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Tandem Hydroformylation/Aldol Addition of Silyl Enol Ethers Bearing Remote Olefinic Functionalities

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Abstract—Rhodium(I) complex catalysed hydroformylation of unsaturated silyl enol ethers leads to products of an intramolecular aldol addition in a one-pot procedure. Thus β,γ- or γ,δ-unsaturated silyl enol ethers undergo tandem hydroformylation/Mukaiyama aldol reaction to form cyclic *O*-silylated aldol adducts with high selectivity and good yields.

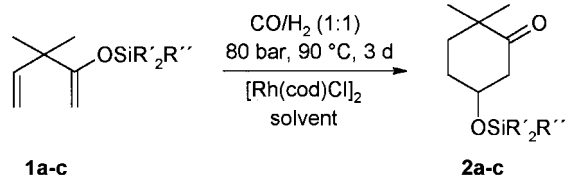
Introduction

Reaction sequences combining hydroformylation with various subsequent transformations of the oxo-aldehydes to one-pot procedures are gaining growing interest.[1] Following our own investigations in developing synthetic procedures of this type we recently reported various examples of novel rhodium(I) complex catalysed tandem hydroformylation/aldol reactions of a selected β,γ-unsaturated ketone and its silyl enol ethers.[2] Here we now describe in more detail the sequential intramolecular hydroformylation/aldol addition of the latter and similar silyl enol ethers of type **A** bearing remote olefinic functionalities to give β-silyloxy substituted cyclic ketones of type **C** (Scheme 1).

For directed aldol additions[3] a large number of transition metal catalysed procedures are reported.[4] Among various other examples, rhodium(I) complex catalysed reactions of enol silanes and aldehydes were investigated by Matsuda,[5] Reetz[6] and Heathcock.[7] According to the results of Matsuda et al.,[5] who described rhodium carbonyl complex catalysed Mukaiyama aldol addition, we expected that a rhodium hydrido carbonyl species,[8] as it is formed under hydroformylation conditions, should equally catalyse hydroformylation and a sequential aldol reaction of the hydroformylation product. This assumption has been verified with the unsaturated silyl enol ethers of type **1**.[2]

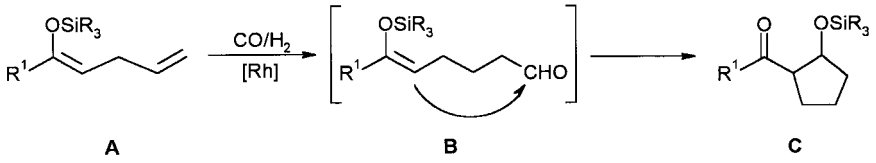
Results

As summarised in Table 1 indeed the trimethylsilyl enol ether **1a** undergoes selective *n*-hydroformylation at the olefinic double bond followed by an intramolecular Mukaiyama type aldol addition. The *O*-silylated aldol adduct is obtained in up to 76% yield (Scheme 2). This one-pot reaction was carried out using various solvents (entries 1–4) and different silyl moieties, e.g. the *tert*-butyldimethylsilyl or the diphenylmethylsilyl group (entries 5, 6).



1a-c **2a-c**

Scheme 2.



A **B** **C**

Scheme 1.

Keywords: hydroformylation; rhodium catalysis; aldol reaction; ring synthesis.

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Table 1. Reactions of silyl enol ethers **1a**–**c** in the presence of CO/H_2 and Cat. Rh(I)

Entry	Solvent	R′	R″	Product	Yield (%)
1	*n*-hexane	Me	Me	**2a**	14
2	THF	Me	Me	**2a**	40
3	CH_3CN	Me	Me	**2a**	76
4	CH_2Cl_2	Me	Me	**2a**	68
5	CH_2Cl_2	Me	*t*-Bu	**2b**	27
6	CH_2Cl_2	Ph	Me	**2c**	29

Best conversions and selectivities were obtained using the trimethyl silyl group. In the case of the diphenyl methyl silyl enol ether (entry 6) protodesilylation side reaction of the starting material decreases the yield. According to observations of Reetz[6] good results were achieved using the weakly coordinating and polar solvent dichloromethane. In our case, however, the reaction takes place even in stronger coordinating solvents such as THF or acetonitrile with medium to good results (entries 2, 3). Remarkably, under the rather severe reaction conditions of the hydroformylation this procedure proceeds with complete transfer of the silyl fragment. Extensive investigations concerning the mechanism of the rhodium(I) catalysed Mukaiyama aldol reaction have been made by Heathcock and coworkers[7] who proposed rhodium enolate and aldolate intermediates with a final intermolecular transfer of the silyl fragment to generate the *O*-silylated aldols. In contrast to Heathcock's observations our method even allows the Mukaiyama aldol addition with enolizable aldehydes as formed via hydroformylation.

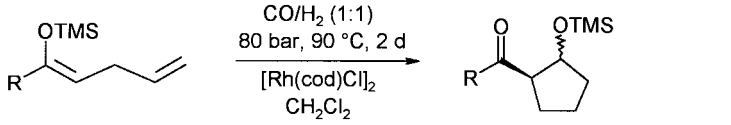
Using our protocol, the same intramolecular aldol addition proceeds with satisfying selectivities applying unsaturated silyl enol ethers of type **3** to generate five membered rings of type **4** (Scheme 3).

Similarly silylated spirocyclic aldol adducts of type **6** (Scheme 4) are obtainable if the reaction is carried out with the trimethyl silyl enol ethers **5a**,**b** of 2-allylcyclopentanone and -hexanone. The silyl enol ethers are obtained by deprotonation of the ketones under thermodynamic reaction control (Et_3N, DMF, 130°C).[9,10] Due to the steric demand of the alkyl silyl moiety hydroformylation here proceeds with rather high *n*-selectivity. Aldol addition then leads to the spirocyclic products (Scheme 5). However, the high reaction temperatures lead to low diastereoselectivities of the aldol addition step.

If starting with silyl enol ether **7b**, the regioisomer of **5b**, prepared under the conditions of kinetic reaction control (LDA, THF, −78°C),[10] unexpectedly again the spirocyclic aldol product **6b** was obtained. Here obviously a rhodium catalysed isomerisation of the silyl enol ether double bond to form the thermodynamically favored species is involved. Using the analogous five membered silyl enol ether **7a** this isomerisation does not occur under the reaction conditions, apparently due to geometric effects of the smaller ring size. Only the hydroformylated silyl enol ethers were detected in this case.

If starting with 3-vinyl substituted cyclic silyl enol ethers **8a**–**c** the tandem reaction offers an approach to hydropentalene and hydroindane derivatives (Scheme 6). The γ,δ-unsaturated silyl enol ethers **8a**–**c** are easily prepared by 1,4-addition of organomagnesium cuprates to conjugated enones in a one-pot procedure.[11] In the presence of trimethylsilyl chloride the generated metal enolates undergo an in situ trapping reaction to form **8a**–**c** in good yields.

