Electronic Supplementary Information for Organic & Biomolecular Chemistry

Mechanistic insights into triterpene synthesis from quantum mechanical calculations. Detection of systematic errors in B3LYP cyclization energies

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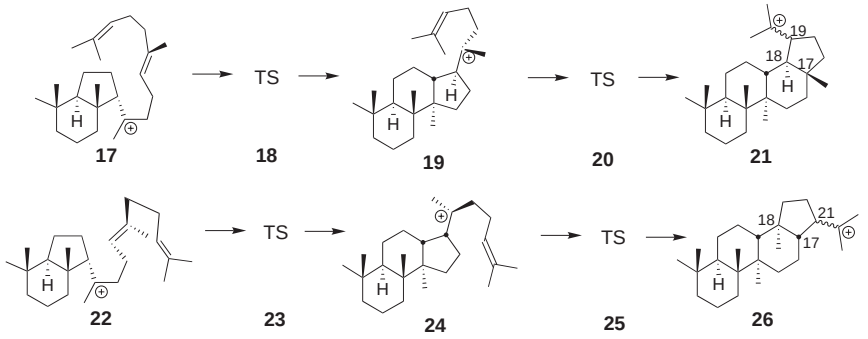
Energetics of D- and E-ring formation in hopene and lupeol synthesis

Table S1 Predicted energetics of D- and E-ring formation for $C_{25}H_{43}$ models of lupeol and hopene biosynthesis[a] (Corresponds to Fig. 1)



	Lupeol Model					Hopene Model				
	17	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**
	Relative Energy (kcal/mol)					*Relative Energy (kcal/mol)*				
HF/6-31G*	0.0	11.0	-9.8	-1.5	-16.3	0.0	12.7	0.1	9.2	-1.4
B3LYP/6-31G*	0.0	5.2	-8.3	-1.7	-14.4	0.0	6.8	-2.7	4.4	-3.0
B3LYP/6-311+G(2d,p)	0.0	6.3	-5.9	0.7	-9.4	0.0	7.5	0.3	7.5	2.0
MPW1K/6-31G*	0.0	4.9	-18.2	-13.3	-33.6	0.0	7.4	-11.5	-4.8	-21.2
MPW1K/6-311+G(2d,p)	0.0	5.7	-16.2	-11.5	-29.6	0.0	7.9	-9.2	-2.6	-17.3
mPW1PW91/6-31G*	0.0	4.5	-15.0	-9.6	-27.5	0.0	6.8	-9.1	-2.1	-15.4
mPW1PW91/6-311+G(2d,p)	0.0	5.3	-13.1	-7.9	-23.5	0.0	7.3	-6.8	0.2	-11.5
MP2/6-31G*	0.0	-1.4	-18.6	-18.1	-36.1	0.0	0.7	-13.0	-13.2	-25.8
ZPE increment	0.0	0.7	1.6	2.0	3.4	0.0	0.5	2.3	2.7	4.7
ΔH increment	0.0	-0.1	0.9	0.7	1.5	0.0	-0.1	1.3	1.2	2.6
ΔG increment	0.0	3.2	3.0	5.1	8.3	0.0	1.7	5.5	7.4	11.0
Relative entropy	0.0	-10.9	-7.1	-14.9	-22.9	0.0	-5.8	-14.0	-20.8	-28.2

[a] Quantum mechanical electron energies relative to **17** or **22** in kcal/mol. Geometry optimization and frequency calculations were done with B3LYP/6-31G(d). Energies for E-ring formation (**19**, **21**, **24**, and **26**; corresponding to **29a**, **30a**, **31a**, and **32a** of Ref. 10) are taken from Table 4 of Ref. 10. Here and elsewhere, the ZPE increment and the thermal energy contributions to the ΔH and ΔG increments were scaled, unless mentioned otherwise. Here and in most tables below, mPW1PW91/6-311+G(2d,p) electron energies and ΔH increments are highlighted in blue text.

Comment: Unlike the $C_{21}H_{37}$ models for D-ring formation in Table 1 of Ref. 10 (without the Δ24 bond), these energies are for the $C_{25}H_{43}$ models with a Δ24 bond. This addition of the cation-stabilizing Δ24 double bond led to only a 3-4 kcal/mol change toward exothermicity, thus suggesting that cation-olefin stabilization is of limited importance in D-ring formation.

Results of combustion analysis for benchmark test samples sent to a major commercial analytical laboratory

Fresh commercial samples of adamantane and *cis*-decalin of high purity were sent to a major analytical service laboratory. Samples were dried in vacuo before analysis, and CH combustion analyses suggested negligible solvent contamination (C 88.27, H 11.82 (theory C 88.16, H 11.84) for adamantane; C 87.08, H 13.24 (theory C 86.88, H 13.12) for *cis*-decalin). However, results were lower than reported values by 6-9 kcal/mol (~0.5% error), and monoterpene samples gave similar errors (see below). These analyses were done by ASTM method D5865-00; the more precise D4809 method was not available. Determination of heats of formation for oxidosqualene and lupeol would also require gram quantities of these precious substances, application of Washburn corrections, and measurement or estimation of heats of vaporization and sublimation. Specific results are given below.

Analyses done on 12-Feb-04:

Adamantane, Heat of combustion: 18931 Btu/lb*
cis-Decahydronaphthalene, Heat of combustion: 19464 Btu/lb**
*Raw data: sample mass 0.50514 g, spike mass 0.63608 g, titration volume (for nitrogen) 12.65 mL; 9.00 cm of fuse wire, initial temperature 25.54°C, delta T 3.8647.
**Raw data: sample mass 0.50139 g, spike mass 0.34455 g, titration volume (for nitrogen) 10.00 mL; 9.00 cm of fuse wire, initial temperature 25.63°C, delta T 3.1485.

Analyses done on the same samples on 23-Feb-04:

Adamantane, Heat of combustion: 18947 Btu/lb (1434 kcal/mol, calculated)
cis-Decahydronaphthalene, Heat of combustion: 19434 Btu/lb (1493 kcal/mol, calculated)

Analyses done on freshly purchased terpene samples from Aldrich on 9-Jan-04:

Geraniol, Heat of combustion: 17307 Btu/lb (1483 kcal/mol, calculated)
Borneol, Heat of combustion: 16661 Btu/lb (1428 kcal/mol, calculated)
Nerol, Heat of combustion: 17248 Btu/lb (1478 kcal/mol, calculated)
Cineole, Heat of combustion: 17065 Btu/lb (1462 kcal/mol, calculated)

Relevant ASTM methods for combustion calorimetry:

D5865-00	for coal, coke, superceded by 2002 version
D240-02	for liquid hydrocarbons, less reproducible than D4809
D4809	for liquid hydrocarbons, 0.2% reproducibility
D2015-00	for coal, coke, withdrawn in 2000

Comparison of our heats of combustion with literature data.

