

Supporting Information

Structure and Reactivity of the Dammarenyl Cation: Configurational Transmission in Triterpene Synthesis

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NMR Spectra

NMR conditions

^1H and ^{13}C NMR spectra were acquired on a Bruker Avance 500 or Varian Inova 500 MHz spectrometer at 25 °C in relatively dilute solution (<15 mM in CDCl_3) with tetramethylsilane as internal standard. Spectra shown in the figures were transformed with mild resolution enhancement (Gaussian apodization with line broadening (LB) of -0.8 Hz and GB of 0.08. Coupling constants were measured from strongly resolution-enhanced spectra (LB of -2 and GB of 0.4 or greater). Many of the fine couplings are visible only in resolution-enhanced spectra and not in the figures shown herein.

NMR spectra are shown in Figures S1–8.

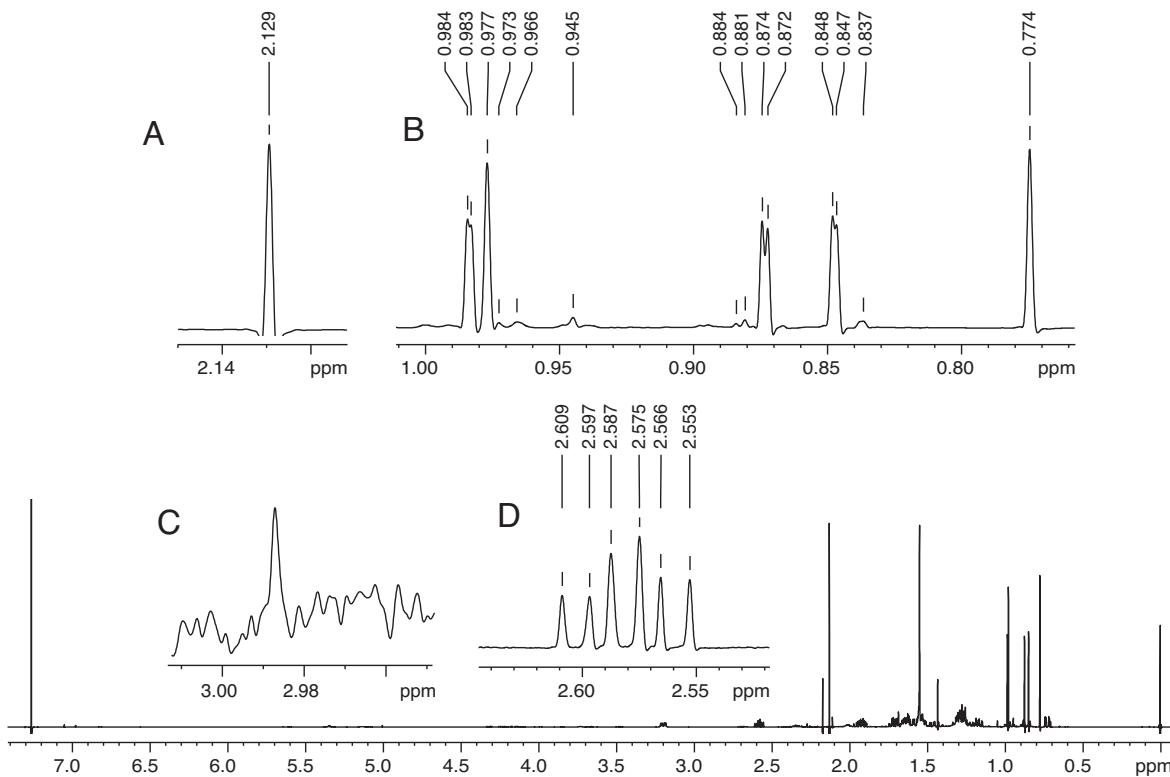


Figure S1. ^1H NMR spectrum of **24b** obtained from the enzymatic product purified by preparative TLC. Lack of signals for **24a** in the inset C (a 15000-fold vertical expansion relative to the main spectrum) compared with the multiplet in the inset D (30-fold vertical expansion) indicates that this sample contained <0.1% **24a** relative to **24b**. A similar conclusion was reached by comparing the intensity of the singlet at δ 2.130 with the absence of a singlet at δ 2.105 (not shown). The singlet at δ 2.172 is from residual acetone. Minor signals at δ 6.98 (s), 5.01 (s), 2.27 (s), and 1.43 (s) are from butylated hydroxytoluene.

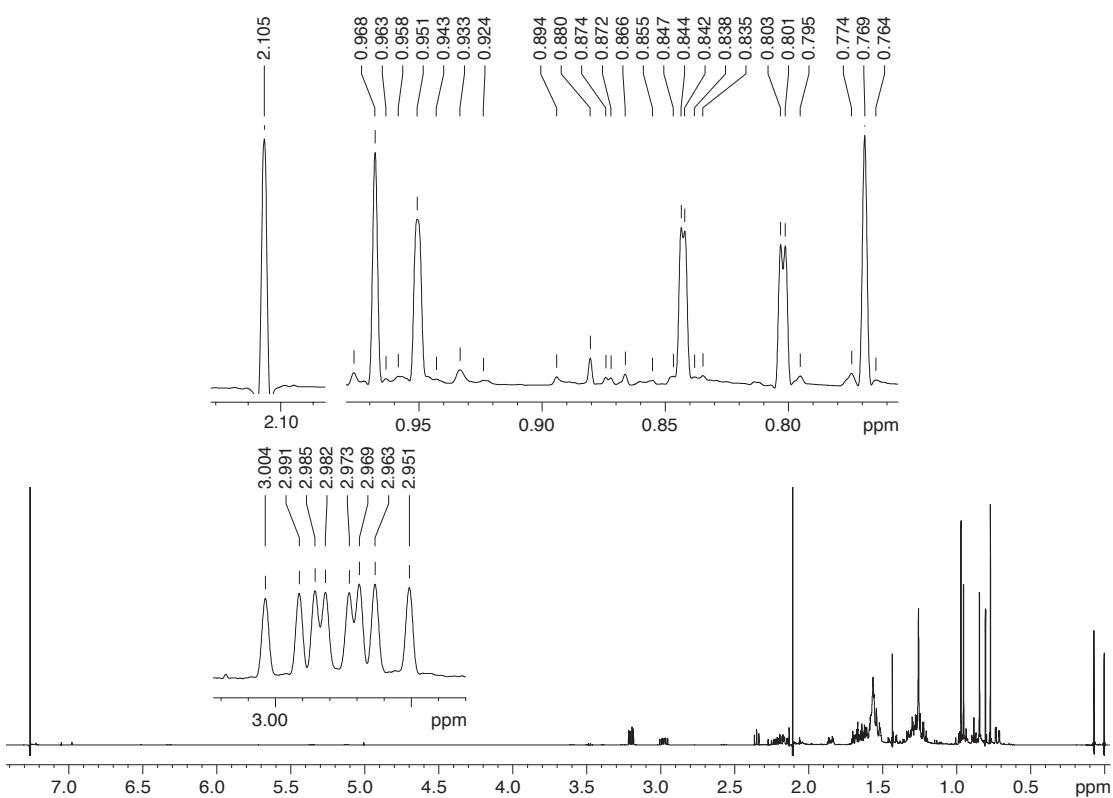


Figure S2. ^1H NMR spectrum of the 17 α -acetyl epimer **24a**.

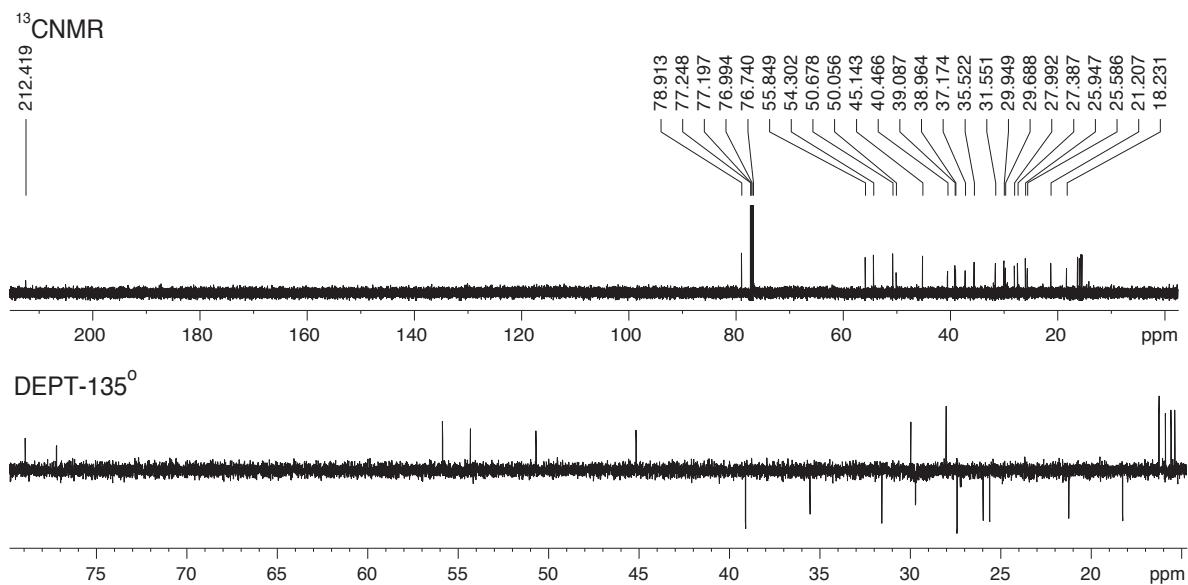


Figure S3. ¹³C NMR and DEPT spectra of **24b**.

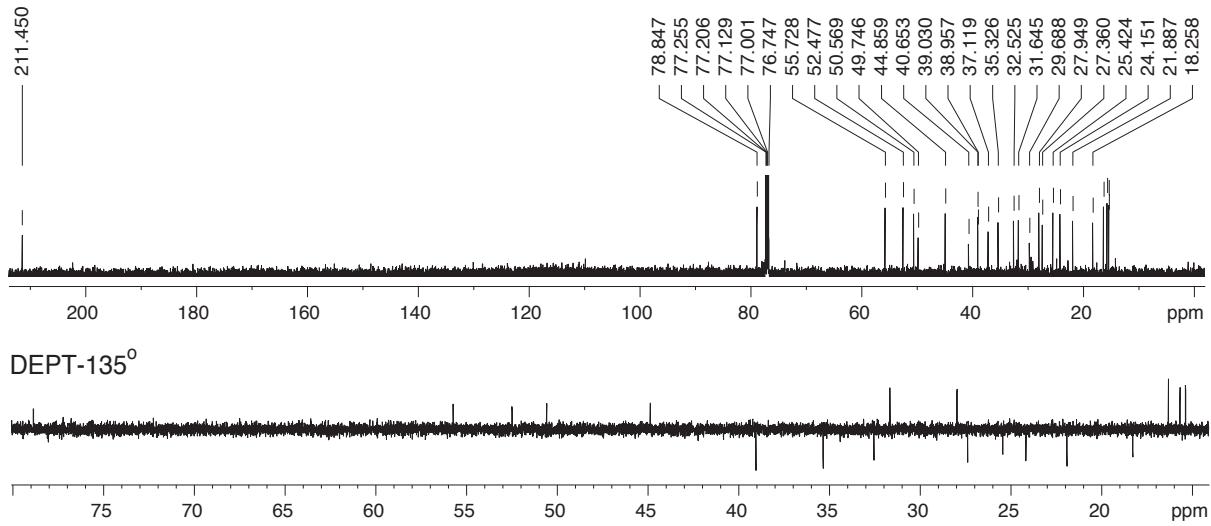


Figure S4. ¹³C NMR and DEPT spectra of **24a**.

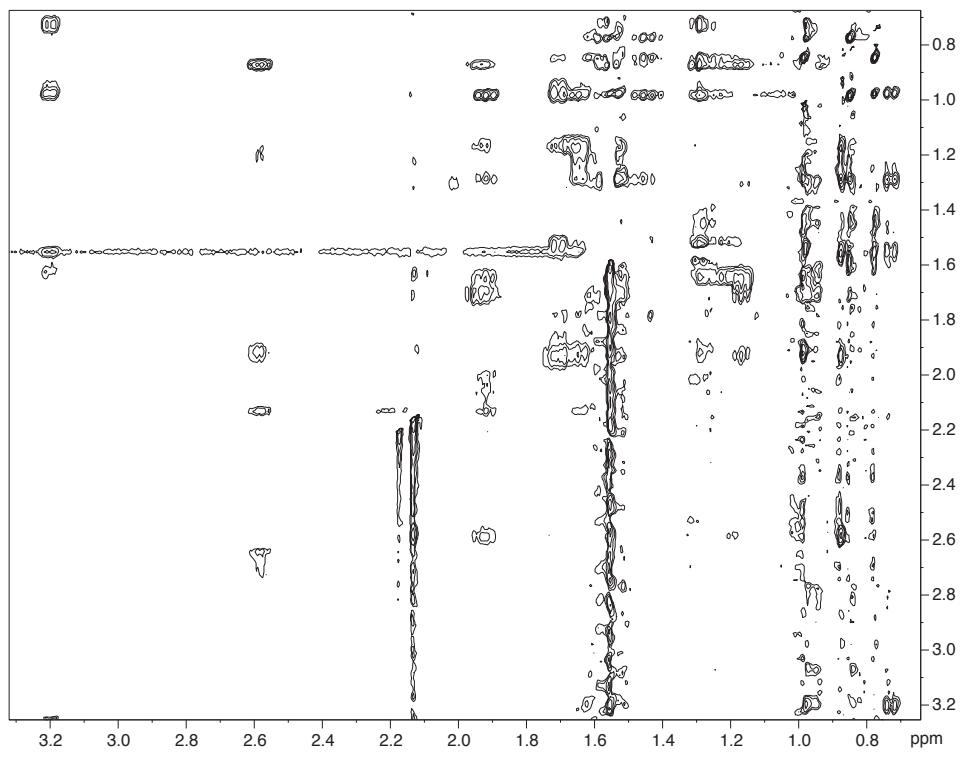


Figure S5. NOESY spectrum of **24b**.

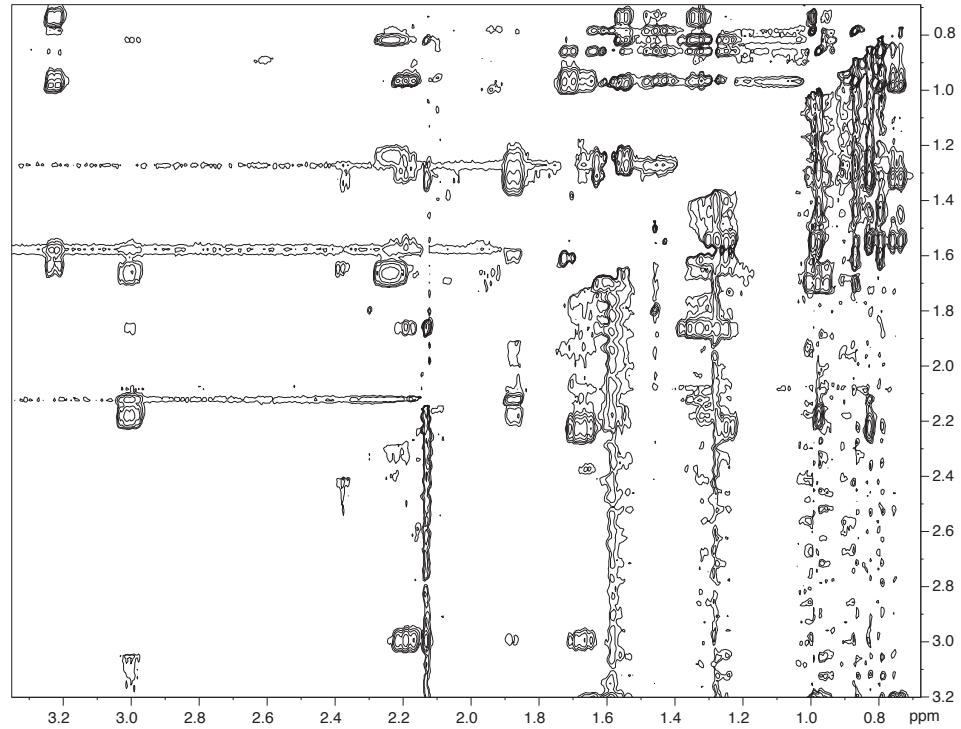


Figure S6. NOESY spectrum of **24a**.

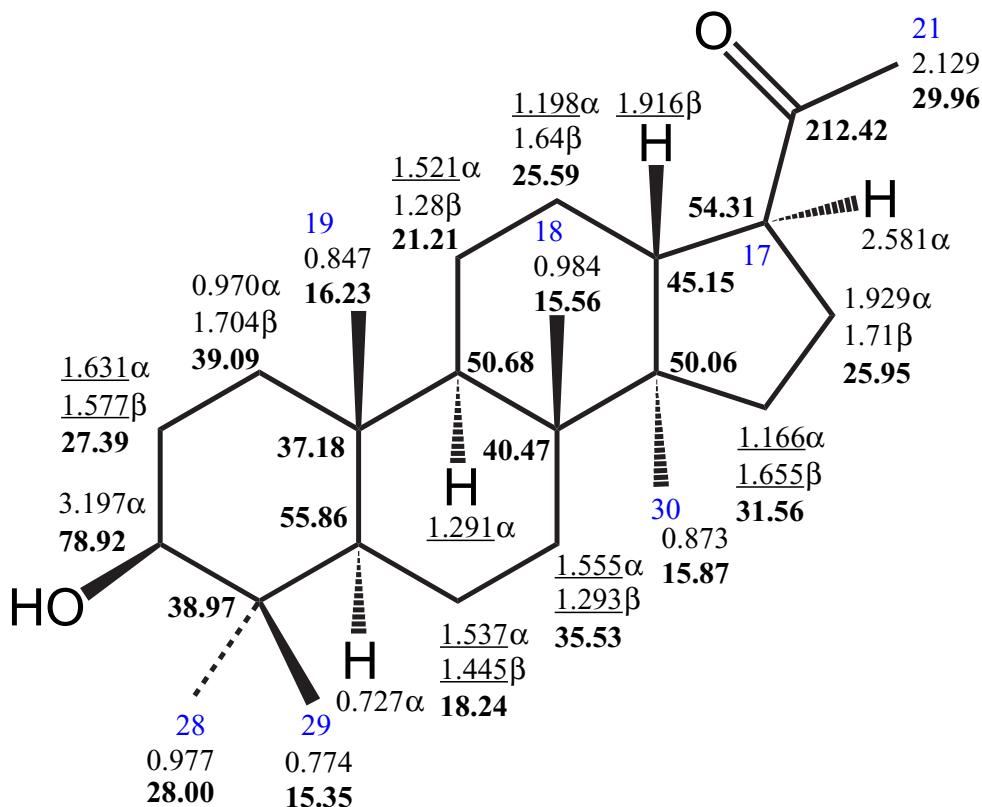
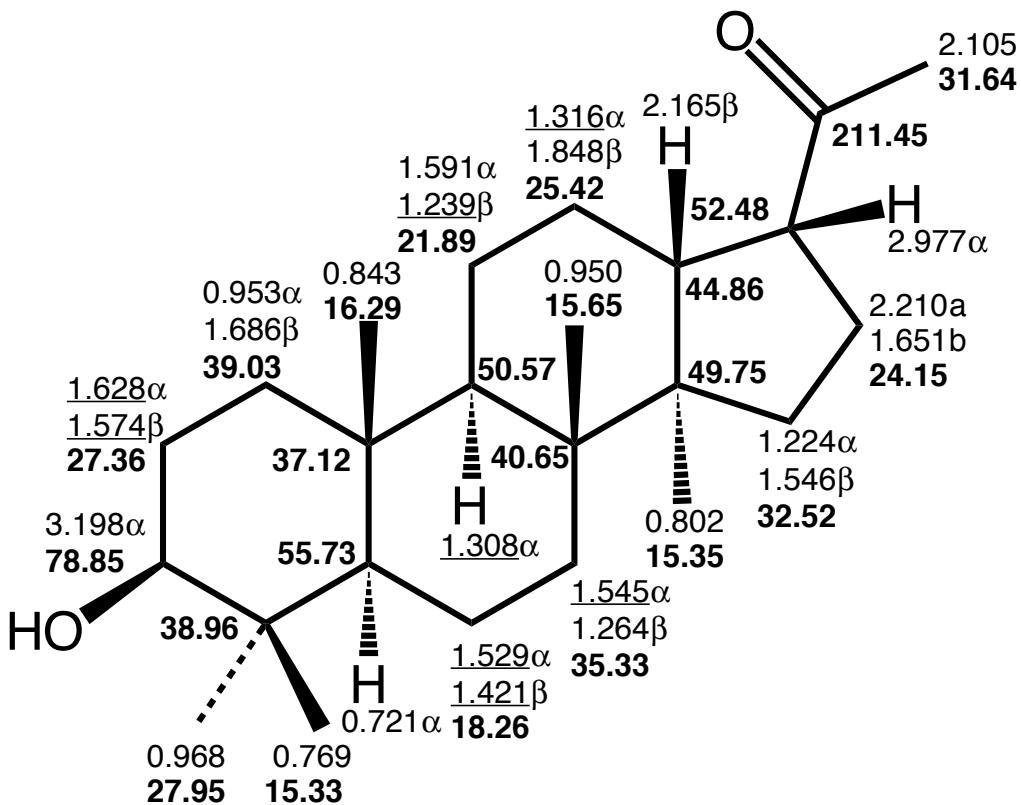


Figure S7. Detailed ¹H and ¹³C NMR chemical shifts of compound 24b. ¹³C values are in boldface. The accuracy of ¹H chemical shifts is ca. ± 0.001 ppm, while that of the underlined values is ca. ± 0.003 ppm (values to 2 decimal places are accurate to ca. ± 0.01 ppm). Nonstandard methyl numbering is indicated.



¹H NMR couplings (Hz)

H-3^α: dd, 11.4, 4.9 Hz
 H-5^α: dd, 11.8, 2.2 Hz
 H-12^β: dtd, 12.3, 4.2, 2.5
 H-13^β: br ddd, 13.1, 11.1, 3.4 Hz
 H-16^α: dddd, 13.5, 11.0, 8.2, 6.3 Hz
 H-16^β: dtd, 13.5, 9.1, 1.1 Hz
 H-17^β: ddd, 11.1, 9.1, 6.2 Hz
 H-18: d, 0.9 Hz
 H-19: d, 0.9 Hz
 H-28: d, 0.4 Hz
 H-29: d, 0.3 Hz
 H-30: d, 1.0 Hz

NOESY connectivities

H-3^α: H-1^α, H-2^α, H-2^β, H-5^α, H-28
 H-5^α: H-3^α, H-9^α, H-28
 H-13^β: H-12^β, H-17^β, H-18
 H-16^α: H-16^β, H-15^α, H-30
 H-16^β: H-16^α, H-17^β
 H-17^β: H-13^β, H-16^β, H-21
 H-18: H-6^β, H-7^β, H-11^β, H-13^β, H-15^β
 H-19: H-1^β, H-2^β, H-6^β, H-11^β, H-18, H-29
 H-21: H-12^β, H-17^β
 H-29: H-2^β, H-6^β, H-19, H-28

Figure S8. Detailed ¹H and ¹³C NMR chemical shifts of **24a**. ¹³C values are in boldface. The accuracy of ¹H chemical shift is ca. ±0.001 ppm, while that of the underlined values is ca. ±0.003 ppm. Nonstandard methyl numbering is indicated in Figure S7.

TABLE S1. ^1H and ^{13}C NMR data for **24a** and **24b**^a

Atom	24b	24a	Atom	24b	24a
C-1	39.09	39.03	H-1 α	0.970	0.953
C-2	27.39	27.36	H-1 β	1.704	1.686
C-3	78.92	78.85	H-2 α	<u>1.631</u>	<u>1.628</u>
C-4	38.97	38.96	H-2 β	<u>1.577</u>	<u>1.574</u>
C-5	55.86	55.73	H-3 α	3.197	3.198
C-6	18.24	18.26	H-5 α	0.727	0.721
C-7	35.53	35.33	H-6 α	<u>1.537</u>	<u>1.529</u>
C-8	40.47	40.65	H-6 β	<u>1.445</u>	<u>1.421</u>
C-9	50.68	50.57	H-7 α	<u>1.555</u>	<u>1.545</u>
C-10	37.18	37.12	H-7 β	<u>1.293</u>	1.264
C-11	21.21	21.89	H-9 α	<u>1.291</u>	<u>1.308</u>
C-12	25.59	25.42	H-11 α	<u>1.521</u>	1.591
C-13	45.15	44.86	H-11 β	1.28	<u>1.239</u>
C-14	50.06	49.75	H-12 α	<u>1.198</u>	<u>1.316</u>
C-15	31.56	32.52	H-12 β	1.64	1.848
C-16	25.95	24.15	H-13 β	<u>1.916</u>	2.165
C-17	54.31	52.48	H-15 α	<u>1.166</u>	1.224
8 β -Me	15.56	15.65	H-15 β	<u>1.655</u>	1.546
10 β -Me	16.23	16.29	H-16 α	1.929	2.210
C-20	212.42	211.45	H-16 β	1.71	1.651
C-21	29.96	31.64	H-17 α	2.581	2.977
4 α -Me	28.00	27.95	8 β -Me	0.984	0.950
4 β -Me	15.35	15.33	10 β -Me	0.847	0.843
14 α -Me	15.87	15.35	H-21	2.129	2.105
			4 α -Me	0.977	0.968
			4 β -Me	0.774	0.769
			14 α -Me	0.873	0.802

^a These data are identical to those in the preceding figures. The accuracy of ^1H chemical shifts is ca. ± 0.001 ppm, while that of the underlined values is ca. ± 0.003 ppm (values to 2 decimal places are accurate to ca. ± 0.01 ppm).

GC/MS and GC Analyses

Derivatization for gas chromatography (GC)

Each sample was converted to the acetate derivative by reaction with acetic anhydride-pyridine (1:1) for 2 h at ambient temperature. The derivatization reaction mixtures were used directly for GC–MS or GC analysis without evaporation of the reagents.

GC/MS conditions

GC/MS was performed on a ZAB-HF reverse-geometry double-focusing instrument interfaced to a Hewlett-Packard 5890A GC equipped with a DB-5ms column (J & W Scientific, 30 m × 0.25 mm i.d., 0.10 mm df). The column head pressure was 105 kPa. Samples were injected in the splitless mode, with the following temperature program: 150 °C for 2 min, increased at 6.5 °C /min to 280 °C. Mass spectra (m/z 60 to 600) were obtained at 70 eV with an electron-impact ion source (200 °C). The accelerating voltage was 8 kV and the resolution was 1000 (10% valley).

EI-MS of acetylated compound **24b**

MS spectrum of the acetate of compound **24b**: m/z 402 (7, M^+), 359 (23, $M - CH_3CO$), 342 (33, $M - CH_3COOH$), 327 (16, $M - CH_3COOH - Me$), 299 (100, $M - CH_3CO - CH_3COOH$), 189 (fragment a – CH_3COOH , see Tanaka, R.; Matsuda, M.; Matsunaga, S. *Phytochemistry* **1987**, 26, 3365-3366). The spectrum is shown in Figure S9.

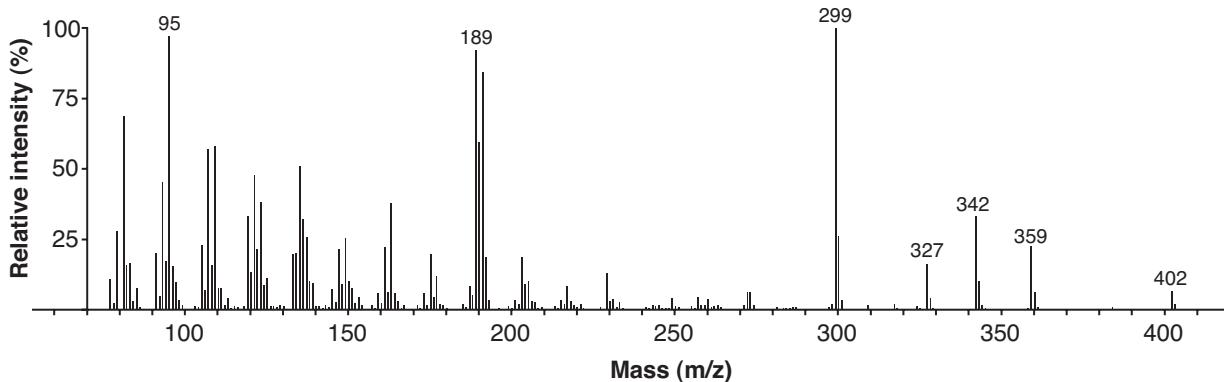


Figure S9. Mass spectrum of the acetate derivative of **24b**.

