Pergamon

Tetrahedron 56 (2000) 2739–2751

TETRAHEDRON

Functionalised Allylsilanes from Silylcopper Reagents and Allene. A Useful Strategy for Cyclopentane Annulations

Asuncion Barbero, Carlos García and Francisco J. Pulido*

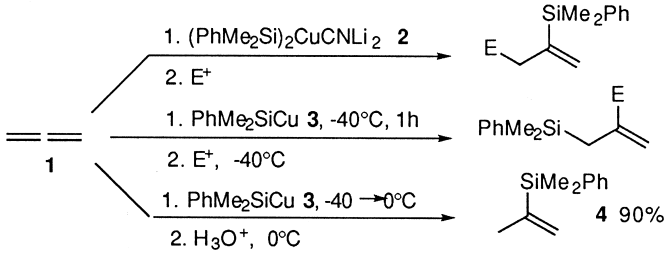
Departamento de Química Orgánica, Universidad de Valladolid, 47011 Valladolid, Spain

Received 15 September 1999; revised 6 January 2000; accepted 13 January 2000

Abstract—Silylcupration of allene using phenyldimethylsilylcopper or *t*-butyldiphenylsilylcopper followed by reaction with α,β-unsaturated acyl chlorides, aldehydes or ketones affords allylsilane-containing divinyl ketones and oxoallylsilanes, respectively. They undergo highly stereocontrolled silicon-assisted intramolecular cyclizations when treated with protic or Lewis acid leading to cyclopentane ring-formation.

Ten years ago, we reported the stoichiometric silylcupration of allenes for the first time.[1] Since then the silylcupration of allenes has become a powerful tool for the synthesis of vinyl- and allylsilanes.[2–6] Moreover, the high versatility that allyl- and vinylsilanes show in synthetic organic chemistry as masked carbon nucleophiles has attracted much attention among organic chemists.[7] The readily prepared lithium bis(phenyldimethylsilyl)cuprate[1] **2** and other cuprates react stereoselectively[8] with allenes by *syn* addition of the silyl–copper pair to one of the double bonds to give, after addition of an electrophile, allyl- or vinylsilanes differently functionalised. Addition is usually regioselective and the formation of allyl- or vinylsilanes depends on the substitution pattern of the allene. In a recent review[9] we reported the reactivity of higher order silyl- and stannylcuprates toward unactivated allenes and acetylenes showing the scope of the reaction and the synthetic applicability of our methodology. In particular, the reaction of **2** with allene **1** itself is not temperature dependent leading invariably to vinylsilanes at low (−78°C) and high (0°C) temperatures[1,2] (Scheme 1). More recently, we noted[10] that phenyldimethylsilyl–copper **3** prepared by mixing one equivalent of phenyldimethylsilyl–lithium and one equivalent of copper(I) cyanide reacted with **1** at −40°C in THF showing a regiochemistry opposite to that of the corresponding higher order silylcuprate **2**. This route allowed us to prepare a wide variety of functionalised allylsilanes (Scheme 1). Contrarily to **2**, the silylcopper reagent **3** shows a temperature dependence when reacting with allene **1** giving allylsilanes after protonation at −40°C, but vinylsilanes at 0°C (Scheme 1).

Silylcupration reactions are a particular example of a more general procedure known as metallo-metallation reactions. They are a relatively new class of reactions closely related to the better-known hydrometallations and carbometallations. Although known for the addition of two different main group metals to a triple bond,[11] stoichiometric metallo-metallations usually involve the addition of copper to one end of a triple bond and a silyl,[12] gerrmyl[13] or stannyl[14] group to the other. Addition of the bimetallic species generates two adjacent nucleophilic carbons which react sequentially with a wide range of electrophiles due to their well differentiated reactivity. The stereochemistry of



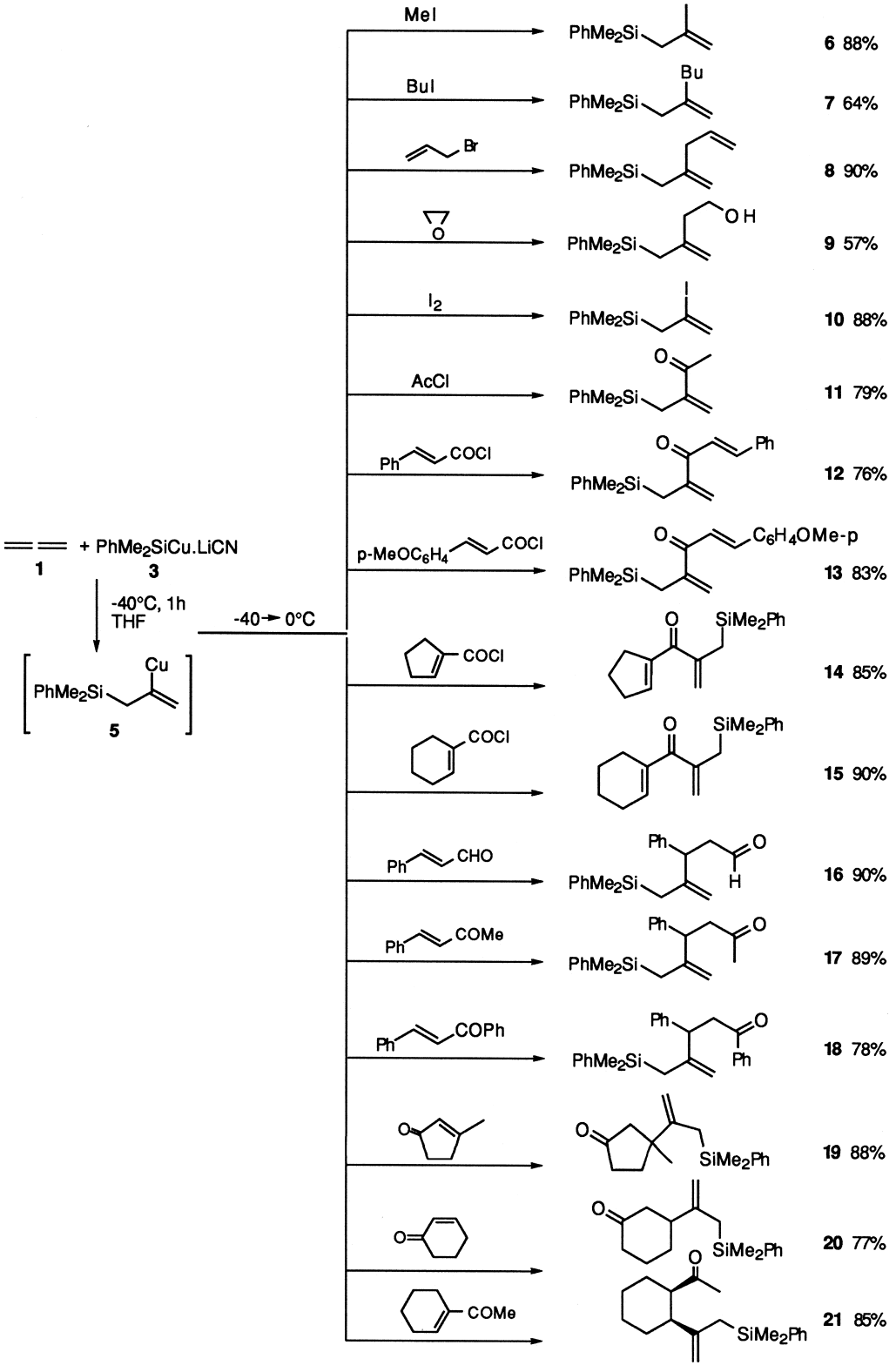
Scheme 1.

Keywords: silylcupration; allene; allylsilane; cyclization.

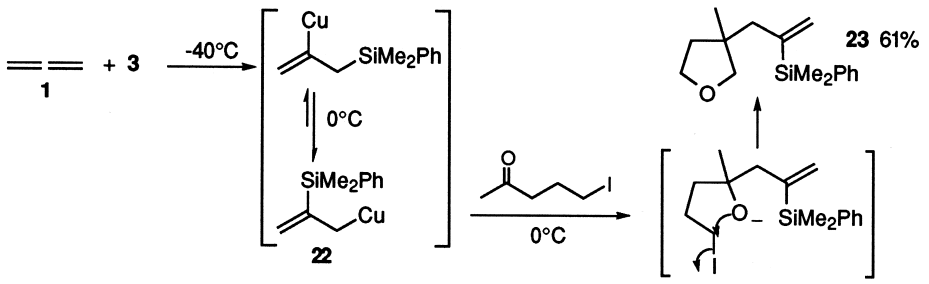
* Corresponding author. Tel.: 34-983-423210; fax: 34-983-423013; e-mail: pulido@qo.uva.es

0040–4020/00/$ - see front matter
PII: S0040-4020(00)00129-0

metallo-metallations of multiple bonds has been abundantly proved to be *syn*[8,15] but occasionally the overall process is *anti*[11,13,16] rather than *syn*. Metallo-metallations of double bonds are much less common but are known for the transition metal-catalysed addition of silicon–silicon bonds to 1,3-dienes,[17] for the transition metal-catalysed addition of silicon–magnesium,[18] silicon–aluminium[18] and silicon–zinc[18] bonds to allenes, for the stoichiometric silylzirconation[19] of allenes, for the platinum-catalysed silylsilylation[20] of double bonds and we[21] and others[22] reported the stoichiometric stannylcupration of allenes and acetylenes.



Scheme 2.



Scheme 3.

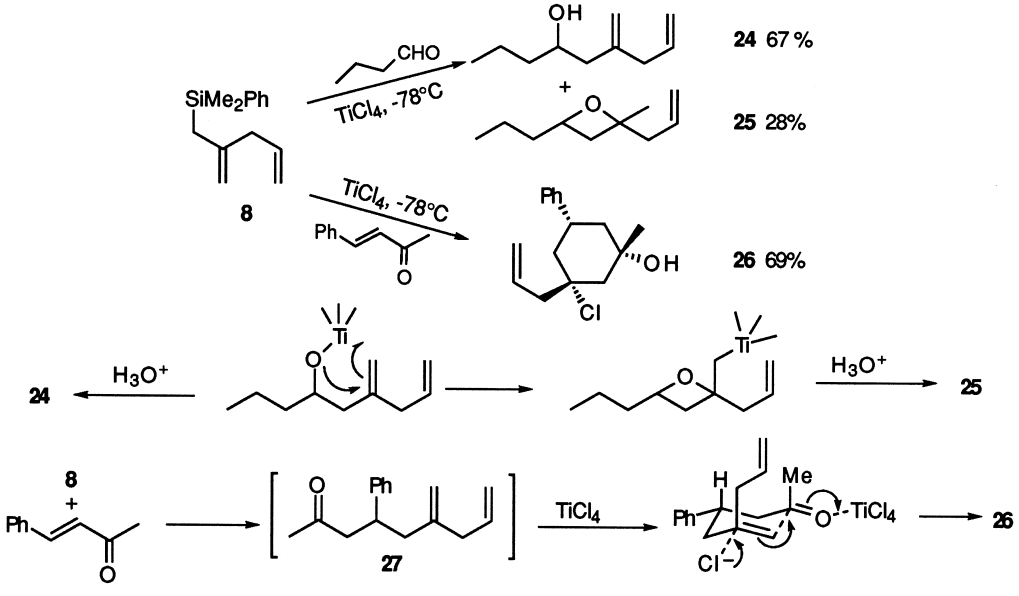
In this paper we report in full the scope and synthetic applications of the silylcupration of allene using silylcopper reagents. We provide details of the work published in preliminary form[10] and we also extend the reaction to other bulkier silylcopper reagents as *t*-butyldiphenylsilyl–copper. Moreover, we describe several new strategies for ring formation via allylsilane intramolecular cyclization discussing factors controlling the stereochemistry.