	Hcomb BTU/lb liq/solid provided	Hcomb cal/g liq/solid calcd	FW liq/solid calcd	Hcomb kcal/mol liq/solid calcd	Hcomb kcal/mol liq/solid provided	10 x Hf CO_2 gas literature	9 x Hf H_2O gas literature	Hf kcal/mol liq/solid calcd	Hcomb kcal/mol liq/solid literature	Hf kcal/mol liq/solid literature	Hf kcal/mol gas literature
Geraniol	17307	9621.5	154.25	1484.1	1483	940.5	614.8	-72.3	-1472.5		
Borneol	16661	9262.3	154.25	1428.7	1428	940.5	614.8	-127.3	-1489.3	-66.0	
Nerol	17248	9588.7	154.25	1479.1	1478	940.5	614.8	-77.3			
Cineole	17065	9486.9	154.25	1463.4	1462	940.5	614.8	-93.3			
Adamantane	18931	10524.3	136.23	1433.7		940.5	546.5	-53.3	-1441.5	-45.6	-31.6
Adamantane	18947	10533.2	136.23	1434.9	1434	940.5	546.5	-53.0	-1441.5	-45.6	-31.6
cis-Decalin	19464	10820.6	138.25	1495.9		940.5	614.8	-59.4	-1502.9	-52.5	-40.5
cis-Decalin	19434	10803.9	138.25	1493.6	1493	940.5	614.8	-62.3	-1502.9	-52.5	-40.5

Notes: Hcomb=heat of combustion; Hf=heat of formation; liq=liquid. "Provided" indicates values given by the commercial analytical laboratory. "Calcd" indicates values we calculated from the data provided. The heats of formation values for CO_2 and H_2O are based on formation of 10 and 9 moles of CO_2 and H_2O, with heats of formation of –94.051 and –68.315 kcal/mol, respectively. The heat of formation for borneol (-66.0 kcal/mol) was calculated by NIST without Washburn corrections; other literature heats of formation were given in the original reports. The literature data for adamantane and *cis*-decalin are particularly reliable, as similar values have been obtained independently by several groups with established expertise in this demanding technique. The older literature values for borneol and geraniol appear to be much less accurate.

References (from the NIST webbook):

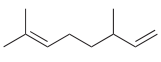
cis-Decalin: D. M. Speros and F. D. Rossini, *J. Phys. Chem.*, 1960, **64**, 1723-1727.

Adamantane (above is shown the average of Clark *et al.* and Boyd *et al.* values as reanalyzed by Pedley *et al.*): (*a*) T. Clark, T. M. O. Knox, M. A. McKervey, H. Mackle and J. J. Rooney, *J. Am. Chem. Soc.* 1979, **101**, 2404-2410. (*b*) J. B. Pedley, R. D. Naylor and S. P. Kirby, *Thermochemical Data of Organic Compounds*; Chapman and Hall, New York, 1986, pp. 1-792. (*c*) R. H. Boyd, S. N. Sanwal, S. Shary-Tehrany and D. McNally, *J. Phys. Chem.*, 1971, **75**, 1264-1271.

Borneol and geraniol: S. Yamada, *Bull. Chem. Soc. Jpn.*, 1941, **16**, 187-196.

Conclusion: The substantial differences between the established literature values (shown in blue) and results from the commercial analytical laboratory (shown in red) indicate that combustion analyses based on ASTM method D5865-00 are not useful for estimating heats of formation to the 1-2 kcal/mol accuracy we needed.

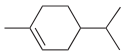
Table S2 Part a Energies of $C_{10}H_{18}$ isomers relative to 5-decyne (extended conformation) from DFT, *ab initio*, and molecular mechanics calculations[a] (Corresponds to Table 1)



