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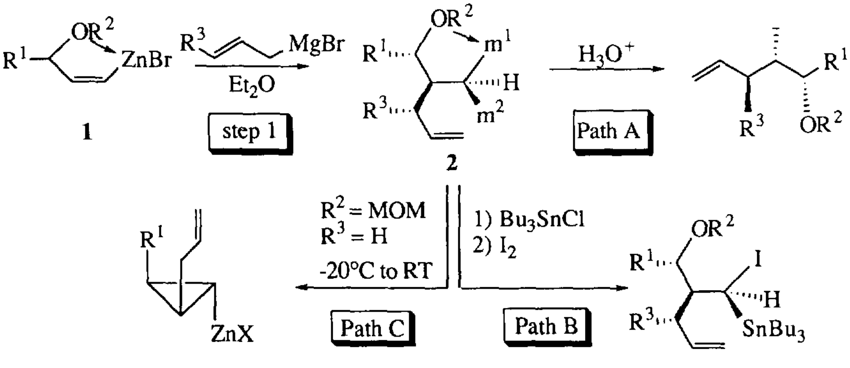
Diastereoselective Synthesis of Heterosubstituted Organogembismetallic Reagents. Application to a New Propargylmetalation Reaction of Vinyl Metals.

Denis Brasseur, Ilane Marek* and Jean-F. Normant*

Laboratoire de Chimie des Organoéléments, associé au CNRS, Tour 44-45
Université P. et M. Curie, 4 Place Jussieu, 75231 Paris Cedex 05
Fax (+33) 44 27 71 50

Abstract: The allylzincation and propargylzincation of various γ-heterosubstituted vinyl metals proceed diastereoselectively. This represents a new synthetic approach to construct two or three adjacent stereogenic centers in acyclic systems. Copyright © 1996 Elsevier Science Ltd

We have already reported on the high diastereoselections which operate when a substituted allylzinc reagent is added to a γ-oxygenated substituted vinyl metal to give the corresponding organogembismetallic[1] (Scheme 1, step 1). The latter can be hydrolyzed (Scheme 1, path A) to afford the creation of three contiguous stereogenic centers, in an acyclic system, with a very good diastereoselectivity[1], but also, it can react with two different electrophiles to give the functionalized α-iodo stannanes with one more asymmetric center[2a] (Scheme 1, path B). Furthermore, from these studies, we have deduced that such organozinc halide on a sp^3 carbon atom was configurationally stable[2]. However, when the chelating moiety is a methoxymethyl ether, the formed bismetallic species **2** leads, by a 1,3-elimination reaction, to an unique polysubstituted metallated cyclopropane[3] (Scheme 1, path C) :

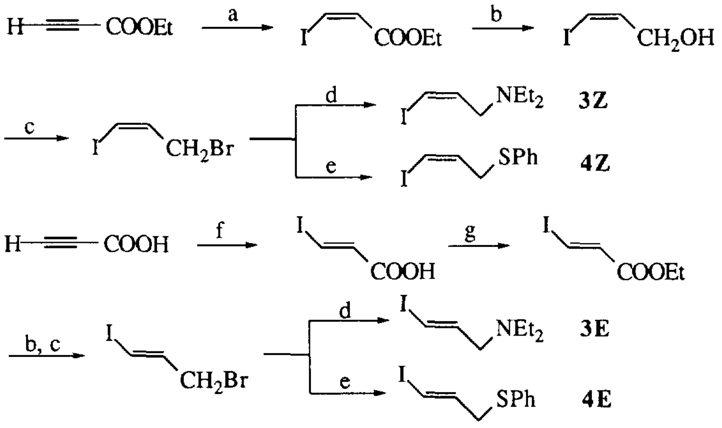


Scheme 1

The diastereoselectivity generated during the allylmetalation (step 1, Scheme 1) has been explained by an intramolecular chelation between the zinc atom and the ether moiety, forming a rigid five-membered ring[1a].

Thus, the substituted allyl metal approaches the vinyl moiety with a diastereofacial selectivity *anti* to the alkyl group. These results agree well with the NMR results established by Van Der Kerk *et al* who demonstrated[4] that dialkylzinc reagents that bear heteroatoms at the γ-position such as $Zn[(CH_2)_3 - ZR]_2$ with Z = N, O, S are chelated (with nitrogen, coordinating better than oxygen, and oxygen better than sulfur). However, in the organometallic field, it is well known that the nature of the heteroatom can have a tremendous effect on the chemical transformation, and we have previously shown that not only, a stronger chelating heteroatom considerably slows down the allylmetalation reaction[5], but also that no diastereoselectivity was obtained in the absence of a chelating moiety[6].

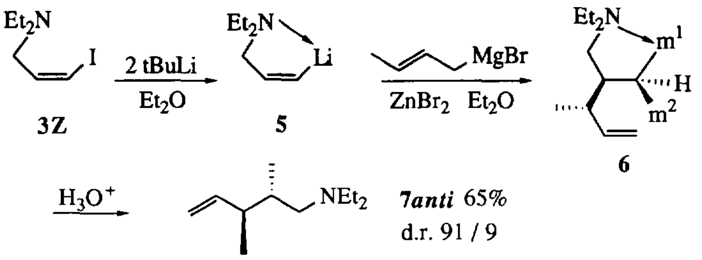
Thus, we have decided to investigate the diastereoselectivity of the carbometalation reaction of γ-nitrogen- and sulfur vinyl metals. Our first study was to determine, the diastereoselectivity resulting from the metallotropic equilibrium of substituted allylic zinc reagents towards the E and Z unsubstituted vinyl metals. These substrates were prepared according to the following Scheme :



Reagents. a) NaI, AcOH$^{7a\text{-}d}$*, 70°C, 88%. b) DIBAL-H /* CH_2Cl_2*, -78°C, 92%. c)* PPh_3*,* Br_2/Et_3N*,* CH_2Cl_2*, 81%. d)* $HNEt_2$ */* CH_3CN*,* Na_2CO_3*, 65%. e) PhSH, NaOH/toluene,* H_2O *aliquat 336, 78%. f) HI, 57%*$^{7e\text{-}f}$*, followed by 2 cristallisations E/Z = 99/1. g) EtOH, Δ/toluene,sulfuric acid*$^{7e\text{-}f}$*, 75%.*

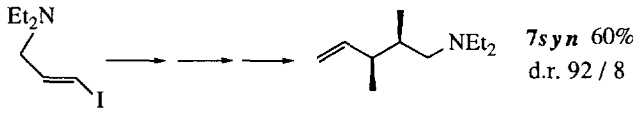
Scheme 2

Starting from **3Z**, metal-halogen exchange affords an alkenyllithium reagent **5**, which can react with crotylmagnesium bromide and zinc dibromide in ether to give, after 5h at -50°C, the corresponding organogembismetallic **6**. After hydrolysis, the (S*,S*)-3,4-dimethyl-5-(N,N-diethyl)-amino pent-1-ene **7*anti*** was isolated in 65% yield with a diastereoselection of 91/9 :



