Pergamon

Tetrahedron, Vol. 52, No. 35, pp. 11405-11420, 1996
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0040-4020/96 $15.00 + 0.00

PII: S0040-4020(96)00634-5

Variations on Radical Cascades of Vinyl Radicals Generated from Bromomethyldimethylsilyl Propargyl Ethers

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Abstract : Vinyl radicals generated from bromomethyldimethylsilyl propargyl ethers have been efficiently engaged in cascades of radical cyclizations. Through the enchainment of 5-*exo-dig*-5-(*π-endo*)-*exo-trig*-6-*endo-trig* or 5-*exo-dig*-5-(*π-endo*)-*exo-trig*-6-*exo-trig* radical processes, hydrindene and a steroid skeleton could be assembled. Appending on the alkyne a suitable chain bearing a dioxolane for 1,5-radical translocations proved also very rewarding since a very diastereoselective access to cyclopentanone derivatives could be devised. Copyright © 1996 Elsevier Science Ltd

Introduction

The new age of radical chemistry has witnessed the development of very efficient new synthetic routes essentially based on the chemo-, regio- and stereoselective carbon-carbon bond forming reactions in cascade sequences.[1,2,3,4,5] Over the past five years in the laboratory, we have demonstrated the synthetic usefulness of the tin hydride mediated radical cyclization of polyunsaturated bromomethyldimethylsilyl propargyl ethers.[6,7] These studies have resulted in the totally stereoselective one-pot preparation of a highly functionalized diquinane framework.[8,9] In this example, two consecutive intramolecular 5-*exo-dig* and 5-*exo-trig* cyclizations provide a homoallyl radical intermediate in a totally stereoselective manner. This homoallyl radical appears to be a convenient intermediate for a Curran [3+2] radical annulation[10] in the presence of acrylonitrile, thus allowing the construction of a second five-membered ring. This one-pot reaction creates four carbon-carbon bonds with two contiguous quaternary centers and controls the stereoselective construction of four stereogenic centers. In connection with other synthetic programs, we decided to fully exploit the potentialities offered by the two remarkable intermediates of the above sequence, namely : the initial vinyl radical **B** generated from **A** and the homoallyl radical **C** (figure 1). First, aiming at the selective one-pot preparation of hydrindenes and synthetic analogs of fusidic acid,[11] we became attracted with the potential formation of six-membered rings from this homoallyl radical. This could be envisaged either *via* 6-*endo-trig* or 6-*exo-trig* cyclization modes. In the latter case (n = 2), we certainly have to fear a competitive and easy 1,5-hydrogen atom transfer while the former mode (n = 1), which is *a priori* less favored, could succeed due to the presence of at least one sp^2-hybridized carbon atom in the tether.[12] Second, a fast 1,5-hydrogen atom transfer may occur from the vinyl radical intermediate, leading to a 5-hexenyl radical which could subsequently cyclize.[13] The overall cascade sequence would allow the preparation of highly functionalized cyclopentanone derivatives with the stereocontrolled formation of two contiguous stereogenic centers from two *sp*-hybridized carbon atoms. In this paper, we will describe full details of our synthetic efforts devoted to these goals.

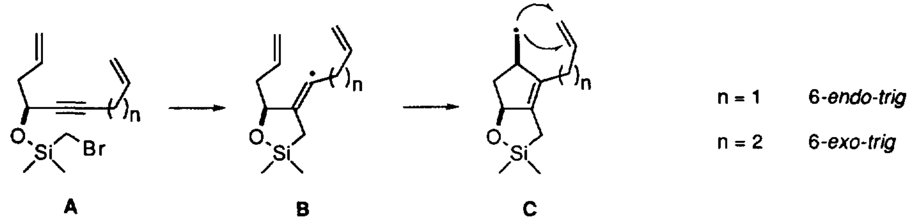


Figure 1

Results and Discussion

Trans-hydrindans are found in many biologically important compounds such as steroid derivatives and therefore have attracted a great deal of interest in organic synthesis.[14] The main methodologies are based on catalytic hydrogenation or conjugate addition on hydrindene derivatives, Diels-Alder approaches, tandem Michael addition, intramolecular aldol reactions, etc. Radical methodologies have also led to interesting approaches. Although it is well known that radical cyclizations involving intermediate **D** (figure 2) give exclusively or predominantly *cis*-fused products,[15] Clive and Shibasaki[14] have proposed solutions to allow the direct formation of *trans*-fused compounds.

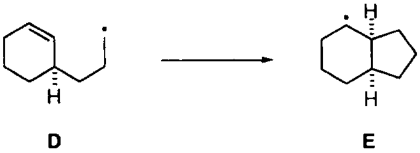
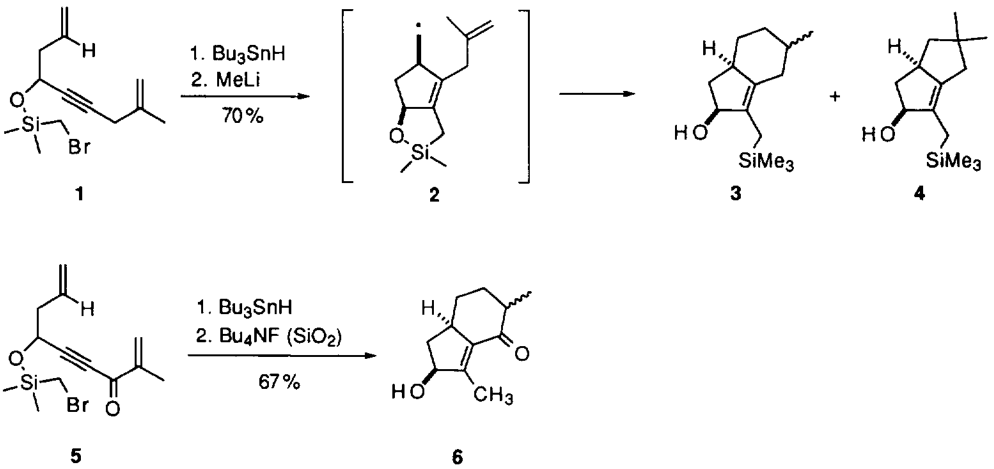


Figure 2

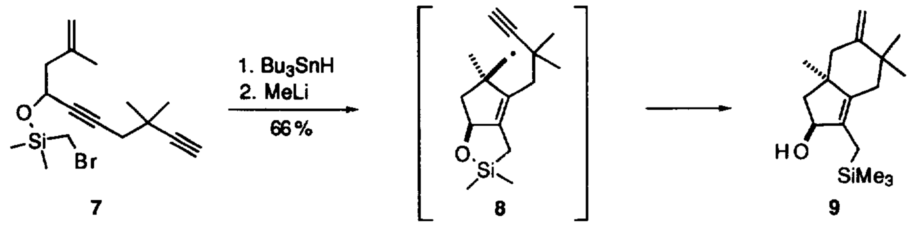
Other radical approaches involve the acyl radical dienes cascade cyclization,[16] the Snider manganese (III) based oxidation free radical method,[17] exploited by Zoretic[18] and the Scheffold cascade[19] using the Nishiyama[20]-Stork[21] methodology. In all these examples, an initial 6-*endo-trig* cyclization allowed the stereoselective construction of the hydrindan system. In our approach, we envisaged the stereoselective construction of hydrindene systems *via* the initial formation of a cyclopentene derivative followed by a 6-*endo* or a 6-*exo* cyclization (figure 1). We first considered a 5-*exo-dig*-5-(*π-endo*)-*exo-trig*-6-*endo-trig* strategy. The readily prepared acyclic bromomethyldimethylsilyl ether **1** was treated with the classical tin mediated radical procedure (scheme 1). We anticipated that the presence of a sp^2-hybridized carbon atom in the tether of the 5-hexenyl radical **2** would facilitate the formation of the hydrindene framework. After treatment of the crude mixture with methyllithium, we isolated in a good chemical yield, a 2 : 1 mixture of two bicyclic structures. The minor one was the diquinane **4** isolated as a single diastereomer, whereas the major compound **3** was a 3 : 2 inseparable diasteromeric mixture having the hydrindene skeleton. Consistent with our previous findings, the complete diastereoselective formation of **2** was the result of a chairlike transition state during the cyclization of the vinyl radical so that the mixture of diastereomers **3** was the consequence of a lack of stereoselectivity during the final 6-*endo-trig* process. This encouraging result was explained by the synergic effect of the presence of an unsatured carbon in the tether and the steric influence of the methyl substituent on the sp^2 carbon of the 5-*exo* cyclization position. In order to better favor the formation of the 5,6-bicyclic system, we decided to check the influence of a carbonyl group in the tether. When the ether **5** was treated with tin hydride, we were pleased to observe, as evidenced by TLC, the formation of a single compound. The crude mixture was then treated with fluoride anion and we isolated in a 67 % overall yield the highly functionalized hydrindenone **6** as a 3 : 1 mixture of diastereomers. As before, the formation of the stereogenic center bearing the methyl substituent was not controlled. The presence of the carbonyl group[12] here plays a crucial role in determining the cyclization regiochemistry, which now proceeds exclusively *via* a 6-*endo* mode, corresponding to the Michael orientation.