Reaction with Electrophiles

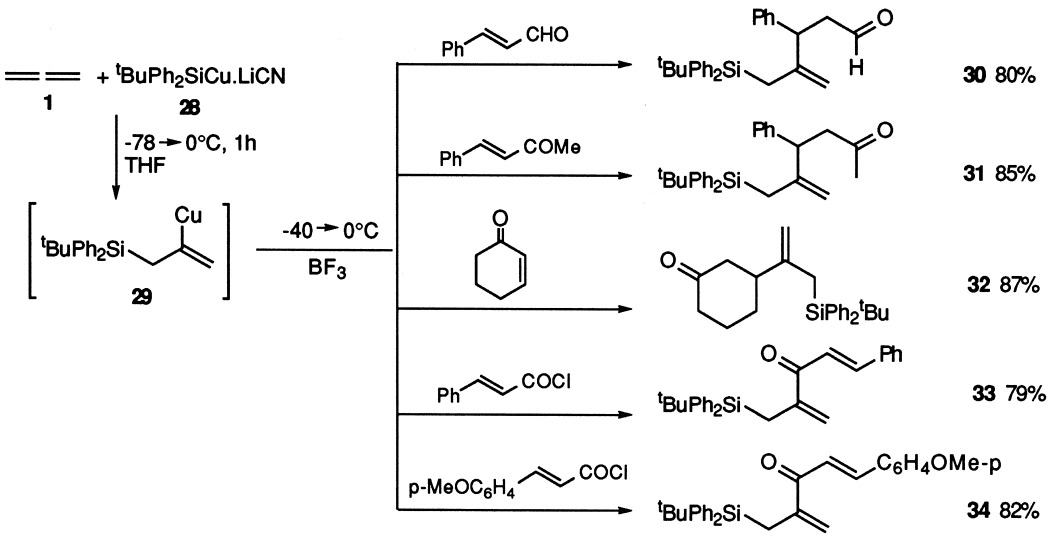
The silylcopper reagent **3**, prepared by stirring one equivalent of phenyldimethylsilyl–lithium[12a] and copper(I) cyanide at 0°C in THF for 30 min, reacts with 1,2-propadiene (allene) **1** at −40°C in THF for 1 h leading to the allylsilane–vinylcopper intermediate **5**. In addition to proton, several more common carbon electrophiles react with **5** at temperatures between −40°C and 0°C giving good yields of allylsilanes **6**–**21** (Scheme 2).

The procedure herein described is quite general, thus providing an efficient entry to the preparation of functionalised allylsilanes. Reactions leading to the formation of **16**–**21** were carried out in the presence of BF_3 for better yields. α,β-Unsaturated aldehydes and ketones undergo conjugate addition as the only observed reaction. Compound **21** undergoes isomerization to the *trans*-isomer in 97% yield, when stirred with a 0.5 M solution of NaOH in H_2O/EtOH/THF. Intermediate **5** is regiochemically stable at temperatures around −40°C however, as was mentioned before (Scheme 1), near 0°C interconversion of **5** to the corresponding vinylsilane–allylcopper **22** occurs rapidly. Therefore, care must be taken with the temperature control of the process to avoid that the reversibility of the reaction may influence the outcome. This effect can be seen in the reaction of 5-iodopentan-2-one with 1,2-propadiene and the silylcopper reagent **3** (Scheme 3). In standard conditions (THF, BF_3, −40 to 0°C) the reaction leads to the formation of the anomalous tetrahydrofuran **23** (Scheme 3). This result suggests that reaction of the iodoketone with intermediate **5** at −40°C proceeds very slowly. As the temperature increases, intermediate **5** equilibrates to the vinylsilane–allylcopper intermediate **22**, then addition of **22** to the carbonyl group followed by intramolecular nucleophilic displacement of iodine gives **23** (Scheme 3).

Although the behaviour of allylsilanes toward carbonyl compounds can be predicted, some anomalous cyclizations, mechanistically not very well set up, have also been observed and are at present, a matter of study. Thus, allylsilane **8** reacts with butyraldehyde and benzalacetone under Lewis acid activation by $TiCl_4$ to yield the expected alcohol **24** and the unexpected oxetane **25** and chlorocyclohexanol



Scheme 4.



Scheme 5.

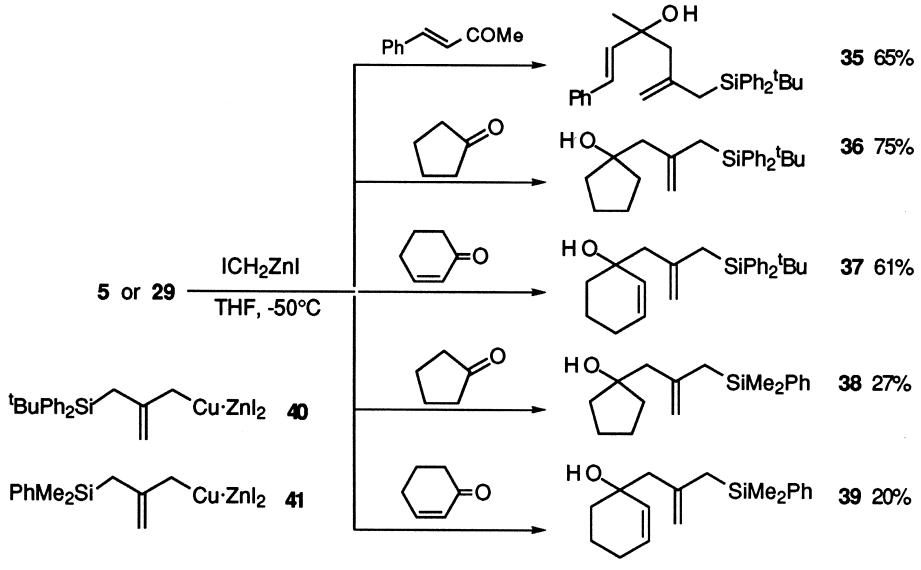
26 (Scheme 4). Although we defer any definitive statements regarding mechanisms, a plausible pathway leading to **25** and **26** has been outlined below (Scheme 4).

The source of chloride anion for the formation of **26** is matter of discussion. It could be due to $TiCl_4$ impurities (HCl) although bidistilled and purified $TiCl_4$ gives similar results. This leaves only the $TiCl_4$ as the source of chlorine. It should be noted that ketone **27** was never isolated.

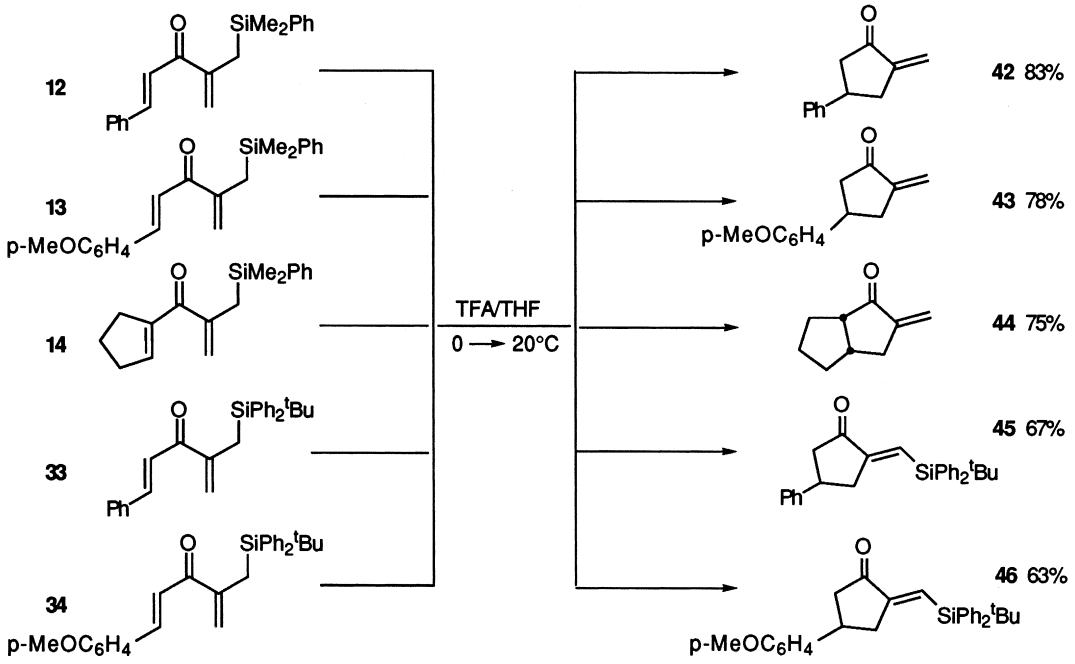
t-Butyldiphenylsilyl–copper **28** was prepared as before by mixing one equivalent of *t*-butyldiphenylsilyl–lithium[23] and copper(I) cyanide at 0°C. It reacts with allene at any temperature between −78 and 0°C leading invariably to allylsilanes after quenching with common electrophiles (proton, alkyl halides, epoxides, acyl chlorides, etc). Now intermediate **29** seems to be the only species present in a long range of temperatures (Scheme 5). These results are quite similar to those we reported for the lithium bis(*t*-butyldiphenylsilyl)cuprate some time ago[4] and therefore, they do not need to be described in this paper. Consequently, it could be thought that the use of **28** has no advantages over the bis(silylcuprate); however, reaction of **28** with allene and α,β-unsaturated oxocompounds shows a different reactivity pattern. Thus, we showed before[4] that α,β-unsaturated oxocompounds undergo carbonyl addition when reacting with the intermediate cuprate resulting from addition of lithium bis(*t*-butyldiphenylsilyl)cuprate to allene whereas reaction of **29** with the same enones, in the presence of BF_3, affords the allylsilanes **30**-**32** resulting from conjugate addition (Scheme 5). Reaction of **29** with α,β-unsaturated acyl chlorides gives the divinylketones **33** and **34** (Scheme 5).

Knochel Homologations

Recently Knochel et al.[24] published an excellent method for the homologation of vinylic organocopper reagents to allylic copper–zinc organometallics by reaction of the



Scheme 6.



Scheme 7.

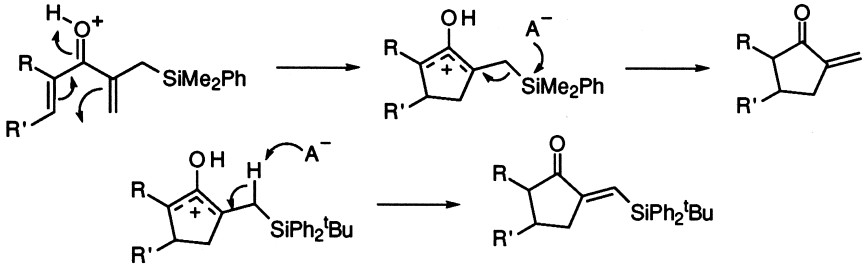
former with (iodomethyl)zinc iodide. We wondered how far this possibility could be taken with our vinylcopper intermediates **5** and **29**. Obviously if the Knochel homologation can be extended to the general reaction, this would increase significantly the synthetic versatility of our methodology. We now report examples of these possibilities. Reaction of intermediate **29** with (iodomethyl)zinc iodide in THF at −50°C followed by addition of ketones or enones gives the homoallyllic alcohols **35**–**37** resulting from carbonyl addition of the homologated copper–zinc organometallic reagent **40** (Scheme 6). Conjugate addition products were not isolated. On the contrary, reaction of the phenyldimethylsilyl analogue **5** in the same conditions leads to poor yields of the alcohols **38** and **39** (Scheme 6). All efforts to improve yields were unsuccessful.