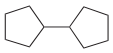
27 Dihydromyrcene

28 cis-Decalin
29 trans-Decalin

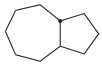
30 Spiro[4,5]-decane



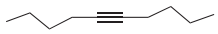
31 Δ^1-*p*-Menthene



32 Dicyclopentyl



33 Bicyclo[5.3.0]-decane



34 5-Decyne

Method	RMS ΔE[b]	RMSD ΔH[c]	MSE ΔH[d]	Energies (kcal/mol) relative to 5-decyne (**34**) **27**	**28**	**29**	**30**	**31**	**32**	**33**
Experimental Hf		0.0	0.0	-11.4	-48.0	-44.9	-39.1	-30.9	-35.8	-35.6
MM3-94		1.5	1.0	-9.8	-45.8	-43.0	-39.4	-30.7	-35.3	-33.3
MM3 (PCMODEL)		1.5	0.9	-10.2	-45.8	-43.0	-39.4	-31.0	-35.3	-33.3
MMX (PCMODEL)		1.2	0.6	-10.4	-46.4	-43.6	-39.4	-31.9	-35.1	-33.7
AM1	*3.5*	2.3	-0.1	-1.8	-50.6	-47.8	-42.3	-26.2	-40.6	-37.7
HF/3-21G	*3.0*	3.8	3.1	-1.6	-47.0	-44.2	-40.3	-24.8	-34.8	-31.8
HF/6-31G*	*3.6*	4.8	4.4	-3.8	-45.2	-41.8	-36.4	-25.9	-32.6	-31.4
B3LYP/6-31G*	*2.9*	4.3	3.9	-7.0	-45.2	-41.9	-36.8	-28.5	-32.5	-32.4
B3LYP/6-311+G(2d,p)	*8.2*	9.2	8.4	-7.3	-39.1	-35.7	-31.2	-25.2	-27.5	-26.8
BV5LYP/6-31G*	*3.1*	4.5	4.1	-7.0	-45.0	-41.6	-36.6	-28.4	-32.3	-32.1
BV5LYP/6-311+G(2d,p)	*8.5*	9.5	8.6	-7.2	-38.9	-35.5	-30.9	-25.1	-27.3	-26.6
MPW1K/6-31G*	*11.7*	9.1	-8.3	-6.6	-60.9	-57.7	-52.6	-36.4	-47.5	-47.3
MPW1K/6-311+G(2d,p)	*7.5*	5.3	-4.8	-7.4	-56.2	-52.9	-48.1	-34.3	-43.4	-42.9
mPW1/6-31G*	*7.4*	5.2	-4.7	-6.9	-56.1	-52.9	-48.0	-34.2	-43.2	-42.9
mPW1/6-311+G(2d,p)	*3.1*	1.3	-1.1	-7.5	-51.2	-47.9	-43.4	-31.8	-39.2	-38.5
B3PW91/6-31G*	*4.0*	2.1	-1.8	-6.5	-52.4	-49.1	-44.2	-32.0	-40.0	-39.4
B3PW91/6-311+G(2d,p)	*0.7*	2.0	1.7	-7.1	-47.5	-44.2	-39.8	-29.6	-36.0	-35.1
B1LYP/6-31G*	*3.2*	4.6	4.1	-6.8	-44.9	-41.6	-36.5	-28.2	-32.2	-32.0
B1LYP/6-311+G(2d,p)	*8.6*	9.6	8.8	-7.1	-38.8	-35.3	-30.7	-24.9	-27.1	-26.4
B3P86P/6-31G*	*6.4*	4.3	-3.9	-7.4	-55.2	-51.9	-46.9	-34.1	-42.0	-42.0
B3P86P/6-311+G(2d,p)	*2.2*	0.6	-0.4	-8.0	-50.3	-47.0	-42.4	-31.6	-38.0	-37.6
PBE1PBE/6-31G*	*9.4*	7.1	-6.4	-7.3	-58.3	-55.2	-50.2	-35.6	-45.1	-45.1
PBE1PBE/6-3111+G(2d,p)	*5.1*	3.1	-2.8	-7.9	-53.4	-50.1	-45.6	-33.2	-41.1	-40.6
HCTH/6-31G*	*5.9*	7.1	6.4	-5.9	-41.7	-37.9	-33.4	-25.9	-30.9	-29.5
HCTH/6-311+G(2d,p)	*10.9*	11.7	10.7	-6.1	-36.0	-32.0	-28.2	-22.8	-26.5	-24.5
VSXC/6-31G*	*11.7*	9.4	-8.1	-18.1	-57.6	-58.1	-55.8	-43.6	-42.3	-44.0
VSXC/6-311+G(2d,p)	*8.6*	6.7	-5.2	-19.2	-53.8	-53.9	-52.4	-42.0	-38.8	-40.0
TPSS/6-31G*	*0.9*	2.3	2.0	-7.5	-46.8	-43.8	-39.6	-29.7	-35.6	-34.7
TPSS/6-311+G(2d,p)	*5.1*	6.4	5.7	-7.8	-41.7	-38.6	-35.0	-27.0	-31.7	-30.2
TPSSh10/6-31G*	*2.0*	0.6	-0.1	-7.2	-49.6	-46.6	-42.3	-30.9	-38.1	-37.3
TPSSh10/6-311+G(2d,p)	*2.6*	4.0	3.6	-7.7	-44.6	-41.5	-37.7	-28.4	-34.2	-32.8
TPSSh25/6-31G*	*5.7*	3.6	-3.2	-6.8	-53.9	-50.9	-46.3	-32.9	-41.9	-41.1
TPSSh25/6-311+G(2d,p)	*1.6*	0.8	0.4	-7.4	-49.0	-45.9	-41.8	-30.5	-37.9	-36.7
O3LYP/6-31G*	*3.3*	4.6	4.2	-5.1	-44.6	-40.8	-36.5	-26.7	-34.2	-32.4
O3LYP/6-311+G(2d,p)	*7.8*	8.9	8.1	-5.4	-39.2	-35.3	-31.6	-24.0	-30.1	-27.7
MP2/6-31G*	*6.8*	4.7	-4.1	-6.4	-55.4	-52.7	-48.5	-34.0	-41.5	-41.2
MP3/6-31G*	*7.6*	5.4	-4.9	-9.2	-56.2	-53.3	-48.6	-35.5	-42.7	-42.4
CCSD(T)/6-31G*	*5.8*	3.8	-3.4	-9.7	-54.1	-51.4	-47.0	-34.7	-40.5	-40.4
ZPE increment				-0.7	4.6	4.8	4.3	1.4	3.5	4.4
ΔH increment				-0.9	2.0	2.2	1.9	0.2	1.7	2.1
ΔG increment				0.2	10.0	10.3	9.2	4.8	5.7	9.1
Relative entropy				-3.7	-26.7	-27.4	-24.7	-15.4	-13.6	-23.3

[a] Values for quantum mechanical methods are electron energies; thermochemical increments are from B3LYP/6-31G* frequency calculations. Energies are for the most stable conformer only. Here and in some other tables, mPW1 denotes mPW1PW91. BV5LYP calculations were done with added parameters specified in Gaussian by IOp(3/76=1000002000) IOp(3/77=0720008000) IOp(3/78=0810010000); BV5LYP differs from Gaussian B3LYP in the use of equation V rather than equation III of Vosko, Wilk, and Nusair (*Can. J. Phys.*, 1980, **58**, 1200-1211). The RMSD (root mean square deviation) and MSE (mean signed error, i.e. average error) calculations describe only cyclization enthalpies and thus exclude dihydromyrcene data. [b] RMSD of predicted electron energy differences relative to experimental heat of formation differences, without ZPE or thermal energy corrections. [c] RMSD of predicted enthalpy differences relative to experimental heat of formation differences. For quantum mechanical methods, enthalpies were obtained by adding the ΔH increment to the electron energy. [d] MSE of predicted enthalpy (or heat of formation) differences relative to experimental heat of formation differences. Deviation=theory-experiment

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Comments:

1. This table shows energies for basis set entries not included in Table 1. Comparisons of 6-31G* and 6-311+G(2d,p) cyclization enthalpies indicate that for all the DFT methods, larger basis sets give lower (less negative) cyclization energies. This matter is addressed in further detail in Table S2b.
2. The purpose of this table is to reveal fundamental trends in DFT energies of cyclization. The data lack the breadth and accuracy of Hf values needed to evaluate the general usefulness of specific DFT methods. For example, B3P86 performs superbly here but is known to have serious faults in other situations. Other DFT methods may perform poorly here but behave well over a wide range of applications. We particularly caution against snap judgments about the best method for estimating cyclization energies, lest AM1, TPSSh/6-31G*, or MMX be impetuously chosen as optimal.
3. Deviations of predicted cyclization enthalpies from experimental values varied considerably among the DFT methods. The spread of these deviations (as rms error, data not shown) was largest for cyclizations that generate two rings and lowest for conversion of 5-decyne to dihydromyrcene. Among DFT methods (excluding VSXC), the predicted enthalpies for this non-cyclization reaction averaged -7.0 kcal/mol with a rms error of only 0.7 kcal/mol. Analogous energy comparisons among bicyclic compounds (**28**, **29**, **30**, and **33**) showed a similar consistency of energy predictions among all the DFT methods except VSXC. These analyses are compatible with our view that empirical DFT methods usually model organic reactions well but sometimes generate systematic errors, notably for cyclization energies..
4. The BV5LYP cyclization energies differed from B3LYP values by <0.3 kcal/mol. Our results suggest that differences in B3LYP energies among software packages using VWN equation III or V will be very minor. The BV5LYP deviations were about 0.25 kcal/mol for formation of two rings, ca. 0.15 kcal/mol for formation of one ring, and ca. 0.01 for no ring formation (dihydromyrcene). The BV5LYP errors were slightly higher than the B3LYP errors, here and in Table S7a, suggesting that the use of VWN equation V exacerbates

slightly the cyclization energy problem. These tiny discrepancies may provide a critical clue to origin of the cyclization energy errors.