The 5-*exo-dig*-5-(π-*endo*)-*exo-trig*-6-*endo-trig* strategy

Scheme 1

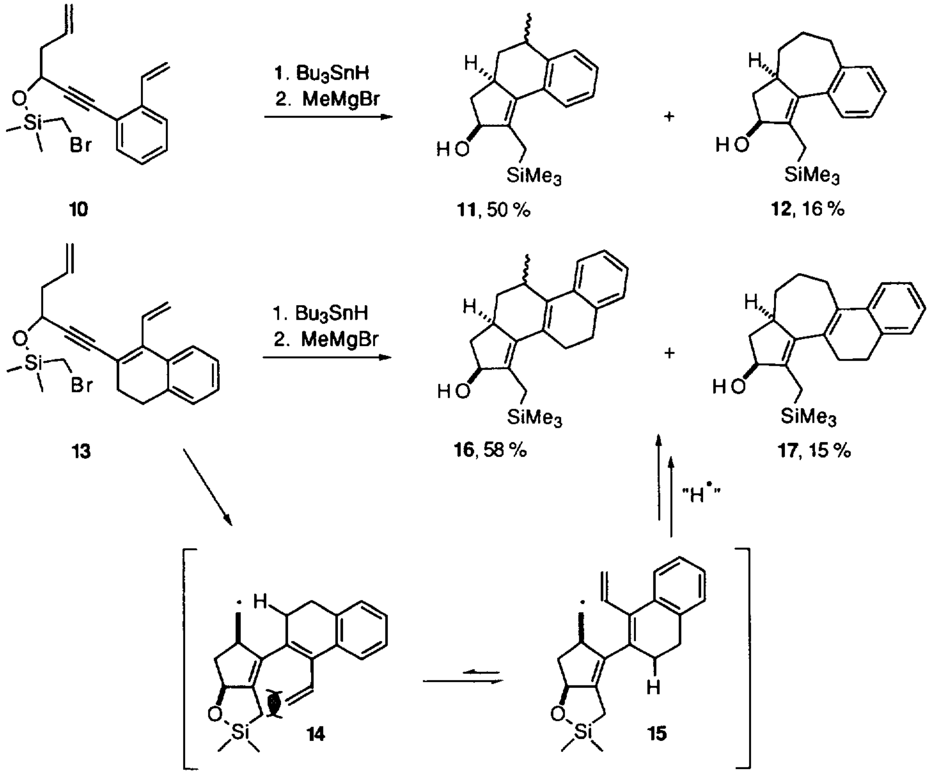
We next turned our attention to a possible formation of six-membered ring through a 6-*exo* process. In this sequence, the main problem is associated with the existence of a competitive and fast 1,5-hydrogen atom transfer involving an activated allylic or propargylic methylene group.[22] Thus, attempts realized with substrates possessing this structural feature met with failure. We then decided to suppress this competitive hydrogen translocation by preparing substrate **7** displaying a *gem*-dimethyl group at the propargylic position (scheme 2).[23] As expected, the homoallyl radical intermediate **8** now cyclized *via* a 6-*exo-dig* process instead of being reduced ; a favorable Thorpe-Ingold effect[24] probably intervened and we observed the exclusive formation of the desired hydrindene **9** as a single diastereomer in 66 % overall yield.



The 5-*exo-dig*-5-(*π-endo*)-*exo-trig*-6-*exo-dig* strategy

Scheme 2

Introduction of an unsaturation as in precursors **10** and **13** could also solve the issue of hydrogen translocation and could appear as synthetically useful (scheme 3). The preparation of the needed precursors was straightforward using the palladium catalyzed coupling reaction[25] between an alkyne and an aryl or vinyl bromide.[26]

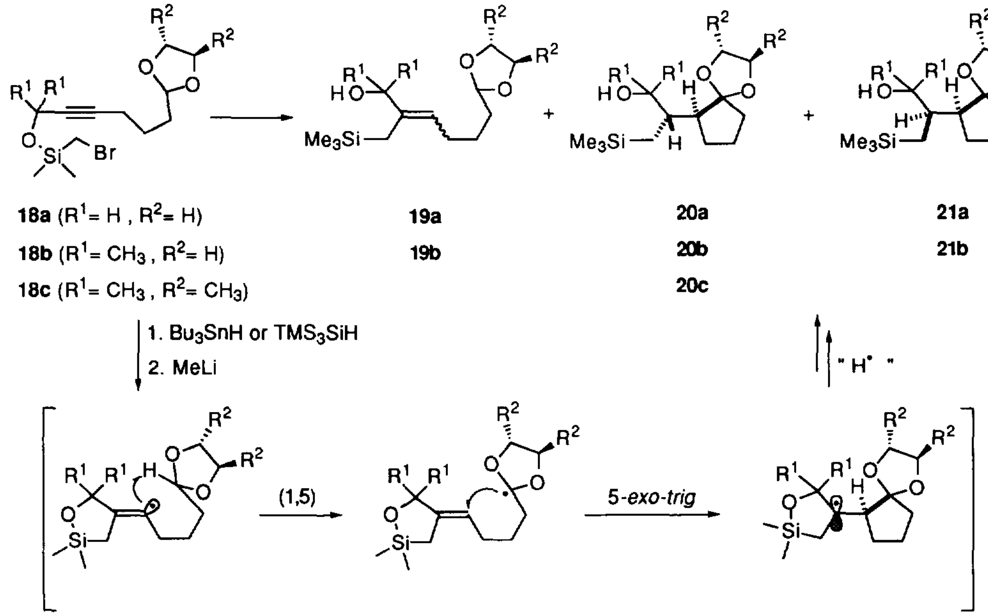


The 5-*exo-dig*-5-(*π-endo*)-*exo-trig*-6-*exo-trig* strategy

Scheme 3

The cyclization of **10** afforded the tricyclic compound **11** as an inseparable 4 : 1 mixture of diastereomers in 50 % isolated yield as the major product of the reaction. The minor product **12** isolated in 16 % yield resulted from a final 7-*endo-trig* mode cyclization, rarely observed but easily explained by the stabilized generated benzylic radical. Finally the related precursor **13** provided an even more impressive example of the efficiency of this radical cascade sequence since it affords in 58 % isolated yield the steroid framework **16** with the same level of stereoselectivity as observed in the preceding example. Here again, generation of the stabilized allylic radical in the 7-*endo* process may account for the fact that compound **17** was obtained in 15 % yield. The remarkable feature of this sequence is the complete chemoselectivity of the homoallyl radical in favor of the cyclization processes. Indeed, the reaction proceeded through the most stable rotamer **15** *vs* **14** in which a strong repulsion between the vinyl moiety and the heterocycle was present. Consequently, it was not surprising that the apparently easy 1,5-hydrogen atom transfer did not compete with the cyclization. This work has delineated the structural requirements needed to afford two new cascades of radical cyclizations, featuring either a 6-*endo* or a 6-*exo* mode cyclization in the last radical step, and which afford the stereoselective preparation of highly functionalized hydrindene systems from simple and easily accessible polyunsaturated bromomethyl dimethylsilyl propargyl ethers.