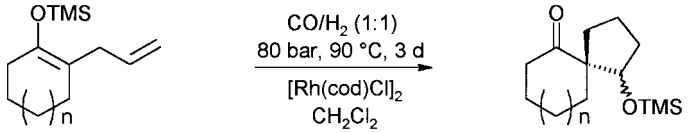
The hydroformylation of **8a**–**c** proceeds with high



3a: R = *t*Bu
3b: R = Me

4a: R = *t*Bu: 54 %, dr = 1.4:1 (rac)
4b: R = Me: 64 %, dr = 1:1 (rac)

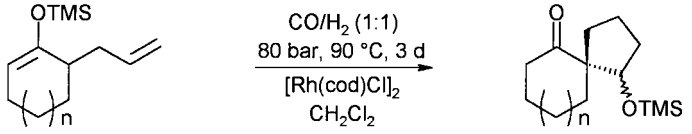
Scheme 3.



5a: n = 0
5b: n = 1

6a: n = 0: 56 %, dr = 1:1 (rac)
6b: n = 1: 47 %, dr = 2:1 (rac)

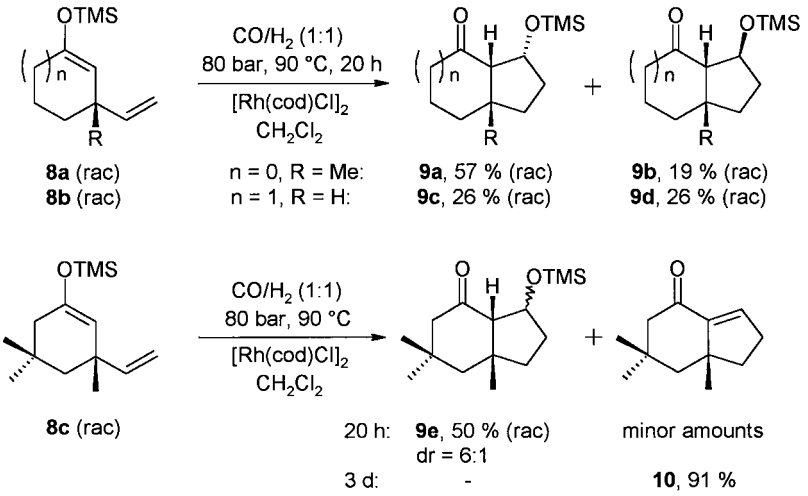
Scheme 4.



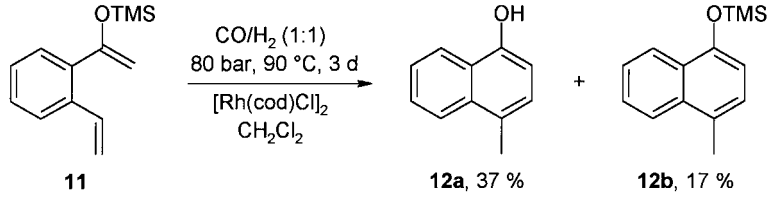
7a: n = 0
7b: n = 1

6a: n = 0:(hydroformylation only)
6b: n = 1: 40 %, dr = 2:1 (rac)

Scheme 5.



Scheme 6.



Scheme 7.

n-selectivity and the cyclisation then leads to the *O*-silylated aldol adducts. In the case of **8a** and **8c** the ring annulation step shows a 3:1 and 6:1 diastereoselectivity. The preference of the (3a*R**,6*R**,6a*S**)-diastereoisomer **9a** is in line with the result of a comparable aldol type cyclisation leading to the analogous unprotected 6-hydroxy-pentalone.[12] Remarkably, if running the reaction for 3 d the 3-vinyl substituted cyclic silyl enol ether **8c** gives the hydroindenone **10** which results from an additional desilylation and dehydration reaction (91% yield).

The overall procedure described here can be used for completely different substrates such as the unsaturated enol silane **11** to give the of naphthol derivatives **12a** and **12b**. In this case the intermediate product undergoes desilylation and dehydration followed by tautomerisation of the enone form to the more stable naphthol derivatives **12a** and **12b** (Scheme 7).

Conclusions

In conclusion, the hydroformylation of unsaturated silyl enol ethers leads to products of an intramolecular aldol reaction in a one-pot procedure. This sequential reaction proceeds in medium to good yields using a rhodium(I) complex without further additives. In contrast, according to preliminary results[13] the corresponding intermolecular reaction of silyl enol ethers and olefins under hydroformylation conditions up to now only provides minor yields of aldol products. As described above, a series of mono-, bi- and spirocyclic trimethylsilyl protected aldol adducts are obtained starting from easily available β,γ- or γ,δ-unsaturated silyl enol ethers. Generally, as reported previously,[5,6] rhodium complex catalysed Mukaiyama aldol additions show only low diastereoselectivities even at low temperatures. Despite the high reaction temperatures as used in our procedure the intramolecular aldol addition step in some cases proceeds with surprisingly high diastereoselectivities up to 6:1.

Experimental

General methods

^{1}H and ^{13}C NMR spectra were recorded on Bruker spectrometers DPX 300 and DRX 400 using $CDCl_3$ as solvent and CH_2Cl_2 as internal standard. IR spectra were performed on a Nicolet Impact 400 D, mass spectra on a Finnigan CA 5 and elementary analysis with a Leco CHNS-932. Analytical gas chromatography was carried out on a Fisons 8130 gas chromatograph with 30 m CP sil-5 capillaries. GC-MS spectra were obtained by using a comparable capillary and a Finnigan ITD 800 (MS). Column chromatography was performed on silica gel 60 from Merck, Darmstadt. Pressure reactions have been carried in autoclaves (250 ml, type A, PTFE-insert) from Berghof, Eningen, Germany and similar autoclaves (70 ml, stainless steel).

Starting materials

The unsaturated ketones, 3,3-dimethyl-4-penten-2-one,[14] 2,2-dimethyl-6-hepten-3-one,[15] 2-allylcyclopentanone,[16] 2-allylcyclohexanone,[17] 1-(2-vinyl-phenyl)-ethanone[18] were prepared according to literature procedures. The catalyst

precursor $[RhCl(cod)]_2$ was prepared as described by Crabtree.[19]

General procedures for silyl enol ether synthesis

A:[9,10] To a solution of 60 mmol trimethylsilyl chloride and 125 mmol triethyl amine in anhydrous DMF (20 ml) a solution of 50 mmol of the unsaturated ketone in DMF (10 ml) was added dropwise at room temperature. The resulting mixture was stirred at 130°C for 3–5 d under argon atmosphere. The reaction mixture was diluted with *n*-pentane (100 ml) and washed with saturated $NaHCO_3$ solution (3×100 ml). The aqueous phase was extracted with *n*-pentane (80 ml), and the combined organic fractions were washed rapidly with 1 M hydrochloric acid (100 ml), saturated $NaHCO_3$ solution (100 ml) and water (100 ml). The organic layer was dried with Na_2SO_4 and evaporated in vacuo. Flash chromatography on silica gel using *n*-hexane as eluent of fractional distillation gave the silyl enol ethers.

