20.4, 31.0 Hz, 1H), 7.31–7.70 (m, 16H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = −3.2, 127.9, 128.5 (d, J = 12.0 Hz), 129.5, 131.3 (d, J = 9.8 Hz), 131.7 (d, J = 1.6 Hz), 132.3 (d, J = 102.8 Hz), 133.8, 136.2, 138.7 (d, J = 89.9 Hz), 152.7 (d, J = 4.5 Hz); ^{31}P NMR (121 MHz, $CDCl_3$): δ = 23.42; IR (CH_2Cl_2): $\tilde{\nu}$ = 1250, 1190, 1110, 995 cm^{-1}; elemental analysis calcd (%) for $C_{22}H_{23}OPSi$ (362.13): C 72.90, H 6.40; found: C 72.79, H 6.33.

(*E*)-(2-Trimethylsilylethenyl)diphenylphosphine oxide (3l): Yield = 28%; R_f = 0.51 (AcOEt); m.p. 115–117 °C (from CH_2Cl_2/hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.15 (s, 9H), 6.85 (dd, J = 20.4, 31.5 Hz, 1H), 7.27 (dd, J = 20.4, 29.6 Hz, 1H), 7.43–7.55 (m, 6H), 7.64–7.72 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = −1.9, 128.5 (d, J = 11.9 Hz), 131.3 (d, J = 9.8 Hz), 131.8, 132.5 (d, J = 105.0 Hz), 136.8 (d, J = 90.3 Hz), 155.2 (d, J = 4.8 Hz); ^{31}P NMR (121 MHz, $CDCl_3$): δ = 23.42; IR (CH_2Cl_2): $\tilde{\nu}$ = 1245, 1185, 995 cm^{-1}; MS m/z (%): 300 (3) [M^+], 285 (9), 227 (13), 202 (58), 185 (13), 73 (100); elemental analysis calcd (%) for $C_{17}H_{21}OPSi$ (300.11): C 67.97, H 7.05; found: C 68.10, H 7.12.

(*E*)-(2-*tert*-Butyldiphenylsilylethenyl)diphenylphosphine oxide (3m): Yield = 45%; R_f = 0.54 (AcOEt); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.10 (s, 9H), 6.90 (dd, J = 20.5, 32.0 Hz, 1H), 7.32–7.85 (m, 21H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.3, 27.6, 127.8, 128.5 (d, J = 11.9 Hz), 129.6, 131.3 (d, J = 9.7 Hz), 131.8, 132.0, 132.5 (d, J = 100.8 Hz), 136.1, 142.6 (d, J = 88.1 Hz), 148.8; ^{31}P NMR (121 MHz, $CDCl_3$): δ = 23.23; IR (film): $\tilde{\nu}$ = 1190, 1100, 998 cm^{-1}; elemental analysis calcd (%) for $C_{30}H_{31}OPSi$ (466.19): C 77.22, H 6.70; found: C 77.31, H 6.63.

(*E*)-(2-Dimethylphenylsilyl-1-propenyl)diphenylphosphine oxide (3n): Yield = 73%; R_f = 0.53 (AcOEt); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.43 (s, 6H), 2.16 (dd, J = 1.7, 2.9 Hz, 3H), 6.51 (dq, J = 1.7, 30.5 Hz, 1H), 7.36–7.74 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = −4.0, 19.6 (d, J = 12.9 Hz), 127.9, 128.5 (d, J = 11.9 Hz), 129.4, 130.7 (d, J = 9.7 Hz), 130.9 (d, J = 89.3 Hz), 131.3, 133.8, 134.5 (d, J = 101.4 Hz), 135.9, 167.2 (d, J = 5.1 Hz); ^{31}P NMR (121 MHz, $CDCl_3$): δ = 20.31; IR (film): $\tilde{\nu}$ = 1250, 1185,1110, 820 cm^{-1}; elemental analysis calcd (%) for $C_{23}H_{25}OPSi$ (376.14): C 73.37, H 6.69; found: C 73.29, H 6.72.