GC quantitation

GC analysis was done on a Hewlett-Packard 6890 system equipped with an Rtx-5 capillary column (Restek, 30 m × 0.25 mm i.d., 0.10 mm df). A 5 µL aliquot of each sample was injected in the split mode (split ratio of 40:1), with a helium flow rate of 20 cm/s. Epicoprostanol (Sigma, purity > 95%) was used as internal standard. The oven, injector and flame ionization detector were all at 280 °C for 30 min. Figure S10 shows the GC of the nonsaponifiable lipids from a LUP1 incubation with substrate analog **21**.

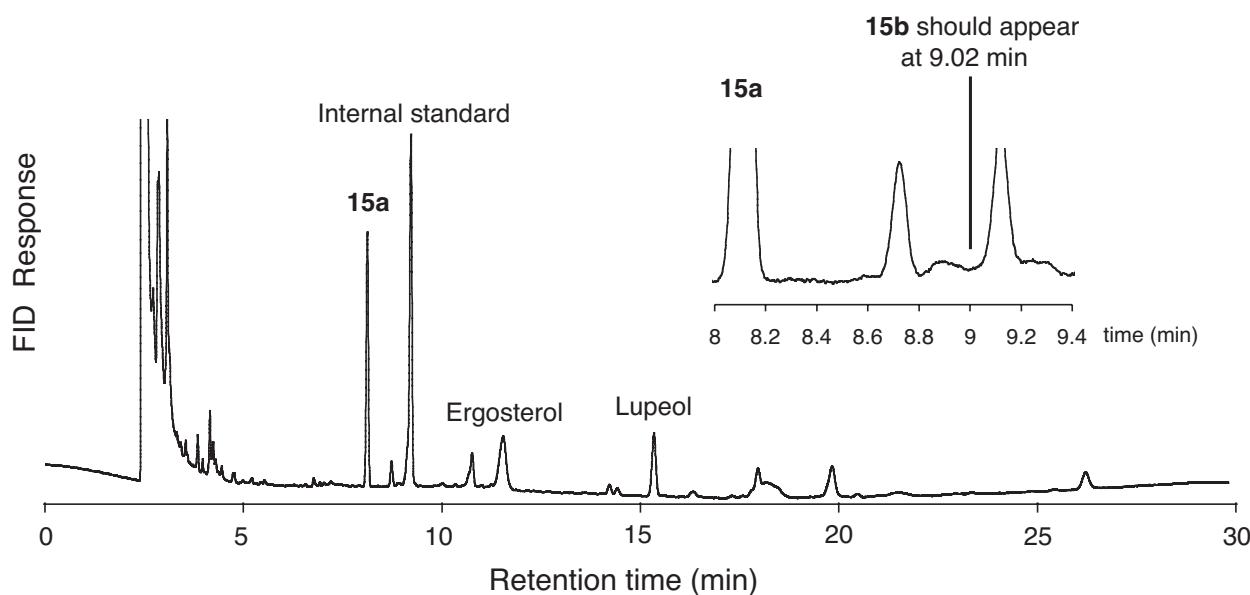


Figure S10. GC trace of the acetylated ether soluble fraction of the crude mixture from incubation of **21** with LUP1 cell homogenate (before purification by preparative TLC). The absence of a signal for **24a** at 9 min indicates that the sample contained <0.5% of **24a**.

A chromatogram similar to Figure S10 but without internal standard indicated the complete absence of **24a** (0.5% detection limit).

Although no apparent epimerization occurred in the above acetate derivatizations, another GC analysis of the acetate of **24a** indicated 0.5% of the acetate of **24b**. However, subsequent ¹H NMR analysis (Figure S1) showed that this same sample of **24a** contained <0.1% **24b**. In the same set of experiments, a sample shown by NMR to comprise a 16:1 mixture of **24b** and **24a** gave a 1:1 ratio of the acetates of **24b** and **24a** by GC analysis. These results indicate partial epimerization during derivatization or in the GC injector.

Molecular Modeling

Molecular mechanics calculations were done in PCMODEL version 8 using either the MM3 force field (neutral molecules) or MMX force field (cations). PCMODEL was obtained from Serena Software, Inc. (Bloomington, IN).

Quantum mechanical calculations were done with Gaussian 98 (Linux version A.9 or Windows version A.11) except that path calculations in Figure 2 were done with Gaussian 03 (Linux and Windows version B.02 or C.01). Geometry optimizations and vibrational frequency calculations were performed with B3LYP/6-31G*, and mPW1PW91/6-311+G(2d,p) was used for single-point energies. All models were considered as closed-shell systems (restricted calculations) with the frozen-core approximation. Zero-point energies and thermal energies at the B3LYP/6-31G* level were scaled by 0.96. Only the thermal energy contribution to enthalpies and free energies was scaled. All energy calculations were done with SCF=tight, except as noted in Table S2.

Comparison of mPW1PW91 energies between Gaussian 98 and 03 was avoided because mPW1PW91 of Gaussian 03 differs slightly from mPW1PW91 of Gaussian 98 owing to an error in the original mPW exchange functional. Because the original functional was optimized with this error, the corrected functional is not fully optimized. In comparing energy differences, deviations between the two versions of mPW1PW91 are usually <<1 kcal/mol. However, inadvertent mixing of the two versions can give errors of a few kcal/mol. For background on this subject, see: http://www.gaussian.com/g_tech/g03_rel.htm#updatedman

All energies are given as kcal/mol.

Relative energies of **24a** and **24b**

The following energy comparisons were made to determine the Boltzmann distribution for an equilibrium mixture of isomers for **24a** and **24b**.

The following minima were found in a cursory study (the designations of conformer A and conformer B are unrelated to their structures):

24a, conformer B: H17-C17-C20-O20 153°, hyperconjugation to C13-C17

24b, conformer A: H17-C17-C20-O20 -172°

24b, conformer B: H17-C17-C20-O20 147°, hyperconjugation to C16-C17

TABLE S2. Relative electron energies (kcal/mol) for **24a** and **24b**^a

<i>Theoretical method</i>	24b , conformer B	24b , conformer A	24a , conformer B
HF/3-21G	0.00	0.77	2.18
B3LYP/6-31G*	0.00	0.37	2.22
B3LYP/6-311+G(2d,p)	0.00	0.22	3.09
mPW1PW91/6-31G*	0.00	0.24	2.23
mPW1PW91/6-311+G(2d,p)	0.00	0.28	2.92
<hr/>			
<i>Thermodynamic results</i>			
ZPE increment, scaled	0.00	0.22	0.15
ΔH increment, scaled	0.00	0.18	0.06
ΔG increment, scaled	0.00	0.18	0.62
ΔS	0.00	-0.03	1.89

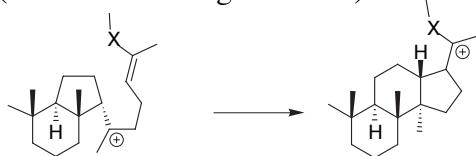
^a Geometry optimization and frequency calculations were done with B3LYP/6-31G*. The B3LYP/6-311+G(2d,p) energy calculations were done without SCF=tight.

Because the conformational analysis was incomplete, we used only one conformer of each stereoisomer in the Boltzmann distribution. For the mPW1PW91/6-311+G(2d,p) enthalpy difference of 2.98 kcal/mol (electron energy difference plus ΔH increment of 0.06 kcal/mol), this gave a ratio of **24b** to **24a** of 99.3% to 0.7%. The free energy difference (ΔG increment of 0.62) would give a 99.7 to 0.3 ratio. If conformer A of **24b** were included, the Boltzmann distribution from enthalpy calculations would be 68.1 : 31.5 : 0.5 for **24b** (B) : **24b** (A) : **24a** (B).

The above results have two serious limitations: (1) A thorough conformational analysis of the side-chain rotamers was not done. The cross section of the PES along the H17-C17-C20-O20 torsion angle appears to have a rather flat topography, and use of energy minima to calculate the Boltzmann distribution may not give accurate rotamer populations. (2) Solvation in CDCl₃ is likely to affect the relative enthalpies and free energies, and our calculations were done for gas-phase models. Consequently, we use a round figure of 0.5% as a rough estimate for the amount of **24a** in an equilibrium mixture.

It should be noted that the stability of side-chain epimers is reversed in 20-keto derivatives of the protosteryl cation. Whereas the 17β side chain is more stable for dammarenyl cation derivatives, the 17α side chain is preferred in 20-keto-protosteryl cation derivatives (see ref. 11d).

TABLE S3. Part A. Relative energies in the formation of 17α (**26a**, **28a**) and 17β (**26b**, **28b**) dammarenyl cation models (B3LYP/6-31G* geometries)^{a-c}



25a	X=C	26a	X=C	17α SC
25b	X=C	26b	X=C	17β SC
27a	X=O	28a	X=O	17α SC
27b	X=O	28b	X=O	17β SC

Theoretical method for energy calculation	Activation energies				Cyclization energies			
	17α		17β		26a	26b	28a	28b
	20-oxa	20-oxa	20-oxa	20-oxa	17α	17β	17α	17β
<i>Electron energies relative to the bicyclic reactant (kcal/mol)</i>								
HF/6-31G*	12.3	13.7	11.6	12.8	0.9	-5.6	-17.7	-24.3
B3LYP/6-31G*	6.7	7.9	6.9	7.8	0.9	-4.5	-12.9	-18.7
B3LYP/6-311+G(2d,p)	7.4	8.6	7.2	8.1	3.1	-2.1	-10.3	-15.9
MPW1K/6-31G*	6.8	7.9	7.2	8.2	-8.5	-14.6	-24.3	-30.3
MPW1K/6-311+G(2d,p)	7.4	8.5	7.5	8.5	-6.8	-12.8	-22.1	-28.0
mPW1PW91/6-31G*	6.4	7.5	6.9	7.8	-5.4	-11.2	-19.7	-25.5
mPW1PW91/6-311+G(2d,p)	6.9	8.1	7.2	7.9	-3.6	-9.4	-17.6	-23.5
MP2/6-31G*	0.4	1.4	0.5	0.8	-10.8	-16.6	-28.7	-35.2
<i>Thermodynamic results^b</i>								
ZPE increment, scaled	0.9	0.7	0.8	0.3	2.5	2.2	3.4	3.0
ΔH increment, scaled	0.1	0.0	0.1	-0.3	1.4	1.2	2.1	1.9
ΔG increment, scaled	3.6	2.8	3.1	2.0	6.1	5.0	7.0	5.9
ΔS	-11.7	-9.4	-10.2	-7.7	-15.9	-12.7	-16.2	-13.4

^a This is an expansion of Table 1, which contained only mPW1PW91/6-311+G(2d,p)//B3LYP/6-31G(d) enthalpies and free energies. This table has a different format from Table 1 and contains electron energies rather than enthalpies or free energies. Estimates of enthalpies and free energies can be obtained by adding the scaled ΔH or ΔG increment to the electron energy in the same column. The preferred mPW1PW91/6-311+G(2d,p) cyclization energies are shown in boldface type.

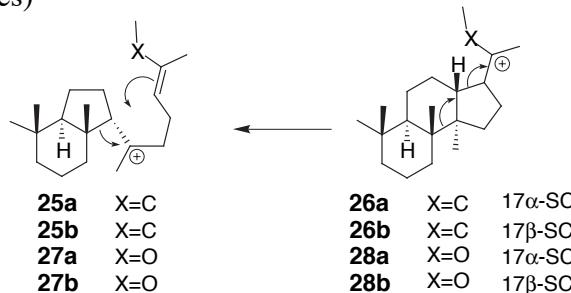
^b The thermodynamic results were obtained from B3LYP/6-31G* frequency calculations. Scaling with a factor of 0.96 was done only for the thermal energy contributions to the ΔH and ΔG increments.

^c The mPW1PW91/6-311+G(2d,p)//B3LYP/6-31G* enthalpy (free energy) of **25a** relative to **25b** was -0.1 (-0.5) kcal/mol; values for **27a** relative to **27b** were -0.3 (-0.8) kcal/mol. These values, which differed by at most ca. 0.2 kcal/mol among correlated methods, indicate essentially identical energies for pairs of conformers that, upon C-ring expansion and D-ring formation, lead to a pair of C17 epimers.

Observations from data in Table S3:

1. The four reactions had similar activation energies but differed markedly in cyclization energies. The latter differences are attributable to (a) stabilization of the product cation by oxygen and (b) steric interactions between the C20 and C14 methyl groups in products with a 17 α side chain.
2. Thermodynamic increments for activation and cyclization energies were fairly similar in all four reactions.
3. All DFT methods predicted similar activation energies but differed markedly in prediction of cyclization energies.

TABLE S3. Part B. Relative activation energies and net energies for the reversal of D-ring formation, i.e. formation **25a**, **25b**, **27a**, and **27b** from the dammarenyl cation models (B3LYP/6-31G* geometries)^a



Theoretical method for Energy Calculation	Activation energies				Reverse cyclization energies			
	17 α	17 β	17 α 20-oxa	17 β 20-oxa	25b	25a	27b	27a
HF/6-31G*	11.4	19.3	29.3	37.1	-0.9	5.6	17.7	24.3
B3LYP/6-31G*	5.8	12.4	19.8	26.5	-0.9	4.5	12.9	18.7
B3LYP/6-311+G(2d,p)	4.3	10.7	17.4	24.1	-3.1	2.1	10.3	15.9
MPW1K/6-31G*	15.3	22.6	31.6	38.4	8.5	14.6	24.3	30.3
MPW1K/6-311+G(2d,p)	14.2	21.3	29.6	36.5	6.8	12.8	22.1	28.0
mPW1PW91/6-31G*	11.8	18.7	26.6	33.3	5.4	11.2	19.7	25.5
mPW1PW91/6-311+G(2d,p)	10.6	17.5	24.8	31.4	3.6	9.4	17.6	23.5
MP2/6-31G*	11.2	17.9	29.3	36.0	10.8	16.6	28.7	35.2
<i>Thermodynamic results^b</i>								
ZPE increment, scaled	-1.6	-1.5	-2.5	-2.7	-2.5	-2.2	-3.4	-3.0
ΔH increment, scaled	-1.2	-1.2	-2.0	-2.2	-1.4	-1.2	-2.1	-1.9
ΔG increment, scaled	-2.5	-2.2	-3.8	-3.9	-6.1	-5.0	-7.0	-5.9
ΔS	4.2	3.4	6.0	5.7	15.9	12.7	16.2	13.4

^a This table is analogous to Table S3, part A except that the energies are for the reverse reaction. The preferred mPW1PW91/6-311+G(2d,p) cyclization energies are shown in boldface type.

Predictions: 20-oxa reactions are irreversible; 17 β -dammarenyl cation formation possibly has slight reversible character; 17 α -dammarenyl cation formation probably has some reversible character (depending on the kinetics of E-ring formation).

TABLE S4. Part A. Geometry changes during ring-C enlargement/D-ring formation in 17 β -dammarenyl cation synthesis, as modeled by a path calculation for the conversion of **25b** to **26b**.^a



Point on path	1	2	3	4	5	6=TS	7	8	9
<i>Energy relative to 25b (kcal/mol)</i>									
B3LYP/6-31G*	0.0	0.5	1.4	2.1	5.3	7.9	3.9	-2.6	-4.5
HF/3-21G	0.0	1.1	4.7	6.3	8.6	9.9	2.3	-9.3	-12.2
mPW1PW91 ^b	0.0	0.6	2.6	3.9	6.3	8.1	2.2	-7.3	-9.3
<i>Interatomic distance (Å)</i>									
C8-C13	1.722	1.808	2.110	2.333	2.354	2.363	2.410	2.507	2.544
C8-C14	2.550	2.524	2.588	2.563	2.276	1.970	1.697	1.611	1.608
C13-C17	3.377	3.444	3.477	3.326	3.072	2.782	2.312	1.797	1.655
C14-C17	3.119	3.102	3.088	3.010	2.944	2.881	2.736	2.535	2.485
C16-C17	1.496	1.498	1.504	1.508	1.510	1.511	1.516	1.543	1.560
C17-H17	1.090	1.091	1.091	1.091	1.091	1.091	1.090	1.091	1.093
C22-C23	1.541	1.541	1.540	1.540	1.541	1.542	1.546	1.557	1.564
<i>Valence angle (°)</i>									
C8-C13-C14	107.1	102.1	93.1	83.1	69.6	56.4	44.1	38.3	37.3
C16-C17-C20	126.9	127.4	127.6	127.4	127.4	127.5	127.1	123.0	119.9
C13-C17-C20	121.1	126.1	122.5	109.8	101.7	95.6	89.6	95.1	103.0
<i>Torsion angle (°)</i>									
8-13-14-15	-90.2	-91.2	-91.8	-96.5	-104.3	-112.1	-119.6	-123.0	-123.1
8-14-15-16	-137.4	-147.2	-160.4	-166.7	-168.7	-170.3	-169.8	-165.0	-159.0
13-14-15-16	-93.3	-98.5	-101.5	-96.5	-85.2	-73.8	-61.1	-50.5	-43.4
14-15-16-17	66.0	63.6	61.1	53.2	47.5	43.1	37.1	31.6	22.9
15-16-17-20	96.0	104.8	101.9	91.9	86.8	84.3	86.0	101.4	119.5
16-17-20-22	177.2	177.3	177.8	178.1	177.8	176.9	173.3	160.2	147.6
H17-17-20-22	-0.9	-0.8	-0.8	-0.5	0.0	0.9	3.9	12.9	13.8
17-20-22-23	-113.9	-112.8	-111.5	-109.8	-108.3	-107.4	-106.6	-104.9	-88.4
13-17-20-22	-84.9	-80.2	-83.3	-89.6	-91.4	-91.8	-91.4	-92.0	-98.6

^a The path calculation was done in Gaussian 03 with B3LYP/6-31G* (geometry and electron energy). The product is not necessarily more stable than one with C16-C17 hyperconjugation. Steroid numbering is used. Point 1 is **25b**, and point 9 is **26b**. ^b mPW1PW91/6-311+G(2d,p) energies; these preferred energy values are shown in boldface type.

Observations from data in Table S4:

1. The C8-C13 bond, initially lengthened by hyperconjugation to the cation, is broken. The newly formed C13-C17 bond is in hyperconjugation with the cation at the end of the reaction. (No special significance should be given to hyperconjugation with the C13-C17 bond, because a slightly different calculation might lead to hyperconjugation to the C16-C17 bond.)
2. Bonds C16-C17, C22-C23, and C17-H17 are lengthened only slightly by hyperconjugation at the end of the reaction (points 8 and 9 of the reaction path).
3. Hyperconjugation is also reflected in certain torsion angles that are about 90°, i.e. 8-13-14-15 and 13-17-20-22.
4. The C16-C17 bond lengthens as it changes from an allylic bond to a bond slightly hyperconjugated to cation C20.

TABLE S4. Part B. Energy changes during ring-C enlargement/D-ring formation of 20-oxa analogs in 17 β -dammarenyl cation synthesis, as modeled by a path calculation for the conversion of **27b** to **28b**^{a-c}



Point on path	1	2	3	4=TS	5	6	7	8	9
<i>Energy relative to 27b (kcal/mol)</i>									
B3LYP/6-31G*	0.0	0.2	2.5	7.8	4.7	-2.8	-13.8	-18.3	-18.7
HF/3-21G	0.0	0.1	5.1	9.7	5.3	-6.8	-23.6	-29.3	-29.5
mPW1PW91 ^b	0.0	0.2	3.9	8.2	4.2	-5.2	-18.2	-23.0	-23.2

^{a,b} See footnotes to Table S4, part A. ^c The transition state is at point 4 in this path calculation but at point 6 in the path calculation of Part A. In Figure 2, these data were compared so that the transition states occur in the center of the energy profile. The different positions of the transition state in the two paths are an accident of the optimization process and should not be interpreted as early or late transition states.

TABLE S5. Illustration of the close fit between SHC and squalene as judged by approximate distances between selected atoms in the 2-azasqualene substrate analog and protein residues^{a,b}

Substrate	Enzyme	R (Å)	Substrate	Enzyme	R (Å)
15-Me	L607	3.23	H17	F605	3.26
15-Me	G600	2.59	H20	F601	3.29
19-Me	F437	2.14	H20	P263	2.87
19-Me	P263	2.62	H21	P263	2.81
19-Me	F605	3.23	H18	P263	3.14

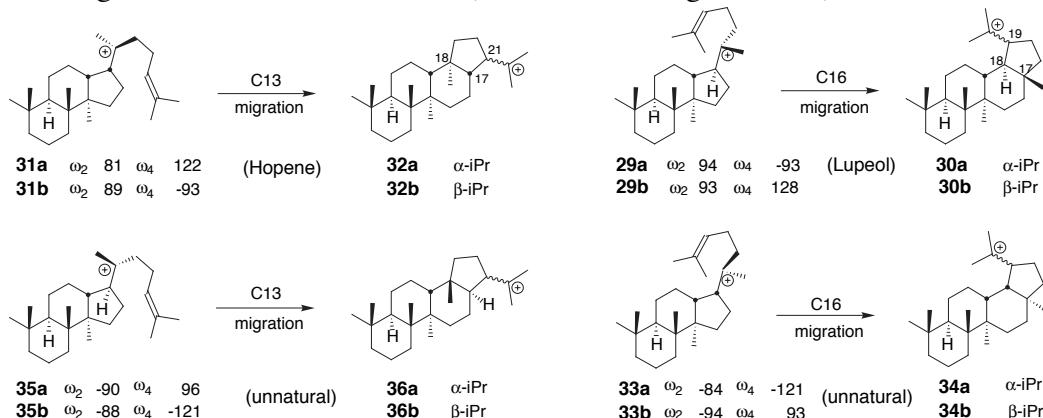
^a Carbon coordinates are from a protein crystal structure (subunit A);⁸ hydrogen atoms were added in PCMODEL without minimization. Partially minimized structures of A-ring substrate models in a rigid enzyme carbon framework also showed interatomic distances of <2.2 Å.^{29b} After tetracyclization, the 19-Me (20-Me in sterol numbering) adopts a position near that originally occupied by the 15-Me according to a molecular dynamics study.⁸ Distances (R) are between hydrogen atoms except for H17-F605 (H-C).

TABLE S6. Geometries and relative energies of various side-chain conformers of the tetracyclic hopene precursor (corresponds to Table 3)^a

	Energy (kcal/mol)					ω_1	ω_2	ω_3	ω_4	C13-C17	C16-C17
	mPW1PW91/ 6-311+G(2d,p)	mPW1PW91/ 6-31G*	B3LYP/ 6-31G*	HF/ 3-21G	HF/ 6-31G*	°	°	°	°	Å	Å
0.0^b	0.0	0.0	0.0	.0	144	81	-81	122	1.66	1.55	
3.8	4.4	4.2	3.6	1.5	165	180 ^d	179	114	1.70	1.55	
4.4	5.5	5.7	4.9	1.6	30	180 ^d	-179	115	1.57	1.63	
0.7	1.0	0.5	-0.6	-1.5	160	96	-178	110	1.69	1.55	
3.3	3.3	3.2	2.2	.1	26	112	179	115	1.57	1.63	
3.7^c	4.0	4.0	3.2	1.7	164	-1	177	115	1.74	1.54	
13.8	14.7	14.7	15.7	11.5	21	7 ^d	-177	117	1.58	1.64	
3.2	3.5	3.7	3.2	.6	90 ^d	86	174	107	1.58	1.57	
3.3	3.9	4.2	3.4	.3	-90 ^d	110	179	110	1.58	1.57	
4.9	6.0	6.8	6.5	1.6	90 ^d	150 ^d	-176	115	1.58	1.57	
4.9	6.2	7.1	6.9	1.8	-90 ^d	-150 ^d	172	113	1.58	1.58	

^a Relative electron energies without ZPE corrections for B3LYP/6-31G* geometries of conformers of model **31a**. Dihedral angles ω_1 - ω_4 are defined in Scheme 4. Thermodynamic parameters for entry 4 vs. entry 1: ZPE, 0.1, ΔH , 0.2, ΔG , -0.2 kcal/mol. ^b Conformer folded for direct E-ring formation. ^c Conformer whose side-chain dihedrals resemble those of the x-ray structure of 2-azasqualene in SHC. ^d Torsion angle frozen during geometry optimization.

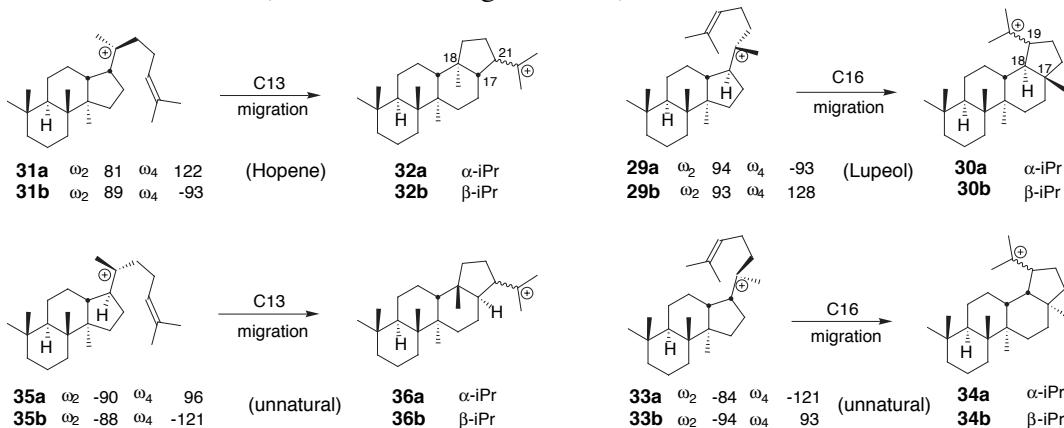
TABLE S7. Part A. Relative energies of reactants and of products for folded dammarenyl cation models differing in side-chain conformation (B3LYP/6-31G* geometries)^{a,b}



Configuration (Me/H/iPr) ^c	C13 migration				C16 migration			
	17 α -SC		17 β -SC		17 α -SC		17 β -SC	
	Hopene $\alpha\beta\alpha$	unnatural $\beta\alpha\beta$	unnatural $\alpha\beta\alpha$	$\beta\alpha\beta$	unnatural $\alpha\beta\alpha$	unnatural $\alpha\beta\beta$	Lupeol $\beta\alpha\alpha$	$\beta\alpha\beta$
ΔH Reactant vs. 31a or 29a	<i>Electron energies (kcal/mol)</i>							
Theoretical model	31a	31b	35a	35b	33a	33b	29a	29b
HF/6-31G*	0.0	6.7	0.0	0.1	8.0	7.4	0.0	0.0
B3LYP/6-31G*	0.0	3.4	-1.7	-1.6	5.5	5.5	0.0	0.4
B3LYP/6-311+G(2d,p)	0.0	3.6	-1.7	-1.5	5.7	5.6	0.0	0.5
MPW1K/6-31G*	0.0	4.4	-1.2	-1.2	5.9	5.9	0.0	0.1
MPW1K/6-311+G(2d,p)	0.0	4.4	-1.2	-1.2	5.8	5.8	0.0	0.1
mPW1PW91/6-31G*	0.0	3.7	-1.7	-1.6	5.5	5.6	0.0	0.3
mPW1PW91/6-311+G(2d,p)	0.0	3.9	-1.5	-1.5	5.6	5.6	0.0	0.3
MP2/6-31G*	0.0	4.7	-1.4	-1.6	6.4	6.8	0.0	0.0
ZPE increment, scaled	0.0	-0.1	-0.1	0.0	0.1	0.4	0.0	0.1
ΔH increment, scaled	0.0	0.0	0.0	0.1	0.0	0.2	0.0	0.0
ΔG increment, scaled	0.0	-0.4	-0.9	-0.3	0.7	1.3	0.0	0.1
ΔS	0.0	1.3	3.2	1.5	-2.3	-3.9	0.0	-0.4
ΔH Product vs. 32a or 30a	<i>Electron energies (kcal/mol)</i>							
Theoretical model	32a	32b	36a	35b	34a	34b	30a	30b
HF/6-31G*	0.0	-6.7	0.1	7.7	27.6	19.1	0.0	6.6
B3LYP/6-31G*	0.0	-5.4	1.3	7.0	23.2	18.0	0.0	6.4
B3LYP/6-311+G(2d,p)	0.0	-5.2	1.4	7.0	23.7	18.1	0.0	6.6
MPW1K/6-31G*	0.0	-6.1	0.6	7.3	24.3	17.8	0.0	6.1
MPW1K/6-311+G(2d,p)	0.0	-5.9	0.7	7.3	24.1	17.8	0.0	5.8
mPW1PW91/6-31G*	0.0	-5.8	0.8	7.1	23.4	17.7	0.0	6.3
mPW1PW91/6-311+G(2d,p)	0.0	-5.7	0.7	6.9	23.2	17.1	0.0	6.0
MP2/6-31G*	0.0	-5.7	1.0	7.1	25.0	18.0	0.0	6.3
ZPE increment, scaled	0.0	-0.3	-0.3	0.0	0.8	0.5	0.0	0.4
ΔH increment, scaled	0.0	-0.2	-0.2	0.0	0.6	0.6	0.0	0.4
ΔG increment, scaled	0.0	-0.6	-0.8	-0.1	1.5	0.0	0.0	0.8
ΔS	0.0	1.3	1.9	0.6	-2.6	2.4	0.0	-1.5

^a This table corresponds to Table 4 but compares energies for a variety of DFT and ab initio methods. Electron energies and thermodynamic data are from B3LYP/6-31G* geometries. ^b In the optimization of **33a**, ω_1 was frozen at -144° to prevent optimization to -107° (hyperconjugation with the C17-H17 bond). ^c Configuration of the angular methyl and hydrogen at the DE ring junction and of the isopropyl cation substituent, respectively.