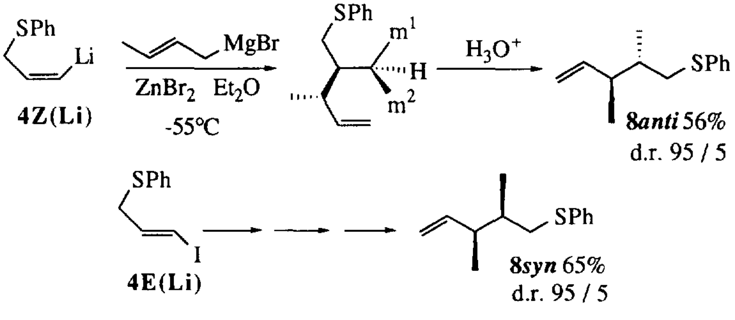
Scheme 3

Thus, for a vinyl metal of determined stereochemistry, the diastereoselectivity resulting from the carbometalation process is only dependent of the metallotropic equilibrium of the substituted allylic system[1b]. The other diastereoisomer 7*syn* was easily obtained, under the same experimental conditions as above, with a very high diastereoselectivity only by changing the stereochemistry of the starting vinyl iodide[8] (Scheme 4):



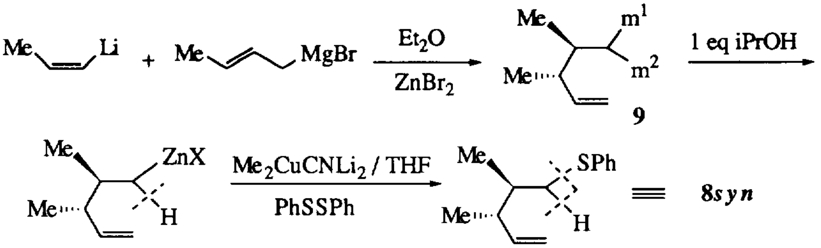
Scheme 4

Thus, in spite of the possible chelation of the zinc atom by the diethylamino group, these substrates undergo diastereoselectively the substituted allylmetalation reaction. The same stereochemical outcome has been observed when treating the pure metalated **4 Z(Li)** and **4 E(Li)** (with a thiophenyl ether instead of the diethylamino group) with crotyl magnesium bromide and zinc salt according to the following Scheme :



Scheme 5

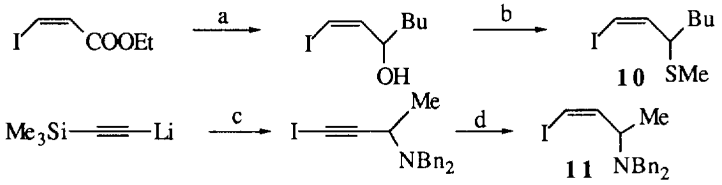
Here again, a very good diastereoselection was obtained, although in a moderate yield, at will, from the two diastereoisomers. The relative configuration of 8*syn* was attributed by a chemical correlation with an authentical sample, prepared by our procedure, already described[1b], as depicted in Scheme 6 :



Scheme 6

Then, subsequent treatment of the organogembismetallic reagent **9** with 1 equiv of a 1N solution of isopropanol in toluene, followed by a transmetalation reaction of the resulting organometallic to an organocuprate derivative and reaction with PhSSPh leads to ***8syn***, in a single-pot operation, in 54% yield with a diastereoselection of 95/5. Thus, starting from two vinylic prochiral carbon atoms, two stereogenic centers were created, whatever the nature of the heteroatom (N,S,O) with a good diastereoselection simply by the use of the E or Z stereochemistry of the starting vinyl metal and by the definite metallotropic equilibrium of the substituted allylic substrate at low temperature in Et_2O.

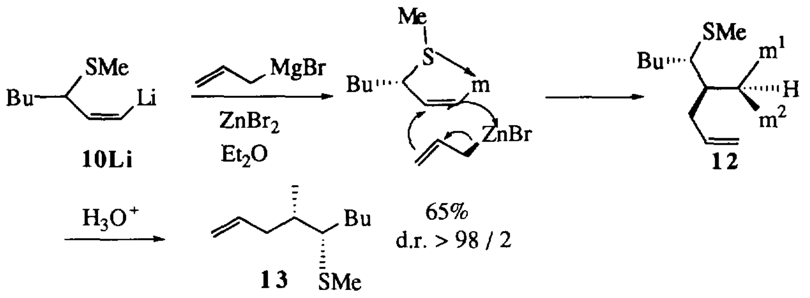
The scope of the allylmetalation reaction was further explored using a γ-secondary nitrogen or sulfur substituted vinyl metal derivative. Indeed, if the intramolecular chelation operates, for the amino as well as for the thioether derivatives, a face differentiation between the two prochiral faces of the vinyl zinc moiety will be effective, since one is shielded by an alkyl group. So, the synthesis of the (Z)-γ-iodo allylic thiomethyl ether was carried out from the already reported synthesis of the corresponding alcohol[7], whereas the amino derivative was prepared via the semi-reduction of the corresponding iodo alkyne, as described in Scheme 7 :



Reagents. a) 1 equiv DIBAL-H/CH_2Cl_2, -78°C, 15 min then BuMgBr/Et_2O, -78°C to r.t., 80%. b) PBu_3, MeSSMe 61%. c) i. N-benzylethanimine, BF_3, Et_2O 50% ; ii. $PhCH_2Br/CH_3CN$, Et_3N 33%. iii. KF, DMF, H_2O 87% ; iiii. n-BuLi/THF then I_2 94%. d) KOOC-N = N-COOK, AcOH / MeOH, pyridine 83%.

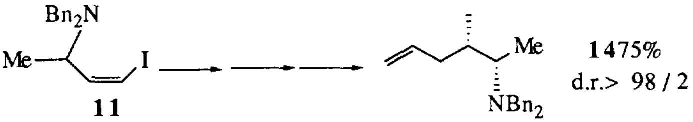
Scheme 7

When **10** was treated with 2 equiv of *tert*-BuLi followed by the addition of 1.5 equiv of allylmagnesium bromide and 1.5 equiv of zinc bromide in Et_2O for 5h at -30°C, the corresponding organogembismetallic **12**, was obtained in more than 80% yield as judged by the analysis of hydrolyzed aliquots. Hydrolysis of the reaction mixture afforded **13**, prior to purification, as a single diastereoisomer[8] :



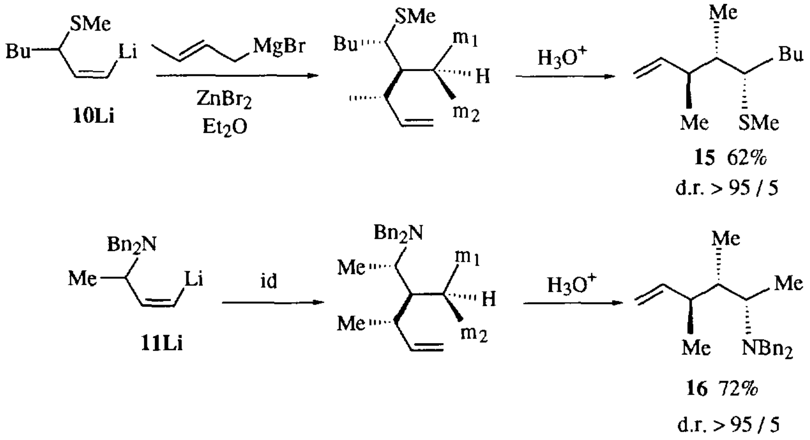
Scheme 8

The same result was obtained from the dibenzylamino derivative[9] **11** as described in the following Scheme :



Scheme 9

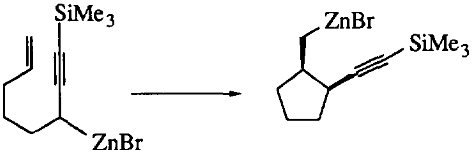
So, the thioether derivative **10**, which was supposed to lead to a weakly chelated zinc compound[4], as well as the amino derivatives **11** considered to lead to a strongly chelated vinyl zinc reagents[9], were both able to induce a face differentiation of the vinyl metals to lead, in a single-pot operation, to the creation of two asymmetric centers in an acyclic system. Now, if we combine this facial selectivity with the selectivity arising from the use of crotylzinc bromide, we have been able to create two new adjacent stereogenic centers out of a single initial stereogenic center, whatever the nature of the heteroatom present in the vinyl metal moiety :



