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Studies Towards the Total Synthesis of Pentacyclic Triterpenes of the Arborane and Fernane Family

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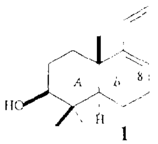
Abstract: *Stereo- and regiochemical variations in conjugate addition reactions leading to isoarborinol and fernenol-like triterpenes via a five-step protocol are described. The Grignard addition on 9, 10, 15, 18 served to establish the relative stereochemical details.*

In connection with our work on the synthesis of pentacyclic triterpenes, we have investigated several ways for assembling the C-ring using a Diels-Alder strategy.[1] In a successful approach to the pentacyclic ring system characteristic of isoarborinol and its CDE-antipodal fernenol, we demonstrated that the Diels-Alder reaction of the diene 1 and the quinone 2 could be efficiently controlled using suitable Lewis acid catalysts.[2] An appropriate manipulation of the functionalities in the D-ring followed by the introduction of the E ring furnished isoarborinol 3 and fernenol 4 derivatives.[3]



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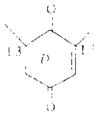

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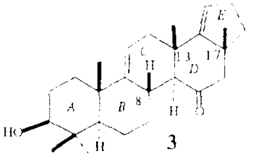

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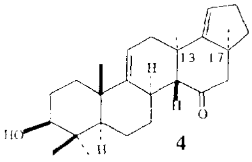

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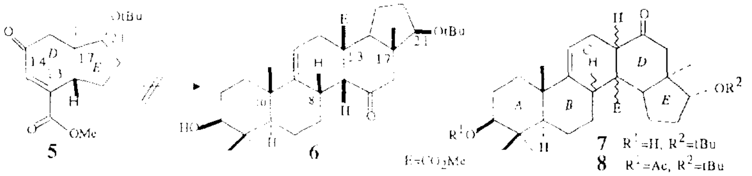


5 6 E=CO₂Me
7 R¹=H, R²=tBu
8 R¹=Ac, R²=tBu

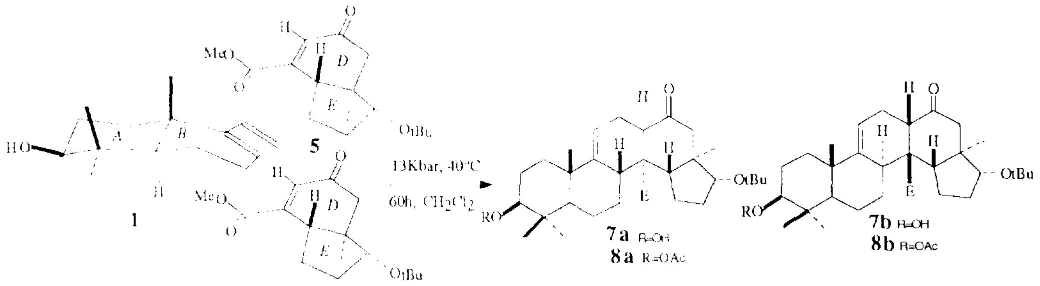
An attractive alternative to this approach would incorporate the D/E rings into the dienophilic partner. Such a convergent synthesis joining the AB and DE ring precursors 1 and 5 should correctly situate the chiral centers at C-10 and C-17 and furthermore ensure the right orientation. We reported the preparation of the D/E ring dienophile 5, that we anticipated would deliver the isoarborinol skeleton if the C-2 carbonyl group guided *endo*-addition to the diene 1, setting up the stereogenic centers present on the pentacyclic backbone. The ester group should initially serve to activate the dienophile during the cycloaddition[4] before its transformation to the C-13 angular methyl substituent, thus satisfying our prerequisites.

This plan was thwarted, as we shall first show, by the wrong orientation of the reactants. However, we report also in this paper the combined use of regio- and stereochemical variations of the Diels-Alder reaction and of nucleophilic additions on the resulting adducts in the construction of selected pentacyclic targets.

Results and discussions

The AB+DE route:

Whereas under thermal or catalyzed conditions, partners **1** and **5** did not react,.the high pressure-mediated Diels-Alder reaction (13 kbar), of diene **1** (2mmol) with dienophile **5** (2mmol) in dry dichloromethane afforded 68% of adducts **7a** and **7b** in a 1:1.2 ratio respectively. The carbonyl thus prefered an *exo*-orientation and led to the unnatural skeleton **7**, the ester group having served both as a good activating group and as an exclusive control element. The formation of the two diastereomers **7a** and **7b** results from the top and bottom face attacks of the dienophile to the diastereotopic faces of the diene **1** (approach of the dienophile *anti* to the C-10 angular methyl group was expected to be prefered). It should be pointed out that the DE dienophile with a *cis* ring junction[5] was recovered intact under the same reaction conditions with diene **1**.



Structural assignements (orientation and *syn/anti*, *endo/exo* selectivities), first deduced from a high field NMR analysis (at 400 and 600 MHz), using the 1D NOEDIFF[6] technique in combination with two-dimensional experiments, were later supported by a computer-assisted conformational analysis via Still's Macromodel Program.[7] The stereochemical analysis of this reaction left some ambiguities as "no observation" of nuclear Overhauser enhancements cannot be construed as a positive structural proof, especially when proximities may be altered by the adopted conformation. An unambiguous answer (Figure 1) was obtained by X-ray crystallography[8] of the 3β-acetate of **7a**, confirming what had been deduced from the NMR data and molecular dynamics. Since the synthetis was performed on optically homogeneous segments for both the diene and dienophile, Figure 1 represents the relative and absolute configurations on all stereogenic centers.

The 3β-acetate derivative of **7b**, which did not give suitable crystals for X-ray analysis, was useful in differentiating between the free (A-ring) and the tBu-protected hydroxy spin systems (E-ring) by shifting the free hydroxy-associated resonances downfield. Assignement of all methyls and ring protons was straightforward using ^{1}H-^{1}H, ^{1}H-^{13}C correlation spectroscopy (long range homo and hetero-coupling experiments included). The signals of the angular methyl groups, which are well separated from each other (600 MHz, resolution enhanced spectra of **7**, **8** in $CDCl_3$) and from most of the ring protons, allowed methyl to methyl, methyl to methine and methyl to methylene n. O. e. measurements. Thus, a series of n.O.e difference experiments on the ring protons (when possible) and methyl signals allowed us to establish a complete set of assignements together with the relative (and absolute) configurations at the newly created centers (C-8, C-13, C-14).

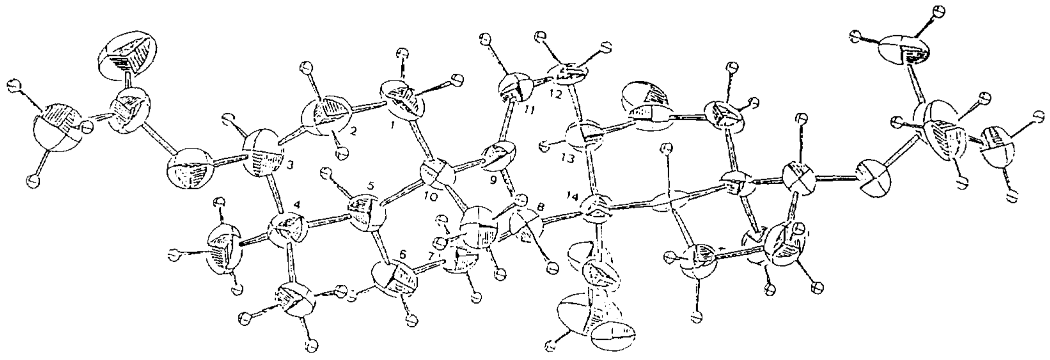
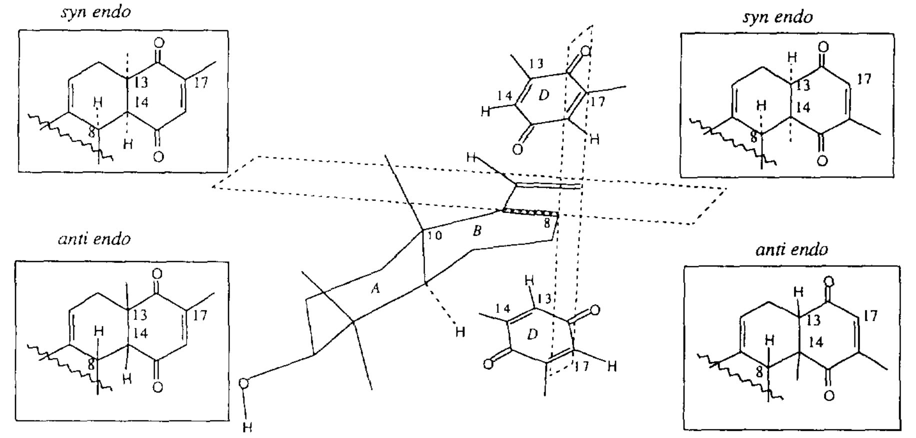


Figure 1: Computer generated drawing of **7a**-3β-acetate derived from the X-ray coordinates .



"meta-endo" Adducts

$AlCl_3$, $BF_3.Et_2O$, $EtAlCl_2$, $SnCl_4$, $TiCl_4$
$Sc(OTf)_3$-DCM or CH_3CN

"ortho-endo" Adducts

Δ, H_2O, High-Pressure, $Eu(fod)_3$
LiCl 5M-H_2O, $Sc(OTf)_3$-H_2O

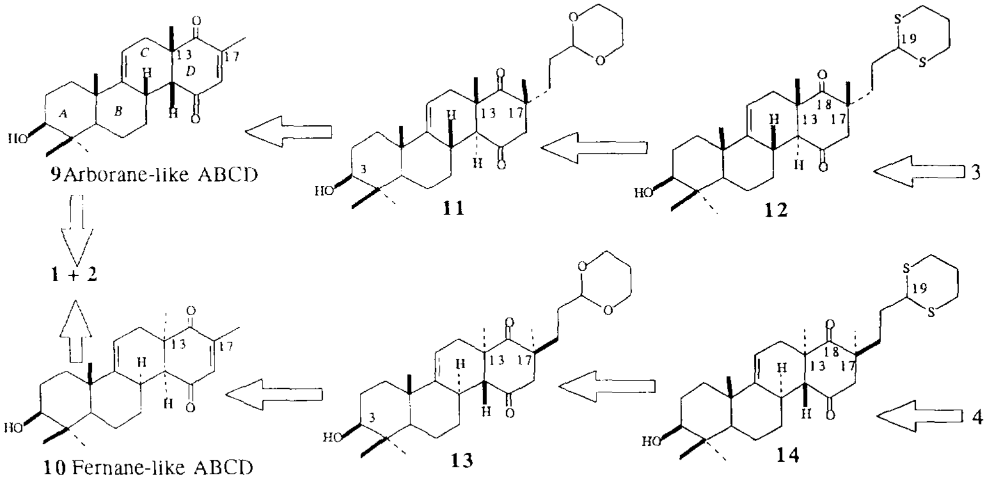
Figure 2

The AB+D--->ABCD-->ABCDE route:

We have shown earlier that the diastereofacial selectivity and orientation can be altered by simply changing the nature of the Lewis acid catalyst or the solvent : better yields of ***meta-anti*** diastereomers (arborane-like) are obtained with $SnCl_4$ or $TiCl_4$, while $AlCl_3$, $EtAlCl_2$ or $BF_3.OEt_2$ give more *meta-syn* adduct (fernane-like, nearly 1:1) (Figure 2).[9] Change of the Lewis acid catalyst could also lead to a reversal of regioselectivity. Thus, Eu^{3+} catalysis increased the reaction rate, but also led exclusively to an *ortho* orientation (opposite to the one obtained by the other Lewis acid catalysts cited above). Scandium triflate, prepared according to Kobayashi's procedure,[10] again favored an *endo* orientation, with comparable facial selectivity, but showed a rather unique "medium dependent" orientation. On the basis of chemical yields and diastereofacial selectivity, $TiCl_4$ was selected as a representative catalyst for the *meta-anti* adducts (arborane precursors) and $AlCl_3$ for the *meta-syn* adducts (fernane precursors).

The synthesis of pentacyclic substances containing the key features found in the natural products of the arborane and fernane families started from common intermediates, the AB-ring precursor **1** and the D-ring precursor **2**, leading to the required tetracyclic targets **15** and **18**. For the elaboration of the E-ring, we used a three carbon homologation, the C-14 center directing the addition and establishing the configuration at the newly created C-17 center. The homologated tetracylic intermediates thus obtained should be readily convertible to 1,3-dithianes by trans-acetalization in the presence of a Lewis acid catalyst, securing the needed "umpolung"[11] for the next carbon-carbon bond forming step. The intramolecular C-18/C-19 carbon bond formation would yield an intermediate such as **38**. The desired chemoselectivity in differentiating the two free carbonyls at C-15 and C-18 would thus be a consequence of the method used (the C-15 carbonyl being enolizable).

With the desired Diels-Alder adducts in hand, the appropriately functionalized C-17 quaternary center was introduced stereo- and regiospecifically by the Grignard addition step. To that end, the tetracyclic intermediates obtained by the suitable Lewis acid catalyzed Diels-Alder reaction were treated either as such or following an epimerization ($NaHCO_3$, MeOH, reflux, 3 h) with the Grignard reagent derived from 2-(2-bromoethyl)-1,3-dioxane at -78°C in THF. The acetal-containing Grignard or organolithium reagents,[12] generated from the



commercially available 2-(2-bromoethyl)-1,3-dioxane are known to undergo 1,2-[13] or 1,4-[14] additions with carbonyl compounds or α,β-unsaturated ketones respectively.

We initially studied the nucleophilic additions on the 3-OTBS protected derivatives, and observed that the products resulting from a 1,4-conjugate addition were mainly deprotected at C-3. When the reactions were repeated on the free 3-hydroxy derivatives **9**, **10**, **15** and **18**, the sole products were **16**, **19**, **11** and **13** respectively (>85%) and in no case did we detect any undesirable by-product. Applying the three-carbon homologation to all four diastereomers (two of them cis and two trans C/D-ring junction), we completed our study on the consequences of varying the C/D-ring junction on facial discrimination during nucleophilic addition and discovered that, depending upon the nature of the C/D-ring junction, we can obtain both configurations at the C-17 stereogenic center. Thus, on the arborane-like cis C/D-ring adducts, the concavity of the α-face controlled the sense of addition, leading to **16**, while on the trans adducts the C-13 angular methyl group hindered the β face, with the nucleophile adding exclusively from the α-face and affording **11** (Figure 3). The regiospecificity is rationalized by MINDO/3 calculations.[15] Thus, the Grignard addition regiospecifically generates a new stereogenic center at C-17, the electrophilic terminus, while proving also to be stereospecific. Isolated yields higher than 88% (exclusive formation of a single diastereomer) were obtained. The regiochemistry of the Grignard addition was in each case easily assigned from the observation of the ^1H signals of the D-ring (characteristic C-16 methylene pattern, C-17 methyl singlet), while the configuration of C-17 was established by n.O.e. studies. Assignements were supported by the determination of interatomic distances, dihedral angles and of the coupling constants for ring protons using the Karplus relationship for the energy minimized structures.