Another opportunity offered by the initially generated vinyl radical **B** of synthetic usefulness may imply a consecutive translocation step,[27] involving a suitably located activating group, to deliver new radical species, which could in turn stereoselectively cyclize onto the remaining double bond. In order to check the validity of this approach in the case of these propargyl derivatives, we began our study by examining the behavior of the simplest example **18a** (R^1 = R^2 = H) with 1.3 equivalents of tributyltin hydride in refluxing benzene (scheme 4).



Scheme 4

	R^1	R^2	Hydrogen-donor	19[a]	20 / 21[b]	d.e (%)	20 + 21[a]
1	H	H	Bu_3SnH	21	30 / 70	40	71
2	H	H	TTMSS	18	20 / 80	60	69
3	CH_3	H	Bu_3SnH	6	90 / 10	80	92
4	CH_3	H	TTMSS	< 2	≥ 98 / 2	≥ 96	92

a) Percent isolated yield; b) The diastereomers were separated on silica by flash chromatography.

Table 1

As expected, a 1,5-hydrogen shift occured and the resulting 5-hexenyl radical subsequently cyclized leading to a diastereomeric mixture of functionalized cyclopentanone precursors **20a** and **21a** in 71 % yield (table 1). Nevertheless, this sequence suffered from two major drawbacks : i) a substantial amount of olefin **19a** was isolated (21 % yield), ii) the diastereomeric excess was very modest (40 %). In an attempt to solve these problems, we next carried out the reaction in the presence of the bulky tris(trimethylsilyl)silane.[28] The diastereomeric excess increased to 60 %, but we did not suppress the competitive intermolecular reduction of the vinyl radical (18 % of **19a**). Gratifyingly, when the reaction was carried out using the propargyl ether **18b** (R^1 = Me, R^2 = H), the formation of olefin **19b** became a very minor pathway (6 % only) even with tin hydride reagent. Moreover the isolated yield of the annelated products **20b** and **21b** was 92 % and the diastereomeric ratio increased to 9 : 1. Finally, using the Chatgilialoglu reagent we observed a perfectly selective reaction : the cyclopentane derivative **20b** was isolated in 92 % isolated yield as a single diastereomer. The diastereomeric ratio was influenced by the size of the hydrogen donor and the sense of the diastereoselection depended on the nature of the substituents at the propargyl position.[29] The cyclization of **18a** led to **21a** as the major product of the reaction, whereas a reversed stereoselectivity was found when the two hydrogen atoms were replaced by a *gem*-dimethyl group.

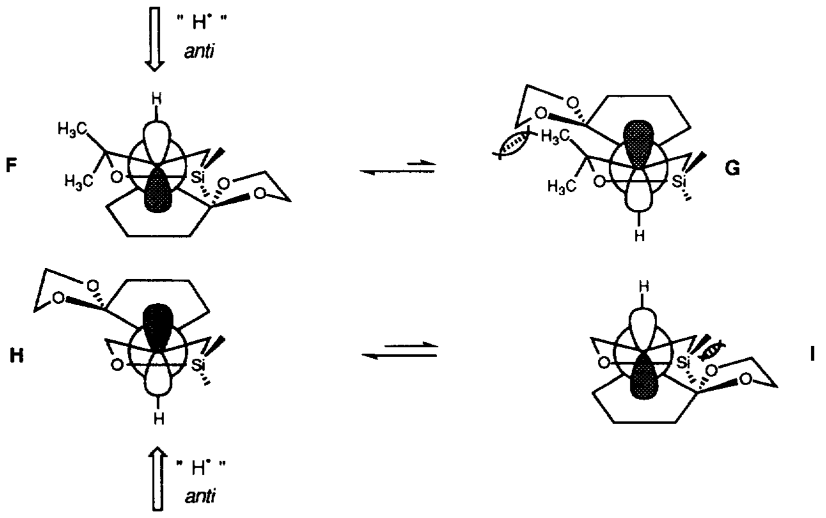


Figure 3

The highly diastereoselective formation of **20b** can be explained by the reduction step which takes place through the most reactive rotamer (**F** *vs* **G**) where a non-bonding interaction between the *gem* dimethyl group and the acetal function was not present (figure 3). The weaker difference of stability between both rotamers **H** and **I** may account for a lower diastereoselectivity in the case of **18a**. Here, the only differentiation originates from the dimethylsilyl group, which is nevertheless a bit far from the acetal function. In order to determine the relative stereochemistry of each diastereomers, these cyclopentane derivatives were transacetalized in the presence of catalytic amount of *para*-toluenesulfonic acid in methanol. ^{1}H-NMR NOE measurements of the heterodiquinanes **22** and **23** confirmed the proposed stereochemistry (Scheme 5).

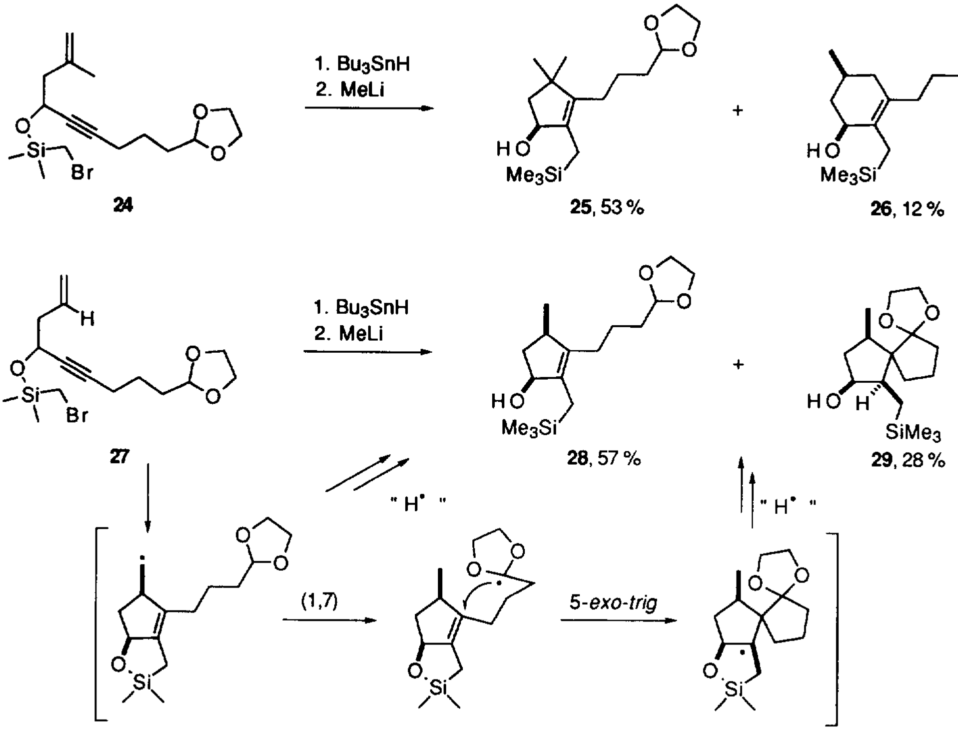
22 (R^1= CH_3) **23** (R^1= H)

i. : *p*-TSA cat.; MeOH; r.t.; 5 min

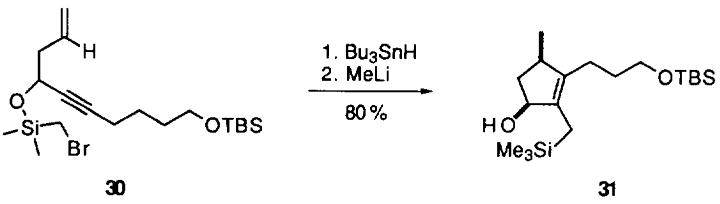
Scheme 5

This new efficient reaction involving a 1,5-hydrogen atom transfer allowed the stereoselective formation of two contiguous stereogenic centers from two *sp*-hydridized carbons belonging to achiral starting materials. Consequently, we decided to study a possible asymmetric version of this sequence using homochiral acetals prepared from C_2-symmetric (2*R*,3*R*)-(-)-2,3-butanediol. Radical cyclization of **18c** afforded **20c** in 79 % and 50 % of diastereomeric excess. Further studies using other homochiral acetals and aminals are under progress.