It is uncertain whether homologation of **5** occurs in little extent or the reactivity of **41** toward ketones is low. However, after quenching with ammonium chloride solution much vinylsilane **4** is recovered, which suggests that homologation of **5** is not complete.

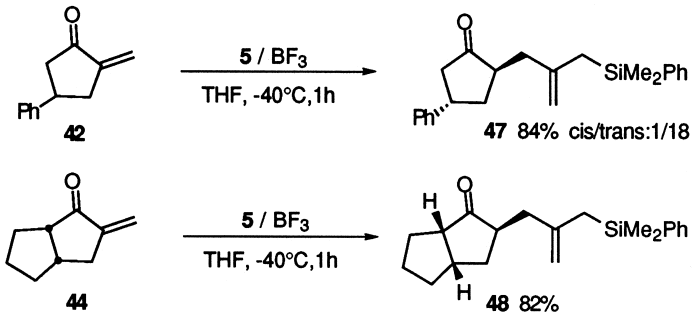
Directed Nazarov Reactions

Cyclopentenone annelations have been largely achieved using the classical Nazarov[25] cyclization reaction. A major limitation of the general method is the lack of control over the position of the double bond in the cyclopentenone moiety. In recent years, Denmark[26] and others found that silicon-assisted Nazarov reactions were an excellent solution to this problem. In most known examples of this type of reaction a directing vinylsilane group is involved, and we now report representative examples of silicon directed Nazarov reactions of divinyl ketones bearing an allylsilane unit. Silyldienones **12**–**14**, **33** and **34** are readily prepared, using our methodology, by reaction of α,β-unsaturated acyl chlorides with intermediates **5** and **29** (Schemes 2 and 5). Cyclization of the former divinyl ketones in the presence of trifluoroacetic acid (TFA)/THF affords good yields of the methylenecyclopentanones **42**–**46** (Scheme 7). It should be noted that in the *t*-butyldiphenylsilyl series the silyl group is not removed during cyclization.

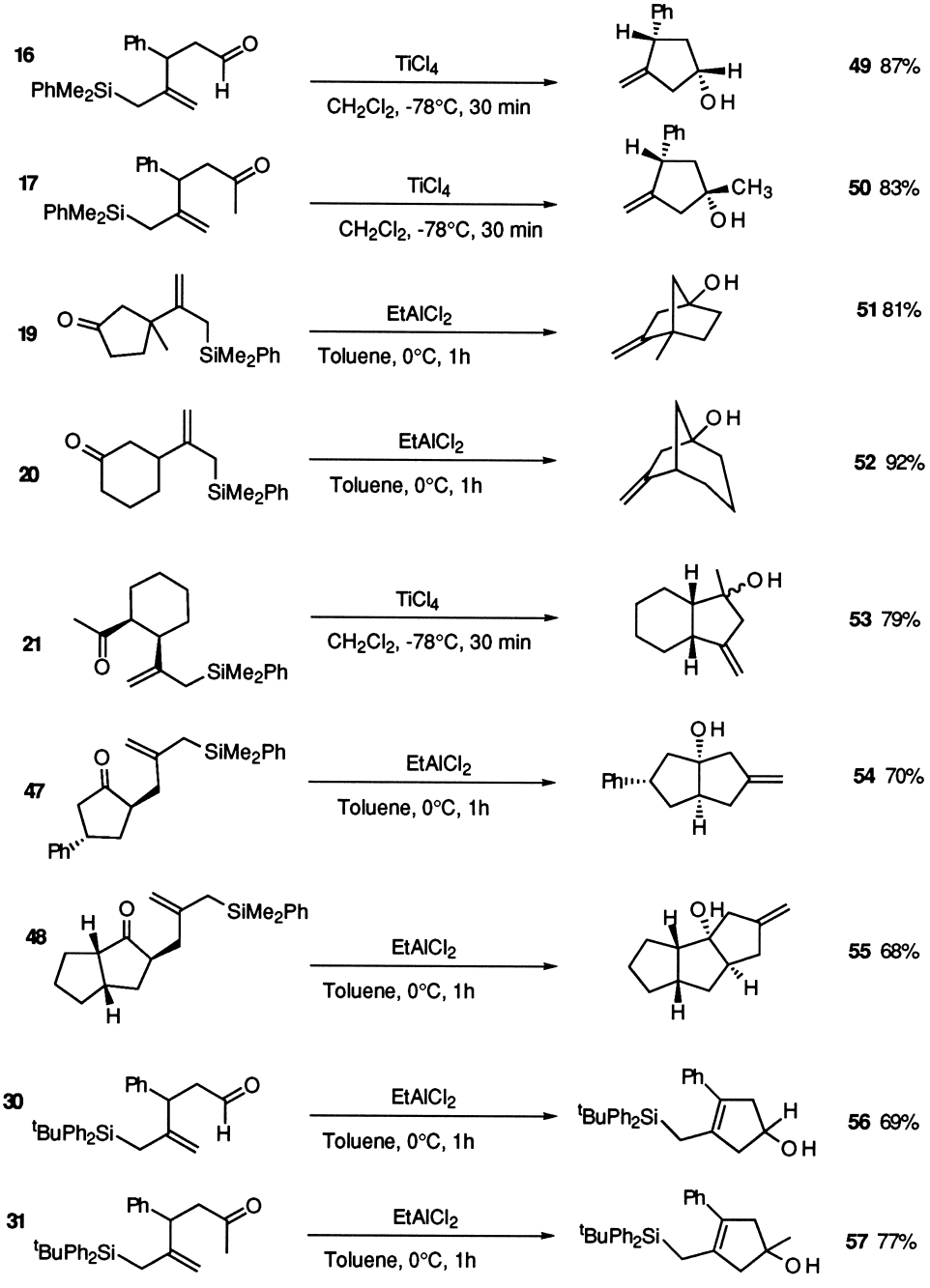
We tested different protic and Lewis acids (TFA, $FeCl_3$, $TiCl_4$, $EtAlCl_2$, BF_3), solvents (THF, CH_2Cl_2) and temperatures (−20 to 40°C) for the best conditions. Of all the acids examined TFA (3 equivalents) in THF has proven to be the most efficient. The procedure herein described constitutes a convenient method for the preparation of conjugated methylenecyclopentanones where the strategic placement of the silyl group directs the introduction of the new exocyclic



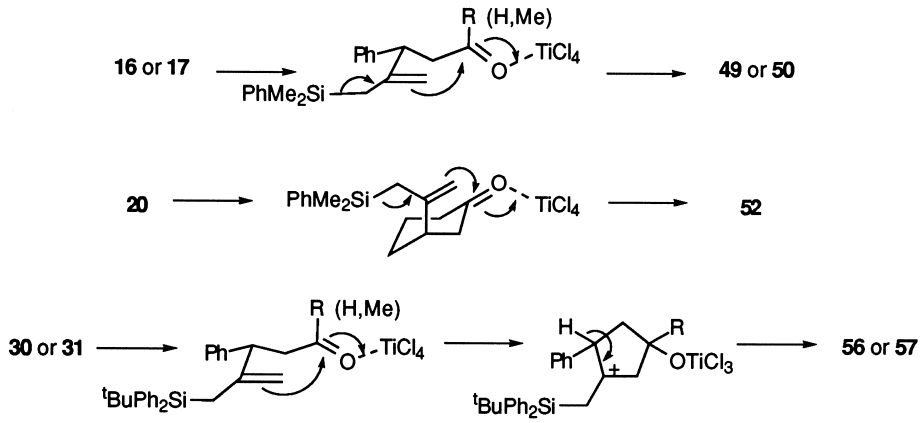
Scheme 8.



Scheme 9.



Scheme 10.



Scheme 11.

double bond. The key to this modification of the classical Nazarov sense is the well-documented ability of silicon to stabilize β-carbocations.[7] In the studied examples, the so-called β-effect of the silyl moiety exerts a perfect control over the electrocyclization of the starting divinyl ketones (Scheme 8). A unique feature of this cyclization is the formation of **45** and **46** in which the silyl group is retained. This result might be due to the low electrofugacity of the *t*-butyldiphenylsilyl group compared to the phenyldimethylsilyl group. Moreover, the higher electronegativity of *t*-butyldiphenylsilyl group enhances the acidity of the hydrogens alpha to silicon, thus assuring elimination in the observed sense (Scheme 8). The *E* geometry of the silyl-substituted double bond was assigned by NOESY and COSY experiments.

Allylsilane Terminated Cyclizations

We have shown in Scheme 2 and 5 the reaction of allylsilane–vinylcopper intermediates **5** and **29** with α,β-unsaturated aldehydes and ketones. Exocyclic α,β-unsaturated enones **42** and **44** resulting from directed Nazarov cyclization (Scheme 7) react even faster than endocyclic or acyclic enones, giving good yields of **47** and **48** with a high degree of stereocontrol (Scheme 9). Oxoallylsilanes **16**, **17**, **19**–**21**, **47** and **48** containing a nucleophilic allylsilane unit and an electrophilic carbonyl moiety, undergo intramolecular allylsilane terminated cyclization[27] when treated with a Lewis acid leading to methylenecyclopentan-1-ols **49**–**55** (Scheme 10). Cyclization of the oxoallylsilanes **30** and **31** bearing the *t*-butyldiphenylsilyl group occurs without loss of the silyl moiety giving cyclopenten-1-ols **56** and **57** (Scheme 10). For the general procedure, $TiCl_4$ was first used but in many of the studied reactions better yields are obtained if $EtAlCl_2$ is used instead. The stereochemistry of the resulting compounds has been assigned on the basis of the observed NMR coupling constants, NOESY experiments and from previously reported data.[28] The easy access to exocyclic methylenecyclopentanes is one of the features of this methodology. The methylenecyclopentanol moiety is very common in some terpene families[10b] moreover, the previous results suggest that a combination of the directed Nazarov reaction (**14**→**44**), followed by conjugate addition of intermediate cuprate **5** (**44**→**48**) and finally allylsilane terminated cyclization (**48**→**55**) might be expeditiously applied to a connective annulation procedure for the synthesis of fused *cis*,*anti*,*cis*-tricyclopentanoids, thus providing an easy approach to linearly fused triquinane natural products.[29] High levels of stereocontrol were found in all cyclizations carried out, with the exception of **53** which was isolated as a mixture of epimeric alcohols in 3:1 ratio (Scheme 10).

The stereochemistry observed in the formation of monocyclic methylenecyclopentanols (NOESY) might indicate a preference for the transition state depicted in Scheme 11, where bulky groups attain an equatorial conformation which minimizes steric repulsions. However, formation of bridged bicyclic methylenecyclopentanols **51** and **52** requires an axially arranged allylsilane unit for the final cyclization step (Scheme 11). Obtention of *cis*-fused geometry for the bi- and tricyclopentanols **54** and **55** is unexceptional in view of their higher thermodynamic stability. As was observed before for the directed Nazarov reactions, the *t*-butyldiphenylsilyl group may not be the electrofugal group following cyclization. Formation of **56** and **57** seems to be consistent with the mechanism outlined below (Scheme 11). This result is remarkable because the *t*-butyldiphenylsilyl moiety is still capable of undergoing electrophilic substitution,[12b] thus making this reaction presumably more useful than we expected before.

We conclude that reaction of allene with silylcopper reagents followed by addition of carbonyl derivatives is a simple and efficient methodology for the synthesis of a large number of allylsilanes with a wide variety of substitution patterns. They undergo highly stereocontrolled intramolecular cyclizations allowing the design and development of new strategies for cyclopentane annulation. Moreover, a simple protocol for triquinane systems based on the consecutive application of directed Nazarov reaction and allylsilane terminated cyclization has been outlined.