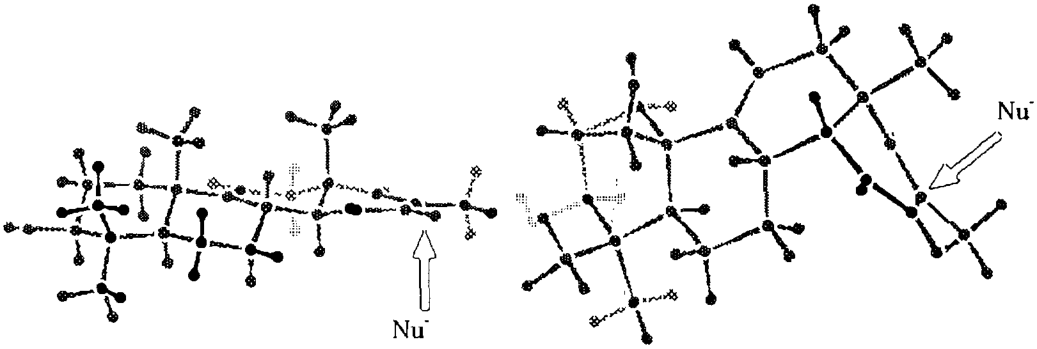
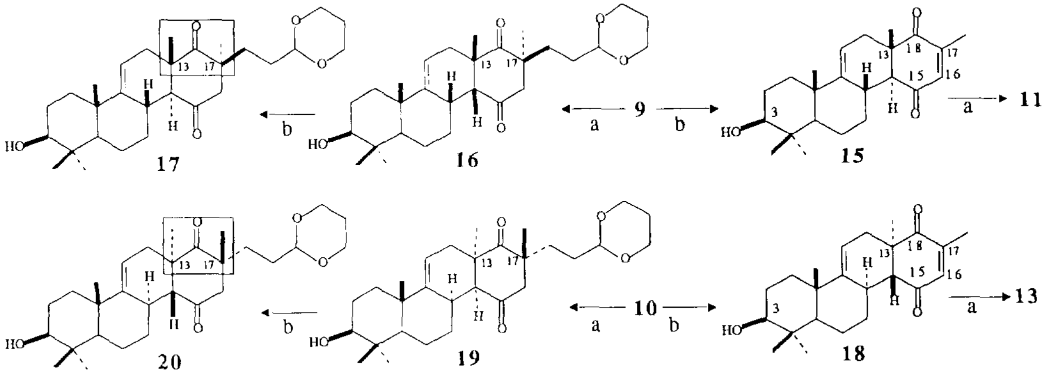


Figure 3 : Lowest energy conformers of **15** and **9** as determined by molecular mechanics calculations.

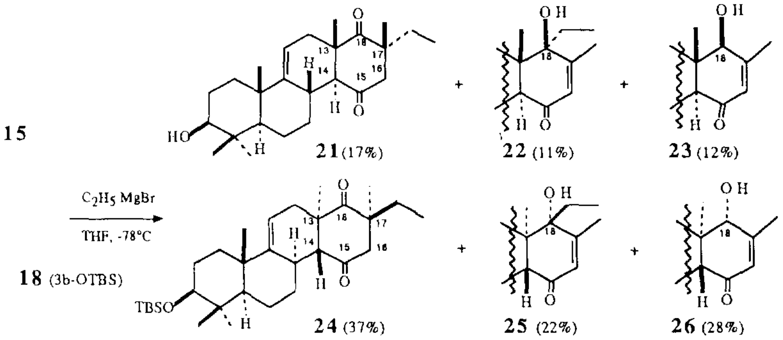
The charge distribution as calculated by MINDO/3, STO-3G, 4-31G showed clearly the C-17 carbon as the electrophilic terminus, thus corroborating the exclusive conjugate addition on C-17. The observed stereospecificity is in agreement with MM2 calculations. In order to rationalize the diastereofacial preference of the conjugate addition, we investigated the reaction of a negatively charged species (the carbanion corresponding to the acetal containing Grignard reagent) with **15**, using MINDO/3 (AM1 gives the same results). A negative charge was brought up to the C-17 carbon along the Bürgi-Dunitz trajectory to both α– and β–faces of the MINDO/3-minimized **15**. The charge to C-17 distance was optimized at 4Å for the α-face approach and at 4.5Å for the β-face approach. Comparing the energies of the optimized systems, we found that the α-face approach was favored over the β-face approach by 2.1 Kcal/mol.

As shown above, the task of establishing the C-17 configurations required the adoption of two divergent protocols. An alternative mode of reactivity on the cis and trans CD-ring junctions, exploiting the diastereofacial preference exhibited in the conversions of **9** to **16**, **15** to **11**, **10** to **19** and **18** to **13**, did provide stereodivergent syntheses of the natural and non-natural (the C-17 configuration being inverted) analogues of arboranes and fernanes.

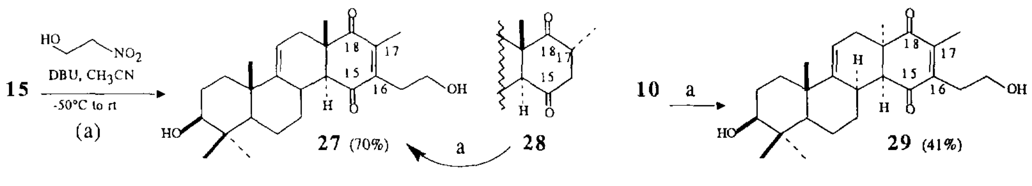


a) 2-(2-bromoethyl)-1,3-dioxane, Mg, THF (reflux 2.5 h), then -78°C, 0.5 h; b) $NaHCO_3$, MeOH, Reflux, 2 h.

We also investigated the reactivity of arborane and fernane-like tetracyclic intermediates towards simple Grignard reagents and other nucleophiles, such as α-nitro alkanes, dithianes and nucleophilic reducing agents. Ethyl magnesium bromide added to **15** and 3β-OTBS-protected **18** (TBSCl, DMF-CH_2Cl_2, 2:8, imidazol, rt, argon, quantitative), in THF at -78°C to give 1,4- (**21**, **24**), 1,2- (**22**, **25**) and reduced adducts (**23**, **26**) :

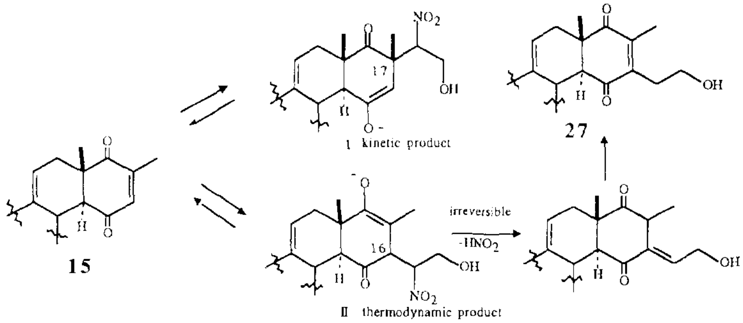


The reaction of **15** and **10** with α-nitro carbanions gave the C-16 substituted compounds **27** and **29**. The conjugate addition of nitroethanol [16] (0.35 mmol) to **15** (0.28 mmol) in CH_3CN (6 ml) was catalyzed by



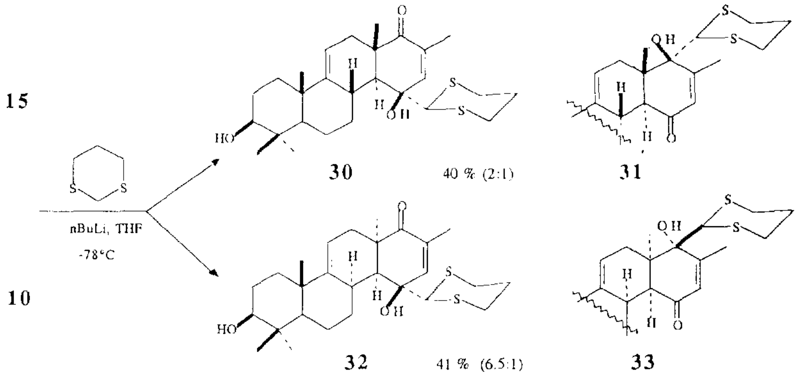
using DBU at -50°C to rt. TLC monitoring indicated that a less polar compound **28**, formed at the beginning, was slowly converted to **27** upon prolonged reaction. Stopping the reaction earlier (after 1 h rt stirring), **28** could be isolated by SiO_2 flash chromatography, characterized, and then converted back to **27** via **15** by simply resubjecting it to the reaction conditions cited above. Similarly, **10** was subjected to the same conditions as above to give **29** (41%).

The overall transformation using α-nitro carbanions (a two-step sequence: Michael addition of the nitroalkane-spontaneous denitration followed by reconjugation) appeared to be a two-carbon homologation process with the C-C bonding occuring at C-16. The regiochemistry of the C-C bond formation could be rationalized by assuming that the conjugate addition of the nucleophile is reversible, both C-16 and C-17 additions occuring competitively. Thus, the overall α-nitro carbanion addition process can be described by equation 1 with the nucleophile adding to the electrophilic positions C-16 and C-17 in the conjugate carbonyl system, to give enolate anions I and II. The reversible addition to C-17 should be faster (kinetic product) than the reversible addition to C-16 (thermodynamic product) and the reverse C-17 addition should ensure formation of **27** as the sole product, following an irreversible spontaneous denitration.

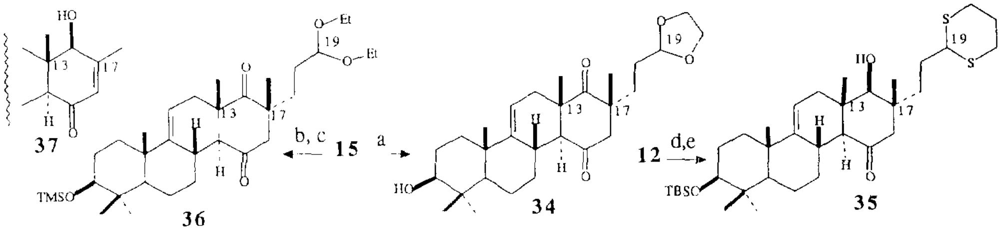


(eq.1)

The use of dithianes as nucleophiles led to exclusive 1,2-addition on both carbonyls. Thus, 2-lithio-1,3-dithiane[17] reacted with **15** at -78°C to rt over 8 h, to give a 40% yield of crude adduct, from which **30** and **31** were obtained after SiO_2 flash chromatography in a 2:1 ratio respectively. Likewise 2-lithio-1,3-dithiane added to enedione **10** to give a 41% yield of a 6.5:1 mixture of 1,2-adducts **32** and **33**. In both runs, *ca* 50% of the starting material was recovered.

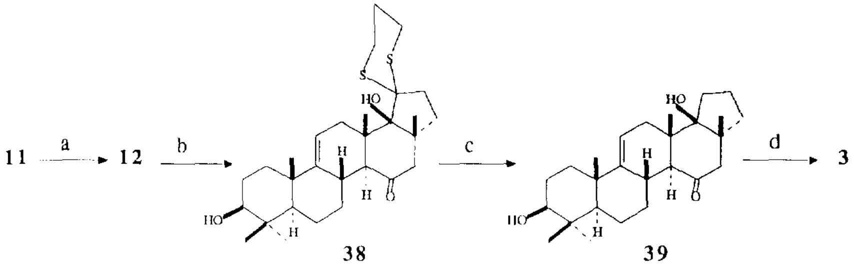


The conjugate additions of **15** with the acetal-substituted Grignard reagent in the presence of copper bromide-dimethyl sulfide complex and cerium trichloride were examined next. A dramatic acceleration of the conjugate Grignard addition was observed when cerium chloride was used as a Lewis acid catalyst, the reaction being completed in less then ten minutes at -78°C (over 85% isolated yield of **19** or **11**); the product deriving from nucleophilic addition to the C-16 electrophilic terminus was only detected in trace amounts. The use of the cuprous bromide-dimethyl sulfide complex (0.25 mmol for 2.6 mmol of the acetal-containing Grignard) on **9** and **15** (1 mmol, 1 h, -78°C) led to lower yields of **16** (29%) and **11** (36%), along with recovered starting materials. On the other hand, the reaction of 3β-OTMS-protected **15** (bis-trimethylsilylacetamide, DMF, Δ, 95%) with 3,3-diethoxypropyl-lithium led to **36** in 50% isolated yield, but the reaction was rather sluggish and unidentified side products were also obtained. Having encountered some difficulties in deprotecting the dioxane-protected acetals, we synthesized the dioxolane analogues whose acetal protection was easily removed by acid treatment. Thus, the 2-(2-bromoethyl)-1,3-dioxolane-derived Grignard reagent gave a 90% isolated yield of **34**. Finally, bulky nucleophilic reducing agents, such as lithium-tri-*tert*-butoxyaluminohydride, in THF at low temperature, chemo- and stereoselectively reduced the C-18 carbonyl (the more easily accessible one, considering the Bürgi-Dunitz trajectory[18]), on **15**- and **12**-3β-OTMS, leading to **37** and **35** respectively and leaving the C-15 carbonyl group intact.



a) 2-(2-bromoethyl)-1,3-dioxolan, Mg, THF; b) BSA, DMF, Δ.; c) 3,3-diethoxypropyl-lithium, THF, -78°C
d) TBDMSCl, Imidazol, DMF; e) LiAl(OtBu)$_3$H, THF, -20°C to rt, 12 h.

This approach has now culminated in a five-step synthesis of the arborane and fernane pentacyclic systems starting from the tetracyclic Diels-Alder adducts **15** and **18**. An alternative mode of reactivity on the cis ring junctions has provided stereodivergent syntheses of the non-natural analogues (the C-17 configuration being inverted: *anti* disposition of C-13/C-17 angular methyl groups) starting from **9** and **10**. Addition of a Grignard reagent to **15** provided **11** in high yield (90%), with complete control of the C-17 configuration. Subsequent treatment of **11** at room temperature with propane dithiol-BF$_3$.Et$_2$O in CH$_2$Cl$_2$ provided the 1,3-dithiane **12** (95%), which was easily deprotonated by *tert*-BuLi at -78°C, leading to **38** (the E-ring formation proceeded in 73% yield) along with 15% recovered starting material. The C-15 carbonyl group was unaffected during this conversion. The Raney-Ni desulfurization of **38** initially proved troublesome. A 15% yield of direct co-formation of the desulfurized-deoxygenated-fully reduced product was obtained in several runs, accompanied with the reduction of the 9,11-double bond, in varying ratios and yields. Such Raney-nickel mediated deoxygenations of tertiary alcohols have precedents in the literature.[19] Experiments conducted under milder conditions (only 10 min reflux in ethanol) were found to give **39**, the desired reductive desulfurization product, in 85% yield. Dehydration (treatment with p-toluenesulfonic acid in refluxing toluene over 6 h) completed the synthetic scheme in a 38% overall yield from **15**. A four-step synthesis of optically homogeneous **3** is detailed below.



38 **39**

a) 1,3-propanedithiol, $BF_3.Et_2O$, CH_2Cl_2, r.t.; b) tBuLi, THF, 10% HMPA, -78°C, 2h., c) Ra-Ni, EtOH, 10 min. reflux;.d) pTosOH, Toluene, 6 h reflux.

The significant ^1H and ^{13}C NMR (the arcs indicate diagnostic n.O.e.'s) data for compounds **11** and **3** are summarized in figures 4 and 5 respectively. The structures depicted are the lowest energy conformations from molecular mechanics calculations carried out with Still's Macromodel program (version 3.1) using the MM2 force field. The vicinal coupling constants given by the program are in agreement with those measured from the 400 and 600 MHz ^1H NMR spectra, which supports the validity of the calculated conformations. The relative configurations of the chiral centers C-8, C-10, C-13, C-14 and C-17 on all compounds investigated were determined via diagnostic n.O.e.'s from 1D difference n.O.e. experiments in $CDCl_3$ solution at 400 and 600 MHz.