TABLE S7. Part B. Calculated annulation energies of folded dammarenyl cation models differing in side-chain conformation (B3LYP/6-31G* geometries)^{a,b}



	C13 migration				C16 migration			
	17 α -SC		17 β -SC		17 α -SC		17 β -SC	
	$\alpha\beta\alpha$	$\beta\alpha\beta$	$\alpha\beta\alpha$	$\beta\alpha\beta$	$\alpha\beta\alpha$	$\alpha\beta\beta$	$\beta\alpha\alpha$	$\beta\alpha\beta$
C17 configuration	Hopene		unnatural		unnatural		Lupeol	
Configuration (Me/H/iPr) ^c	31a	31b	35a	35b	33a	33b	29a	29b
	↓	↓	↓	↓	↓	↓	↓	↓
	32a	32b	36a	35b	34a	34b	30a	30b
ΔH for Cyclization	<i>Electron energies (kcal/mol)</i>				<i>Electron energies (kcal/mol)</i>			
HF/6-31G*	-1.5	-7.5	6.0	13.5	13.0	5.2	-6.5	0.0
B3LYP/6-31G*	-0.3	-6.0	5.9	11.5	11.6	6.3	-6.2	-0.1
B3LYP/6-311+G(2d,p)	1.7	-3.6	8.2	13.6	14.5	8.9	-3.6	2.6
MPW1K/6-31G*	-9.7	-16.1	-3.8	2.9	3.0	-3.6	-15.4	-9.5
MPW1K/6-311+G(2d,p)	-8.1	-14.2	-2.1	4.5	4.9	-1.5	-13.4	-7.7
mPW1PW91/6-31G*	-6.3	-12.6	-0.7	5.5	5.4	-0.4	-12.5	-6.5
mPW1PW91/6-311+G(2d,p)	-4.6	-10.8	1.0	7.1	7.3	1.1	-10.4	-4.6
MP2/6-31G*	-12.8	-18.9	-6.1	0.2	1.1	-6.2	-17.4	-11.2
ZPE increment, scaled	2.4	2.3	2.2	2.3	2.5	1.9	1.8	2.2
ΔH increment, scaled	1.4	1.1	1.1	1.3	1.3	1.1	0.6	1.0
ΔG increment, scaled	5.6	5.4	5.7	5.8	6.0	4.0	5.3	6.0
ΔS	-14.2	-14.2	-15.5	-15.2	-16.0	-9.6	-15.8	-16.8

^a This table, which corresponds to Table 4, gives annulation energies, whereas Part A compares the energies among reactants and among annulation products. Geometries and thermodynamic data are from B3LYP/6-31G* calculations. ^b During optimization of **33a**, ω_1 was frozen at -144° to prevent minimization to a -107° angle (hyperconjugation with the C17-H17 bond). ^c Configuration of the angular methyl and hydrogen at the DE ring junction and of the isopropyl cation substituent, respectively.

Relative energies of lupeol and its stereoisomer **37a**

Neutral species: At the mPW1PW91/6-311+G(2d,p)/B3LYP/6-31G* level, **37a** was 1.3 (1.5, 1.2) kcal/mol lower in electron energy (enthalpy, free energy) than lupeol. The B3LYP/6-31G* electron energy difference was 1.6 kcal/mol. Corrections for the Boltzmann distribution of rotamer enthalpies would probably alter these energy differences only modestly compared to other sources of error in the theoretical methods.

Cations: Lupyl cation model **30a** (described in Table 4) and its stereoisomer corresponding to **37a** had almost identical enthalpies:

Method	Energy (cation 30a) – Energy (37a cation) kcal/mol
HF/6-31G*	-1.4
B3LYP/6-31G*	-0.1
B3LYP/6-311+G(2d,p)	-0.3
MPW1K/6-31G*	-0.4
MPW1K/6-311+G(2d,p)	-0.6
mPW1PW91/6-31G*	-0.1
mPW1PW91/6-311+G(2d,p)	-0.3
MP2/6-31G*	-0.3
ZPE, scaled	0.3
ΔH increment, scaled in part	0.2
ΔG increment, scaled in part	0.5
ΔS (cal/mol-K)	-1.0

These energies were roughly 10 kcal/mol lower than those of the cation corresponding to stereoisomer **37b**.

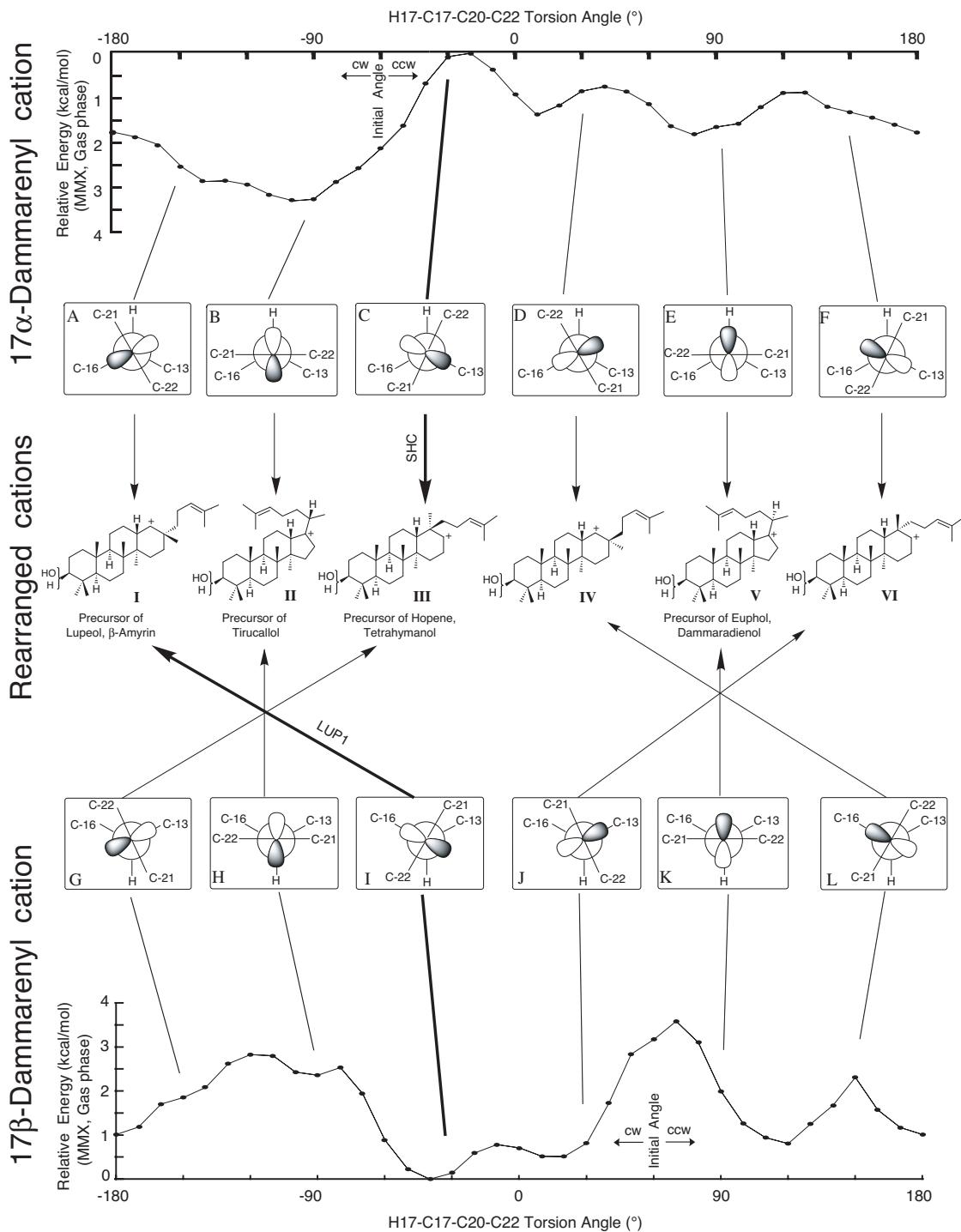


Figure S11. Reactivity of dammarenyl cations. Curves at the top and bottom indicate barriers to rotation about the H17-C17-C20-C22 torsion angle (similar to ω_1) as judged by molecular mechanics energies from MMX (PCMODEL). These relaxed PES scans do not consider enzymatic effects, solvation, hyperconjugation, or other quantum mechanical effects. Each rearranged cation can be formed in two ways, as indicated in Table 2. For example, cation **III** can be formed from the 17 α -dammarenyl cation via intermediate **C** (thick lines/arrows) or from the 17 β -dammarenyl cation via intermediate **G**. Torsion angles leading to H17 migration or ring expansion are approximate. Secondary cations **I**, **III**, **IV**, and **VI** are actually bridged cations (cyclopropane/carbonium ion structures).^{29a}

Steric arguments against 180° ω_1 rotation and C16 migration for the 17 α -dammarenyl cation

Below are the steric arguments mentioned in the main text:

“Additional arguments stemming from steric interactions between the side chain and the 14 α -methyl suggest that 180° ω_1 rotation and C16 migration are energetically unfavorable for the 17 α -dammarenyl cation (see Supporting Information).”

The relative energies of reactants in Table 5 suggested that the 17 α -dammarenyl cation favors hyperconjugation with C13-C17, perhaps because C16-C17 hyperconjugation leads to steric congestion between the C20 methyl and H12 α and the 14 α methyl. In fact, the ω_1 value needed to be frozen in the geometry optimization of **33a** in order to assure optimization to the desired ω_1 conformer.

Energetically, ω_1 rotation is unfavorable for the following reason. Rotations of ω_2 and ω_3 are needed in preparation for E-ring formation, a process that appears to be slow for SHC⁸ and probably other cyclases. During this time, a Boltzmann distribution of rotamers accessible within the active site cavity will begin to form. In a study of several side-chain conformers of the folded hopene precursor model **31a** (Tables 4 and S6), we found that the ω_1 *syn* conformers are >3 kcal/mol higher in enthalpy than **31a**. Thus, even if geometry of the active site permitted 180° rotation for **13a**, the resulting rotamer would have a negligible Boltzmann population. (Enzyme geometry can block an exothermic reaction pathway, but enzymatic facilitation of an endothermic pathway would require unusual stabilization of these hydrocarbon conformers; we show in a separate study^{29b} that the cyclase cannot ordinarily stabilize a particular cation position or orientation.) Thus, lupeol formation is unlikely to proceed via the 17 α -dammarenyl cation **13a** unless none of the many alternative conformers can undergo annulation, rearrangement, or deprotonation. Analogous arguments against intermediate **13b** for hopene-like products are weaker because the gas-phase energy differences between *syn* and *anti* conformers are diminished since the 17 β side chain has fewer steric constraints

Structural Considerations Regarding a C₃₅ Homolog of Hopene

As described in reference 16d, incubation of a C₃₅ homolog of squalene with SHC^{16d,m} gave a single product, whose structure was determined by 1D and 2D NMR methods. The DE ring junction in the unnatural cyclization of a C₃₅ homolog of squalene by SHC^{16d,m} indicates its formation from an analog of **13a**. The reported ¹H and ¹³C NMR chemical shifts are compatible with predicted shieldings for the proposed product stereochemistry in rings ABCD (Guo, L.-W.; Wilson, W. K.; Shackleton, C. H. L., unpublished results).

Steric and electronic effects from F601, F605, and F437 (mainly below) and P263 (above) of the SHC active site⁸ presumably determine the stereochemistry of the EF ring junction and the terminal isopropenyl side chain. Discussion of this matter awaits a more definitive determination of the F-ring stereochemistry.

The interesting results of Abe et al.^{16d} were foreshadowed by Ruzicka, who suggested in 1963 the use of cyclases to prepare unnatural heptacyclic triterpenes.^{6e}

Evolutionary Relationships of Triterpene Synthases

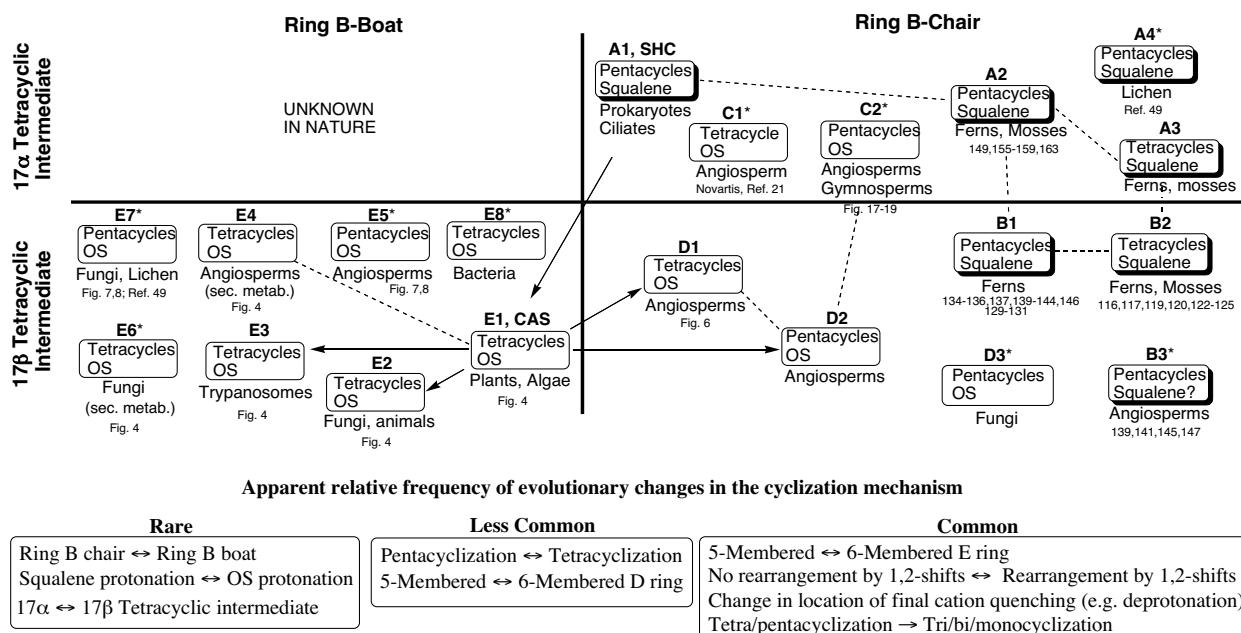


Figure S12. Evolutionary relationships of triterpene synthases. Cyclases are classified into eight possible categories based on mechanistic criteria corresponding to the 3 rare evolutionary changes. Five categories (A-E) are known in nature. Categories of cyclases using squalene as substrate (A-B) are shown as shadowed boxes; cyclases in other categories (C-E) use oxidosqualene (OS). Cyclases are further divided into groups according to taxonomic and structural features (i.e. whether the triterpene product is tetracyclic or pentacyclic). Minor groups (not widely distributed in the specified taxa) are denoted by an asterisk. Cycloartenol is regarded as tetracyclic. Solid arrows represent evolutionary pathways suggested by phylogenetic reconstructions from sequence data, and dashed lines represent tentative pathways. The stereochemistry of C17 and ring B refers to that of the unrearranged tetracyclic intermediate (**3**, **9**, **13a**, or **13b**). Cyclase groups producing mono-, bi-, and tricyclic products or unusual cyclization patterns are not shown. **Unlike Figure 5, this figure contains citations to compound numbers and figures from reference 3. References (ref. 21, 49) are citations from the present paper.**

Note: The difficulty of crossing evolutionary barriers depends on the number of rings being formed. For example, cyclases can probably cross the B-ring chair/boat transition more easily when the product is a bicyclic rather than a tetracycle. Similarly, mutation results suggest that the $17\alpha/17\beta$ transition is easier for cyclases producing tetracycles rather than pentacycles. (This transition has never been achieved artificially for pentacycles.) A change in substrate folding is required in both cases, but the pentacyclic product also requires a change in shape of the active-site cavity to accommodate a lupeol-type skeleton instead of a hopene skeleton.

Atomic coordinates from B3LYP/6-31G* geometry optimizations

For economy of space, coordinates are given in condensed format. These data are easily converted to tabular form by global find-and-replace routines available in most word processors. First, replace the paragraph mark with nothing; spaces might also need to be deleted; then replace “l” with the paragraph mark. If desired, commas can be replaced by the tab mark.

Compound **24a**, conformer B: H17-C17-C20-O20 153°, hyperconjugation to C13-C17.

```
1|1|UNPC-UNK|FOpt|RB3LYP|6-31G(d)|C24H40O2|PCUSER|16-Sep-2003|0||# B3L
YP/6-31G* GEOM=ALLCHECK OPT=READFC| |XQ-OOS-17aConfB||0,1|C,2.152536947
9,-1.4619768622,1.2831756901|C,3.6814942976,-1.5836341333,1.2922323518
|C,4.2988534591,-1.2414739689,-0.0627421152|C,3.9189214374,0.171922678
1,-0.5746579695|C,2.3524252509,0.2761710723,-0.5301532894|C,1.78670678
09,1.5692622035,-1.1445909007|C,0.2891688451,1.4203811874,-1.451460192
6|C,-0.572270159,1.0473530017,-0.2193158519|C,0.0957075688,-0.18531002
93,0.5130944379|C,1.6426269912,-0.0622481796,0.833473312|C,-0.76220832
25,-0.6904190326,1.6986229761|C,-2.2108491066,-1.0409971665,1.29498742
46|C,-2.8379072555,0.1599281257,0.5900006691|C,-2.0339887029,0.5946754
087,-0.6708424893|C,-2.9813601057,1.6879360073,-1.2326212931|C,-4.3953
548781,1.0743807778,-1.0955716515|C,-4.3575158805,0.1670743419,0.16951
17161|C,1.9409030892,0.940048151,1.9802061982|C,-4.9864046372,-1.21250
23839,-0.0447696758|C,-5.6851072709,-1.8307594431,1.1550834188|O,5.725
9410428,-1.3339307456,-0.0162342603|H,5.9485083667,-2.2327744629,0.271
0831948|C,4.4016794099,0.2599662352,-2.0431806934|C,4.6584250966,1.270
1670018,0.218930977|C,-0.6444606037,2.3067960417,0.6829516265|C,-1.990
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220914269|H,0.0724202401,-0.9985215743,-0.222516423|H,-0.3008868169,-1
.578642747,2.1414244459|H,-0.8004061809,0.0610273308,2.4978954196|H,-2
.7741279743,-1.3093684843,2.1989562213|H,-2.2208067758,-1.9260119576,0
.6450720421|H,-2.7673870195,0.9937596644,1.2981691779|H,-2.7522970858,
1.9635960038,-2.2680477283|H,-2.9287703247,2.6029904651,-0.6341107869|H,-5.1682680618,1.845844037,-1.0124757136|H,-4.6417269787,0.4628571449
,-1.967746143|H,-4.9174839191,0.6305020223,0.9908249625|H,2.8345462822
,0.65253435,2.5404461474|H,1.1190114214,0.9696717365,2.7017974914|H,2.
1067362662,1.9613188195,1.6319775606|H,-5.963961061,-2.8632652315,0.93
49161675|H,-5.0520053072,-1.7940561481,2.0488308035|H,-6.5912689269,-1
.2541766087,1.3849583765|H,3.8098731365,-0.3904920348,-2.7000834593|H,
5.4462600996,-0.0582445634,-2.10357397|H,4.3414199109,1.2799422344,-2.
4356832985|H,4.498550043,1.2075813262,1.2971737886|H,4.3357259554,2.26
44825621,-0.1095225968|H,5.734747822,1.1906427669,0.0433027646|H,0.347
3888653,2.710803333,0.8841252717|H,-1.1137851952,2.1287550168,1.654033
7043|H,-1.2054271473,3.1043775313,0.1877845817|H,-1.2824906245,-1.3325
447789,-1.5070359587|H,-1.7104139274,-0.1251286969,-2.7151174418|H,-2.
9671049653,-1.0068338586,-1.8574646538||Version=x86-Win32-G98RevA.11.2
|HF=-1089.0794342|RMSD=7.975e-009|RMSF=5.091e-006|PG=C01 [X(C24H40O2)] ||@
```

Compound 24b, conformer A: H17-C17-C20-O20 -172°.

```
1|1|UNPC-UNK|SP|RB3LYP|6-31G(d)|C24H40O2|PCUSER|16-Sep-2003|0||# B3LYP
/6-31G* SP||XQ-OOS 17b-SC conf A||0,1|C,0,2.536376,-2.002839,-0.373581
|C,0,4.06534,-2.111689,-0.312189|C,0,4.755725,-0.856733,-0.844436|C,0,
4.326665,0.441013,-0.112562|C,0,2.757236,0.497951,-0.15018|C,0,2.15726
6,1.79806,0.4145|C,0,0.702274,1.969661,-0.044549|C,0,-0.227463,0.79445
9,0.34917|C,0,0.46277,-0.567361,-0.066791|C,0,1.97241,-0.760923,0.3753
44|C,0,-0.44598,-1.785418,0.232321|C,0,-1.832982,-1.679224,-0.43335|C,
0,-2.487128,-0.352221,-0.059262|C,0,-1.615159,0.881543,-0.4314|C,0,-2.
585786,2.028834,-0.040136|C,0,-4.000574,1.52585,-0.449978|C,0,-3.90086
3,-0.026772,-0.609983|C,0,2.124452,-1.019452,1.897994|C,0,-4.977786,-0
.776136,0.172253|C,0,-5.739708,-1.867419,-0.557684|O,0,6.178841,-0.972
718,-0.754633|H,0,6.435894,-1.770911,-1.241287|C,0,4.90477,1.625321,-0
.925624|C,0,4.940059,0.513041,1.30223|C,0,-0.460903,0.889794,1.878778|
C,0,-1.424126,0.981996,-1.969401|O,0,-5.202216,-0.516019,1.341366|H,0,
2.103013,-2.924052,0.032091|H,0,2.229014,-1.954718,-1.428906|H,0,4.411
426,-2.302506,0.710254|H,0,4.388275,-2.978981,-0.907606|H,0,4.466676,-
0.734739,-1.904633|H,0,2.52734,0.517993,-1.229707|H,0,2.728839,2.66273
9,0.061803|H,0,2.228573,1.819984,1.508112|H,0,0.291156,2.907692,0.3531
86|H,0,0.723757,2.081754,-1.134159|H,0,0.540691,-0.524229,-1.160867|H,
0,0.03588,-2.706369,-0.110876|H,0,-0.590075,-1.903484,1.313236|H,0,-2.
454058,-2.526292,-0.111003|H,0,-1.734268,-1.764982,-1.524539|H,0,-2.60
6988,-0.338825,1.031219|H,0,-2.33301,2.978981,-0.523756|H,0,-2.573075,
2.203853,1.038169|H,0,-4.73712,1.779922,0.316658|H,0,-4.334733,1.98186
,-1.387555|H,0,-3.96767,-0.314124,-1.66585|H,0,3.00066,-1.636467,2.112
58|H,0,1.259972,-1.559942,2.294478|H,0,2.235406,-0.105439,2.484613|H,0
,-6.293454,-1.438204,-1.403083|H,0,-5.044472,-2.604377,-0.980071|H,0,-
6.435893,-2.361758,0.123012|H,0,4.401675,1.730045,-1.895626|H,0,5.9687
02,1.454929,-1.112902|H,0,4.808684,2.57632,-0.392196|H,0,4.712197,-0.3
58229,1.919546|H,0,4.58037,1.40181,1.832534|H,0,6.028766,0.583429,1.22
8065|H,0,0.483411,0.915497,2.421221|H,0,-1.039367,0.058844,2.289494|H,
0,-0.98734,1.813292,2.135576|H,0,-0.80536,0.188203,-2.394641|H,0,-0.97
0856,1.937949,-2.246929|H,0,-2.38835,0.939416,-2.484612||Version=x86-W
in32-G98RevA.11.2|HF=-1089.0823774|RMSD=2.304e-006|PG=C01 [X(C24H40O2)
|||@
```

Compound 24b, conformer B: H17-C17-C20-O20 147°, hyperconjugation to C16-C17.

```
1|1|UNPC-UNK|FOpt|RB3LYP|6-31G(d)|C24H40O2|PCUSER|15-Sep-2003|0||# B3L
YP/6-31G* GEOM=ALLCHECK OPT=READFC||XQ-OOS17bconfB||0,1|C,-2.325047858
4,0.8516737193,-1.6882823259|C,-3.8413647181,0.6630059606,-1.824838999
9|C,-4.278413526,-0.7653778272,-1.5033474915|C,-3.8511768493,-1.236727
2419,-0.0894067559|C,-2.3051844278,-0.987115504,0.0347816791|C,-1.6793
434556,-1.5290551199,1.3321545995|C,-0.1546577894,-1.643776277,1.19379
79012|C,0.5494782299,-0.310691842,0.8366552912|C,-0.1969991007,0.34689
49281,-0.3949926873|C,-1.7743006066,0.4589290357,-0.2869994636|C,0.502
1248312,1.6455837296,-0.8681315172|C,1.9878198213,1.4312611989,-1.2199
337293|C,2.7017176922,0.781370343,-0.0393673563|C,2.0585803225,-0.5651
040354,0.3950221754|C,3.0655183026,-0.9966526722,1.4957408636|C,4.4645
817895,-0.6214777222,0.9312960434|C,4.209345588,0.5011596192,-0.146180
8874|C,-2.2318229992,1.5469811699,0.7212311414|C,5.0796814011,1.725520
2085,0.1302322249|C,6.494311675,1.6888158004,-0.4239595861|O,-5.69763
77968,-0.9084785846,-1.6145625794|H,-5.946728571,-0.6363873249,-2.5111
852283|C,-4.1350576925,-2.7573899612,-0.0185655793|C,-4.7036833952,-0.
```