Scheme 10

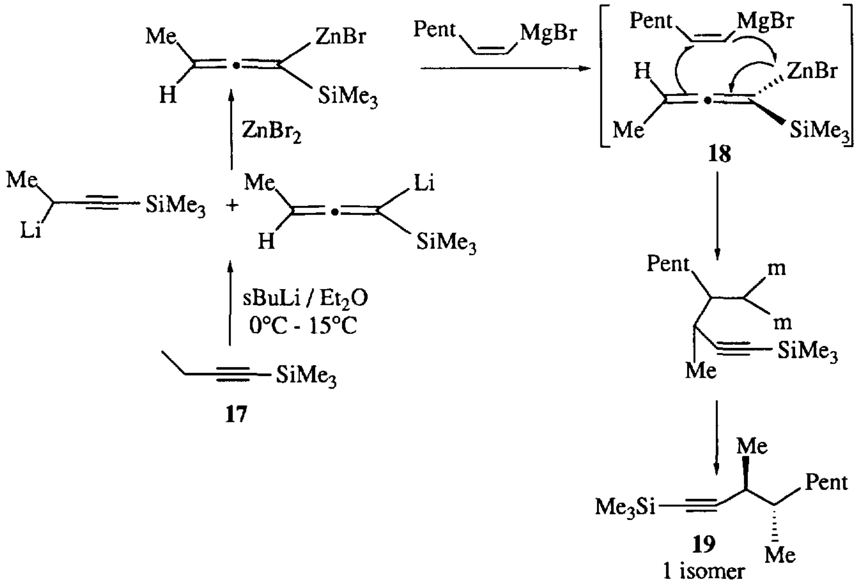
Propargylmetalation of vinyl metals

We have, recently described a new carbocycle synthesis via an intramolecular zinca-ene-allene reaction[10], in which an allenyl zinc bromide undergoes a 5-exo-Trig (Scheme 11) or 5-exo-Dig cyclization[11] on a terminal inactivated unsaturation in an extremely fast (2-3 min at r.t.) and diastereoselective way (only 1 isomer is formed) :



Scheme 11

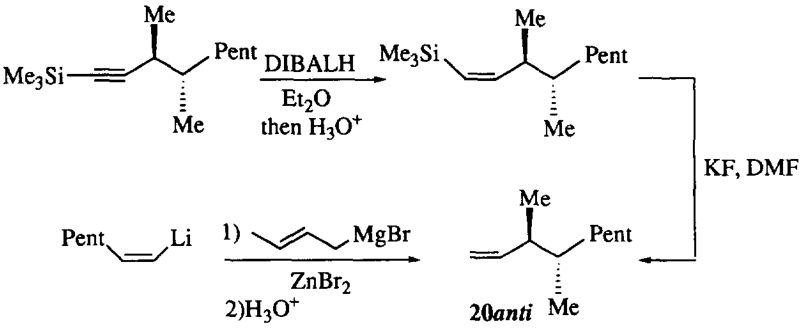
Since then, we have been interested by the potentiality of the carbometalation reaction of a propargylic metal (or its allenic counterpart via the metallotropic equilibrium) towards different unsaturated systems (cyclic or acyclic). So, we wish to report, now, our preliminary results in the area of propargylic metalation of vinyl metals[12] which is, to the best of our knowledge, unprecedented. The 1-trimethylsilyl-but-1-yne **17** was cleanly metalated which *sec*-BuLi in Et_2O between 0°C and 15°C to give the corresponding organolithium reagent since hydrolysis of the reaction mixture produced the starting alkyne and its allenic isomer in a 60/40 ratio[10a]. Addition of zinc salt (1 equiv at -20°C) not only modified the propargyl/allenyl ratio of the hydrocarbons arising from protonation of the organometallic species[13] (respectively 98/2) but also resulted in an addition reaction to the pure 1(Z)-magnesio-1-heptene[14] in 4 to 5 h at -20°C. Hydrolysis of the reaction mixture afforded **19** in 68% yield as a single diastereoisomer :



Scheme 12

The presence of zinc salt *is absolutely necessary* for the addition to occur.

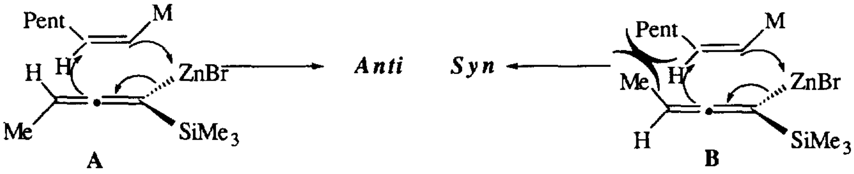
The *anti* stereochemistry was determined after subsequent cis-reduction of the alkyne moiety into the Z-vinyl silane[15] (74%) followed by a desilylation to the corresponding (3S*,4R*)-dimethyl non-1-ene **20*anti*** (78%), already prepared in our laboratory from the known crotylmetalation of vinyl metal[1]:



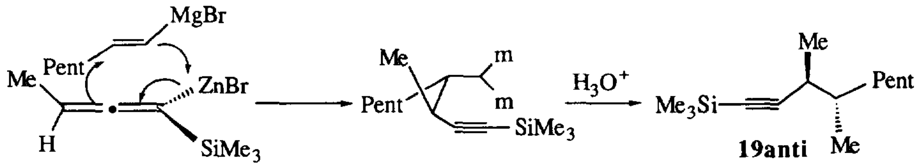
20*anti*

Scheme 13

How can we interpret the result obtained in Scheme 12 ? Knowing that the addition of zinc salt to the propargyl / allenyl organolithium leads quantitatively to the allenyl zinc bromide[10a,13] and considering that this latter reacts with the vinyl metal moiety via a S_E2' process[16], we can interpret the stereochemical result, thus obtained, according to the transition state **18** described in Scheme 12. In this transition state, the stereocontrol is attributed to a minimum of steric interactions between the methyl group located on a sp_2 carbon atom of the allenic system and the prochiral carbon atom of the vinyl metal moiety (*figure* A). The other transition state, leading to the *syn* isomer, is highly disfavored by the repulsion between the two alkyl groups (*figure* B):



If this transition state is correct, the same diastereoisomer should be obtained starting from the 1-magnesiohept-1(E)-ene. The methyl group of the allenyl moiety should be still *anti* to the alkyl group of the vinyl derivative :



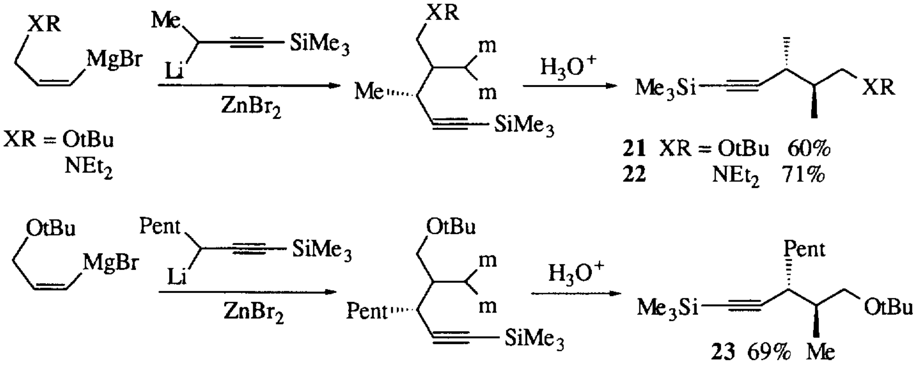
19anti

Scheme 14

This is indeed the case as **19*anti*** is obtained from either E or Z heptenyl magnesium bromide.