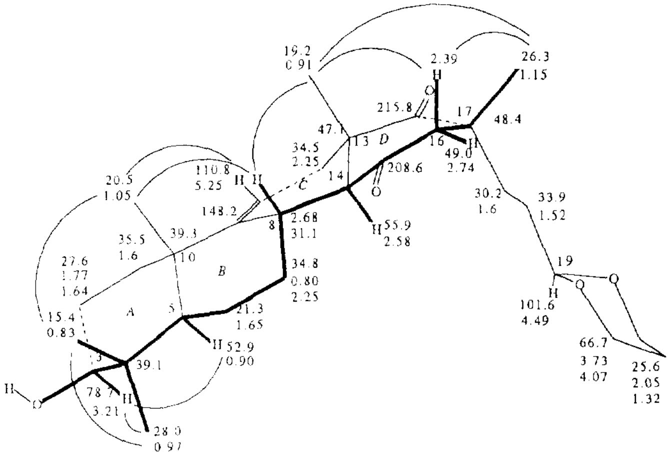


Figure 4: NMR data (chemical shifts and spatial proximities) of **11** shown on the lowest energy conformer, as determined by molecular mechanics calculations.

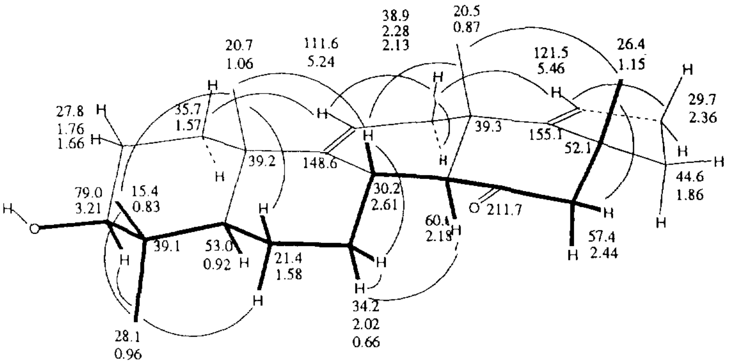
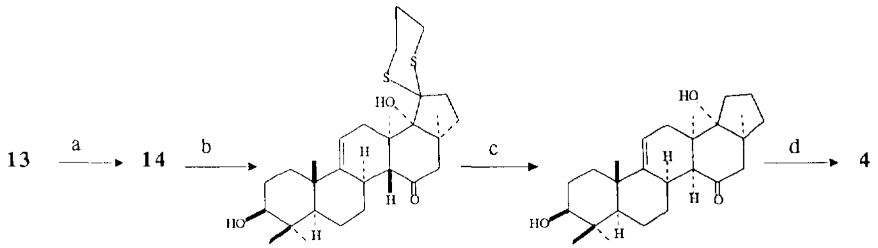


Figure 5: NMR data (chemical shifts and spatial proximities) of **3** shown on the lowest energy conformer as determined by molecular mechanics calculations.

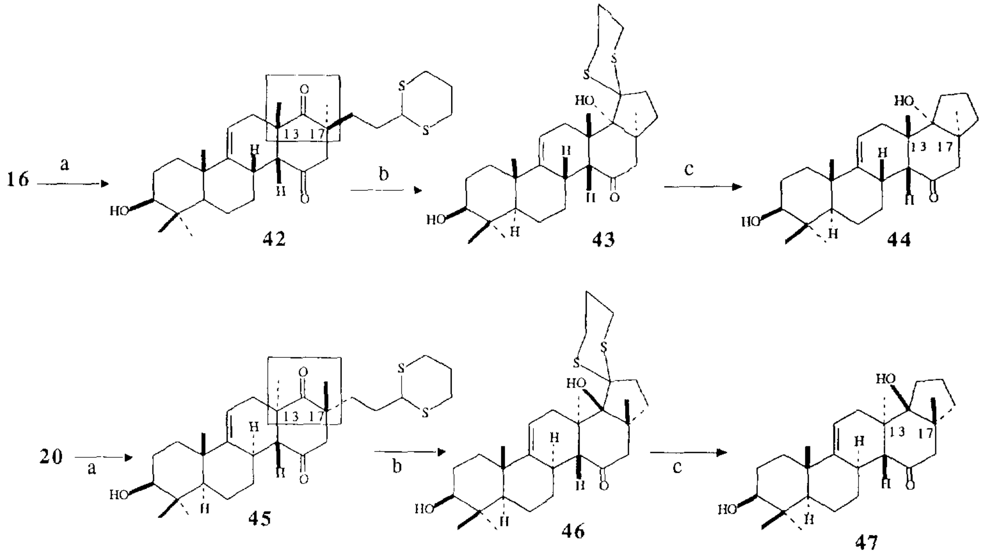
The fernane route proceeded by direct analogy to that followed for the arborane skeleton. Thus the possibility of securing a regiospecific, stereocontrolable three-carbon homologation through an organomagnesium addition was pursued. Direct access to the absolute configurations present in fernenol would require tetracyclic intermediate **10** (fernane-like ABCD), which was first subjected to alkaline epimerization (sodium bicarbonate, methanol, reflux, 2 h, under nitrogen) to afford the desired starting ene-dione **18**. Similarly to the results obtained in the arborane series, addition of an acetal-substituted Grignard to **18** provided **13** in 86% isolated yield, with complete control of the C-17 configuration. Subsequent room temperature treatment of **13** with propane dithiol-$BF_3.Et_2O$ in CH_2Cl_2 provided the dithioacetal **14** (95%), which was cyclized (metallation-C-C bond formation with tBuLi, in THF-10% HMPA) to **40** (71%) and subjected to Raney-nickel desulfurization as above, to afford **41** in 85% yield. Finally, dehydration (p-toluenesulfonic acid in refluxing toluene, 6 h), afforded the fernane-like pentacyclic triterpene **4** (60%, along with unreacted starting carbinol) in 30% overall yield from **18**. The four-step synthesis of optically homogeneous **4** is detailled below.



40 **41**

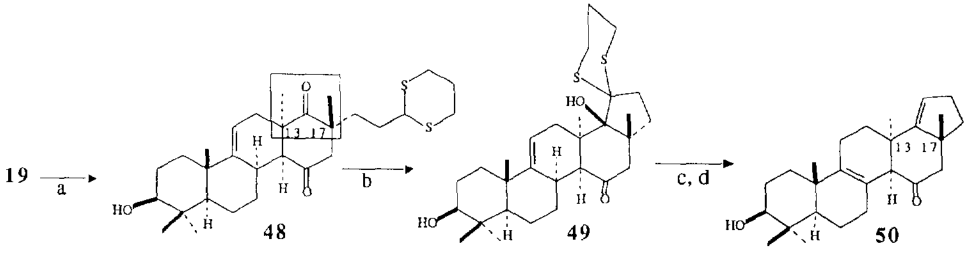
a) 1,3-propanedithiol, $BF_3.Et_2O$, CH_2Cl_2, r.t.; b) tBuLi, THF, 10% HMPA, -78°C, 2h.; c) Ra-Ni, EtOH, 10 min.r. reflux; d) p-TosOH, Toluene, 6 h reflux.

The diastereofacial preference exhibited in the conversion of **9** to **16** and **10** to **19** was also exploited for the synthesis of the pentacyclic intermediates **44** and **47** with the unnatural disposition of C-13/C-17 angular methyl groups. Sequential treatment of **16** and **20** with 1,3-propanedithiol in the presence of boron trifluoride-etherate in CH_2Cl_2 at rt and tBuLi in THF-HMPA at -78°C gave the pentacyclic products **43** and **46** in 67 and 53% yields respectively. Reductive removal of the dithiane (Ra-Ni , EtOH, 10 min reflux) provided **44** and **47** in 72 and 63% isolated yields, accompagnied with unreacted starting material.



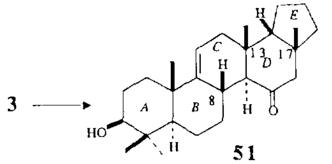
a) 1,3-propanedithiol, $BF_3.Et_2O$, CH_2Cl_2, r.t.; b) tBuLi, THF, 10% HMPA, -78°C, 2h.; c) Ra-Ni, EtOH, 10 min. reflux.

The whole sequence, applied to **19**, led by double bond migration from $\Delta^{9(11)}$ to $\Delta^{8(9)}$ to **50**. Thus, conjugate addition of the acetal-substituted Grignard on **10** (fernane-like ABCD) afforded **19** as a single diastereomer in 87% isolated yield. Transacetalization (**48**, 99%) and subsequent cyclization (**49**, 77%) completed the E-ring formation as for the routes described above. The Raney-nickel desulfurization product being rather insoluble, the reaction mixture was carried forward as such for the dehydration step. Heating the crude product thus obtained in toluene in the presence of p-toluenesulfonic acid led to **50** in 29% overall yield.

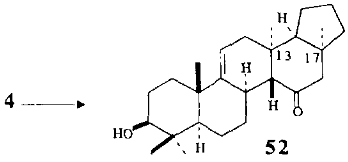


a) 1,3-propanedithiol, $BF_3.Et_2O$, CH_2Cl_2, r.t.; b) tBuLi, THF, 10% HMPA, -78°C, 2h.;
c) Ra-Ni, EtOH, 10 min. reflux; d) p-TosOH, toluene, 6 h reflux.

Selective hydrogenation of the C-18/C-19 double bond of the arborane and fernane derivatives **3** and **4** (H_2, Pd-C in acetic acid, 12 h at 50 psi), afforded **51** and **52** respectively in 95% yield. In each case, the inaccessible C_9-C_{11} double bond remained intact. Again, the concavity of the system, not the angular methyl groups at C-13 and C-17, proved to be the prevailing control element for the stereochemical outcome of this reduction, leading to the *cis* D/E fused pentacycles.



51



52

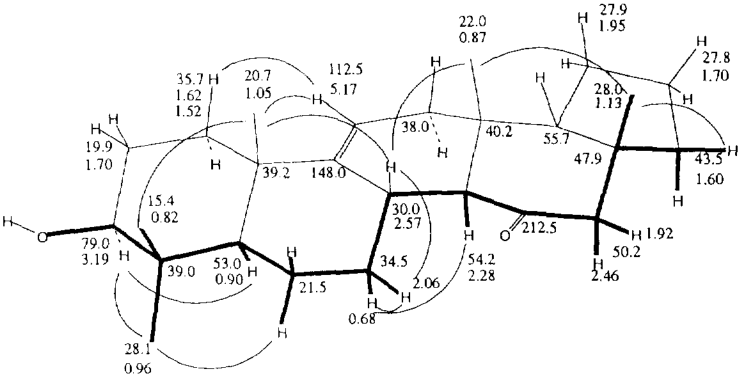


Figure 6: NMR data (chemical shifts and spatial proximities) of **51** shown on the lowest energy conformer as determined by molecular mechanics calculations.

MM2 calculations (Figure 7), or simply inspection of Dreiding models, safely predict the sense of hydrogenation which was further proved by extensive 600 MHz ^{1}H-NMR experiments.

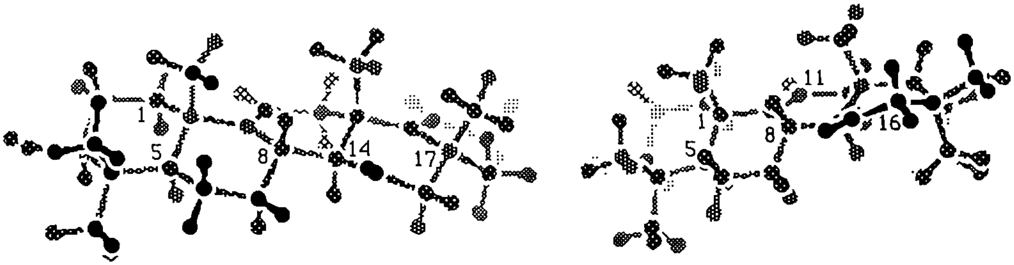


Figure 7: Lowest energy conformers of **3**, used to predict the face selectivity and of **51** to confirm structure elucidation.

In summary, a general route to arboranes and fernanes from common starting materials has been developed, yielding the title compounds. Molecular mechanics calculations as well as NMR experiments were extensively used in this investigation.[20] From a more general point of view, the results obtained give "*a series of nice examples of configuration-directed (trans-decalins) and conformation-directed (cis-decalins) conjugate additions*", as one of the referees has kindly remarked.

Acknowledgements: The authors wish to thank Dr. André Guingant (ESPCI, Paris) and Dr. Gérard Jenner (Université Louis Pasteur, Strasbourg) for kindly performing the high-pressure mediated Diels-Alder experiments, and Mr. Rolando Spanevello for technical help.

Experimental section :

General experimental details were as previously described[21]; complete ^1H and ^{13}C NMR data (1D and 2D experiments) were obtained for each compound synthesized in $CDCl_3$ at 400 (occasionnally 600) and 75 MHz, and optical rotations were measured in chloroform, unless otherwise specified.

General procedures:

Three-carbon homologation :

1- A solution of 3-bromopropionaldehyde trimethylene acetal (10 mmol) in dry THF (10 ml) was added dropwise to magnesium powder (20 g-atom) in the same solvent (10 ml). The reaction was initiated with iodine, and the rate of addition was controlled to moderate the reflux rate. The reaction mixture was then heated for 2.5 h then cooled to room temperature. The Grignard reagent thus derived (7.7 mmol) was added dropwise to a solution of ene-diones **9**, **10**, **15**, **18** (3 mmol) in dry THF (15 ml) at -78°C. The reaction was kept at -78°C for 30 min, at which time TLC analysis indicated the disappearance of starting material. Quenched with saturated ammonium chloride solution and extracted with CH_2Cl_2, the combined layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. Silica gel flash-chromatography (elution with heptane-ethyl acetate, 2:1) afforded the three-carbon homologated adducts **11**, **13**, **16**, **19**.

A solution of Grignard reagent prepared from 2-(2-bromoethyl)-1,3-dioxolane as above was added dropwise to **15** to give **34** in excellent isolated yield.

2- **Copper-catalyzed 1,4-conjugate Grignard addition** : A solution of the Grignard reagent of 3-bromopropionaldehyde trimethylene acetal (2.6 mmol) was prepared in the predescribed manner, cooled to -78°C and treated in one portion with a solution of cuprous bromide-dimethylsulfide complex (0.25 mmol) in dry THF (10 ml). The yellow solution was stirred at -78°C for one hour, before a solution of **10**, **15** (1 mmol) in dry THF (10 ml) was added dropwise. Stirring was maintained for 1 h at this temperature. The resulting oil, after workup as befor,e was taken up in CH_2Cl_2 and water, and processed in the manner described earlier.

3- **Cerium (III) accelerated 1,4-conjugate Grignard addition** : $CeCl_3$ was dried by heating it under vacuum at 140°C for 2 h, cooled and diluted with dry THF to a known volume. The dry $CeCl_3$ and the enedione were stirred in THF during 2 h at room temperature (for 1.5 mmol of $CeCl_3$, 1.0 mmol of ene-dione **10** or **15**) under an inert atmosphere. The mixture was then cooled to -78°C and a solution of the Grignard reagent (2.6 mmol) prepared as above was added. After 20 min stirring at this temperature, the reaction mixture was diluted with CH_2Cl_2, washed with citric acid until neutral, then with brine, and worked up as usual.

4-**Organolithium addition** : To a suspension of lithium metal (100 mg) in dry, oxygen-free, ether at -10°C, was added dropwise 0.15 ml of 3-chloropropionaldehyde diethyl acetal in ether (*ca* 3 h). After the addition was complete, the solution was stirred a further 1.5 h. Then 0.5 ml (3 equiv) of the solution was added to a precooled (-78°C) solution of the 3β-OTMS protected adduct **15** in ether (2 ml) and THF (1 ml), left 5 min then warmed to rt over 1.5 h, left a further 1.5 h at rt and worked up as usual to give the corresponding three-carbon homologated adduct.