(*E*)-(2-Trimethylsilyl-1-propenyl)diphenylphosphine oxide (3o): Yield = 69%; R_f = 0.54 (AcOEt); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.11 (s, 9H), 2.13 (dd, J = 1.5, 2.7 Hz, 3H), 6.39 (dq, J = 30.9, 1.5 Hz, 1H), 7.38–7.47 (m, 6H), 7.66–7.73 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = −2.6, 19.3 (d, J = 13.4 Hz), 128.4 (d, J = 11.8 Hz), 128.8 (d, J = 90.2 Hz), 130.6 (d, J = 9.7 Hz), 131.2, 134.5 (d, J = 101.0 Hz), 169.3 (d, J = 5.5 Hz); ^{31}P NMR (121 MHz, $CDCl_3$): δ = 20.32; IR (film): $\tilde{\nu}$ = 1240, 1184, 829 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{23}OPSi$ (314.13): C 68.76, H 7.37; found: C 68.64, H 7.45.

(*E*)-(2-Dimethylphenylsilyl-2-phenyl)ethenyldiphenylphosphine oxide (3p): Yield = 60%; R_f = 0.55 (AcOEt); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.39 (s, 6H), 6.79 (d, J = 18.0 Hz, 1H), 7.62–7.83 (m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = −3.4, 126.4, 127.3, 127.9, 128.1 (d, J = 11.9 Hz), 128.3, 129.5, 130.7 (d, J = 9.6 Hz), 130.9, 133.8 (d, J = 89.2 Hz), 134.0 (d, J = 100.3 Hz), 134.2, 135.7, 139.5 (d, J = 11.6 Hz), 169.1; ^{31}P NMR (121 MHz, $CDCl_3$): δ = 18.61; IR (film): $\tilde{\nu}$ = 1248, 1185, 1100, 820 cm^{-1}; elemental analysis calcd (%) for $C_{28}H_{27}OPSi$ (438.16): C 76.68, H 6.21; found: C 76.84, H 6.30.

Diphenylmethyl-2-propenylphosphonium iodide (4a): see ref. [1].

(*E*)-1-Hexenyldiphenylmethylphosphonium iodide (4b): Yield = 71% from **1f** and 76% from **1h**; m.p. 152–154 °C (from EtOH); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.3 Hz, 3H), 1.33 (m, 2H), 1.50 (m, 2H), 2.49 (m, 2H), 2.88 (d, J = 13.4 Hz, 3H), 6.68 (dd, J = 16.5, 23.8 Hz, 1H), 6.86 (tt, J = 6.6, 16.5 Hz, 1H), 7.27–7.81 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.9 (d, J = 57.7 Hz), 13.7, 22.2, 29.4, 35.1 (d, J = 18.0 Hz), 109.1 (d, J = 85.8), 119.2 (d, J = 89.2 Hz), 130.3 (d, J = 12.6 Hz), 132.7 (d, J = 10.5 Hz), 134.8, 162.8; ^{31}P NMR (121 MHz, $CDCl_3$): δ = 17.33; IR (CH_2Cl_2): $\tilde{\nu}$ = 990 cm^{-1}; MS (EI, 70 eV): m/z (%): 283 (16) [M^+], 268 (3), 253 (67), 215 (14), 200 (71), 185 (100), 108 (10), 77 (69); elemental analysis calcd (%) for $C_{19}H_{24}IP$ (410.07): C 55.62, H 5.90; found: C 55.58, H 5.78.