A rapid examination of the effect of solvents and metallic salts revealed that, while the reaction occurred in THF with or without magnesium salt, the carbometalation reaction is considerably faster and cleaner in ether and in the presence of 1 equiv of magnesium bromide.

The scope of the reaction is quite broad : the use of functionalized vinyl metals as well as the introduction of an alkyl group different from the methyl group on the allenyl zinc bromide were possible without altering the diastereoselectivity : only one isomer is formed.



Scheme 15

In conclusion, we have shown that the allyl or crotylzincation of vinyl metals were possible with a large variety of heteroatoms (N,S,O) in allylic position on the vinyl metal reagent with a very good diastereoselectivity but also that a new and very diastereoselective approach to the synthesis of alkynes with two adjacent stereogenic centers was possible by the propargylzincation of vinyl metals.

We are currently investigating an extension of the work described above to homochiral substrates.

Experimental Section[17]

3-bromo-1-iodoprop-1(Z)-ene

To a solution of triphenylphosphine (17.1 g, 65.2 mmol) in dry dichloromethane (70 mL) was added dropwise at 0°C 1 equiv of bromine (3.25 mL, 65.2 mmol). The pale yellow solution of PPh_3Br_2 thus obtained, was stirred for 5-10 mn at 0°C. A solution of 1-iodoprop-1(Z)-en-3-ol (10 g, 54.25 mmol) and dry triethylamine (9.1 mL, 65.2 mmol) in dry dichloromethane (50 mL) were then added dropwise. After stirring for 5 minutes at 0°C, TLC on SiO_2 (eluant cyclohexane / ethyl acetate = 9/1) indicated a complete reaction. The reaction mixture was concentrated under vacuo to give a solid residue which was stirred overnight in 250 mL of dry pentane. The solids were then filtrated off through a pad of celite, washed with pentane. Concentration afforded a yellow oil which was then distilled under reduced pressure (75°C, 15mmHg) to yield 10.87 g of the title product (81%): I.R. ν_{max} 1595, 1350, 1425, 1295, 1195 ,1140, 720 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.53 (d, 1H, J = 7.69 Hz), 6.49 (d.t, 1H, J = 6.49, 6.15 Hz), 4.01 (d, 2H, J = 7.15 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 136.5, 87.8, 32.4 ; Anal. Calcd for C_3H_4IBr: C, 14.60; H, 1.63. Found: C, 14.86; H, 1.67.

3-bromo-1-iodoprop-1(E)-ene

The same procedure as described for 3-bromo-1-iodoprop-1-(Z)-ene was used, starting with 1-iodoprop-1(E)-en-3-ol (3.22 g, 17.5 mmol), to give the title compound (3.07g) in 71% yield: ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.68 (m, 1H), 6.51 (d, 1H, J = 14.35 Hz), 3.84 (d, 2H, J = 7.34 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 140.9, 82.2, 32.8 .

3-(N,N-diethyl)-amino-1-iodoprop-1(Z)-ene 3(Z)

To a solution of 3-bromo-1-iodoprop-1-(Z)-ene (1.234 g, 5 mmol) in acetonitrile (10 mL) were added 2 equiv of diethylamine (730 mg, 10 mmol) and 2 equiv of sodium carbonate (1.06 g, 10 mmol). The reaction mixture was stirred for 2 h at room temperature. The adduct was checked by TLC on Al_2O_3 (cyclohexane / ethyl acetate 9/1). The hydrolysis was done with brine (10mL), the aqueous phase was extracted twice with ether (2 x 20 mL) and the combinated organic phases were washed with water (10mL), dried over Na_2CO_3 and evaporated *in vacuo*. The crude mixture was purified on SiO_2 (eluent: cyclohexane / ethyl acetate 1/1) to yield **3 Z** (781.8 mg, 65.4%): I.R. ν_{max} 2960, 2920, 2860, 1610, 1450, 1380, 1270, 1195, 1060 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.30 (m, 2H), 3.20 (d, 2H, J = 4.0 Hz), 2.51 (q, 4H, J = 7.2 Hz), 1.02 (t, 6H, J = 7.1 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 138.7, 83.1, 57.1, 47.2, 12,0.

1-iodo-3-phenylthioprop-1(Z)-ene 4(Z)

To a solution of thiophenol (890 mg, 830μL, 8mmol) in toluene (6 mL) were sequentially added 1 equiv of 3-bromo-1-iodoprop-1(Z)-ene (2 g, 8 mmol), a solution of sodium hydroxyde (500 mg in 8.3 mL of water) and 10 mg of aliquat 336 (MeN^+Oct_3 Cl^-). The reaction mixture was vigourously stirred for 30 mn at room temperature. The adduct was checked by GC. The organic layer was washed with water (10mL) then dried over $MgSO_4$ and evaporated *in vacuo* to yield, after flash chromatography on SiO_2 (eluent: cyclohexane / ethyl acetate 98/2), **4(Z)** as a pure product. (1.72 g, 78%): I.R. ν_{max} 3045, 1575, 1475, 1430, 1290, 1220, 1020, 735, 685, 650 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.2-7.4 (Aro, 5H), 6.23-6.38 (m, 2H), 3.63 (d, 2H J = 6.2 Hz); ^{13}C (50 MHz, $CDCl_3$) δ 137.1, 135, 130.5, 128.9, 126.7, 85.2, 38.1; Anal. Calcd for C_9H_9IS: C, 39.15; H, 3.29. Found: C, 39.45; H, 3.64.

3-(N,N-diethyl)-amino-1-iodoprop-1(E)-ene 3(E)

The same procedure as described for **3Z** was used, from 3-bromol-iodoprop-1(E)-ene (2 g, 8 mmol), and the residue was chromatographed on SiO_2 (eluent : cyclohexane / ethyl acetate = 1/1) to yield **3E** (1.17 g, 61%), I.R. ν_{max} 2955, 2920, 2860, 2790, 1610, 1450, 1380, 1350, 1190, 1155, 1065 , 935 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.62 (d.t, 1H, J = 14.3, 6.6 Hz), 6.30 (d, 1H, J = 14.3 Hz), 3.15 (d, 2H, J = 6.6 Hz), 2.59 (q, 4H, J = 7.1 Hz), 1.07 (t, 6H, J = 7.1 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 142.3, 78.5, 56.8, 46.5, 11,4; Anal. Calcd for $C_7H_{14}IN$: C, 35.16; H, 5.90. Found: C, 35.25; H, 5.98.

1-iodo-3-phenylthioprop-1(E)-ene 4(E)

The same procedure as described for **4Z** was used, from 3-bromo-1-iodoprop-1(E)-en (2 g, 8 mmol), and the residue was chromatographed on SiO_2 (eluent : cyclohexane / ethyl acetate = 98/2) to yield **4E** (1.68 g, 76%), ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.16-7.31 (Aro, 5H), 6.5 (d.t., 1H, J = 14.3, 1.2 Hz), 6.06 (d.t., 1H, J = 14.3, 7.15 Hz), 3.43 (d.d., 2H J = 7.15, 1.2 Hz); ^{13}C (50 MHz, $CDCl_3$) δ 141.0, 135.0, 131.0, 129.2, 127.2, 78.7, 39.6.

