Silylformylation of Chiral 1-Alkynes, Catalysed by Solvated Rhodium Atoms

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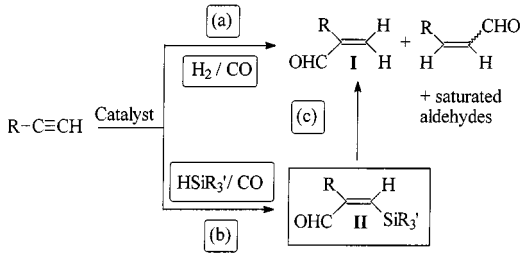
Solvated rhodium atoms, prepared by the metal vapour synthesis technique, promote the silylformylation reaction of variously substituted alkynes $R^1R^2CH(CH_2)_nC{\equiv}CH$, with catalytic activities comparable with and even higher than more common species such as $Rh_4(CO)_{12}$. *Z*-Silylalkenals are exclusively formed in high yields (60–95%) indicating *syn* addition both of CO and of the silane (Me_2PhSiH) to the triple bond. The chemoselectivity of the process (silylformylation vs. hydrosilylation) is highly affected by the amount of catalyst employed (mmol of Rh species with respect to the alkyne reagent), by the steric requirements of the acetylenic substrates and by the hydrosilane/alkyne molar ratio. When optically active acetylenes are treated in the presence of Me_2PhSiH under carbon monoxide pressure, the silylformylation reaction occurs with total retention of stereochemistry of the stereogenic centre, even if it is at the α-position of the unsaturated moiety, to afford enantiomerically enriched β-silylalkenals.

Introduction

Transition metal-catalysed carbonylation of unsaturated compounds with carbon monoxide is one of the most important reactions in synthetic organic chemistry.[1] Among the different methods used to incorporate a formyl moiety into a carbon-carbon multiple bond, the hydroformylation (oxo) reaction of alkenes[2] is one of the most commonly employed and is the basis of well-known industrial processes.[3] The reaction involving acetylenic compounds[4] (Scheme 1, a) has received relatively scant attention, due to its low yields, lack of selectivity and overreduction. Nevertheless, hydroformylation of alkynes can be particularly interesting since it represents an easy route to the synthesis of α,β-unsaturated aldehydes and ketones,[5] esters,[6] lactones,[7] amides and lactams.[8]



Scheme 1

When the H_2 molecule is replaced by a hydrosilane compound ($HSiR_3'$), the silylformylation reaction occurs[9] (Scheme 1, b). This process can generally be performed under mild experimental conditions and yields (*Z*)-3-silyl-2-alkenals with very high regio- and stereoselectivities. Thanks to its high levels of regiocontrollability, the silylformylation of alkynes has been studied intensely in recent years[10] as it provides a direct path to the synthesis of β-silylenals, which are important building blocks in organic synthesis.[11] These substrates can be easily transformed into silyl-substituted dienes,[12] dienones[13] and α,β-unsaturated ketones.[14] Furthermore, they can also be important precursors for the synthesis of more complex molecules by Peterson olefination,[15] Nazarov-type cyclopentenone annulation[16] or Trost-type cyclopentane annulation.[17] Moreover, the β-silylenals can undergo a protodesilylation process[18] to afford a particular α,β-unsaturated aldehyde exclusively: formal hydroformylation of a triple bond with total regio- and stereoselectivity (Scheme 1, c).

The silylformylation reaction can be considered as a hydrosilylation process performed under CO atmosphere. Actually, the hydrosilylation and the silylformylation often occur in competition with each other, and the relative rates of these transformations are mainly determined by the reactivity of the organosilane[19] and by the nature of the alkyne[20] and the catalyst.[21] The hydrosilane structure has a pronounced influence on the chemoselectivity of the reaction: it was found that silylformylation performed with hydrosilanes bearing phenyl groups proceeds approximately ten times more rapidly than that with trialkylsilanes, resulting in drastic suppression of the hydrosilylation side reaction. The rate of silylformylation may also be strongly dependent on the substituents linked to the *sp* carbons of the acetylene functionality: a competitive reaction using Me_2PhSiH as hydrosilane found that phenylacetylene reacted more rapidly than 1-hexyne.[19] Many different catalysts were found to be effective in the silylformylation of alkynes. Rh^I and Rh^{II} species[22] and Rh−Co mixed complexes such as $(t\text{BuNC})_4RhCo(CO)_4$ [23] and $Co_2Rh_2(CO)_{12}$ [24] have been reported to be highly reactive. $Rh_4(CO)_{12}$ is the most commonly used catalyst,[25] even if it sometimes displays lower chemoselectivity[19] (hydrosilylation vs. silylformylation). A great deal of attention is therefore still being focused on the

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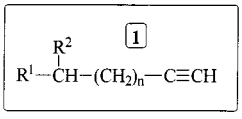
development of very active and more selective new catalysts. Recently we found that homogeneous and heterogeneous catalysts derived from solvated metal atoms (Rh, Pt), generated by the reaction between metal vapours and weakly stabilising organic ligands (metal vapours synthesis technique,[26] MVS), are very efficient for promotion of many different synthetic transformations such as the hydrosilylation of acetylenes[27] and nitriles.[28]

For this paper the catalytic activity of mesitylene-solvated Rh atoms in the silylformylation process of acetylenes was investigated. The influence of the substrates' steric hindrance on the regio- and chemoselectivity of the silylformylation reaction was studied extensively, using several substituted alkynes. Indeed, while the silylformylation of linear alkynes has been the subject of great attention, only a few examples of addition of CO and a hydrosilane to branched acetylenic compounds have been reported in the literature.[22a] Particular attention was devoted to examination of the silylformylation of enantiomerically enriched acetylenes in order to explore the possibility of extending this reaction to the preparation of useful chiral building blocks.

Results and Discussion

Synthesis of the Acetylenes

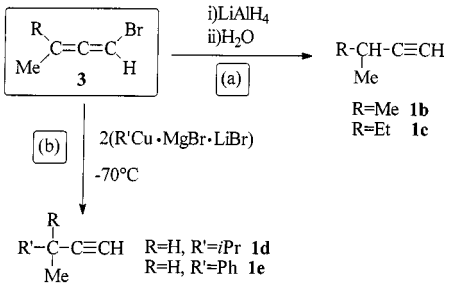
Alkynes **1a**−**g** were chosen as model substrates for this study. Except for commercially available 1-hexyne (**1a**), all of the acetylenes were synthesized according to experimental procedures that represent an improvement and/or an extension of already reported methodologies.[29−34]



n	R^1	R^2	1
0	*n*Pr	H	**a**
0	Me	Me	**b**
0	Et	Me	**c**
0	*i*Pr	Me	**d**
0	Ph	Me	**e**
1	Et	Me	**f**
2	Et	Me	**g**