B:[10] To a solution of anhydrous diisopropylamine (4.4 ml, 31 mmol) in anhydrous THF (60 ml) under argon was added at −78°C a solution of *n*-butyl lithium (18 ml, 29 mmol) in hexane (c=1.6 mol/l). After stirring for 1 h at 0°C, the LDA solution was cooled to −78°C and a solution of the ketone (25 mmol) in THF (10 ml) was added dropwise. After 1 h the trialkylsilyl chloride (43 mmol) was added, the solution was warmed to room temperature and stirred for 1–2 h. The solvent was evaporated and the residue was treated with *n*-hexane (30 ml). Separated LiCl was removed by filtration, the solvent was removed and the residue was separated by flash chromatography on silica gel using *n*-hexane as eluent or by Kugelrohr distillation.

C:[11] Mg (2.1 g, 85 mmol) was suspended in anhydrous THF (20 ml) under argon inert gas atmosphere. A solution of the alkyl bromide (85 mmol) in THF (100 ml) was added dropwise over 90 min maintaining the temperature at below 40°C. The resulting solution was stirred for 1 h at room temperature and then cooled to −10°C. CuI (8.1 g, 43 mmol) was added in one portion and after 2 min the black mixture was cooled to −78°C. A solution of the cyclohexenone (42 mmol) in THF (30 ml) was added dropwise over 30 min. After sequential addition of DMPU (10.1 ml, 83 mmol), triethyl amine (17.4 ml, 125 mmol) and trimethylsilyl chloride (15.8 ml, 125 mmol) the reaction mixture was allowed to warm to room temperature. The mixture was diluted with pentane (200 ml) and washed with a 9:1 mixture of saturated NH_4Cl: conc. NH_3 solution until the aqueous layer was no longer blue (ca. 4–5 times). The organic layer was then washed with water and brine. After drying the solvents were removed by rotary evaporation and the crude product was distilled or flash chromatographed on silica gel using *n*-hexane as eluent.

(2,2-Dimethyl-1-methylene-but-3-enyloxy)-trimethyl-silane[20] (1a). Obtained from 3,3-dimethyl-4-penten-2-one[14] as a colourless liquid in 76% yield (method B).

***tert*-Butyl-(2,2-dimethyl-1-methylene-but-3-enyloxy)-dimethyl-silane (1b).** Obtained from 3,3-dimethyl-4-penten-2-one[14] as a colourless liquid in 91% yield (method B). ^{1}H NMR (400 MHz, $CDCl_3$, 20°C) δ=0.15 (s, 6 H), 0.92 (s, 9 H), 1.14 (s, 6 H), 3.93 (d, ^2J=1.4 Hz, 1 H), 4.06 (d, ^2J=1.4 Hz, 1 H), 4.94 (dd, ^3J=10.6 Hz, ^2J=1.3 Hz, 1 H), 4.99 (dd, ^3J=18.3 Hz, ^2J=1.3 Hz, 1 H), 5.92 (dd, ^3J=18.3 Hz, ^3J=10.6 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 20°C) δ=−4.8 (CH_3), −3.0 (CH_3), 25.3 (CH_3), 25.7 (CH_3), 25.7 (CH_3), 42.9 (Cq), 53.4 (Cq), 86.6 (CH_2), 111.0 (CH_2), 145.8 (CH), 164.9 (Cq). IR (NaCl, neat) $\tilde{\nu}$ = 3086 (m), 2961 (s), 2930 (s), 2887 (s), 2859 (s), 1659 (m), 1620 (s), 1472 (s), 1259 (s), 1017 (s), 812 (s) cm^{-1}. GC-MS (EI, 70 eV) *m*/*z* (%)=227 (M^++1, 44), 211 (50), 169 (100), 155 (28), 127 (18), 95 (90), 75 (57).

(2,2-Dimethyl-1-methylene-but-3-enyloxy)-methyl-diphenyl-silane (1c). Obtained from 3,3-dimethyl-4-penten-2-one[14] as a colourless oil in 49% yield (method B). ^{1}H NMR (400 MHz, $CDCl_3$, 20°C) δ=0.72 (s, 3 H), 1.23 (s, 6 H), 3.93 (s, 1 H), 4.12 (s, 1 H), 5.00 (d, ^3J=10.5 Hz, 1 H), 5.07 (d, ^3J=17.3 Hz, 1 H), 5.99 (dd, ^3J=17.3 Hz, ^3J=10.5 Hz, 1 H), 7.38 (m, 6 H), 7.62 (d, ^3J=7.5 Hz, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$, 20°C) δ=−3.2 (CH_3), 25.4 (CH_3), 42.9 (Cq), 88.8 (CH_2), 111.4 (CH_2), 127.8 (CH), 129.8 (CH), 134.2 (CH), 136.0 (Cq), 145.6 (CH), 164.2 (Cq). IR (NaCl, neat) $\tilde{\nu}$ = 3070 (m), 3050 (w), 3001 (w), 2969 (s), 2930 (w), 1625 (s), 1429 (s), 1278 (s), 1120 (s), 1015 (s), 798 (s) cm^{-1}. MS (EI, 70 eV) *m*/*z* (%)=308 (M^+, 24), 293 (46), 217 (63), 197 (100), 137 (28), 119 (9). $C_{20}H_{24}OSi$ (308.50): Calcd C, 77.87; H, 7.84; Found C, 77.8; H, 7.9.

(1*Z*-1-*tert*-Butyl-penta-1,4-dienyloxy)-trimethyl-silane (3a). Obtained from 2,2-dimethyl-6-hepten-3-one[15] as a colourless liquid in 70% yield (method B). ^{1}H NMR (400 MHz, $CDCl_3$, 20°C) δ=0.22 (s, 9 H), 1.04 (s, 9 H), 2.72 (t, ^3J=6.5 Hz, 2 H), 4.54 (t, ^3J=6.5 Hz, 1 H), 4.94 (dd, ^3J=10.1 Hz, ^2J=1.6 Hz, 1 H), 5.02 (dd, ^3J=15.2 Hz, ^2J=1.6 Hz, 1 H), 5.80 (ddt, ^3J=15.2 Hz, ^3J=10.1 Hz, ^3J=6.5 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 20°C) δ=1.1 (CH_3), 28.6 (CH_3), 30.4 (CH_2), 36.3 (Cq), 101.4 (CH), 114.2 (CH_2), 137.8 (CH), 158.9 (Cq). IR (NaCl, neat) $\tilde{\nu}$ = 3079 (w), 2958 (s), 2906 (m), 2871 (m), 1658 (s), 1639 (w), 1481 (w), 1331 (s), 1253 (s), 1144 (s), 844 (vs) cm^{-1}. GC-MS (EI, 70 eV) *m*/*z* (%)=213 (M^++1, 10), 197 (29), 155 (68), 143 (20), 123 (13), 81 (50), 73 (100), 57 (38).