3β-TBDMS protection : To a stirred solution of alcohols (2 mmol) in DMF-CH_2Cl_2 (2:8) was added *t*-butyldimethylsilyl chloride (2.1 mmol) and imidazol (2.1 mmol) at room temperature under a nitrogen atmosphere. The resulting mixture was stirred at room temperature and TLC monitored. Work-up in the usual way followed by chromatography (heptane-ethyl acetate, 2:1) afforded the 3β-OTBS protected products in 85-88% yields.

3β-Acetylation : To a stirred solution of the alcohols (1 mmol) in 2 ml of pyridine and 0.05 mmol of DMAP was added 2.5 mmol of acetic anhydride. The reaction mixture was stirred at 0°C and TLC monitored. After completion, water was added and the reaction mixture was extracted with dichloromethane, washed with 1 M hydrochloric acid, then with saturated sodium bicarbonate and finally with brine, dried over magnesium sulfate, and concentrated under reduced pressure. The residue was chromatographed on silica gel; the yields were often quantitative.

Addition of ethyl-magnesium Grignard : Commercial ethylmagnesium bromide (2 mmol, c 1.0 M in THF) was added dropwise to a stirred solution of **15**[2] and **18**-3β-OTBS (1.5 mmol) in 15 ml of dry THF, at -78°C under nitrogen. After 30 min at this temperature, the reaction was quenched with a saturated ammonium chloride solution, the THF was removed under reduced pressure and the residue extracted with dichloromethane, washed with water and brine, dried ($MgSO_4$), concentrated, and chromatographed (heptane-ethyl acetate, 2:1) to afford 1,2- and 1,4- adducts, and the C-18 carbonyl reduced products in varying yields.

Addition of 2-nitroethanol : To a solution of ene-diones **15**, **10** (0.28 mmol) and 2-nitroethanol (0.35 mmol) in 6 ml of CH_3CN at -50°C, DBU (0.71 mmol) was added. The resulting solution was allowed to warm to rt over 3 h, stirred at this temperature for 6 h more, and quenched with a saturated NH_4Cl solution. After dilution with ether, the organic layer was washed with brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude reaction product was then flash-chromatographed (heptane-ethyl acetate, 4:1) to afford the two-carbon homologated adducts **27** and **29**.

Addition of 1,3-dithiane : A solution of 0.25 mmol of ene-diones **15**, **10**, in 3 ml of THF was added over 15 min to 2-lithio-1,3-dithiane (from 1.01 mmol of dithiane and 1.01 mmol of nBuLi) at -78°C. After the solution had been stirred for 5 h at -78°C, it was allowed to warm to rt over 3 h and quenched with a saturated NH_4Cl solution. The reaction mixture was then partitioned between CH_2Cl_2 and water, the organic phase was dried over $MgSO_4$ and concentrated, to afford after silica gel flash chromatography (heptane-ethyl acetate, 2:1) the 1,2-adducts **30**, **31**, **32**, **33**. About 50% of starting material was recovered in each run.

Selective reduction of C-18 carbonyl : To a solution of 0.05 mmol of ene-dione **15**-(3β-OTMS), **12**-(3β-OTBS) in 1 ml of THF cooled at -25°C were added dropwise 0.05 mmol of a 1.0 M solution of $LiAl(OtBu)_3H$ over 5 min. The reaction was TLC monitored, quenched with wet ether and 5% aqueous KOH to afford after extraction, washing with brine, drying over magnesium sulfate, evaporation and chromatography (heptane-ethyl acetate, 1:1) **35**, **37** in 70-85% yields along with unreacted starting material.

Preparation of thioacetals by trans-acetalization with 1,3-propanedithiol : The acetals **11**, **13**, **16**, **19**, **20** (2.6 mmol) were dissolved in dry CH_2Cl_2 (15 ml), and 1,3-propanedithiol (5.17 mmol) and $BF_3.OEt_2$ (0.5 ml) were added. After being stirred at room temperature for 12h, the reaction mixture was diluted with CH_2Cl_2 and neutralized with aqueous sodium bicarbonate. The organic layer was washed with brine, dried over $MgSO_4$ and evaporated. The residue was purified by silica gel flash column chromatography (heptane-ethyl acetate, 2:1) to give the thioacetals **12**, **14**, **42**, **48**, **45** respectively.

E-ring formation : To a stirred solution (0.01 M) of thioacetals **12, 14, 42, 45, 48** (3.6 mmol), in dry THF (350 ml) at -78°C was added HMPA (35 ml) and tBuLi (8.33 mmol). The resulting yellow solution turned red during the reaction (2 to 5 h, TLC monitoring). The reaction mixture was quenched with NH_4Cl aq. at low temperature, the solvent was removed under reduced pressure and the residue taken up in dichloromethane. The organic layer was washed with brine and water, dried ($MgSO_4$), concentrated and purified by silica gel flash chromatography, eluting with 1:2 v/v ethyl acetate-heptane, to afford **38, 40, 43, 46, 49** (70-77% along with 15-20% of recovered starting materials) .

Raney nickel desulfurization : Commercially available (Aldrich Chemical Co.) Raney nickel was used for the reactions. We encountered some side reactions beside desulfurization, such as reduction of the 9(11) double bond, or direct deoxygenation. A good deal of experimentation led to the following procedure : To a solution of the thioketal **38, 40, 43, 46, 49** (1.78 mmol) in absolute ethanol (90 ml) was added 5g of Raney nickel (we did not found it necessary to wash the catalyst with water until neutral; on the other hand, deactivation of the catalyst to suppress side reactions failed to give any desulfurization) and the reaction mixture was refluxed for 10 min (oil bath temperature 100°C). After cooling to room temperature and diluting with ethyl acetate, the nickel was removed by filtration through Celite and rinsed with ethanol. These conditions gave high yields of the expected products **39, 41, 44, 47,** and the product of double bond migration **50**.

Acid-catalyzed dehydration : A 250 ml reaction flask equiped with a Dean-Stark apparatus, a nitrogen bubbler and a magnetic stirrer was charged with the appropriate alcohol **39** or **41** (1.5 mmol) in toluene (20 ml) and THF (20 ml) in the presence of p-toluenesulfonic acid (1.5 mmol). The reaction mixture was refluxed for 6 h. After cooling at 0°C, solid sodium bicarbonate was added and the mixture was concentrated under reduced pressure. Following dilution with ether, washing with 10% aqueous NaOH, water, and brine, the residue was subjected to column chromatography on silica gel (heptane-ethyl acetate, 2:1) to give the corresponding olefins **3** and **4** in 60-72% yield along with 15-20% recovered starting carbinols.

Reduction of the $\Delta^{18(19)}$ double bond : To a solution of **3** or **4** (0.94 mmol) in acetic acid (50 ml) was added 460 mg of the catalyst (Pd/C, 10 %). The mixture was placed in a Parr apparatus and pressurized with hydrogen until 45 psi (3 atm). It was shaken for 12 h at room temperature. After dilution with ethyl acetate, the catalyst was filtered through Celite, the solvent was evaporated under reduced pressure and the residue chromatographed (heptane-ethyl acetate, 2:1) to give **51** and **52** in 95% yield. The $\Delta^{9(11)}$ double bond remained intact.

High pressure mediated Diels-Alder reaction : 2 mmol of diene **1** and 2 mmol of dienophile **5** in 2 ml of CH_2Cl_2 were heated at 45°C under a pressure of 13 Kbar for 60 hrs. Depressurization followed by concentration and SiO_2 flash chromatography (ether- CH_2Cl_2, 1:5) afforded adducts **7a** and **7b** in a 1:1.2 ratio. The same conditions were used for the reaction of **1** with **2** and for the unsuccesful $ZnBr_2$-catalyzed high pressure experiments.

3 : 72 % m.p. 205-207°C (heptane). $[\alpha]_D$ - 63 (c = 1.11). **IR** : 3385, 2935, 2957, 1711, 1654, 1597, 1376, 1281, 1277, 1185, 1085, 1056, 1044, 984, 755. **^{1}H-NMR** (600 MHz): δ 0.66 (1H, m, H-7ax), 0.83 (3H, s, Me-4ax), 0.87 (3H, s, Me-13), 0.92 (1H, m, H-5), 0.96 (3H, s, Me-4eq), 1.06 (3H, s, Me-10), 1.15 (3H, s, Me-17), 1.51-1.68 (5H, m), 1.86 (1H, m, H-21), 2.02 (1H, dt, J= 2.2, 7.2, 12.2, H-7eq), 2.13 (1H, dd, J= 6.3, 16.6, H-12eq), 2.18 (1H, d, J= 8.5, H-14), 2.31 (1H, m), 2.44 (2H, AB quartet, J= 12, H-16), 2.61

(1H, m, H-8), 3.21 (1H, dd, J= 4.4, 11.1, H-3), 5.24 (1H, d, J= 6.3, H-11), 5.46 (1H, t, J= 1.9, H-19). **^{13}C-NMR** : δ 15.4, 20.5, 20.8, 21.5, 26.4, 27.8, 28.1, 29.8, 30.2, 34.2, 35.7, 38.9, 39.2, 39.3, 44.6, 52.1, 53.0, 57.4, 60.0, 78.9, 111.6, 121.5, 148.6, 155.1, 211.7. **EIMS** : 382 ($M^{+\cdot}$, 100), 367 (45), 364 (56), 349 (52), 105 (59), 91 (58), 69 (44), 55 (72). **CIMS** : 383 $[M + H]^+$, 364 $[M - H_2O]^+$. **HREIMS** : calcd for $C_{26}H_{38}O_2$:m/z 382.2872, found: 382.2865.

4 : 60 % **m.p.** 195°C (pentane). $[\alpha]_D$ + 22 (c = 1.1). **IR** : 3380, 2957, 2940, 1709, 1654, 1265, 1180, 1080, 1047, 757. **^{1}H-NMR** (600 MHz): δ 0.87 (3H, s, Me-4ax), 0.93 (3H, s, Me-13), 1.01 (3H, s, Me-4eq), 1.08 (3H, s, Me-10), 1.14 (3H, s, Me-17), 1.32 (1H, dd, J= 8.2, 13.1, H-1ax), 1.40-1.70 (9H, m), 1.85 (1H, dt, J= 2.1, 13.5, H-1eq), 1.86 (1H, d, J= 7.4, H-16), 2.15 (1H, d, J= 10.3 H, H-14), 2.19 (1H, m, H-12), 2.20-2.50 (5H, m), 2.56 (1H, m, H-8), 3.24 (1H, dd, J= 6.1, 9.7, H-3), 5.34 (1H, d, J= 5.3, H-11), 5.46 (1H, s, H-19). **^{13}C-NMR** : δ 15.4, 18.2, 21.0, 24.9, 25.2, 26.2, 27.8, 28.2, 28.6, 29.7, 37.8, 39.1, 39.4, 39.6, 42.2, 44.4, 44.5, 45.7, 57.9, 58.8, 79.1, 114.9, 121.6, 150.7, 165.9, 211.9. **EIMS** : 382 ($M^{+\cdot}$, 100), 364 (28), 349 (31), 331 (26), 323 (19), 195 (39), 105 (75), 99 (78), 91 (71.2), 55 (84.4). **HREIMS** : calcd for $C_{26}H_{38}O_2$: m/z 382.2871, found: 382.2888.

7a : 30.9 % $[\alpha]_D$ - 157 (c = 0.94). **IR** : 3474, 2964, 2867, 1736, 1454, 1394, 1364, 1197, 1001, 1038, 756. **^{1}H-NMR** (600 MHz) : δ 0.67 (3H, s), 0.81 (3H, s), 0.918 (3H, s), 0.92 (1H, m), 1.102 (9H, s), 1.103 (3H, s), 1.40-1.80 (7H, m), 1.93 (1H, m), 2.10-2.30 (6H, m), 2.49 (2H, m), 2.98 (1H, t, J= 9.4), 3.20 (1H, m), 3.52 (1H, m), 3.64 (3H, s), 5.24 (1H, s). **^{13}C-NMR** : δ 12.8, 15.0, 19.8, 20.4, 22.6, 26.9, 27.8, 28.0, 28.6, 30.4, 31.8, 34.3, 37.9, 39.5, 40.5, 42.0, 45.0, 46.1, 48.8, 49.8, 50.9, 55.2, 72.5, 78.7, 79.9, 108.8, 148.1, 175.5, 212.2. **EIMS** : 500 ($M^{+\cdot}$, 18), 441 (8), 385 (8), 367 (5), 235 (11), 57 (100). **HREIMS** : calcd for $C_{31}H_{48}O_5$: m/z 500.3502, found: 500.3509.

7b : 37.1 % $[\alpha]_D$ - 131 (c = 1). **IR** : 3405, 2932, 2855, 1723, 1459, 1217, 1095, 1035, 759. **^{1}H-NMR** (600 MHz) : δ 0.65 (3H, s), 0.89 (3H, s), 0.92 (3H, s), 1.11 (9H, s), 1.14 (3H, s), 1.20 (1H, m), 1.35 (1H, m), 1.45-1.60 (1H, m), 1.61-1.70 (6H, m), 1.80-1.95 (3H, m), 2.11 (1H, d, J= 14.4), 2.12-2.32 (5H, m), 2.42 (1H, m), 2.48 (1H, d, J=14.4), 3.12 (1H, t, J= 9), 3.19 (1H, dd, J= 10.4, 4.8), 3.49 (1H, t, J= 8.0), 3.65 (3H, s), 5.45 (1H, s). **^{13}C-NMR** : δ 14.0, 14.7, 19.5, 21.6, 23.5, 25.1, 27.0, 27.2, 27.6, 28.5, 30.6, 38.2, 38.7, 39.2, 40.3, 41.6, 43.4, 46.6, 48.2, 49.6, 51.0, 51.3, 72.4, 78.4, 78.8, 113.5, 149.0, 175.1, 212.5. **EIMS** : 500 ($M^{+\cdot}$, 15), 57 (100). **HREIMS** : calcd for $C_{31}H_{48}O_5$: m/z 500.3502, found: 500.3507.

8a : 92 % **m.p.** 278°C (pentane). $[\alpha]_D$ - 119 (c = 1.3). **IR** : 2969, 2950, 2872, 1729, 1454, 1364, 1243, 1198,1029. **^{1}H-NMR** (600 MHz): δ 0.68 (3H, s, Me-17), 0.81 (3H, s, Me-4eq), 0.89 (3H, s, Me-4ax), 0.99 (1H, m, H-5), 1.11 (9H, s), 1.13 (3H, s, Me-10), 1.30-1.90 (5H, m), 2.05 (3H, s), 2.10-2.40 (11H, m), 2.49 (1H, m, H-8), 2.51 (1H, d, J= 14.8, H-16), 2.99 (1H, t, J= 8.2, H-13), 3.51 (1H, t, J= 8.5, H-21), 3.65 (3H, s), 4.45 (1H, m, H-3), 5.25 (1H, m, H-11). **^{13}C-NMR** : δ 12.8, 16.1, 19.9, 20.4, 21.1, 22.3, 24.1, 26.8, 27.7, 28.6, 30.4, 31.7, 33.9, 37.9, 38.3, 40.5, 41.9, 44.9, 46.0, 48.7, 49.7, 50.9, 55.2, 72.5, 79.9, 80.5, 109.1, 147.5, 170.1, 175.5, 212.0. **EIMS** : 542 ($M^{+\cdot}$,23), 483 (13), 427 (11), 235 (15), 57 (100). **HREIMS**: calcd for $C_{33}H_{50}O_6$: m/z 542.3607, found: 542.3608.