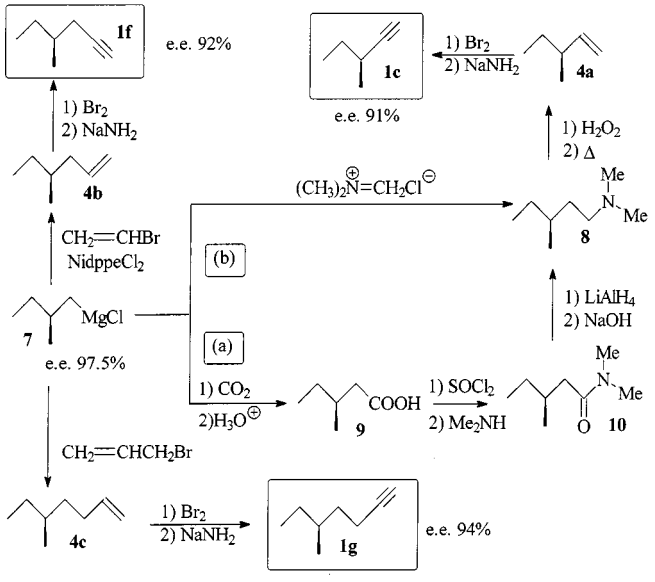
3-Methyl-1-butyne (**1b**) and (*R*,*S*)-3-methyl-1-pentyne (**1c**) were prepared by lithium aluminium hydride reduction[30] of the corresponding 3,3-dialkyl-1-bromoallenes **3**,[31] which were easily obtained from commercially available propargylic alcohols **2** (Scheme 2, a). (*R*,*S*)-3,4-Dimethyl-1-pentyne (**1d**) and (*R*,*S*)-3-phenyl-1-butyne (**1e**) were obtained through cross-coupling reactions between 1-bromo-1,2-butadiene and the appropriate alkyl or aryl cuprate (Scheme 2, b).[32]

The optically active acetylenes (*S*)-3-methyl-1-pentyne (**1c**), (*S*)-4-methyl-1-hexyne (**1f**) and (*S*)-5-methyl-1-heptyne (**1g**) were prepared by bromination-dehydrobromination[33] of the corresponding alkenes **4a**−**c**. Olefins **4a**−**c** were obtained from the Grignard reagent of (*S*)-1-chloro-2-methyl-



Scheme 2

butane (**6**, >97% *ee*) according to the synthetic strategies[34] described in Scheme 3. (*S*)-3-Methyl-1-pentene (**4a**) was prepared by the pyrolysis[35] (130° C, 1 Torr) of *N*,*N*-dimethyl(3-methylpentyl)amine *N*-oxide generated in situ by H_2O_2 oxidation of the corresponding amine **8**. The latter was synthesized by a multistep sequence involving the carboxylation of the Grignard reagent **7** followed by treatment with $SOCl_2$ and Me_2NH and subsequent reduction ($LiAlH_4$) of the *N*,*N*-dimethylamide **10** (Scheme 3, a).[36] Even though a good total yield of amine **8** (70%) and subsequent olefin **4a** was achieved by this long synthetic pathway, a very easy and direct route to the desired amine product was also obtained by the reaction between (*S*)-2-methylbutylmagnesium chloride **7** and a slight excess of commercially available dimethyl(methylene)iminium chloride (Eschenmoser's salt).[37] The reaction proceeds with quite a high yield (82%) and nearly total stereoselectivity (Scheme 3, b).



Scheme 3

(*S*)-4-Methyl-1-hexene **4b** and (*S*)-5-methyl-1-heptene **4c** were synthesized by cross-coupling processes as shown in Scheme 3. Both reactions were performed by addition of the Grignard reagent **7** to an ethereal solution of the suitable bromide (vinyl bromide or allyl bromide). The preparation of **4b** required a catalytic amount of $Ni(dppe)Cl_2$,[38]

while **4c** was easily obtained by direct coupling (method of Tiffeneau−Grignard).[39] The reported procedures did not involve any significant racemization and afforded the desired products **4b−c** with high stereoselectivity. Previously, (*S*)-3-methyl-1-pentene (**4a**) and (*S*)-4-methyl-1-hexene (**4b**) had been prepared according to quite complex synthetic pathways involving the pyrolysis of the corresponding acetates, performed in a quartz tube at 500 °C. The low overall yields (16−18%) and the severe experimental conditions required by these sequences make the methodologies developed here very attractive.

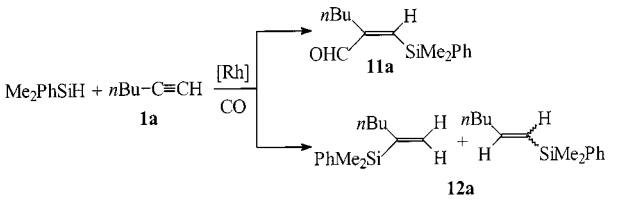
Silylformylation of 1-Hexyne

At the beginning of our study, $Rh_4(CO)_{12}$ and Rh/mesitylene species, obtained by the MVS technique, were both used as catalytic precursors and their activities (turnover numbers, TONs) were compared. The rhodium/mesitylene cocondensate was prepared by simultaneous evaporation of both the metal and the organic solvent inside a glass reactor, cooled to liquid nitrogen temperature.[40] On warming of the obtained solid matrix to −40° C, a red-brown "solution" was produced; this was used directly as the catalyst source. 1-Hexyne and dimethylphenylsilane were chosen as model compounds and equimolar amounts of both substrates were treated at room temperature in the presence of 0.1 mol% of the rhodium species with respect to the silane. The reaction occurred with high regio- and stereoselectivity with both catalytic species. (*Z*)-2-(Dimethylphenylsilylmethylene)hexanal (**11a)** was formed, together with minor amounts of hydrosilylation by-products **12a** (Table 1). Both silylformylation and hydrosilylation derivatives were detected by gas chromatography and identified by GC-MS spectrometry and by IR and NMR (^1H and ^{13}C) spectroscopy.

As it is evident from Table 1, both rhodium species displayed good catalytic activity in the silylformylation process, but the Rh/mesitylene cocondensate showed better TONs, probably due to its highly reactive small rhodium metal clusters.[27,28,41] Very low TONs were observed for both catalysts when the reactions were carried out under one atmosphere pressure of carbon monoxide (Table 1, entries 1−2), while improved reaction rates resulted on increasing P_{CO} to 10 bar (Table1, entries 3−8). When the reaction was performed under 10 bar of CO and in the presence of 1 mol% of Rh/mesitylene cocondensate with respect to the silane (Table 1, entry 4), a strong reduction in chemoselectivity was observed, large quantities (43%) of hydrosilylation by-products **12a** being formed, together with the desired aldehyde **11a**.

These results clearly indicate that the amount of catalyst has a drastic influence on the chemoselectivity of the reaction (silylformylation versus hydrosilylation). The observed trend was confirmed when $Rh_4(CO)_{12}$ was used as catalytic species. In the presence of a very small quantity (0.01 mol%) of the catalyst (Table 1, entry 5), a marked decrease in the reaction rate was measured. When 0.1 mol% of $Rh_4(CO)_{12}$ was employed (Table 1, entry 6), the β-silylalkenal **11a** was obtained in nearly quantitative yield. When the amount of the rhodium species was increased to 1 mol% (Table 1, entry 7) a strong reduction in chemoselectivity resulted, the hydrosilylation products **12a** constituting 38% of the reaction mixture. Total absence of the silylformylation product was observed if a relatively large amount of catalyst was used (3 mol%, Table 1, entry 8), even under 25 bar of carbon monoxide pressure.