Trimethyl-(1-methyl-penta-1,4-dienyloxy)-silane[15,21] (3b). Obtained from 5-hexen-2-one as a colourless liquid in 71% yield as a 70:30 mixture of the 1-*E*/*Z*-stereoisomers (method A).

(2-Allyl-cyclopent-1-enyloxy)-trimethyl-silane (5a). Obtained from 2-allylcyclopentanone[16] as a colourless liquid in 61% yield (method A). ^{1}H NMR (400 MHz, $CDCl_3$, 20°C) δ=0.16 (s, 9 H), 1.78 (m, 2 H), 2.17 (m, 2 H), 2.28 (m, 2 H), 2.73 (dm, ^3J=6.8 Hz, 2 H), 4.93 (ddt, ^3J=10.0 Hz, J=2.2 Hz, J=1.3 Hz, 1 H), 4.98 (dm, ^3J=17.0 Hz, 1 H), 5.72 (ddt, ^3J=17.0 Hz, ^3J=10.0 Hz, ^3J=6.8 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 20°C) δ=0.5 (CH_3), 19.7 (CH_2), 30.9 (CH_2), 31.1 (CH_2), 33.7 (CH_2), 114.7 (CH_2), 114.9 (Cq), 136.5 (CH), 146.9 (Cq). IR (NaCl, neat) $\tilde{\nu}$ = 3078 (m), 2959 (s), 2900 (s), 2848 (s), 1683 (s), 1640 (m), 1343 (s), 1255 (s), 842 (s) cm^{-1}. GC-MS (EI, 70 eV)

m/*z* (%)=197 (M^++1, 90), 183 (52), 169 (100), 89 (23), 73 (82).

(2-Allyl-cyclohex-1-enyloxy)-trimethyl-silane[22] **(5b).** Obtained from 2-allylcyclohexanone[17] as a colourless liquid in 70% yield (method A).

(5-Allyl-cyclopent-1-enyloxy)-trimethyl-silane (7a). Obtained from 2-allylcyclopentanone[16] as a colourless liquid in 77% yield (method B). ^{1}H NMR (400 MHz, $CDCl_3$, 20°C) δ=0.19 (s, 9 H), 1.51 (m, 1 H), 1.95 (m, 2 H), 2.34 (m, 1 H), 2.50 (m, 1 H), 4.57 (dd, ^3J=4.3 Hz, ^3J=4.0 Hz, 2 H), 4.96 (dm, ^3J=10.3 Hz, 1 H), 5.01 (dm, ^3J=17.3 Hz, 1 H), 5.78 (ddt, ^3J=17.3 Hz, ^3J=10.3 Hz, ^3J=7.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 20°C) δ=−0.1 (CH_3), 26.9 (CH_2), 27.1 (CH_2), 37.4 (CH_2), 44.3 (CH), 101.3 (CH), 115.4 (CH_2), 137.3 (CH), 156.9 (Cq). IR (NaCl, neat) $\tilde{\nu}$ = 3075 (m), 2958 (s), 2908 (s), 2854 (s), 1643 (s), 1440 (m), 1350 (s), 1253 (s), 845 (s) cm^{-1}. GC-MS (EI, 70 eV) *m*/*z* (%)=196 (M^+, 40), 195 (94), 181 (34), 167 (20), 155 (100), 105 (18), 74 (6).

(6-Allyl-cyclohex-1-enyloxy)-trimethyl-silane (7b). Obtained from 2-allylcyclohexanone[17] as a colourless liquid in 64% yield (method B). ^{1}H NMR (400 MHz, $CDCl_3$, 20°C) δ=0.16 (s, 9 H), 1.38–1.71 (m, 4 H), 1.99 (m, 4 H), 2.43 (m, 1 H), 4.81 (td, ^3J=3.9 Hz, ^4J=1.0 Hz, 2 H), 4.98 (m, 2 H), 5.75 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 20°C) δ=0.3 (CH_3), 20.1 (CH_2), 24.1 (CH_2), 27.7 (CH_2), 36.8 (CH_2), 38.5 (CH), 104.1 (CH), 115.6 (CH_2), 137.7 (CH), 152.6 (Cq). IR (NaCl, neat) $\tilde{\nu}$ = 3076 (m), 3049 (w), 2933 (s), 2859 (s), 1662 (s), 1640 (m), 1446 (m), 1368 (m), 1255 (s), 1179 (s), 841 (s) cm^{-1}. GC-MS (EI, 70 eV) *m*/*z* (%)=210 (M^+, 54), 195 (29), 181 (10), 169 (100), 119 (23), 93 (9), 73 (43).

Trimethyl-(3-methyl-3-vinyl-cyclopent-1-enyloxy)-silane[23] **(8a).** Obtained from 3-methyl-2-cyclopenten-1-one as a colourless liquid in 24% yield (method C).

Trimethyl-(3-vinyl-cyclohex-1-enyloxy)-silane[11] **(8b).** Obtained from 2-cyclohexen-1-one as a colourless liquid in 78% yield (method C).

Trimethyl-(3,5,5-trimethyl-3-vinyl-cyclohex-1-enyloxy)-silane[24] **(8c).** Obtained from isophorone as a colourless liquid in 93% yield (method C).

Trimethyl-[1-(2-vinyl-phenyl)-vinyloxy]-silane (11). Obtained from 1-(2-vinyl-phenyl)-ethanone[18] as a colourless liquid in 70% yield (method B). ^{1}H NMR (400 MHz, $CDCl_3$, 20°C) δ=0.21 (s, 9 H), 4.47 (d, ^2J=0.8 Hz, 1 H), 4.67 (d, ^2J=0.8 Hz, 1 H), 5.26 (dd, ^3J=11.0 Hz, ^2J=0.8 Hz, 1 H), 5.68 (dd, ^3J=17.5 Hz, ^2J=0.8 Hz, 1 H), 7.14 (dd, ^3J=17.5 Hz, ^3J=11.0 Hz, 1 H), 7.25 (t, ^3J=7.5 Hz, 1 H), 7.31 (t, ^3J=7.5 Hz, 1 H), 7.41 (d, ^3J=7.5 Hz, 1 H), 7.56 (d, ^3J=7.5 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 20°C) δ=0.1 (CH_3), 96.7 (CH_2), 114.2 (CH_2), 125.7 (CH), 127.3 (CH), 128.2 (CH), 128.7 (CH), 135.9 (Cq), 136.2 (CH), 137.9 (Cq), 156.1 (Cq). IR (NaCl, neat) $\tilde{\nu}$ = 3114 (w), 3087 (w), 3064 (w), 2961 (m), 2901 (w), 1624 (m), 1479 (w), 1303 (s), 1254 (s), 1015 (s), 848 (s) cm^{-1}.