5. B3LYP and BV5LYP differ in the equation used for calculating the non-local correlation by the local spin density approximation (LSDA). Vosko, Wilk, and Nusair (VWN) suggested five possible equations for estimating $\Delta\varepsilon_c(r_s,\zeta)$, which is defined by the equation $\varepsilon_c(r_s,\zeta) = \varepsilon_c^P(r_s) + \Delta\varepsilon_c(r_s,\zeta)$, where $\varepsilon_c(r_s,\zeta)$ is the electron correlation as a function of density (r_s) and spin polarization (ζ) and $\varepsilon_c^P(r_s)$ is the paramagnetic term, which can be calculated in closed form. Equation I was considered too crude; equation V was favored over equation III for ease of calculation and better "high density behavior." B3LYP, as implemented in Gaussian, uses VWN equation III, whereas BV5LYP of Gaussian uses equation V. Some other software packages use equation V for B3LYP.

As described in the Gaussian 03 manual, a general pattern for DFT calculations is:

P_2*(HF exchange)+P_4*(local exchange)+P_3*(non-local exchange)+P_6*(local correlation)+P_5*(non-local correlation)

B3LYP is a stand-alone Gaussian hybrid functional; parameters P_1-P_6 are built in.

BV5LYP is a user-defined functional made by combining the Becke 88 exchange functional with the V5LYP correlation functional. V5LYP differs from LYP in using VWN equation V rather than equation III for the LSDA portion of local correlation. We defined parameters P_1-P_6 to match the built-in B3LYP values through the IOp entries given in footnotes to Table S2a.

Thus, B3LYP and our implementation of BV5LYP both use the following parameters:

0.20*(HF exchange)+0.80*(local exchange)+0.72*(non-local exchange)+1.00*(local correlation)+0.81*(non-local correlation)

Specifically:

0.20*(HF exchange)+0.80*(Slater exchange)+0.72*(Becke 88)+0.19*(VWN)+0.81*(LYP local + LYP non-local)

The LYP functional provides local (VWN-like) and non-local correlation; the VWN term provides additional local correlation. The LYP functional is described in C. Lee, W. Yang and R. B. Parr, *Phys. Rev. B*, 1988, **37**, 785-789 and B. Miehlich, A. Savin, H. Stoll and H. Preuss, *Chem. Phys. Lett.*, 1989, **157**, 200-206. The Becke 88 functional is described in: A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098-3100. The combination of these functionals into B3PW91 is described in A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652. Modification of B3PW91 by replacing PW91 correlation with LYP correlation is described in P. J. Stevens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623-11627. This paper points out the practical merits of B3LYP, already implemented in Gaussian 92.

References for experimental heats of formation from the NIST WebBook:

Compound	Hf	Phase	Reference
cyclohexen-4-isopropyl-1-methyl (**31**)	-26.48	gas	Kalechits *et al.* 1990
1,1'-bicyclopentyl (**32**)	-42.86	liq	Good and Lee 1976
5-decyne (**34**)	4.46	gas	Rogers *et al.* 1979
bicyclo-5,3,0-decane (**33**)	-31.10	gas	Chang *et al.* 1970
spiro-(4-5)-decane (**30**)	-34.68	gas	Subach and Zwolinski 1975
trans-decalin (**29**)	-43.54	gas	Speros and Rossini, 1960
cis-decalin (**28**)	-40.45	gas	Speros and Rossini, 1960

S.-j. Chang, D. McNally, S. Shary-Tehrany, S. M. J. Hickey and R. H. Boyd, *J. Am. Chem. Soc.*, 1970, **92**, 3109-3118.

W. D. Good and S. H. Lee, *J. Chem. Thermodyn.*, 1976, **8**, 643-650.

G. V. Kalechits, V. A. Luk'yanova, M. P. Kozina and G. L. Gal'chenko, *J. Gen. Chem. USSR*, 1990, **60**, 169-172.

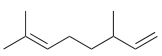
D. W. Rogers, O. A. Dagdagan and N. L. Allinger, *J. Am. Chem. Soc.*, 1979, **101**, 671-676.

D. M. Speros and F. D. Rossini, *J. Phys. Chem.*, 1960, **64**, 1723-1727.

D. J. Subach and B. J. Zwolinski, *J. Chem. Eng. Data*, 1975, **20**, 232-235.

The heat of formation for 1,1'-bicyclopentyl was converted to a gas-phase value by estimating the heat of vaporization from tables of related isomeric substances. For alternative methods of estimating these increments, see: S. W. Benson, *J. Phys. Chem. A*, 1999, **103**, 11481-11485.

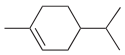
Table S2 Part b mPW1PW91 energies of $C_{10}H_{18}$ isomers relative to 5-decyne (extended conformation) for different basis sets [a] (Corresponds to Table 1)



27 Dihydromyrcene

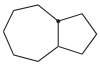
28 cis-Decalin
29 trans-Decalin

30
Spiro[4,5]-decane

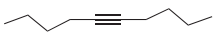


31
Δ^1-*p*-Menthene

32
Dicyclopentyl



33
Bicyclo[5.3.0]-decane



34
5-Decyne

	Energies (kcal/mol) relative to 5-decyne (**34**)						
	27	**28**	**29**	**30**	**31**	**32**	**33**
MPW1K/6-31G*	-6.9	-56.1	-52.9	-48.0	-34.2	-43.2	-42.9
MPW1K/6-31G**		-56.1	-52.9	-48.0	-34.5	-43.3	-43.0
MPW1K/6-31+G**		-53.7	-50.5	-46.0	-33.3	-41.5	-40.9
MPW1K/6-311+G**		-52.0	-48.8	-44.4	-32.2	-39.7	-39.2
MPW1PW91/6-311+G(2d,p)	-7.5	-51.2	-47.9	-43.4	-31.8	-39.2	-38.5
MPW1PW91/6-311+G(2df,2p)				-42.5	-31.3	-38.2	-37.5
MPW1PW91/cc-pVDZ		-56.4	-53.2	-48.0	-34.6	-43.4	-43.4
MPW1PW91/cc-pVTZ		-50.0	-46.7	-42.3	-31.1	-38.3	-37.5

[a] Values for quantum mechanical methods are electron energies. See Table S2a for thermochemistry increments, which are from B3LYP/6-31G* frequency calculations. Energies are for the most stable conformer only.

Comment: This table shows the effect of increasing basis set size on cyclization energies. Larger basis sets give lower (less negative) cyclization energies. Substantial changes result from adding diffuse functions, whereas adding *p* functions to hydrogen had negligible effect. Additional data and discussion on basis set effects are found in Table S7c.