Table 1. Silylformylation of 1-hexyne (**1a**), catalysed by Rh species.



Entry[a]	Cat.	Cat.[b] (%)	t (h)	P_{CO} (bar)	Conv.[c] (%)	TON[d]	Yield[e] (%) 11a:12a
1	$Rh_4(CO)_{12}$	0.1	24	1	38	4	68:16
2	Rh/MVS[f]	0.1	24	1	41	17	72:28
3	Rh/MVS[f]	0.1	6	10	91	152	92:3
4	Rh/MVS[f]	1	6	10	92	15	50:43
5	$Rh_4(CO)_{12}$	0.01	24	10	47	n.d.	93:4
6	$Rh_4(CO)_{12}$	0.1	6	10	98	41	96:1
7	$Rh_4(CO)_{12}$	1	6	10	100	4	51:38
8	$Rh_4(CO)_{12}$	3	24	25	95	n.d.	0:86

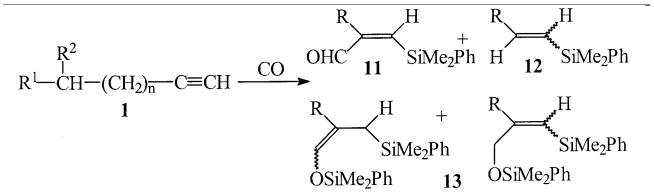
[a] The reactions were carried out with Me_2PhSiH (3 mmol) and 1-hexyne (3 mmol) in toluene (3 mL) at 25 °C. − [b] Mol% with respect to Me_2PhSiH. − [c] GC conversion of the hydrosilane. − [d] Turnover/hours = [mmol (silane)/mmol Rh × time of reaction (h)] × conv.%. − [e] Calculated from GC areas of the GC peaks; hydrosilylation by-products **12a** were detected by GC and GC-MS analysis. − [f] Rh/mesitylene cocondensate.

The importance of the amount of catalyst in the silylformylation reaction is underestimated in the literature. Murai[42] reported competitive formation of *n*-hexylsilanes in the silylformylation of 1-hexene, performed with a 1:10 catalyst/hydrosilane ratio [10 mol% $Co_2(CO)_{12}$]. Cobalt species display catalytic behaviour markedly similar to that of rhodium ones. The effect of the amount of rhodium on the chemoselectivity of the process could be explained in terms of the fact that the silylformylation and the hydrosilylation reactions are competitive processes, since both of them involve a metal-catalysed interaction between an acetylene and a hydrosilane. The presence of large quantities of the rhodium species causes the hydrosilylation process to prevail. Because of this, 0.1 mol% of rhodium species was used in all the following experiments.

Silylformylation of Branched 1-Alkynes

The 1-alkynes **1b−g** were treated with Me_2PhSiH in the presence of the rhodium/mesitylene cocondensate under 10 bar of CO. All substrates, were active in the silylformylation, yielding the aldehydes **11** with high selectivity, as summarised in Table 2.

Table 2. Silylformylation of alkynes **1** with Rh/mesitylene catalysis



Entry[a]	1	n	R^1	R^2	t (h)	P_{CO} (bar)	≡C/Si[b]	Cat.[c] (%)	Conv.[d] (%)	Yield[e] (%) 11:12:13
1	a	0	nPr	H	24	10	1	0.1	100	97:2:1
2	g	2	Et	Me	24	10	1	0.1	94	98:1:1
3	f	1	Et	Me	24	10	1	0.1	95	69:2:29
4	b	0	Me	Me	24	10	1	0.1	78	75:0:25
5	c	0	Et	Me	24	10	1	0.1	51	84:4:12
6	c	0	Et	Me	48	10	1	0.1	80	74:1:25
7	c	0	Et	Me	48	25	1	0.1	80	91:1:8
8	c	0	Et	Me	24	25	2	0.1	94	89:2:9
9	c	0	Et	Me	24	25	2	1	100	94:2:4
10	d	0	iPr	Me	48	25	2	1	95	41:20:39
11	d	0	iPr	Me	48	50	2	1	96	55:12:33
12	e	0	Ph	Me	24	10	1	0.1	38	70:30:0
13	e	0	Ph	Me	24	50	1	0.1	84	82:18:0

[a] The reactions were carried out with Me_2PhSiH (3 mmol) in toluene (3 mL) at 25 °C. – [b] Mmol/mmol. – [c] Mol% with respect to Me_2PhSiH. – [d] GC conversion of Me_2PhSiH. – [e] Calculated from GC areas of the GC peaks; silylformylation-hydrosilylation by-products **13** were detected by GC-MS analysis.

The obtained results attested that the silylformylation process is remarkably affected by the structure of the acetylenic substrate. 5-Methyl-1-heptyne (**1g**) displayed a chemoselectivity quite similar to that of 1-hexyne (**1a**) (Table 2, entries 1, 2). On the other hand, decreases in both the reaction rate and selectivity were observed when the reaction was carried out with acetylenes characterised by methyl substituents at positions α or β to the triple bond (Table 2, entries 3–6). In particular, in the case of 3-methylbutyne (**1b**) and of 3-methyl-1-pentyne (**1c**), conversions after 24 hours were 78% and 51%, respectively, and considerable amounts (12–25%) of silylformylation-hydrosilylation by-products[24a] **13** were detected by GC-MS analysis (Table 2, entries 4–6). Products **13** are probably formed by 1,2- and 1,4-addition of Me_2PhSiH to the α,β-unsaturated aldehydes **11** generated in the silylformylation process.[24a]

In order to reduce the levels of by-products **13**, treatment of 3-methyl-1-pentyne (**1c**) was carried out in the presence both of a smaller quantity of silane and of a higher pressure of CO. An increase in the carbon monoxide pressure to 25 bar resulted in nearly total silylformylation chemoselectivity (Table 2, entry 6 vs. 7). When the reaction was carried out with a 2:1 alkyne:silane ratio, a higher reaction rate was achieved, conversion being 94% after 24 h (Table 2, entry 8). Finally, when the amount of catalyst was increased to 1 mol% (Table 2, entry 9), quantitative conversion and 94% chemoselectivity were obtained. Thus, use of a larger quantity of the Rh/mesitylene species did not produce any reduction in chemoselectivity, since the presence of a 2:1 C≡C/Me_2PhSiH ratio favours the silylformylation process, which occurs with total regio- and stereoselectivity. (*Z*)-2-(Dimethylphenylsilylmethylene)-3-methylpentanal (**11c**) was formed exclusively and its configuration was confirmed by NOE experiments; when the C**H**O resonance was irradiated, a marked enhancement of both aliphatic C**H** and $C_6\mathbf{H}_6$ resonances was detected (Figure 1).