Experimental

Allene **1** was supplied by Air Liquide in lecture bottles. Compounds **4**, **6**, **10**, **17** and **50** were described in previous papers.[1,10b]

Silylcupration of allene. Preparation of intermediate 5

A solution of phenyldimethylsilyl–lithium[12a] (3 mmol) prepared in THF (3 ml) was added by syringe to a stirred suspension of copper(I) cyanide (269 mg, 3 mmol) in THF (5 ml) at 0°C. The resulting black mixture was stirred at this temperature for an additional period of 30 min, and then used immediately. The solution of phenyldimethylsilyl–copper **3** (3 mmol) in THF (8 ml) was cooled at −40°C and a slight excess of allene **1** was added from a balloon. The mixture was stirred for 1 h at this temperature and the reagent **5** used immediately.

Silylcupration of allene. Preparation of intermediate 29

A solution of *t*-butyldiphenylsilyl-lithium[23] (3 mmol) prepared in THF (3 ml) was added by syringe to a stirred suspension of copper(I) cyanide (269 mg, 3 mmol) in THF (5 ml) at 0°C. The resulting green–black mixture was stirred at this temperature for 30 min, and then used immediately. The solution of *t*-butyldiphenylsilyl–copper **28** (3 mmol) in THF (8 ml) was cooled at −78°C and a slight excess of allene **1** was added from a balloon. The mixture was allowed to warm up to 0°C with continuous stirring for 1 h. The reagent **29** was used immediately.

Reaction of intermediate 5 with electrophiles

Procedure 1: methyl iodide (10 mmol), butyl iodide (10 mmol), allyl bromide (6 mmol), ethylene oxide (4 mmol), iodine (3.6 mmol), acetyl chloride (3.6 mmol), cinnamoyl chloride (3.6 mmol), *p*-metoxycinnamoyl chloride (3.6 mmol), cyclopent-1-enecarbonyl chloride (3.6 mmol) or cyclohex-1-enecarbonyl chloride (3.6 mmol) was added to the cuprate reagent **5** (3 mmol) at −40°C and the resulting solution was kept at this temperature for 1 h. After gentle warming to 0°C (over 0.5 h) the mixture was quenched with saturated ammonium chloride solution and extracted twice with Et_2O. The organic layer was dried over $MgSO_4$ and rotoevaporated. Purification by flash-chromatography (EtOAc:hexanes) gave the allylsilanes **6**–**15** (Scheme 2).

Procedure 2: $BF_3{\cdot}Et_2O$ (0.38 ml, 3 mmol) was added at −78°C to a stirred solution of cuprate **5** (3 mmol) and the mixture stirred for 10 min at this temperature, then 3.6 mmol of cinnamaldehyde, benzalacetone, chalcone, 3-methylcyclopent-2-en-1-one, cyclohex-2-en-1-one, 1-acetylcyclohex-1-ene or 5-iodopentan-2-one in THF (5 ml) were added dropwise at −40°C and the resulting mixture was kept at this temperature for 1 h. After gentle warming to 0°C (over 0.5 h) the mixture was quenched as before and extracted with Et_2O. The organic phase was dried, evaporated and chromatographed (EtOAc:hexanes) to give the allylsilanes **16**–**21** and the vinylsilane **23** (Schemes 2 and 3).

2-Dimethyl(phenyl)silylmethylhex-1-ene (7). Oil, 64%; IR (neat): 1629, 1251, 1110, 885, 830; ^{1}H NMR ($CDCl_3$, 300 MHz): 7.60–7.38 (m, 5H), 4.67 (s with fine couplings, 1H), 4.59 (s with fine couplings, 1H), 1.91 (t, *J*=7.2 Hz, 2H), 1.83 (s with fine couplings, 2H), 1.47–1.25 (m, 4H), 0.92 (t, *J*=7.3 Hz, 3H), 0.35 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): 140.1, 138.5, 133.2, 129.6, 127.4, 113.3, 37.6, 30.1, 23.7, 22.5, 14.3, −3.1; MS(EI) *m/z*: 232 (M^+, 0.4%), 217, 189, 135 (100). Anal. Calcd for $C_{15}H_{24}Si$: C, 77.51; H, 10.41. Found: C, 77.73; H, 10.52.

2-Dimethyl(phenyl)silylmethylpenta-1,4-diene (8). Oil, 90%; IR (neat): 1625, 1250, 1110, 985, 922, 875, 832; ^{1}H NMR: 7.58–7.36 (m, 5H), 5.79 (ddt, *J*=10.1 Hz, 17.1 and 7.1, 1H), 5.06 (d with fine couplings, *J*=10.1 Hz, 1H), 4.99 (d with fine couplings, *J*=17.1 Hz, 1H), 4.67 (s with fine couplings, 1H), 4.60 (s with fine couplings, 1H), 2.62 (d with fine couplings, *J*=7.1 Hz, 2H), 1.83 (s, 2H), 0.37 (s, 6H); ^{13}C NMR: 145.4, 138.9, 136.4, 133.6, 129.0, 127.7, 116.1, 108.8, 42.8, 25.7, −2.9; MS(EI) *m/z*: 216 (M^+, 0.14%), 201, 135 (100). Anal. Calcd for $C_{14}H_{20}Si$: C, 77.71; H, 9.32. Found: C, 78.02; H, 9.51.

3-Dimethyl(phenyl)silylmethylbut-3-en-1-ol (9). Oil, 57%; IR (neat): 3260, 1633, 1252, 1110, 1060, 878, 831; ^{1}H NMR: 7.54–7.34 (m, 5H), 4.71 (s, 1H), 4.68 (s, 1H), 3.62 (t, *J*=6.2 Hz, 2H), 2.11 (t, *J*=6.2 Hz, 2H), 1.78 (s, 2H), 1.51 (br s, 1H), 0.33 (s, 6H); ^{13}C NMR: 143.3, 138.6, 133.5, 129.1, 127.8, 110.5, 59.9, 41.1, 25.6, −3.0; MS(EI) *m/z*: 220 (M^+, 0.24%), 205, 202, 135 (100). Anal. Calcd for $C_{13}H_{20}SiO$: C, 70.85; H, 9.15. Found: C, 70.91; H, 9.13.

3-Dimethyl(phenyl)silylmethylbut-3-en-2-one (11). Oil, 79%; IR (neat): 1672, 1610, 1243, 1113, 935, 836; ^{1}H NMR: 7.55–7.34 (m, 5H), 5.83 (s, 1H), 5.51 (s, 1H), 2.26 (s, 3H), 2.04 (s, 2H), 0.26 (s, 6H); ^{13}C NMR: 199.4, 146.7, 138.3, 133.6, 129.0, 127.6, 122.7, 25.3, 19.8, −3.2; MS(EI) *m/z*: 218 (M^+, 5%), 203, 175, 135 (100). Anal. Calcd for $C_{13}H_{18}SiO$: C, 71.50; H, 8.31. Found: C, 71.73; H, 8.46.

(*E*)-1-Phenyl-4-dimethyl(phenyl)silylmethylpenta-1,4-dien-3-one (12). Oil, 76%; IR (neat): 1692, 1661, 1604, 1250, 1110, 982, 925, 837; ^{1}H NMR: 7.60–7.34 (m, 10H), 7.58 (d, *J*=16.1 Hz, 1H), 7.28 (d, *J*=16.1 Hz, 1H), 5.92 (s, 1H), 5.58 (s, 1H), 2.22 (s, 2H), 0.34 (s, 6H); ^{13}C NMR: 191.4, 147.5, 143.2, 138.3, 134.9, 133.6, 130.1, 129.0, 128.8, 128.1, 127.6, 121.5, 121.3, 20.9, −3.1; MS(EI) *m/z*: 306 (M^+, 9%), 291, 229, 135 (100). Anal. Calcd for $C_{20}H_{22}SiO$: C, 78.38; H, 7.24. Found: C, 78.75; H, 7.45

(*E*)-1-(4-Methoxyphenyl)-4-dimethyl(phenyl)silylmethylpenta-1,4-dien-3-one (13). Viscous oil, 83%; IR (Cl_4C): 1650, 1633, 1601, 1257, 1115, 978, 915; ^{1}H NMR: 7.58–7.34 (m, 8H), 7.13 (d, *J*=15.7 Hz, 1H), 6.92 (d, *J*=8.9 Hz, 2H), 5.86 (s, 1H), 5.51 (s, 1H), 3.86 (s, 3H), 2.17 (s with fine couplings, 2H), 0.29 (s, 6H); ^{13}C NMR: 191.6, 161.4, 147.6, 143.2, 138.5, 133.7, 130.0, 129.1, 127.7, 127.5, 121.1, 119.1, 114.3, 55.3, 21.1, −3.2; MS(EI) *m/z*: 336 (M^+, 40%), 321, 305, 258, 135 (100).

1-(Cyclopent-1-en-1-yl)-2-dimethyl(phenyl)silylmethylprop-2-en-1-one (14). Oil, 85%; IR (neat): 1702, 1630, 1600, 1250, 1113, 927, 834; ^{1}H NMR: 7.53–7.33 (m, 5H), 6.39 (m, 1H), 5.51 (s, 1H), 5.36 (s, 1H), 2.59–2.48 (m, 4H), 2.14 (s, 2H), 1.91 (quintet, *J*=7.5 Hz, 2H), 0.28 (s, 6H); ^{13}C NMR: 195.5, 146.3, 144.4, 143.7, 138.3, 133.7, 129.0, 127.6, 120.9, 33.9, 31.7, 22.6, 21.7, −3.1; MS(EI) *m/z*: 270 (M^+, 19%), 255, 241, 135 (100). Anal. Calcd for $C_{17}H_{22}SiO$: C, 75.50; H, 8.20. Found: C, 75.29; H, 8.08.

1-(Cyclohex-1-en-1-yl)-2-dimethyl(phenyl)silylmethylprop-2-en-1-one (15). Oil, 90%; IR (neat): 1703, 1638, 1610, 1255, 1116, 930, 839; ^{1}H NMR: 7.55–7.34 (m, 5H), 6.49 (m, 1H), 5.35 (s, 1H), 5.31 (s, 1H), 2.23–2.14 (m, 4H), 2.14 (s, 2H), 1.65–1.59 (m, 4H), 0.31 (s, 6H); ^{13}C NMR: 199.4, 145.2, 141.1, 138.3, 137.7, 133.7, 129.0, 127.6, 120.7, 25.8, 23.9, 22.2, 22.0, 21.6, −3.3; MS(EI) *m/z*: 284 (M^+, 86%), 269, 255, 210, 135 (100). Anal. Calcd for $C_{18}H_{24}SiO$: C, 76.00; H, 8.50. Found: 75.86; H, 8.58.

3-Phenyl-4-dimethyl(phenyl)silylmethylpent-4-enal (16). Oil, 90%; IR (neat): 2731, 2833, 1734, 1642, 1253, 1110, 889, 833; ^{1}H NMR: 9.46 (dd, *J*=1.8 Hz and 2.6, 1H), 7.59–7.11 (m, 10H), 4.85 (s, 1H), 4.81 (s, 1H), 3.51 (t, *J*=7.6 Hz, 1H), 2.82 (ddd, *J*=16.7, 2.6 and 7.6 Hz, 1H), 2.62 (ddd, *J*=16.7, 1.8 and 7.6 Hz, 1H), 1.78 (d, *J*=13.9 Hz, 1H), 1.59 (d, *J*=13.9 Hz, 1H), 0.41 (s, 3H), 0.35 (s, 3H); ^{13}C NMR: 201.4, 147.5, 142.1, 138.7, 133.7, 129.2, 128.6, 128.1, 127.9, 126.8, 108.9, 48.5, 46.5, 25.8, −2.7, −3.3; MS(EI) *m/z*: 308 (M^+, 0.4%), 293, 230, 204, 156, 135 (100). Anal. Calcd for $C_{20}H_{24}SiO$: C, 77.87; H, 7.84. Found: C, 77.75; H, 7.86.