(*E*)-(2-Phenylethenyl)diphenylmethylphosphonium iodide (4c): Yield = 64%; m.p. 177–178 °C (from EtOH); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.95 (d, J = 13.6 Hz, 3H), 6.95 (dd, J = 15.7, 26.5 Hz, 1H), 7.08 (t, J = 15.7 Hz, 1H), 7.27–7.91 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.1 (d, J = 58.6 Hz), 106.0 (d, J = 89.5 Hz), 119.4 (d, J = 90.2 Hz), 128.9, 129.2, 130.2 (d, J = 12.5 Hz), 131.8, 132.9 (d, J = 10.7 Hz), 133.5, 134.7, 154.7; ^{31}P NMR (121 MHz, $CDCl_3$): δ = 19.60; IR (CH_2Cl_2): $\tilde{\nu}$ = 995 cm^{-1}; elemental analysis calcd (%) for $C_{21}H_{20}IP$ (430.03): C 58.62, H 4.69; found: C 58.56, H 4.61.

2-Iodoethylidenediphenylmethylphosphorane (5): see ref. [1].

(*Z*)-1-*tert*-Butyldiphenylsilyloxy-2-phenylethene (6a): see ref. [1].

2-*tert*-Butyldiphenylsilyloxypropene (6b): Yield = 76%; R_f = 0.39 (hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.07 (s, 9H), 1.85 (d, J = 0.7 Hz, 3H), 3.85 (s, 1H), 3.97 (d, J = 0.7 Hz, 1H), 7.42–7.44 (m, 6H), 7.77–7.78 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.2, 22.7, 26.5, 92.3, 127.6, 129.7, 133.1, 135.4, 155,6; IR (CH_2Cl_2): $\tilde{\nu}$ = 1100, 795 cm^{-1}; MS (EI, 70 eV): m/z (%): 296 (4) [M^+], 239 (100), 199 (35), 181 (15), 161 (6), 121 (3), 77 (9), 57 (67); elemental analysis calcd (%) for $C_{19}H_{24}OSi$ (296.16): C 76.97, H 8.16; found: C 77.04, H 8.23.

1-*tert*-Butyldiphenylsilyloxy-1-trimethylsilylethene (6c): Yield = 52%; R_f = 0.50 (hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.25 (s, 9H), 1.06 (s, 9H), 4.43 (d, J = 1.5 Hz, 1H), 4.44 (d, J = 1.5 Hz, 1H), 7.41–7.46 (m, 6H), 7.76–7.79 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = −2.3, 19.3, 26.4, 105.3, 127.5, 129.5, 133.2, 135.5, 165.8; IR (film): $\tilde{\nu}$ = 1245, 1100, 790 cm^{-1}; MS (EI, 70 eV): m/z (%): 297 (9) [M^+−*t*Bu], 271 (28), 219 (80), 193 (64), 73 (95), 57 (100); elemental analysis calcd (%) for $C_{21}H_{30}OSi_2$ (354.18): C 71.12, H 8.53; found: C 71.24, H 8.47.

1-*tert*-Butyldiphenylsilyloxy-1-dimethylphenylsilylethene (6d): Yield = 56%; R_f = 0.41 (hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.50 (s, 6H), 0.96 (s, 9H), 4.44 (d, J = 1.6 Hz, 1H), 4.48 (d, J = 1.6 Hz, 1H), 7.34–7.72 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = −3.8, 19.2, 26.3, 107.0, 127.5, 127.7, 129.2, 129.5, 133.0, 134.1, 135.5, 136.6, 164.1; IR (film): $\tilde{\nu}$ = 1250, 1110, 790 cm^{-1}; MS (EI, 70 eV): m/z (%): 416 (2) [M^+], 359 (31), 281 (63), 255 (21), 195 (22), 179 (32), 135 (28), 105 (13), 77 (23), 57 (100); elemental analysis calcd (%) for $C_{26}H_{32}OSi_2$ (416.20): C 74.94, H 7.74; found: C 75.06, H 7.81.