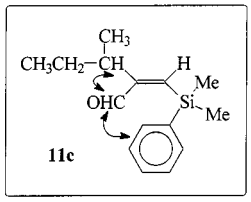


Figure 1. Determination of the configuration of 2-(dimethylphenylsilylmethylene)-3-methylpentanal (**11c**) by NOE experiments.

The optimised experimental conditions were applied to the silylformylation of particularly hindered alkynes such as 3,4-dimethyl-1-pentyne (**1d**). As shown in Table 2 (entries 10–11), despite complete consumption of the silane, the aldehyde yield did not exceed 55%, even if the reaction was performed under 50 bar of CO. The formation of large quantities of silylformylation-hydrosilylation by-products **13d** was observed. However, it is important to underline that the pure aldehydes can easily be separated from the reaction mixture by silica gel column chromatography, confirming the high synthetic potential of the silylformylation process.

A different silylformylation behaviour was observed when 3-phenyl-1-butyne (**1e**) was treated with Me_2PhSiH in the presence of 0.1 mol% of Rh/mesitylene (Table 2, entries 12–13). It is noteworthy that no silylformylation-hydrosilylation by-products **13** were formed in this case. However, when the reaction was performed under the usual reaction conditions (0.1 mol% rhodium catalyst, 10 bar CO, 25 °C), large quantities of hydrosilylation products were detected and a low degree of substrate conversion was observed. The reaction rate was considerably improved by raising the CO pressure to 50 bar (Table 2, entry 13).

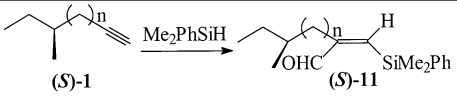
These results, together with the data obtained from the silylformylation of 3,4-dimethyl-1-pentyne (**1d**), confirm the dramatic effect of the alkyne structure on the silylformylation process, which therefore needs to be optimised for each substrate.

Silylformylation of Optically Active Alkynes

In order to evaluate the stereoselectivity of the silylformylation reaction, samples of (*S*)-4-methyl-1-hexyne [(*S*)-**1f**] and (*S*)-5-methyl-1-heptyne [(*S*)-**1g**] were treated with equimolar amounts of Me_2PhSiH under 10 bar of carbon monoxide. Under the optimised experimental conditions reported in Table 2, (*S*)-3-methyl-1-pentyne [(*S*)-**1c**] was treated with dimethylphenylsilane in the presence of 1 mol%

of Rh/mesitylene species. The obtained results are reported in Table 3.

Table 3. Silylformylation of optically active alkynes (*S*)-1c, (*S*)-1f and (*S*)-1g, catalysed by Rh/mesitylene

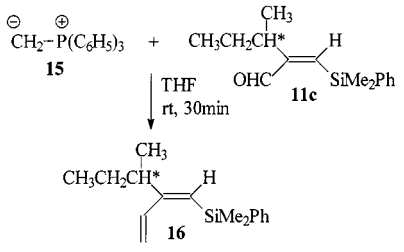


(*S*)-1 (*S*)-11

Entry[a]	1	*ee* (%)	Cat.[b] (%)	≡C/Si[c]	Yield[d] **11** (%)	$[\alpha]_D^{25}$ ($CHCl_3$)
1[e]	c	91	1	2	94 (65)	+19.62
2	f	92	0.1	1	69 (49)	+7.75
3	g	94	0.1	1	92 (64)	+8.52

[a] The reactions were run with Me_2PhSiH (3 mmol) under 10 bar CO at 25 °C for 24 h. – [b] Mol% with respect to Me_2PhSiH. – [c] Mmol/mmol. – [d] Determined by GLC analysis based on Me_2PhSiH consumed; isolated yield of pure compounds in parentheses. – [e] Reaction performed under 25 bar CO.

The dextrorotatory (*S*)-β-silylalkenals [(*S*)-**11c**, (*S*)-**11f** and (*S*)-**11g**] were obtained with total regio- and stereoselectivities and with good yields of the purified products (49−65%). The enantiomeric excesses of the pure aldehydes were determined by ^{195}Pt NMR analyses[43] of the platinum complexes generated by ligand exchange with the ethylene molecule of $[PtCl_3(C_2H_4)]^-Am^*H^+$ (Am* = chiral amine). It was recently reported[44] that ammonium platinum species such as $[PtCl_3(C_2H_4)]^-$[(*S*,*S*′)-α,α′-dimethyldibenzylammonium] **14** acted as very efficient chiral derivatising agents (CADs) for terminal olefins with α or β chiral centres. Thus, both racemic and enantiomerically enriched (*Z*)-2-(Dimethylphenylsilylmethylene)-3-methylpentanal [(*R*,*S*)- and (*S*)-**11c**; the latter with $[\alpha]_D^{25}$ = +42.28, $CHCl_3$, from 91% *ee* (*S*)-3-methyl-1-pentyne] were transformed into the corresponding butadiene derivatives **16**, containing terminal double bonds (Scheme 4).



Scheme 4

Indeed when an excess of the Schlosser−Schaub "instant ylide" **15**, generated in situ from a mixture of methylphenylphosphonium bromide and sodium amide, was treated with the β-silylalkenals (*R*,*S*)- and (*S*)-**11c**, Wittig reactions rapidly occurred, affording (*S*)- and (*R*,*S*)-**16** in very high yields (94−95%). Both the racemic and the enantiomerically enriched derivatives **16** were treated with Pt^{II} complex **14**, and 91% optical purity was determined for the butadiene (*S*)-**16** by comparison of the ^{195}Pt NMR spectra of both dienes. This value agreed perfectly with the original enantiomeric excess in the acetylenic precursor **1c**.

The obtained result confirmed that the silylformylation process takes place with complete retention of stereochemistry of the stereogenic centre, even if it is in the position α with respect to the triple bond, in agreement with the commonly accepted mechanism that exclusively involves the carbon atoms of the unsaturated moiety of the substrate. Enantiomeric excesses of 92% and 94% were found for **11f** ($[\alpha]_D^{25}$+7.75, $CHCl_3$) and **11g** ($[\alpha]_D^{25}$ = +8.52, $CHCl_3$) respectively; these compounds, which have a β and a δ chiral centre, having been obtained from samples of 92% *ee* (*S*)-4-methyl-1-hexyne ($[\alpha]_D^{25}$ = +8.47) and 94% *ee* (*S*)-5-methyl-1-heptyne ($[\alpha]_D^{25}$ = +18.84).[33]

Conclusion

Rh/mesitylene cocondensate, obtained by the metal vapour synthesis technique, was shown to be able to promote the silylformylation process with catalytic activity (turnover numbers) comparable with and even higher than that of the commonest rhodium species, such as $Rh_4(CO)_{12}$. The silylformylation proved to be totally regio- and stereoselective. Only *Z* silylalkenals were formed, indicating *syn* addition both of the silane (Me_2PhSiH) and of CO to the triple bond. The chemoselectivity of the reaction (silylformylation vs. hydrosilylation) was markedly affected by the amount of the catalyst employed (mmolRh/mmolC≡C), regardless of the nature of the rhodium species [$Rh_4(CO)_{12}$ or Rh/mesitylene]. Branched alkynes react under the silylformylation conditions to afford the corresponding β-silylalkenals in good to excellent yields. A dramatic influence of the acetylene structure on the chemoselectivity of the process was observed. Considerable amounts of hydrosilylation and/or hydrosilylation-silylformylation by-products were detected as soon as the steric requirements of the substrates increased. Hence, to achieve better yields, fine-tuning of the reaction conditions is required for each 1-alkyne employed.