8b : 95 % **m.p.**125-127°C (pentane). $[\alpha]_D$ - 43 (c = 0.92). **IR** : 2979, 2884, 1728, 1458, 1368, 1243, 1196, 1087, 1030, 903. **^{1}H-NMR** (600 MHz) : δ 0.60 (3H, s), 0.76 (3H, s), 0.89 (3H, s), 1.06 (9H, s), 1.12 (3H, s), 1.25 (1H, t, J= 10), 1.38 (1H, dt, J= 4.2, 13), 1.46 (1H, m), 1.59 (1H, m), 1.60 (1H, m), 1.61

(2H, m), 1.65 (1H, m), 1.78 (1H, m), 1.84 (1H, m), 1.88 (1H, m), 1.99 (3H, s), 2.06 (1H, d, J= 14), 2.09 (1H, m), 2.14 (1H, dd, J= 7.5, 11.8), 2.23 (2H, m), 2.26 (1H, m), 2.38 (1H, ddd, J= 5, 12), 2.43 (1H, d, J=14), 3.08 (1H, dd, J= 10.7, 7.5), 3.44 (1H, t, J=8.5), 3.60 (3H, s), 4.39 (1H, dd, J=4.4, 11.6), 5.39 (1H, bs). **^{13}C-NMR**: δ 14.0, 15.8, 19.5, 21.1, 21.5, 23.7, 24.2, 25.2, 27.0, 27.2, 28.5, 31.0, 38.1, 38.4, 40.5, 41.7, 43.8, 46.7, 48.3, 49.7, 51.1, 51.3, 72.4, 78.9, 80.4, 113.7, 148.6, 170.6, 175.0, 212.0. **EIMS** : 542 ($M^{+\cdot}$,10), 484 (29), 483 (81), 427 (27), 367 (13), 287 (12), 205 (27), 57 (100). **HREIMS** : calcd for $C_{33}H_{50}O_6$: m/z 542.3607, found: 542.3608.

11 : 88 % **m.p.** 158-160 °C (ether-heptane). $[\alpha]_D$ + 27 (c = 0.86). **IR** : 3499, 2970, 2935, 2857, 1704, 1460, 1377, 1146, 1079, 1043, 1002, 755. **^{1}H-NMR** (600 MHz): δ 0.80 (1H, m, H-7), 0.83 (3H, s, Me-4ax), 0.90 (1H, m, H-5), 0.91 (3H, s, Me-13), 0.97 (3H,s, Me-4eq), 1.05 (3H, s, Me-10), 1.15 (3H, s, Me-17), 1.32 (2H, m), 1.50-1.90 (10H, m), 2.04 (1H, m), 2.24 (3H, m), 2.39 (1H, d, J=17.2 Hz, H-16β), 2.58 (1H, d, J= 9.3 Hz, H-14), 2.68 (1H, m, H-8), 2.74 (1H, d, J= 17.2 Hz, H-16α), 3.21 (1H, dd, J= 4.4, 11.5 Hz, H-3), 3.73 (2H, dt, J= 2.4, 12.2, 14.1 Hz), 4.07 (2H, m), 4.49 (1H, t, J= 4.9 Hz, H-19), 5.25 (1H,d, J= 5.8 Hz, H-11). **^{13}C-NMR** : δ 15.4, 19.2, 20.5, 21.3, 25.6, 26.3, 27.6, 28.0, 30.2, 31.1, 33.9, 34.5, 34.8, 35.5, 39.1, 39.3, 47.1, 48.4, 49.0, 52.9, 55.9, 66.7 (2), 78.7, 101.6, 110.8, 148.2, 208.6, 215.8. **EIMS** : 472 ($M^{+\cdot}$, 27), 115 (100), 103 (39), 87 (50), 59 (24), 57 (26). **HREIMS** : calcd for $C_{29}H_{44}O_5$: m/z 472.3189, found: 472.3170. **Anal** : calcd for $C_{29}H_{44}O_5$: C 73.69, H 9.38. found: C 73.64, H, 9.74.

12 : 95 % **m.p.** 116.5-118.5 °C (MeOH). $[\alpha]_D$ + 22 (c = 1). **IR** : 3499, 2970, 2935, 2857, 1704, 1460, 1377, 1146, 1079, 1043, 1002, 755. **^{1}H-NMR** : δ 0.83 (3H, s), 0.92 (3H, s), 0.97 (3H, s), 1.05 (3H, s), 1.16 (3H, s), 1.40-2.50 (9H, m), 2.43 (1H, d, J= 17.1, H-16), 2.59 (1H, m), 2.73 (1H, d, J=17.1, H-16), 2.85 (4H, m), 3.22 (1H, dd, J= 4.4, 11.5, H-3), 3.98 (1H, t, J= 5.0, H-19), 5.26 (1H, m, H-11). **^{13}C-NMR** : δ 15.4, 19.3, 20.5, 21.5, 25.8, 25.9, 27.7, 28.0, 30.3 (2), 30.6, 31.3, 34.7, 34.9, 35.6, 37.0, 39.3, 39.5, 47.1, 47.4, 48.5, 49.3, 52.9, 56.2, 78.9, 110.9, 148.3, 208.4 , 215.6. **EIMS** : 504 ($M^{+\cdot}$, 48), 285 (7), 147 (78), 145 (100), 119 (44), 105 (33), 87 (33), 69 (29), 55 (40.7). **HREIMS** : calcd for $C_{29}H_{44}O_3S_2$: m/z 504.2732, found: 504.2726. **Anal** : calcd for $C_{29}H_{44}O_3S_2$: C 69.00, H 8.79, found: C 68.21, H 9.14.

12-(3β-OTMS) : 85 % **m.p.** 135-137°C (heptane). $[\alpha]_D$ + 17 (c = 1). **IR** : 2944, 2858, 1709, 1472, 1461, 1375, 1367, 1255, 1093, 978, 910, 880, 835, 774, 734. **^{1}H-NMR** : δ 0.03 (3H, s), 0.05 (3H, s), 0.79 (3H, s), 0.87 (3H, s), 0.89 (9H, s), 0.91 (3H, s), 1.04 (3H, s), 1.16 (3H, s), 1.40-2.00 (10H, m), 2.13 (1H, dt, J= 3.7, 10.8), 2.23 (3H, m), 2.42 (1H, d, J= 17.4, H-16β), 2.60 (1H, d, J= 9.3, H-14), 2.73 (1H, d, J= 17.5, H-16α), 2.85 (3H, m), 3.16 (1H, dd, J= 5.4, 10, H-3), 3.99 (1H, t, J= 6.8, H-19), 5.23 (1H, t, J= 2.9, H-11). **^{13}C-NMR** : δ -4.8, -3.7, 15.9, 18.2, 19.3, 20.6, 21.7, 25.9 (3), 28.2, 28.6, 30.3 (2), 30.7, 31.3, 34.8, 35.1, 35.6, 37.0, 39.4, 39.9, 47.2, 47.4, 48.6, 49.3, 53.1, 56.2, 79.5, 110.7, 148.7, 208.4, 215.7. **EIMS** : 618 ($M^{+\cdot}$, 29), 562 (64), 415 (11), 221 (21), 147 (43), 145 (39), 75 (100). **HREIMS** : calcd for $C_{35}H_{58}O_3S_2Si$: m/z 618.3596, found: 618.3586.

13 : 86 % **m.p.** 176-178 °C (ether-heptane). $[\alpha]_D$ - 9 (c = 1.01). **IR** : 3475, 2965, 2931, 2854, 1702, 1458, 1378, 1144, 1079, 999, 755. **^{1}H-NMR** : δ 0.87 (3H, s, Me-4ax), 0.97 (3H, s, Me-13), 1.05 (3H, s, Me-4eq), 1.08 (3H, s, Me-10), 1.15 (3H, s, Me-17), 1.25-1.39 (3H, m), 1.44 (1H, dd, J= 5.2, 10.4, H-5), 1.59 (7H, m), 1.84 (3H, m), 2.03 (2H, m), 2.26 (2H, m, H-12), 2.35 (1H, d, J= 16.5 , H-16α), 2.54 (1H, d, J= 9.8 Hz, H-14), 2.67 (1H, m, H-8), 2.76 (1H, d, J= 16.5, H-16β), 3.23 (1H, t, J= 7.6, H-3), 3.74 (2H, dd, J= 2.2, 11.9), 4.08 (2H, dd, J= 4.5, 11.3), 4.51 (1H, t, J= 4.7), 5.34 (1H, d, J= 1.3, H-11). **^{13}C-NMR** : δ 15.2, 17.9, 19.6, 23.6, 25.0, 25.1, 25.5, 26.5, 27.7, 27.9, 29.1, 30.1, 33.8, 35.1, 37.7, 38.8, 39.1, 44.2, 47.7, 48.9, 49.0, 54.7, 66.6 (2), 78.5, 101.5, 114.2, 150.0, 208.7, 216.0. **EIMS** : 472 ($M^{+\cdot}$, 9), 457 (13), 454 (16), 381 (21), 339 (14), 285 (17), 229 (19), 171 (12), 115 (29), 87 (100). **Anal** : calcd for $C_{29}H_{44}O_5$: C 73.69, H 9.38, found: C 73.41, H 9.31. **HREIMS** : calcd for $C_{29}H_{44}O_5$: m/z 472.3189, found: 472.3209.

13-(3β-OTBS) : 82 % **m.p.** 137-139°C (heptane). $[\alpha]_D$ - 19 (c = 1.04). **IR** : 2958, 2932, 2856, 1704, 1468, 1378, 1251, 1146, 1101, 1005, 889, 837, 757. **^{1}H-NMR** : δ 0.03 (6H, s), 0.83 (3H, s, Me-4ax), 0.89 (9H, s), 0.92 (3H, s, Me-13), 0.97 (3H, s, Me-4eq), 1.08 (3H, s, Me-10), 1.15 (3H, s, Me-17), 1.20-2.20 (17 (H, m), 2.25 (2H, m, H-12), 2.35 (1H, d, J= 16.5, H-16α), 2.54 (1H, d, J= 9.8, H-14), 2.67 (1H, m, H-8), 2.75 (1H, d, J= 16.5, H-16β), 3.18 (1H, dd, J= 4.1, 11.4, H-3), 3.74 (2H, t, J= 12.1), 4.07 (2H, m), 4.51 (1H, d, J= 4.8), 5.34 (1H, d, J= 1.3, H-11). **^{13}C-NMR** : δ -4.9, -3.9, 15.8, 19.8, 25.3, 25.4, 25.5, 25.9 (3), 26.6, 28.3, 29.4, 30.5, 34.0, 35.5, 37.9, 39.4, 39.6, 44.4, 48.0, 49.0, 49.2, 55.0, 66.8 (2), 79.5, 101.7, 114.2, 150.9, 209.0, 216.5. **EIMS** : 586 ($M^{+\cdot}$, 34.1), 568 (47.1), 530 (70.6), 529 (98.8), 133 (60), 115 (100), 107 (40), 75 (97.6), 73 (42.4). **HREIMS** : calcd for $C_{35}H_{58}O_5Si$: m/z 586.4053, found: 586.4049.

14 : 95 % **m.p.** 60-63°C (hexane). $[\alpha]_D$ - 17 (c = 1.3). **IR** : 3508, 2932, 2868, 1702, 1462, 1375, 1275, 1217, 1076, 1030. **^{1}H-NMR** : δ 0.87 (3H, s), 0.98 (3H, s), 1.01 (3H, s), 1.09 (3H, s), 1.16 (3H, s), 1.20-2.20 (16H, m), 2.26 (2H, t, J= 1.9), 2.38 (1H, d, J= 16.6, H-16), 2.55 (1H, d, J= 9.8), 2.65 (2H, m), 2.75 (1H, d, J= 16.5, H-16), 2.85 (3H, t, J= 4), 3.23 (1H, t, J= 8, H-3), 3.99 (1H, t,J= 6.7, H-19), 5.35 (1H, s, H-11). **^{13}C-NMR** : δ 15.3, 18.0, 19.8, 25.2, 25.3, 25.8, 26.3, 27.8, 28.1, 29.3, 30.2 (2), 30.6, 35.4, 36.9, 37.8, 38.9, 39.3, 44.4, 47.3, 47.9, 49.2, 49.3, 55.1, 78.9, 114.4, 150.2, 208.6, 215.77. **EIMS** : 504 ($M^{+\cdot}$, 100), 489 (6), 471 (4), 285 (21), 147 (66), 145 (73), 119 (50), 87 (38), 55 (36.4). **HREIMS** : calcd for $C_{29}H_{44}O_3S_2$: m/z 504.2732, found.: 504.2729.

15 : see ref. [2].

16 : 90 % **m.p.** 105-107 °C (ether-heptane). $[\alpha]_D$ + 20 (c = 1). **IR** : 3515, 2971, 2931, 2871, 1716, 1702, 1461, 1504, 1379, 1243, 1145, 915, 732. **^{1}H-NMR** : δ 0.83 (3H, s, Me-4ax), 1.02 (3H, s, Me-4eq), 1.04 (3H, s, Me-10), 1.15 (3H, s, Me-17), 1.23 (3H, s, Me-13), 1.30-1.90 (12H, m), 2.00-2.30 (3H, m), 2.29 (1H, d, J= 16.2, H-16β), 2.41 (1H, m, H-8), 2.76 (1H, d, J= 16.3, H-16α), 3.06 (1H, d, J= 3.6, H-14), 3.28 (1H, dd, J= 3.8, 11.1, H-3), 3.76 (2H, dt, J= 2.2, 12.2, 14.3), 4.10 (2H, dd, J=4.7, 10.7), 4.52 (1H, t, J= 4.9), 5.18 (1H, m, H-11). **^{13}C-NMR** : δ 15.5, 20.9, 21.5, 21.9, 25.5, 26.5, 27.4, 27.9, 29.0, 30.1, 31.7, 32.6, 34.3, 35.2, 38.9, 39.1, 49.1, 49.2, 49.6, 51.1, 53.3, 66.6 (2), 78.1, 101.5, 110.2, 147.6, 207.7, 214.8. **EIMS** : 472 ($M^{+\cdot}$, 10), 241 (7), 105 (87), 103 (43), 87 (100), 59 (48), 57 (47), 41 (54). **HREIMS** : calcd for $C_{29}H_{44}O_5$: m/z 472.3189, found: 472.3188.

17 : 95 % **m.p.**160-162°C (heptane). $[\alpha]_D$ + 26 (c = 0.96). **IR** : 3425, 2995, 2931, 1723, 1704, 1457, 1370, 1263, 1145, 955, 732. **^{1}H-NMR** : δ 0.79 (1H, m, H-7ax), 0.83 (3H, s, Me-4ax), 0.87 (3H, s, Me-13), 0.92 (1H, dd, J= 4.2, 10.6, H-5), 0.96 (3H, s, Me-4eq), 1.05 (3H, s, Me-10), 1.26 (3H, s, Me-17), 1.33 (1H, d, J= 13.2), 1.45 (2H, dd, J= 4.6, 8.3), 1.50-1.90 (11H, m), 2.05 (1H, m), 2.20 (1H, d, J= 17.3, H-12α), 2.27 (1H, d, J= 6.1, H-12β), 2.49 (1H, d, J= 18.6, H-16β), 2.54 (1H,d, J= 9.9, H-14), 2.64 (2H, m, H-16α and H-8), 3.21 (1H, dd, J= 4.3, 11.2, H-3), 3.73 (2H, dt, J= 2.4, 11.8, 14.1), 4.08 (1H, d, J= 11.7), 4.48 (1H, d, J= 4.7), 5.26 (1H, d, J= 4.9, H-11). **^{13}C-NMR** : δ 16.2, 19.2, 21.7, 22.2, 23.5, 25.6, 26.3, 27.7, 29.9, 30.3, 31.4, 33.7, 33.9, 35.1, 38.6, 39.4, 44.7, 47.7, 49.2, 52.5, 53.3, 66.6 (2), 78.4, 103.7, 111.8, 147.5, 205.7, 215.3. **EIMS** : 472 ($M^{+\cdot}$, 12), 241 (12), 105 (85), 103 (43), 87 (100), 59 (53), 57 (46).