5599192132, 1.0052346557|C, 0.5023321998, 0.5861634826, 2.0996835234|C, 2.1
 68453332, -1.6283194515, -0.7332197396|O, 4.6789178708, 2.6762662985, 0.777
 7981169|H, -2.0794644163, 1.894987291, -1.9163518361|H, -1.8242563966, 0.24
 07338871, -2.4541060415|H, -4.3900839825, 1.3570824591, -1.1777788426|H, -4
 .1425882659, 0.9074111364, -2.8546984849|H, -3.7869382277, -1.4418020256, -
 2.2266538128|H, -1.8796263618, -1.6078973517, -0.7729271114|H, -2.07627901
 48, -2.5245117413, 1.5562790565|H, -1.9491455285, -0.9011224528, 2.18906642
 19|H, 0.2770209624, -2.0469555734, 2.1203825574|H, 0.0394379185, -2.3893639
 438, 0.414577962|H, -0.067934862, -0.3662292058, -1.2194472289|H, -0.012428
 9697, 2.0480886172, -1.7463882111|H, 0.4395881622, 2.423191878, -0.09674893
 95|H, 2.4496167395, 2.3973848193, -1.4616103763|H, 2.0761845469, 0.80598345
 35, -2.1200609767|H, 2.6110628391, 1.475032624, 0.8046030917|H, 3.000863268
 8, -2.0622568653, 1.743612391|H, 2.8972582187, -0.4388589095, 2.420161063|H
 , 5.1253344084, -0.271785155, 1.7321940261|H, 4.9576242238, -1.4839943299, 0
 .4722536425|H, 4.4769409985, 0.1168997225, -1.1387190191|H, -3.1936166237,
 1.97889329, 0.4329705221|H, -1.5183488205, 2.3753433964, 0.7590529571|H, -2
 .3516406414, 1.1719907809, 1.7397428116|H, 6.9904850411, 0.7427144997, -0.1
 752230649|H, 6.4614605476, 1.7510335993, -1.5197912147|H, 7.073304837, 2.52
 83425099, -0.0336176847|H, -3.4521874315, -3.3246721499, -0.6642912047|H, -
 5.1578222122, -2.9542823593, -0.3520403717|H, -4.036064098, -3.1468410634,
 0.9996758454|H, -4.6901821193, 0.5306475436, 0.9539147579|H, -4.3539658346
 , -0.8518169731, 2.0017538429|H, -5.7456820366, -0.8772880356, 0.9089321607
 |H, -0.5173928879, 0.7034948758, 2.4645442428|H, 0.9001926318, 1.5911805373
 , 1.9408628498|H, 1.0693469758, 0.1339965941, 2.9187127819|H, 1.4987866879,
 -1.4499910669, -1.577562914|H, 1.9533932371, -2.6304300613, -0.3496772757|
 H, 3.1828809139, -1.6647626065, -1.141921322 || Version=x86-Win32-G98RevA.1
 1.2 |HF=-1089.0829649|RMSD=2.633e-009|RMSF=4.881e-006|PG=C01 [X(C24H40
 2)] ||@

Compound 25a, reactant in Table 1, 17 α -side chain, 20-carbo

1\1\GINC-DFTC\FOpt\RB3LYP\6-31G(d)\C21H37(1+)\BILLW\06-Jul-2003\0\\# B
 3LYP/6-31G* OPT=READFC GUESS=READ GEOM=(CHECK,MODREDUNDANT) \A-dammare
 nyl cat carb SM\1,1\C,-1.9671763075,1.3134121583,-0.7519717827\C,-0.7
 001284563,0.7204794364,-1.4148363262\C,0.058888949,-0.1193995772,-0.34
 42212748\C,0.2810433085,-1.528996127,-0.5817421629\C,-0.8693557644,0.0
 758647082,1.0609625261\C,-2.2501559659,0.3498047778,0.4036520765\C,-0.
 5842520271,-2.3374386534,-1.4769737385\C,3.4033101832,-0.6363036415,-0
 .7634552034\C,1.4516845469,-2.1759917896,0.0206937997\C,2.7346803117,-
 1.9595664765,-0.9352595147\C,3.5910729155,0.3273505305,-1.6907200949\C
 ,3.0824035486,0.2559630878,-3.1085423753\C,4.3926624106,1.5644295316,-
 1.341806736\C,-0.1864472837,1.2626437211,1.7628241514\C,-3.439008168,0
 .6192763531,1.3807140852\C,-0.9941422199,-1.120951981,2.0206447976\C,-
 2.106702045,-0.8568857502,3.0589965257\C,-3.4608287946,-0.555176634,2.
 3966943851\C,-3.3940984738,1.9799956005,2.1071040355\C,-4.7466730763,0
 .577614103,0.5576890417\C,5.7225652318,1.6787272497,-2.1122328846\H,-2
 .7967099073,1.3720566135,-1.46119487\H,-1.7826705039,2.3307644986,-0.3
 929555886\H,-0.9785419908,0.1024377229,-2.2730768886\H,-0.0301185465,1
 .4945597797,-1.8000136041\H,1.0296573848,0.3175251642,-0.0870736315\H,
 -2.5271901665,-0.6091457257,-0.0648094654\H,-1.6233083953,-1.995973169
 1,-1.4740613984\H,-0.2295334001,-2.1965662285,-2.5123979252\H,-0.53172
 39607,-3.4064005863,-1.2579151788\H,3.8328027866,-0.4744352291,0.22614
 99007\H,1.7125307354,-1.7314156385,0.9852501099\H,1.3010304695,-3.2516
 064929,0.1369428735\H,3.41071252,-2.7602082342,-0.6127252725\H,2.46254

18548, -2.1769349337, -1.9705716479\H, 3.9119963784, 0.116702379, -3.812711
 6363\H, 2.3719834417, -0.5568554268, -3.2804462462\H, 2.5958344598, 1.19855
 35196, -3.3891377269\H, 4.5983266058, 1.5754611717, -0.2653135627\H, 3.7844
 144355, 2.4549793017, -1.5578053758\H, -0.1290298327, 2.150193865, 1.126948
 8685\H, 0.8344444034, 0.9905759368, 2.0536003909\H, -0.7130431748, 1.543048
 1496, 2.6754489575\H, -1.2597824087, -2.0308650406, 1.4632859189\H, -0.0467
 694204, -1.3247373214, 2.5352832088\H, -1.8131397292, -0.0373765305, 3.7246
 045794\H, -2.2013728898, -1.7412307712, 3.6992758646\H, -4.2109675709, -0.3
 501970498, 3.1700659684\H, -3.8016737945, -1.4604496825, 1.8732031673\H, -2
 .6345291074, 2.0345129423, 2.8901309683\H, -3.2218262999, 2.8088765791, 1.4
 119181565\H, -4.3594150717, 2.1618506004, 2.5920459052\H, -4.8195676978, -0
 .337757116, -0.0423048084\H, -5.6135043465, 0.6040956441, 1.2272435969\H, -
 4.8295170186, 1.4356964876, -0.1182654216\H, 6.3608951094, 0.8087358742, -1
 .9248818807\H, 5.5645715193, 1.7600171232, -3.1924547601\H, 6.2661361904, 2
 .5724080585, -1.7905615281\Version=x86-Linux-G98RevA.9\HF=-822.2531856
 \RMSD=8.066e-09\RMSF=8.408e-05\PG=C01 [X(C21H37)]\\@

Compound 26a, product in Table 1, 17 α -side chain, 20-carbo

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1\1\GINC-DFTC\Fopt\RB3LYP\6-31G(d)\C21H37(1+)\BILLW\04-Jul-2003\0\\# B
3LYP/6-31G* OPT=READFC GEOM=ALLCHECK GUESS=READ\A damm cat carb produ
ct\1,1\C,-1.4763659652,0.8527631655,-0.8982399167\C,-0.1257798849,0.5
067310855,-1.5808502881\C,0.9321661129,0.5014981995,-0.4912402575\C,0.
6965655436,-0.5477832995,0.6151083399\C,-0.6520336936,-0.0802945003,1.
374077655\C,-1.8105254287,-0.060307082,0.3015941104\C,0.575229001,-1.9
849345703,0.047959877\C,2.6431640748,0.3954787448,-0.7846864872\C,2.01
15742194,-0.4949747818,1.4284958539\C,3.1347061344,-0.5030254528,0.368
5170097\C,2.7873499069,0.0613440242,-2.1685696521\C,2.8563302096,-1.31
69810869,-2.7084107033\C,2.848642885,1.163984119,-3.1643283144\C,-0.44
35724884,1.2981909812,2.0527398798\C,-3.2749407633,0.1252001302,0.8539
283714\C,-1.0073435453,-1.1083125633,2.4818374739\C,-2.4012312582,-0.8
771885714,3.0868433808\C,-3.4868525443,-0.8921872822,2.0060018442\C,-3
.6301092668,1.5548375427,1.3182924889\C,-4.2778621569,-0.2456557687,-0
.2650286896\C,4.3449809205,1.523337231,-3.4336724427\H,-2.2608542737,0
.7774591127,-1.6563347163\H,-1.4491899463,1.9050690233,-0.5918403199\H
,-0.199749532,-0.4652968808,-2.0831741742\H,0.0809655327,1.2607974606,
-2.3495488059\H,0.9413881997,1.4983809748,-0.0489405421\H,-1.845055659
3,-1.0803252226,-0.1001700898\H,-0.3475826886,-2.1725613122,-0.5009595
437\H,1.3976849701,-2.217342147,-0.6320990182\H,0.6288710052,-2.716688
5447,0.8576878057\H,2.9452680379,1.435579314,-0.6383630356\H,2.0854092
162,0.425210463,2.0143043177\H,2.1138977041,-1.3310010065,2.1258712582
\H,4.0755329167,-0.1056344329,0.7620904759\H,3.3427369376,-1.519696705
,0.0272683978\H,3.1372155888,-2.0772458035,-1.980464128\H,1.8606566833
,-1.5701211922,-3.1089066798\H,3.5321561208,-1.3524914758,-3.570888288
4\H,2.3421150625,2.057260688,-2.785973093\H,2.385226858,0.8599041581,-
4.1093233815\H,-0.4488092386,2.1434565195,1.3587841284\H,0.4925414451,
1.3346629274,2.6159192211\H,-1.2327494113,1.4940667613,2.7764986003\H,
-0.9964619388,-2.1220679772,2.0662821904\H,-0.2438081081,-1.082072681,
3.2702810055\H,-2.433523695,0.0600482282,3.6544164402\H,-2.6022720274,
-1.6706897658,3.8166570848\H,-4.4707385051,-0.7162921578,2.458896426\
H,-3.5281488618,-1.9020994082,1.5711686135\H,-3.1242898731,1.858369296
2,2.236891147\H,-3.40569407,2.3029759388,0.549639832\H,-4.7067386907,1
.6133685052,1.514741968\H,-4.0371584323,-1.2138906948,-0.7216109807\H,
-5.2883154525,-0.3217720551,0.1520140434\H,-4.3178271967,0.5066425829,

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-1.0603169896\H, 4.8429343597, 1.8703035839, -2.5241551969\H, 4.9002228522
 , 0.6728103282, -3.8382786268\H, 4.369592036, 2.3306020116, -4.1702827619\\
 Version=x86-Linux-G98RevA.9\HF=-822.2518158\RMSD=4.348e-09\RMSF=3.400e
 -06\PG=C01 [X(C21H37)] \\@

Transition state between 25a and 26a, see Table 1, 17 α -side chain, 20-carbo Frequency calculation: 1 imaginary frequency: -166.6 cm⁻¹, IR intensity 247

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1\1\GINC-DFTB\FTS\RB3LYP\6-31G(d)\C21H37(1+)\BILLW\07-Aug-2003\0\\# B3
LYP/6-31G* OPT=QST3\transition state, near optimized from path calc\\
1,1\C,-1.1113295104,-1.9070759325,-0.0824949203\C,0.3956958969,-1.6621
113988,0.2982060473\C,0.7403170143,-0.3510223781,-0.284612532\C,0.4045
881415,0.8944122154,0.2831408123\C,-1.4176893569,0.6092527265,-0.42063
74465\C,-1.9448859552,-0.6696870915,0.2684421407\C,0.3389547727,1.0274
247389,1.8028252306\C,3.2416068062,0.803787077,-0.5771635802\C,1.07136
11616,2.0944671381,-0.3812987314\C,2.6051550136,2.0740719622,-0.090255
9912\C,3.8758735736,-0.1644737529,0.1281941824\C,4.0982158616,-0.13693
55898,1.6189539758\C,4.4828305626,-1.3484066789,-0.5994948441\C,-1.360
7828117,0.6022402904,-1.9489411465\C,-3.5133123798,-0.8673765234,0.132
8259442\C,-2.1289072002,1.8616855072,0.0994220203\C,-3.6581983359,1.71
1898732,-0.0978515569\C,-4.1914313199,0.4512844455,0.5862935771\C,-3.9
884661478,-1.2760116341,-1.2768643712\C,-3.9499579054,-1.9791135721,1.
113979891\C,6.0209662924,-1.2927912842,-0.6916019041\H,-1.4494089526,-
2.7873837138,0.4690811236\H,-1.1780046062,-2.1538781639,-1.1464163894\
H,0.5049527391,-1.6756973032,1.3858008707\H,1.0095040864,-2.459637893,
-0.1303357852\H,1.0046877282,-0.3533686777,-1.3377408626\H,-1.82049012
69,-0.5027099671,1.3450206597\H,-0.3230870545,0.3124077845,2.291146785
2\H,1.339934367,0.869272584,2.2173895644\H,0.0261922163,2.0339234568,2
.0906377596\H,3.2096606276,0.6740547274,-1.6612299193\H,0.9373559759,2
.0707924418,-1.4670466893\H,0.6410790986,3.0329146555,-0.018795843\H,3
.0433011906,2.9296012311,-0.6202094203\H,2.7876243154,2.2440660825,0.9
738372214\H,3.7007376145,0.75541258,2.1069696734\H,3.6517508397,-1.020
5226758,2.0943344001\H,5.1705558773,-0.1809180047,1.8437462032\H,4.070
1635278,-1.4064503873,-1.6139485502\H,4.194835389,-2.2759935355,-0.083
9666725\H,-1.0921663283,-0.3648578476,-2.3779798875\H,-0.6672209801,1.
3536504493,-2.3321201489\H,-2.3411866966,0.8721213257,-2.3483044029\H,
-1.9464684339,1.9967122239,1.169194556\H,-1.7675222503,2.7562597553,-0
.4178313032\H,-3.9114127528,1.7151470623,-1.1637006506\H,-4.136552296,
2.6007668651,0.3291067765\H,-5.2721169076,0.367795486,0.4185905373\H,-
4.0576899145,0.5577529154,1.6725067946\H,-3.867921375,-0.491763238,-2.
027467122\H,-3.4713096328,-2.1709782408,-1.639086505\H,-5.0560782999,-
1.5182059495,-1.2380940213\H,-3.5620811999,-1.8049141962,2.124954432\H
,-5.0431587376,-2.0020043366,1.1804771147\H,-3.6278733468,-2.973676007
6,0.7887830515\H,6.3489313217,-0.3884398382,-1.2145249969\H,6.49227200
43,-1.3046399307,0.2962900549\H,6.3945859289,-2.1597257007,-1.24546919
28\\Version=x86-Linux-G98RevA.9\HF=-822.2425796\RMSD=4.135e-09\RMSF=2.
773e-06\PG=C01 [X(C21H37)] \\@ 
  
```

Compound 25b, reactant in Table 1, 17 β -side chain, 20-carbo

```

1|1|UNPC-UNK|SP|RB3LYP|6-31G(d)|C21H37(1+)|PCUSER|19-Oct-2003|0||# B3L
YP/6-31G* SP SCF=TIGHT|BDammCatCarb-SM-SP||1,1\C,0,-2.116164,-1.45167
4,1.711921\C,0,-0.66481,-0.94225,1.837978\C,0,-0.3283,-0.162504,0.5381
78\C,0,0.188821,1.180759,0.610395\C,0,-1.826359,-0.083303,-0.307572\C,
0,-2.784164,-0.351315,0.885688\C,0,-0.078632,2.080182,1.760317\C,0,3.0
09174,-0.02382,0.042794\C,0,1.065342,1.662497,-0.461943\C,0,2.607541,1
  
```

.413284,-0.058643|C,0,3.603684,-0.76792,-0.913118|C,0,3.931617,-0.2670
 71,-2.297327|C,0,4.001573,-2.199856,-0.620476|C,0,-1.670756,-1.198883,
 -1.354276|C,0,-4.305446,-0.43196,0.535536|C,0,-2.22825,1.237099,-0.990
 409|C,0,-3.709842,1.173711,-1.427384|C,0,-4.653826,0.857948,-0.256264|
 C,0,-4.726946,-1.697827,-0.23896|C,0,-5.098119,-0.416328,1.862007|C,0,
 5.524114,-2.43661,-0.625837|H,0,-2.576459,-1.585654,2.694168|H,0,-2.15
 2682,-2.420945,1.204016|H,0,-0.582495,-0.29329,2.715099|H,0,0.061011,-
 1.7493,1.976581|H,0,0.314177,-0.737331,-0.133237|H,0,-2.718911,0.56126
 1,1.502262|H,0,-1.071809,1.922284,2.191119|H,0,0.635642,1.824438,2.561
 835|H,0,0.066413,3.134181,1.513373|H,0,2.821604,-0.500493,1.005389|H,0
 ,0.900421,1.121294,-1.396716|H,0,0.950452,2.738548,-0.621311|H,0,2.796
 018,1.941401,0.882023|H,0,3.163143,1.941582,-0.837089|H,0,3.524795,0.7
 23091,-2.51698|H,0,5.017334,-0.217285,-2.445413|H,0,3.549142,-0.963675
 ,-3.05403|H,0,-1.465935,-2.173258,-0.903077|H,0,-0.846592,-0.962281,-2
 .036665|H,0,-2.569068,-1.295704,-1.964876|H,0,-2.116838,2.080849,-0.29
 5272|H,0,-1.594137,1.44753,-1.860512|H,0,-3.83344,0.437804,-2.229682|H
 ,0,-3.982522,2.140272,-1.866005|H,0,-4.637624,1.707336,0.442373|H,0,-5
 .684521,0.788,-0.624581|H,0,-4.389556,-1.712266,-1.277998|H,0,-4.36135
 2,-2.609535,0.246209|H,0,-5.820451,-1.761023,-0.261344|H,0,-4.798642,0
 .420623,2.504708|H,0,-6.169085,-0.309245,1.657309|H,0,-4.964241,-1.345
 068,2.427001|H,0,5.742367,-3.479124,-0.374054|H,0,5.966557,-2.235727,-
 1.606679|H,0,6.0237,-1.798418,0.110839|H,0,3.594942,-2.500871,0.352202
 |H,0,3.541348,-2.856647,-1.373084||Version=x86-Win32-G98RevA.11.2|HF=-
 822.2533226|RMSD=4.205e-009|PG=C01 [X(C21H37)]||@

Compound **26b**, product in Table 1, 17 β -side chain, 20-carbo

1|1|UNPC-UNK|SP|RB3LYP|6-31G(d)|C21H37(1+)|PCUSER|21-Oct-2003|0||# B3L
 YP/6-31G* SP SCF=TIGHT||Prod coord from path for freq calc BDammCatCar
 b||1,1|C,0,0.757616,-1.772337,0.075502|C,0,-0.681825,-1.520512,-0.4400
 11|C,0,-1.130579,-0.153998,0.046547|C,0,-0.216706,1.026537,-0.419997|C
 ,0,1.234092,0.767307,0.222543|C,0,1.738025,-0.638261,-0.291727|C,0,-0.
 169002,1.133646,-1.965481|C,0,-2.621673,0.402292,-0.408396|C,0,-1.0086
 2,2.248928,0.0966|C,0,-2.48641,1.948871,-0.255754|C,0,-3.513819,-0.326
 994,0.449446|C,0,-3.769556,0.06766,1.854452|C,0,-4.200678,-1.536699,-0
 .064393|C,0,1.162326,0.848914,1.767478|C,0,3.249742,-0.995127,-0.01515
 7|C,0,2.223644,1.86461,-0.258663|C,0,3.681023,1.56138,0.121282|C,0,4.1
 24766,0.210348,-0.447285|C,0,3.578685,-1.406074,1.438061|C,0,3.647418,
 -2.188399,-0.917631|C,0,-5.545649,-1.106396,-0.73778|H,0,1.103309,-2.7
 19652,-0.347646|H,0,0.721065,-1.919245,1.161796|H,0,-0.704896,-1.56718
 1,-1.535605|H,0,-1.334104,-2.32192,-0.071574|H,0,-1.13081,-0.149719,1.
 139949|H,0,1.713393,-0.565226,-1.386165|H,0,0.358765,0.311845,-2.45068
 4|H,0,-1.170048,1.170402,-2.405929|H,0,0.325141,2.061349,-2.26331|H,0,
 -2.748636,0.088316,-1.447467|H,0,-0.91087,2.356731,1.179679|H,0,-0.674
 813,3.189095,-0.351387|H,0,-2.777473,2.39816,-1.209438|H,0,-3.174066,2
 .353651,0.491845|H,0,-3.210217,0.942633,2.18471|H,0,-4.8463,0.271871,1
 .966835|H,0,-3.571423,-0.781225,2.523047|H,0,0.56747,0.057321,2.23198|
 H,0,0.758972,1.810707,2.096762|H,0,2.15548,0.775171,2.205387|H,0,2.184
 402,1.948542,-1.350144|H,0,1.919411,2.839561,0.144436|H,0,3.819262,1.5
 91051,1.208405|H,0,4.321841,2.355153,-0.281145|H,0,4.107497,0.275666,-
 1.545396|H,0,5.167603,0.008622,-0.171642|H,0,3.553657,-0.575839,2.1472
 37|H,0,2.901919,-2.183962,1.808835|H,0,4.592275,-1.821173,1.474183|H,0
 ,3.352406,-2.024112,-1.961451|H,0,4.735031,-2.320724,-0.900495|H,0,3.2
 06828,-3.133732,-0.582894|H,0,-6.029095,-2.007566,-1.123675|H,0,-6.221

674,-0.634451,-0.019775|H,0,-5.376671,-0.42016,-1.57195|H,0,-3.583535,
-2.027501,-0.824695|H,0,-4.418007,-2.246644,0.739568||Version=x86-Win3
2-G98RevA.11.2|HF=-822.2605636|RMSD=5.477e-009|PG=C01 [X(C21H37)]||@

**Transition state between 25b and 26b, see Table 1, 17 α -side chain, 20-carbo
Frequency calculation: 1 imaginary frequency: -168.1 cm⁻¹, IR intensity 241.2**

1|1|UNPC-UNK|SP|RB3LYP|6-31G(d)|C21H37(1+)|PCUSER|22-Oct-2003|0||# B3L
YP/6-31G* SP SCF=TIGHT||TS coord opt from path for freq calc BDammCatC
arb||1,1|C,0,1.193049,-1.937746,-0.115582|C,0,-0.260361,-1.732241,-0.6
8711|C,0,-0.729832,-0.459102,-0.110879|C,0,-0.373108,0.818439,-0.58534
2|C,0,1.346251,0.573777,0.344384|C,0,2.013956,-0.657746,-0.308405|C,0,
-0.115522,1.017947,-2.076443|C,0,-3.244105,0.590067,-0.675576|C,0,-1.1
78349,1.955934,0.02955|C,0,-2.625361,1.963986,-0.563697|C,0,-3.896354,
-0.101157,0.289314|C,0,-4.090233,0.410612,1.693669|C,0,-4.516953,-1.44
7554,-0.019929|C,0,1.086446,0.509942,1.851047|C,0,3.557453,-0.802682,0
.036391|C,0,2.069195,1.869237,-0.034681|C,0,3.560649,1.769847,0.371881
|C,0,4.236784,0.55695,-0.270226|C,0,3.848049,-1.253396,1.482692|C,0,4.
171687,-1.856079,-0.913502|C,0,-6.057074,-1.41174,-0.087411|H,0,1.6367
25,-2.782115,-0.648307|H,0,1.128549,-2.224838,0.938394|H,0,-0.2216,-1.
706843,-1.779091|H,0,-0.892679,-2.567741,-0.373464|H,0,-1.141111,-0.50
8769,0.892886|H,0,2.029688,-0.453083,-1.385482|H,0,0.620795,0.337384,-
2.504407|H,0,-1.053226,0.859706,-2.620908|H,0,0.205142,2.042067,-2.281
737|H,0,-3.209578,0.134688,-1.66598|H,0,-1.259157,1.82553,1.112295|H,0
,-0.703324,2.924994,-0.151973|H,0,-2.605138,2.424794,-1.556486|H,0,-3.
232074,2.624352,0.064793|H,0,-3.64811,1.3952,1.863326|H,0,-5.157685,0.
481332,1.935387|H,0,-3.661322,-0.289724,2.423882|H,0,0.804064,-0.48132
1,2.211041|H,0,0.317609,1.221734,2.159525|H,0,1.993187,0.801481,2.3857
32|H,0,2.031845,2.033355,-1.115174|H,0,1.60299,2.73153,0.452488|H,0,3.
662705,1.744151,1.462352|H,0,4.055691,2.69117,0.044252|H,0,4.25448,0.7
01207,-1.360068|H,0,5.285215,0.505897,0.047502|H,0,3.583131,-0.510551,
2.238334|H,0,3.330195,-2.18585,1.732412|H,0,4.920901,-1.447567,1.58930
8|H,0,3.919824,-1.655461,-1.961791|H,0,5.26358,-1.835709,-0.828336|H,0
,3.851031,-2.874433,-0.671444|H,0,-6.444464,-2.403754,-0.339788|H,0,-6
.502096,-1.117152,0.868204|H,0,-6.398646,-0.70826,-0.853759|H,0,-4.128
276,-1.819179,-0.975743|H,0,-4.216468,-2.171989,0.750951||Version=x86-
Win32-G98RevA.11.2|HF=-822.2407252|RMSD=3.819e-009|PG=C01 [X(C21H37)]|
|@

Compound 27a, reactant in Table 1, 17 α -side chain, 20-oxa

1\1\GINC-DFT\FOpt\RB3LYP\6-31G(d)\C20H35O1(1+)\BILLW\27-Jul-2003\0\\#
B3LYP/6-31G* OPT\\A Damm Cat Ox model coord from long path calc\\1,1\C
,-1.4395295364,-0.8651042547,1.803424037\C,-0.0316489701,-0.2263110568
,1.8025478406\C,0.2747139721,0.2476854208,0.350115555\C,0.624912235,1.
6378728806,0.1216267156\C,-1.1119006811,-0.1556236728,-0.5185390854\C,
-2.1418196754,-0.1490540831,0.6476389728\C,0.2321522415,2.7271219196,1
.0529982583\C,3.5115672811,0.3511068507,-0.7110131447\C,1.4710996068,1
.9684647731,-1.0208271111\C,3.0355271466,1.7519441345,-0.605456113\C,3
.9869453422,-0.4135105221,0.3083183444\C,4.0645858495,-0.0304090321,1.
7594618656\O,4.498446792,-1.649836598,0.1496095936\C,-0.7699379996,-1.
5249439406,-1.1323772116\C,-3.6159350045,-0.5039769306,0.2745477812\C,
-1.5871078273,0.8161517413,-1.6137633744\C,-3.0145461089,0.4483184219,
-2.073425092\C,-4.0157949088,0.4215882794,-0.9072870203\C,-3.860485961
9,-1.9875792321,-0.0723044107\C,-4.5097862979,-0.1586860075,1.48678648

24\C, 4.602964625, -2.2201192472, -1.1563592734\H, -1.9434035708, -0.718138
 7853, 2.7622432768\H, -1.382256485, -1.9448443883, 1.6336559662\H, -0.00822
 47718, 0.6136458724, 2.5026977057\H, 0.745524054, -0.9229398479, 2.13098140
 94\H, 1.0666636606, -0.3509167153, -0.1183758254\H, -2.2074708804, 0.910269
 8396, 0.9496869235\H, -0.7805599664, 2.5777043482, 1.4430703285\H, 0.318524
 4695, 3.7175919689, 0.6015321909\H, 0.8902115263, 2.7002232243, 1.937121267
 7\H, 3.5408880999, -0.0502104629, -1.7199219181\H, 1.3583872297, 3.01054266
 12, -1.326637663\H, 1.3028426417, 1.3070990793, -1.8740981391\H, 3.21490018
 42, 2.2030832493, 0.3723491569\H, 3.5472416497, 2.3813841394, -1.3420166998
 \H, 3.5570109109, 0.9091347036, 1.9822684254\H, 5.1137817522, 0.0656780183,
 2.0616274124\H, 3.6281334135, -0.8249859581, 2.3738355251\H, -1.6062062438
 , -1.9288115338, -1.7031974561\H, 0.0715351306, -1.4225717845, -1.827499125
 9\H, -0.492286721, -2.2671276945, -0.378724707\H, -0.9084032353, 0.81201698
 49, -2.4760350664\H, -1.6078194535, 1.8454535456, -1.2275376004\H, -3.34086
 42821, 1.1841660301, -2.8173196731\H, -3.0058724288, -0.5158875986, -2.5945
 398009\H, -4.1275152729, 1.4457552623, -0.5218713021\H, -5.0048099711, 0.12
 68003861, -1.2785825698\H, -3.441219454, -2.2874721347, -1.0353024578\H, -4
 .9387482921, -2.1746231249, -0.1246880924\H, -3.4539694142, -2.6559417455,
 0.69468129\H, -4.3409559433, 0.8675389818, 1.8355484478\H, -4.33424904, -0.
 8378035461, 2.3282694999\H, -5.5668933424, -0.2448471504, 1.2118133802\H, 5
 .0662217316, -3.1961662684, -1.0136508649\H, 5.2335404387, -1.6010046513, -
 1.8039937707\H, 3.612895572, -2.3447207727, -1.6109503198\Version=x86-Linux-G98RevA.9\HF=-858.1504837\RMSD=6.263e-09\RMSF=4.196e-06\PG=C01 [X(C20H35O1)]\\@\n

Compound 28a, product in Table 1, 17 α -side chain, 20-oxa

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1\1\GINC-DFT\FOpt\RB3LYP\6-31G(d)\C20H35O1(1+)\BILLW\13-Jun-2003\0\\#  

B3LYP/6-31G(D) OPT=READFC GUESS=READ GEOM=ALLCHECK\a-dammarenly oxy c  

at Product\\1,1\C,-1.228840831,0.7685232947,-1.1750018779\C,0.26658877  

19,0.6058951827,-1.5437949953\C,1.0637389315,0.5893974332,-0.241991926  

6\C,0.6614809427,-0.5800042205,0.6998727651\C,-0.842781182,-0.28426748  

84,1.1723338551\C,-1.7348261246,-0.2598989824,-0.1348134182\C,0.789108  

8392,-1.9675081912,0.0169820277\C,2.6965912196,0.6487959941,-0.1977788  

788\C,1.7792989119,-0.5168159757,1.7706965622\C,3.0829735106,-0.315020  

0898,0.9636869955\C,3.3027232395,0.4283367847,-1.5176184094\C,3.703370  

6077,-0.8893553399,-2.0770796701\O,3.5258584397,1.3943586051,-2.338485  

2439\C,-0.9145705533,1.0481360428,1.9650950768\C,-3.2948208761,-0.2207  

168833,0.0829421372\C,-1.3522066953,-1.411062221,2.1112409393\C,-2.859  

797684,-1.3249356483,2.3948300668\C,-3.6687282669,-1.3367784561,1.0940  

071485\C,-3.862778807,1.1402620993,0.5430017107\C,-3.9949875803,-0.571  

4579433,-1.2520221039\C,3.2925868572,2.8097923789,-2.042315132\H,-1.81  

68373958,0.6838210392,-2.0932084687\H,-1.3833236487,1.7915432393,-0.81  

04481579\H,0.4166397876,-0.3147445871,-2.1213384566\H,0.5613988411,1.4  

375847359,-2.1980266486\H,0.8164188268,1.5169782291,0.2788995227\H,-1.  

5913768984,-1.2455147465,-0.5938740538\H,0.1076201827,-2.1219466215,-0  

.8201713389\H,1.7996854122,-2.1424427296,-0.3595052092\H,0.601677508,-  

2.7644688987,0.7402285152\H,2.9364877575,1.6730568356,0.0975775532\H,1  

.6433950541,0.3321365664,2.4464295784\H,1.8320859931,-1.4173793838,2.3  

893974121\H,3.455958011,-1.2698886589,0.5863372338\H,3.8854735612,0.12  

09658136,1.5658148401\H,4.5206270043,-1.304251557,-1.4725173728\H,2.87  

46449919,-1.6006443924,-2.0145348534\H,4.0338718657,-0.7844300212,-3.1  

110398671\H,-0.8744183557,1.9440893989,1.3394567984\H,-0.1135828833,1.  

1222211444,2.7061422443\H,-1.8456283451,1.1113180454,2.5257793351\H,-1
  