General procedure: Hydroformylation/aldol reaction of unsaturated silyl enol ethers

The reactions were carried out in an autoclave. A solution of the unsaturated silyl enol ether (10.0 mmol) and $[RhCl(cod)]_2$ (1 mol%) in anhydrous dichloromethane (10 ml) were placed in an autoclave. After flushing with argon the reactor was pressurized with 40 bar carbon monoxide and 40 bar hydrogen, magnetically stirred and heated to 90 or 100°C for 1–3 d. Then the autoclave was allowed to cool to room temperature. After expanding the syngas, the remaining solution was filtered through alumina using diethyl ether as eluent. The solvent was removed by rotary evaporation and the residue was analysed by gas chromatography. The products were then separated by column chromatography using mixtures of petrol ether (30/60) and methyl *t*-butyl ether as eluent.

2,2-Dimethyl-5-trimethylsilanyloxy-cyclohexanone (2a). Obtained from (2,2-dimethyl-1-methylene-but-3-enyloxy)-trimethyl-silane[20] (**1a**) as a colourless liquid in up to 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 20°C) δ=0.06 (s, 9 H), 1.03 (s, 3 H), 1.08 (s, 3 H), 1.40 (m, 1 H), 1.75 (m, 2 H), 1.85 (m, 1 H), 2.45 (dd, ^2J=14.0 Hz, ^3J=8.0 Hz, 1 H), 2.52 (ddd, ^2J=14.0 Hz, ^3J=4.7 Hz, J=1.4 Hz, 1 H), 3.95 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 20°C) δ=0.0 (CH_3), 24.7 (CH_3), 24.9 (CH_3), 30.5 (CH_2), 34.9 (CH_2), 44.2 (Cq), 47.6 (CH_2), 70.6 (CH), 213.7 (Cq). IR (NaCl, neat) $\tilde{\nu}$ = 2963 (vs), 2874 (m), 1714 (vs), 1456 (m), 1252 (s), 1101 (s), 1055 (m), 1010 (m), 841 (vs) cm^{-1}. GC-MS (EI, 70 eV) *m*/*z* (%)=287 (M^++$Si(CH_3)_3$, 95), 197 (100), 169 (16), 141 (58), 125 (50), 107 (81), 95 (62), 73 (64). $C_{11}H_{22}O_2Si$ (214.38): Calcd C, 61.63; H, 10.34; Found C, 61.5; H, 10.2.

5-(*tert*-Butyl-dimethyl-silanyloxy)-2,2-dimethyl-cyclohexanone (2b). Obtained from *tert*-butyl-(2,2- dimethyl-1-methylene-but-3-enyloxy)-dimethyl-silane (**1b**) as a colourless liquid in 27% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 20°C) δ=0.02 (s, 6 H), 0.84 (s, 9 H), 1.07 (s, 3 H), 1.09 (s, 3 H), 1.44 (m, 1 H), 1.75 (m, 1 H), 1.86 (m, 1 H), 1.89 (m, 1 H), 2.43 (ddd, ^2J=14.1 Hz, ^3J=6.7 Hz, J=0.7 Hz, 1 H), 2.56 (ddd, ^2J=14.1 Hz, ^3J=3.2 Hz, J=1.0 Hz, 1 H), 4.05 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 20°C) δ=−4.9 (CH_3), −4.9 (CH_3), 18.0 (Cq), 24.8 (CH_3), 25.0 (CH_3), 25.7 (CH_3), 30.3 (CH_2), 34.9 (CH_2), 44.3 (Cq), 47.4 (CH_2), 70.7 (CH), 213.9 (Cq). IR (NaCl, neat) $\tilde{\nu}$ = 2957 (s), 2930 (s), 2857 (s), 1713 (vs), 1472 (m), 1254 (m), 1101 (s), 1059 (m), 836 (s) cm^{-1}. GC-MS (EI, 70 eV) *m*/*z* (%)=257 (M^++1, 10), 239 (100), 199 (81), 157 (10), 143 (60), 125 (38), 107 (42), 89 (58).

2,2-Dimethyl-5-(methyl-diphenyl-silanyloxy)-cyclohexanone (2c). Obtained from (2,2-dimethyl-1-methylene-but-3-enyloxy)-methyl-diphenyl-silane (**1c**) as a colourless oil in 29% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 20°C) δ=0.69 (s, 9 H), 1.09 (s, 3 H), 1.16 (s, 3 H), 1.45 (m, 1 H), 1.90 (m, 3 H), 2.61 (m, 2 H), 4.19 (m, 1 H), 7.41 (m, 6 H), 7.61 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$, 20°C) δ=−2.5 (CH_3), 24.7 (CH_3), 24.9 (CH_3), 30.0 (CH_2), 34.7 (CH_2), 44.2 (Cq), 47.1 (CH_2), 71.2 (CH), 127.8 (CH), 129.8 (CH), 134.1 (CH), 135.9 (Cq), 213.4 (Cq). IR (NaCl, neat) $\tilde{\nu}$ = 3069 (m), 3049 (w), 2965 (s), 2867 (m), 1712 (vs), 1429 (s), 1255 (m), 1119 (s), 791 (s) cm^{-1}. MS (EI, 70 eV) *m*/*z*

(%)=339 (M^+, 2), 323 (16), 267 (28), 261 (100), 199 (44), 183 (22), 137 (23), 107 (10). $C_{21}H_{26}O_2Si$ (338.52): Calcd C, 74.51; H, 7.74; Found C, 74.5; H, 7.8.

2,2-Dimethyl-1-(2-trimethylsilanyloxy-cyclopentyl)-propan-1-one (4a). Obtained from (1*Z*-1-*tert*-butyl-penta-1,4-dienyloxy)-trimethyl-silane (**3a**) as a colourless liquid in 54% yield as a 1.4:1 mixture of diastereoisomers. ^{1}H NMR (400 MHz, $CDCl_3$, 20°C) δ=0.00 and 0.02 (s, 9 H), 1.08 and 1.09 (s, 9 H), 1.31–2.10 (6 H), 3.22 (dt, ^3J=8.8 Hz, ^3J=6.6 Hz) and 3.35 (q*, ^3J=7.5 Hz) [1H], 4.32 (q*, ^3J=6.7 Hz) and 4.42 (m) [1H]. ^{13}C NMR (100 MHz, $CDCl_3$, 20°C) δ=−0.1 0.2 (CH_3), 22.4 23.0 (CH_2), 25.7 26.1 (CH_3), 27.2 27.5 (CH_2), 35.3 35.6 (CH_2), 44.2 44.3 (Cq), 49.8 54.1 (CH), 76.2 77.8 (CH), 215.4 218.7 (Cq). IR (NaCl, neat) $\tilde{\nu}$ = 2961 (s), 2906 (m), 2872 (m), 1703 (s), 1366 (m), 1252 (s), 1112 (s), 843 (vs) cm^{-1}. **Diastereoisomer a:** GC-MS (EI, 70 eV) *m*/*z* (%)=243 (M^++1, 100), 227 (90), 191 (42), 135 (76), 73 (50), 57 (98). **Diastereoisomer b:** GC-MS (EI, 70 eV) *m*/*z* (%)=243 (M^++1, 94), 227 (86), 191 (20), 135 (60), 73 (78), 57 (100).