1,3-Diphenyl-4-dimethyl(phenyl)silylmethylpent-4-en-1-one (18). Viscous oil, 78%; IR (neat): 1682, 1628, 1258, 1111, 877, 834; ^{1}H NMR: 7.89–7.15 (m, 15H), 4.81 (s, 1H), 4.74 (s, 1H), 3.90 (t, *J*=7.2 Hz, 1H), 3.51 (dd, *J*=16.7 and 7.2 Hz, 1H), 3.23 (dd, *J*=16.7 and 7.2 Hz, 1H), 1.77 (d, *J*=13.9 Hz, 1H), 1.61 (d, *J*=13.9 Hz, 1H), 0.41 (s, 3H), 0.34 (s, 3H); ^{13}C NMR: 198.2, 148.2, 142.9, 139.0, 137.2, 133.7, 132.8, 128.9, 128.5, 128.3, 128.1, 127.9, 127.7, 126.5, 108.0, 47.6, 43.8, 25.9, −2.9, −2.7; MS(EI) *m/z*: 384 (M^+, 0.3%), 369, 307, 279, 135 (100).

3-Methyl-3-[3-dimethyl(phenyl)silylprop-1-en-2-yl]cyclopentan-1-one (19). Oil, 88%; IR (neat): 1742, 1618, 1249, 1108, 875, 830; ^{1}H NMR: 7.56–7.35 (m, 5H), 4.76 (s, 1H), 4.67 (s, 1H), 2.34 (d, *J*=17.7 Hz, 1H), 2.29–1.71 (m, 5H), 1.78 (s, 2H), 1.12 (s, 3H), 0.38 (s, 3H), 0.37 (s, 3H); ^{13}C NMR: 218.9, 151.3, 139.1, 133.6, 129.1, 127.8, 108.4, 51.1, 45.9, 36.5, 33.6, 25.7, 20.4, −2.3; MS(EI) *m/z*: 272 (M^+, 1%), 257, 244, 135 (100). Anal. Calcd for $C_{17}H_{24}SiO$: C, 74.94; H, 8.88. Found: C, 75.26; H, 9.13.

3-[3-Dimethyl(phenyl)silylprop-1-en-2-yl]cyclohexan-1-one (20). Oil, 77%; IR (neat): 1714, 1631, 1253, 1109, 880, 841; ^{1}H NMR: 7.55–7.33 (m, 5H), 4.65 (s with fine couplings, 1H), 4.61 (s with fine couplings, 1H), 2.42–1.82 (m, 7H), 1.78 (s with fine couplings, 2H), 1.49–1.40 (m, 2H), 0.32 (s, 6H); ^{13}C NMR: 211.6, 149.2, 138.5, 133.5, 129.1, 127.7, 107.2, 47.0, 45.4, 41.2, 30.3, 25.1, 25.0, −3.1; MS(EI) *m/z*: 272 (M^+, 2%), 257, 229, 135 (100). Anal. Calcd for $C_{17}H_{24}SiO$: C, 74.94; H, 8.88. Found: C, 75.15; H, 8.98.

***cis*-1-Acetyl-2-[3-dimethyl(phenyl)silylprop-1-en-2-yl]-cyclohexane (21).** White crystals mp=50–51°C (hexane), 85%; IR (Cl_4C): 1709, 1633, 1255, 1113, 881; ^{1}H NMR: 7.57–7.35 m, 5H), 4.65 (s, 1H), 4.59 (s, 1H), 2.93 (q, *J*=4.5 Hz, 1H), 2.02 (s, 3H), 1.96–1.29 (m, 9H), 1.88 (d, *J*=13.7 Hz, 1H), 1.76 (d, *J*=13.7, 1H), 0.33 (s, 3H), 0.31 (s, 3H); ^{13}C NMR: 211.7, 147.9, 138.8, 133.5, 129.0, 127.7, 108.8, 48.7, 45.7, 31.7, 27.5, 26.3, 25.8, 25.5, 21.2, −2.9, −3.4; MS(EI) *m/z*: 300 (M^+, 0.7%), 285, 257, 223, 135 (100). Anal. Calcd for $C_{19}H_{28}SiO$: C, 75.94; H, 9.39. Found: C, 76.05; H, 9.32.

2-Methyl-2-[2-dimethyl(phenyl)silylprop-2-en-1-yl]tetrahydrofuran (23). Oil, 61%; IR (neat): 1605, 1595, 1243, 1115, 1047, 921; ^{1}H NMR: 7.55–7.30 (m, 5H), 5.85 (s with fine couplings, 1H), 5.59 (s with fine couplings, 1H), 3.78–3.52 (m, 2H), 2.41 (d with fine couplings, *J*=15.1 Hz, 1H), 2.34 (d with fine couplings, *J*=15.1 Hz, 1H), 1.92–1.51 (m, 4H), 1.12 (s, 3H), 0.40 (s, 3H), 0.38 (s, 3H); ^{13}C NMR: 147.2, 139.0, 134.0, 130.7, 128.6, 127.5, 82.6, 66.7, 46.6, 36.9, 26.1, 25.8, −2.1, −2.6; MS(EI) *m/z*: 260 (M^+, 0.12%), 245, 183, 135, 85 (100). Anal. Calcd for $C_{16}H_{24}SiO$: C, 73.79; H, 9.29. Found: C, 74.15; H, 9.50.

Reaction of intermediate 29 with electrophiles

Reaction of **29** (3 mmol) with cinnamoyl chloride (3.6 mmol) or *p*-metoxycinnamoyl chloride (3.6 mmol) was carried out in the same conditions as described before in *Procedure 1*, leading to **33** and **34** (Scheme 5). Reaction of **29** (3 mmol) with cinnamaldehyde (3.6 mmol), benzalacetone (3.6 mmol) or cyclohex-2-en-1-one (3.6 mmol) was carried out in the presence of BF_3 in the same conditions as described above in *Procedure 2*, leading to **30**–**32** (Scheme 5).

3-Phenyl-4-*tert*-butyl(diphenyl)silylmethylpent-4-enal (30). Oil, 80%; IR (neat): 2826, 2737, 1728, 1625, 1110, 882; ^{1}H NMR: 9.01 (t, *J*=2.4 Hz, 1H), 7.69–7.02 (m, 15H), 4.93 (s, 1H), 4.77 (s, 1H), 3.24 (t, *J*=7.6 Hz, 1H), 2.47 (dd, *J*=2.4 and 7.6 Hz, 2H), 2.28 (d, *J*=14.5 Hz, 1H), 1.87 (d, *J*=14.5 Hz, 1H), 1.05 (s, 9H); ^{13}C NMR: 201.7, 147.4, 141.7, 136.7, 136.3, 134.5, 134.0, 129.3, 129.1, 128.5, 128.0, 127.6, 127.5, 126,8, 110.9, 48.4, 46.5, 27.7, 19.3, 18.5; MS(EI) *m/z*: 412 (M^+, 0.1%), 397, 395, 355, 335, 199 (100). Anal. Calcd for $C_{28}H_{32}SiO$: C, 81.50; H, 7.82. Found: C, 81.78; H, 7.99.

4-Phenyl-5-*tert*-butyl(diphenyl)silylmethylhex-5-en-2-one (31). Oil, 85%; IR (neat): 1723, 1633, 1112, 875; ^{1}H NMR: 7.68–7.03 (m, 15H), 4.82 (s, 1H), 4.78 (s, 1H), 3.36 (dd, *J*=5.4 and 9.5 Hz, 1H), 2.66 (dd, *J*=15.6 and 9.5 Hz, 1H), 2.52 (dd, *J*=15.6 and 5.4 Hz, 1H), 2.23 (d, *J*=14.7 Hz, 1H), 1.91 (d, *J*=14.7 Hz, 1H), 1.81 (s, 3H), 1.05 (s, 9H); ^{13}C NMR: 207.1, 148.0, 142.2, 136.4, 136.3, 134.6, 134.3, 129.2, 129.0, 128.3, 128.1, 127.5(2C), 126.6, 110.1, 48.8, 47.9, 30.0, 27.7, 19.2, 18.5; MS(EI) *m/z*: 426 (M^+, 0.1%), 369, 239, 199 (100).

3-[3-*tert*-Butyl(diphenyl)silylprop-1-en-2-yl]cyclohexan-1-one (32). Oil, 87%; IR (neat): 1697, 1642, 1111, 866; ^{1}H NMR: 7.75–7.34 (m, 10H), 4.72 (s, 1H), 4.58 (s, 1H), 2.29–2.18 (m, 3H), 2.15 (dd, *J*=14.0 and 4.4 Hz, 1H), 2.05 (d, *J*=14.0 Hz, 1H), 1.86–1.71 (m, 2H), 1.65 (s, 2H), 1.40–1.23 (m, 2H), 1.08 (s, 9H); ^{13}C NMR: 211.7, 149.0, 136.0, 132.9, 129.6, 127.6, 109.2, 46.8, 45.1, 41.1, 29.7, 26.5, 24.7, 19.3, 18.5; MS(EI) *m/z*: 376 (M^+, 0.2%), 319, 241, 239, 199, 135, 41 (100). Anal. Calcd for $C_{25}H_{32}SiO$: C, 79.73; H, 8.56. Found: C, 79.80; H, 8.53.

(*E*)-1-Phenyl-4-*tert*-butyl(diphenyl)silylmethylpenta-1,4-dien-3-one (33). Oil, 79%; IR (neat): 1669, 1600, 1110,

986, 927; ^{1}H NMR: 7.65–7.32 (m, 15H), 7.44 (d, J=15.8 Hz, 1H), 6.89 (d, J=15.8 Hz, 1H), 5.71 (s, 1H), 5.41 (s, 1H), 2.64 (s, 2H), 1.11 (s, 9H); ^{13}C NMR: 192.2, 147.2, 142.9, 136.4, 135.0, 133.8, 130.0, 129.1, 128.7, 128.1, 127.4, 122.4, 121.8, 27.7, 18.5, 14.0; MS(EI) *m/z*: 410 (M^+, 0.15%), 353 (100), 199, 105. Anal. Calcd for $C_{28}H_{30}SiO$: C, 81.90; H, 7.36. Found: C, 82.11; H, 7.48.

(*E*)-1-(4-Methoxyphenyl)-4-*tert*-butyl(diphenyl)silylmethylpenta-1,4-dien-3-one (34). Viscous oil, 82%; IR (neat): 1660, 1600, 1113, 975, 915; ^{1}H NMR: 7.65–7.29 (m, 12H), 7.27 (d, J=15.7 Hz, 1H), 6.88 (d, J=8.8 Hz, 1H), 6.77 (d, J=15.7 Hz, 1H), 5.67 (s, 1H), 5.35 (s, 1H), 3.84 (s, 3H), 2.62 (s, 2H), 1.09 (s, 9H); ^{13}C NMR: 192.4, 161.2, 147.3, 142.8, 136.4, 133.9, 129.8, 129.1, 127.7, 127.5, 121.9, 119.6, 114.2, 55.3, 27.8, 18.5, 14.1; MS(EI) *m/z*: 440 (M^+, 0.5%), 383, 199 (100).

Reaction of 8 with carbonyl derivatives

To 0.22 ml of $TiCl_4$ (2 mmol) in 10 ml of dry CH_2Cl_2 was added at −78°C, under nitrogen, butyraldehyde or benzalacetone (2 mmol) and immediately a solution of **8** (432 mg, 2 mmol) in CH_2Cl_2 (1 ml). The resulting mixture was stirred at −78°C for 30 min and quenched with MeOH at this temperature. The solution was allowed to warm up to room temperature, washed with a saturated solution of sodium bicarbonate, extracted with CH_2Cl_2, dried over $MgSO_4$ and evaporated. Purification by flash-chromatography (EtOAc:hexanes) gave **24–26** (Scheme 4).