Table S3 Energies of $C_{10}H_{16}$ isomers relative to adamantane from DFT, *ab initio*, and molecular mechanics calculations[a]

	α-Pinene	β-Pinene	Limonene	Proto-adamantane	3-Carene	Camphene	Ocimene	Myrcene
MMX (PCMODEL 8.5, Hf)	39.6	44.6	30.7	10.8	34.4	28.4	47.7	48.0
MM3 (PCMODEL 8.5, Hf)	40.6	46.8	31.0	12.3	42.0	29.1	37.0	43.3
AM1	61.3	62.2	40.4	11.8	53.1	48.0	61.1	63.3
HF/3-21G	52.7	54.3	45.3	12.4	57.4	34.5	66.6	65.9
HF/6-31G*	46.7	49.4	34.7	12.1	41.9	34.1	53.7	54.1
B3LYP/6-31G*	41.2	44.4	30.6	11.0	36.5	30.7	46.3	48.0
B3LYP/6-311+G(2d,p)	38.4	41.0	24.7	10.6	32.8	27.5	37.5	39.1
MPW1K/6-31G*	50.3	53.8	47.2	11.3	47.8	39.0	71.7	73.1
MPW1K/6-311+G(2d,p)	47.3	50.6	41.7	11.0	44.4	35.9	63.7	65.2
mPW1PW91/6-31G*	46.7	48.2	42.0	10.9	43.6	36.0	63.5	65.2
mPW1PW91/6-311+G(2d,p)	43.9	45.1	36.7	10.5	40.3	33.0	55.7	57.4
B3PW91/6-31G*	44.7	48.2	38.7	10.8	41.1	34.3	58.3	60.2
B3PW91/6-311+G(2d,p)	42.1	45.2	33.6	10.4	37.9	31.4	50.9	52.7
B1LYP/6-31G*	41.5	44.6	30.6	11.1	36.8	30.8	46.3	47.8
B1LYP/6-311+G(2d,p)	38.6	41.1	24.5	10.7	33.0	27.6	37.3	38.7
B3P86P/6-31G*	46.0	49.3	40.3	11.0	42.7	35.3	60.8	62.7
B3P86P/6-311+G(2d,p)	43.4	46.3	35.1	10.6	39.5	32.4	53.3	55.1
PBE1PBE/6-31G*	47.5	50.9	43.7	10.9	44.5	36.7	66.1	67.8
PBE1PBE/6-311+G(2d,p)	44.6	47.7	38.3	10.5	41.2	33.5	58.3	60.0
HCTH/6-31G*	37.4	41.4	28.2	10.6	29.5	28.6	42.1	44.0
HCTH/6-311+G(2d,p)	34.0	37.5	22.6	10.0	25.8	25.0	33.9	35.8
VSXC/6-31G*	37.9	39.1	35.3	8.5	40.4	24.3	52.3	52.7
VSXC/6-311+G(2d,p)	35.2	35.7	30.1	8.6	37.4	20.6	45.4	45.2
MP2/6-31G*	46.0	49.5	44.1	11.1	45.7	33.8	66.9	68.2
MP3/6-31G*	46.1	49.6	40.4	11.2	44.1	34.6	62.7	63.5
MP4/6-31G*	44.8	47.7	40.1					62.4
MP2/6-311+G(2d,p)	43.5	46.3	39.5	10.8				61.6
MP3/6-311+G(2d,p)	43.6	46.1	35.2	11.0				56.0
ZPE increment	-4.5	-4.2	-5.1	-0.2	-5.0	-3.7	-7.3	-7.0
ΔH increment	-2.6	-2.6	-2.8	-0.1	-2.9	-2.3	-3.4	-3.9
ΔG increment (unscaled)	-7.0	-6.1	-8.6	-0.4	-7.7	-5.5	-13.3	-12.6
Relative entropy (cal/K-mol)	14.2	11.2	18.8	1.1	15.7	10.1	30.6	28.8

[a] Values for quantum mechanical methods are electron energies; thermochemistry increments are from B3LYP/6-31G* frequency calculations. Energies are for the most stable conformer only. The relative ΔG values are unscaled.

Comment: Table S3 shows the same trends as Table S2a, i.e. underestimation of cyclization energies by B3LYP, overestimation by MPW1K, and reasonable agreement with mPW1PW91 (although this is obscured by the referencing to adamantane energies). Because reliable benchmark energies were unavailable from either experiment or G3 calculation, RMSD and MSE statistics are not given. Many of the MM3 values are in reasonable agreement with mPW1PW91/6-311+G(2d,p) enthalpies, but some MM3 values suffer from inadequate parameterization.

Table S4 Energies of $C_{10}H_{16}O$ isomers relative to geraniol (**35**, extended conformation) from DFT, *ab initio*, and molecular mechanics calculations[a]

	Cineole	Isoborneol	Borneol	Myrtanol	Nerol	1-Decalol	Isopino-campheol
	45	**46**	**47**	**48**	**49**	**50**	**51**
	Energies relative to geraniol, kcal/mol						
MMX (PCMODEL 8.5, Hf)	-31.5	-23.0	-23.3	-2.9	0.8	-37.6	-6.4
MM3 (PCMODEL 8.5, Hf)	-32.5	-25.8	-26.5	-2.9	-0.3	-40.4	-6.4
AM1	-12.6	-8.6	-7.8	7.1	0.8	-37.0	7.6
HF/3-21G	-46.5	-36.8	-36.1	-7.8	-0.8	-52.5	-10.4
HF/6-31G*	-33.7	-20.7	-20.8	0.0	0.0	-42.0	-2.2
B3LYP/6-31G*	-31.2	-18.8	-18.2	2.0	-1.1	-37.3	-1.3
B3LYP/6-311+G(2d,p)	-19.8	-12.5	-12.3	7.2	0.0	-30.2	4.3
MPW1K/6-31G*	-45.9	-36.5	-36.0	-13.8	-1.4	-54.1	-16.9
MPW1K/6-311+G(2d,p)	-36.0	-31.2	-31.0	-9.3	-0.7	-48.0	-12.1
mPW1PW91/6-31G*	-41.0	-31.2	-30.6	-9.2	-1.3	-48.4	-12.5
mPW1PW91/6-311+G(2d,p)	-30.8	-25.9	-25.7	-4.8	-0.6	-42.2	-7.8
B3PW91/6-31G*	-37.4	-27.2	-26.6	-5.8	-0.7	-44.5	-9.0
B3PW91/6-311+G(2d,p)	-27.3	-22.1	-21.9	-1.5	-0.1	-38.4	-4.4
B1LYP/6-31G*	-31.2	-18.6	-18.0	2.2	-1.0	-37.4	-1.1
B1LYP/6-311+G(2d,p)	-19.7	-12.1	-12.0	7.6	0.1	-30.1	4.7
B3P86P/6-31G*	-39.8	-29.5	-28.8	-7.5	-1.3	-46.9	-10.9
B3P86P/6-311+G(2d,p)	-29.7	-24.3	-24.0	-3.2	-0.6	-40.8	-6.2
PBE1PBE/6-31G*	-42.9	-33.6	-32.9	-11.2	-1.7	-50.5	-14.6
PBE1PBE/6-311+G(2d,p)	-32.7	-28.4	-28.1	-6.9	-0.9	-44.2	-10.0
HCTH/6-31G*	-25.1	-14.8	-14.2	4.2	-0.6	-32.6	0.8
HCTH/6-311+G(2d,p)	-14.6	-9.4	-9.4	8.4	0.4	-25.9	5.2
VSXC/6-31G*	-47.9	-48.0	-45.9	-16.7	-9.7	-50.9	-21.4
VSXC/6-311+G(2d,p)	-39.8	-44.1	-42.7	-13.4	-11.1	-46.3	-18.6
MP2/6-31G*	-47.2	-39.3	-38.7	-14.1	-3.5	-52.8	-17.8
MP3/6-31G*	-42.9	-33.4	-33.0	-10.2	-2.6	-50.1	-13.6
ZPE increment (scaled)	3.3	3.3	3.1	3.2	0.4	4.8	2.9
ΔH increment	1.3	1.3	1.2	1.4	0.1	2.3	1.1
ΔG increment (unscaled)	8.0	8.4	8.0	7.6	1.3	10.2	7.5
Relative entropy (cal/K-mol)	-22.3	-23.8	-22.8	-20.3	-3.9	-26.3	-21.3