(S*,S*)-3,4-dimethyl-5-(N,N-diethyl)-aminopent-1-ene 7*anti*

To a solution of **3(Z)** (716.7 mg, 3 mmol) in Et_2O (20 mL) was added at -78°C, 2 equiv of *ter*-BuLi (1.7 M solution in hexane, 3.5 mL, 6 mmol). The solution was warmed to -65°C for 10 mn to complete the lithium-iodine exchange, and then, at -60°C, 2 equiv of crotylmagnesium bromide were added (0.94M solution in Et_2O, 6.4 mL, 6 mmol) and 2 equiv of $ZnBr_2$ in Et_2O were slowly added at -50°C (1M solution in Et_2O, 6 mL, 6 mmol). The reaction mixture was stirred at -40°C for 4h 30 min and the quantitative formation of the adduct **7** is checked by TLC. The hydrolysis was done with an aqueous solution of (ammonia 33% / sat.ammonium chloride) in the ratio of (1/2). The aqueous phase was extracted twice with ether (2 x 20 mL) and the combinated organic phases were treated overnight with an aqueous solution of Na_2S and then washed with $NaHCO_3$ (2 x 20 mL), dried over Na_2CO_3 and concentrated *in vacuo*. The residue was chromatographed on Al_2O_3 (eluent : cyclohexane / ethyl acetate = 9/1), to yield **7*anti;*** (330 mg, 65%) d. r. : 91/9 I.R. ν_{max} 2950, 2920, 2860, 2590, 1450, 1380, 1200, 1060, 995, 905 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.72 (m, 1H), 5.00 (m, 2H), 2.50 (q, 4H, J = 7.1 Hz), 2.29 (m, 1H), 2.28 (dd, 1H, J = 6.5, 12.6 Hz), 2.05 (dd, 1H, J = 7.8, 12.7 Hz), 1.60 (m, 1H), 1.03 (d, 3H, J = 7.0 Hz), 1.00 (t, 6H, J = 7.1 Hz), 0.84 (d, 3H, J = 7.0 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 141.6, 114.0, 57.9, 47.5, 40.0, 36.3, 17.8, 13.1, 11.7; Anal. Calcd for $C_{11}H_{23}N$: C, 78.63; H, 13.69; Found: C, 79.21; H, 13.72.

(3S*,4R*)-dimethyl-5-(N,N-diethyl)-aminopent-1-ene 7*syn*

The same procedure as described for **7*anti*** was used, from **3E** (378 mg, 1.58 mmol), and the residue was chromatographed on Al_2O_3 (eluent : cyclohexane / ethyl acetate = 9/1) to yield **7*syn;*** (300 mg, 60 %) d.r. : 92/8 ^1H NMR (200 MHz, $CDCl_3$) δ 5.75 (m, 1H), 4.95 (m, 2H), 2.46 (q, 4H, J = 7.0 Hz), 2.31 (dd, 1H, J = 6.0, 13.1 Hz), 2.24 (m, 1H), 2.04 (dd, 1H, J = 8.4, 13.1 Hz), 1.62 (m, 1H), 0.96 (t, 6H, J = 7.5 Hz), 0.91 (d, 3H, J = 6.8 Hz), 0.80 (d, 3H, J = 5.8 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 144.1, 112.9, 57.5, 47.5, 39.8, 37.5, 18.7, 14.4, 11.7.

(S*,S*)-3,4-dimethyl-5-phenylthiopent-1-ene 8*anti*

To a solution of **4(Z)** (551 mg, 2 mmol) in Et_2O (20 mL) was added at -78°C, 2 equiv of *ter*-BuLi (1.6 M solution in hexane, 2.5 mL, 4 mmol). The solution was warmed to -65°C for 10 mn to complete the lithium-iodine exchange, and then, at -60°C, 2 equiv of crotylmagnesium bromide were added (0.73M solution in Et_2O, 5.5 mL, 4 mmol) and 2 equiv of $ZnBr_2$ in Et_2O were slowly added at -50°C (1M solution in Et_2O, 4 mL, 4 mmol). The reaction mixture was stirred at -45°C for 4h and the quantitative formation of the adduct **8*anti*** was checked by GC. The hydrolysis was done with an aqueous solution of hydrochloric acid (1N solution, 20 mL). The aqueous phase was extracted twice with ether (2 x 20 mL) and the combinated organic phases were washed with HCl 1N (2 x 20 mL). The organic layer was treated overnight with an aqueous solution of Na_2S, then washed with $NaHCO_3$ (2 x 20 mL) and then dried over $MgSO_4$ and concentrated *in vacuo*. The residue was chromatographed on SiO_2 (eluent : cyclohexane / ethyl acetate 95/5). to yield **8*anti*** : (230 mg, 56%); d.r.: 95/5; I.R. ν_{max} 3060, 2950, 2905, 2830, 1580, 1470, 1445, 1430, 1370, 1020, 995, 910, 770, 685 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.11-7.34 (Aro, 5H), 5.7 (m, 1H), 5.05 (m, 1H), 4.98 (m, 1H), 2.99 (dd, 1H, J = 5.8, 12.6 Hz), 2.69 (dd, 1H, J = 7.9, 12.6 Hz), 2.38 (m, 1H), 1.72 (m, 1H), 1 (d, 3H, J = 7.7 Hz), 0.97 (t, 3H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 137.5, 129.1, 128.9, 125.8, 114.9, 41.4, 39.1, 37.8, 17.5, 15.6. Anal. Calcd for $C_{13}H_{18}S$: C, 75.67; H, 8.79, Found: C, 75.72; H, 8.82.

(3S*,4R*)-dimethyl-5-phenylthiopent-1-ene **8*syn***

The same procedure as above was used, starting from **4(E)** (550 mg, 2 mmol);to yield **8*syn*** (65%, 270 mg); d.r.: 95/5; I.R. ν max 3060, 2950, 2905, 2830, 1580, 1470, 1445, 1430, 1370, 1020, 995, 910, 770, 685 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.11-7.34 (m, 5H), 5.71 (m, 1H), 5.02 (m, 1H), 4.96 (m, 1H), 3.08 (dd, 1H, *J* = 4.9, 12.6 Hz), 2.64 (dd, 1H, *J* = 8.8, 12.7 Hz), 2.25 (m, 1H), 1.7 ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 137.3, 129.1, 128.9, 125.6, 114.1, 41.7, 38.7, 37.4, 15.8, 15.5.

The same procedure as above was used, starting from prop-1(Z)-enyl-lithium (5 mL, 0.65 N, 3.25 mmol), 2 equiv of crotylmagnesium chloride (8.9 mL, 0.73 N) and 6.5 mL $ZnBr_2$ (1 M in ether). The reaction mixture was stirred at -45°C for 5h, then 2 equiv of propan-(2)-ol in solution in toluene (2 mL, 1 M) were added,and the resulting organozinc derivative was transmetalated into organocuprate with $Me_2CuCNLi_2$ [prepared from 291 mg of CuCN in 25 mL of ether and 2 equiv of MeLi (3.78 mL, 1.71 N)]. After stirring for 30 mn at -20°C, 2 equiv of diphenyldisulfide (1.417 g, 6.5 mmol) were added. The hydrolysis was done with an aqueous solution of hydrochloric acid (1N solution, 20 mL). The aqueous phase was extracted twice with ether (2 x 20 ml) and the combinated organic phases were washed with HCl 1N (2 x 20 mL). The organic layer was treated overnight with an aqueous solution of Na_2S, then washed with $NaHCO_3$ (2 x 20 mL) and then dried over $MgSO_4$ and concentrated *in vacuo*. The residue was chromatographed on SiO_2 (eluent : cyclohexane / ethyl acetate 95/5) to give **8syn** in 54% yield (225mg) d.r.: 95/5.