6-Methylenenon-8-en-4-ol (24). Oil, 67%; IR (neat): 3390, 1638, 1122, 1020, 991, 911, 893; ^{1}H NMR: 5.80 (ddt, J=17.5, 9.6 and 7.0 Hz, 1H), 5.11–5.03 (m, 2H), 4.92 (s with fine couplings, 1H), 4.88 (s with fine couplings, 1H), 3.73 (m, 1H), 2.82 (dd, J=17.2 and 7.0 Hz, 1H), 2.76 (dd, J=17.2 and 7.0 Hz, 1H), 2.25 (dd, J=2.5 and 14.1, 1H), 2.06 (dd, J=9.1 and 14.1, 1H), 1.74 (br s, 1H), 1.51–1.32 (m, 4H), 0.93 (t, J=7.1 Hz, 3H); ^{13}C NMR: 145.1, 135.9, 116.6, 113.5, 68.5, 44.3, 40.5, 39.2, 18.9, 14.1; MS(EI) *m/z*: 154 (M^+, 10%), 155, 137, 111, 93, 82, 73, 67, 55, 43, 41 (100).

2-Allyl-2-methyl-4-propyloxetane (25). Oil, 28%; IR (neat): 1648, 1034, 988, 905; ^{1}H NMR: 5.92 (ddt, J=17.1, 10.1 and 7.0 Hz, 1H), 5.19–5.10 (m, 2H), 3.99 (m, 1H), 2.65 (dd, J=17.0 and 10.1 Hz, 1H), 2.61 (dd, J=17.0 and 10.1 Hz, 1H), 1.95 (dd, J=8.4 and 15.1 Hz, 1H), 1.83 (dd, J=2.0 and 15.1 Hz, 1H), 1.59 (s, 3H), 1.53–1.30 (m, 4H), 0.94 (t, J=7.0 Hz, 3H); ^{13}C NMR: 133.3, 119.0, 73.3, 68.4, 50.3, 49.3, 40.6, 30.1, 18.6, 14.0; MS(EI) *m/z*: 154 (M^+, 0.2%), 139, 82, 67 (100), 55, 41. Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 78.25; H, 12.01.

[1*S,3*R**,5*R**]-1-Methyl-3-allyl-3-chloro-5-phenylcyclohexan-1-ol (26).** Oil, 69%; IR (neat): 3560, 3450, 1644, 1153, 995, 923; ^{1}H NMR ($CDCl_3$, 500 MHz): 7.35–7.19 (m, 5H), 5.95 (ddt, J=17.0, 9.9 and 7.0 Hz, 1H), 5.21 (d, J=9.9 Hz, 1H), 5.16 (d, J=17.0 Hz, 1H), 3.57 (br s, 1H), 3.38 (tt, J=12.7 and 3.1 Hz, 1H), 2.59 (dd, J=14.1 and 7.0 Hz, 1H), 2.57 (dd, J=14.1 and 7.0 Hz, 1H), 2.27–2.18 (m, 2H), 2.02 (dd with other fine couplings, J=13.2 and 3.1 Hz, 1H), 1.69 (d, J=15.2 Hz, 1H), 1.63 (dd, J=13.7 and 12.7 Hz, 1H), 1.52 (dd, J=13.2 and 12.7 Hz, 1H), 1.27 (s, 3H); ^{13}C NMR: 145.0, 128.5, 127.0, 126.5, 132.2, 119.7, 79.4, 70.4, 51.0, 48.2, 46.3, 46.0, 35.3, 31.1; MS(EI) *m/z*: 264 and 266 (M^+ and M^+2, 0.4%), 246 and 248, 211, 205 and 207, 169, 129, 91, 77, 43 (100); Found: M^+-18, 246.1177. $C_{16}H_{19}Cl$ requires: 246.1175. Anal. Calcd for $C_{16}H_{21}OCl$: C, 72.58; H, 7.99. Found: C, 72.49; H, 8.05.

Homologation of cuprates 5 and 29 and reaction with electrophiles

A solution of (iodomethyl)zinc iodide (5 mmol) freshly prepared[24] in THF (5 ml) was added at −40°C to a solution of intermediate **5** or **29** (3 mmol) which was prepared using the general procedure. The reaction mixture was stirred at this temperature for 30 min, then 3.6 mmol of benzalacetone, cyclopentanone or cyclohex-2-en-1-one in THF (3 ml) were added dropwise and the resulting solution was kept at −40°C for 2 h. After allowing the mixture to warm up to 0°C, it was quenched with saturated ammonium chloride solution and extracted twice with Et_2O. The organic layer was dried, rotoevaporated and chromatographed (EtOAc:hexanes) to give **35–39** (Scheme 6).

(*E*)-1-Phenyl-3-methyl-5-*tert*-butyl(diphenyl)silylmethylhexa-1,5-dien-3-ol (35). Oil, 65%; IR (neat): 3550, 1632, 1599, 1230, 1112, 985, 892; ^{1}H NMR: 7.68–7.28 (m, 15H), 6.51 (d, J=16.2 Hz, 1H), 6.14 (d, J=16.2 Hz, 1H), 4.87 (d, J=1.6 Hz, 1H), 4.72 (d, J=1.6 Hz, 1H), 2.35 (d, J=13.9 Hz, 1H), 2.28 (d, J=13.9 Hz, 1H), 2.04 (br s, 1H), 1.99 (s, 2H), 1.23 (s, 3H), 1.05 (s, 9H); ^{13}C NMR: 143.4, 137.0, 136.9, 136.3, 136.1, 135.9, 134.7, 134.5, 129.2, 128.5, 127.5, 127.4, 127.2, 126.4, 126.2, 115.2, 71.9, 50.6, 28.6, 27.7, 22.2, 18.5; MS(CI) *m/z*: 441 (M^+1, 1%), 440 (M^+, 2%), 423, 345, 383, 239 (100). Anal. Calcd for $C_{30}H_{36}SiO$: C, 81.76; H, 8.23. Found: C, 81.50; H, 8.11.

1-[2-*tert*-Butyl(diphenyl)silylmethylprop-2-en-1-yl]cyclopentan-1-ol (36). Oil, 75%; IR (neat): 3555, 1624, 1240, 1100, 900; ^{1}H NMR: 7.69–7.34 (m, 10H), 4.82 (d, J=0.8 Hz, 1H), 4.68 (d, J=0.8 Hz, 1H), 2.35 (s, 2H), 1.91 (s, 2H), 1.80–1.35 (m, 8H), 1.63 (br s, 1H), 1.10 (s, 9H); ^{13}C NMR: 144.2, 136.3, 134.6, 129.1, 127.4, 113.8, 80.8, 48.5, 39.8, 27.8, 23.4, 22.0, 18.5; MS(CI) *m/z*: 379 (M^+1, 2%), 378 (M^+, 1%), 361, 321, 239, 123 (100). Anal. Calcd for $C_{25}H_{34}SiO$: C, 79.31; H, 9.05. Found: C, 79.52; H, 9.16.

1-[2-*tert*-Butyl(diphenyl)silylmethylprop-2-en-1-yl]cyclohex-2-en-1-ol (37).Z Oil, 61%; IR (neat): 3650, 3400, 1635, 1243, 1180, 1105, 902; ^{1}H NMR: 7.70–7.32 (m, 10H), 5.71 (dt, J=10.2 and 3.6 Hz, 1H), 5.46 (d with fine couplings, J=10.2 Hz, 1H), 4.81 (d with fine couplings, J=1.8 Hz, 1H), 4.64 (d, J=1.8 Hz, 1H), 2.40 (d with fine couplings, J=13.8 Hz, 1H), 2.33 (d with fine couplings, J=13.8 Hz, 1H), 1.98–1.47 (m, 6H), 1.92 (d, J=13.6 Hz, 1H), 1.83 (d, J=13.6 Hz, 1H), 1.72 (br s, 1H), 1.08 (s, 9H); ^{13}C NMR: 143.4, 136.4, 134.6, 132.8, 129.1, 127.5, 128.9, 114.7, 69.5, 49.6, 35.9, 27.8, 25.1, 22.4, 19.2, 18.6; MS(CI) *m/z*: 391 (M^+1, 9%), 390 (M^+, 2%), 373, 333, 295 (100), 239. Anal. Calcd for $C_{26}H_{34}SiO$: C, 79.94; H, 8.77. Found: C, 80.34; H, 9.08.

1-[2-Dimethyl(phenyl)silylmethylprop-2-en-1-yl]cyclopentan-1-ol (38). Oil, 27%; IR (neat): 3580, 3500, 1620,

1252, 1161, 1115, 885, 832; ^{1}H NMR: 7.54–7.34 (m, 5H), 4.71 (s, 2H), 2.14 (s, 2H), 1.89 (s, 2H), 1.84–1.47 (m, 8H), 1.76 (br s, 1H), 0.33 (s, 6H); ^{13}C NMR: 144.3, 138.8, 133.6, 129.0, 127.7, 111.9, 80.8, 48.6, 39.9, 27.7, 23.4, −3.1; MS(EI) *m/z*: 274 (M^+, 0.2%), 259, 219, 135 (100).

1-[2-Dimethyl(phenyl)silylmethylprop-2-en-1-yl]cyclohex-2-en-1-ol (39). Oil, 20%; IR (neat): 3450, 1630, 1246, 1145, 1105, 871, 830; ^{1}H NMR: 7.57–7.32 (m, 5H), 5.75 (dt, *J*=10.1 and 3.4 Hz, 1H), 5.56 (d with fine couplings, *J*=10.1 Hz, 1H), 4.72 (m, 2H), 2.42–1.40 (m, 6H), 2.13 (s with fine couplings, 2H), 1.92 (s with fine couplings, 2H), 1.63 (br s, 1H), 0.32 (s, 6H); ^{13}C NMR: 143.5, 138.8, 134.3, 133.6, 129.0, 128.2, 127.7, 112.5, 77.2, 49.8, 35.9, 28.0, 25.1, 19.2, −2.9; MS(EI) *m/z*: 286 (M^+, 0.3%), 268, 209, 190, 135 (100).

Directed Nazarov reactions

A solution of **12**–**14**, **33** or **34** (2 mmol) in THF (3 ml) was cooled at 0°C and TFA (0.46 ml, 6 mmol) was added with continuous stirring. After 30 min at 0°C, the solution was warmed up to room temperature and stirred for an additional period of 2 h. In the case of compounds **33** and **34** bearing the *t*-butyldiphenylsilyl group the reaction temperature was increased to 40–50°C and the mixture stirred for 1 h. The reaction was stopped by adding a saturated solution of sodium bicarbonate (5 ml). After extraction with Et_2O, the ethereal layer was washed twice with brine, dried and concentrated. The crude was purified by flash-chromatography (EtOAc:hexanes) to give **42**–**46** (Scheme 7).

2-Methylene-4-phenylcyclopentan-1-one (42). Oil, 83%; IR (neat): 1722, 1638, 936, 750, 697; ^{1}H NMR: 7.39–7.22 (m, 5H), 6.07 (s with fine couplings, 1H), 5.38 (s with fine couplings, 1H), 3.42 (tt, *J*=10.1 and 7.5 Hz, 1H), 3.14 (dd with fine couplings, *J*=16.4 and 7.5 Hz, 1H), 2.87–2.70 (m, 2H), 2.53 (dd, *J*=10.1 and 17.7 Hz, 1H); ^{13}C NMR: 205.6, 144.5, 143.2, 128.7, 126.8, 126.6, 117.5, 45.9, 38.9, 38.0; MS(EI) *m/z*: 172 (M^+, 58%), 143, 128, 115, 103, 91, 68 (100). Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.80; H, 7.11.