[a] Values for quantum mechanical methods are electron energies; thermochemistry increments are from B3LYP/6-31G* frequency calculations. Energies are for the most stable conformer only. The relative ΔG values are unscaled.

Comment: Table S4 shows the same trends as Table S2a, i.e. underestimation of cyclization energies by B3LYP, overestimation by MPW1K, and reasonable agreement with mPW1PW91. Because reliable benchmark energies were unavailable from either experiment or G3 calculation, RMSD and MSE statistics are not given. Nevertheless, the MM3 values are in rather good agreement with mPW1PW91/6-311+G(2d,p) enthalpies (unlike in Table S3, where some MM3 values suffered from inadequate parameterization).

Table S5 Comparison of relative energies predicted by various DFT, *ab initio*, and molecular mechanics methods for a series of methylated derivatives of ethylene oxide and their isomers[a] (Corresponds to Table 2)

Part a C_2H_4O isomers, C_3H_6O isomers, and C_4H_8O isomers:

C_2H_4O isomers: acetaldehyde (**52**) and ethylene oxide (**53**)

C_3H_6O isomers: acetone (**54**), propylene oxide (**55**), propanal (**56**), and oxetane (**57**)

C_4H_8O isomers: 2-butanone (**58**), cyclobutanol (**59**), *trans*-2,3-dimethyloxirane (**60**), cis-2,3-dimethyloxirane (**61**), and tetrahydrofuran (**62**)

	C_2H_4O isomers		C_3H_6O isomers				C_4H_8O isomers				
	52	**53**	**54**	**55**	**56**	**57**	**58**	**59**	**60**	**61**	**62**
	Relative Energy (kcal/mol)										
Experimental Hf	0.0	28.2	0.0	29.6	7.1	33.0	0.0	22.4	26.8	27.8	13.0
MMX (PCMODEL)	0.0	28.2	0.0	31.7	7.8		0.0	38.5	28.4	30.1	10.8
MM3 (PCMODEL)	0.0	27.7	0.0	28.3	7.2	33.1	0.0	23.2	22.8	24.3	12.1
G3B3	0.0	27.2	0.0	29.2	7.7	32.6	0.0	22.8	24.4	25.7	13.4
CCSD(T)/6-31+G**	0.0	27.4	0.0	29.4	7.4	32.2					
CCSD(T)/6-311+G**	0.0	28.2	0.0	30.0	6.9	32.1	0.0	22.0	25.7	27.1	12.8
HF/ 6-31G*	0.0	30.7	0.0	33.2	7.5	33.3	0.0	29.8	29.1	30.7	13.5
B3LYP/6-31G*	0.0	27.5	0.0	29.6	7.7	31.8	0.0	29.1	25.0	26.4	13.3
B3LYP/6-311+G(2d,p)	**0.0**	**28.8**	**0.0**	**31.3**	**7.8**	**33.7**	**0.0**	**25.7**	**26.6**	**27.9**	**14.9**
mPW1/6-31G*	0.0	24.6	0.0	26.9	7.8	28.9	0.0	24.4	22.5	23.9	9.8
mPW1/91/6-311+G(2d,p)	**0.0**	**25.7**	**0.0**	**28.3**	**7.9**	**30.3**	**0.0**	**21.0**	**23.7**	**25.0**	**10.9**
MP2/6-31G*	0.0	27.1	0.0	28.9	7.6	32.9	0.0	26.8	24.3	25.7	12.9
MP2/6-311+G**	0.0	27.6	0.0	29.4	7.0	32.8	0.0	21.0	24.8	26.2	12.8
MP3/6-311+G**	0.0	26.9	0.0	29.0	7.0	30.4	0.0	19.8	24.8	26.2	10.9
MP4/6-311+G**	0.0	28.4	0.0	30.3	6.9	32.2	0.0	22.3	26.0	27.4	12.9
CCSD(T)/cc-pVDZ	0.0	30.0									
CCSD(T)/cc-pVTZ	0.0	26.8									
ZPE increment	0.0	1.1	0.0	1.2	0.5	2.1	0.0	1.6	0.6	0.7	2.6
ΔH increment	0.0	0.6	0.0	0.5	0.3	1.3	0.0	0.7	0.2	0.2	1.6
ΔG increment	0.0	1.7	0.0	2.2	0.7	2.8	0.0	3.3	2.0	2.0	3.8
Relative entropy	0.0	-3.4	0.0	-5.5	-1.3	-5.2	0.0	-8.8	-6.2	-6.0	-7.5

[a] For quantum mechanical methods, thermochemistry increments are from B3LYP/6-31G* frequency calculations. The ΔH and ΔG values are appropriately scaled in part. For comparison, B3LYP and mPW1PW91 energies with the 6-311+G(2d,p) basis set are shown in boldface type.

Table S5 Part b $C_5H_{10}O$ isomers and $C_6H_{12}O$ isomers: [a]

$C_5H_{10}O$, methyl isopropyl ketone (**63**), trimethyloxirane (**64**), cyclopentanol (**65**), 2*H*-tetrahydropyran (**66**)

$C_6H_{12}O$, methyl *t*-butyl ketone (**67**), tetramethyloxirane (**68**), cyclohexanol (**69**), and 1-methylcyclopentanol (**70**)