When optically active acetylenes were treated with a hydrosilane under carbon monoxide pressure, the Rh/mesitylene-catalysed silylformylation took place with complete stereoselectivity, generating optically active β-silylalkenals. These molecules are new and useful chiral building blocks of high added value, and can be converted into chiral α,β-unsaturated aldehydes by means of a protodesilylation process. The complete sequence (silylformylation-protodesilylation) represents a convenient route to the syntheses of the hydroformylation products of enantiomerically enriched alkynes, with high chemo- and stereoselectivities.

Experimental Section

General Remarks: All solvents were reagent grade materials, purified by standard methods. Diethyl ether, diethyl carbitol and toluene were distilled from sodium immediately before use. Dimethylphenylsilane and 1-hexyne were distilled and stored over molecular sieves. Dimethylamine, vinyl bromide, *N*,*N*-dimethyl(methylene)im-

monium chloride, and Schlosser−Schaub "instant ylide" (methyltriphenylphosphonium bromide, mixture with sodium amide) were used without purification. Lithium bromide and cuprous bromide were dried under vacuum before use. $Ni(dppe)Cl_2$ [45] and $Rh_4(CO)_{12}$ [46] were prepared and purified as previously reported. (+)-(*S*)-3-Methyl-1-pentyne (**1c**) (58% yield, 91% *ee*), (+)-(*S*)-4-methyl-1-hexyne (**1f**) (68% yield, 92% *ee*) and (+)-(*S*)-5-methyl-1-heptyne (**1g**) (42% yield, 94% *ee*) were synthesised from the corresponding olefins **4a−c** by bromination−dehydrobromination (Scheme 4) according to literature methods.[33] (*S*)-2-Methylbutylmagnesium chloride (**7**) was prepared from (+)-(*S*)-1-chloro-2-methylbutane (**6**) (97.5% *ee*) as previously reported.[34] (*R*,*S*)-1-Bromo-1,2-butadiene (**3a**), 1-bromo-3-methyl-1,2-butadiene (**3b**) and (*R*,*S*)-1-bromo-3-methyl-1,2-pentadiene (**3c**) were synthesised and purified (70−90% yields) according to literature methods,[31] starting from the appropriate propargylic alcohols. − IR spectra were measured on KBr plates as neat films. − ^1H NMR (200 MHz) and ^{13}C NMR (50.3 MHz) spectra were recorded in $CDCl_3$ solution with Me_4Si or $CHCl_3$ as internal standards; δ values are given in ppm and coupling constants (*J*) in Hz. − Mass spectra were obtained with a Perkin−Elmer Q-Mass 910 connected to a Perkin−Elmer 8500 gas chromatograph. Optical rotations were measured on a Perkin−Elmer 142 automatic polarimeter using standard cuvettes (*l* = 0.1 and 1 dm). − GLC analyses were performed with a DB1 capillary column (30 m × 0.52 mm, 5 micron), using He as the carrier gas and a flame ionisation detector (FID). Column chromatography was performed on silica gel 60 (230−400 mesh) purchased from Fluka.

General Procedure for the Preparation of 1-Alkynes 1b−c by $LiAlH_4$ Reduction: A solution of the appropriate 1-bromo-1,2-diene **3** (R = Me, Et, Scheme 2) in anhydrous diethylcarbitol was added dropwise at 0 °C to a suspension of $LiAlH_4$ in the same solvent. The reaction mixture was stirred overnight at room temperature and hydrolysed with water. The crude product was distilled (17 Torr) directly from the reaction vessel and collected in a liquid nitrogen trap. Subsequent careful distillation yielded pure **1b−c**.

3-Methyl-1-butyne (1b): 76% (10.5 g) yield. − B.p. 28 °C (760 Torr). − ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 1.19 (d, *J* = 6.5 Hz, 6 H), 2.02 (d, *J* = 2.3 Hz, 1 H), 2.56 (dhept, *J* = 2.3, *J* = 6.5 Hz, 1 H). − ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 20.3 (CH_3), 22.8 (CH), 67.1 (CH), 90.2 (Cq).

(*R*,*S*)-3-Methyl-1-pentyne (1c):[33] 71% (33.7 g) yield. − B.p. 58 °C (760 Torr). − ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 1.00 (t, *J* = 7.3 Hz, 3 H), 1.17 (d, *J* = 6.9 Hz, 3 H), 1.47 (m, 2 H), 2.02 (d, *J* = 2.4 Hz, 1 H,), 2.36 (m, 1 H). − ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 11.5 (CH_3), 20.5 (CH_3), 27.3 (CH_2), 29.7 (CH), 68.1 (CH), 88.9 (Cq).

General Procedure for the Preparation of 1-Alkynes 1d−e by Alkylcuprate Chemistry: A solution of the suitable alkylmagnesium bromide (*i*PrMgBr or PhMgBr, Scheme 2) in THF was added at 0 °C to an equimolar stirred solution of $LiCuBr_2$, prepared from stoichiometric amounts of cuprous bromide and lithium bromide in tetrahydrofuran. Stirring was continued at 0 °C for 30 min, the reaction mixture was then cooled to −70 °C and a solution of 1-bromo-1,2-butadiene (**3**, R = H, Scheme 2) in THF was added dropwise. After 10 min, the cooling bath was removed and the mixture was allowed to warm to room temperature. The reaction mixture was quenched with saturated ammonium chloride solution and the organic materials were extracted with ether. The combined extracts were washed with additional aqueous ammonium chloride and water, dried (Na_2SO_4) and concentrated. After fractional distillation, the obtained crude products yielded pure **1d−e**.

(*R*,*S*)-3,4-Dimethyl-1-pentyne (1d):[32] 77% (0.94 g) yield. − B.p. 81 °C (760 Torr). − ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.97 (d, *J* = 6.6 Hz, 6 H), 1.15 (d, *J* = 7.0 Hz, 3 H), 1.55−1.74 (m, 1 H), 2.02 (d, *J* = 2.4 Hz, 1 H), 2.25−2.42 (m, 1 H). − ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 18.4 (CH_3), 18.5 (CH_3), 20.4 (CH_3), 32.6 (CH), 32.8 (CH), 68.9 (CH), 87.5 (Cq).

(*R*,*S*)-3-Phenyl-1-butyne (1e):[32] 71% (5.38 g) yield. − B.p. 116 °C (760 Torr). − ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 1.47 (d, *J* = 7.0 Hz, 3 H), 2.15 (d, *J* = 2.5 Hz, 1 H), 3.43 (dq, *J* = 7 and 2.5 Hz), 7.30−7.50 (m, 5 H).