2-Methylene-4-(4-methoxyphenyl)cyclopentan-1-one (43). Oil, 78%; IR (neat): 1726, 1640, 1250, 942, 834; ^{1}H NMR: 7.22 (d, *J*=8.7 Hz, 2H), 6.88 (d, *J*=8.7 Hz, 2H), 6.06 (s with fine couplings, 1H), 5.37 (s with fine couplings, 1H), 3.81 (s, 3H), 3.37 (tt, *J*=10.2 and 7.2 Hz, 1H), 3.11 (dd with fine couplings, *J*=16.3 and 7.2 Hz, 1H), 2.77–2.65 (m, 2H), 2.48 (dd, *J*=10.2 and 17.9 Hz, 1H); ^{13}C NMR: 205.7, 158.3, 144.7, 135.2, 127.6, 117.4, 114.0, 55.2, 46.1, 38.2, 38.0; MS(EI) *m/z*: 202 (M^+, 100%), 187, 171, 159, 134, 119, 91, 68.

***cis*-3-Methylenebicyclo[3.3.0]octan-2-one (44).** Oil, 75%; IR (neat): 1720, 1635, 932; ^{1}H NMR: 5.96 (m, 1H), 5.29 (m, 1H), 2.85 (ddt, *J*=17.3, 8.1 and 2.9 Hz, 1H), 2.75–2.60 (m, 2H), 2.42 (dq, *J*=17.3 and 2.1 Hz, 1H), 2.03–1.77 (m, 3H), 1.56 (quintet, *J*=7.0 Hz, 2H), 1.21 (sextet, *J*=7.1 Hz, 1H); ^{13}C NMR: 210.9, 144.8, 118.0, 53.1, 37.9, 33.8, 33.5, 29.8, 26.1; MS(EI) *m/z*: 136 (M^+, 48%), 121, 108, 93, 79, 67 (100). Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.60; H, 9.01.

(*E*)-2-*tert*-Butyl(diphenyl)silylmethylene-4-phenylcyclopentan-1-one (45). Oil, 67%; IR (neat): 1708, 1612, 1100, 750, 700; ^{1}H NMR: 7.78–7.30 (m, 10H), 7.23–6.70 (m, 5H), 6.61 (s with fine couplings, 1H), 3.75 (m, 1H), 2.75 (dd, *J*=18.8 and 6.9 Hz, 1H), 2.46 (dt, *J*=14.8 and 1.2 Hz, 1H), 2.29 (dt, *J*=14.8 and 1.4 Hz, 1H), 2.10 (dd, *J*=18.8 and 2.4 Hz, 1H), 1.11 (s, 9H); ^{13}C NMR: 209.3, 158.8, 142.6, 136.2, 134.8, 133.7, 129.6, 128.6, 127.7, 126.9, 126.6, 43.9, 43.7, 27.7, 18.5, 6.4; MS(CI) *m/z*: 411 (M^+1, 0.8%), 353 (100), 199. Anal. Calcd for $C_{28}H_{30}SiO$: C, 81.90; H, 7.36. Found: C, 81.61; H, 7.57.

(*E*)-2-*tert*-Butyl(diphenyl)silylmethylene-4-(4-methoxyphenyl)cyclopentan-1-one (46). Oil, 63%; IR (neat): 1700, 1605, 1240, 1105, 835, 740, 690; ^{1}H NMR: 7.70–7.33 (m, 10H), 6.72 (d, *J*=8.8 Hz, 2H), 6.60 (d, *J*=8.8 Hz, 2H), 6.59 (s, 1H), 3.77 (s, 3H), 3.72 (m, 1H), 2.73 (dd, *J*=18.8 and 6.8 Hz, 1H), 2.46 (dt, *J*=14.7 and 1.3 Hz, 1H), 2.27 (dt, *J*=14.7 and 1.6 Hz, 1H), 2.06 (dd, *J*=18.8 and 2.6 Hz, 1H), 1.10 (s, 9H); ^{13}C NMR: 209.4, 159.0, 158.2, 142.4, 136.1, 134.5, 133.7, 129.3, 127.9, 127.6, 113.9, 55.2, 43.9, 43.1, 27.6, 18.5, 6.3; MS(CI) *m/z*: 441 (M^+1, 1.5%), 425, 383 (100), 199.

Reaction of 42 and 44 with intermediate 5

Following *Procedure 2* ketones **42** and **44** (2 mmol) were allowed to react with cuprate **5** (2.2 mmol) in the presence of BF_3 (2 mmol) to give **47** and **48** respectively (Scheme 9).

***trans*-2-[2-Dimethyl(phenyl)silylmethylprop-2-en-1-yl]-4-phenylcyclopentan-1-one (47).** Oil, 84%; IR (neat): 1747, 1636, 1250, 1110, 885, 832; ^{1}H NMR: 7.57–7.22 (m, 10H), 4.67 (s, 1H), 4.60 (s, 1H), 3.29 (tt, *J*=12.1 and 8.2 Hz, 1H), 2.78 (dd with fine couplings, *J*=18.5 and 8.2 Hz, 1H), 2.60–2.38 (m, 3H), 2.30 (dd, *J*=18.5 and 12.1 Hz, 1H), 1.86 (dd, *J*=15.4 and 10.3 Hz, 1H), 1.84 (d, *J*=13.9 Hz, 1H), 1.74 (d, *J*=13.9 Hz, 1H), 1.53 (q, *J*=12.0 Hz, 1H), 0.36 (s, 6H); ^{13}C NMR: 218.6, 144.4, 142.9, 138.7, 133.6, 129.0, 128.6, 127.8, 126.7, 126.6, 109.3, 49.3, 45.6, 39.9, 38.5, 38.1, 25.6, −2.9, −3.0; MS(EI) *m/z*: 348 (M^+, 2%), 333, 292, 270, 255, 135 (100). Anal. Calcd for $C_{23}H_{28}SiO$: C, 79.26; H, 8.10. Found: C, 79.45; H, 8.30.

[1*S,3*R**,5*S**]-3-[2-Dimethyl(phenyl)silylmethylprop-2-en-1-yl]bicyclo[3.3.0]octan-2-one (48).** Oil, 82%; IR (neat): 1738, 1630, 1255, 1115, 874, 835; ^{1}H NMR: 7.55–7.34 (m, 5H), 4.62 (s with fine couplings, 1H), 4.56 (s with fine couplings, 1H), 2.71 (m, 1H), 2.70–2.30 (m, 4H), 1.96–1.31 (m, 8H), 1.78 (d, *J*=13.7 Hz, 1H), 1.70 (d, *J*=13.7 Hz, 1H), 0.34 (s, 6H); ^{13}C NMR: 221.5, 144.9, 138.8, 133.5, 129.0, 127.7, 108.7, 51.4, 48.7, 38.0, 37.7, 34.5, 33.6, 29.0, 25.7, 24.9, −3.0; MS(EI) *m/z*: 312 (M^+, 11%), 297, 269, 257, 235, 135 (100). Anal. Calcd for $C_{20}H_{28}SiO$: C, 76.86; H, 9.03. Found: C, 77.10; H, 8.95.

Allylsilane terminated cyclizations

$TiCl_4$ catalyzed reactions. $TiCl_4$ (0.13 ml, 1.2 mmol) was added slowly to a solution of **16**, **17** or **21** (2 mmol) in CH_2Cl_2 (8 ml) at −78°C, under nitrogen. After stirring for 30 min at this temperature, 2 ml of MeOH were added at

once and the mixture was allowed to warm up to 0°C. The reaction mixture was washed with a saturated solution of sodium bicarbonate, extracted with Et_2O, dried over $MgSO_4$ and rotoevaporated. Purification by flash-chromatography (EtOAc:hexanes) gave **49**, **50** and **53** (Scheme 10).

***cis*-3-Methylene-4-phenylcyclopentan-1-ol (49).** Oil, 87%; IR (neat): 3350, 1648, 1075, 882, 750, 690; ^{1}H NMR: 7.36–7.20 (m, 5H), 5.03 (d with fine couplings, J=2.3 Hz, 1H), 4.56 (d with fine couplings, J=2.3 Hz, 1H), 4.42 (quintet, J=7.1 Hz, 1H), 3.64, (t with fine couplings, J=10.3 Hz, 1H), 2.87 (dd with fine couplings, J=16.2 and 7.1 Hz, 1H), 2.56–2.45 (m, 2H), 1.94 (br s, 1H), 1.89 (ddd, J=12.6, 10.3 and 7.1 Hz, 1H); ^{13}C NMR: 153, 143, 128.4, 128.3, 126.2, 109.1, 71.5, 48.7, 44.5, 43.0; MS(CI) *m/z*: 175 (M^+1, 28%), 157 (100), 131, 97. Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.90; H, 8.13.

[1*R,6*S**,7*R**]- and [1*R**,6*S**,7*S**]-7-Methyl-9-methylenebicyclo[4.3.0]nonan-7-ol (53).** Oil, 79%; IR (neat): 3430, 1657, 1110, 880; ^{1}H NMR: 4.92 (q, J=2.2 Hz, 1H), 4.84 (q, J=2.2 Hz, 1H), 2.67 (m, 1H), 2.54 (d with fine couplings, J=17.6 Hz, 1H), 2.49 (d with fine couplings, J=17.6 Hz, 1H), 1.88 (dq, J=14.0 and 3.4 Hz, 1H), 1.80–1.50 (m, 4H), 1.72 (br s, 1H), 1.50–1.10 (m, 4H), 1.34 (s, 3H). The epimeric alcohol shows a methyl signal at 1.35 (ratio 3:1); ^{13}C NMR: 150.5, 105.6, 78.1, 48.7, 46.0, 42.0, 28.5, 25.9, 24.5, 23.3, 21.3; MS(EI) *m/z*: 166 (M^+, 34%), 151, 148, 133, 123 (100). Anal. Calcd for $C_11H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.88; H, 11.22.

Allylsilane terminated cyclizations. $EtAlCl_2$ catalyzed reactions

$EtAlCl_2$ (2.4 mmol, 1.8 M in toluene) was added slowly to a solution of **19**, **20**, **47**, **48**, **30** or **31** (2 mmol) in toluene (8 ml) at 0°C, under nitrogen. After stirring for 1 h at 0°C, brine was added (5 ml) and the mixture extracted with Et_2O, dried and evaporated. Purification by flash-chromatography gave **51**, **52** and **54**–**57** (Scheme 10).

3-Methylene-4-methylbicyclo[2.2.1]heptan-1-ol (51). White crystals mp=50–51°C (hexane), 81%; IR (Cl_4C): 3615, 3355, 1660, 1305, 1107, 884; ^{1}H NMR: 4.71 (t, J=1.9 Hz, 1H), 4.62 (t, J=1.9 Hz, 1H), 2.46 (dt, J=15.4 and 1.9 Hz, 1H), 2.38 (dt, J=15.4 and 1.9 Hz, 1H), 1.95–1.35 (m, 7H), 1.19 (s, 3H); ^{13}C NMR: 156.2, 101.0, 80.1, 51.0, 47.3, 44.9, 36.7, 36.1, 17.9; MS(EI) *m/z*: 138 (M^+, 27%), 123 (100), 110, 109, 95. Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.39; H, 10.30.

6-Methylenebicyclo[3.2.1]octan-1-ol (52). White crystals mp=53–54°C (hexane), 92%; IR (Cl_4C): 3595, 3355, 1653, 1120, 877; ^{1}H NMR: 4.76 (s with fine couplings, 2H), 2.68 (m, 1H), 2.61 (br s, 1H), 2.38 (d with fine couplings, J=16.7 Hz, 1H), 2.29 (d with fine couplings, J=16.7 Hz, 1H), 1.87 (m, 1H), 1.75–1.36 (m, 7H);); ^{13}C NMR: 152.9, 105.1, 77.7, 46.1, 44.0, 43.7, 39.4, 32.8, 20.0; MS(EI) *m/z*: 138 (M^+, 5%), 123, 110, 109, 95 (100). Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.17; H, 10.22.