Related to a study aiming at the synthesis of an angular triquinane framework, a point remained to be addressed : what is the chemoselectivity of these vinyl radicals bearing both an external acetal group and an internal double bond. The reaction of **24** in the presence of tributyltin hydride yielded mainly the cyclopentene derivative **25** (Scheme 6). No product resulting from a 1,5-hydrogen translocation was isolated. The only side-product, cyclohexene **26**, resulted from a competitive 6-*endo-trig* cyclization of the vinyl radical, probably due to the presence of a methyl group on the double bond and of the bulky acetal group. Thus, this reaction was totally chemoselective. We followed our study focusing on bromoether **27**, where no methyl substituent was present onto the radical terminator. We were surprised to isolate, beside the expected cyclopentene **28** (57 %, one diasteromer) the spirobicyclic compound **29** as a 2 : 1 mixture of diastereomers. Its formation can be rationalized by a new cascade process involving a 1,7-translocation between the homoallylic radical and the acetal hydrogen atom, after the 5-*exo-trig* cyclization. The resulting radical then cyclized probably mainly *anti* to the methyl substituent following a 5-*exo-trig* process to deliver the bicyclic adduct. We next examined the case of **30** possessing a TBS ether, which is claimed to be among the best activating groups for a hydrogen atom translocation (Scheme 7).[13] Interestingly, this group completely inhibited 1,5- or 1,7-hydrogen migration. Instead, we observed the selective formation of cyclopentene **31** in 80 % chemical yield as a single diastereomer.



Scheme 6



Scheme 7

Conclusion

In this paper, we have shown that the vinyl radical resulting from the radical cyclization of variously functionalized bromomethyldimethylsilyl propargyl ethers represents an attractive building block for new selective and synthetically useful cascade processes. On one hand, it allows the stereoselective formation of hydrindene systems following either a *5-exo-dig-5-(π-endo)exo-trig-6-endo-trig* sequence or a *5-exo-dig-5-(π-endo)-exo-trig-6-exo-trig* process. In the latter, the one-pot construction of a steroid skeleton was achieved. On the other hand, the diastereoselective synthesis of functionalized cyclopentanone precursors implying a 1,5-hydrogen translocation and the controlled construction of two stereogenic centers from two *sp*-hybridized carbon atoms was rendered possible. We could also precise the chemoselectivity of the vinyl radical between a *5-exo-trig* process and a 1,5-hydrogen translocation. In this course, we have observed a sequence involving a 1,7-hydrogen translocation leading to spirobicyclic compounds rich in synthetic potentialities, whose optimization is under active progress in our laboratory.

Experimental Section

^{1}H-NMR and ^{13}C-NMR spectra were recorded with 200 MHz Bruker AC 200, 400 MHz JEOL 65X 400 and Bruker ARX 400 spectrometers. Chemical shifts are reported in ppm referenced to the residual proton resonances of the solvants. Infrared (IR) spectra were recorded by using a Perkin Elmer 1420 spectrometer. Mass spectra (MS) were obtained on GC-MS Hewlett-Packard HP 5971 apparatus. Thin-layer chromatography (TLC) was performed on Merck silica gel 60 F 254. *Rf* are reported using a solvant mixture of ether (E) and petroleum ether (PE). Silica gel Merck Geduran SI (40-63 μm) was used for column chromatography using Still method.[30]

1) Preparation of bromomethyldimethylsilyl ethers. To a mixture of the corresponding alcohol, triethylamine (1.5 eq.) and a catalytic amount of DMAP (10 mol %) in CH_2Cl_2, is added at 0°C *via* syringe bromomethyldimethylchlorosilane (0.9 - 1 eq.). After stirring at rt for 15 min, the reaction mixture is diluted with CH_2Cl_2, washed twice with a saturated solution of ammonium chloride, and twice with brine. After drying over $MgSO_4$, and concentrating *in vacuo*, the crude product is purified by flash chromatography, to afford as a colorless oil :

1, *Rf* (PE : E, 90 : 10) = 0.5; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 5.87 (m, 1H), 5.17-5.10 (m, 2H), 5.00 (br s, 1H), 4.85 (br s, 1H), 4.49 (m, 1H), 2.94 (s, 2H), 2.57 (m_{AB}, 2H), 2.48-2.44 (m, 2H), 1.80 (s, 3H), 0.35 (s, 6H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 140.3, 133.8, 117.9, 111.9, 83.0 (2C), 63.4, 43.3, 27.6, 22.2, 16.5, -2.5, -2.6; IR (neat) 3070, 2960, 2930, 2220, 1650, 1640, 1435, 1340, 1250 cm^{-1}.

5, *Rf* (PE : E, 90 : 10) = 0.71; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 6.41 (s, 1H), 5.91-5.80 (m, 1H), 5.61 (d, *J*=1.0 Hz, 1H), 5.15 (s, 1H), 5.12 (d, *J*=4.4 Hz, 1H), 4.44 (m, 1H), 2.48-2.37 (m, 2H), 2.36 (m_{AB}, 2H), 1.83 (s, 3H), 0.31 (s, 3H), 0.28 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 179.5, 145.1, 132.6, 131.3, 118.9, 92.0, 82.0, 63.0, 42.2, 16.1, 15.9, -2.6 (2C); IR (neat) 3060, 2950, 2210, 1640, 1250, 1140, 1075, 835 cm^{-1}.

7, *Rf* (PE : E, 90 : 10) = 0.95; ^{1}H-NMR (C_6D_6, 200 MHz) δ 4.83-4.81 (m, 1H), 4.79-4.77 (m, 1H), 4.60 (tt, *J*=7.0, 2.0 Hz, 1H), 2.60 (m_{AB}, 2H), 2.40 (m, 2H), 2.35 (d, *J*=2.0 Hz, 2H), 2.10 (s, 1H), 1.80 (s, 3H), 1.25 (s, 6H), 0.31 (s, 3H), 0.27 (s, 3H); ^{13}C-NMR (C_6D_6, 50 MHz) δ 142.2, 114.4, 91.6, 84.2, 83.1, 69.1, 63.5, 47.8, 34.2, 31.8, 29.2, 23.8, 17.4, -2.0, -2.1; IR (neat) 3300, 3060, 2940, 2220, 2100, 1640 cm^{-1}; GC/EIMS *m/z* 341 (M^+, 1), 287 (100), 285 (100).

10, *Rf* (PE : E, 95 : 5) = 0.45; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.58 (d, *J*=8.8 Hz, 1H), 7.42 (d, *J*=7.7 Hz, 1H), 7.30 (dt, *J*=1.6-7.7 Hz, 1H), 7.23-7.14 (m, 2H), 5.98-5.88 (m, 1H), 5.80 (d, *J*=17.6 Hz, 1H), 5.36 (d, *J*=11.0 Hz, 1H), 5.23-5.16 (m, 2H), 4.75 (t, *J*=6.6 Hz, 1H), 2.64-2.56 (m, 4H), 0.38 (s, 3H), 0.37 (s, 3H); ^{13}C-NMR (CDCl$_3$, 100 MHz) δ 139.1, 134.8, 133.4, 132.5, 128.6, 127.4, 124.6, 121.2, 118.2 115.6, 94.2, 83.7, 63.6, 43.0, 16.3, -2.5, -2.6; IR (neat) 3065, 2950, 2210, 1830, 1620, 1645, 1470, 1335, 1250, 1070, 910 cm^{-1}; GC/EIMS *m/z* 349 (M$^+$, 1), 153 (100), 151 (84), 139 (41), 125 (72), 123 (72). Anal. Calcd. for $C_{17}H_{21}OSiBr$: C, 58.46, H, 6.06. Found : C, 59.5, H, 6.21.