1-(2-Trimethylsilanyloxy-cyclopentyl)-ethanone (4b). Obtained from trimethyl-(1-methyl-penta-1,4-dienyloxy)-silane[15,21] (**3c**) as a colourless liquid in 64% yield as a 1:1 mixture of diastereoisomers. IR (NaCl, neat) $\tilde{\nu}$ = 2961 (s), 2875 (m), 1715 (s), 1358 (m), 1253 (s), 1107 (s), 1059 (s), 841 (vs) cm^{-1}. The diastereoisomers were separated by column chromatography on silica gel using a 20:1 mixture of petrol ether (30/60) and diethyl ether as eluent. The assignment of the diastereoisomers is based on literature data[25] of similar compounds. **(1*R**, 2*R**)-Diastereoisomer:** ^{1}H NMR (400 MHz, $CDCl_3$, 20°C) δ=0.06 (s, 9 H), 1.51–1.93 (6 H), 2.14 (s, 3 H), 2.84 (m, 1 H), 4.26 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 20°C) δ=−0.2 (CH_3), 22.4 (CH_2), 26.6 (CH_2), 30.0 (CH_3), 35.5 (CH_2), 60.4 (CH), 75.8 (CH), 210.0 (Cq). GC-MS (EI, 70 eV) *m*/*z* (%)=201 (M^++1, 30), 185 (100), 129 (18), 110 (28), 95 (16), 75 (13). **(1*R**, 2*S**)-Diastereoisomer:** ^{1}H NMR (400 MHz, $CDCl_3$, 20°C) δ=0.10 (s, 9 H), 1.47–1.88 (5 H), 2.12 (s, 3 H), 2.15 (m, 1 H), 2.78 (dt, ^3J=8.5 Hz, ^3J=5.8 Hz, 1 H), 4.54 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 20°C) δ=0.0 (CH_3), 22.1 (CH_2), 24.0 (CH_2), 30.0 (CH_3), 35.5 (CH_2), 58.5 (CH), 75.4 (CH), 208.5 (Cq). GC-MS (EI, 70 eV) *m*/*z* (%)=201 (M^++1, 34), 185 (100), 143 (6), 129 (8), 112 (8), 93 (7), 75 (13).

6-Trimethylsilanyloxy-spiro[4.4]nonan-1-one (6a). Obtained from (2-allyl-cyclopent-1-enyloxy)-trimethyl-silane (**5a**) as a colourless liquid in 56% yield as a 1:1 mixture of diastereoisomers. The diastereoisomers were separated by column chromatography on silica gel using a 20:1 mixture of petrol ether (30/60) and methyl *t*-butyl ether as eluent. The assignment of the diastereoisomers is based on literature data[26,27] of similar compounds. **(5*R**, 6*S**)-Diastereoisomer:** ^{1}H NMR (400 MHz, $CDCl_3$, 20°C) δ=0.02 (s, 9 H), 1.49 (m, 2 H), 1.65 (m, 4 H), 1.78 (m, 1 H), 1.90 (m, 2 H), 2.10 (m, 1 H), 2.25 (m, 2 H), 4.15 (t*, ^3J=7.3 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 20°C) δ=−0.1 (CH_3), 19.7 (CH_2), 20.6 (CH_2), 30.6 (CH_2), 33.9 (CH_2), 34.5 (CH_2), 38.7 (CH_2), 59.9 (Cq), 77.4 (CH), 224.0 (Cq). IR (NaCl, neat) $\tilde{\nu}$ = 2960 (s), 2900 (m), 2878 (m), 1733 (s), 1408 (w), 1252 (s), 1115 (s), 843 (s) cm^{-1}. GC-MS (EI, 70 eV) *m*/*z* (%)=211 (M^++1, 100), 191 (10), 169 (20), 137 (50), 119 (38), 91 (15), 73 (23). **(5*R**, 6*R**)-Diastereoisomer:** ^{1}H NMR (400 MHz, $CDCl_3$, 20°C) δ=0.07 (s, 9 H), 1.35 (m, 1 H), 1.53 (m, 1 H), 1.83 (m, 5 H), 2.03 (m, 4 H), 2.23 (m, 1 H), 3.93 (dd, ^3J=7.6 Hz, ^3J=6.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 20°C) δ=0.0 (CH_3), 19.3 (CH_2), 21.1 (CH_2), 32.3 (CH_2), 34.3 (CH_2), 37.0 (CH_2), 38.5 (CH_2), 58.6 (Cq), 82.6 (CH), 221.2 (Cq). IR (NaCl, neat) $\tilde{\nu}$ = 2958 (s), 2865 (m), 1739 (s), 1448 (w), 1252 (s), 1111 (s), 842 (s) cm^{-1}. GC-MS (EI, 70 eV) *m*/*z* (%)=211 (M^++1, 100), 169 (10), 143 (20), 119 (45), 91 (20), 73 (25).

1-Trimethylsilanyloxy-spiro[4.5]decan-6-one (6b). Obtained from (6-allyl-cyclohex-1-enyloxy)-trimethyl-silane (**7b**) as a colourless liquid in 40% yield as a 2:1 mixture of diastereoisomers. $C_{13}H_{24}O_2Si$ (240.42): Calcd C, 64.95; H, 10.06; Found C, 64.7; H, 9.9. The diastereoisomers were separated by column chromatography on silica gel using a 40:1 mixture of petrol ether (30/60) and diethyl ether as eluent. **Diastereoisomer a:** ^{1}H NMR (400 MHz, $CDCl_3$, 20°C) δ=0.00 (s, 9 H), 0.76 (m, 1 H), 1.41 (m, 1 H), 1.36–1.85 (m, 10 H), 2.25 (m, 2 H), 4.37 (t*, ^3J=5.5 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 20°C) δ=0.2 (CH_3), 20.7 (CH_2), 22.2 (CH_2), 26.9 (CH_2), 32.6 (CH_2), 33.8 (CH_2), 33.9 (CH_2), 39.8 (CH_2), 60.3 (Cq), 75.2 (CH), 214.5 (Cq). IR (NaCl, neat) $\tilde{\nu}$ = 2961 (s), 2936 (s), 2862 (m), 1712 (s), 1449 (m), 1261 (s), 1095 (s), 844 (s) cm^{-1}. GC-MS (EI, 70 eV) *m*/*z* (%)=241 (M^++1, 70), 225 (80), 191 (35), 151 (55), 130 (66), 91 (42), 73 (100). **Diastereoisomer b:** ^{1}H NMR (400 MHz, $CDCl_3$, 20°C) δ=−0.05 (s, 9 H), 0.90 (m, 1 H), 1.30–1.76 (m, 9 H), 1.90 (m, 1 H), 2.21 (m, 1 H), 2.35 (m, 2 H), 4.16 (t*, ^3J=4.8 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 20°C) δ=0.0 (CH_3), 20.7 (CH_2), 22.3 (CH_2), 27.1 (CH_2), 32.1 (CH_2), 34.4 (CH_2), 38.5 (CH_2), 41.6 (CH_2), 60.9 (Cq), 79.3 (CH), 211.6 (Cq). IR (NaCl, neat) $\tilde{\nu}$ = 2956 (s), 2940 (s), 2864 (m), 1714 (s), 1448 (m), 1251 (s), 1116 (s), 1061 (s), 842 (s) cm^{-1}. GC-MS (EI, 70 eV) *m*/*z* (%)=241 (M^++1, 100), 225 (50), 191 (12), 151 (14), 130 (48), 91 (26), 73 (58).