[1*R,5*R**,7*S**]-3-Methylene-7-phenylbicyclo[3.3.0]octan-1-ol (54).** White crystals mp=67–68°C (hexane), 70%; IR (Cl_4C): 3610, 3350, 1664, 1070, 890; ^{1}H NMR: 7.34–7.18 (m, 5H), 4.87 (s with fine couplings, 1H), 4.85 (s with fine couplings, 1H), 3.22 (tt, J=12.4 and 6.2 Hz, 1H), 2.77 (dd with fine couplings, J=15.0 and 9.4 Hz, 1H), 2.57 (d with fine couplings, J=15.4 Hz, 1H), 2.49 (d with fine couplings, J=15.4 Hz, 1H), 2.52–2.38 (m, 2H), 2.22 (dd with fine couplings, J=12.4 and 6.2 Hz, 1H), 2.03 (d with fine couplings, J=15.0 Hz, 1H), 1.78 (t, J=12.4 Hz, 1H), 1.61 (br s, 1H), 1.36 (dd with other couplings, J=12.4 and 3.5 Hz, 1H); ^{13}C NMR: 150.2, 143.8, 128.3, 126.9, 126.1, 107.6, 88.8, 51.7, 48.6, 48.4, 44.2, 42.3, 39.2; MS(EI) *m/z*: 214 (M^+, 50%), 199, 171, 156, 143, 129, 104 (100), 91. Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.27; H, 8.60.

10-Methylene-*cis*,*anti*,*cis*-tricyclo[6.3.0.0^{2,6}]undecan-1-ol (55). Oil, 68%; IR (neat): 3595, 3450, 1655, 1065, 878; ^{1}H NMR: 4.91 (s with fine couplings, 2H), 2.65 (dd with fine couplings, J=16.7 and 7.2 Hz, 1H), 2.55–2.15 (m, 6H), 1.84 (ddd, J=12.5, 8.1 and 6.4 Hz, 1H), 1.70–1.40 (m, 7H), 1.29 (sextet, J=6.4 Hz, 1H); ^{13}C NMR: 150.8, 107.5, 90.5, 51.4, 49.2, 47.4, 41.9, 37.2, 36.6, 35.2, 28.5, 27.3; MS(EI) *m/z*: 178 (M^+, 10%), 163, 135, 123, 95, 82, 67, 41 (100). Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 81.21; H, 10.46.

3-*tert*-Butyl(diphenyl)silylmethyl-4-phenylcyclopent-3-en-1-ol (56). Oil, 69%; IR (neat): 3400, 1621, 1600, 1590, 1250, 1105, 1037, 700; ^{1}H NMR: 7.61–7.17 (m, 15H), 4.12 (t with fine couplings, J=5.9 Hz, 1H), 2.87 (dd with fine couplings, J=16.2 and 5.9 Hz, 1H), 2.53–2.39 (m, 4H), 2.02 (d, J=17.4 Hz, 1H), 1.31 (br s, 1H), 0.98 (s, 9H); ^{13}C NMR: 138.3, 136.1, 134.4, 133.5, 131.4, 129.2, 128.1, 127.6, 127.4, 126.2, 70.0, 49.1, 46.9, 27.4, 18.3, 13.0; MS(EI) *m/z*: 412 (M^+, 0.2%), 355, 199 (100), 156, 135. Anal. Calcd for $C_{28}H_{32}SiO$: C, 81.50; H, 7.82. Found: C, 81.64; H, 7.94.

3-*tert*-Butyl(diphenyl)silylmethyl-1-methyl-4-phenylcyclopent-3-en-1-ol (57). Oil, 77%; IR (neat): 3570, 3450, 1628, 1600, 1590, 1235, 1110, 1080, 705; ^{1}H NMR: 7.66–7.22 (m, 15H), 2.73 (d, J=16.2 Hz, 1H), 2.58 (d, J=16.2 Hz, 1H), 2.56 (d, J=14.1 Hz, 1H), 2.41 (d, J=14.1 Hz, 1H), 2.32 (d, J=17.1 Hz, 1H), 2.19 (d, J=17.1 Hz, 1H), 1.40 (br s, 1H), 1.21 (s, 3H), 1.02 (s, 9H); ^{13}C NMR: 138.3, 136.1, 134.3, 134.1, 132.2, 129.3, 128.1, 127.7, 127.5, 126.2, 76.5, 54.5, 52.6, 27.4, 27.2, 18.4, 12.8; MS(EI) *m/z*: 426 (M^+, 10%), 369, 199 (100), 135. Anal. Calcd for $C_{29}H_{34}SiO$: C, 81.64; H, 8.03. Found: C, 81.92; H, 7.83.

Acknowledgements

We gratefully acknowledge financial support from the Ministry of Education and Culture of Spain (DGES PB96/0357 project) and from the 'Junta de Castilla y León' (VA43/98 project).

References

1. Cuadrado, P.; González, A. M.; Pulido, F. J.; Fleming, I.; Rowley, M. *Tetrahedron* **1989**, *45*, 413.

2. Fleming, I.; Pulido, F. J. *J. Chem. Soc., Chem. Commun.* **1986**, 1010.
3. Cuadrado, P.; González, A. M.; Pulido, F. J.; Fleming, I. *Tetrahedron Lett.* **1988**, *29*, 1825.
4. Barbero, A.; Cuadrado, P.; González, A. M.; Pulido, F. J.; Fleming, I. *J. Chem. Soc., Perkin Trans I* **1991**, 2811.
5. Blanco, F. J.; Cuadrado, P.; González, A. M.; Pulido, F. J. *Synthesis* **1996**, 42.
6. Barbero, A.; Cuadrado, P.; González, A. M.; Pulido, F. J.; Fleming, I. *J. Chem. Res.* **1990**, *297*, 291.
7. Chan, T. H.; Fleming, I. *Synthesis*, **1979**, 761; Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Heidelberg; 1983; Fleming, I.; Dunogues, J.; Smithers, R. H. *Org. React*. **1989**, *37*, 57.
8. Fleming, I.; Landais, Y.; Raithby, P. R. *J. Chem. Soc., Perkin Trans I* **1991**, 715.
9. Pulido, F. J.; Barbero, A. *Recent Res. Devel. Synth. Organic Chem.* **1999**, *2*, 1–22.
10. (a) Blanco, F. J.; Cuadrado, P.; González, A. M.; Pulido, F. J.; Fleming, I. *Tetrahedron Lett*. **1994**, *35*, 8881. (b) Barbero, A.; García, C.; Pulido, F. J. *Tetrahedron Lett*. **1999**, *40*, 6649.
11. Zavgorodnii, V. S.; Simin, V. B.; Zubova, T. P.; Petrov, A. A. *Zh. Obshch. Khim.* **1976**, *46*, 197; Zavgorodnii, V. S.; Simin, V. B.; Zubova, T. P.; Petrov, A. A. *Zh. Obshch. Khim.* **1981**, *51*, 2048; Lysenko, Yu. A.; Troshina, E. A.; Pekhtereva, T. M. *Zh. Obshch. Khim*. **1981**, *51*, 2058.
12. (a) Fleming, I.; Newton, T. W.; Roessler, F. *J. Chem. Soc., Perkin Trans. I* **1981**, 2527. (b) Sharma, S.; Oehlschlager, A. C. *Tetrahedron* **1989**, *45*, 557. (c) Barbero, A.; Cuadrado, P.; Fleming, I.; González, A. M.; Pulido, F. J.; Sanchez, A. *J. Chem. Soc., Perkin Trans. I* **1995**, 1525. See also Ref. 1 and citations therein.
13. Oda, H.; Morizawa, Y.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1984**, *25*, 3217.
14. Barbero, A.; Cuadrado, P.; Fleming, I.; González, A. M.; Pulido, F. J. *J. Chem. Soc., Chem. Commun.* **1992**, 351; Barbero, A.; Cuadrado, P.; Fleming, I.; González, A. M.; Pulido, F. J.; Rubio, R. *J. Chem. Soc., Perkin Trans. I* **1993**, 1657; Barbero, A.; Cuadrado, P.; González, A. M.; Pulido, F. J.; Rubio, R.; Fleming, I. *Tetrahedron Lett.* **1992**, *33*, 5841; Barbero, A.; Cuadrado, P.; Garcia, C.; Pulido, F. J.; Rincon, J. A. *J. Org. Chem.* **1998**, *63*, 7531 and citations therein.
15. Piers, E.; Tillyer, R. D. *J. Org. Chem.* **1988**, *53*, 5366; Marino, J. P.; Emonds, M. V. M.; Stengel, P. J.; Oliveira, A. R. M.; Simonelli, J.; Ferreira, J. T. B. *Tetrahedron Lett.* **1992**, *33*, 49; see also Refs. 12 and 14.
16. Bulten, E. J.; Buddind, H. A. *J. Organomet. Chem.* **1974**, *78*, 385.
17. Sakurai, H.; Eriyama, Y.; Kamiyama, Y.; Nakadaira, Y. *J. Organomet. Chem.* **1984**, *264*, 229; Carlson, C. W.; West, R. *Organometallics* **1983**, *2*, 1801.
18. Morizawa, Y.; Oda, H.; Oshima, K.; Nozaki, H. *Tetrahedron. Lett.* **1984**, *25*, 1163.
19. Arnold, J.; Engeler, M. P.; Elsner, F. H.; Heyn, R. H.; Tilley, T. D. *Organometallics* **1989**, *8*, 2284.
20. Hayashi, T.; Kobayashi, T.; Kawamoto, A. M.; Yamashita, H.; Tanaka, M. *Organometallics* **1990**, *9*, 280.
21. Barbero, A.; Cuadrado, P.; Fleming, I.; González, A. M.; Pulido, F. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1030. Barbero, A.; Cuadrado, P.; Fleming, I.; González, A. M.; Pulido, F. J. *J. Chem. Soc., Perkin Trans. I* **1992**, 327; see also Refs. 1 and 6.
22. Singh, S. M.; Oehlschager, A. C.; Can *J. Chem.* **1991**, *69*, 1872.
23. Cuadrado, P.; Gonzalez, A. M.; Gonzalez, B.; Pulido, F. J. *Synth. Commun.* **1989**, *19*, 275.
24. Knochel, P.; Rao, S. A. *J. Am. Chem. Soc.* **1990**, *112*, 6146.
25. Nazarov, I. N.; Zaretskoya, I. I. *J. Gen. Chem. USSR* **1957**, *27*, 693; Sorensen, T. S. *J. Am. Chem. Soc*. **1967**, *89*, 3782; Santelli-Rouvier, C.; Santelli, M. *Synthesis* **1983**, 429.
26. Denmark, S. E.; Jones, T. K. *J. Am. Chem. Soc* **1982**, *104*, 2642; Denmark, S. E.; Wallace, M. A.; Walker, C. B. *J. Org. Chem.* **1990**, *55*, 5543.
27. For a review on intramolecular allylsilane cyclizations see: Schinzer, D. *Synthesis* **1988**, 263; Trost, B. M.; Coppola, B. P. *J. Am. Chem. Soc*. **1982**, *104*, 6879.
28. Marchand, A. P. *Stereochemical Applications of NMR Studies in Rigid Bicyclic Systems, Methods in Stereochemical Analysis*; Verlag Chemie Int: Deerfield Beach, 1982; Vol. 1–2.
29. Mehta, G.; Murthy, A. N.; Reddy, D. S.; Reddy, A. V. *J. Am. Chem. Soc.* **1986**, *108*, 3443.