18 (3β-OTBS) : 88 % $[\alpha]_D$ - 13 (c = 0.96). **m.p.** 168-170°C (heptane). **IR** : 2959, 2932, 2865, 1681, 1462, 1380, 1363, 1253, 1103, 1089, 847. **^{1}H-NMR** : δ 00.3 (6 H, s), 0.82 (3H, s), 0.91 (3H, s), 0.99 (3H, s), 1.07 (3H, s), 0.90-1.80 (10H, m), 1.89 (3H, s), 2.26 (2H, m), 2.47 (1H, d, J= 9.8, H-14), 2.66 (1H, m, H-8), 3.16 (1H, dd, J= 6.1, 9.7, H-3), 5.31 (1H, m, H-11), 6.54 (1H, s, H-16). **^{13}C-NMR** : δ -4.7, -3.8, 15.3, 16.0, 18.1, 20.2, 24.8, 25.3, 27.8, 29.2, 29.9, 35.2, 37.8, 38.6, 39.1, 45.7, 47.6, 56.7, 78.5, 113.9,- 136.8, 146.8, 150.2, 200.1, 205.3. **EIMS** : 470 ($M^{+\cdot}$, 1), 413 (11), 105 (10), 91 (12), 75 (100), 73 (48), 57 (22), 55 (13). **HREIMS** : calcd for $C_{29}H_{46}O_3Si$: m/z 470.3216, found: 470.3253.

19 : 87 % **m.p.**158-160°C (heptane). $[\alpha]_D$ - 5 (c = 0.92). **IR** : 3493, 2970, 2934, 2866, 1702, 1458, 1378, 1146, 1081, 1040, 1007, 755. **^{1}H-NMR** : δ 0.91 (3H, s, Me-4ax), 0.96 (3H, s, Me-4eq), 1.14 (3H, s, Me-17), 1.17 (3H, s, Me-10), 1.29 (3H, s, Me-13), 1.30 (1H, m, H-2ax), 1.30 (1H, m, H-5), 1.50-2.20 (15H, m), 2.38 (1H, d, J=17.4, H-16β), 2.44 (1H, m, H-8), 2.63 (1H, d, J= 17.3, H-16α), 2.81 (1H, d, J= 3.3, H-14), 3.19 (1H, t, J= 7.6, H-3), 3.60-3.80 (2H, m), 4.09 (2H, dd, J= 4.7, 11.0), 4.49 (1H, t, J= 4.8), 5.19 (1H, m, H-11). **^{13}C-NMR** : δ 14.9, 19.2, 21.8, 22.3, 24.5, 25.7, 25.8, 27.4, 27.7, 30.1, 31.6, 33.5, 33.9, 38.0, 38.3, 39.4, 44.7, 47.8, 48.3, 49.3, 53.4, 66.8 (2), 78.9, 101.6, 111.9, 150.2, 207.5, 215.0. **EIMS** : 472 ($M^{+\cdot}$, 8), 269 (9), 115 (52), 113 (26), 105 (27), 87 (100), 59 (33), 41 (31). **HREIMS** : calcd for $C_{29}H_{44}O_5$: m/z 472.3189, found: 472.3192.

21 : 17 % **IR** : 3469, 2977, 2944, 2866, 1706, 1462, 1376, 1290, 1218, 1071, 1038,752. **^{1}H-NMR** : δ 0.83 (3H, s), 0.89 (3H, t, J= 7.4), 0.92 (3H, s), 0.97 (3H, s), 1.05 (3H, s), 1.14 (3H, s), 1.30 (3H, m), 1.50-1.70 (6H, m), 2.00-2.30 (5H, m), 2.35 (1H, d, J= 18, H-16), 2.55 (1H, d, J= 9, H-14), 2.65 (1H, m, H-8), 2.75 (1H, d, J= 18.1, H-16), 3.19 (1H, dd, J= 4, 11.2, H-3), 5.35 (1H, t, J= 1.8 Hz, H-11). **^{13}C-NMR** : δ 14.7, 15.9, 19.7, 21.1, 24.3, 25.5, 25.9, 26.9, 28.7, 29.8, 32.3, 34.6, 35.7, 37.9, 39.2, 44.1, 45.8, 55.9, 78.6, 80.9, 110.7, 131.3, 144.7, 149.9, 200.2. **EIMS** : 386 ($M^{+\cdot}$, 25), 279 (36), 165 (20), 149 (74), 133 (12),75 (100), 73 (67).

22 : 11 % **IR** : 3475, 2970, 2944, 2871, 1709, 1662, 1463, 1377, 1031,760. **^{1}H-NMR** : δ 0.83 (6H, s), 0.94 (3H, s), 0.97 (3H, s), 1.05 (3H, m), 1.28 (3H, s), 1.20-1.90 (11H, m), 1.99 (3H, s), 2.30-2.60 (3H, m), 3.20 (1H, m, H-3), 5.35 (1H, m, H-11), 6.15 (1H, s, H-16). **^{13}C-NMR** : δ 16.8, 17.6, 18.3, 21.1, 21.7, 24.1, 25.2, 26.9, 27.2, 28.7, 29.1, 33.1, 35.7, 38.3, 39.5, 42.4, 47.7, 56.6, 78.1, 81.3, 111.7, 135.9, 145.8, 150.0, 199.9. **EIMS** : 386 ($M^{+\cdot}$, 5), 279 (16), 205 (24), 133 (50), 75 (100), 57 (96), 55 (72).

23 : 12 % **IR** : 3442, 2970, 2937, 2871, 1712, 1669, 1649, 1462, 1374, 1276, 1374, 1061, 1028, 757. **^{1}H-NMR** : δ 0.75 (3H, s), 0.83 (3H, s), 0.97 (3H, s), 1.05 (3H, s), 1.20-1.90 (11H, m), 1.98 (3H, s), 2.30-2.60 (4H, m), 3.20 (1H, dd, J= 5, 10, H-3), 4.25 (1H, s, H-18), 5.25 (1H, m, H-11), 5.85 (1H, s, H-16). **^{13}C-NMR** : δ 12.3, 15.9, 19.7, 21.1, 28.4, 28.6, 30.9, 35.8, 36.2, 37.5, 39.4, 42.4, 53.6, 56.7, 79.8, 80.1, 111.1, 128.5, 148.7, 159.3, 199.7. **EIMS** : 358 ($M^{+\cdot}$, 25), 430 (50), 383 (34), 325 (25), 204 (22), 157 (31), 57 (100).

24 : 37 % **m.p.** 128-130°C (heptane). $[\alpha]_D$ - 12 (c = 1.37). **IR** : 2956, 2938, 2856, 1706, 1462, 1380, 1363, 1251, 1100, 835. **^{1}H-NMR** (600MHz): δ 0.01 (3H, s), 0.03 (3H, s), 0.88 (3H, s), 0.91 (3H, t, J= 7.4), 0.93 (9H, s), 0.97 (3H, s), 1.02 (3H, s), 1.13 (3H, s), 1.18 (3H, s), 1.30 (4H, m), 1.50-1.70 (4H, m), 1.82 (1H, m), 1.88 (1H, m), 2.08 (1H, m), 2.30 (2H, m, H-12), 2.39 (1H, d, J= 16.8, H-16α), 2.58 (1H, d, J= 9.7, H-14), 2.71 (1H, m, H-8), 2.78 (1H, d, J= 16.8, H-16β), 3.22 (1H, dd, J= 4.0, 11.2, H-3), 5.34 (1H, t, J= 2.4, H-11). **^{13}C-NMR** : δ -4.7, -3.8, 15.3, 17.2, 18.5, 22.2, 23.7, 24.1, 25.3, 25.9, 26.8, 29.5, 29.9, 35.4, 36.8, 38.6, 39.7, 44.7, 49.5, 56.7, 78.3, 113.9, 144.3, 150.7, 200.9, 203.3. **EIMS** : 500 ($M^{+\cdot}$, 54), 443 (38), 279 (15), 167 (19), 149 (54), 75 (100), 73 (46). **HREIMS** : calcd for $C_{31}H_{52}O_3Si$: m/z 500.3685, found: 500.3700.

25 : 22 % **m.p.** 174-176°C (heptane). $[\alpha]_D$ + 58. (c = 0.81). **IR** : 3487, 2941, 2856, 1715, 1647, 1465, 1370, 1252, 1099, 836. **^{1}H-NMR** (600MHz): δ 0.01 (3H, s), 0.04 (3H, s), 0.84 (3H, s), 0.90 (9H, s), 0.926 (3H, s), 0.933 (3H, s), 1.04 (3H, t, J= 7.5), 1.12 (3H, s), 1.27 (2H, t, J= 16.1), 1.40-1.70 (5H, m), 1.75 (1H, m, H-1), 1.91 (4H, m), 1.99 (3H, s), 2.24 (1H, d, J= 8.6, H-14), 2.48 (3H, m), 3.19 (1H, dd, J= 3.9, 11.3, H-3), 5.38 (1H, d, J= 4.8, H-11), 5.81 (1H, s, H-16). **^{13}C-NMR** : δ -4.7, -3.1, 17.2, 17.8, 18.3, 22.2, 22.5, 24.4, 25.1, 26.9, 27.4, 29.2, 29.9, 34.2, 36.8, 38.6, 39.9, 44.7, 47.7, 58.7, 78.1, 80.5, 113.1, 134.8, 146.5, 150.2, 200.1. **EIMS** : 500 ($M^{+\cdot}$, 1), 443 (35), 205 (40), 149 (50), 75 (100), 57 (85), 55 (75). **HREIMS** : calcd for $C_{31}H_{52}O_3Si$: m/z 500.3685, found: 500.3703.

26 : 28 % $[\alpha]_D$ - 7 (c = 0.81). **IR** : 3458, 2937, 1714, 1639, 1460, 1119, 1099, 843. **^{1}H-NMR** : δ 0.01 (3H, s), 0.04 (3H, s), 0.80 (3H, s), 0.84 (3H, s), 0.89 (9H,s), 0.93 (3H, s), 1.11 (3H, s), 1.20-1.70 (8H, m), 1.75 (1H, dt, J= 3.3, 13.5 Hz, H-1eq), 1.98 (3H, s), 2.22 (4H, m); 2.56 (1H, m, H-8), 3.19 (1H, dd, J= 4.3, 11.4 Hz, H-3), 4.24 (1H, s, H-18), 5.35 (1H, t, J= 2.6 Hz, H-11), 5.84 (1H, d, J= 1.4 Hz, H-16). **^{13}C-NMR** : δ -4.8, -3.1, 15.2, 16.3, 18.0, 20.0, 24.0, 25.7, 26.9, 29.7, 29.9, 35.0, 37.1, 38.9, 39.1, 45.0, 47.6, 52.6, 78.5, 81.2, 112.8, 134.8, 145.9, 150.0, 199.1. **EIMS** : 472 ($M^{+\cdot}$, 25), 430 (50.), 383 (34), 325 (25), 204 (22), 157 (31), 57 (100).

27 : 70 % **m.p.** 224-226°C (heptane). $[\alpha]_D$ + 18 (c = 1.02). **IR** :3435, 2987, 2935, 1671, 1621, 1510, 1395, 1375, 1115, 1029, 755. **^{1}H-NMR** : δ 0.84 (3H, s), 0.97 (3H, s), 0.99 (3H, s), 1.08 (3H, s), 1.20-1.90 (8H, m), 2.01 (3H, s), 2.20-2.40 (3H, m), 2.60-3.00 (4H, m), 3.2 (1.H, m, H-3), 3.77 (2H, m), 5.31 (1H, d, J= 6.6 Hz, H-11). **^{13}C-NMR** : δ 12.6, 15.4, 19.9, 20.6, 21.5, 22.3, 27.7, 28.1, 30.9, 31.1, 33.4, 34.9, 35.5, 39.1, 47.3, 53.1, 57.6, 61.2, 78.9, 110.5, 143.2, 148.7, 172.3, 202.3, 205.7. **EIMS** : 400 ($M^{+\cdot}$, 100), 385 (11), 382 (8), 372 (27), 367 (20), 285 (21), 271 (24), 105 (51), 55 (62.5). **HREIMS** : calcd for $C_{25}H_{36}O_4$: m/z 400.2613, found: 400.2641.

29 : 41 % $[\alpha]_D$ + 10 (c = 0.66). **IR** : 3409, 2966, 2935, 2875, 1673, 1617, 1553, 1455, 1375, 1045, 1029, 735. **^{1}H-NMR** : δ 0.87 (3H, s), 1.02 (3H, s), 1.04 (3H, s), 1.20 (3H, s), 0.90-3.00 (15H, m), 1.99 (3H, s), 3.25 (1H, dd, J= 5, 10.5 Hz, H-3), 3.70 (2H, m), 5.42 (1H, m, H-11). **^{13}C-NMR** : δ 12.4, 15.4, 18.2, 20.4, 25.2, 25.5, 27.8, 28.2, 29.1, 31.1, 34.1, 38.0, 39.1, 39.3, 44.6, 47.6, 56.2, 61.2, 79.0, 114.5, 142.6, 147.5, 149.8, 202.1, 204.7. **EIMS** : 400 ($M^{+\cdot}$, 100), 382 (25), 367 (23), 285 (14), 271 (16), 213 (27), 105 (20), 91 (19). **HREIMS** : calcd for $C_{25}H_{36}O_4$: m/z 400.2613, found: 400.2617.

30 : 27 % $[\alpha]_D$ - 20 (c = 0.8). **IR** :3489, 2976, 2937, 2869, 1710, 1675, 1454, 1423, 1374, 1279, 1032, 755. **^{1}H-NMR** : δ 0.82 (6H, s), 1.01 (3H, s), 1.07 (3H, s), 1.85 (3H, s), 1.00-2.20 (10H, m), 2.80-3.00 (5H, m), 3.23 (2H, dd, J= 4.2, 10.6 Hz, H-3), 4.84 (1H, s, -CHS_2-), 5.45 (1H, m, H-11), 6.50 (1H, s, H-16). **^{13}C-NMR** : δ 12.9, 15.9, 16.1, 20.2, 21.6, 22.3, 22.7, 25.6, 27.7 (2), 28.0, 29.1, 30.5, 30.7, 31.0, 34.2, 35.5, 39.2, 44.5, 51.4, 60.1, 78.6, 110.7, 120.9, 140.9, 152.8, 216.9. **EIMS** : 476 ($M^{+\cdot}$, 9), 356 (6), 121 (11), 120 (14), 119 (100). **HREIMS** : calcd for $C_{27}H_{40}O_3S_2$: m/z 476.2419, found: 476.2408.