3a-Methyl-6-trimethylsilanyloxy-hexahydro-pentalen-1-one (9a,b). Obtained from trimethyl-(3-methyl-3-vinyl-cyclopent-1-enyloxy)-silane[23] (**8a**) as a colourless liquid in 76% yield as a 3:1 mixture of the 3a*R**,6*R**,6a*S**- and 3a*R**,6*S**,6a*S**-diastereoisomers. $C_{12}H_{22}O_2Si$ (226.39): Calcd. C, 63.67; H, 9.79; Found C, 63.6; H, 9.7. The diastereoisomers were separated by column chromatography on silica gel using a 20:1 mixture of *n*-hexane and methyl *t*-butyl ether as eluent. The assignment of the diastereoisomers is based on NOESY experiments and literature data[12] of the desilylated 6-hydroxy-pentalones. **(3a*R**,6*R**, 6a*S**)-Diastereoisomer (9a):** ^{1}H NMR (400 MHz, $CDCl_3$, 20°C) δ=0.02 (s, 9 H), 1.11 (s, 3 H), 1.59 (ddd, ^2J=11.6 Hz, ^3J=7.6 Hz, ^3J=3.8 Hz, 1 H), 1.73 (m, 1 H), 1.80 (m, 1 H), 1.96 (m, 2 H), 2.15 (m, 1 H), 2.21 (ddd, ^2J=17.4 Hz, ^3J=8.5 Hz, ^3J=6.3 Hz, 1 H), 2.33 (ddd, ^2J=17.4 Hz, ^3J=9.5 Hz, ^3J=7.5 Hz, 1 H), 4.44 (ddd, ^3J=6.8 Hz, ^3J=4.4 Hz, ^3J=2.5 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 20°C) δ=−0.2 (CH_3), 28.2 (CH_3), 35.4 (CH_2), 37.0 (CH_2), 38.9 (CH_2), 40.4 (CH_2), 47.5 (Cq), 65.7 (CH), 76.1 (CH), 218.7 (Cq). IR (NaCl, neat) $\tilde{\nu}$ = 2954 (*s*), 2868 (s), 1744 (s), 1455 (m), 1377 (m), 1251 (s), 1147 (s),

1048 (s), 842 (s) cm^{-1}. MS (EI, 70 eV) *m/z* (%)=226 (M^+, 60), 211 (100), 198 (3), 183 (3), 167 (6), 155 (9), 129 (13), 119 (20), 93 (21), 75 (41). **(3a*R**,6*S**,6a*S**)-Diastereoisomer (9b):** ^{1}H NMR (400 MHz, $CDCl_3$, 20°C) δ=0.08 (s, 9 H), 1.11 (s, 3 H), 1.35–1.54 (m, 4 H), 1.72 (m, 1 H), 1.84 (m, 1 H), 1.90 (d*, ^2J=18.4 Hz, 1 H), 2.04 (dd, ^2J=18.4, ^3J=3.5 Hz, 1 H), 2.37 (dm, J=9.4 Hz, 1 H), 3.77 (ddd, J=9.4 Hz, ^3J=5.9 Hz, ^3J=3.3 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 20°C) δ=0.1 (CH_3), 26.6 (CH_3), 30.6 (CH_2), 36.7 (CH_2), 36.9 (Cq), 41.9 (CH_2), 50.0 (CH_2), 55.8 (CH), 72.4 (CH), 217.4 (Cq). IR (NaCl, neat) $\tilde{\nu}$ = 2951 (s), 2903 (s), 2870 (s), 1747 (s), 1459 (m), 1368 (m), 1251 (s), 1165 (m), 1093 (s), 841 (s) cm^{-1}. MS (EI, 70 eV) *m/z* (%)=226 (M^+, 4), 211 (100), 193 (2), 183 (4), 170 (7), 155 (9), 129 (44), 119 (19), 94 (30), 75 (40).

3-Trimethylsilanyloxy-octahydro-inden-4-one (9c,d). Obtained from trimethyl-(3-vinyl-cyclohex-1-enyloxy)-silane[11] (**8b**) as a colourless liquid in 51% yield as a 1:1 mixture of diastereoisomers. $C_{12}H_{22}O_2Si$ (226.39): Calcd C, 63.67; H, 9.79; Found C, 63.9; H, 9.7. The diastereoisomers were separated by column chromatography on silica gel using a 8:1 mixture of petrol ether (30/60) and diethyl ether as eluent. **Diastereoisomer a:** ^{1}H NMR (400 MHz, $CDCl_3$, 20°C) δ=0.04 (s, 9 H), 1.22 (m, 1 H), 1.46 (m, 2 H), 1.78 (m, 4 H), 1.96 (m, 1 H), 2.25 (t*, ^3J=6.8 Hz, 2 H), 2.49 (dd, ^3J=8.5 Hz, ^3J=3.7 Hz, 1 H), 2.67 (m, 1 H), 4.61 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 20°C) δ=−0.1 (CH_3), 23.3 (CH_2), 27.3 (CH_2), 28.4 (CH_2), 34.1 (CH_2), 40.6 (CH_2), 40.7 (CH), 61.5 (CH), 73.7 (CH), 212.2 (Cq). IR (NaCl, neat) $\tilde{\nu}$ = 2956 (vs), 2872 (s), 1712 (s), 1463 (m), 1251 (s), 1059 (s), 1029 (s), 841 (s) cm^{-1}. GC-MS (EI, 70 eV) *m/z* (%)=227 (M^++1, 60), 211 (70), 136 (39), 119 (100), 108 (20), 91 (41), 80 (32). **Diastereoisomer b:** ^{1}H NMR (400 MHz, $CDCl_3$, 20°C) δ=−0.04 (s, 9 H), 1.51 (m, 2 H), 1.65 (m, 4 H), 1.85 (m, 2 H), 2.11 (m, 1 H), 2.25 (m, 2 H), 2.41 (dd, ^3J=8.8 Hz, ^3J=5.5 Hz, 1 H), 4.38 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 20°C) δ=−0.3 (CH_3), 23.4 (CH_2), 30.4 (CH_2), 31.0 (CH_2), 35.0 (CH_2), 39.3 (CH), 42.1 (CH_2), 58.2 (CH), 77.1 (CH), 213.6 (Cq). IR (NaCl, neat) $\tilde{\nu}$ = 2955 (s), 2939 (s), 2866 (m), 1705 (vs), 1449 (w), 1251 (s), 1073 (s), 1044 (s), 842 (vs) cm^{-1}. GC-MS (EI, 70 eV) *m/z* (%)=227 (M^++1, 60), 211 (80), 129 (38), 119 (100), 107 (8), 91 (62), 75 (26).