```

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.1649965539,-2.3905079491,1.6575278267\H,-0.7875284893,-1.3887001579,3
.0531188102\H,-3.0995966066,-0.4360451396,2.9898687271\H,-3.152217929,
-2.1816261001,3.0138249504\H,-3.5195496102,-2.3103582453,0.6034993418\
H,-4.7411763965,-1.2697934513,1.3165260386\H,-3.5795414425,1.413364000
5,1.561366743\H,-3.5559860366,1.9575500046,-0.1196201518\H,-4.95786553
15,1.103080915,0.5154314102\H,-3.5779957287,-1.4805160037,-1.703043620
5\H,-5.0614563587,-0.7521585516,-1.0763142686\H,-3.9265259235,0.236690
4733,-1.9882527431\H,3.5147786436,3.3154648734,-2.9795022176\H,2.25403
20618,2.9648292564,-1.7523314046\H,3.9832017268,3.1279471586,-1.259253
3327\\Version=x86-Linux-G03RevB.02\HF=-858.1710586\RMSD=9.978e-09\RMSF
=5.860e-06\Dipole=4.3335622,1.3965234,0.5328778\PG=C01 [X(C20H35O1)]\\
@

```

Transition state between **27a** and **28a**, see Table 1, 17 α -side chain, 20-oxa

Frequency calculation: 1 imaginary frequency: -175.6 cm⁻¹, IR intensity 276.9

```

1|1\GINC-DFTC\SP\RB3LYP\6-31G(d)\C20H35O1(1+)\BILLW\24-Oct-2003\0\\# B
3LYP/6-31G* SP SCF=TIGHT\ADammCatOxa-TS-SP\1,1\C,0,-1.027848,1.41494
6,-1.498351\C,0,0.393586,0.765683,-1.646225\C,0,0.789218,0.329532,-0.2
89069\C,0,0.381466,-0.861247,0.329192\C,0,-1.361926,0.141209,0.691012\
C,0,-1.939356,0.480271,-0.695462\C,0,0.065423,-2.088255,-0.514754\C,0,
3.332379,-0.515302,0.60934\C,0,1.094663,-1.192147,1.629034\C,0,2.57373
4,-1.596622,1.325805\C,0,3.920783,-0.599036,-0.613853\C,0,3.917223,-1.
779639,-1.544382\O,0,4.649411,0.394425,-1.174429\C,0,-1.063292,1.29795
4,1.640088\C,0,-3.467475,0.913263,-0.645576\C,0,-2.155583,-0.964001,1.
383175\C,0,-3.638549,-0.526189,1.505914\C,0,-4.236837,-0.179295,0.1407
05\C,0,-3.713834,2.309429,-0.038043\C,0,-4.015666,0.927193,-2.090332\C
,0,4.917411,1.586146,-0.43887\H,0,-1.421869,1.590059,-2.502175\H,0,-0.
93042,2.39492,-1.020816\H,0,0.344171,-0.068777,-2.350781\H,0,1.093799,
1.509528,-2.03788\H,0,1.205161,1.097067,0.356149\H,0,-1.979971,-0.4686
1,-1.244062\H,0,-0.631936,-1.906186,-1.332523\H,0,-0.332769,-2.896672,
0.103358\H,0,0.994041,-2.455244,-0.965792\H,0,3.490043,0.391606,1.1880
95\H,0,0.594705,-2.008772,2.158952\H,0,1.115638,-0.328203,2.300795\H,0
,2.590638,-2.539802,0.774004\H,0,3.049372,-1.801303,2.293704\H,0,3.344
783,-2.624049,-1.159757\H,0,4.948321,-2.110307,-1.711472\H,0,3.516036,
-1.489439,-2.521929\H,0,-1.970834,1.548534,2.195651\H,0,-0.321861,1.02
2052,2.393259\H,0,-0.726464,2.207008,1.138658\H,0,-1.743316,-1.180465,
2.373867\H,0,-2.132307,-1.887887,0.798624\H,0,-4.19277,-1.356479,1.958
141\H,0,-3.733732,0.315217,2.201132\H,0,-4.270375,-1.092419,-0.470813\
H,0,-5.277767,0.143223,0.264655\H,0,-3.508262,2.366129,1.033328\H,0,-4
.766773,2.579092,-0.174541\H,0,-3.119501,3.082796,-0.536439\H,0,-3.782
831,-0.002221,-2.623864\H,0,-3.626225,1.766568,-2.675317\H,0,-5.106063
,1.029999,-2.068422\H,0,5.554248,2.193237,-1.082519\H,0,5.442227,1.362
23,0.496714\H,0,3.992751,2.13465,-0.217763\\Version=x86-Linux-G98RevA.
9\HF=-858.1395595\RMSD=9.657e-09\PG=C01 [X(C20H35O1)]\\
@

```

Compound **27b**, reactant in Table 1, 17 β -side chain, 20-oxa

```

1|1|UNPC-UNK|SP|RB3LYP|6-31G(d)|C20H35O1(1+)|PCUSER|24-Oct-2003|0||# B
3LYP/6-31G(D) SP SCF=TIGHT\BDammCatOx-SM\1,1\C,0,-1.59203,1.172495,-
1.807273\C,0,-0.102009,0.738516,-1.866318\C,0,0.217652,-0.094159,-0.58
6788\C,0,0.466417,-1.519216,-0.728714\C,0,-1.117092,0.174834,0.384436\
C,0,-2.205944,0.283402,-0.718981\C,0,-0.131693,-2.366421,-1.790164\C,0
,3.508348,-0.662213,-0.318049\C,0,1.381455,-2.162856,0.20565\C,0,2.918
242,-2.024837,-0.338505\C,0,4.219122,-0.143432,0.719396\C,0,4.47449,-0

```

.805367,2.043716|O,0,4.816483,1.063204,0.699846|C,0,-0.758483,1.476435
 ,1.126522|C,0,-3.665847,0.54497,-0.232639|C,0,-1.509841,-0.921117,1.38
 9116|C,0,-2.918835,-0.645589,1.958195|C,0,-3.977793,-0.523785,0.850254
 |C,0,-3.935541,1.966698,0.302633|C,0,-4.614098,0.316671,-1.431841|C,0,
 4.778703,1.860213,-0.484276|H,0,-2.086616,1.043426,-2.773518|H,0,-1.67
 3485,2.232939,-1.550244|H,0,0.110341,0.166284,-2.773747|H,0,0.568762,1
 .602121,-1.894737|H,0,1.06409,0.315392,-0.022052|H,0,-2.262033,-0.7298
 31,-1.148885|H,0,-0.59418,-1.813532,-2.606644|H,0,0.612357,-3.069201,-
 2.189049|H,0,-0.902237,-3.000944,-1.321593|H,0,3.398508,-0.071768,-1.2
 21779|H,0,1.371886,-1.688566,1.189219|H,0,1.189595,-3.235873,0.294788|
 H,0,2.941489,-2.450617,-1.346032|H,0,3.456628,-2.718037,0.312088|H,0,3
 .937576,-1.747846,2.160578|H,0,5.546852,-0.99833,2.161885|H,0,4.180705
 ,-0.130007,2.854312|H,0,-0.52626,2.299097,0.444695|H,0,0.114012,1.3137
 36,1.769|H,0,-1.573825,1.804665,1.771959|H,0,-1.53295,-1.903357,0.8961
 02|H,0,-0.781781,-0.991983,2.207456|H,0,-2.90495,0.258187,2.577894|H,0
 ,-3.188921,-1.465356,2.633636|H,0,-4.077269,-1.501251,0.355544|H,0,-4.
 955811,-0.309524,1.2981|H,0,-3.473355,2.166444,1.27225|H,0,-3.595997,2
 .738074,-0.396905|H,0,-5.014553,2.104107,0.433206|H,0,-4.44297,-0.6582
 88,-1.904863|H,0,-5.657632,0.343919,-1.098827|H,0,-4.494737,1.091424,-
 2.197354|H,0,5.359196,2.753851,-0.25589|H,0,5.231261,1.32798,-1.328306
 |H,0,3.748973,2.144143,-0.733748||Version=x86-Win32-G98RevA.11.2|HF=-8
 58.1503889|RMSD=4.048e-009|PG=C01 [X(C20H35O1)]||@

Compound 28b, product in Table 1, 17 β -side chain, 20-oxa

1|1|UNPC-UNK|SP|RB3LYP|6-31G(d)|C20H35O1(1+)|PCUSER|27-Oct-2003|0||# B
 3LYP/6-31G(D) SP SCF=TIGHT||BDammCatOx-Prod||1,1|C,0,-0.558563,1.36625
 ,-1.140857|C,0,0.887584,0.83005,-1.227169|C,0,1.212495,0.088614,0.0632
 55|C,0,0.241125,-1.088801,0.388267|C,0,-1.229827,-0.478562,0.554453|C,
 0,-1.586929,0.266378,-0.794622|C,0,0.304502,-2.191896,-0.700479|C,0,2.
 651674,-0.587725,0.21579|C,0,0.914784,-1.66927,1.656029|C,0,2.438268,-
 1.642814,1.361036|C,0,3.628046,0.46618,0.499993|C,0,3.771236,1.116529,
 1.832324|O,0,4.428277,0.957553,-0.378947|C,0,-1.285898,0.461046,1.7844
 72|C,0,-3.085253,0.725734,-0.977841|C,0,-2.262448,-1.61471,0.787733|C,
 0,-3.716948,-1.124718,0.729915|C,0,-4.013964,-0.463544,-0.619096|C,0,-
 3.494763,1.986071,-0.181747|C,0,-3.32352,1.046134,-2.473941|C,0,4.5630
 46,0.453988,-1.749787|H,0,-0.811011,1.824654,-2.101154|H,0,-0.591194,2
 .174927,-0.40071|H,0,0.988181,0.159911,-2.091411|H,0,1.574966,1.67228,
 -1.390363|H,0,1.127193,0.803833,0.888689|H,0,-1.4795,-0.497499,-1.5753
 44|H,0,-0.111871,-1.888453,-1.662185|H,0,0.1.330835,-2.523844,-0.889492|
 H,0,-0.24175,-3.079468,-0.373166|H,0,2.899448,-1.080851,-0.725072|H,0,
 0.708759,-1.051045,2.532858|H,0,0.577223,-2.682818,1.89043|H,0,2.80509
 7,-2.608212,1.002776|H,0,3.017926,-1.409156,2.258154|H,0,2.865024,1.02
 3003,2.432271|H,0,4.584996,0.610459,2.372468|H,0,4.058697,2.164779,1.7
 18838|H,0,-0.641419,1.341576,1.705448|H,0,-1.01811,-0.070691,2.702351|
 H,0,-2.29435,0.838103,1.939695|H,0,-2.150218,-2.384133,0.015835|H,0,-2
 .062346,-2.10413,1.750376|H,0,-3.934935,-0.438489,1.556467|H,0,-4.3858
 37,-1.982164,0.871154|H,0,-3.91887,-1.227698,-1.404914|H,0,-5.056331,-
 0.121979,-0.652179|H,0,-3.59368,1.815698,0.89266|H,0,-2.788806,2.81143
 8,-0.326141|H,0,-4.471213,2.334972,-0.536619|H,0,-2.969962,0.235828,-3
 .123559|H,0,-4.395966,1.171999,-2.660316|H,0,-2.834683,1.97422,-2.7898
 37|H,0,5.317012,1.099773,-2.194508|H,0,4.907793,-0.580709,-1.720466|H,
 0,3.611098,0.54939,-2.270531||Version=x86-Win32-G98RevA.11.2|HF=-858.1
 801798|RMSD=2.985e-009|PG=C01 [X(C20H35O1)]||@

Transition state between **27b** and **28b**, see Table 1, 17 β -side chain, 20-oxa

Frequency calculation: 1 imaginary frequency: -191.0 cm⁻¹, IR intensity 301.4

```
1|1|UNPC-UNK|SP|RB3LYP|6-31G(d)|C20H35O1(1+)|PCUSER|26-Oct-2003|0||# B
3LYP/6-31G(D) SP SCF=TIGHT||BDammCatOx-TS||1,1|C,0,-1.014298,1.273428,
-1.58743|C,0,0.490005,0.822584,-1.598464|C,0,0.780504,0.324008,-0.2359
15|C,0,0.455308,-0.95482,0.241452|C,0,-1.423473,-0.20643,0.4532|C,0,-1
.88048,0.171509,-0.96834|C,0,0.41007,-2.13671,-0.716914|C,0,3.326805,-
0.576295,0.601761|C,0,1.050251,-1.301513,1.594078|C,0,2.582266,-1.5866
8,1.441276|C,0,3.841126,0.595153,1.062306|C,0,3.703989,1.128737,2.4601
9|O,0,4.570432,1.457796,0.321375|C,0,-1.386062,0.89896,1.505363|C,0,-3
.448156,0.412446,-1.079017|C,0,-2.147049,-1.447765,0.970806|C,0,-3.677
119,-1.196512,0.942709|C,0,-4.157358,-0.819765,-0.460509|C,0,-3.939154
,1.719337,-0.423384|C,0,-3.825959,0.468741,-2.57648|C,0,4.925408,1.114
092,-1.016536|H,0,-1.308622,1.479663,-2.619157|H,0,-1.103969,2.21536,-
1.038123|H,0,0.635092,0.052772,-2.361086|H,0,1.120737,1.682079,-1.8439
61|H,0,1.023599,1.075884,0.508361|H,0,-1.734138,-0.727974,-1.578676|H,
0,-0.184725,-1.968799,-1.614925|H,0,1.432273,-2.358592,-1.046442|H,0,0
.034224,-3.032893,-0.217161|H,0,3.552053,-0.871708,-0.418335|H,0,0.930
628,-0.468113,2.292612|H,0,0.560099,-2.175718,2.034292|H,0,2.715778,-2
.578371,0.997265|H,0,2.999364,-1.654135,2.451627|H,0,3.111955,0.475413
,3.102573|H,0,4.697341,1.250012,2.906575|H,0,3.243219,2.123424,2.44239
3|H,0,-1.106044,1.877245,1.110684|H,0,-0.71173,0.650857,2.328057|H,0,-
2.377359,0.999875,1.954424|H,0,-1.943712,-2.313372,0.334275|H,0,-1.824
872,-1.69329,1.987569|H,0,-3.953318,-0.427061,1.672045|H,0,-4.170171,-
2.117787,1.273205|H,0,-4.006649,-1.681712,-1.126264|H,0,-5.237969,-0.6
3268,-0.444049|H,0,-3.858381,1.723777,0.665998|H,0,-3.402176,2.594631,
-0.804423|H,0,-4.997888,1.864943,-0.664225|H,0,-3.419019,-0.384699,-3.
132101|H,0,-4.915991,0.440106,-2.681747|H,0,-3.481896,1.389203,-3.0588
81|H,0,5.53803,1.938537,-1.381478|H,0,5.501818,0.182486,-1.042279|H,0,
4.033659,1.009916,-1.64767||Version=x86-Win32-G98RevA.11.2|HF=-858.137
9998|RMSD=3.815e-009|PG=C01 [X(C20H35O1)]||@
```

Transition state of Figure 3, E-ring formation for lupeol skeleton

Frequency calculation: 1 imaginary frequency: -189.4 cm⁻¹, IR intensity 77.4

```
1\1\GINC-DFT\SP\RB3LYP\6-31G(d)\C25H43(1+)\BILLW\15-Oct-2003\0\\# B3LY
P/6-31G(D) SP GEOM=CHECK GUESS=READ SCF=TIGHT\\lupeol E ring SM for QS
T3\\1,1|C,0,-1.482579,1.639857,0.748137|C,0,-0.031486,1.409616,0.28697
8|C,0,0.272383,-0.098752,0.314798|C,0,-0.719556,-0.918365,-0.615199|C,
0,-2.200581,-0.719381,-0.055232|C,0,-2.513284,0.832318,-0.071083|C,0,-
0.588824,-0.484863,-2.100328|C,0,1.646864,-0.482285,-0.094907|C,0,-0.1
48487,-2.359587,-0.507585|C,0,1.356021,-2.36583,-0.749562|C,0,2.444454
,-1.488757,0.475524|C,0,2.179188,-2.061782,1.854016|C,0,3.877774,-1.61
0395,-0.015652|C,0,-2.326558,-1.333685,1.361313|C,0,-4.008775,1.255589
,0.193428|C,0,-3.222346,-1.444391,-0.974431|C,0,-4.681831,-1.111807,-0
.632836|C,0,-4.930594,0.397629,-0.711998|C,0,-4.475309,1.177813,1.6653
21|C,0,-4.186522,2.728471,-0.250349|C,0,4.838465,-0.644873,0.741394|C,
0,4.420457,0.80429,0.700211|C,0,4.822183,1.744584,-0.175785|C,0,4.3418
77,3.169989,-0.053545|C,0,5.784397,1.498905,-1.311125|H,0,-1.698138,2.
708919,0.665922|H,0,-1.558588,1.397136,1.815322|H,0,0.121578,1.81061,-
0.722529|H,0,0.65978,1.945948,0.947545|H,0,0.109284,-0.448615,1.335955
|H,0,-2.369542,1.138396,-1.114693|H,0,-1.020267,0.49493,-2.305033|H,0,
0.451831,-0.437302,-2.435921|H,0,-1.092247,-1.203502,-2.75211|H,0,2.07
2605,0.023485,-0.959633|H,0,-0.353068,-2.805845,0.467614|H,0,-0.599092
```

$, -3.024662, -1.255009 \text{H}, 0, 1.832875, -3.304494, -0.454426 \text{H}, 0, 1.671819, -2.$
 136153, -1.766499 H , 0, 1.121948, -2.124032, 2.112389 H , 0, 2.620581, -3.05850
 3, 1.946324 H , 0, 2.665158, -1.41794, 2.595898 H , 0, 3.922957, -1.376618, -1.08
 5621 H , 0, 4.225366, -2.642064, 0.111876 H , 0, -1.699883, -0.849982, 2.115919
 H , 0, -2.088728, -2.402188, 1.358243 H , 0, -3.348538, -1.259598, 1.725841 H , 0,
 -3.059054, -1.151235, -2.01748 H , 0, -3.061232, -2.529979, -0.923547 H , 0, -4.
 952104, -1.499885, 0.35606 H , 0, -5.338234, -1.627757, -1.343694 H , 0, -5.9768
 92, 0.621404, -0.468911 H , 0, -4.785136, 0.715731, -1.755233 H , 0, -4.642002, 0
 .159267, 2.023132 H , 0, -3.76799, 1.661105, 2.348156 H , 0, -5.430167, 1.705548
 $, 1.768418 \text{H}, 0, -3.784929, 2.902558, -1.256345 \text{H}, 0, -5.252137, 2.982664, -0.2$
 74129 H , 0, -3.706159, 3.434536, 0.435452 H , 0, 5.830032, -0.786281, 0.301072
 H , 0, 4.924167, -0.97135, 1.784738 H , 0, 3.743828, 1.121519, 1.495532 H , 0, 3.64
 0151, 3.300758, 0.775928 H , 0, 3.853322, 3.505468, -0.978158 H , 0, 5.188923, 3.
 849158, 0.109855 H , 0, 6.118073, 0.461339, -1.389172 H , 0, 5.330436, 1.78172, -
 2.270189 H , 0, 6.675453, 2.129953, -1.197865 \Version=x86-Linux-G98RevA.9
 HF=-978.2791361 RMSD=3.148e-09 PG=C01 [X(C25H43)] \\ @

Transition state of Figure 3, E-ring formation for hopene skeleton

Frequency calculation: 1 imaginary frequency: -145.0 cm⁻¹, IR intensity 96.5

```

1\1\GINC-DFTB\FTS\RB3LYP\6-31G(d)\C25H43(1+)\BILLW\04-Sep-2003\0\\# B3
LYP/6-31G(D) OPT=QST3\TS guess HF geom frozen 1.9=old 2.2=new bond\1
,1\c,1.9552464328,1.8134137694,-0.3070292153\c,0.4823744774,1.82795328
42,0.1918187788\c,-0.1452598333,0.4672940649,-0.0948103756\c,0.5968025
217,-0.7299387491,0.5375024472\c,2.0386357766,-0.7484563293,-0.2341405
629\c,2.7681285287,0.5897750442,0.157725375\c,0.7719847389,-0.58645458
68,2.0740893795\c,-2.0844945357,-0.5431658157,-0.0740855678\c,-0.20788
87098,-2.0265480709,0.2856983714\c,-1.7172664743,-1.7899274165,0.63004
23852\c,-2.0153868746,0.7662630805,0.415056611\c,-2.1285138259,1.09091
51145,1.8912877284\c,-2.5776185038,1.8404343902,-0.5089870961\c,1.8432
587273,-0.8874512924,-1.768887206\c,4.3023613696,0.689690586,-0.187897
8634\c,2.8699432703,-1.9771686028,0.2274224526\c,4.3462885422,-1.89714
54137,-0.1921837105\c,4.99555405,-0.6046100105,0.3075593748\c,4.620670
9311,0.934020911,-1.6794309086\c,4.9130990997,1.8682235831,0.606696045
8\c,-4.1350783474,1.781511897,-0.5628891488\c,-4.6608030284,0.48100267
41,-1.101875987\c,-5.4410492198,-0.4324766625,-0.4869275415\c,-5.90967
70937,-1.6605154213,-1.2297143629\c,-5.9664767553,-0.3171041555,0.9223
643704\h,2.4152797315,2.7356433406,0.0610568969\h,1.9563862396,1.88901
51962,-1.3990761569\h,0.4592104815,2.0573653442,1.2595664376\h,-0.0523
330829,2.6269233906,-0.3268742824\h,-0.2346555722,0.3413318925,-1.1723
830185\h,2.7656929965,0.6093928971,1.254763131\h,0.953853921,0.4340209
24,2.4112877303\h,-0.1095351005,-0.9474102582,2.6085784543\h,1.6058928
734,-1.1936009298,2.4286739685\h,-2.2399453059,-0.6454102512,-1.145673
6211\h,-0.1482014053,-2.3429754907,-0.7583432601\h,0.1674783088,-2.855
544725,0.8927445833\h,-2.3064905912,-2.6271394153,0.2421282769\h,-1.87
5547091,-1.7282358094,1.708068315\h,-1.5929467668,2.0129296474,2.13284
04232\h,-3.184985581,1.2676282469,2.1212365036\h,-1.7741040776,0.30065
7358,2.5497611116\h,-2.186269483,1.7091911049,-1.5257588789\h,-2.27320
13025,2.8343729842,-0.1682442787\h,1.5501728617,0.0374848515,-2.270544
3609\h,1.1019739015,-1.650099748,-2.0243461462\h,2.771014028,-1.210202
2096,-2.2402067955\h,2.8501570935,-2.0726839271,1.3180992184\h,2.41909
70395,-2.8942980702,-0.1723588254\h,4.4503183248,-1.9829810094,-1.2802
450971\h,4.8754423854,-2.7620782071,0.2249425048\h,6.0528166738,-0.576
3755932,0.0156943595\h,4.9826956898,-0.6094079378,1.4078222937\h,4.351