13, *Rf* (PE : E, 95 : 5) = 0.70; ^{1}H-NMR (CDCl$_3$, 400 MHz) δ 7.49-7.47 (m, 1H), 7.22-7.17 (m, 3H), 6.88 (dd, *J*=17.9, 11.3 Hz, 1H), 5.95-5.85 (m, 1H), 5.63 (dd, *J*=17.6, 1.6 Hz, 1H), 5.48 (dd, *J*=11.6, 1.6 Hz, 1H), 5.21-5.13 (m, 2H), 4.72-4.69 (m, 1H), 2.76-2.72 (m, 2H), 2.63-2.58 (m, 2H), 2.54-2.51 (m, 2H), 2.44-2.40 (m, 2H), 0.36 (s, 6H); ^{13}C-NMR (CDCl$_3$, 100 MHz) δ 140.7, 137.0, 133.5, 133.3, 127.6, 127.5, 126.2 (2C) , 125.9, 119.4, 118.1, 118.0, 97.3, 85.9, 63.8, 43.02, 28.9, 28.0, 16.4, -2.5, -2.6; IR (neat) 3060, 2930, 2200, 1640, 1480, 1250, 1070, 910, 835, 810 cm^{-1}; GC/EIMS *m/z* 401 (M$^+$, 5), 321 (28), 262 (36), 260 (100), 258 (64), 179 (46), 178 (42). Anal. Calcd. for $C_{21}H_{25}OSiBr$: C, 62.83, H, 6.28. Found : C, 62.67, H, 6.46.

18a, *Rf* (PE : E, 70 : 30) = 0.28; ^{1}H-NMR (CDCl$_3$, 400 MHz) δ 4.86 (t, *J*= 4.9 Hz, 1H), 4.33 (t, *J*= 2.2 Hz, 2H), 3.98-3.92 (m, 2H), 3.88-3.82 (m, 2H), 2.54 (s, 2H), 2.27 (tt, *J*= 7.2, 2.2 Hz, 2H), 1.78-1.73 (m, 2H), 1.67-1.60 (m, 2H), 0.31 (s, 6H); ^{13}C-NMR (CDCl$_3$, 100 MHz) δ 104.1, 85.8, 78.3, 64.9, 52.0, 32.9, 22.9, 18.7, 16.0, -3.0; IR (neat) 2960, 2220, 1400, 1350, 1250, 1150, 1030, 830 cm^{-1}. Anal. Calcd. for $C_{12}H_{21}O_3SiBr$: C, 44.86, H : 6.59. Found : C, 44.88, H, 6.63.

18b, *Rf* (PE : E, 70 : 30) = 0.30; ^{1}H-NMR (CDCl$_3$, 200 MHz) δ 4.87 (t, *J*= 4.3 Hz, 1H), 3.97-3.92 (m, 2H), 3.89-3.83 (m, 2H), 2.58 (s, 2H), 2.24 (t, *J* = 7.1 Hz, 2H), 1.77-1.62 (m, 4H), 1.44 (s, 6H), 0.32 (s, 6H); ^{13}C-NMR (CDCl$_3$, 50 MHz) δ 104.1, 85.4, 83.4, 67.1, 64.8, 33.2, 33.0, 23.0, 18.6, 17.6, -1.2; IR (neat) 2960, 2220, 1400, 1350, 1250, 1150, 1030, 830 cm^{-1}. Anal. Calcd. for $C_{14}H_{25}O_3SiBr$: C, 48.13, H : 7.21. Found : C, 47.99, H, 7.24.

18c, *Rf* (PE : E, 90 : 10) = 0.34; $[\alpha]_D^{20}$ -5,1 (c 0,2 ; CHCl$_3$); ^{1}H-NMR (CDCl$_3$, 400 MHz) δ 5.04 (t, *J*= 4.4 Hz, 1H), 3.61-3.56 (m, 2H), 2.57 (s, 2H), 2.22 (t, *J*= 7.1 Hz, 2H), 1.71-1.68 (m, 2H), 1.65-1.59 (m, 2H), 1.43 (s, 6H), 1.27 (d, *J*= 5.5 Hz, 3H), 1.21 (d, *J*= 5.5 Hz, 3H), 0.31 (s, 6H); ^{13}C-NMR (CDCl$_3$, 100 MHz) δ 102.7, 85.2,83.4, 79.8, 78.1, 67.1, 33.7, 33.1, 22.8, 18.5, 17.7, 17.2, 16.8, -1.2; IR (neat) 2950, 2220, 1480, 1250, 1140, 1050, 850 cm^{-1}. Anal. Calcd. for $C_{16}H_{29}O_3SiBr$: C, 50.92, H : 7.75. Found : C, 50.91, H, 7.82.

24, *Rf* (PE : E, 70 : 30) = 0.55; ^{1}H-NMR (CDCl$_3$, 400 MHz) δ 4.90 (t, *J*= 4.5 Hz, 1H), 4.84 (s, 1H), 4.79 (s, 1H), 4.54 (t, *J*=7.7 Hz, 1H), 4.00 (m, 2H), 3.85 (m, 2H), 2.56 (m$_{AB}$, 2H), 2.32 (m, 2H), 2.27 (m, 2H), 1.80 (m, 5H), 1.65 (m, 2H), 0.30 (s, 6H); ^{13}C-NMR (CDCl$_3$, 100 MHz) δ 141.4, 113.5, 104.2, 85.3, 81.4, 64.9, 62.7, 47.0, 33.0, 23.1, 23.0, 18.7, 16.5, -2.5, -2.6; IR (neat) 3060, 2940, 2860, 1640, 1250, 1080 cm^{-1}. Anal. Calcd. for $C_{16}H_{27}O_3SiBr$: C, 51.20, H : 7.19. Found : C, 51.29, H, 7.15.

27, *Rf* (PE : E, 70 : 30) = 0.50; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 5.84 (ddt, *J*= 17.2, 10.2, 7.1 Hz, 1H), 5.13-5.06 (m, 2H), 4.86 (t, *J*=4.6 Hz, 1H), 4.42 (tt, *J*=6.1, 2.0 Hz, 1H), 3.97-3.82 (m, 4H), 2.58-2-50 (m_{AB}, 2H), 2.42-2.37 (m, 2H), 2.25 (td, *J*=7.1, 2.0, 2H), 1.77-1.59 (m, 4H), 0.31 (s, 3H), 0.30 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 133.9, 117.8, 104.2, 85.5, 81.2, 65.0, 63.3, 43.3, 33.0, 23.1, 18.7, 16.5, -2.4, -2.6; IR (neat) 3030, 2960, 2220, 1640, 1410, 1250, 1140, 1070, 840 cm^{-1}. Anal. Calcd. for $C_{15}H_{25}O_3SiBr$: C, 49.85, H: 6.97. Found : C, 49.90, H, 6.96.

30, *Rf* (PE : E, 95 : 5) = 0.65; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 5.85 (ddt, *J*=17.3, 10.1, 7.1 Hz, 1H), 5.12 (m, 2H), 4.44 (tt, *J*=6.6, 2.0 Hz, 1H), 3.64 (t, *J*=6.1 Hz, 2H), 2.61-2.53 (mAB, 2H), 2.42 (tt, *J*=7.1, 1.5 Hz, 2H), 2.25 (td, *J*=7.1, 2.0 Hz, 2H), 1.64-1.55 (m, 4H), 0.91 (s, 9H), 0.34 (s, 3H), 0.33 (s, 3H), 0.07 (s, 6H); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 134.7, 118.6, 86.8, 81.7, 64.2, 63.5, 44.2, 32.9, 26.9, 26.0, 19.2, 19.4, 17.3, -1.6, -1.7, -4.4; IR (neat) 3070, 2960, 2220, 1640, 1460, 1250, 1180, 830 cm^{-1}. Anal. Calcd. for $C_{19}H_{37}O_2Si_2Br$: C, 52.63, H, 8.60. Found : C, 52.68, H, 8.68.