6,6,7a-Trimethyl-3-trimethylsilanyloxy-octahydro-inden-4-one (9e). Obtained from trimethyl-(3,5,5-trimethyl-3-vinyl-cyclohex-1-enyloxy)-silane[24] (**8c**) as a colourless liquid in 50% yield as a 6:1 mixture of diastereoisomers. $C_{15}H_{28}O_2Si$ (268.47): Calcd. C, 67.11; H, 10.51; Found C, 67.5; H, 10.4. The diastereoisomers were separated by column chromatography on silica gel using a 15:1 mixture of *n*-hexane and methyl *t*-butyl ether as eluent. **(minor) Diastereoisomer a:** ^{1}H NMR (400 MHz, $CDCl_3$, 20°C) δ=0.03 (s, 9 H), 0.93 (s, 3 H), 0.97 (s, 3 H), 1.21 (s, 3 H), 1.44 (d, ^2J=14.9 Hz, 1 H), 1.52 (d, ^2J=14.9 Hz, 1 H), 1.58 (m, 3 H), 1.95 (m, 1 H), 2.08 (d, ^2J=13.3 Hz, 1 H), 2.16 (d, ^2J=13.3 Hz, 1 H), 2.21 (d, ^3J=5.0 Hz, 1 H), 4.50 (dt, ^3J=5.0 Hz, ^3J=5.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 20°C) δ=0.0 (CH_3), 29.8 (CH_3), 31.2 (CH_3), 31.7 (CH_3), 34.2 (CH_2), 36.0 (Cq), 40.8 (CH_2), 45.5 (Cq), 49.1 (CH_2), 51.9 (CH_2), 67.9 (CH), 76.4 (CH), 212.6 (Cq). **(major) Diastereoisomer b:** ^{1}H NMR (400 MHz, $CDCl_3$, 20°C) δ=0.01 (s, 9 H), 0.90 (s, 3 H), 0.97 (s, 3 H), 1.11 (s, 3 H), 1.53 (m, 1 H), 1.59 (dm, ^2J=13.3 Hz, 1 H), 1.68 (m, 2 H), 1.72 (d, ^2J=13.3 Hz, 1 H), 1.87 (m, 1 H), 2.06 (dm, ^2J=13.1 Hz, 1 H), 2.19 (d, ^2J=13.1 Hz, 1 H), 2.20 (m, 1 H), 4.44 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 20°C) δ=−0.2 (CH_3), 28.0 (CH_3), 32.1 (CH_3), 33.2 (CH_3), 34.6 (CH_2), 35.2 (Cq), 43.1 (Cq), 43.8 (CH_2), 51.5 (CH_2), 55.5 (CH_2), 63.9 (CH), 77.9 (CH), 214.3 (Cq). IR (NaCl, neat) $\tilde{\nu}$ = 2956 (s), 2871 (s), 1706 (s), 1458 (m), 1369 (m), 1251 (s), 1055 (s), 843 (s) cm^{-1}. MS (EI, 70 eV) *m/z* (%)=268 (M^+, 56), 253 (100), 237 (3), 211 (11), 197 (17), 178 (87), 163 (89), 129 (35), 123 (45), 105 (17), 73 (67).

6,6,7a-Trimethyl-1,2,5,6,7,7a-hexahydro-inden-4-one (10). Obtained from trimethyl-(3,5,5-trimethyl-3-vinyl-cyclohex-1-enyloxy)-silane[24] (**8c**) as a colourless liquid in 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 20°C) δ=0.93 (s, 3 H), 1.04 (s, 3 H), 1.12 (s, 3 H), 1.64 (d, ^2J=14.0 Hz, 1 H), 1.70 (d,^2J=14.0 Hz, 1 H), 1.86 (m, 1 H), 2.03 (dd, J=12.1 Hz, J=6.5 Hz, 1 H), 2.14 (d, ^2J=16.3 Hz, 1 H), 2.30 (d, ^2J=16.3 Hz, 1 H), 2.42 (m, 2 H), 6.61 (t, ^3J=3.1 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 20°C) δ=28.5 (CH_3), 29.3 (CH_3), 30.1 (CH_2), 31.7 (CH_3), 32.8 (Cq), 45.0 (CH_2), 45.1 (Cq), 51.1 (CH_2), 52.6 (CH_2), 137.5 (CH), 148.3 (Cq), 199.3 (Cq). IR (NaCl, neat) $\tilde{\nu}$ = 3055 (w), 2953 (s), 2866 (s), 2843 (s), 1689 (vs), 1617 (s), 1452 (s), 1367 (m), 1266 (s), 1106 (m) cm^{-1}. MS (EI, 70 eV) *m/z* (%)=179 (M^++1, 100), 164 (70), 122 (28), 107 (59), 94 (77), 79 (65), 55 (19). $C_{12}H_{18}O$ (178.27): Calcd C, 80.85; H, 10.18; Found C, 80.6; H, 10.3.

4-Methyl-naphthalene-1-ol[28] (12a). Obtained from trimethyl-[1-(2-vinyl-phenyl)-vinyloxy]-silane (**11**) as colourless crystals in 37% yield.

Trimethyl-(4-methyl-naphthalen-1-yloxy)-silane (12b). Obtained from trimethyl-[1-(2-vinyl-phenyl)-vinyloxy]-silane (**11**) as a colourless oil in 17% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 20°C) δ=0.39 (s, 9 H), 2.65 (s, 3 H), 6.82 (d, ^3J=7.7 Hz, 1 H), 7.19 (d,^3J=7.7 Hz, 1 H), 7.54 (m, 2 H), 7.96 (dd, ^3J=7.6 Hz, ^4J=1.8 Hz, 1 H), 8.22 (dd, ^3J=7.6 Hz, ^4J=1.8 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 20°C) δ=0.3 (CH_3), 18.8 (CH_3), 112.4 (CH), 123.0 (CH), 124.1 (CH), 124.8 (CH), 125.9 (CH), 126.3 (CH), 127.0 (Cq), 128.0 (Cq), 133.7 (Cq), 149.8 (Cq). IR (NaCl, neat) $\tilde{\nu}$ = 3071 (m), 3034 (w), 2960 (s), 2900 (m), 2869 (m), 1586 (s), 1464 (s), 1391 (s), 1253 (s), 1072 (s), 846 (s) cm^{-1}. GC-MS (EI, 70 eV) *m/z* (%)=231 (M^++1, 99), 230 (M^+, 100), 215 (45), 159 (5), 140 (4), 73 (12).

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