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2983029, 0.0991837404, -2.3300795478\H, 4.1211745299, 1.8306477519, -2.0625
 133778\H, 5.6982221624, 1.0956996264, -1.7964191148\H, 4.6692387886, 1.8062
 6461, 1.6744998248\H, 6.0051623144, 1.8519289791, 0.5177607359\H, 4.5776219
 249, 2.8432082776, 0.2366392674\H, -4.4520164161, 2.6022512528, -1.21972650
 33\H, -4.5471003195, 2.0076066254, 0.4244033687\H, -4.3976071726, 0.2854945
 645, -2.1437424581\H, -5.4991560153, -1.7150261653, -2.242384503\H, -7.0047
 706403, -1.6677292203, -1.3088384666\H, -5.636143912, -2.5786852331, -0.692
 5165017\H, -5.6140988484, 0.5688211098, 1.4555765408\H, -7.0636106337, -0.2
 816245432, 0.9112779356\H, -5.6964928405, -1.2027702053, 1.5124306706\\Version=x86-Linux-G98RevA.9\HF=-978.273353\RMSD=4.002e-09\RMSF=6.302e-06\
 PG=C01 [X(C25H43)] \\@

TABLE 5: ENTRIES WITH C13 MIGRATION

Compound **31a**, reactant in Table 5, 17 α -side chain, C13 migration, $\alpha\beta\alpha$ configuration

1|1|UNPC-UNK|FOpt|RB3LYP|6-31G(d)|C25H43(1+)|PCUSER|16-Aug-2003|0||# B
 3LYP/6-31G(D) OPT=READFC GEOM=ALLCHECK GUESS=READ||E ring mod 17a hope
 ne SM||1,1|C,-0.2410281139,2.4062759028,-0.2160868485|C,0.7603198118,1
 .3106967371,-0.6541743778|C,0.3210598498,-0.0040639478,-0.0302134274|C
 ,-1.109294902,-0.4453311457,-0.4361814521|C,-2.1343582945,0.671920881,
 0.0942888826|C,-1.7052349161,2.0500535732,-0.5463536725|C,-1.226330103
 ,-0.6590665715,-1.9666876322|C,1.2115629707,-1.4026936274,-0.172433357
 3|C,-1.1943621291,-1.8400863809,0.228257742|C,0.14161209,-2.5252961111
 ,-0.1378002259|C,2.2237858538,-1.375836261,-1.2120806982|C,2.148788333
 2,-2.0927326841,-2.5105156866|C,3.4786211389,-0.6561625598,-0.94813511
 21|C,-2.1400744867,0.7021888853,1.6428497499|C,-2.7092512683,3.2540447
 28,-0.3806805204|C,-3.5745631875,0.331927052,-0.3749323023|C,-4.574389
 8001,1.4666644378,-0.1053828235|C,-4.1261502218,2.7654303277,-0.782453
 8567|C,-2.7400756364,3.9082178717,1.0191211509|C,-2.3157133908,4.36692
 70044,-1.3824510455|C,4.4596137919,-1.6007322494,-0.0884328411|C,4.159
 045774,-1.6130159766,1.3725302414|C,3.8500313187,-2.6748897809,2.15000
 3877|C,3.6762702906,-2.5027123935,3.6377282461|C,3.7005601965,-4.09073
 32321,1.6566283562|H,0.0422180422,3.3390996831,-0.7122945844|H,-0.1175
 814912,2.5842704319,0.859203338|H,0.7954108274,1.244779179,-1.74977528
 35|H,1.761799114,1.6072560075,-0.3192082762|H,0.3304824253,0.139081376
 6,1.0523756198|H,-1.7305047574,1.8796166034,-1.630247455|H,-1.29003282
 69,0.2673263408,-2.5387650113|H,-0.3683642566,-1.2098685312,-2.3626497
 644|H,-2.1123348233,-1.2534200523,-2.2057100576|H,1.7962321808,-1.3822
 711888,0.7649020644|H,-1.2665925062,-1.7544630421,1.3155649297|H,-2.05
 3886671,-2.4259072832,-0.1102609467|H,0.4266286877,-3.290950855,0.5907
 052451|H,0.0536202987,-3.0334844392,-1.1003000576|H,2.0138169743,-1.33
 81606717,-3.3028346236|H,3.1105895319,-2.5714161774,-2.7365692522|H,1.
 3452743636,-2.8227658364,-2.5887966637|H,3.3226824495,0.2468454317,-0.
 3534290055|H,3.9948573654,-0.4014289978,-1.8774677293|H,-1.1904245085,
 1.0127328122,2.0880056057|H,-2.3982523795,-0.277605663,2.0549080396|H,
 -2.8920577929,1.3937698835,2.017273787|H,-3.5787616723,0.1433858201,-1
 .4545342812|H,-3.9126249462,-0.5947314324,0.1074426403|H,-4.7149459758
 ,1.618039199,0.9710971963|H,-5.5568824688,1.1728674146,-0.4944281971|H
 ,-4.8488116692,3.5663362171,-0.5804343982|H,-4.1414318698,2.6087316213
 ,-1.8714821141|H,-3.2229133062,3.2944807494,1.7824986462|H,-1.73537345
 01,4.1590460869,1.3772024482|H,-3.3042475276,4.8463109897,0.9655768347
 |H,-2.168827961,3.9694569296,-2.3944093533|H,-3.1129583019,5.116860261
 9,-1.4370505103|H,-1.4022112691,4.8945973696,-1.0875739308|H,5.4439900

472,-1.1489988089,-0.2594218867|H,4.4908978581,-2.5996515798,-0.530132
 7787|H,4.2642632194,-0.6447713653,1.8635682073|H,3.7874216459,-1.46104
 64045,3.9512114286|H,4.4166936658,-3.103462648,4.1819623734|H,2.690750
 8959,-2.8612981376,3.9625159639|H,3.7538184932,-4.1942379494,0.5701898
 171|H,4.4878871257,-4.7235304485,2.0870847334|H,2.7480174023,-4.517385
 7717,1.9960130453||Version=x86-Win32-G98RevA.11.2|HF=-978.2847095|RMSD
 =6.612e-009|RMSF=9.067e-006|PG=C01 [X(C25H43)]||@

Compound 32a, product in Table 5, 17 α -side chain, C13 migration, $\alpha\beta\alpha$ configuration

1|1|UNPC-UNK|FOpt|RB3LYP|6-31G(d)|C25H43(1+)|PCUSER|18-Aug-2003|0||# B
 3LYP/6-31G(D) OPT=READFC GEOM=ALLCHECK GUESS=READ||17-hopene E ring mo
 del product||1,1|C,-1.8476198601,1.4957767624,-1.4322793267|C,-0.39457
 85989,1.0923509819,-1.7422387123|C,0.3495111504,0.580959907,-0.4919542
 993|C,-0.4346306302,-0.5915360766,0.211108954|C,-1.861204191,0.0205018
 405,0.6701678122|C,-2.6299877079,0.4208774362,-0.6476388926|C,-0.62597
 66051,-1.8143044107,-0.7344641193|C,2.4232209094,-0.0616157685,0.63735
 13256|C,0.356840055,-1.1163743407,1.4459482377|C,1.8748904304,-1.35344
 71634,1.2085568016|C,1.8850018603,0.321784997,-0.7509300312|C,2.159942
 4428,-0.7038032421,-1.8689329248|C,2.6816003517,1.6099939466,-1.061219
 5881|C,-1.6686825499,1.2385229504,1.6173351986|C,-4.1667712183,0.73652
 25464,-0.5171444276|C,-2.6783179131,-1.0320002638,1.4740562558|C,-4.15
 58422835,-0.6563204334,1.6602448685|C,-4.8308930182,-0.3900058368,0.31
 34788025|C,-4.5002539409,2.1173111029,0.0895498042|C,-4.8061728691,0.6
 956964169,-1.925254833|C,4.1481588356,1.279524635,-0.6948854142|C,4.11
 63375087,0.3714891827,0.5517651048|C,4.8081309495,-0.8713133464,0.6527
 906149|C,5.1425098175,-1.396513134,2.0015420585|C,5.1997671154,-1.7311
 96661,-0.4911820771|H,-2.3492244708,1.7018775234,-2.3833212815|H,-1.84
 73237456,2.445064365,-0.8852725877|H,-0.395213835,0.3296605704,-2.5289
 548597|H,0.1358992707,1.9574690431,-2.1596176143|H,0.348207728,1.41342
 03781,0.2219562704|H,-2.619531923,-0.4839320395,-1.2693456461|H,-0.766
 9501339,-1.5445473078,-1.7817132287|H,0.2326223007,-2.4906894642,-0.69
 29830153|H,-1.4900003398,-2.4135013219,-0.442114566|H,2.1494491146,0.7
 347478598,1.3371544048|H,0.2767357733,-0.4189091542,2.2849989578|H,-0.
 0819542895,-2.0586205349,1.7909446636|H,2.327586284,-1.6016440069,2.17
 53311562|H,2.0464687297,-2.2046413005,0.5405428533|H,1.6119449336,-0.4
 192297985,-2.7708625985|H,3.2161277427,-0.7264795563,-2.1491189712|H,1
 .8607614731,-1.7213182661,-1.6182456675|H,2.3181301056,2.4375921738,-0
 .4393563906|H,2.5978903413,1.9274246696,-2.1042391296|H,-0.9253378569,
 1.0425546814,2.3963538387|H,-2.5965862245,1.4622320366,2.1439318109|H,
 -1.3730131754,2.1588555091,1.1099439196|H,-2.6564246235,-2.0059520336,
 0.9726138075|H,-2.2130073478,-1.1833109603,2.4568347092|H,-4.260370734
 7,0.2142102451,2.3188730146|H,-4.6676650066,-1.4791591656,2.1743120894
 |H,-5.8912468327,-0.1488241967,0.4621133148|H,-4.8085219982,-1.3183806
 069,-0.2772811226|H,-4.1982264673,2.2232047902,1.1337828512|H,-4.03617
 45333,2.9335197349,-0.4748508376|H,-5.5838963878,2.2792066265,0.051078
 6285|H,-4.5571800618,-0.2323519864,-2.4546195794|H,-5.8980534221,0.743
 8729202,-1.8417342881|H,-4.4958003261,1.5381549794,-2.552237574|H,4.72
 77559232,2.1797066844,-0.4692952008|H,4.6528435057,0.787205219,-1.5296
 965677|H,4.2398801545,0.931969386,1.4810215954|H,6.2216959547,-1.21835
 38174,2.1497461407|H,5.0053843795,-2.4817637494,2.0689143179|H,4.61311
 61001,-0.88735426,2.8091406345|H,4.4476986449,-2.5300561454,-0.5921948
 023|H,5.2671342311,-1.2080694442,-1.4443118962|H,6.1444908038,-2.24215
 24481,-0.27284871||Version=x86-Win32-G98RevA.11.2|HF=-978.2851416|RMSD

=6.195e-009|RMSF=2.101e-006|PG=C01 [X(C25H43)]||@

Compound 31b, reactant in Table 5, 17 α -side chain, C13 migration, $\alpha\beta\beta$ configuration

1|1|UNPC-UNK|FOpt|RB3LYP|6-31G(d)|C25H43(1+)|PCUSER|22-Aug-2003|0||# B
3LYP/6-31G(D) OPT=READFC GEOM=ALLCHECK GUESS=READ||E ring mod hopene 1
7a SM||1,1|C,-1.2726724982,1.6554568265,0.9544474568|C,-0.1830502552,1
.4765482451,-0.1299416218|C,0.1871993618,0.0022840808,-0.1756108671|C,
-0.9967780655,-0.9378257654,-0.5156814211|C,-2.0716754706,-0.792617011
4,0.6719373246|C,-2.4899431739,0.7290538526,0.7455848701|C,-1.61455713
69,-0.6130842595,-1.8984693766|C,1.446029018,-0.583428127,-1.111390264
2|C,-0.2773832416,-2.3016282884,-0.6486585472|C,0.9694273839,-2.003492
4584,-1.5124160194|C,1.8864689038,0.3738547343,-2.1078298394|C,1.50339
80925,0.3650581327,-3.5410968064|C,2.8280013409,1.4192415272,-1.692220
6353|C,-1.4780215519,-1.318231869,2.0026038713|C,-3.7224710036,1.08237
66417,1.6626413754|C,-3.3318915796,-1.6413401656,0.3520110434|C,-4.492
6952581,-1.3755866389,1.3229730856|C,-4.8796777117,0.1067288929,1.3224
78609|C,-3.4402332453,1.0801483012,3.1822323558|C,-4.21448233,2.505646
0591,1.30343173|C,4.3445136903,0.8962936482,-1.8802325987|C,4.75296191
87,-0.2276223826,-0.9838224994|C,5.3646780478,-0.1195553005,0.21528330
61|C,5.7843595126,-1.3515282917,0.9750329025|C,5.7023665913,1.18524673
75,0.8889084323|H,-1.5912425621,2.7017894681,0.9447853991|H,-0.8194069
254,1.484689862,1.9385207557|H,-0.5554811673,1.8290076679,-1.100923041
|H,0.6775044815,2.1044973433,0.1315866922|H,0.5497519948,-0.2643348749
,0.819157452|H,-2.8727967782,0.966079278,-0.2548759197|H,-2.2147818261
,0.2971814111,-1.9127775965|H,-0.8437825664,-0.4917235896,-2.663546802
5|H,-2.2544641748,-1.4332391259,-2.2343900446|H,2.2639748649,-0.630830
7165,-0.3777400519|H,0.0463309263,-2.6750712179,0.3263869536|H,-0.9037
733647,-3.0760741015,-1.1010138276|H,1.7723479058,-2.7269761665,-1.339
1595393|H,0.7221004076,-2.0650234075,-2.5745603144|H,0.7451782549,1.15
15787233,-3.6896263358|H,2.3536028765,0.6620485691,-4.1676096023|H,1.0
888662904,-0.577279731,-3.8966266304|H,2.7208337872,1.6741869848,-0.63
59372886|H,2.7303948688,2.3159938899,-2.3119448446|H,-0.6523760836,-0.
7168645407,2.3930788328|H,-1.123210325,-2.3476705817,1.8994775301|H,-2
.2363166825,-1.3397993178,2.7825890817|H,-3.6917380835,-1.4081275552,-
0.6564721441|H,-3.0705350921,-2.7077090992,0.354906791|H,-4.2420636894
,-1.7106051329,2.3362917676|H,-5.3562091252,-1.9779945833,1.0159713225
|H,-5.7090448417,0.2816518737,2.0196013529|H,-5.2629731296,0.361215453
,0.3229659731|H,-3.295211047,0.0828870743,3.6030584117|H,-2.559972725,
1.6814453213,3.4363534624|H,-4.2930880064,1.5240816535,3.708414766|H,-
4.3460063606,2.628811917,0.2212131313|H,-5.1855207224,2.6936250316,1.7
753466208|H,-3.5328097415,3.287624424,1.6551991704|H,4.9412608971,1.79
50115081,-1.7060163001|H,4.4768526979,0.6237876463,-2.932264897|H,4.56
89343988,-1.2314957799,-1.3656354843|H,5.516499508,-2.2741004639,0.452
2578459|H,5.3284093778,-1.3717185805,1.973621106|H,6.87080441,-1.35244
9364,1.1328016825|H,5.37067647,2.0698897783,0.3399245531|H,5.257678023
8,1.2227100902,1.8917426285|H,6.7875745424,1.267310234,1.0326921841||V
ersion=x86-Win32-G98RevA.11.2|HF=-978.2841916|RMSD=5.999e-009|RMSF=6.6
500e-006|PG=C01 [X(C25H43)]||@

Compound 32b, product in Table 5, 17 α -side chain, C13 migration, $\alpha\beta\beta$ configuration

1|1|UNPC-UNK|FOpt|RB3LYP|6-31G(d)|C25H43(1+)|PCUSER|11-Sep-2003|0||# B
3LYP/6-31G(D) OPT=READFC GEOM=ALLCHECK||ERing-17aHopUP-Prod||1,1|C,-2.
3610996942,0.7727016115,-1.2086390321|C,-0.9673479983,0.5672028969,-1.
8300094892|C,0.1284063269,0.3639951863,-0.7635531125|C,-0.2365455262,-

0.7985295242, 0.2332689393|C, -1.6110594727, -0.3604234228, 0.9697948745|C
 , -2.7214817469, -0.2895621659, -0.1486391825|C, -0.4027243078, -2.16352367
 44, -0.4979679363|C, 2.5244562406, 0.2127248238, -0.1547110264|C, 0.9047049
 397, -0.9948636959, 1.2737911367|C, 2.3368726806, -1.0410523121, 0.67623643
 24|C, 1.5708652885, 0.313297448, -1.3843638782|C, 1.783614222, -0.802865811
 5, -2.4270675996|C, 2.0256385652, 1.6502847977, -2.0103378188|C, -1.4457438
 716, 0.9996120776, 1.7038115193|C, -4.2202863276, -0.2165428433, 0.32832077
 08|C, -2.0053624063, -1.398128259, 2.0603347689|C, -3.4458046527, -1.244066
 1181, 2.5689814024|C, -4.4460063173, -1.2989876606, 1.4130433932|C, -4.6728
 82303, 1.1660983484, 0.8485657541|C, -5.1402741194, -0.5723991468, -0.86355
 29953|C, 3.5763832414, 1.6217489224, -1.9488292274|C, 3.9791035782, 0.54390
 85636, -0.9033602898|C, 4.825021917, 0.8716323831, 0.2025124735|C, 5.618530
 3098, -0.182273583, 0.876423515|C, 4.9213865496, 2.2487426661, 0.7476244177
 |H, -3.0966440285, 0.7552107112, -2.0193491708|H, -2.418236443, 1.778620371
 1, -0.7778395922|H, -1.0016978387, -0.2907217002, -2.5104539793|H, -0.71955
 86503, 1.4367754581, -2.4518340699|H, 0.1452628088, 1.2805363311, -0.160759
 0586|H, -2.6749047102, -1.2617430684, -0.6562206062|H, -0.8306181724, -2.07
 95541462, -1.4978421876|H, 0.5554513044, -2.6795937926, -0.6043732995|H, -1
 .0447016164, -2.8429467369, 0.0652496638|H, 2.3204026723, 1.0875614969, 0.4
 750093286|H, 0.897581552, -0.1900552511, 2.0154088069|H, 0.7388344527, -1.9
 233607773, 1.8302704467|H, 3.0471915844, -1.0974899917, 1.509365967|H, 2.49
 24549623, -1.938744935, 0.0686109963|H, 1.0122033588, -0.7334762452, -3.198
 4900517|H, 2.743580694, -0.7012038176, -2.9446147673|H, 1.7370124117, -1.80
 8993351, -2.0115585931|H, 1.6385902628, 2.4924664368, -1.4240789739|H, 1.67
 04791467, 1.7812685789, -3.0358998759|H, -1.4377013113, 1.8680507437, 1.042
 3047281|H, -0.5299608299, 1.0357106826, 2.3022034103|H, -2.2652430057, 1.15
 5073421, 2.4056945261|H, -1.9085012495, -2.4195808487, 1.6764091896|H, -1.3
 092885853, -1.321891211, 2.9057475008|H, -3.5660433593, -0.3122901056, 3.13
 48979989|H, -3.6578860152, -2.051533884, 3.2805738885|H, -5.4717700403, -1.
 2155947031, 1.7945249908|H, -4.3761665515, -2.2893061489, 0.938155761|H, -4
 .173353747, 1.4750472251, 1.7695531042|H, -4.512731349, 1.952984389, 0.1034
 197835|H, -5.7483139556, 1.1405297174, 1.0600196452|H, -4.8441708414, -1.51
 83774305, -1.3335242108|H, -6.1739098432, -0.6867952395, -0.5170613473|H, -
 5.1456600938, 0.2037361737, -1.6361618674|H, 3.9875339864, 2.6049722747, -1
 .7064874656|H, 4.018815931, 1.3354703255, -2.9074381416|H, 4.2766951374, -0
 .4051287235, -1.3556801571|H, 5.5056665337, -1.1690910307, 0.4258917969|H,
 5.3722879449, -0.2236985021, 1.9469157221|H, 6.6808038565, 0.1087796754, 0.
 8399750694|H, 4.0337537043, 2.8534767628, 0.547285021|H, 5.161942096, 2.259
 3202486, 1.8142006708|H, 5.7603271422, 2.74319157, 0.2279125422||Version=x
 86-Win32-G98RevA.11.2|HF=-978.2936844|RMSD=8.224e-009|RMSF=5.722e-006|
 Dipole=6.1308349, 1.1029936, 0.0168896|PG=C01 [X(C25H43)]||@

Compound 35a, reactant in Table 5, 17 β -side chain, C13 migration, $\beta\alpha\alpha$ configuration

1\1\GINC-DFTC\Fopt\RB3LYP\6-31G(d)\C25H43(1+)\BILLW\15-Aug-2003\0\\# B
 3LYP/6-31G(D) OPT=READFC GEOM=ALLCHECK GUESS=READ\E ring model hopene
 17bSC SM\1,1\C,-2.0572782743,0.7512719816,-0.9803897883\C,-0.5239295
 738,0.6361720207,-1.156362698\C,0.1162122704,0.6088824471,0.2215942777
 \C,-0.3781560392,-0.5612619137,1.1326583688\C,-1.9531302862,-0.3514930
 064,1.359996299\C,-2.6409069877,-0.3445867187,-0.0622537817\C,-0.04914
 68147,-1.9422665572,0.5099359546\C,1.7427084348,0.4527378357,0.3369442
 176\C,0.5404127136,-0.3880200921,2.3642586497\C,1.9471718975,-0.106651
 0055,1.7798537153\C,2.2636098047,1.7589189907,0.0060582409\C,2.3579546
 779,2.8486904995,1.0095108817\C,2.7329094818,2.0281761657,-1.356157163

8\C,-2.2158201095,0.9500439405,2.157298944\C,-4.2155262359,-0.42255016
 12,-0.0910741615\C,-2.5283063466,-1.5314780646,2.1912952222\C,-4.06307
 46406,-1.5255983251,2.2559308675\C,-4.6683783204,-1.5701018053,0.84930
 9204\C,-4.9505711404,0.8890618193,0.2659523649\C,-4.6633345565,-0.8100
 581022,-1.5214032076\C,4.3034530812,1.6769852128,-1.4765590334\C,4.656
 1866175,0.2327389875,-1.318728362\C,4.8473730843,-0.6630211376,-2.3086
 72695\C,5.2657217423,-2.0762890199,-1.9913938674\C,4.691065458,-0.3661
 286602,-3.7779149988\H,-2.5152109038,0.6946529372,-1.97199644\H,-2.293
 1512572,1.7498362808,-0.5930655543\H,-0.2745482024,-0.274714779,-1.714
 9231339\H,-0.1676898982,1.4846466404,-1.753742943\H,-0.1303945997,1.54
 22884755,0.7367125565\H,-2.3520384636,-1.2987196044,-0.5203950359\H,-0
 .6401269939,-2.1815124795,-0.3752764198\H,1.0025530028,-2.0177992385,0
 .217417611\H,-0.2188645858,-2.7363438691,1.241130758\H,2.0355820978,-0
 .263408197,-0.4364727383\H,0.2264082322,0.4633024856,2.9734318339\H,0.
 5469726695,-1.265685921,3.0171045282\H,2.5214783945,0.5727054174,2.415
 8587221\H,2.5420156903,-1.0209358597,1.6981038169\H,1.8347102662,2.634
 606142,1.942178785\H,3.4243485908,2.9977835545,1.250434214\H,2.0144928
 848,3.8015916223,0.5911651599\H,2.624235485,3.0833172879,-1.6227540838
 \H,2.2214630039,1.3970069085,-2.0875021351\H,-1.9244596892,1.864613931
 4,1.6329089993\H,-1.6988188912,0.936243807,3.1211321643\H,-3.273812221
 2,1.0566752834,2.3874797747\H,-2.2272215017,-2.4845369722,1.7427897885
 \H,-2.1040754052,-1.5118348615,3.2039738769\H,-4.4310935883,-0.6545456
 22,2.810592823\H,-4.3963738919,-2.402318423,2.8242515239\H,-5.76425601
 6,-1.5685295335,0.9084686624\H,-4.3899188684,-2.528290835,0.3856098507
 \H,-4.90162048,1.1471834325,1.3260204251\H,-4.5681118514,1.7426335258,
 -0.3045801995\H,-6.0127702131,0.7875168552,0.0153132039\H,-4.111668898
 7,-1.6807800801,-1.8970258374\H,-5.7276813958,-1.0707882788,-1.5191253
 357\H,-4.5367780406,0.0087118422,-2.2380046499\H,4.8360357203,2.292435
 7416,-0.7435722714\H,4.5708202474,2.0575034942,-2.4652589403\H,4.80495
 32008,-0.1104566159,-0.2948229031\H,5.3678127556,-2.2478935167,-0.9159
 652107\H,6.2279398311,-2.3082230095,-2.4662498404\H,4.5424156503,-2.79
 87764081,-2.3920845704\H,4.3573816422,0.6515557284,-3.9946912091\H,5.6
 431871432,-0.525302961,-4.3004221703\H,3.9725597217,-1.0604663164,-4.2
 322721575\\Version=x86-Linux-G98RevA.9\HF=-978.2924158\RMSD=6.696e-09\R
 RMSF=2.463e-06\PG=C01 [X(C25H43)] \\@

Compound 36a, product in Table 5, 17 β -side chain, C13 migration, $\beta\alpha\alpha$ configuration

1\1\GINC-LNX\FOpt\RB3LYP\6-31G(d)\C25H43(1+)\BILLW\20-Feb-2004\0\\# B3
 LYP/6-31G* OPT=READFC GEOM=ALLCHECK\\ERing 17b Hopen Prod\\1,1\C,-2.38
 00167917,1.0571650111,-0.8605642278\C,-0.9141037545,1.3100333489,-1.25
 8001062\C,0.0196580815,1.0377708527,-0.0689276555\C,-0.1412147046,-0.4
 333090365,0.4701221446\C,-1.6588961363,-0.577151504,1.0013876318\C,-2.
 6021916483,-0.3399160991,-0.24455476\C,0.1532749407,-1.5149464419,-0.6
 279311709\C,2.466092035,0.3218297135,-0.1400141655\C,0.8931946024,-0.6
 134925528,1.6164869045\C,2.3835698586,-0.4617860812,1.1616933302\C,1.5
 178035327,1.5500290466,-0.2393947744\C,1.7942136165,2.5978866625,0.862
 0546861\C,1.924930422,2.136923444,-1.6063951491\C,-1.9469297356,0.4217
 745652,2.1543573595\C,-4.1186300552,-0.7281950528,-0.0813292241\C,-1.8
 986626092,-1.998944318,1.5871891636\C,-3.3817938682,-2.3294487367,1.81
 33211594\C,-4.1953622087,-2.150426987,0.5298691795\C,-4.9630057971,0.2
 621566267,0.7505173342\C,-4.7691410622,-0.8052286756,-1.4832263712\C,3
 .473493349,2.0789873578,-1.6254117843\C,3.9101569345,1.0269962492,-0.5
 627097095\C,4.6984103259,-0.1090483838,-0.9350342111\C,5.6325231556,-0