2) General procedure for the radical cyclization of the bromomethyldimethylsilyl ethers (**1**, **5**, **7**, **10**, **13**, **18a**, **18b**, **18c**, **24**, **27**, **30**) : To a refluxing benzene solution, under nitrogen, of the bromomethyldimethylsilyl ether (1 mmol) in 40 mL of benzene, and 8 mg of AIBN (5 mol %) is added a 13.5 mL benzene solution of tributyltin hydride (360 µL, 1.30 mmol) and AIBN (15 mol %) *via* a syringe-pump (2.10^{-4} $mol.h^{-1}$). After completion of the reaction, the mixture is allowed to reflux for 2 additional hours. Five equivalents of methyllithium (methylmagnesium bromide for compounds **11**, **12**, **14**, **15**) are then added at 0°C and the mixture is stirred for 30 min at rt. After quenching with a saturated solution of ammonium chloride, and extracting with ether, the organic phase is then washed with brine and dried over $MgSO_4$ and concentrated *in vacuo*. The crude product is then purified by flash chromatography with a solvent mixture to afford as a colorless oil :

3 + **4**, 167 mg (**3** (2 diastereomers.3 : $\underline{\underline{2}}$) and **3**:$\underline{\mathbf{4}}$, 2:1) ; *Rf* (MeOH : AcOEt :PE, 2.5 : 2.5 : 95) = 0.27; ^{1}H-NMR (C_6D_6, 400 MHz) δ 4.79-4.66 (m, $\underline{\text{1H}}$), 4.50-4.41 (m, 1H+$\underline{\text{1H}}$), 2.78-1.02 (m, $\underline{\text{9H}}$+12H+$\underline{\underline{\text{12H}}}$), 0.99 (s, $\underline{\text{3H}}$), 0.95 (s, 3H), 0.87 (d, *J*=7 Hz, 3H), 0.86 (d, *J*=6.6 Hz, $\underline{\underline{\text{3H}}}$), 0.02 (s, 9H), 0.00 (s, $\underline{\underline{\text{9H}}}$), -0.02 (s, 9H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ $\underline{143.9}$, 137.5, $\underline{\underline{136.5}}$, $\underline{135.}$5, 134.2, $\underline{\underline{133.5}}$, $\underline{83.9}$, 80.4, $\underline{\underline{80.1}}$, 48.9, 44.8, $\underline{\underline{44.4}}$, 43.8, 41.9, 41.8, 40.7, 36.6, 36.3, 35.8, 34.0, 33.7, 32.5, 31.5, 31.1, 30.1, $\underline{\underline{29.4}}$, 23.6 (2C), 16.0, 15.4, 15.2, 0.0, -0.2. IR (neat) 3320, 2940, 2900, 1450, 1240, 1155, 1045, 850, 830 cm^{-1}; GC/EIMS *m/z* : **3** (major diastereomer) (MH^+-H_2O, 38), 220 (14), 146 (48), 133 (38), 91 (42), 73 (100), 45 (35), **4**, 220 (MH^+-H_2O, 14), 133 (44), 92 (35), 91 (49), 73 (100), 45 (32). Anal. Calcd. for $C_{18}H_{26}OSi$: C, 75.02, H, 9.09. Found : C, 75.13, H, 9.05.

9, 183 mg (66 %), *Rf* (PE : E, 70 : 30) = 0.3; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.77 (s, 1H), 4.66 (m, 2H), 2.33 (d, *J*=12.6 Hz, 1H), 2.30-2.25 (m, 2H), 2.13 (d, *J*=12.6 Hz, 1H), 2.04 (d, *J*=12.6 Hz, 1H), 1.84-1.45 (m, 2H), 1.59 (d, *J*=12.6 Hz, 1H), 1.18 (s, 3H), 0.98 (s, 3H), 0.93 (s, 3H), 0.05 (s, 9H); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 153.9, 139.3, 134.1, 107.5, 76.9, 50.0, 48.2, 46.4, 38.7, 37.9, 28.4, 26.6, 24.9, 15.00, -0.9. IR (neat) 3300, 3060, 2930, 1630 cm^{-1}; GC/EIMS *m/z* : 271 (MH^+ - H_2O, 100). Anal. Calcd. for $C_{17}H_{30}OSi$: C, 73.31, H, 10.86. Found : C, 73.22, H, 10.86.

11, 143 mg (50 %, 2 dia : 4 : 1), (major diastereomer), *Rf* (PE : E, 60 : 40) = 0.39. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.52-7.58 (m, 1H), 7.12-7.21 (m, 3H), 4.72 (t, *J*=7.7 Hz, 1H), 2.90-2.98 (m, 1H), 2.82-2.88 (m, 1H), 2.63 (dt, *J*=12.4, 6.7 Hz, 1H), 2.15 (m_{AB}, 2H), 1.85 (ddd, *J*=14.3, 6.6, 2.9 Hz, 1H), 1.68 (t, *J*=12.4, 5.6 Hz, 1H), 1.29 (d, *J*=7.1 Hz, 3H), 1.21-1.27 (m, 1H), 0.18 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 143.3, 138.0, 133.1, 132.4, 129.1, 126.6, 126.3, 125.4, 79.8, 41.2, 38.5, 36.7, 33.7, 24.0, 17.3, 0.00 (3C). IR (neat) 3420, 3060, 2940, 1600, 1550, 1500, 1240, 1030, 840 cm^{-1}; GC/EIMS *m/z* : 286 (MH^+, 1), 196 (51), 181 (100), 165 (22), 154 (24). Anal. Calcd. for $C_{18}H_{26}OSi$: C, 75.02, H, 9.09. Found : C, 75.13, H, 9.05.

12, 46 mg (16 %); *Rf* (PE : E, 60 : 40) = 0.34; ^{1}H-NMR ($CDCl_3$, 400 MHz) 7.19-7.10 (m, 4H), 4.87 (br t, *J*=6.6 Hz, 1H), 2.74-2.50 (m, 3H), 2.12-2.06 (m, 2H), 1.96-1.87 (m, 1H), 1.76 (m_{AB}, 2H), 1.50-1.20 (m, 3H), -0.11 (s, 9H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 142.8, 142.0, 139.9, 138.8, 130.2, 129.9, 127.4, 126.6, 80.1, 46.9, 43.7, 41.3, 38.2, 28.7, 16.5, 0.00 (3C); IR (neat) 3420, 3060, 2940, 1600, 1550, 1440, 1240, 1030, 840, 740 cm^{-1}; GC/EIMS *m/z* : 286 (MH^+- H_2O, 1), 268 (11), 196 (51), 181 (100), 165 (24), 154 (25). Anal. Calcd. for $C_{18}H_{26}OSi$: C, 75.02, H, 9.09. Found : C, 74.95, H, 9.02.

16, 196 mg (58 %, 2 diastereomers $\underline{70}$: 30); *Rf* (PE: AcOEt : MeOH, 90 : 5 : 5) = 0.35; ^{1}H-NMR ($CDCl_3$, 400 MHz) 7.32 (d,*J*=7.7 Hz, $\underline{1H}$), 7.22-7.06 (m, $\underline{3H}$+4H), 4.60 (t, *J*=7.7 Hz, $\underline{1H}$), 4.51 (t, *J*=7.7 Hz, 1H), 3.10-1.90 (m, 1H+1H), 2.82-2.65 (m, 2H+$\underline{2H}$), 2.59-1.10 (m, 9H+$\underline{9H}$), 1.16 (d, *J*=7.2 Hz, 3H), 1.13 (d,*J*=7.2 Hz, 3H), 0.16 (s, $\underline{9H}$), 0.13 (s, 9H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 138.7, $\underline{138.5}$, 138.3, $\underline{137.3}$, 137.2, $\underline{136.5}$, 136.4, $\underline{135.8}$, $\underline{134.1}$, 133.2, 132.2, $\underline{130.3}$, $\underline{127.7}$, 127.3, $\underline{127.0}$, $\underline{126.6}$, 126.3, 126.2, 124.5, $\underline{123.8}$, 80.2, $\underline{80.0}$, 41.9, 41.6, 41.1, 40.9, $\underline{38.6}$, $\underline{36.2}$, 31.5, $\underline{29.2}$, 29.0, $\underline{27.0}$, 26.1, 22.9, $\underline{20.9}$, $\underline{19.1}$, 18.7, 0.00 (3C+$\underline{3C}$); IR (neat) 3430, 2960, 2840, 1590, 1480, 1445, 1375, 1240, 1110, 840 cm^{-1}; GC/EIMS *m/z* : 338 (100), 247 (54), 191 (58), 178 (62), 165 (61), 141 (50). Anal. Calcd. for $C_{22}H_{30}OSi$: C, 78.05, H, 8.93. Found : C, 78.19, H, 8.90.