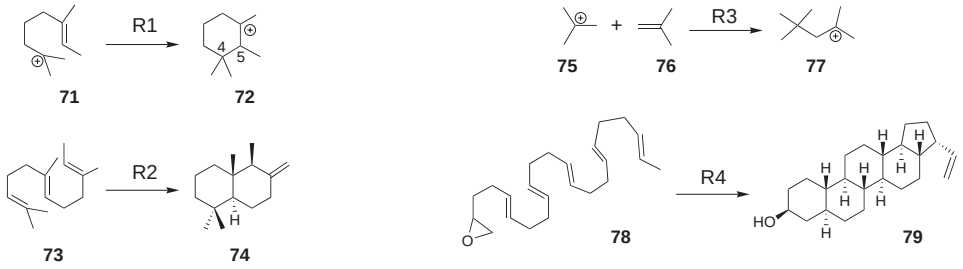
	$C_5H_{10}O$ isomers				$C_6H_{12}O$ isomers			
	63	**64**	**65**	**66**	**67**	**68**	**69**	**70**
	Relative Energy (kcal/mol							
Experimental Hf	0.0	23.8	4.8	9.3	0.0	20.1	0.9	1.5
MMX (PCMODEL)	0.0	25.3	2.9	6.8	0.0	23.3	-2.3	0.1
MM3 (PCMODEL)	0.0	19.7	3.6	8.6	0.0	19.7	-0.2	1.8
G3B3	0.0	20.8	4.5	9.4	0.0	19.9	0.6	2.6
CCSD(T)/6-31+G**	0.0	21.4	4.4	8.3	0.0	20.6	0.0	2.4
HF/ 6-31G*	0.0	26.0	9.5	8.0	0.0	24.4	2.1	6.9
B3LYP/6-31G*	0.0	21.4	10.2	7.7	0.0	19.2	3.1	7.7
B3LYP/6-311+G(2d,p)	**0.0**	**23.0**	**6.9**	**10.0**	**0.0**	**20.7**	**0.2**	**4.4**
mPW1/6-31G*	0.0	19.1	5.3	4.4	0.0	17.2	-1.5	3.0
mPW1/6-311+G(2d,p)	**0.0**	**20.1**	**1.9**	**6.1**	**0.0**	**18.1**	**-4.6**	**-0.6**
MP2/6-31G*	0.0	20.7	7.0	8.2	0.0	19.8	2.7	5.5
MP3/6-31G*	0.0	20.7	5.0	6.1	0.0	19.5	-0.4	3.0
MP2/6-31+G**	0.0	20.4	3.5	8.5	0.0	19.8	-0.4	1.8
MP3/6-31+G**	0.0	20.6	2.0	6.3	0.0	19.7	-3.0	-0.2
MP4/6-31+G**	0.0	21.6	4.4	8.1	0.0	20.7	-0.3	2.4
ZPE increment (scaled)	0.0	0.2	2.5	3.4	0.0	-0.1	3.4	-0.1
ΔH increment	0.0	-0.1	1.5	2.0	0.0	-0.1	2.1	-0.1
ΔG increment	0.0	1.2	3.6	5.6	0.0	0.0	5.2	0.0
Relative entropy	0.0	-4.2	-7.2	-12.0	0.0	-0.5	-10.1	-0.5

[a] See footnote for Table S5a.

Comments:

1. Table S5 shows relative energy differences for individual compounds, whereas Table 2 showed only a statistical summary. These results show that the B3LYP energies for conversion of a double bond to two single bonds are too positive. For ease of comparison, the relevant rows of B3LYP and mPW1PW91 energies are highlighted in boldface.
2. These transformations are rather different from the olefin cyclizations, and the trends are not entirely parallel. For example, the MP2 energies for olefin cyclizations were too negative but here are too positive. For these transformations, the mPW1PW91 energies were consistently too negative (and by about the same amount that the B3LYP energies were too positive).
3. The G3B3 energies appear to be quite accurate, and we considered these as more reliable when they differed substantially from experimental values.

Table S6 Predicted electron energies for model reactions related to (oxido)squalene cyclization [a] (Corresponds to Table 3)



	Reaction				
	R1-3.8 Å	R1-3.28 Å	R2	R3	R4
	Reaction energies for cation-olefin addition or cyclization (kcal/mol)				
MM3-94			-27.5		-106.3
MMX (PCMODEL 8.5)			-30.3		-108.8
MM3 (PCMODEL 8.5)			-26.7		-106.5
AM1	-11.3	-11.9	-17.6	-16.8	-109.2
HF/3-21G	-25.1	-22.1	-34.5		-121.1
HF/6-31G*	-16.8	-14.5	-21.1	-19.3	-90.8
B3LYP/6-31G*	-15.6	-12.2	-19.6	-22.7	-86.1
B3LYP/6-31+G*		-11.6	-17.3		
B3LYP/6-31+G**		-11.2	-17.1		
B3LYP/6-311+G(2d,p)	-12.8	-10.1	-14.0	-18.0	-77.9
B3LYP/6-311+(G(3df,2p)		-10.0	-13.5		
MPW1K/6-31G*	-24.8	-20.9	-37.8	-29.8	-125.2
MPW1K/6-311+G(2d,p)	-22.0	-18.8	-33.1	-25.8	-119.1
mPW1PW91/6-31G*	-21.7	-17.8	-31.9	-28.0	-112.2
mPW1PW91/6-311+G(2d,p)	-19.0	-15.9	-27.2	-23.8	-106.0
MP2/6-31G*	-27.7	-23.0	-43.9	-32.1	-124.1
MP3/6-31G*	-24.0	-20.2	-38.1	-28.5	
MP4/6-31G*	-25.6	-21.0		-30.1	
G3MP2B3 enthalpy	-21.6			-26.3	
G3MP2B3 free energy	-18.9			-10.9	
ZPE increment	2.7	2.4	4.7	3.8	9.9
ΔH increment	2.1	1.8	2.2	*3.1	5.5
ΔG increment	4.7	3.8	11.8	*18.1	22.3
Relative entropy	-8.8	-6.7	-32.0	-51.9	-56.4

[a] For quantum mechanical methods, geometries and frequencies are from B3LYP/6-31G* calculations. G3MP2B3 values are enthalpies. In reaction R1, the C4-C5 bond of the reactant was frozen at either 3.8 Å or 3.28 Å, as indicated in the heading. Force-field energies were not calculated for cationic species. The ΔH and ΔG increments marked by an asterisk were calculated without consideration for the difference in the number of reactants and products.

Comment: Relative to Table 3, this table shows energies with additional theoretical methods or basis sets. These data show some details of the effects of increasing basis set size. Also, relative entropies and G3MP2B3 free energies are shown. Overall, this table supports the data in Table 3 but does not provide additional insights.