Synthesis of (*S*)-3-methylpentanoic Acid (9):[47] An ethereal solution of (*S*)-2-methylbutylmagnesium chloride (373 mL, 2.99 M) was slowly added to a dispersion of excess solid CO_2 in 200 mL of Et_2O. The obtained mixture was stirred for 72 h, quenched with aqueous H_2SO_4 (10%) and extracted with diethyl ether. The combined extracts were treated with aqueous NaOH (10%). The basic solution was extracted with Et_2O, acidified with diluted sulfuric acid and extracted with ether, and the extract was dried (Na_2SO_4) and concentrated in vacuum. Distillation (b.p. 108 °C/17 Torr) gave pure **9** in 96% yield (125 g). − $[\alpha]_D^{25}$ = +8.47. − ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.91 (t, *J* = 7.3 Hz, 3 H), 0.97 (d, *J* = 6.6 Hz, 3 H), 1.12−1.54 (m, 2 H), 1.90 (m, 1 H), 2.14 (dd, *J* = 15.0, *J* = 8.0 Hz, 1 H), 2.37 (dd, *J* = 15.0 *J* = 6.1 Hz, 1 H), 11.80 (s, 1 H). − ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 11.2 (CH_3), 19.2 (CH_3), 29.2 (CH), 31.7 (CH_2), 41.3 (CH_2), 180.3 (CO).

Synthesis of (*S*)-*N*,*N*-Dimethyl-3-methylpentanamide (10): $SOCl_2$ (83 mL, 1.14 mol) was slowly added, at −10 °C under nitrogen, to a solution of (*S*)-3-methylpentanoic acid (66 g, 0.57 mol; $[\alpha]_D^{25}$ = +8.47) in 225 mL of diethyl ether. The solution was refluxed for 5 h and the solvent and the excess $SOCl_2$ were distilled off. A solution of dimethylamine (68 g, 1.5 mol) in 150 mL of Et_2O was added at −10 °C to the crude acyl chloride, diluted in 100 mL of ether. The reaction mixture was stirred at room temperature for 24 h, quenched with water and extracted with Et_2O. The combined organic layers were successively washed with 5% aqueous HCl and water and dried over Na_2SO_4. After evaporation of the solvent in vacuum, the crude material was distilled (b.p. 95 °C/17 Torr), affording **10** in 87% (71 g) yield. − α_D^{25} = +13.36° (*l* = 1). − ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.90 (t, *J* = 7.4 Hz, 3 H), 0.94 (d, *J* = 6.4 Hz, 3 H), 1.12 (m, 1 H), 1.40 (m, 1 H), 1.93 (m, 1 H), 2.12 (dd, *J* = 14.6, *J* = 7.9 Hz, 1 H), 2.32 (dd, *J* = 14.6, *J* = 5.9 Hz, 1 H), 2.95 (s, 3 H), 3.02 (s, 3 H). − ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 11.3 (CH_3), 19.3 (CH_3), 29.5 (CH_2), 31.7 (CH), 35.2 (CH_3), 37.3 (CH_3), 40.1 (CH_2), 172.6 (CO). − GC-MS: *m*/*z* (%) = 143 (0.7) [M^+], 45 (100). − $C_8H_{17}NO$: calcd. C 67.09, H 11.96; found C 67.14, H 11.67.

Synthesis of (*S*)-*N*,*N*-Dimethyl-3-methylpentylamine (8) by $LiAlH_4$ Reduction: A solution of (*S*)-*N*,*N*-dimethyl-3-methylpentanamide (**10**) [71 g, 0.15 mol; α_D^{25} = +13.36° (*l* = 1)] in 150 mL of Et_2O was added to a suspension of $LiAlH_4$ (20 g, 0.53 mol) in 150 mL of diethyl ether. The reaction mixture was stirred at room temperature overnight, refluxed for 8 h, hydrolysed with water and 40% aqueous NaOH, and steam distilled. The distillate was extracted with ether and the combined organic phases were acidified with dilute (10%) HCl. The aqueous layer was washed with ether and treated with aqueous NaOH (10%) and the alkaline solution was extracted with Et_2O. The organic fractions were dried over KOH. Fractional distillation (b.p. 96 °C/175 Torr), gave pure **8** in 84% yield (54 g). − α_D^{25} = +11.62° (*l* = 1). − ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.84 (t, *J* = 7.0 Hz, 3 H), 0.84 (d, *J* = 6.1 Hz, 3 H), 1.15−1.55 (m, 5 H), 2.18 (s, 6 H), 2.22 (t, *J* = 7.6 Hz, 2 H). − ^{13}C NMR

(50.3 MHz, $CDCl_3$, 25 °C): δ = 11.3 (CH_3), 19.3 (CH_3), 29.7 (CH_2), 32.9 (CH), 34.5 (CH_2), 45.6 (CH_3), 58.0 (CH_2). − GC-MS: *m*/*z* (%) = 129 (2.5) [M^+], 58 (100). − $C_8H_{19}N$: calcd. C 74.35, H 14.84; found C 74.11, H 14.66.

Synthesis of (*S*)-*N*,*N*-Dimethyl-3-methylpentylamine (8) by using Eschenmoser's Salt: A solution of (*S*)-2-methylbutylmagnesium chloride (**7**) in Et_2O (1 M, 120 mL) was slowly dropped into a suspension of *N*,*N*-dimethyl(methylene)iminium chloride (25 g, **0.1**35 mol) in of diethyl ether (100 mL). The reaction mixture was stirred for one hour, then hydrolysed with water and extracted with ether. The combined organic phases were washed with water, dried over Na_2SO_4 and concentrated (760 Torr). The crude oil was distilled under reduced pressure, affording **8** in 82% (14.3 g) yield. − α_D^{25} = +11.54° (*l* = 1).

Synthesis of (*S*)-3-Methyl-1-pentene (4a):[29] H_2O_2 (30%, 130 mL) was slowly added to (*S*)-*N*,*N*-dimethyl-3-methylpentylamine {54 g, 0.42 mol; $[\alpha]_D^{25}$ = +11.62 (*l* = 1)} according to the procedure reported by Cram.[48] The reaction mixture was stirred for 15 h at room temperature until a clear solution resulted. The excess hydrogen peroxide was decomposed with an extract of catalase, and water was removed by distillation under reduced pressure (40 °C, 17 Torr). The obtained *N*-oxide was pyrolyzed at 130 °C for 120 min (0.5 Torr). The crude olefin was collected in a liquid nitrogen trap, diluted with pentane, washed with 5% aqueous HCl, aqueous $NaHCO_3$ and water, and dried (Na_2SO_4). Fractional distillation (b.p. 54 °C/760 Torr) gave **4a** in 86% (30.3 g) yield. − $[\alpha]_D^{25}$ = +34.61. − ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.86 (t, *J* = 7.4 Hz, 3 H), 0.98 (d, *J* = 6.7 Hz, 3 H), 1.31 (m, 2 H), 2.03 (m, 1 H), 4.91 (ddd, *J* = 0.9, *J* = 2.0, *J* = 10.3 Hz, 1 H), 4.94 (ddd, *J* = 0.9, *J* = 2.0, *J* = 17.5 Hz, 1 H), 5.69 (ddd, *J* = 7.5, *J* = 10.3, *J* = 17.5 Hz, 1 H). − ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 11.6 (CH_3), 19.7 (CH_3), 29.4 (CH_2), 39.4 (CH), 112.4 (=CH), 144.7 (=C).