31: 14 % $[\alpha]_D$ - 38 (c = 0.75). **IR** : 3496, 2971, 2933, 2875, 1712, 1671, 1374, 1277, 1066, 1032,755. **^{1}H-NMR** : δ 0.82 (3H, s), 1.02 (3H, s), 1.03 (3H, s), 1.18 (3H, s), 2.08 (3H, s), 1.00-2.70 (10H, m), 2.80-3.00 (5H, m), 3.25 (2H, m), 4.84 (1H, s, -CHS_2-), 5.16 (1H, dd, J= 3.2, 5.6 Hz, H-11), 5.83 (1H, s, H-16). **^{13}C-NMR** : δ 17.0, 17.7, 19.9, 21.8, 22.3, 22.8, 26.9, 27.7 (2), 28.2, 30.0, 32.5, 32.9, 33.2, 34.1, 35.5, 50.9, 51.5, 51.7, 55.9, 56.4, 78.7, 112.9, 129.7, 140.9, 152.8, 229.3. **EIMS** : 476 ($M^{+\cdot}$, 9), 356 (15), 122 (26), 120 (27), 119 (100), 57 (34).

32 : 5 % $[\alpha]_D$ - 22 (c = 0.3). **IR** : 3450, 2975, 2925, 1666, 1447, 1379, 1081, 1035, 909. **^{1}H-NMR** : δ 0.91 (3H, s); 0.99 (3H, s); 1.20 (3H, s); 1.22 (3H, s); 1.86 (3H, s); 1.40-2.60 (10H, m); 2.70-3.00 (5H, m); 3.20 (2H, m); 4.76 (1H, s, -CHS_2-); 5.55 (1H, m, H-11); 6.46 (1H, s, H-16). **^{13}C-NMR** : δ 14.3, 16.1, 19.5, 20.8, 22.3, 22.9, 23.7, 25.7, 27.4, 27.8 (2), 30.9, 31.2, 32.2, 33.1, 34.4, 38.7, 42.9, 43.8, 59.9, 74.4, 78.8, 114.6, 139.6, 150.2, 155.8, 201.7. **EIMS** : 476 ($M^{+\cdot}$, 17), 457(3), 355 (22), 338 (7), 322 (6), 253 (11), 200 (20), 118 (100). **HREIMS** : calcd for $C_{27}H_{40}O_3S_2$: m/z 476.2419, found.: 476.2396.

33 : 33 % $[\alpha]_D$ - 74 (c = 0.77). **IR** : 3455, 2940, 2869, 1726, 1666, 1379, 1276, 1087, 1037,756. **^{1}H-NMR** : δ 0.90 (3H, s), 0.96 (3H, s), 1.12 (3H, s), 1.25 (3H, s), 2.07 (3H, s), 1.40-2.00 (8H, m), 2.20-2.50 (2H, m), 2.80-3.00 (5H, m), 3.20 (2H, m), 4.82 (1H, s, -CHS_2-), 5.16 (1H, s, H-11), 5.80 (1H, d, J= 1, H-16). **^{13}C-NMR** : δ 14.9, 15.6, 19.8, 20.3, 22.8, 24.4, 25.9, 27.5, 27.9 (2), 32.6, 33.2, 33.2, 33.8, 37.9, 38.6, 39.7, 44.9, 52.1, 55.7, 79.3, 79.5, 114.1, 129.3, 150.2, 155.8, 199.8. **EIMS** : 476 ($M^{+\cdot}$, 2), 400 (1), 356 (6), 201 (3), 138 (8), 59 (100).

34 : 90 % **m.p.** 177-179°C (heptane-ether). $[\alpha]_D$ +8 (c = 1.1). **IR** : 3402, 2938, 2360, 1704, 1458, 1376, 1125, 1039, 980, 940. **^{1}H-NMR** : δ 0.78 (1H, m, H-7α), 0.83 (3H, s, Me-4ax), 0.915 (1H, m, H-5), 0.92 (3H, s; Me-13), 0.97 (3H, s, Me-4eq), 1.05 (3H, s, Me-10), 1.16 (3H, s, Me-17), 1.45-1.85 (10H, m), 2.20-2.34 (4H, m, H-12α, H-12β, H-7β, H-20), 2.42 (1H, d, J=17.2, H-16β), 2.58 (1H, d, J=9.3, H-14), 2.69 (1H, m, H-8), 2.75 (1H, d, J=17.2, H-16α), 3.21 (1H, dd, J=4.5, 11.3), 3.90 (4H, m), 4.83 (1H, t, J=4.5, H-19), 5.25 (1H, d, J=5.6, H-11). **^{13}C-NMR** : δ 15.3 (Me-4ax), 19.1 (Me-13), 20.4 (Me-10), 21.3 (C-6), 26.1 (Me-17), 27.6 (C-2), 28.0 (Me-4eq), 28.8, 31.1 (Me-8), 33.7, 34.5, 34.8 (C-7), 35.5 (C-1), 39.1, 39.3 (C-10), 47.1(C-13), 48.3 (C-17), 49.1 (C-16), 52.9 (C-5), 55.9 (C-14), 64.4 and 64.8(O-$\underline{CH_2CH_2}$-O), 78.6 (C-3), 103.8 (C-19), 110.8 (C-11), 148.2 (C-9), 208.6 (C-15), 215.7 (C-18). **EIMS** : 458 ($M^{+\cdot}$, 22), 443 (13), 440 (13), 298 (15), 287 (35), 285 (18), 172 (18), 101 (100), 99 (87), 73 (88). **HREIMS** : calcd for $C_{28}H_{42}O_5$: m/z 458.3032, found.: 458.3039.

35 : 70 % **m.p.** 184-186°C (heptane). $[\alpha]_D$ - 19 (c = 0.98). **IR** : 3508, 2944, 2858, 1693, 1656, 1474, 1388, 1362, 1275, 1253, 1110, 1097, 1075, 886, 839, 773. **^{1}H-NMR** : δ 0.03 (3H, s), 0.05 (3H, s), 0.73 (3H, s), 0.78 (3H, s), 0.87 (3H, s), 0.89 (9H, s), 0.93 (3H, s), 1.03 (3H, s), 0.50-2.20 (18 H, m), 2.35 (1H, d, J= 12.3), 2.57 (1H, m), 2.85 (4H, m), 3.16 (1H, dd, J= 5.1, 10.2), 3.55 (1H, s), 4.00 (1H, t, J= 6.4), 5.18 (1H, d, J= 5.26). **^{13}C-NMR** : δ -4.8, -3.7, 13.4, 16.0, 18.2, 18.9, 20.9, 21.7, 26.0 (3), 26.1, 28.3, 28.7, 29.8, 30.0, 30.6(2), 34.5, 35.8, 39.4, 39.9, 40.3, 42.6, 44.0, 48.1, 51.6, 53.1, 59.2, 79.6, 82.8, 110.9, 149.4, 209.9. **EIMS** : 620 ($M^{+\cdot}$, 55), 563 (95), 545 (19), 455 (20), 126 (52), 75 (100). **HREIMS** : calcd for $C_{35}H_{60}O_3S_2Si$: m/z 620.3753, found: 620.3743.

36 : 52% **IR** : 2940, 1695, 1375, 1150, 1130. **^{1}H-NMR** : δ 0.10 (9H, s), 0.70 (3H, s), 0.80 (3H, s), 0.92 (3H, s), 1.04 (3H, s), 1.06 (3H, s), 1.15 (6H, t, J=7.0), 1.16 (3H, s), 2.20 (1H, d, J=17.0), 2.30 (1H, m), 2.65 (1H, d, J=17.0), 2.95 (1H, d, J=9.2), 3.15 (1H, m), 3.30-3.60 (4H, m), 4.35 (1H, t, J=5.2), 5.05 (1H, m). ^{13}**C-NMR** : δ 0.4, 15.3, 16.0, 21.2, 21.8, 22.1, 26.8, 28.1, 28.5, 29.0, 29.40, 32.0, 32.9, 35.3, 35.5, 39.3, 39.5, 49.4, 49.6, 50.0, 51.4, 53.8, 61.3, 61.6, 78.3, 102.7, 110.4, 148.1, 207.8, 215.1. **EIMS**: 545 (3), 515 (3), 514 (59), 499 (19), 409 (5), 363 (11), 339 (11), 241 (8), 155 (22), 129 (38), 103 (38), 85 (100).

37 : $[\alpha]_D$ - 29 (c = 4.1). ^{1}**H-NMR** : δ 0.1 (9H, s), 0.75 (3H, s), 0.79 (3H, s), 0.85 (3H, s), 0.91 (1H, dd, J=6.5, 9.2, H-5), 1.05 (3H, s), 1.50-1.80 (7H, m), 1.98 (3H, s), 2.03 (1H, d, J=9Hz, H-14), 2.12 (1H, d, J=16.7, H-12), 2.22 (1H, dd, J=6.2, 16.5, H-12), 2.38 (1H, dt, J=3.9, 8.2, 12.3, H-1), 2.58 (1H, m, H-8), 3.18 (1H, dd, J=4.2, 11.3, H-3), 4.25 (1H, s, H-18), 5.20 (1H, d, J=4.6, H-11), 5.85 (1H, s, H-16). ^{13}**C-NMR** : δ 0.6, 12.1, 15.9, 19.8 (Me-17), 20.6, 21.9, 28.3, 28.6, 30.9 (C-8), 35.7, 36.2 (C-1), 37.4, 39.6, 42.4, 53.6 (C-5), 56.8 (C-14), 79.8 (C-3), 80.1 (C-18), 110.1 (C-11), 127.1 (C-16), 149.5, 159.3, 199.8. **EIMS** : 430($M^{+\cdot}$, 38), 415 (4), 383(3), 325 (5), 231 (19), 204 (17), 157 (31), 129 (42), 73 (100). **HREIMS**: calcd for $C_{26}H_{42}O_3Si$: m/z 430.2903, found: 430.2912.

38 : 70 % **m.p.** 238-240 °C (MeOH). $[\alpha]_D$ - 92 (c = 0.81, THF). **IR** : 3691, 3426, 2965, 2882, 1706, 1603, 1454, 1368, 1273, 1113. ^{1}**H-NMR** : δ 0.82 (3H, s); 0.89 (3H, s); 0.95 (3H, s); 1.05 (3H, s); 1.16 (3H, s); 1.50-2.20 (12 H, m); 2.50-3.50 (15 H, m); 3.65 (1H, d, J= 17, H-12); 5.30 (1H, m, H-11). ^{13}**C-NMR** : δ 15.5, 17.6, 20.7, 21.6, 25.3, 25.6, 27.9, 28.2, 28.8, 29.9, 31.2, 35.1, 35.2, 35.7, 39.4, 39.5, 39.7, 40.1, 46.9, 52.1, 52.9, 54.1, 57.8, 69.0, 79.1, 88.6, 112.2, 147.5, 211.2. **EIMS** : 504 ($M^{+\cdot}$, 34), 147 (47), 145 (100), 119 (18), 115 (24), 55 (26). **HREIMS** : calcd for $C_{29}H_{44}O_3S_2$:m/z 504.2732, found: 504.2717.

39 : 85% **m.p.** 122-125 °C (MeOH). $[\alpha]_D$ - 79 (c = 0.73, THF). **IR** : 3431, 2968, 2937, 2874, 1702, 1585, 1460, 1382, 1059, 1042, 982. ^{1}**H-NMR** : δ 0.82 (3H, s); 0.89 (3H, s); 0.95 (3H, s); 1.05 (3H, s); 1.16 (3H, s); 1.25-2.50 (21 H, m); 2.54 (1H, m); 3.27 (1H, t, J= 8.5 Hz, H-3); 3.65 (1H, d, J= 17 Hz, H-12); 5.30 (1H, m, H-11). ^{13}**C-NMR** : δ 14.7, 15.4, 18.0, 20.7, 21.2, 21.5, 27.8, 28.1, 28.2, 29.7, 30.5, 34.6, 35.3, 35.7, 36.2, 39.3, 40.7, 51.3, 51.6, 53.1, 57.1 79.1, 84.8, 111.8, 114.9, 147.4, 210.2. **CIMS** : 401 $[M + H]^+$, 383 $[M + H - H_2O]^+$, 365 $[383 - H_2O]^+$. **HREIMS** : calcd for $C_{26}H_{40}O_3$: m/z 400.2977, found: 400.2969. **Anal** : calcd for $C_{26}H_{40}O_3$: C 77.95, H 10.07, found: C, 79.29; H, 9.83.

40 : 71 % **m.p.** 215-218 °C (MeOH). $[\alpha]_D$ + 22 (c = 1.18). **IR** : 3489, 2936, 2864, 1702, 1388, 1028, 756. ^{1}**H-NMR** : δ 0.86 (3H, s); 0.96 (3H, s); 0.99 (3H, s); 1.13 (3H, s); 1.15 (3H, s); 1.60 (7H, m); 1.80-2.20 (7H, m); 2.60-3.20 (9H, m); 3.24 (1H, t, J= 9.5); 3.33 (2H, d, J= 12.4); 3.62 (2H, d, 17.4); 5.40 (1H, t, J= 2.7, H-11). ^{13}**C-NMR** : δ 15.3, 17.7, 18.1, 24.5, 25.2, 25.3, 25.4, 27.7, 28.1, 28.5, 29.2, 29.3, 35.4, 37.7, 38.9, 39.2, 39.3, 40.0, 44.3, 46.8, 51.8, 52.9, 56.3, 68.7, 78.9, 88.4, 115.2, 149.2, 211.3. **EIMS** : 504 ($M^{+\cdot}$, 45), 489 (7), 486 (6), 471 (5), 339 (9), 285 (25), 213 (19), 147(52), 145 (41), 55 (100). **Anal** : calcd for $C_{29}H_{44}O_3S_2$: C 69.00, H 8.79, found: C 67.85, H 8.94. **HREIMS** : calcd for $C_{29}H_{44}O_3S_2$: m/z 504.2732, found: 504.2737.

41 ; 85% **m.p.** 116-117°C (heptane). $[\alpha]_D$ + 13 (c = 1.18). **IR** : 3472, 2944, 2866, 1702, 157, 1384, 1072, 1025, 998. ^{1}**H-NMR** : δ 0.85 (6H, s); 0.99 (6H, s); 1.08 (3H, s); 1.20-2.20 (20H, m); 2.28 (1H, d, J= 9.2 Hz); 2.47 (1H, d, J= 12.8 Hz); 2.54 (1H, m); 3.23 (1H, t, J= 8.5 Hz, H-3); 5.31 (1H, m, H-11).

^{13}C-NMR : δ 15.3, 18.1, 20.9, 25.2, 25.3, 27.8, 28.1, 28.7, 29.3, 35.2, 36.1, 36.7, 37.8, 39.2, 39.8, 44.4, 48.2, 51.3, 53.7, 54.9, 55.8, 79.9, 84.7, 114.8, 150.1, 201.7. **EIMS** : 400 ($M^{+\cdot}$, 24), 283 (14), 289 (26), 261 (26), 243 (72), 139 (51), 98 (87),96 (100). **HREIMS** : calcd for $C_{26}H_{40}O_3$: m/z 400.2977, found: 400.2983.

42 : 95 % **m.p.**160-162 °C (MeOH). $[\alpha]_D$ + 14 (c = 1). **IR** : 3540, 2973, 2935, 2872, 1717, 1702, 1460, 1375, 1278, 1243, 1215, 1033, 943, 908, 755, 669. **^{1}H-NMR** : δ 0.82 (3H,s); 1.02 (3H, s); 1.03 (3H, s); 1.15 (3H, s); 1.24 (3H, s); 1.50-2.20 (20 H, m); 2.30 (1H, d, J= 16.5, H-16); 2.73 (1H, d, J= 16.5, H-16); 2.86 (3H, m); 3.06 (1H, d, J= 4.6, H-14); 3.26 (1H, dd, J= 4.3, 10.6, H-3); 4.00 (1H, t, J= 6, H-19); 5.18 (1H, d, J= 5.6, H-11). **^{13}C-NMR** : δ 15.4, 21.1, 21.4, 21.9, 25.6, 26.2, 27.4, 27.9, 29.1, 30.1, 30.4 (2), 31.8, 32.6, 35.2, 37.3, 38.9, 39.1, 47.1, 48.9, 49.3, 49.7, 51.1, 53.4, 78.2, 110.2, 147.5, 207.3, 214.4. **EIMS** : 504 ($M^{+\cdot}$, 26), 476 (14), 357 (10), 217 (28), 147 (45), 145 (100), 119 (55), 41(48). **HREIMS** : calcd for $C_{29}H_{44}O_3S_2$: m/z 504.2732, found: 504.2758. **Anal** : calcd for $C_{29}H_{44}O_3S_2$: C 69.00, H 8.79, found: C 68.53, H 9.14.