.7073738184, 0.0486584151\c, 4.606080237, -0.7480025448, -2.2687568901\h, -3.0019483897, 1.1737342579, -1.7536041779\h, -2.6998261386, 1.8438851642, -0.1667660146\h, -0.6572262888, 0.6838655722, -2.122449017\h, -0.8063829012, 2.3497300734, -1.5910125578\h, -0.3578976152, 1.6663714791, 0.7413100624\h, -2.2570220234, -1.0527922077, -1.0054317188\h, 0.3477060923, -1.0809131857, -1.6132709558\h, 1.0158858033, -2.1374136695, -0.3652834242\h, -0.6747215183, -2.209014809, -0.7715372852\h, 2.2178796387, -0.3325024302, -0.9757535276\h, 0.705635612, 0.1265369291, 2.3977058313\h, 0.7781438325, -1.5944607264, 2.0863987637\h, 2.9459490775, 0.0416074035, 1.9578399062\h, 2.8400254996, -1.4499685879, 1.0353892438\h, 2.7975796833, 3.0347592993, 0.8113084274\h, 1.6583226735, 2.1855035708, 1.8664760812\h, 1.0853295675, 3.4256082439, 0.7532503929\h, 1.5158899351, 1.5309153697, -2.4212850136\h, 1.5641411646, 3.1587263818, -1.7545623963\h, -2.0327377731, 1.4639102552, 1.8384004142\h, -2.885690822, 0.1741630373, 2.6491522724\h, -1.1783720806, 0.3734855502, 2.9314057787\h, -1.3570665403, -2.0996278181, 2.5366121887\h, -1.489290247, -2.7674258003, 0.9207232203\h, -3.4647705255, -3.3665353377, 2.1610245295\h, -3.7995118457, -1.7136122566, 2.6187290749\h, -3.8303906644, -2.8709059011, -0.2180753488\h, -5.2472321972, -2.4067567281, 0.7106528451\h, -4.7025489716, 0.278387846, 1.8107513247\h, -6.0209755126, -0.0178418145, 0.6856255069\h, -4.8792822456, 1.2864174749, 0.3711411245\h, -4.1778796895, -1.4232181864, -2.1706013628\h, -4.9000418855, 0.1812965142, -1.9399835352\h, -5.7648665207, -1.2573339231, -1.4080741686\h, 3.8616561408, 1.8505335326, -2.6215779768\h, 3.9201561618, 3.0350910249, -1.3377699674\h, 4.2908673889, 1.4819202933, 0.3547738708\h, 5.3223845681, -0.5234312553, 1.0815184583\h, 5.82079341, -1.7705831468, -0.1208701267\h, 6.5958654198, -0.1815477742, -0.0784865194\h, 3.8523313046, -0.3109439006, -2.9233163142\h, 4.43810921, -1.8277312634, -2.1639063976\h, 5.5903138947, -0.6575844237, -2.7570084279\\Version=x86-Linux-G98RevA.9\HF=-978.2829942\RMSD=4.326e-09\RMSF=3.057e-06\PG=C01 [X(C25H43)]\\@

Compound 35b, reactant in Table 5, 17 β -side chain, C13 migration, $\beta\alpha\beta$ configuration

1\1\GINC-APSARA\FOpt\RB3LYP\6-31G(d)\C25H43(1+)\BILLW\21-Feb-2004\0\\#
 B3LYP/6-31G* OPT\ERing17bHopenUP-SM\\1,1\c, -2.1551961652, 0.7984998058, -1.125560504\c, -0.6921095742, 0.3997898736, -1.4366941576\c, 0.1370185281, 0.5753793609, -0.1750490175\c, -0.3754586667, -0.263705036, 1.0409172005\c, -1.8524206622, 0.2587232149, 1.3864996928\c, -2.73920575, 0.0558328121, 0.0951161844\c, -0.3388954507, -1.783056552, 0.7331240672\c, 1.7265737332, 0.1779232682, -0.2049658278\c, 0.7316724654, 0.0101032484, 2.085475837\c, 2.0616415214, -0.0802284581, 1.2961967727\c, 2.3676960312, 1.2729107469, -0.8956622467\c, 2.8245537338, 2.4887167134, -0.1748364325\c, 2.6109448786, 1.1801585693, -2.3387013305\c, -1.8086787381, 1.735584784, 1.8523672516\c, -4.2960283814, 0.2386508814, 0.2638854868\c, -2.452378395, -0.5801547355, 2.5486274148\c, -3.9459249108, -0.3058805997, 2.7779069154\c, -4.7529081168, -0.5737258613, 1.5040742023\c, -4.7855551928, 1.7004695456, 0.369244275\c, -5.0018174429, -0.3815744522, -0.9662821313\c, 4.0307974149, 0.4647440012, -2.598269282\c, 4.0092886427, -1.0204898766, -2.4418233282\c, 4.7336049589, -1.7752115047, -1.5915447799\c, 4.6459559647, -3.2800462051, -1.6455558066\c, 5.6960589152, -1.2387237893, -0.5629050202\h, -2.756438377, 0.5889211679, -2.014749652\h, -2.1995413403, 1.8844407357, -0.9784627012\h, -0.6492336064, -0.6399467235, -1.7840056683\h, -0.3230954204, 1.026265706, -2.2580307785\h, 0.099700387, 1.6277173425, 0.1222410132\h, -2.6559646131, -1.0128442999, -0.1382339684\h, -1.0657547289, -2.1027542286, -0.0145975997\h, 0.6444360043, -2.1019898437, 0.3742166992\h, -0.5305207858, -2.3567859689, 1.642

8886399\H, 1.8026121139, -0.728423394, -0.8129655694\H, 0.6337480259, 1.010
 8337426, 2.5137113091\H, 0.7113237842, -0.6980917232, 2.9187388068\H, 2.808
 1344291, 0.6174899595, 1.6849202543\H, 2.5093693499, -1.0752757371, 1.36998
 0886\H, 2.2677363028, 2.6676332685, 0.7483522627\H, 3.874394048, 2.32823870
 64, 0.1242108487\H, 2.8087276869, 3.3783914686, -0.8096841377\H, 2.64878037
 02, 2.1670410663, -2.8064366266\H, 1.8603382768, 0.5590697498, -2.836178086
 1\H, -1.5088722464, 2.4427610836, 1.0737591055\H, -1.1333859616, 1.86573790
 02, 2.7028685203\H, -2.787776936, 2.0629320912, 2.1960381848\H, -2.35024894
 41, -1.6483412593, 2.3281565439\H, -1.8846769186, -0.3935023294, 3.46978876
 97\H, -4.108900562, 0.7181017971, 3.1333644991\H, -4.3052250978, -0.9593632
 915, 3.5820276567\H, -5.8179360848, -0.3795541991, 1.6837227273\H, -4.67459
 43804, -1.6447774415, 1.2648722551\H, -4.5216161327, 2.1860140385, 1.311118
 9386\H, -4.4027874564, 2.32274611, -0.4471688101\H, -5.8791507635, 1.720471
 3502, 0.2999424988\H, -4.6431882178, -1.3980908298, -1.1701096352\H, -6.080
 4880565, -0.4440299617, -0.7840267006\H, -4.8660751698, 0.2158292638, -1.87
 43040869\H, 4.7981937337, 0.9529330866, -1.9934455542\H, 4.2402194368, 0.72
 45754402, -3.6428279512\H, 3.3638606142, -1.5387292319, -3.151951711\H, 3.9
 273257726, -3.6266277438, -2.3933819528\H, 4.3586857173, -3.6932286272, -0.
 6695756857\H, 5.6246483361, -3.7144694576, -1.8875079659\H, 5.7321540218, -
 0.1477111413, -0.5116287537\H, 5.442387465, -1.6191104904, 0.4352114139\H,
 6.7133198765, -1.5926356842, -0.7743708537\Version=x86-Linux-G98RevA.9\
 HF=-978.2922309\RMSD=7.780e-09\RMSF=4.776e-05\PG=C01 [X(C25H43)]\@\n

Compound 36b, product in Table 5, 17 β -side chain, C13 migration, $\beta\alpha\beta$ configuration

1\1\GINC-DFTB\FOpt\RB3LYP\6-31G(d)\C25H43(1+)\BILLW\10-Dec-2003\0\\# B
 3LYP/6-31G* OPT=READFC GEOM=ALLCHECK GUESS=READ\ERing17bHopUP-Prod\1
 ,1\C,-2.066297367,0.513421252,-1.7869181023\C,-0.5345109671,0.63369667
 7,-1.904699363\C,0.1011741072,0.7574655851,-0.5125434738\C,-0.27205578
 53,-0.4687620377,0.405542916\C,-1.8732380561,-0.4279460523,0.607858901
 \C,-2.5132573386,-0.608440637,-0.8258523739\C,0.1599030101,-1.8456650
 563,-0.211112008\C,2.4190412096,0.0571695081,0.1685497092\C,0.48783538
 77,-0.2898906105,1.7500686699\C,2.0525209966,-0.2531925516,1.611561964
 7\C,1.6412384387,1.2021638679,-0.4852860913\C,1.7220236021,2.531503108
 5,0.2970423302\C,2.3523255769,1.3660849808,-1.8452819621\C,-2.32032376
 71,0.8950089547,1.2869459688\C,-4.0546930265,-0.9198234166,-0.88649885
 21\C,-2.3338610041,-1.5784764191,1.5489284473\C,-3.8508792178,-1.81962
 54094,1.5307340473\C,-4.3605298809,-2.0671407002,0.1094121768\C,-4.976
 6866877,0.289272376,-0.614697095\C,-4.4046533931,-1.4445424414,-2.2994
 147356\C,3.8606855162,1.3652645443,-1.5099947556\C,4.0688889182,0.3106
 346837,-0.4087236753\C,4.814229742,0.5272206072,0.7834271421\C,5.36925
 12849,-0.6463470903,1.5081548787\C,5.0622755175,1.8495742067,1.4087497
 902\H,-2.4732002504,0.3308480618,-2.7863661427\H,-2.4728864426,1.48079
 83547,-1.4690487673\H,-0.139612235,-0.2309544354,-2.4533219291\H,-0.29
 15682513,1.5156212568,-2.5099275299\H,-0.3967104991,1.6104836469,-0.04
 57142964\H,-2.068964345,-1.5304029773,-1.2247230086\H,0.5444983811,-1.
 7569627096,-1.2315833867\H,0.9325242152,-2.336824865,0.3907896465\H,-0
 .6607215142,-2.5608101131,-0.2685766739\H,2.264804666,-0.8458057505,-0
 .4166198375\H,0.1783969634,0.6426817003,2.2269504388\H,0.2281658522,-1
 .0936307307,2.4446999445\H,2.4398060264,0.4974938592,2.3099679557\H,2.
 4810107499,-1.2162146966,1.9082036072\H,2.7366763809,2.9319001737,0.37
 22986743\H,1.3225724289,2.437447047,1.3110374692\H,1.1208135466,3.2882
 993683,-0.2178266676\H,2.1203076519,0.5232226811,-2.5056145262\H,2.064
 1589624,2.2793758168,-2.3734108899\H,-2.2878521224,1.7695691719,0.6336

932435\H,-3.3481180318,0.8152407945,1.6404759419\H,-1.7174865076,1.119
 5912345,2.1718706333\H,-2.0141118865,-1.3598455836,2.5762129019\H,-1.8
 489190692,-2.522345302,1.2737047451\H,-4.0788550678,-2.6879608211,2.16
 10506396\H,-4.385095294,-0.9765442665,1.9852447361\H,-3.8996159224,-2.
 9911322306,-0.2717314131\H,-5.4425583387,-2.2508195934,0.12339892\H,-4
 .9283126935,0.6562438018,0.4126960266\H,-6.0178253008,0.0027319997,-0.
 8040413248\H,-4.7508566143,1.1306358478,-1.2790156554\H,-3.7304849628,
 -2.252887259,-2.6091733528\H,-4.3655136596,-0.6586888562,-3.0609995715
 \H,-5.4247285973,-1.8457150356,-2.3060806757\H,4.4766515681,1.10874454
 11,-2.3774964751\H,4.1816557412,2.3556742884,-1.1788643877\H,4.3003315
 666,-0.6753850012,-0.8164914765\H,4.9444383603,-1.5967613001,1.1796002
 669\H,6.4504284539,-0.672498796,1.2896171318\H,5.2828759129,-0.5389698
 976,2.5951610184\H,4.9189823905,2.6986355207,0.7418672476\H,6.07225948
 01,1.8752216728,1.8354201938\H,4.3801974093,1.9613523642,2.2669398801\
 \Version=x86-Linux-G98RevA.9\HF=-978.2739088\RMSD=5.083e-09\RMSF=4.885
 e-06\PG=C01 [X(C25H43)]\\@

TABLE 5: ENTRIES WITH C16 MIGRATION

Compound **33a**, reactant in Table 5, 17 α -side chain, C16 migration, $\alpha\beta\alpha$ configuration

1|1|UNPC-UNK|FOpt|RB3LYP|6-31G(d)|C25H43(1+)|PCUSER|25-Mar-2004|0||# B
 3LYP/6-31G(D) OPT FREQ GEOM=CHECK GUESS=READ||ERing17aLupSM-REDO C25H4
 3(1+) frozen torsion||1,1|C,1.2733937189,1.3133973113,1.0303899741|C,-
 0.0371250742,0.5435799836,1.2998164429|C,-0.3975955616,-0.2449103815,0
 .0384995765|C,0.711333269,-1.2475544908,-0.3996448408|C,2.0435699754,-
 0.430816533,-0.7338572728|C,2.4232183135,0.3901496257,0.565051394|C,0.
 9549722534,-2.3452357267,0.6684746212|C,-1.777666711,-0.9493806208,-0.
 1732567524|C,0.0027241172,-1.9427660653,-1.5935144215|C,-1.4360018866,
 -2.2246856942,-1.1189264185|C,-2.6635755705,-1.4124611364,0.8879909792
 |C,-2.2472522777,-1.6030992136,2.2955298089|C,-4.0713262102,-1.6431545
 191,0.5463598368|C,1.820900091,0.4727023417,-1.9730360257|C,3.83743434
 85,1.0885249929,0.580992148|C,3.2166129918,-1.3898233402,-1.0716719752
 |C,4.5691917906,-0.671993457,-1.1832221726|C,4.9036089472,0.0599767935
 ,0.1203044973|C,3.9460651245,2.3844585347,-0.2536868261|C,4.1834630244
 ,1.4694233879,2.0414394527|C,-4.8763403303,-0.2463556647,0.664925974|C
 ,-4.7440013292,0.6239124525,-0.5385054268|C,-4.2803096369,1.8913909026
 ,-0.601707639|C,-4.3232605838,2.6527302597,-1.9022621558|C,-3.73730449
 44,2.6707014215,0.5676796704|H,1.5631478101,1.8348258747,1.9472392697|
 H,1.0789682966,2.0942182233,0.2844084547|H,0.1055687191,-0.1102526727,
 2.1681324372|H,-0.8328456133,1.2555454343,1.5610843847|H,-0.431774426,
 0.5115027866,-0.7533693875|H,2.5308231845,-0.368485861,1.3520051812|H,
 1.4011002827,-1.9691330001,1.5910861038|H,0.0259488791,-2.8534594725,0
 .9443103604|H,1.6155020691,-3.1244915224,0.2806163884|H,-2.4204851911,
 -0.3194262936,-0.8125481163|H,-0.0424123113,-1.2831847922,-2.463636196
 7|H,0.4915583566,-2.8721846558,-1.9034315356|H,-2.1616409113,-2.283610
 5096,-1.9329359754|H,-1.4951408045,-3.1608129868,-0.5580001767|H,-1.28
 93613441,-2.1304321987,2.3538132769|H,-2.0465687148,-0.6157182712,2.74
 03025347|H,-3.0000641848,-2.1159465764,2.8963394129|H,-4.5376967726,-2
 .3527699063,1.2328953277|H,-4.1992376331,-1.9830149176,-0.4851699945|H
 ,1.0332966292,1.2212519021,-1.8485626633|H,1.5762962874,-0.1251293835,
 -2.856600072|H,2.7249201549,1.0231467092,-2.2240157291|H,3.3214727396,
 -2.1469202591,-0.2864428656|H,2.9954662057,-1.9319213633,-2.0012032826
 |H,4.5794357237,0.0208508709,-2.0328277278|H,5.3498401473,-1.412663708
 8,-1.394811996|H,5.8726898333,0.5677322615,0.0323140962|H,5.0255754249

, -0.6919227217, 0.9144548497 | H, 3.9600108415, 2.2122097343, -1.332045343 | H
, 3.1303952051, 3.0830806687, -0.0365670386 | H, 4.8821996537, 2.8977583001, -
0.0050726827 | H, 4.0331962822, 0.6259277302, 2.7268067266 | H, 5.2367304147, 1
.7647684345, 2.1091046211 | H, 3.5917865013, 2.3153551792, 2.4076550691 | H, -4
.6114822, 0.2561373527, 1.5979374802 | H, -5.9148709012, -0.581219358, 0.7703
792382 | H, -5.1328846993, 0.1839381141, -1.45755916 | H, -4.7172306402, 2.0491
436998, -2.724473345 | H, -3.3234533711, 3.0111181237, -2.1805924646 | H, -4.95
363329, 3.5459863912, -1.8025989357 | H, -3.653311242, 2.0911999848, 1.490313
2424 | H, -2.7477336335, 3.0809147433, 0.3284959331 | H, -4.3824715512, 3.53382
09263, 0.777795607 || Version=x86-Win32-G98RevA.11.2 | HF=-978.280897 | RMSD=
6.066e-009 | RMSF=1.618e-004 | PG=C01 [X(C25H43)] || @

Compound 34a, product in Table 5, 17 α -side chain, C16 migration, $\alpha\beta\alpha$ configuration

1 | 1 | UNPC-UNK | FOpt | RB3LYP | 6-31G(d) | C25H43(1+) | PCUSER | 20-Nov-2003 | 0 || # B
3LYP/6-31G(D) OPT=READFC GEOM=ALLCHECK GUESS=READ || 17a lupeol prod C25
H43 || 1,1 | C, -1.9197609765, 0.5986409656, -0.6716864365 | C, -0.5523643976, 0.
2760085005, -1.3154476166 | C, 0.5104461471, 0.3325622131, -0.2237031025 | C, 0.
2353400006, -0.8112992094, 0.8470528018 | C, -1.0810939257, -0.3221595609, 1
.6347542522 | C, -2.2571977431, -0.2643127702, 0.5763075325 | C, -0.0034234804
,-2.2155802268, 0.2279334859 | C, 2.0114909736, 0.4602977272, -0.5190582988 |
C, 1.522278102, -0.9576623409, 1.7057915793 | C, 2.7681620532, -1.4199889245,
0.8841352671 | C, 2.9302366628, -0.7741794655, -0.5497620018 | C, 2.7037259556
,-1.7916000773, -1.6985685083 | C, 4.297256347, -0.0913788055, -0.7811514025
| C, -0.8221545075, 1.0477962839, 2.3264174325 | C, -3.6983132749, 0.013426972
6, 1.1489951296 | C, -1.4791066593, -1.3329126275, 2.7480740008 | C, -2.8604008
124, -1.0522377649, 3.3607744677 | C, -3.9532213577, -1.0072916246, 2.2893141
409 | C, -3.9484549982, 1.4531821108, 1.6480953777 | C, -4.7458479119, -0.27239
90722, 0.046821062 | C, 4.0356151636, 0.9339801748, -1.9053865813 | C, 2.596283
7637, 1.5259198732, -1.6626790723 | C, 1.7720727806, 1.7353726338, -2.8364944
125 | C, 1.0795297073, 3.0409640337, -2.9894444717 | C, 1.7211113837, 0.7967528
615, -3.9812804518 | H, -2.7072083116, 0.4724464699, -1.4203078775 | H, -1.9220
584186, 1.6627731007, -0.4017619194 | H, -0.5727887723, -0.6834304364, -1.843
7626141 | H, -0.3442666912, 1.0423628031, -2.0841289122 | H, 0.2964728151, 1.27
03441833, 0.2966594843 | H, -2.3550821938, -1.2914473452, 0.2081137364 | H, -0.
1359646512, -2.9466032873, 1.0298126673 | H, -0.8785483667, -2.2877399709, -0
.4169108145 | H, 0.8437682791, -2.5647744438, -0.3545992925 | H, 2.3925520243,
1.01077055, 0.3467105815 | H, 1.7599457146, -0.0160407776, 2.2123167684 | H, 1.
3585696576, -1.6903778995, 2.5031210558 | H, 3.6606254768, -1.1878001223, 1.4
76788684 | H, 2.7554356162, -2.5082075293, 0.7800262442 | H, 3.277698931, -1.52
72020875, -2.5926397794 | H, 1.6591856514, -1.8925272608, -2.0000826129 | H, 3.
055143523, -2.7841306563, -1.3986000312 | H, 4.6250042154, 0.425481713, 0.128
4656926 | H, 5.0896853761, -0.793578146, -1.0601391438 | H, -1.0287076484, 1.91
10106419, 1.6878668241 | H, -1.4479932738, 1.1663629027, 3.2114634742 | H, 0.21
02292624, 1.1362402806, 2.6772324711 | H, -0.717273216, -1.3304876088, 3.5383
19612 | H, -1.5059201264, -2.3496189748, 2.342151292 | H, -3.0914663254, -1.843
1638425, 4.0847512861 | H, -2.8530826217, -0.1193995727, 3.9370068955 | H, -4.0
444265201, -2.0082191107, 1.8417044551 | H, -4.925010181, -0.7904466879, 2.75
13463459 | H, -3.3829208554, 1.7085920989, 2.5458965756 | H, -5.0105455252, 1.5
725723804, 1.8919527269 | H, -3.7128566436, 2.1990019663, 0.8800729832 | H, -4.
5709784128, -1.2408159687, -0.4385600346 | H, -4.7608640827, 0.5006721811, -0
.7291184554 | H, -5.7493637716, -0.3023065104, 0.4863969105 | H, 4.7602040072,
1.7537277723, -1.9125528884 | H, 4.092015296, 0.4539608874, -2.885251352 | H, 2
.6564743096, 2.4787479481, -1.1299167645 | H, 1.8327784186, 3.7395405889, -3.

3987241947|H,0.2434978929,3.0164534394,-3.6912323817|H,0.7722518517,3.
 4639307174,-2.0282008607|H,0.7469979883,0.813294447,-4.4772320371|H,2.
 0082193253,-0.2220694577,-3.7271317142|H,2.4473170037,1.1706893441,-4.
 7261481256||Version=x86-Win32-G98RevA.11.2|HF=-978.2624534|RMSD=9.464e
 -009|RMSF=3.451e-006|PG=C01 [X(C25H43)]||@

Compound 33b, reactant in Table 5, 17 α -side chain, C16 migration, $\alpha\beta\beta$ configuration

1|1|UNPC-UNK|FOpt|RB3LYP|6-31G(d)|C25H43(1+)|PCUSER|30-Aug-2003|0||# B
 3LYP/6-31G(D) OPT||ERing17aLupUP-SMC||1,1|C,1.4339259868,1.594613616,0
 .8374754841|C,0.0835635477,0.9353719615,1.189628709|C,-0.2361193762,-0
 .1013418585,0.1104455293|C,0.8546282297,-1.2042629707,-0.0369512231|C,
 2.2367345387,-0.5145702432,-0.4474829671|C,2.5689321213,0.5586900867,0
 .6673854071|C,0.9941020767,-2.0592255818,1.2487976289|C,-1.6304030826,
 -0.7970109006,-0.0254637138|C,0.1827561014,-2.1116265835,-1.1022836268
 |C,-1.2885563802,-2.250594801,-0.6626023402|C,-2.5796060501,-1.0097201
 37,1.0629173745|C,-2.2396560605,-0.9202498647,2.4999563619|C,-3.979166
 6717,-1.2388478886,0.704141017|C,2.1251481568,0.1047600267,-1.86304251
 06|C,4.0099403585,1.1992818703,0.6370960901|C,3.3877690061,-1.55488802
 26,-0.4904687755|C,4.7712046085,-0.913570175,-0.6677337426|C,5.0580068
 733,0.0671650068,0.4737468578|C,4.2292090814,2.2882722284,-0.438615465
 4|C,4.2810012635,1.8667492497,2.0076978248|C,-4.7810271344,0.171002174
 2,0.7412757657|C,-4.3771187326,1.1575849013,-0.3039683265|C,-4.9482514
 185,1.3251129388,-1.5164850386|C,-4.4719386483,2.4159616486,-2.4406966
 28|C,-6.0870126993,0.4952489595,-2.0497197775|H,1.6921908792,2.3032084
 602,1.6296790081|H,1.3108769222,2.1897322557,-0.0760522716|H,0.1573518
 481,0.483292445,2.1857529016|H,-0.6993299491,1.7053217117,1.242479179|
 H,-0.2019155135,0.4648090137,-0.8272276312|H,2.5874497989,-0.012901664
 ,1.6051345322|H,1.4115703839,-1.5124044113,2.0968170656|H,0.0307046852
 ,-2.4653187546,1.5702528072|H,1.6361613029,-2.9254152952,1.0711228325|
 H,-2.2181440372,-0.2920696811,-0.8093396272|H,0.2085279373,-1.64417912
 14,-2.0900746083|H,0.6493086402,-3.0986305475,-1.1875712593|H,-1.97534
 03952,-2.4619160618,-1.484836337|H,-1.4087336369,-3.0456891103,0.07788
 39805|H,-1.301921514,-1.4365813248,2.7265450339|H,-2.0401903463,0.1377
 365108,2.7357568078|H,-3.0393591324,-1.2810080082,3.149311931|H,-4.474
 8537351,-1.890089922,1.4295043871|H,-4.0930551581,-1.6337696603,-0.307
 5450359|H,1.334120839,0.8531180058,-1.9650862174|H,1.9513484785,-0.670
 1028011,-2.6164152811|H,3.0503699581,0.6014180376,-2.1462762923|H,3.41
 67258025,-2.1199803451,0.4477572043|H,3.1985410635,-2.2834692823,-1.29
 05038442|H,4.8546445433,-0.4165241867,-1.6414740965|H,5.5332960567,-1.
 7022646784,-0.669997706|H,6.0506274568,0.5181825944,0.3478242228|H,5.0
 998762912,-0.5047306318,1.4129405044|H,4.3185546229,1.89107665,-1.4523
 473244|H,3.4268024642,3.0342020991,-0.440550817|H,5.1629180162,2.82181
 73688,-0.2272190746|H,4.0558905193,1.1892777671,2.8407905078|H,5.33930
 88052,2.1407254236,2.0848007991|H,3.7028642146,2.7860645463,2.15055845
 81|H,-4.6716240396,0.590826346,1.7459689387|H,-5.8231443349,-0.1384139
 652,0.6332915547|H,-3.5619302381,1.8296756012,-0.0363018838|H,-3.63855
 67072,2.9840800319,-2.0178610403|H,-5.2879561578,3.1173569634,-2.65813
 92922|H,-4.1566950016,2.0011083211,-3.4070662751|H,-6.416990792,-0.297
 8850494,-1.3744152779|H,-6.9527794587,1.1350225806,-2.2639410679|H,-5.
 8059055571,0.031857921,-3.0042298834||Version=x86-Win32-G98RevA.11.2|H
 F=-978.2808556|RMSD=6.095e-009|RMSF=6.993e-006|PG=C01 [X(C25H43)]||@

Compound 34b, product in Table 5, 17 α -side chain, C16 migration, $\alpha\beta\beta$ configuration