1-iodo-3-methylthiohept-1(Z)-ene **10**

To a solution of 1-iodohept-1(Z)-en-3-ol (4.8 g, 20 mmol), in toluene (40 mL) were sequentially added 3 equiv of tributylphophine (12.12 g or 14.8 mL, 60 mmol) and 3 equiv of dimethyldisulfide (5.64 g, 60mmol). The reaction mixture was stirred overnight and the formation of the adduct was checked by TLC. The hydrolysis was done with a solution of sodium hydoxide (80mL, 1M), the aqueous phase was extracted twice with ether (2 x 20 mL) and the combinated organic phases were washed with water (10 mL) then dried over $MgSO_4$ and evaporated *in vacuo*. The residue was chromatographed on SiO_2 (eluent : cyclohexane) to yield **10** (3.3 g, 61%), I.R. ν max 2950, 2900, 2850, 1460, 1430, 1380, 1300, 1290, 1270, 1250, 1230 , 685 cm^{-1}; ^{1}H NMR (200, $CDCl_3$) δ 6.62 (d.t, 1H, *J* = 14.3, 6.6 Hz), 6.30 (d, 1H, *J* = 14.3 Hz), 3.15 (d, 2H, *J* = 6.6 Hz), 2.59 (q, 4H, *J* = 7.1 Hz), 1.07 (t, 6H, *J* = 7.1 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 142.5, 82.8, 50.1, 33.7, 29.6, 22.9, 14.4, 14.3 ; Anal. Calcd for $C_8H_{15}IS$: C, 35.57; H, 5.60, Found: C, 35.83; H, 5;66.

3-(N-benzyl)-amino-1-trimethylsilylbut-1-yne

To a solution of bistrimethylsilylacetylene (17 g, 100 mmol) in THF was added at -20° C 1 equiv of methyllithium in ether (100 mL, 100 mmol), the mixture was warmed to room temperature for 2 hours and then 1 equiv of BF_3,OEt_2 (12.3 mL, 100 mmol) was added at -78°C. After stirring for 10 mn 1 equiv of N-benzylethanimine (13.3 g,100 mmol) was added, the mixture was stirred at the same temperature for 1 h and was allowed to warmed to room temperature for 1 hour. The hydrolysis was done with an aqueous solution of NaOH (100 mL, 10 %). The aqueous phase was extracted three times with ether (3 x 20 ml) and the combinated organic phases were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was chromatographed on SiO_2 (eluent : cyclohexane / ether = 1/1) to yield the title compound (12 g, 50%); ^{1}H NMR (400, $CDCl_3$) δ 7.28-7.41 (Aro, 5H), 4.03 (d, 1H, *J* = 12.7 Hz), 3.84 (d, 1H, *J* = 12.7 Hz), 3.51 (q, 1H, *J* = 7.1 Hz), 1.38 (d, 3H, *J* = 6.6 Hz), 0.17 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 139.8, 128.6, 128.2, 126.9, 108.4, 87.0, 51.2, 44.9, 22.1, 0.1.

3-(N,N-dibenzyl)-amino-1-trimethylsilylbut-1-yne

To a solution of N-benzyl-1-trimethylsilyl-but-1-yn-3-amine (6 g, 26 mmol), in acetonitrile (50 mL) were added 2 equiv of benzyl bromide (6.18 mL, 52 mmol) followed by 2 equiv of sodium carbonate (5.51 g, 52 mmol). Then, water (20 mL) was added and the aqueous phase was extracted twice with ether and the combinated organic phases were washed with $NaHCO_3$ (2 x 20 mL). The organic layer was dried over Na_2CO_3 and concentrated *in vacuo* to give after purification, the title compound in 33% yield (2.74 g); ^{1}H NMR (400, $CDCl_3$) δ 7.19-7.41 (Aro, 10H), 3.58 (q, 1H, J = 7.0 Hz), 3.78 (d, 2H,J = 13.8 Hz), 3.38 (d, 2H J = 13.8 Hz), 1.31 (d, 3H, J = 7.1 Hz), 0.23 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 139.9, 128.7, 128.2, 126.8, 105.2, 88.5, 54.7, 47.3, 20.0, 0.4.

3-(N,N-dibenzyl)-aminobut-1-yne

To a solution of N,N-dibenzyl-1-trimethylsilyl-but-1-ynyl-3 amine (2.74 g, 8.53 mmol) in wet dimethylformamide (30 mL) was added 1.17 equiv of potassium fluoride (500 mg, 10 mmol). The mixture was stirred overnight at room temperature.Then brine (20 mL) was added and the aqueous phase was extracted twice with ether (2 x 20 mL) and the combinated organic phases were washed with $NaHCO_3$ (2 x 20 mL). The organic layers were dried over Na_2CO_3 and concentrated *in vacuo*. The residue was used without further purification. (Yield 87.3 %).^{1}H NMR (400, $CDCl_3$) δ 7.20-7.41 (Aro, 10H), 3.58 (qd, 1H, J = 7.2, 2.0 Hz), 3.81 (d, 2H,J = 14.0 Hz), 3.41 (d, 2H J = 14.0 Hz), 1.35 (d, 3H, J = 7.2 Hz), 2.30 (d, 1H, 2Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 140.0, 128.9, 128.4, 127.1, 82.9, 72.2, 54.8, 46.6, 20.2.

3-(N,N-dibenzyl)-amino-1-iodobut-1-yne

To a solution of N,N-dibenzyl-but-1-ynyl-3-amine (1.85 g, 7.44 mmol) in THF (20 mL) was added at -20°C 1.2 equiv of nBuLi (5 mL 1.6 N in hexane). This solution was warmed to room temperature for 30 mn then cooled to -50°C and 1.2 equiv of iodine (2 g dissolved in 20 mL of THF) was added, the reaction mixture was allowed to warm overnight to room temperature. The hydrolysis was done with a solution of sodium hydoxyde (10 mL, 1N), the organic layer was washed with a solution of Na_2SO_3, and then the aqueous phase was extracted twice with ether (2 x 20 mL) and the combinated organic phases were washed with water, dried over Na_2CO_3 and concentrated *in vacuo* to yield the title compound (2.63 g, 94%); ^{1}H NMR (400, $CDCl_3$) δ 7.24-7.45 (Aro, 10H), 3.85 (d, 2H, J = 13.8 Hz), 3.74 (q, 1H,J = 7.0 Hz), 3.43 (d, 2H J = 13.8 Hz), 1.37 (d, 3H, J = 7.0 Hz); ^{13}C (50 MHz, $CDCl_3$) δ 139.8, 128.9, 128.4, 127.1, 94.6, 55.0, 48.9, 20.3, -1.9.

3-(N,N-dibenzyl)-amino-1-iodobut-1(Z)-ene 11

To a stirred solution of N,N-dibenzyl-1-iodo-but-1-ynyl-3-amine (2.63 g, 7 mmol) in MeOH (10 mL) were added 3.5 mL of pyridine, dipotassium azodicarboxylate (1.71 g, 8.85 mmol) and acetic acid (1mL added in five portions during two hours).The reaction mixture was stirred overnight and dipotassium azodicarboxylate (514 mg), acetic acid (0.3 mL) were added again. The hydrolysis was done with an aqueous solution of hydrochloric acid (1N solution, 20 mL). The aqueous phase was extracted twice with ether (2 x 20 mL) and the combinated organic phases were washed with HCl 1N (2 x 20 mL). dried over $MgSO_4$ and concentrated *in vacuo*. The residue was chromatographed on SiO_2 (eluent : cyclohexane / ethyl acetate 95 / 5) to yield **11** (2.12 g, 80.3%); ^{1}H NMR (400, $CDCl_3$) δ 7.24-7.41 (Aro, 10H), 6.40 (m., 2H), 3.83 (d, 2H, J = 13.9 Hz), 3.64 (m, 1H), 3.49 (d, 2H J = 13.9 Hz), 1.23 (d, 3H, J = 7.0 Hz); ^{13}C (50 MHz, $CDCl_3$) δ 140.7, 139.7, 128.3, 127.7, 126.7, 83.0, 58.4, 54.3, 17.5.; Anal. Calcd for $C_{18}H_{20}IN$: C, 57.31; H, 5.34 Found: C, 57.48; H, 5.45.