Synthesis of (*S*)-4-Methyl-1-hexene (4b):[38] Vinyl bromide (12 mL) was added at −10 °C to a solution of $NidppeCl_2$ (0.23 g, 1 mmol) in diethyl ether (100 mL). An ethereal solution of (*S*)-2-methylbutylmagnesium chloride (**7**) (32 mL, 2.99 M) was slowly added dropwise and the reaction mixture was stirred at room temperature overnight. After hydrolysis with saturated NH_4Cl solution, the aqueous layer was extracted with Et_2O and the organic phases were washed with water and dried over Na_2SO_4. Fractional distillation (b.p. 87 °C/760 Torr) afforded **4b** in 84% (7.7 g) yield. − $[\alpha]_D^{25}$ = −2.95. − ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.87 (d, *J* = 6.5 Hz, 3 H), 0.88 (t, *J* = 7.2 Hz, 3 H), 1.08−1.47 (m, 3 H), 1.88 (m, 1 H), 2.07 (m, 1 H), 4.96 (m, 1 H), 4.98 (m, 1 H), 5.78 (ddt, *J* = 7.0, *J* = 10.6, *J* = 16.3 Hz, 1 H). − ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 11.4 (CH_3), 18.9 (CH_3), 29.1 (CH_2), 34.5 (CH), 41.1 (CH_2), 115.3 (=CH), 137.8 (=C); GC-MS: *m*/*z* (%) = 83 (100) [M^+ − 15].

Synthesis of (*S*)-5-Methyl-1-heptene (4c):[39] A solution of allyl bromide in Et_2O (70 g, 0.58 mol) was added to a solution of (*S*)-2-methylbutylmagnesium chloride (**7**) in ether (93 mL, 2.99 M). The reaction mixture was refluxed for 1 h, hydrolysed with saturated NH_4Cl solution and extracted with diethyl ether. The combined organic layers were washed with water and dried over Na_2SO_4. Fractional distillation (b.p. 113 °C/760 Torr) gave **4c** in 62% (19 g) yield. − $[\alpha]_D^{25}$ = + 10.28. − ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.85 (d, *J* = 6.1 Hz, 3 H), 0.86 (t, *J* = 7.2 Hz, 3 H), 1.10−1.50 (m, 5 H), 2.05 (m, 2 H), 4.91 (m, 1 H), 4.99 (m, 1 H), 5.80 (ddt, *J* = 6.7, *J* = 10.2, *J* = 16.9 Hz, 1 H). − ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 11.3 (CH_3), 19.0 (CH_3), 29.4 (CH_2), 31.5 (CH_3), 33.9 (CH), 35.9 (CH_2), 113.9 (=CH), 139.4 (=C). − GC-MS: *m*/*z* (%) = 102 (0.7) [M^+], 70 (100).

General Procedure for the Rhodium-Catalysed Silylformylation of 1-Alkynes 1a−g: Carbonylation reactions were run in a 25 mL stainless steel autoclave fitted with a Teflon inner crucible and a stirring bar. In a typical run, Me_2PhSiH (3 mmol), the required 1-alkyne (3 mmol), toluene (3 mL) and the chosen amount of rhodium catalyst were put under CO atmosphere in a Pyrex "Schlenk" tube. This solution was introduced into the previously evacuated (0.1 Torr) autoclave by a steel siphon. The reactor was pressurised with carbon monoxide and the mixture was stirred at room temperature for a specified time. After removal of excess CO (fume hood), the reaction mixture was diluted with pentane, filtered (Celite) and concentrated by bulb to bulb distillation (1 Torr). The residue was purified by column chromatography on silica gel, using pentane/EtOAc (95:5) as eluent, to afford the pure aldehydes **11a−g** (Table 1−3).

(*Z*)-2-(Dimethylphenylsilylmethylene)hexanal (11a):[21] Yield 95% (0.70 g) . − ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.51 (s, 6 H), 0.91 (t, *J* = 7.0 Hz, 3 H), 1.22−1.45 (m, 4 H), 2.31 (t, *J* = 7.3, 2 H), 6.93 (s, 1 H), 7.35−7.40 (m, 3 H), 7.48−7.55 (m, 2 H), 9.78 (s, 1 H). − GC-MS: *m*/*z* (%) = 231 (30) [M^+ − 15], 189 (100).

(*Z*)-2-(Dimethylphenylsilylmethylene)-3-methylbutanal (11b): Yield 51% (0.35 g) . − ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.51 (s, 6 H), 1.06 (d, *J* = 6.8 Hz, 6 H), 2.94 (sept, *J* = 6.8 Hz, 1 H), 6.92 (s, 1 H), 7.32−7.42 (m, 3 H), 7.47−7.62 (m, 2 H), 9.80 (s, 1 H). − ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = −0.08 (CH_3), 21.76 (CH_3), 28.27 (CH), 128.12 (CH), 129.38 (CH), 133.48 (CH), 138.11 (Cq), 145.48 (=CH), 163.16 (=C), 193.08 (CO). − GC-MS: *m*/*z* (%) = 217 (100) [M^+ − 15]. − IR (neat): $\tilde{\nu}$ = 2727, 1686, 1587, 1428, 1252 cm^{-1}. − $C_{14}H_{20}SiO$: calcd. C 72.36, H 8.67; found C 72.58, H 8.81.

(*Z*)-2-(Dimethylphenylsilylmethylene)-3-methylpentanal (11c):[22a] Yield 65% (0.48 g) . − ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.49 (s, 6 H), 0.81 (t, *J* = 7.3 Hz, 3 H), 1.02 (d, *J* = 6.9 Hz, 3 H), 1.22−1.54 (m, 2 H), 2.75 (m, 1 H), 6.87 (s, 1 H), 7.30−7.45 (m, 3 H), 7.45−7.55 (m, 2 H), 9.77 (s, 1 H). − ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = −0.01 (CH_3), 11.68 (CH_3), 19.50 (CH_3), 28.87 (CH_2), 35.03 (CH), 128.21 (CH), 129.15 (CH), 133.53 (CH), 138.18 (Cq), 146.72 (=CH), 162.22 (=C), 193.34 (CO). − GC-MS: *m*/*z* (%) = 231 (55) [M^+ − 15], 43 (100). − IR (neat): $\tilde{\nu}$ = 2730, 1686, 1586, 1427, 1260 cm^{-1}.