1|1|UNPC-UNK|FOpt|RB3LYP|6-31G(d)|C25H43(1+)|PCUSER|15-Nov-2003|0||# B

3LYP/6-31G(D) OPT=READFC GEOM=ALLCHECK GUESS=READ || 17a lupeol UP prod
 | 1,1|C,-1.6631462574,0.0421949913,-1.4820521312|C,-0.1296573874,-0.124
 9862387,-1.6077700564|C,0.4925170126,0.192789287,-0.24492534|C,-0.0085
 799614,-0.826556133,0.8509340717|C,-1.5614565131,-0.4622024059,1.08421
 90974|C,-2.3040342548,-0.7184931137,-0.2914334251|C,0.1294962809,-2.31
 85352593,0.441234477|C,2.0036745162,0.5272991039,-0.0948814143|C,0.906
 3117712,-0.6481039005,2.0963721402|C,2.3950121368,-1.0344981928,1.8390
 539354|C,2.9798119904,-0.5338798475,0.476209202|C,3.320829104,-1.68288
 53454,-0.5091586412|C,4.2478833781,0.3439064207,0.6045270756|C,-1.7071
 999278,1.0056005523,1.5817474097|C,-3.876476574,-0.6215957298,-0.26474
 96865|C,-2.2015925763,-1.3744965436,2.1672195773|C,-3.7310611888,-1.24
 84777077,2.2468162221|C,-4.3875695135,-1.5214243304,0.891188806|C,-4.4
 494574836,0.8057005645,-0.1272765494|C,-4.4433791814,-1.2127943444,-1.
 5772362054|C,4.3119664362,1.2177944295,-0.6819147748|C,2.7746454259,1.
 1113157647,-1.2911755672|C,2.5863617579,2.4624144633,-1.7493683404|C,2
 .9322606828,2.8314576576,-3.1415129301|C,2.0666169963,3.5334258776,-0.
 8679631941|H,-2.1307960474,-0.2849082548,-2.4155202722|H,-1.8785097489
 ,1.116052863,-1.3980849072|H,0.1305635494,-1.1292755977,-1.9616558423|
 H,0.2327153385,0.57288825,-2.3797073416|H,0.0272883607,1.1446584049,0.
 0290665077|H,-2.147901295,-1.7827421627,-0.4991436198|H,-0.2072391915,
 -2.9583107525,1.2610401411|H,-0.4432711992,-2.600667188,-0.4416644653|
 H,1.1595005036,-2.6038064307,0.2479536481|H,2.022920328,1.3077200941,0
 .6773322031|H,0.8689497158,0.3870796527,2.4542734744|H,0.541167251,-1.
 26267352,2.926019167|H,2.9921943653,-0.6290121437,2.665189799|H,2.5083
 090469,-2.1203273735,1.903924948|H,4.0471250875,-1.3712220742,-1.26879
 65201|H,2.4525926113,-2.0714809517,-1.0437067581|H,3.7800693403,-2.516
 1339276,0.0329439926|H,4.1830494431,0.9910696891,1.4849797882|H,5.1713
 294515,-0.2403735475,0.6895561391|H,-1.7478762555,1.7440758395,0.77601
 62337|H,-2.6236762215,1.1345393499,2.1581681028|H,-0.8892747792,1.2889
 131303,2.2512931923|H,-1.7616289655,-1.149367241,3.1474980769|H,-1.975
 8602075,-2.4253624688,1.9579428516|H,-4.106635296,-1.9663711104,2.9863
 009042|H,-4.0262815488,-0.2605689129,2.6204284929|H,-4.202045564,-2.57
 13864257,0.6191600535|H,-5.4772715412,-1.4160698528,0.9720548907|H,-4.
 2536120832,1.2620728006,0.8447865671|H,-5.5379060083,0.7738565688,-0.2
 544083109|H,-4.0582792124,1.4783703479,-0.8992710848|H,-3.9988301566,-
 2.1891652909,-1.8069769062|H,-4.2839677365,-0.5554389964,-2.438872156|
 H,-5.5256943896,-1.3585692506,-1.4832845005|H,4.6195415349,2.243224376
 9,-0.4561258247|H,4.979446474,0.8389295226,-1.4574216253|H,2.826882198
 ,0.4211758486,-2.1352272587|H,2.0352455275,3.2548370023,-3.6217061331|
 H,3.6656672151,3.6500331524,-3.1451144528|H,3.295988753,1.9940256878,-
 3.7386259416|H,2.3740494892,4.5330146164,-1.1844614239|H,2.292991321,3
 .3702355273,0.18829915|H,0.9663105251,3.4866406306,-0.9530755293||Vers
 ion=x86-Win32-G98RevA.11.2|HF=-978.2708329|RMSD=3.840e-009|RMSF=3.233e
 -006|PG=C01 [X(C25H43)]||@

Compound 29a, reactant in Table 5, 17 β -side chain, C16 migration, $\beta\alpha\alpha$ configuration
 (This model corresponds to an intermediate leading to lupeol)

1|1|UNPC-UNK|FOpt|RB3LYP|6-31G(d)|C25H43(1+)|PCUSER|12-Aug-2003|0||# B
 3LYP/6-31G(D) OPT=READFC GEOM=ALLCHECK GUESS=READ||E ring model 17bSC
 lupeol cat SM||1,1|C,-1.4741154204,1.6342087551,0.2591107268|C,-0.2473
 945052,1.0986894619,-0.5070944859|C,0.5460459016,0.1682155833,0.409532
 372|C,-0.2956950224,-1.0208743026,0.9665351925|C,-1.5109940503,-0.4404
 215897,1.8217138185|C,-2.3428198425,0.5073427642,0.8641859187|C,-0.771

7941793, -1.9615187193, -0.1734875734 | C, 1.8216843415, -0.4855440022, -0.15
 58636302 | C, 0.8080969696, -1.7859809405, 1.7401866713 | C, 2.0697655903, -1.7
 588525571, 0.839923048 | C, 3.0984922832, 0.2086637557, -0.1121136802 | C, 3.36
 55519603, 1.2909031875, 0.866858642 | C, 4.1376405792, -0.1433117325, -1.0765
 253262 | C, -0.9796333042, 0.299879929, 3.0746588544 | C, -3.741963319, 1.00533
 79444, 1.3958598906 | C, -2.4355430979, -1.5852602809, 2.3155800957 | C, -3.740
 3704032, -1.079269667, 2.9461943497 | C, -4.5230943061, -0.2131591675, 1.9539
 888039 | C, -3.687224489, 2.1354045366, 2.4486977942 | C, -4.5580640051, 1.5514
 433481, 0.1987029755 | C, 4.0481727772, 0.859992698, -2.3475488014 | C, 2.84848
 82447, 0.6718809129, -3.2172656172 | C, 2.7733191891, -0.095102359, -4.324865
 1474 | C, 1.5069805635, -0.1369789567, -5.1411264512 | C, 3.8978367525, -0.9435
 498143, -4.8601688305 | H, -2.0741915903, 2.2393459633, -0.4264959557 | H, -1.1
 27968814, 2.3183462282, 1.0440735626 | H, -0.5670282165, 0.5640059976, -1.411
 4110975 | H, 0.3718346059, 1.9414301534, -0.8466718213 | H, 0.8509750284, 0.759
 4836901, 1.280280439 | H, -2.6285230741, -0.1315932542, 0.0185164767 | H, -1.53
 15518972, -1.5176663724, -0.8187598973 | H, 0.0534331285, -2.2663014611, -0.8
 257403157 | H, -1.1890568863, -2.8833548156, 0.238968363 | H, 1.6751064772, -0.
 8927129437, -1.1617082988 | H, 1.0403538115, -1.299658638, 2.6898249601 | H, 0.
 5408091835, -2.824714796, 1.9636930361 | H, 2.984973018, -1.6719687132, 1.434
 4459583 | H, 2.1838217196, -2.6413413667, 0.2073465037 | H, 3.0110190174, 1.018
 9683599, 1.8680324982 | H, 4.4176994359, 1.5770532443, 0.9108096068 | H, 2.7685
 52658, 2.1721516016, 0.5815133633 | H, 4.012461894, -1.1545921256, -1.4700135
 015 | H, 5.1372908479, -0.0154056897, -0.6518082098 | H, -0.3532908771, 1.16763
 43182, 2.8480660235 | H, -0.4027078098, -0.3721061611, 3.7178221314 | H, -1.798
 5105855, 0.6701645672, 3.687735387 | H, -2.7141590961, -2.2280384126, 1.47303
 74538 | H, -1.890091464, -2.220482074, 3.0270393695 | H, -3.5427116501, -0.5272
 033915, 3.8726008323 | H, -4.3528246755, -1.9405220466, 3.239240795 | H, -5.454
 0756836, 0.142263863, 2.4138470514 | H, -4.8247792223, -0.8481548161, 1.10761
 06845 | H, -3.3448264312, 1.8048706851, 3.431880038 | H, -3.0434244739, 2.96287
 37158, 2.1306224813 | H, -4.6930554211, 2.5482122477, 2.5887297092 | H, -4.5644
 845368, 0.8469133645, -0.6423370303 | H, -5.5990651002, 1.7131330115, 0.50081
 97405 | H, -4.178819165, 2.5125065269, -0.1652159845 | H, 4.9793963743, 0.65884
 41573, -2.8822817487 | H, 4.1106684437, 1.8860144243, -1.9717369485 | H, 1.9618
 188485, 1.2390201718, -2.9354288456 | H, 0.7174313851, 0.4889055135, -4.71552
 87419 | H, 1.1292610131, -1.1645150373, -5.2253361384 | H, 1.6991472314, 0.2057
 926332, -6.1661378461 | H, 4.8035837557, -0.9250708841, -4.2489065762 | H, 3.57
 49471834, -1.9885207766, -4.9529997103 | H, 4.1703463609, -0.6168433871, -5.8
 720554573 || Version=x86-Win32-G98RevA.11.2 | HF=-978.2896322 | RMSD=6.527e-
 009 | RMSF=2.654e-006 | PG=C01 [X(C25H43)] || @

**Compound 30a, product in Table 5, 17 β -side chain, C16 migration, $\beta\alpha\alpha$ configuration
(This model corresponds to an intermediate leading to lupeol)**

```

1|1|UNPC-UNK|FOpt|RB3LYP|6-31G(d)|C25H43(1+)|PCUSER|14-Aug-2003|0||# B
3LYP/6-31G* OPT=READFC GEOM=ALICHECK GUESS=READ||E ring mod 17b lupeol
product||1,1|C,-0.7937623318,1.9418936638,0.5753782205|C,0.3172676429
,1.4126644408,-0.341576134|C,0.6809523975,-0.0393594511,-0.019033376|C
,-0.587252479,-0.988992362,-0.1413102629|C,-1.7063370588,-0.4482458016
,0.8898416945|C,-2.0493014512,1.0468361522,0.519275908|C,-1.1212786146
,-1.0042818912,-1.6001600923|C,1.8384673766,-0.5964438851,-0.844169384
3|C,-0.1458527421,-2.4502281416,0.1833999233|C,1.0710652857,-2.9509395
591,-0.6243841806|C,2.292830336,-2.0274455478,-0.4401008261|C,2.829818
1421,-2.1369836603,1.0056587533|C,3.4541575524,-2.2401636487,-1.424925
7517|C,-1.202535534,-0.5835136018,2.3492043112|C,-3.3126473914,1.69900

```

64111, 1.2056991879|C, -3.0057751055, -1.2953282643, 0.7706839685|C, -4.188
 4835139, -0.7104177231, 1.5565282353|C, -4.5021526391, 0.7123131467, 1.0890
 310619|C, -3.1242195002, 2.1352761298, 2.6772644503|C, -3.701179671, 2.9701
 397052, 0.4114874599|C, 4.2184682995, -0.8883435111, -1.4562861068|C, 3.210
 8492148, 0.2041153245, -0.8355655752|C, 3.2592284471, 1.4189552994, -1.6210
 697662|C, 3.8384661177, 2.658125552, -1.0529207493|C, 2.8324603939, 1.46309
 96027, -3.0385010005|H, -1.0459854133, 2.9638281796, 0.2757815907|H, -0.410
 899297, 2.008033733, 1.6008471708|H, 0.005283915, 1.5052887092, -1.39137149
 61|H, 1.2117830772, 2.0498811612, -0.2253091187|H, 1.0000545649, -0.0631625
 532, 1.0284836683|H, -2.3504192828, 1.0166805124, -0.5353216508|H, -1.54359
 97147, -0.0534575105, -1.9294237859|H, -0.3413736392, -1.2696644247, -2.319
 0173739|H, -1.9018321483, -1.7605357623, -1.7130613759|H, 1.536712518, -0.6
 508224607, -1.8965898488|H, 0.0885035672, -2.5514035802, 1.2458287938|H, -0
 .9855884092, -3.1277657841, -0.0040986144|H, 1.3239193668, -3.9684204424, -
 0.3012475452|H, 0.825172395, -3.0212205159, -1.6914451704|H, 2.108127238, -
 1.8134132946, 1.7596138171|H, 3.0725636194, -3.1840671982, 1.2167995346|H,
 3.74896711, -1.5624630716, 1.1645728679|H, 3.0685169796, -2.4770376324, -2.
 4231667312|H, 4.1270249651, -3.0534374693, -1.1328974362|H, -0.2820699604,
 -0.0310119883, 2.5568497516|H, -1.0279687524, -1.6300868347, 2.6133900938|
 H, -1.9454385533, -0.2129386569, 3.0520376391|H, -3.3153556612, -1.35993643
 47, -0.278614551|H, -2.8108699764, -2.3219576694, 1.1042420196|H, -3.990946
 9313, -0.7302280456, 2.6346947768|H, -5.0670033638, -1.3487545035, 1.402283
 5708|H, -5.3567696967, 1.1177156036, 1.6460249213|H, -4.8171126643, 0.66799
 3541, 0.0356291419|H, -3.0869958079, 1.3007685976, 3.3811497714|H, -2.21628
 16372, 2.732370743, 2.8173727423|H, -3.9705085221, 2.76350158, 2.9783345458
 |H, -3.7684158025, 2.7706049558, -0.6652607134|H, -4.6830345752, 3.32842871
 28, 0.7410086091|H, -2.9945685881, 3.7937260433, 0.5622942103|H, 4.54217345
 51, -0.6275367079, -2.4676217291|H, 5.1116200524, -0.8843284855, -0.8264847
 89|H, 3.4994076378, 0.419020543, 0.1953507953|H, 3.7235212199, 2.724944793,
 0.0315510486|H, 3.4809815317, 3.5664173985, -1.5467066429|H, 4.9252886704,
 2.6021898085, -1.2529962641|H, 2.6511334788, 0.4854177415, -3.484824483|H, 1
 .8947603651, 2.041316373, -3.076440499|H, 3.5480036288, 2.0350920199, -3.64
 29410748||Version=x86-Win32-G98RevA.11.2|HF=-978.2994442|RMSD=5.226e-0
 09|RMSF=2.389e-005|PG=C01 [X(C25H43)]||@

Compound 29b, reactant in Table 5, 17 β -side chain, C16 migration, $\beta\alpha\beta$ configuration

1\1\GINC-LNX\FOpt\RB3LYP\6-31G(d)\C25H43(1+)\BILLW\27-Mar-2004\0\#\ B3
 LYP/6-31G* OPT FREQ\ERing17bLupUP-SM C25H43(1+) still another restart
 \\\1,1\C, -1.0179340704, 1.6958286828, 0.0017390904\C, 0.286154166, 0.966384
 9197, -0.3805943846\C, 0.4557474544, -0.2599894508, 0.51577448\C, -0.751759
 3014, -1.2459954282, 0.4516130795\C, -2.0701176325, -0.486620027, 0.9311623
 83\C, -2.2529066677, 0.7664984733, -0.0182263634\C, -0.9076230371, -1.86203
 99923, -0.9654700238\C, 1.6963107562, -1.146607322, 0.3006620459\C, -0.2183
 677619, -2.3744336284, 1.37019061\C, 1.2722170397, -2.5701644081, 0.9976654
 29\C, 2.9546124449, -0.8661032843, 0.9665284265\C, 3.022671285, -0.03095735
 81, 2.1909841582\C, 4.197359316, -1.4107934436, 0.4116683741\C, -1.94809620
 13, -0.087537207, 2.4230251926\C, -3.6264927545, 1.5361319829, 0.0712413247
 \C, -3.3151703876, -1.403486772, 0.796495635\C, -4.639349365, -0.6596397258
 , 1.0183140226\C, -4.7797001045, 0.4995485467, 0.0264180066\C, -3.789925558
 4, 2.4650859788, 1.2963070589\C, -3.7742497675, 2.4279404582, -1.1856637903
 \C, 4.8663351148, -0.3317825199, -0.5774083996\C, 4.2265894984, -0.26378236
 1, -1.9260828241\C, 3.7602536874, 0.8268863862, -2.5658728362\C, 3.23353043
 36, 0.7148347777, -3.9748460514\C, 3.7486801137, 2.2248336646, -2.002113856

$\backslash H, -1.1671639148, 2.5271090253, -0.6936692666 \backslash H, -0.8925010568, 2.14922200$
 85, 0.9929930246 $\backslash H, 0.258197798, 0.6648306322, -1.43584997 \backslash H, 1.1384759956,$
 1.6519111467, -0.2757530922 $\backslash H, 0.4987169413, 0.1006613362, 1.5494831444 \backslash H,$
 -2.2889239098, 0.3456962859, -1.0313329945 $\backslash H, -1.2584939373, -1.151983282,$
 -1.7160192664 $\backslash H, 0.0349779915, -2.2729251793, -1.3419411814 \backslash H, -1.61608839$
 41, -2.6938777429, -0.946257382 $\backslash H, 1.8893248673, -1.3539886212, -0.75657030$
 $\backslash H, -0.2886096184, -2.097125287, 2.424221758 \backslash H, -0.7514974448, -3.3236679$
 806, 1.2469349212 $\backslash H, 1.8758824687, -2.8245551461, 1.8748773601 \backslash H, 1.4475268$
 866, -3.3500930348, 0.2542663857 $\backslash H, 2.2622523229, -0.338545435, 2.919522298$
 $\backslash H, 4.0074663606, -0.0418223075, 2.6606621587 \backslash H, 2.7595310338, 1.0050718872$
 $, 1.9263860365 \backslash H, 4.0198186093, -2.3134868731, -0.1801621162 \backslash H, 4.923187534$
 3, -1.6174951978, 1.2026560721 $\backslash H, -1.1101656986, 0.5813750711, 2.6404978005$
 $\backslash H, -1.8473704887, -0.9703426223, 3.062290203 \backslash H, -2.8432513117, 0.428905037$
 7, 2.7623346931 $\backslash H, -3.3539025799, -1.8344920682, -0.2100796686 \backslash H, -3.229827$
 9692, -2.2472300559, 1.4949870794 $\backslash H, -4.72238809, -0.3008868806, 2.05111139$
 3 $\backslash H, -5.4710393675, -1.3608271744, 0.8792884282 \backslash H, -5.7326136354, 1.0208851$
 679, 0.1838676242 $\backslash H, -4.8274310045, 0.0780002176, -0.9889109167 \backslash H, -3.94757$
 07945, 1.9300427156, 2.235497273 $\backslash H, -2.9276809179, 3.1279980419, 1.42891966$
 51 $\backslash H, -4.6667825786, 3.1060351928, 1.1492571004 \backslash H, -3.5758626592, 1.8668186$
 174, -2.107299208 $\backslash H, -4.7980642407, 2.8134757501, -1.249896776 \backslash H, -3.107270$
 0407, 3.2966382208, -1.1655732502 $\backslash H, 5.8945788052, -0.7031697643, -0.668000$
 2813 $\backslash H, 4.9262566617, 0.6377604206, -0.0774888078 \backslash H, 4.21057665, -1.2115259$
 134, -2.4659166351 $\backslash H, 3.2601627085, -0.3129907692, -4.3474377424 \backslash H, 3.82269$
 91589, 1.340246036, -4.6580573862 $\backslash H, 2.1996839257, 1.0800656575, -4.0363220$
 435 $\backslash H, 4.0917802217, 2.2929485692, -0.9666952863 \backslash H, 4.391594628, 2.87915611$
 53, -2.605067046 $\backslash H, 2.7391958804, 2.6519325274, -2.0568185209 \backslash Version=x86$
 $-Linux-G98RevA.9 \backslash HF=-978.2890306 \backslash RMSD=5.354e-09 \backslash RMSF=2.674e-06 \backslash PG=C01$
 $[X(C25H43)] \backslash @$

Compound 30b, product in Table 5, 17 β -side chain, C16 migration, $\beta\alpha\beta$ configuration

1 | 1 | UNPC-UNK | FOpt | RB3LYP | 6-31G(d) | C25H43 (1+) | PCUSER | 08-Oct-2003 | 0 || # B
 3LYP/6-31G* OPT=READFC GEOM=ALLCHECK GUESS=READ || ERing-LupeolUP-Prod ||
 1, 1 | C, -1.9081498627, 0.7565495018, -0.796367714 | C, -0.5262948081, 0.488459
 5606, -1.4151682333 | C, 0.5316192702, 0.1334064735, -0.362493734 | C, 0.073925
 7988, -1.1010442977, 0.5170021136 | C, -1.2865018091, -0.6629807501, 1.266647
 5461 | C, -2.3723441145, -0.3643227848, 0.1613133493 | C, -0.140247314, -2.3578
 760083, -0.3725737599 | C, 1.9237390015, -0.1428225033, -0.9399906497 | C, 1.20
 66606836, -1.4775368829, 1.52648649 | C, 2.624009891, -1.6111885288, 0.919229
 3279 | C, 3.0288086137, -0.3484201496, 0.1286235012 | C, 3.2517721131, 0.821737
 4156, 1.1136455941 | C, 4.2695697576, -0.488823538, -0.77440459 | C, -1.0346379
 205, 0.5740006822, 2.1728606573 | C, -3.8613551625, -0.1867227442, 0.64681474
 55 | C, -1.7941803207, -1.8096085092, 2.1864672157 | C, -3.2142509863, -1.58568
 2804, 2.7259923598 | C, -4.2112284362, -1.3693272231, 1.5853987049 | C, -4.1725
 653438, 1.1585938468, 1.3390945909 | C, -4.8011545409, -0.2906158537, -0.5783
 453441 | C, 4.1415364928, 0.6470967453, -1.8132945177 | C, 2.5383558536, 0.7222
 156867, -2.1121916683 | C, 2.2310764734, 2.1225233736, -2.3177336356 | C, 2.179
 6488665, 2.6428390046, -3.704750343 | C, 2.0297163952, 3.1035310797, -1.23073
 31702 | H, -2.6348715043, 0.87899814, -1.6054058498 | H, -1.8802720568, 1.71750
 41478, -0.2690662765 | H, -0.5948060582, -0.3066917447, -2.168652646 | H, -0.20
 9812075, 1.391702588, -1.9686998951 | H, 0.6055197723, 0.985815291, 0.3212896
 42 | H, -2.4279790331, -1.2802410016, -0.4394109424 | H, -0.8470101863, -2.2136
 053637, -1.1908039912 | H, 0.7957736034, -2.7015010875, -0.8219693716 | H, -0.5
 059211641, -3.1951322519, 0.2259312839 | H, 1.854165231, -1.1081126633, -1.45

53303491|H,1.2569599181,-0.7491493466,2.3394604653|H,0.9510595458,-2.4
 306324749,2.0016220632|H,3.3403935963,-1.7997702883,1.7280609709|H,2.6
 773355722,-2.4833738039,0.255561778|H,2.3461702474,1.1037252765,1.6566
 432874|H,3.991849003,0.5193989009,1.8627791283|H,3.6454454001,1.723631
 9123,0.6339339292|H,4.2634635602,-1.4583973642,-1.2863036259|H,5.21982
 95725,-0.401084238,-0.2359605403|H,-0.975786135,1.5194277482,1.627541
 9089|H,-0.1157967889,0.4744361688,2.7570349091|H,-1.836264447,0.691080
 8096,2.9016474477|H,-1.8052496299,-2.7566069995,1.6355579288|H,-1.0985
 410871,-1.9448966591,3.023882372|H,-3.2418597987,-0.7414793014,3.42539
 97274|H,-3.5117378225,-2.4639419827,3.3118527923|H,-5.2216722307,-1.21
 96449179,1.9872478385|H,-4.2551132173,-2.2891247365,0.982928786|H,-3.6
 799998223,1.27921567,2.3059823621|H,-3.8933819043,2.0137775656,0.71339
 49709|H,-5.2515891095,1.2328656212,1.5174551742|H,-4.5861024773,-1.183
 7284589,-1.1781257701|H,-5.8427586042,-0.361730807,-0.2446103748|H,-4.
 7359827845,0.5838838107,-1.2348836674|H,4.6661205277,0.462105249,-2.75
 29268167|H,4.51332877,1.5901325809,-1.40515784|H,2.3943030877,0.207046
 6605,-3.0666238876|H,2.7939547327,2.0595732528,-4.3968517258|H,2.41114
 40776,3.7096967281,-3.7702594923|H,1.1342630414,2.5233318706,-4.041769
 9858|H,1.7735907586,2.6597157572,-0.2720109608|H,2.9783913601,3.656782
 8466,-1.1139411673|H,1.2942754857,3.8611121385,-1.5256166078||Version=
 x86-Win32-G98RevA.11.2|HF=-978.289187|RMSD=8.064e-009|RMSF=2.295e-006|
 PG=C01 [X(C25H43)]||@

Compound 37a, stereoisomer of products in Table 5, $\beta\alpha\alpha$ configuration

1|1|UNPC-UNK|FOpt|RB3LYP|6-31G(d)|C25H43(1+)|PCUSER|12-Mar-2004|0||# B
 3LYP/6-31G* OPT GEOM=CHECK||ERingLup-13b17a18aProd C25H4||1,1|C,-1.349
 1908896,1.7980980905,0.0829202914|C,0.0631276733,1.4731092733,-0.42003
 1041|C,0.5593600211,0.1187365388,0.1043849103|C,-0.4100875136,-1.05653
 9374,-0.2500448999|C,-1.8839853708,-0.7079585006,0.3058095954|C,-2.339
 8299322,0.679444853,-0.2901548209|C,-0.4299183258,-1.3169627151,-1.779
 8089721|C,2.0371938661,-0.1294899716,-0.3228505793|C,0.1845055859,-2.3
 036775125,0.453220294|C,1.5593968682,-2.700160864,-0.0955755394|C,2.62
 55884552,-1.5726939405,-0.0955163477|C,3.6570885847,-1.9176257501,-1.1
 919931345|C,3.3428113717,-1.4413384895,1.2649293274|C,-1.8764143266,-0
 .7088808298,1.8557005016|C,-3.8537904879,1.0897301336,-0.1149559809|C,
 -2.89761732,-1.7918808122,-0.156853033|C,-4.3547797255,-1.434025403,0.
 1653784984|C,-4.7484467997,-0.1148072039,-0.5033635734|C,-4.2420662699
 ,1.6106763979,1.2880792901|C,-4.1710207177,2.228503036,-1.1146540009|C
 ,4.0659294439,-0.087298326,1.2296044991|C,2.9218105598,0.8395206326,0.
 5407105702|C,3.6693114089,1.9207243011,-0.0522474342|C,4.0109114646,3.
 1160390025,0.7529802007|C,4.1511821689,1.8835515834,-1.4499104903|H,-1
 .6702948795,2.7499455665,-0.3513125887|H,-1.3224277395,1.9501310692,1.
 1692208834|H,0.07089288,1.4648344253,-1.5194979152|H,0.7525390324,2.27
 8629905,-0.1165631897|H,0.5568113669,0.1753772451,1.2013992359|H,-2.25
 43832189,0.56193411,-1.3789484312|H,-1.0377315825,-0.5964140748,-2.330
 4258792|H,0.5725957411,-1.2771463298,-2.2167159112|H,-0.8264189694,-2.
 3119503546,-2.0027788589|H,2.1228263227,0.1275956631,-1.3841371314|H,0
 .2676767943,-2.1164389205,1.5295333091|H,-0.487628702,-3.1616083803,0.
 3424413609|H,1.4444523685,-3.0744829789,-1.1181369649|H,1.9542569168,-
 3.5462555443,0.4816604508|H,3.1934085165,-1.8923252206,-2.1845908588|H
 ,4.0476141268,-2.9300244164,-1.0392017651|H,4.5225367852,-1.2439626037
 ,-1.2123461147|H,2.6195764576,-1.4444852611,2.088860796|H,4.0581935766
 ,-2.2520600885,1.4448324238|H,-1.1425785605,-0.0265878803,2.2951412486

| H,-2.8447348171,-0.4161575734,2.2564549925| H,-1.6711462303,-1.7099619
086,2.2461719153| H,-2.6456828872,-2.7588737247,0.2955784474| H,-2.82824
36602,-1.9270973614,-1.2424682089| H,-5.0080824759,-2.2371720846,-0.196
9131702| H,-4.5150731269,-1.3841277919,1.24903927| H,-4.6943958138,-0.25
25776741,-1.5937341077| H,-5.7945797919,0.1310874993,-0.2794150918| H,-4
.2989986316,0.8267218094,2.0470698239| H,-5.2346241037,2.0735988728,1.2
402333506| H,-3.5475599705,2.3771027485,1.6496081213| H,-3.8446725617,1.
9772408913,-2.1314397397| H,-3.7045289008,3.1789518997,-0.8328328128| H,
-5.2525814479,2.4025089349,-1.1500239888| H,4.3300580084,0.3203290223,2
.207482093| H,4.9721648667,-0.1364221592,0.620462126| H,2.3524926785,1.2
210468745,1.3940481686| H,3.5859530314,3.104895373,1.7575125805| H,5.104
7878023,3.2212456465,0.8072364325| H,3.6700217579,4.0174503023,0.220163
0561| H,5.031915965,2.5105520779,-1.6112667681| H,3.3370480347,2.3073241
273,-2.0648577975| H,4.3121262823,0.8688633684,-1.8210915775|| Version=x
86-Win32-G98RevA.11.2| HF=-978.2995767|RMSD=5.731e-009|RMSF=1.946e-006|
PG=C01 [X(C25H43)] || @