(2-Hydroxy-2-dimethylphenylsilyl)propyldiphenylphosphine oxide (7): Yield = 40%; R_f = 0.55 (AcOEt); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.37 (s, 3H), 0.38 (s, 3H), 1.34 (s, 3H), 2.30 (dd, J = 7.6, 15.0 Hz, 1H), 2.75 (t, J = 15.0, 1H), 4.66 (s, 1H), 7.35–7.73 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = −6.4, −6.3, 25.4, 36.0 (d, J = 65.8 Hz), 66.4 (d, J = 7.9 Hz), 127.7, 128.7 (d, J = 11.3 Hz), 130.0, 130.3 (d, J = 9.1 Hz), 131.6, 134.2 (d, J = 95.2 Hz), 134.5, 135.8; ^{31}P NMR (121 MHz, $CDCl_3$): δ = 35.37; IR (film): $\tilde{\nu}$ = 3500, 1253, 1178, 1100 cm^{-1}; MS (EI, 70 eV): m/z (%): 379 (2) [M^+−Me], 320 (1), 202 (33), 185 (33), 135 (100); elemental analysis calcd (%) for $C_{23}H_{27}O_2PSi$ (394.15): C 70.02, H 6.90; found: C 69.92, H 6.83.

2-Dimethylphenylsilylpropene (8a): see ref. [4].

(*E*)-1-*tert*-Butyldiphenylsilyl-2-trimethylsilylethene (8b): see ref. [3].

1-*tert*-Butyldiphenylsilyl-1-trimethylsilylethene (8c): Yield = 13%; R_f = 0.54 (hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.19 (s, 9H), 1.10 (s, 9H), 6.76 (d, J = 4.6 Hz, 1H), 6.82 (d, J = 4.6 Hz, 1H), 7.34–7.41 (m, 6H), 7.64–7.67 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.1, 19.0, 28.6, 127.4, 128.9, 136.2, 136.4, 145.1, 149.2; IR (film): $\tilde{\nu}$ = 1250, 1110, 840 cm^{-1}; MS (EI, 70 eV): m/z (%): 338 (1) [M^+], 281 (35), 197 (23), 73 (100), 57 (94); elemental analysis calcd (%) for $C_{21}H_{30}Si_2$ (338.19): C 74.48, H 8.93; found: C 74.53, H 9.05.

1-*tert*-Butyldiphenylsilyl-1-dimethylphenylsilylethene (8d): Yield = 16 %; R_f = 0.45 (hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.35 (s, 6H), 1.06 (s, 9H), 6.74 (d, J = 4.5 Hz, 1H), 6.91 (d, J = 4.5 Hz, 1H), 7.27–7.76 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = −1.5, 0.8, 19.0, 28.6, 127.3, 127.7, 128.8, 128.9, 131.4, 134.0, 135.2, 136.4, 147.2, 147.3; IR (film): $\tilde{\nu}$ = 1248, 1122, 885 cm^{-1}; MS (EI, 70 eV): m/z (%): 343 (90) [M^+], 265 (18), 197 (100), 181 (17), 135 (78), 105 (41), 57 (55); elemental analysis calcd (%) for $C_{26}H_{32}Si_2$ (400.20): C 77.93, H 8.05; found: C 78.07, H 7.93.

(*E*)-1-*tert*-Butyldiphenylsilyl-1-trimethylsilylpropene (8e): Yield = 59 %; R_f = 0.35 (hexane); ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.12 (s, 9H), 1.06 (s, 9H), 2.18 (d, J = 6.6 Hz, 3H), 7.41–7.44 (m, 7H), 7.80–7.84 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 1.4, 19.1, 22.2, 28.1, 127.3, 128.7, 136.1, 136.6, 136.8, 155.72; IR (film): $\tilde{\nu}$ = 1253, 1115, 810 cm^{-1}; MS (EI, 70 eV): m/z (%): 337 (2) [M^+−Me], 295 (100), 279 (1), 221 (12), 197 (78), 159 (45), 135 (55), 73 (6); elemental analysis calcd (%) for $C_{22}H_{32}Si_2$ (352.20): C 74.93, H 9.15; found: C 75.11, H 8.99.

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