43 : 70 % **m.p.**165-167°C (heptane). $[\alpha]_D$ + 38 (c = 1.28). **IR** : 3507, 2963, 2930, 2870, 1709, 1461, 1377, 1280, 1065, 755. **^{1}H-NMR** : δ 0.81 (3H, s); 0.99 (3H, s); 1.03 (3H, s); 1.25 (3H, s); 1.51 (3H, s); 1.40-3.30 (27H, m); 3.61 (1H, d, J= 4.1 Hz, H-3); 5.15 (1H, d, J= 5.9 Hz, H-11). **^{13}C-NMR** : δ 15.7, 21.3, 21.8, 21.9, 25.6, 26.7, 27.8, 28.2, 28.9, 29.4, 29.6, 32.9, 35.4, 39.1, 39.2, 41.2, 48.1, 51.4, 51.6, 55.0, 55.9, 69.7, 78.8, 88.1, 112.5, 146.5, 210.2. **EIMS** : 504 ($M^{+\cdot}$, 18), 476 (9), 357 (6), 279 (5), 217 (19), 145 (100), 119 (19), 105 (22), 91 (20), 55 (27), 41 (35). **HREIMS** : calcd for $C_{29}H_{44}O_3S_2$: m/z 504.2732, found: 504.2723.

44 : 72 % **m.p.**110-112°C (heptane). $[\alpha]_D$ + 50 (c = 1.39). **IR** : 3482, 2977, 2931, 2871, 1702, 1457, 1370, 1277, 1217, 1131, 1071, 1038, 978, 752, 666. **^{1}H-NMR** : δ 0.81 (3H, s); 1.00 (3H, s); 1.02 (6H, s); 1.08 (3H, s); 1.10-2.10 (22H, m); 2.21 (1H, d, J= 17.5 Hz); 2.32 (1H, m); 2.52 (2H, dd, J= 4.2, 11.5 Hz); 2.74 (1H, d, J= 4.6 Hz); 3.27 (1H, dd, J= 5.9, 10.1 Hz, H-3); 5.21 (1H, d, J= 3.5 Hz, H-11). **^{13}C-NMR** : δ 15.6, 18.1, 21.1, 21.6, 21.8, 22.1, 27.7, 28.2, 29.4, 29.8, 32.2, 35.6, 36.1, 39.2, 41.6, 45.9, 51.4, 51.7, 51.9, 54.9, 78.8, 84.8, 112.2, 146.9, 209.7. **EIMS** : 400 ($M^{+\cdot}$, 100), 382 (74), 367 (46), 364 (44), 349 (39), 243 (38), 181 (83), 139 (99), 105 (52), 95 (48).

45 : 95 % **m.p.**72-74°C (heptane). $[\alpha]_D$ - 19 (c = 1.19). **IR** : 3502, 2969, 2938, 2875, 1702, 1456, 1376, 1269, 1171, 1029, 739. **^{1}H-NMR** : δ 0.87 (3H, s); 0.94 (3H, s); 1.01 (3H, s); 1.09 (3H, s); 1.27 (3H, s); 1.30-2.00 (18H, m); 2.11 (2H, m); 2.28 (1H, t, J= 2.8); 2.57 (2H, d, J= 1.8); 2.84 (3H, m); 3.23 (1H, t, J= 7.9, H-3); 3.96 (1H, t, J= 6.9, H-19); 5.36 (1H, s, H-11). **^{13}C-NMR** : δ 15.3, 18.1, 18.6, 25.2, 25.6, 25.8, 26.9, 27.8, 28.1, 29.5, 30.2, 30.4 (2), 35.7, 36.7, 37.9, 38.9, 39.3, 44.4, 46.9, 47.4, 48.1, 48.4, 54.9, 78.9, 114.3, 150.3, 208.3, 215.4. **EIMS** : 504 ($M^{+\cdot}$, 26), 269 (37), 145 (100), 119 (50), 105 (95), 55 (40), 41 (58). **HREIMS** : calcd for $C_{29}H_{44}O_3S_2$: m/z 504.2732, found: 504.2732.

46 : 55 % **m.p.**117-119°C (heptane). $[\alpha]_D$ - 27 (c = 1.3). **IR** : 3439, 2936, 2877, 1704, 1456, 1382, 1073, 1025,755. **^{1}H-NMR** : δ 0.86 (3H, s); 0.99 (3H, s); 1.09 (3H, s); 1.23 (3H, s); 1.30 (3H, s); 1.40-2.20 (18H, m); 2.29 (1H, d, J= 16.8, H-16); 2.40 (1H, dt, J= 3.5, 9.2); 2.55 (1H, d, J= 16.7, H-16); 2.83 (3H, m); 2.99 (1H, dd, J= 4.5, 8.9); 3.18 (2H, m); 3.52 (1H, m); 5.33 (1H, dd, J= 2.8, 5.4, H-11). **^{13}C-NMR** : δ 15.4, 18.3, 19.2, 23.9, 25.3, 26.6, 27.8, 28.2, 28.9, 29.1, 29.9, 30.4, 34.5, 37.6, 38.9, 39.3, 39.6, 39.9, 44.3, 45.3, 48.1, 52.9, 54.0, 66.9, 79.0, 88.6, 115.4, 148.2, 213.3. **EIMS** : 504 ($M^{+\cdot}$, 17), 287 (18), 147 (67), 145 (100), 119 (90), 105 (69), 55 (88), 43 (80).

47 : 63 % **m.p.**182-184°C (heptane). $[\alpha]_D$ - 9 (c = 0.97). **IR** : 3449, 2967, 2939, 2873, 1699, 1461, 1382, 1186, 1118, 1077, 1027, 734. **^{1}H-NMR** : δ 0.86 (6H, s); 0.99 (3H, s); 1.07 (3H, s); 1.16 (3H, s); 1.40-2.20 (21H, m); 2.33 (1H, d, J= 3.6); 2.57 (1H, d, J= 2.6); 3.24 (1H, dd, J= 7.9, 9.7, H-3); 5.33 (1H, d, J= 5.2, H-11). **^{13}C-NMR** : δ 15.3, 17.9, 18.2, 20.2, 25.4, 25.9, 27.3, 27.8, 28.2, 28.3, 28.9, 33.5, 33.8, 37.1, 39.1, 44.4, 45.1, 47.8, 49.9, 50.9, 53.5, 79.1, 83.4, 114.9, 149.1, 212.1. **EIMS** : 400 ($M^{+\cdot}$, 28), 364 (81), 349 (69), 243 (75), 105 (100), 55 (94), 43 (62).

48 : 99 % **m.p.**84-86°C (heptane). $[\alpha]_D$ - 24 (c = 1.05). **IR** : 3509, 2979, 2925, 1715, 1456, 1366, 1247, 1170, 1029, 755. **^{1}H-NMR** : δ 0.87 (3H, s); 0.94 (3H, s); 1.01 (3H, s); 1.09 (3H, s); 1.27 (3H, s); 1.30-2.00 (18H, m); 2.11 (2H, dt, J= 14); 2.28 (1H, t, J= 2.8); 2.57 (2H, d, J= 1.8); 2.84 (3H, t, J= 9.6); 3.23 (1H, t, J= 7.9, H-3); 3.96 (1H, t, J= 6.9, H-19); 5.36 (1H, s, H-11). **^{13}C-NMR** : δ 15.3, 18.3, 19.2, 25.3, 25.6, 25.7, 26.9, 27.1, 28.1, 29.9, 30.2, 30.7 (2), 34.6, 36.6, 37.9, 38.9, 39.5, 42.1, 46.6, 47.5, 48.1, 48.8, 54.2, 78.8, 113.9, 149.5, 206.3, 215.1. **EIMS** : 504 ($M^{+\cdot}$, 25), 269 (30), 163 (100), 114 (15), 105 (92), 55 (46), 41 (50).

49: 77 % **m.p.**120-122°C (heptane). $[\alpha]_D$ - 22 (c = 1.07). **IR** : 3450, 2944, 2865, 1704, 1456, 1376, 1184, 1095, 1061, 1035, 756. **^{1}H-NMR** : δ 0.69 (3H,s); 0.96 (3H, s); 1.18 (3H, s); 1.24 (3H, s); 1.55 (3H, s); 1.40-3.30 (25H, m); 3.42 (1H, d, J= 3.9 Hz, H-3); 5.18 (1H, d, J= 4.2 Hz, H-11). **^{13}C-NMR** : δ 14.9, 17.9, 19.3, 22.1, 22.6, 25.6, 27.1, 27.5, 28.1, 28.8, 29.0, 34.1, 35.6, 37.2, 38.5, 38.9, 39.5, 40.7, 44.9, 48.7, 54.6, 55.5, 66.9, 79.2, 87.9, 113.8, 143.2, 209.8. **EIMS** : 504 ($M^{+\cdot}$, 43), 486 (21), 287 (36), 147 (61), 145 (100), 119 (64), 105 (42).

50 : 29 % **m.p.**80-82°C (heptane). $[\alpha]_D$ - 35 (c = 1.2). **IR** : 3428, 2939, 2864, 1706, 1458, 1374, 1183, 1091, 1061, 1035, 756. **^{1}H-NMR** : δ 0.84 (3H, s, Me-4eq); 1.00 (3H, s, Me-4ax); 1.08 (3H, s, Me-10); 1.09 (3H, s, Me-13); 1.21 (3H, s, Me-17), 1.50-2.60 (24H, m); 3.24 (1H, dd, J= 5.2, 10.7, H-3); 5.62 (1H, s, H-19). **^{13}C-NMR** : δ 15.5, 18.7, 20.1, 21.4, 23.9, 25.9, 27.7, 28.1, 29.3, 32.4, 33.0, 34.6, 38.9, 40.1, 44.5, 50.9, 56.5, 60.3, 79.1, 118.5, 122.9, 123.8, 138.2, 210.7. **EIMS** : 382 ($M^{+\cdot}$, 26), 367 (19), 349 (22), 163 (28), 105 (34), 84 (45), 69 (32), 55 (49), 43 (100), 41 (78). **CIMS** : 383 $[M + H]^+$ 365 $[M+ H - H_2O]^+$. **HREIMS** : calcd for $C_{26}H_{38}O_2$: m/z 382.2872, found: 382.2851.

51 : 95% **m.p.** 145-148 °C (heptane-AcOEt). $[\alpha]_D$ - 27 (c = 1.3, THF). **IR** : 3420, 2941, 2870, 1709, 1674, 1462, 1386, 1277, 1091, 1069, 1042, 753. **^{1}H-NMR** : δ 0.68 (1H, m, H-7α,ax); 0.82 (3H, s, Me-4ax); 0.87 (3H, s, Me-13); 0.90 (1H, m, H-5); 0.96 (3H, s, Me-4eq); 1.05 (3H, s, Me-10); 1.13 (3H, s, Me-17); 1.50 (1H, dd, J= 3.5, 12.1, H-1eq); 1.51-1.80 (6H: H-2ax, H-6ax, m; H-6eq, dd, J= 3.8, 10.0; H-18, d, J= 7.2; H-12ax, d, J= 5.7; H-2eq, m); 1.92 (1H, d, J= 12.1, H-16β); 2.06 (1H, dd, J= 4.9, 11.9, H-7β); 2.28 (1H, d, J= 9.5, H-14); 2.35 (1H, m, H-12); 2.46 (1H, d, J= 12.4, H-16α); 2.57 (1H, m, H-8); 3.19 (1H, dd, J= 4.8, 9.8 Hz, H-3); 5.17 (1H, d, J= 6.1 Hz, H-11). **^{13}C-NMR** : δ 15.4, 19.4, 20.7, 21.5, 21.9, 27.8, 27.9, 28.0, 28.1, 29.9, 34.6, 35.7, 38.1, 39.2, 40.2, 43.5, 47.9, 50.2, 53.1, 54.2, 55.7, 79.0, 112.5, 148.0, 212.5. **EIMS** : 384 ($M^{+\cdot}$, 100), 351 (47), 333 (32), 287 (37), 197 (68), 81 (63). **HREIMS** : calcd for $C_{26}H_{40}O_2$: m/z 384.3028, found: 384.3030.

52 : 95% $[\alpha]_D$ + 12 (c = 1.18). **m.p.** 212°C (pentane). **IR** : 3420, 2941, 2870, 1711, 1674, 1462, 1386, 1277, 1091, 1069, 1042, 753. **^{1}H-NMR** : δ 0.87 (3H, s, Me-4ax); 0.93 (3H, s, Me-13); 1.01 (3H, s, Me-4eq); 1.08 (3H, s, Me-10); 1.14 (3H, s, Me-17); 1.51 (4H, m); 1.60-1.75 (7H including H-12, d, J= 5.4 and H-21b, t, J=9.8); 1.80-2.10 (6H, including H-1eq, dt, J= 3.7, 10.3); 1.91 (1H, d, J= 12, H-16α); 2.24 (1H, d, J= 9.9, H-14); 2.29 (1H, m); 2.35 (1H, d, J= 7.5, H-12'); 2.47 (1H, d, J= 12, H-16β); 2.56 (1H, m, H-8); 3.25 (1H, m, H-3); 5.29 (1H, m, H-11). **^{13}C-NMR** : δ 14.1, 15.4, 18.2, 19.8, 22.5, 24.7, 25.2, 25.3, 27.7, 27.9, 28.2, 28.3, 29.7, 31.9, 33.6, 43.5, 44.4, 47.9, 50.1, 53.1, 55.7, 57.4, 79.1, 115.0, 150.6, 212.9. **EIMS** : 384 ($M^{+\cdot}$, 26), 369 (15), 350 (22), 162 (28), 105 (34), 83 (45), 69 (32), 43(100). **HREIMS** : calcd for $C_{26}H_{40}O_2$: m/z 384.3028, found: 384.3030.

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$I > \sigma(I)$. After Lorenz and polarization corrections the structure was solved with Semi Invariants Method (SIR88) which reveals all the non-hydrogen atoms of the molecule. After isotropic (R = 0.12) refinement, then anisotropic (0.095) refinement, many hydrogen atoms are located in a Fourier Difference, the remaining ones being set in theoretical position. The whole structure was refined by the full-matrix least-square techniques (use of F magnitude; x, y, z, β_{ij} for C and O atoms, x, y, z and x, y, z fixed for H atoms; 353 variables and 1385 observations; $\omega = 1/\sigma(F_O)^2 = [\sigma^2(I)+(0.04F_O{}^2)^2]^{-1/2})$ with the resulting R = 0.076, Rω = 0.075 and Sω = 2.12 (residual $\Delta\rho \leq 0.024$ eÅ^{-3}). Atomic scattering factors from International Tables for X-ray Crystallography (1974).[22] All the calculations were performed on a Digital MicroVAX 3100 computer with the MolEN package (Enraf-Nonius, 1990).[23] It must be noticed that, due to the size of the sample (great difficulties were encountered to obtain good crystals for diffraction studies), the number of observations is not very large but an anisotropic refinement is possible and do not give any atom non-positive definite.

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