(*Z*)-2-(Dimethylphenylsilylmethylene)-3,4-dimethylpentanal (11d): Yield 44% (0.34 g). − ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.50 (s, 6 H), 0.82 (d, *J* = 6.7 Hz, 3 H), 0.83 (d, *J* = 6.7 Hz, 3 H), 1.00 (d, *J* = 7.0 Hz, 3 H), 1.57−1.77 (m, 1 H), 2.65 (q, *J* = 7.0 Hz, 1 H), 6.86 (s, 1 H), 7.31−7.42 (m, 3 H), 7.47−7.56 (m, 2 H), 9.80 (s, 1 H). − ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = −0.03 (CH_3), 16.36 (CH_3), 19.25 (CH_3), 21.09 (CH_3), 32.12 (CH), 39.81 (CH), 128.17 (CH), 129.43 (CH), 133.52 (CH), 137.84 (Cq), 147.59 (=CH), 161.79 (=C), 193.30 (CO). − GC-MS: *m*/*z* (%) = 245 (30) [M^+ − 15], 137 (100). − IR (neat): $\tilde{\nu}$ = 2723, 1686, 1584, 1428, 1258 cm^{-1}. − $C_{16}H_{24}SiO$: calcd. C 73.79, H 9.29; found C 73.95, H 9.43.

(*Z*)-2-(Dimethylphenylsilylmethylene)-3-phenylbutanal (11e): Yield 58% (0.51 g). − ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.49 (s, 6 H), 1.40 (d, *J* = 7.3 Hz, 3 H), 4.17 (q, *J* = 7.3 Hz, 1 H), 6.94 (s, 1 H), 7.15−7.50 (m, 10 H), 9.76 (s, 1 H). − ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = −0.09 (CH_3), 20.42 (CH_3), 39.55 (CH), 126.32 (CH), 127.60 (CH), 128.23 (CH), 128.44 (CH), 129.51 (CH), 133.54

(CH), 136.54 (Cq), 144.13 (Cq) 147.40 (=CH), 160.54 (=C), 192.60 (CO). − GC-MS: *m/z* (%) = 294 (0.1) [M^+], 105 (100). − IR (neat): $\tilde{\nu}$ = 2727, 1687, 1586, 1428, 1251. − $C_{18}H_{22}SiO$: calcd. C 76.54, H 7.85; found C 76.68, H 7.61.

(*Z*)-2-(Dimethylphenylsilylmethylene)-4-methylhexanal (11f): Yield 49% (0.38 g). − ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.51 (s, 6 H), 0.81 (d, *J* = 6.3 Hz, 3 H), 0.88 (t, *J* = 7.3 Hz, 3 H), 1.03−1.63 (m, 3 H), 2.06 (dd, *J* = 13.4, *J* = 8.2 Hz, 1 H), 2.38 (dd, *J* = 13.4, *J* = 5.9 Hz, 1 H), 6.90 (s, 1 H), 7.40−7.50 (m, 3 H); 7.45−7.55 (m, 2 H), 9.76 (s, 1 H). − ^{13}C NMR (50.3 MHz, $CDCl_3$, 25° C): δ = −0.07 (CH_3), 11.31 (CH_3), 18.83 (CH_3), 29.38 (CH_2), 33.82 (CH), 39.29 (CH_2), 128.23 (CH), 129.52 (CH), 133.51 (CH), 138.10 (Cq), 150.32 (=CH), 156.21 (=C), 193.33 (CO). − GC-MS: *m/z* (%) = 245 (57) [M^+ − 15], 189 (100). − IR (neat): $\tilde{\nu}$ = 2733, 1686, 1587, 1428, 1258 cm^{-1}. − $C_{16}H_{24}SiO$: calcd. C 73.79, H 9.29; found C 73.59, H 9.45.

(*Z*)-2-(Dimethylphenylsilylmethylene)-5-methylheptanal (11g): Yield 64% (0.54 g). − ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.49 (s, 6 H), 0.86 (t, *J* = 7.4 Hz, 3 H), 0.86 (d, *J* = 5.8 Hz, 3 H), 1.07−1.48 (m, 5 H), 2.20−2.40 (m, 2 H), 6.91 (t, *J* = 1.2 Hz, 1 H), 7.35−7.45 (m, 3 H), 7.49 (m, 2 H), 9.76 (s, 1 H). − ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = −0.05 (CH_3), 11.3 (CH_3), 19.1 (CH_3), 29.3 (CH_2), 29.5 (CH_2), 34.4 (CH_2), 35.3 (CH), 128.2 (CH), 129.5 (CH), 133.6 (CH), 138.1 (Cq), 148.6 (=CH), 157.7 (=C), 193.2 (CO). − GC-MS: *m/z* (%) = 259 (3) [M^+ − 15], 189 (100). − IR (neat): $\tilde{\nu}$ = 2730, 1685, 1590, 1428, 1251 cm^{-1}. − $C_{17}H_{26}SiO$: calcd. C 74.39, H 9.55; found C 74.17, H 9.38.

Synthesis of (*R*,*S*)- and (*S*,*Z*)-1-(Dimethylphenylsilyl)-2-(1-methylpropyl)-1,3-butadiene: Schlosser−Schaub "instant ylide" (methyltriphenylphosphonium bromide, mixture with sodium amide; 2 g, 4.8 mmol) was dissolved in anhydrous THF (15 mL). The solution was stirred at room temperature for 30 min, and (*Z*)-2-(Dimethylphenylsilylmethylene)-3-methylpentanal (**11c**, 0.647 g, 2.5 mmol) was then added. After 1 h, the reaction mixture was quenched with a 25% NaOH solution and the aqueous layer was extracted with diethyl ether. The combined organic materials were dried over Na_2SO_4 and concentrated in vacuum. The crude product was transferred to a centrifuge tube and diluted with hexane. After centrifugation, the organic layer was separated from the solid and the solvent was evaporated under reduced pressure to afford **16** in 95% (0.58 g) yield. − $[\alpha]_D^{25}$ = +16.85 (*c* = 5.05, hexane). − ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.43 (s, 6 H), 0.91 (t, *J* = 7.4 Hz, 3 H), 1.12 (d, *J* = 6.8 Hz, 3 H), 1.31−1.67 (m, 2 H), 2.58 (sext, *J* = 6.8 Hz, 1 H), 5.06 (dt, *J* = 11.0, *J* = 1.1 Hz, 1 H), 5.33 (dd, *J* = 17.5, *J* = 1.1 Hz, 1 H), 5.69 (s, 1 H), 6.57 (dd, *J* = 17.5, *J* = 11.0 Hz, 1 H), 7.35−7.45 (m, 3 H), 7.50−7.60 (m, 2 H). − ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 0.38 (CH_3), 11.94 (CH_3), 20.36 (CH_3), 29.46 (CH_2), 37.40 (CH), 113.84 (=C), 124.33 (=CH_2), 127.74 (CH), 128.71 (CH), 137.77 (CH), 138.29 (=C), 139.97 (Cq), 161.34 (=C). − GC-MS: *m/z* (%) = 244 (17) [M^+], 135 (100). − IR (neat): $\tilde{\nu}$ = 1556, 1428, 1248, 1112 cm^{-1}. − $C_{16}H_{24}SiO$: calcd. C 78.61, H 9.90; found C 78.83, 10.05.

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