17, 51 mg (15 %); *Rf* (PE : EA : M, 90 : 5 : 5) = 0,49; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.33 (m, *J*=7.6 Hz, 2H), 7.12 (d, *J*=7.6 Hz, 2H), 4.12-4.10 (m, 1H), 3.00-2.98 (m, 1H), 2.75-1.93 (m, 8H), 1.10-1.07 (m, 2H), 0.99-0.90 (m, 2H), 0.75-0.65 (m, 2H), 0.15 (s, 9H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 142.7, 138.9, 137.7, 137.5, 136.7, 134.2, 128.4, 127.5, 126.9, 124.0, 72.8, 47.7, 47.6, 34.2, 29.8, 28.9, 28.3, 26.6, 14.9, 0.0; IR (neat)

3450, 2920, 1590, 1480, 1450, 1240, 1070, 850 cm^{-1}; GC/EIMS *m/z* : 320 (MH$^+$- H$_2$O, 85), 247 (93), 231 (100), 215 (54), 202 (33).

19a, (2 diastereomers 50 : 50); *Rf* (PE : E, 50 : 50) = 0.20; ^{1}H-NMR (CDCl$_3$, 400 MHz) δ 5.28, 5.05 (t, *J*=7.1 Hz, 1H), 4.84, 4.83 (t, *J*=4.9 Hz, 1H), 3.94-3.81 (m, 6H), 2.11, 2.02 (q, *J* =7.1 Hz, 2H), 1.67-1.61 (m, 2H), 1.58, 1.56 (s, 2H), 1.48-1.42 (m, 2H), 0.02, 0.01 (s, 9H); IR (neat) 3350, 2950, 1650, 1460, 1370, 1245, 840, 750 cm^{-1}.

19b *Rf* (PE : E, 50 : 50) = 0.28; ^{1}H-NMR (CDCl$_3$, 400 MHz) δ 5.27 (t, *J*=7.1 Hz, 1H), 4.84 (t, *J*=4.9 Hz, 1H), 3.96-3.91 (m, 2H), 3.88-3.82 (m, 2H), 1.96 (q, *J*=7.1 Hz, 2H), 1.68-1.64 (m, 2H), 1.61 (s, 2H), 1.53-1.46 (m, 2H), 1.31 (s, 6H); IR (neat) 3450, 2960, 2930, 1640, 1470, 1250, 850 cm^{-1}.

20a *Rf* (PE : E, 50 : 50) = 0,23. ^{1}H-NMR (CDCl$_3$, 400 MHz) 4.00–3.84 (m, 4H), 3.72-3.70 (m, 1H), 3.28-3.25 (m, 1H), 2.11 (q, *J*=8.1 Hz, 1H), 1.91 (m, 1H), 1.76-1.40 (m, 6H), 0.69-0.50 (m$_{ABX}$, 2H), -0.02 (s, 9H); ^{13}C-NMR (CDCl$_3$, 100 MHz) δ 117.7, 65.0, 63.4, 47.6, 36.8, 35.9, 28.4, 20.4, 17.9 , -0.8; IR (neat) 3440, 2950, 1430, 1030, 840 cm^{-1}.

20b *Rf* (PE : E, 60 : 40) = 0,29; ^{1}H-NMR (CDCl$_3$, 400 MHz) δ 3.92-3.80 (m, 4H), 2.37-2.24 (m, 1H), 1.84 (td, *J*=6.1, 3.3 Hz, 1H), 1.65-1.40 (m, 6H), 1.11 (s, 3H), 1.09 (s, 3H), 0.62-0.36 (m$_{ABX}$, 2H), 0.01 (s, 9H); ^{13}C-NMR (CDCl$_3$, 100 MHz) δ 118.3, 73.9, 64.0, 63.9, 46.2, 41.9, 35.5, 28.4, 26.8, 25.8, 21.2 , 15.4, -0.2; IR (neat) 3420, 2940, 1440, 1240, 1030, 840 cm^{-1}. Anal. Calcd. for $C_{15}H_{30}O_3Si$: C, 62.89, H, 10.55. Found : C, 62.85, H, 10.51.

20c *Rf* (PE : E, 70 : 30) = 0,30; $[\alpha]_D^{20}$ 12,5 (c 0,2 ; CHCl3); ^{1}H-NMR (CDCl$_3$, 400 MHz) δ 4.24 (quint, *J*=6.6 Hz, 1H), 4.16 (quint, *J*=6.6 Hz, 1H), 2.22-2.18 (m, 1H), 2.01-1.96 (m, 1H), 1.76-1.73 (m, 2H), 1.68-1.42 (m, 4H), 1.17 (d, *J*= 6.6 Hz, 3H), 1.14 (s, 3H), 1.12 (d, *J*= 6.6 Hz, 3H), 1.09 (s, 3H), 0.64-0.38 (m$_{ABX}$, 2H), 0.03 (s, 9H); ^{13}C-NMR (CDCl$_3$, 100 MHz) δ 116.3, 73.9, 72.9, 72.5, 45.6, 40.8, 35.5, 28.7, 27.1, 25.3, 21.0 , 16.1, 16.0, 15.2, -0.2; IR (neat) 3460, 2960, 1450, 1300, 1210, 850 cm^{-1}. Anal. Calcd. for $C_{17}H_{34}O_3Si$: C, 64.92, H, 10.89. Found : C, 64.87, H, 10.96.

21a *Rf* (PE : E, 50 : 50) = 0,24; ^{1}H-NMR (CDCl$_3$, 400 MHz) δ 3.94–3.80 (m, 4H), 3.51-3.40 (m, 2H), 2.12-2.06 (m, 1H), 2.00-1.96 (m, 1H), 1.76-1.59 (m, 4H), 1.56-1.38 (m, 2H), 0.54-0.42 (m$_{ABX}$, 2H), -0.03 (s, 9H); ^{13}C-NMR (CDCl$_3$, 100 MHz) δ 117.9, 65.8, 64.7, 64.2, 50.7, 36.6 34.5, 24.4, 21.1,19.2, -1.0; IR (neat) 3440, 2950, 1430, 1030, 840 cm^{-1}. Anal. Calcd. for $C_{13}H_{26}O_3Si$: C, 60.42, H, 10.14. Found : C, 60.42, H, 10.12.

21b *Rf* (PE : E, 60 : 40) = 0,30. ^{1}H-NMR (CDCl$_3$, 400 MHz) δ 4.00–3.79 (m, 4H), 2.13-2.10 (m, 1H), 2.00-1.88 (m, 1H),1.81-1.63 (m, 6H), 1.18 (s, 3H), 1.13 (s, 3H), 0.73-0.54 (m$_{ABX}$, 2H), 0.03 (s, 9H); ^{13}C-NMR

($CDCl_3$, 100 MHz) δ 118.4, 73.2, 64.5, 63.7, 51.4, 41.6, 36.9, 33.0, 26.9, 25.3, 22.6, 20.1, -0.8; IR (neat) 3420, 2940, 1440, 1240, 1030, 840 cm^{-1}.

25, 164 mg (53 %); *Rf* (PE: E, 50 : 50) = 0.3; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.85 (t, *J*= 4.6 Hz, 1H), 4.50 (t, J=6 Hz, 1H), 3.95 (m, 2H), 3.82 (m, 2H), 2.1 (dd, *J*=13.2, 7.12 Hz, 1H), 2.00 (m, 1H), 1.91 (m, 1H), 1.70 (m, 3H), 1.55 (m, 3H), 1.45 (m, 2H), 1.10 (s, 3H), 0.97 (s, 3H), 0.03 (s, 9H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 143.1, 135.5, 104.5, 77.9, 64.9, 50.3, 45.0, 34.5, 29.0, 28.7, 25.7, 24.2, 15.9, -0.5; IR (neat) 3400, 2960, 1650, 1420, 1200, 1080 cm^{-1}.

26, 38 mg (12 %); *Rf* (PE: E, 50 : 50) = 0.34; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 4.80 (t, *J*= 4.6 Hz, 1H), 4.05 (m, 1H), 3.95 (m, 2H), 3.85 (m, 2H), 2.31-1.1 (m, 14 H), 0.90 (d, *J*=6.2 Hz, 3H), -0.01 (s, 9H); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 131.3, 127.0, 104.5, 71.1, 64.8, 42.4, 38.7, 33.8, 27.9, 22.2, 21.8, 17.5, -0.6.