(S*,S*)-4-methyl-5-methylthionon-1-ene 13*syn*

The same procedure as for **8*anti*** was used, starting from **10** (540 mg, 2 mmol); 2 equiv of allylmagnesium bromide (instead of crotylmagnesium bromide) and 2 equiv of $ZnBr_2$ in Et_2O were added. The reaction mixture was stirred at -30°C for 5h and the quantitative formation of the adduct **13*syn*** was checked by GC to yield the title compound. The residue was chromatographed on SiO2 (eluent : cyclohexane / ethyl acetate 95/5) (242 mg, 65 %); d.r. >98/2 ; ^1H NMR (400 MHz, $CDCl_3$) δ 5.77 (m, 1H), 5.02 (m, 1H), 2.46 (m, 1H), 2.33 (m, 1H), 2.08 (s, 3H), 1.98 (m, 1H), 1.81 (m, 1H), 1.51 (m, 2H), 1.30 (m, 4H), 0.91 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 116.0, 53.6, 38.7, 36.7, 32.7, 30.0, 22.7, 15.6, 15.5., 14.1 Anal. Calcd for $C_{11}H_{22}S$: C, 70.90; H, 11.90, Found: C, 70.98; H, 12.21.

(S*,S*)-4-methyl-5-(N,N-dibenzyl)-aminohex-1-ene 14*syn*

The same procedure as described for **7*anti*** was used, starting from **11** (753.8 mg, 2 mmol), 2 equiv of allylmagnesium bromide (instead of crotylmagnesium bromide) and 2 equiv of $ZnBr_2$ in Et_2O were added. The reaction mixture was stirred at -30°C for 5h and the quantitative formation of the adduct **14*syn*** was checked by TLC to yield the title product as a pale yellow liquid. After purification on silica gel (cyclohexane / ethyl acetate : 8/2) 440 mg of **14*syn*** was obtained. (75%) d. r. : >95/5; ^1H NMR (400 MHz, $CDCl_3$) δ 7.27-7.50 (aro, 10 H), 5.75 (m, 1H), 5.02 (m, 2H), 3.86 (d, 2H, J = 13.8 Hz), 3.41 (d, 2H, J = 13.8 Hz), 2.46 (m, 1H), 2.26 (m, 1H), 1.76 (m, 2H), 1.12(d, 3H, J = 6.6 Hz), 1.09 (d, 3H, J = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 137.3, 128.9, 128.2, 126.7, 115.7, 58.0, 57.2, 38.6, 36.8, 17.3, 9.7 Anal. Calcd for $C_{21}H_{27}N$: C, 85.95; H, 9.27, Found: C, 86.21; H, 9.36.

(S*,S*,S*)-3,4-dimethyl-5-methylthionon-1-ene 15

The same procedure as for **8*anti*** was used, starting from **10** (540 mg, 2 mmol); 2 equiv of crotylmagnesium bromide and 2 equiv of $ZnBr_2$ in Et_2O were added. The reaction mixture was stirred at -30°C for 5h and the quantitative formation of the adduct **15** was checked by GC. After purification on silica gel (cyclohexane / ethyl acetate : 95/5) 250mg of **15** was obtained (62%); d. r. : >95/5; ^1H NMR (400 MHz, $CDCl_3$) δ 5.67 (m, 1H), 4.97 (m, 1H), 2.57 (m, 1H), 2.37 (m, 1H), 2.09 (s, 3H), 1.65 (m, 2H), 1.45 (m, 1H), 1.35 (m, 4H), 1.02(d, 3H, J = 6.7 Hz), 0.92 (t, 3H, J = 7.1 Hz), 0.88 (d, 3H, J = 6.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 113.9, 51.0, 41.2, 41.1, 33.7, 29.6, 22.7, 19,1, 15.0, 14.1., 13.0 Anal. Calcd for $C_{12}H_{24}S$: C, 71.93; H, 12.07, Found: C, 72.24; H, 12.28

(S*,S*,S*)-3,4-dimethyl-5-(N,N-dibenzyl)-aminohex-1-ene 16

The same procedure as above was used, starting from **11** (753.8 mg, 2 mmol), 2 equiv of crotylmagnesium bromide and 2 equiv of $ZnBr_2$ in Et_2O were added. The reaction mixture was stirred at -30°C overnight and the quantitative formation of the adduct **16** was checked by TLC. After purification on silica gel (cyclohexane / ethyl acetate : 8/2) 445 mg of **16** were obtained (72%) d.r. >95/5; ^1H NMR (400 MHz, $CDCl_3$) δ 7.16-7.40 (aro, 10 H), 5.47 (m, 1H), 4.81 (m, 2H), 3.75 (d, 2H, J = 13.6 Hz), 3.30 (d, 2H, J = 13.6 Hz), 2.43 (m, 1H), 2.30 (m, 1H), 2.02 (d, 3H, J = 6.5 Hz), 1.54 (m, 1H), 0.97(d, 3H, J = 6.9 Hz), 0.1 (d, 3H, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 138.8, 128.9, 128.1, 126.4, 114.3, 58.0, 53.8, 42.1, 38.2, 19.6, 11.6, 9.6 Anal. Calcd for $C_{22}H_{29}N$: C, 85.94; H, 9.51 Found: C, 86.26; H, 9.68.

(S*,S*)-3,4-dimethyl-1-trimethylsilyl-non-1-yne 19*anti*

To a solution of 1(Z)-iodohept-1-ene (448 mg, 2 mmol) in Et_2O (20 mL) was added at -78°C, 2 equiv of *ter*-BuLi (1.6 M solution in hexane, 2.5 mL, 4 mmol). This solution was warmed to -65°C for 10 mn to complete the lithium-iodine exchange, and then, at -60°C, 2 equiv of magnesium bromide were added (4 mmol), and 2 equiv of 1-trimethylsilyl-3-bromozinca-but-1-yne in Et_2O [prepared by metalation of 1-trimethylsilyl-butyne (4 mmol, 504 mg) in Et_2O (20 mL) at -40°C by addition of 1.3 equiv of sBuLi in hexane (4 mL, 1.3 M, 4 mmol) .Then, the reaction mixture was allowed to warm to room temperature (the deprotonation was followed by GC, the equilibrium alcyne / allene is detected) and 1.3 equiv. of $ZnBr_2$ was added at -30°C (5.2 mL, 1M in Et_2O) to give the corresponding allenyl zinc bromide] The reaction mixture was stirred at -20°C for 4h and the quantitative formation of the adduct **19*anti*** was checked by GC. The hydrolysis was done with an aqueous solution of hydrochloric acid (1N solution, 20 mL). The aqueous phase was extracted twice with ether (2 x 20 mL) and the combinated organic phases were washed with HCl 1N (2 x 20 mL). The organic layer was treated overnight with an aqueous solution of Na_2S, then washed with $NaHCO_3$ (2 x 20 mL) and then dried over $MgSO_4$ and concentrated *in vacuo*. The residue was chromatographed on SiO_2 (eluent : cyclohexane / ethyl acetate 98/2) to yield **19*anti*** : (304.7 mg, 68%) d.r.> 95/5; I.R. ν_{max} 2950, 2920, 2860, 2850, 2160, 1450, 1375, 1430, 1245, 900, 840, 755, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.51 (m, 1H), 1.43 (m, 2H), 1.18-1.36 (m, 7H), 1.14 (d, 3H, J = 6.9 Hz), 0.93 (d, 3H, J = 6.2 Hz), 0.91 (t, 3H, J = 7.0 Hz), 0.16 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.7, 85.1, 37.7, 35.0, 32.1, 31.8, 26.9, 22.7, 18.7, 15.5, 14.2, 0.4; Anal. Calcd for $C_{14}H_{28}Si$: C, 74.57; H, 12.57, Found: C, 74.28; H, 12.72.