28, 170 mg (57 %), *Rf* (PE: E, 60 : 40) = 0.25. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.85 (t, *J*= 4.6 Hz, 1H), 4.45 (t, *J*=6.1 Hz, 1H), 3.98 (m, 2H), 3.86 (m, 2H), 2.53 (m, 1H), 2.44 (dt, *J*=13.2, 7.6 Hz, 1H), 2.07 (m, 2H), 1.68-1.58 (m, 6H), 1.35 (m, 1H), 1.14 (dt, *J* = 13.2, 5.08 Hz, 1H), 1.05 (d, *J* = 6.61 Hz, 3H), 0.03 (s, 9H). ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 140.0, 135.7, 104.5, 79.2, 64.8, 42.0, 38.3, 34.1, 26.8, 22.4, 20.8, 16.0, -0.6. IR (neat) 3450, 2960, 2880, 1645, 1450, 1400, 1250, 1130 cm^{-1}; GC/CIMS *m/z* : 281 (MH$^+$- H_2O, 100). Anal Calcd. for $C_{16}H_{30}O_3Si$: C, 64.38, H : 10.12. Found : C, 64.17, H, 10.17.

29, 85 mg (28 %, 2 diastereomers 2 : 1), *Rf* (PE : E, 50 : 50) = 0.45. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.12 (m, 1H), 3.95-3.85 (m, 4H), 2.48 (ddd, *J*=13.7, 9.2, 7.6 Hz, 0.33H), 2.24 (ddd, *J*=13.7, 8.7, 6.7 Hz, 0.66H), 2.05 (m, 1.66H), 1.80-1.60 (m, 6.66H), 1.45 (m, 0.66H), 1.20 (ddd, *J*=13.7, 9.1, 3.6, 0.66H), 1.08 (m, 0.33H), 1,03 (d, *J*=6.8 Hz, 2.33H), 0.98 (d, *J*=6.8 Hz, 1H), 0.80 (m, 1.66H), -0.30 (s, 3H), -0.50 (s, 6H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 120.3, 112.7, 74.9, 73.6, 64.6, 64.1, 63.2, 57.8, 55.8, 54.3, 46.2, 44.2, 43.1, 37.8, 35.9, 33.7, 30.3, 25.4, 22.7, 21.9, 20.9, 20.8, 19.7, 17.2, 12.9, 1.8, -0.7. IR (neat) 3500, 2950, 2880, 1480, 1240, 1050 cm^{-1}; GC/CIMS *m/z* : major diastereomer, 299 (MH$^+$,100), 281 (MH$^+$- H_2O, 27), minor diastereomer, 281 (MH$^+$ - H_2O, 23).

31, 295 mg (80 %), *Rf* (PE : E, 60 : 40) = 0.4. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 4.57 (t, *J*=5.6 Hz, 1H), 3.63 (t, *J*=5.6 Hz, 2H), 2.5 (dd, *J*= 13.2, 6.6 Hz, 1H), 2.4 (dt, *J*=12.7, 7.6 Hz, 1H), 2.05 (m, 2H), 1.60-1.51 (m, 5H), 1.30 (m, 2H), 1.08 (dt, J=13.2, 5.1 Hz, 1H), 1,07 (d, *J*=6.7 Hz, 3H), 0.91 (s, 9H), 0.07 (s, 6H), 0.05 (s, 9H). ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 139.6, 134.2, 78.4, 62.0, 41.0, 37.4, 32.3, 25.7, 24.9, 23.3, 19.7, 17.3, 15.00, -0.0, -1.6, -6.2. IR (neat) 3400, 2960, 2820, 1480, 1260, 1100 cm^{-1}. GC/CIMS *m/z* : 353 (MH$^+$ - H_2O, 100).

Procedure for 6 :

Benzene was then concentrated *in vacuo* and the residue was diluted in 30 mL of DMF. Tetrabutylammonium fluoride on silica gel (2 g, 2 mmol, 2 eq.) was added, and the resulting suspension is vigourously stirred at 50 °C for 3 hours. Ether (60 mL) is then added, and the suspension is filtered over celite. The organic phase is washed with brine, and dried over Na_2SO_4, and concentrated in *vacuo* to afford after flash chromatography :

6, 121 mg (67 %, 2 dia 77 : 23), *Rf* (E) = 0.8. ^{1}H-NMR (C_6D_6, 400 MHz) δ 4.58-4.48 (m, 1H), 4.47-4.37 (m, $\underline{\text{1H}}$), 2.41 (t, *J*=7 Hz, 1H+$\underline{\text{1H}}$), 2.33 (br s, $\underline{\text{3H}}$), 2.26 (br s, 3H), 2.08 (m, 1H+$\underline{\text{1H}}$), 1.71 (m, 2H+$\underline{\text{2H}}$), 1.48-1.18 (m, 4H+$\underline{\text{4H}}$), 1.22 (d, *J*=6.7 Hz, 3H), 1.13 (d, *J*=7.3 Hz, $\underline{\text{3H}}$). ^{13}C-NMR (C_6D_6, 100 MHz) δ $\underline{203.4}$, 202.1, $\underline{153.8}$, 150.7, 136.8, $\underline{135.3}$, 79.0, $\underline{78.9}$, 46.2, 45.1, $\underline{43.4}$, $\underline{42.5}$, 42.4 (C+$\underline{\text{C}}$), 33.8, 32.7, $\underline{30.0}$, $\underline{27.7}$, $\underline{17.2}$, 15.5, $\underline{12.9}$, 12.5. IR (neat) 3410, 2910, 2850, 1675, 1625, 1450, 1170, 1070 cm^{-1}; GC/EIMS *m/z* : 180 (MH$^+$, 40), 109 (100), 95 (38), 81 (31), 79 (30), 77, 67 (30), 41 (33).

Procedure for 22 and 23 :

To a 0.1 M solution of **20b** (0.9 mmole) in MeOH is added 0.09 mmole (0.1 eq.) of *p*-TSA. The solution is stirred at room temperature for 5 min. The mixture is diluted in 50 mL of ether and washed with saturated aqueous $NaHCO_3$. The aqueous layer is extracted with ether (2 x 20 mL) and the combined organic layers are washed with saturated aqueous NH_4Cl and then with brine, dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by chromatography on silica gel.

22, 192 mg (83 %); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.26 (s, 3H), 2.14 (t, *J*=8.2 Hz, 1H), 1.96-1.92 (m, 1H), 1.85-1.75 (m, 1H), 1.69-1.59 (m, 2H), 1.56-1.44 (m, 3H), 1.19 (m, 3H), 1.18 (s, 3H), 0.62-0.50 (m_{ABX}, 2H), 0.02 (s, 9H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 118.6, 85.7, 81.2, 56.7, 53.0, 50.4, 36.3, 32.0, 27.6, 24.1, 22.9, 18.5, -0.8; IR (neat) 2940, 1460, 1250, 1150, 1080, 850 cm^{-1}. Anal. Calcd. for $C_{14}H_{28}O_2Si$: C, 65.57, H : 11.00. Found : C, 65.56, H, 11.15.

23, *Rf* (PE : E, 90 : 10) = 0.22; ^{1}H-NMR ($CDCl_3$, 400 MHz) 4.05 (t, *J*=8.2, 1H), 3.39 (d, *J*=8.2 Hz, 1H), 3.29 (s, 3H), 2.53 (sext, *J*=7.7 Hz, 1H), 2.33 (q, *J*=7.7 Hz, 1H), 1.94-1.86 (m, 2H), 1.67-1.61 (m, 2H), 1.57-1.54 (m, 2H), 0.62-0.48 (m_{ABX}, 2H), 0.02 (m, 9H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 120.2, 75.3, 51.7, 50.6, 36.6, 35.7, 21.6, 21.4, 15.3, -1.0; IR (neat) 2950, 1460, 1240, 1150, 1080, 850 cm^{-1}.

Acknowledgements :

Financial support was provided by the CNRS and MRES. S. B. thanks Glaxo-Wellcome for a grant. S. W. was supported by a fellowship from Roussel-Uclaf.

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(*Received* 12 *April* 1996; *accepted* 20 *May* 1996)