The same procedure as above was used, starting with 1-iodohept-1(E)-ene (448 mg, 2 mmol) to yield (300 mg, 67%) of **19*anti*** ; d.r.> 95/5.

(3R*,4S*)-dimethyl-non-1-ene 20*anti*

To a solution of **19*anti*** (500 mg, 2.22 mmol) in ether (20 mL) was added 2 eq of DIBAL-H (4.5 mL, 1 M in hexane). The mixture was heated until reflux of the solvent and the formation of the reduced product was checked by GC. The hydrolysis was done with an aqueous solution of hydrochloric acid (1N solution, 10 mL). The aqueous phase was extracted twice with ether (2 x 20 mL) and the combinated organic phases were dried over $MgSO_4$ and concentrated in vacuo. After purification on silica gel (cyclohexane / ethyl acetate 98/2) (3S*,4R*)-dimethyl-1-trimethylsilyl-non-1(Z)-ene was isolated as a pure oil (372mg, 73.7%) d.r.>95/5; ^1H NMR (400 MHz, $CDCl_3$) δ 618 (dd, 1H, J = 10.4, 14 Hz), 5.43 (d, 1H, J = 14 Hz), 2.19 (m, 1H), 1.2 -1.4 (m, 8H), 1.1 (m, 1H), 0.96 (d, 3H, J = 6.8 Hz), 0.91 (t, 3H, J = 6.8 Hz), 0.87 (d, 3H, J = 6.8 Hz), 0.13 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 127.2, 42.9, 38.1, 34.1, 32.3, 26.9, 22.8, 18.9., 16.7, 14.2, 0.6. Anal. Calcd for $C_{14}H_{30}Si$: C, 74.25; H, 13.35, Found: C, 74.44; H, 14.05.

To a solution of (3S*, 4S*)-dimethyl-1-trimethylsilylnon-1(Z)-ene *anti* (372 mg, 1.64mmol) in DMF was added KF,DMF in the presence of few drops of water. The mixture was stirred at room temperature and the formation of (3S*, 4R*)-dimethyl-non-(1)-ene **20*anti*** was checked by GC. The hydrolysis was done with an aqueous solution of brine (10 mL). The aqueous phase was extracted twice with ether (2 x 20 mL) and the combinated organic phases were dried over $MgSO_4$ and concentrated *in vacuo* to yield **20*anti*** (198 mg, 78 %) d.r. >95/5; ^1H NMR (200 MHz, $CDCl_3$) δ 5.68 (m, 1H), 4.89 (m, 2H), 2.05 (m, 1H), 1.1 -1.4 (m, 8H), 1.05 (m, 1H), 0.94 (d, 3H, J = 6.8 Hz), 0.84 (t, 3H, J = 6.5 Hz), 0.77 (d, 3H, J = 6.6 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 142.5, 113.4, 42.3, 37.8, 34.1, 32.2, 27.1, 22.8, 17.3., 16.0, 14.1.

(3R*,4S*)-dimethyl-1-trimetylsilyl-5-terbutoxy-pent-1-yne 21*anti*

The same procedure as described for **19*anti*** was used, starting with 1-iodo-3-terbutoxy-prop-1(Z)-ene (480 mg, 2 mmol) to yield the title compound (280 mg, 60%); d.r.> 95/5; ^1H NMR (400 MHz, $CDCl_3$) δ 3.31 (t, 1H, J = 8.6 Hz), 3.21 (dd, 1H, J = 8., 5.2 Hz), 2.85 (qd, 1H, J = 7.2, 4.0 Hz), 1.64 (m, 1H), 1.21 (s, 9H), 1.15 (d, 3H, *J* = 7.2 Hz), 0.91 (d, 3H, *J* = 7.2 Hz), 0.14 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 109.6, 85.2, 72.5, 65.2, 28.0, 27.6, 18.7, 11.8, 0.24. Anal. Calcd for $C_{14}H_{28}OSi$: C, 69.93; H, 11.74, Found: C, 69.53; H, 11.92.

(3R*,4S*)-dimethyl-1-trimetylsilyl-5-(N,N-diethyl)-aminopent-1-yne 22*anti*

The same procedure as described for **19*anti*** was used, starting with 3-(N,N diethyl)-amino-1-iodoprop-1(Z)-ene **3Z** but after the quantitive formation of the bismetallic, the hydrolysis was done with an aqueous solution of 20 mL of ammonia 33% / sat.ammonium chloride (ratio of 1/2). The aqueous phase was extracted twice with ether (2 x 20 mL) and the combinated organic phases were treated overnight with an aqueous solution of Na_2S and then washed with $NaHCO_3$ (2 x 20 mL), dried other $MgSO_4$, and concentrated *in vacuo*. The residue was chromatographed on SiO_2 (eluent : cyclohexane /ethyl acetate : 8/2), yield of (340 mg, 71%); d. r. > 95/5; ^1H NMR (400 MHz, $CDCl_3$) δ 2.84 (qd, 1H, *J* = 7.1, 3.5 Hz), 2.49 (m, 5H),2.15 (dd, 1H, *J* = 13.0., 6.0 Hz), 1.59 (m, 1H), 1.15 (d, 3H, *J* = 7.1 Hz), 1.02 (d, 6H, *J* = 7.1 Hz), 0.90 (d, 3H, *J* = 7.1 Hz), 0.15 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.1, 85.3, 58.3, 48.0, 36.5, 29.3, 18.9, 12.3, 12.1., 0.35; Anal. Calcd for $C_{14}H_{29}NSi$: C, 70.22; H, 12.21 Found: C, 70.59; H, 12.41.

(3R*,4S*)-4-methyl-1-trimetylsilyl-3-pentyl-5-terbutoxypent-1-yne 23*anti*

The same procedure as described for **19*anti*** was used, starting from the 1-iodo-3-terbutoxyprop-1(Z)-ene (480 mg, 2 mmol) with 2 equiv of 1-trimethylsilyl-3-bromozinca-oct-1-yne (4 mmol) in Et_2O to yield 404 mg of **23*anti*** (69%); d.r.> 98/2; ^1H NMR (400 MHz, $CDCl_3$) δ 3.31 (t, 1H, *J* = 8.4 Hz), 3.19 (dd, 1H, *J* = 8.8, 5.2 Hz), 2.66 (m, 1H), 1.68 (m, 1H), 1.48 (m, 2H), 1.34 (m, 6H), 1.18 (s, 9H), 0.89 (m, 6H), 0.13 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 108.8, 86.2, 72.5, 65.4, 36.9, 34.3, 32.9, 31.8, 27.7, 18.7, 11.8, 0.1 Anal. Calcd for $C_{18}H_{36}OSi$: C, 72.90; H, 12.24, Found: C, 72.98 H, 12.45.

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