Table S7 Part a Energies (kcal/mol) for cyclization of neutral (oxido)squalene to neutral tetra- and pentacyclic triterpenes [a,b] (Corresponds to Table 4)

	Oxidosqualene				Squalene	SqualeneX
	Hopen-3β-ol	Lupeol	Lanosterol	Cycloartenol	Hopene	Hopene
	Cyclization energies (kcal/mol)					
MM3-94	-55.6	-66.8	-61.3		-44.2	[c]
MM3 (PCMODEL)	-54.0	-64.5	-56.5		-42.7	[c]
MMX (PCMODEL)	-61.3	-72.2	-68.5		-54.7	[c]
AM1	-50.5	-59.7	-58.5	-46.0	-24.9	-24.9
HF/6-31G*	-31.1	-41.5	-38.5	-29.2	-26.8	-29.3
B3LYP/6-31G*	-31.1	-39.4	-35.9	-25.7	-29.0	-31.0
B3LYP/6-311+G(2d,p)	-22.9	-32.1	-30.0	-18.6	-14.8	-16.6
BV5LYP/6-31G*	-30.4	-38.7	-35.4	-25.1		
MPW1K/6-31G*	-73.4	-82.2	-69.6	-64.4	-73.9	-75.6
MPW1K/6-311+G(2d,p)	-67.9	-76.7	-65.1	-58.6	-62.3	-64.0
mPW1/6-31G*	-59.6	-67.9	-58.4	-52.0	-60.2	-61.9
mPW1/6-311+G(2d,p)	-54.3	-62.7	-54.7	-46.5	-48.5	-50.2
ZPE increment	10.4	10.8	7.6	8.5	11.1	11.4
ΔH increment	5.6	5.7	4.1	4.5	6.3	6.9
ΔG increment	26.8	26.4	19.9	21.4	26.6	26.5
Relative entropy (cal/mol-K)	-71.0	-70.3	-53.2	-56.7	-67.4	-64.5

[a] Values for quantum mechanical methods are electron energies; geometries and frequencies are from B3LYP/6-31G* calculations. BV5LYP is defined in the footnotes and comments to Table S2a. [b] Energies are relative to the appropriately coiled (oxido)squalene except that lanosterol and cycloartenol energies are compared to oxidosqualene coiled for lupeol formation. Lanosterol and cycloartenol were modeled with the same non-extended side chain conformer (arbitrarily chosen). Energies are given for the C-ring boat conformer of cycloartenol, but C-ring chair data are given below. SqualeneX is a squalene conformer derived from 2-azasqualene in an X-ray crystal structure in SHC;[8] the terminal Me_2C=CH- group was constructed manually, followed by B3LYP/6-31G* optimization in which carbon coordinates beyond C5 were frozen. Thus, thermodynamic increments (notably entropies) may be misleading. [c] MM3 and MMX energies were not calculated for SqualeneX because fixing numerous coordinates in a force-field optimization is not practical or meaningful in this context.

Table S7 Part b Comparison of electron energies for (a) extended and folded forms of oxidosqualene and (b) the ring-C chair and ring-C boat forms of cycloartenol [a]

	OxSqual-Extend – OxSqual-Fold	OxSqual-Hairpin – OxSqual-Fold	Cycloart C-boat – OxSqual-Fold	Cycloart Cchair–Cboat
		Relative energies (kcal/mol)		
HF/6-31G*	-2.6	1.0	-29.2	3.2
B3LYP/6-31G*	-2.7	-0.8	-25.7	2.0
B3LYP/6-311+G(2d,p)	-3.7	1.5	-18.6	1.3
MPW1K/6-31G*	-1.9	-1.3	-64.4	2.0
MPW1K/6-311+G(2d,p)	-2.3		-58.6	1.4
mPW1PW91/6-31G*	-2.2	-1.3	-52.0	1.9
mPW1PW91/6-311+G(2d,p)	-2.7		-46.5	1.2
ZPE increment	-2.7		8.5	0.2
ΔH increment	-1.4		4.5	0.1
ΔG increment	-6.2		21.4	0.1
Relative entropy (cal/mol-K)	16.0		-56.7	0.1

[a] Values for quantum mechanical methods are electron energies; geometries and frequencies are from B3LYP/6-31G* calculations. The extended oxidosqualene conformer and the cycloartenol ring-C boat have the lower energies. Abbreviations: OxSqual, 2,3-oxidosqualene; Extend, extended conformation; Fold, folded conformation; Cycloart, cycloartenol. A partially extended conformation of oxidosqualene contains a *gauche* bond leading to a hairpin shape; the DFT energies do not reflect the favorable dispersion energies from close alignment of the chains.

Comments for Table S7a and S7b:

1. These tables give relative entropy data and energies for some additional basis sets.
2. Table S7b shows that folded and extended conformers of oxidosqualene differ in energy by only about 3 kcal/mol. The hairpin conformer is intermediate in energy.
3. Table S7b also shows the relative energies of two major cycloartenol conformers, the C-ring chair and boat. The chair conformer is only about 1 kcal/mol higher in energy than the chair. This is consistent with unpublished results by Guo, Wilson, and Shackleton that comparison of experimental ($CDCl_3$ solution) and empirically corrected quantum mechanical ^{1}H and ^{13}C NMR predictions indicate a ca. 5:1 mixture of boat and chair conformers. The difference in flatness between these conformers is possibly of some relevance to the enzymatic mechanism (although it appears that cyclases can readily accommodate both flat and arced conformers).
4. Table S7a shows the same effect observed in Table S2a from using VWN equation V versus III. Compared with B3LYP energies, BV5LYP energies were slightly more positive, the increment depending on the number of rings formed: 0.72 kcal/mol for hopen-3β-ol and lupeol; 0.61 kcal/mol for cycloartenol, and 0.55 kcal/mol for lanosterol.

Table S7 Part c Energies for formation of hopene (squaleneX side chain) from various conformers of squalene [a]

Squalene conformer:	Folded	Extended-1	Extended-2	SqualeneX
	Cyclization energy from squalene to hopene (kcal/mol)			
AM1	-24.9	-20.5	-20.4	-24.9
HF/3-21G	-59.5	-56.3	-56.4	-61.5
HF/6-31G*	-26.8	-24.1	-24.1	-29.3
B3LYP/6-31G*	-29.0	-26.1	-26.1	-31.0
B3LYP/6-31G**	-29.1	-26.3	-26.3	
B3LYP/6-31+G**	-22.2	-18.7	-18.7	
B3LYP/6-311+G(2d,p)	-14.8	-11.1	-11.1	-16.6
B3LYP/6-311+G(2df,2p)		-8.3	-8.3	
MPW1K/6-31G*	-73.9	-71.7	-71.7	-75.6
MPW1K/6-311+G(2d,p)	-62.3	-59.8	-59.9	-64.0
MPW1PW91/6-31G*	-60.2	-57.6	-57.6	-61.9
MPW1PW91/6-311+G(2d,p)	-48.5	-45.7	-45.7	-50.2
ZPE increment	11.1	11.1	11.1	11.4
ΔH increment	6.3	5.4	5.4	6.9
ΔG increment	26.6	28.9	28.8	26.5
Relative entropy (cal/mol-K)	-67.4	-249.5	-249.5	-64.5

[a] Values for quantum mechanical methods are electron energies; geometries and frequencies are from B3LYP/6-31G* calculations. For the "X-ray" conformer, carbon atoms beyond C5 were frozen in the position observed in the 2-azasqualene/SHC crystal structure.[8]

Comments for Table S7c:

1. The squalene conformer fully folded for hopene synthesis was about 3 kcal/mol less stable than extended conformers and about 2 kcal/mol more stable than a partially folded conformer corresponding to the 2-azasqualene-SHC crystal structure.[8] Because of the many frozen torsion angles in the partially folded conformer and the neglect of enzyme-substrate interactions, these energy differences are not physically meaningful but indicate the modest influence of substrate conformation on cyclization energy.

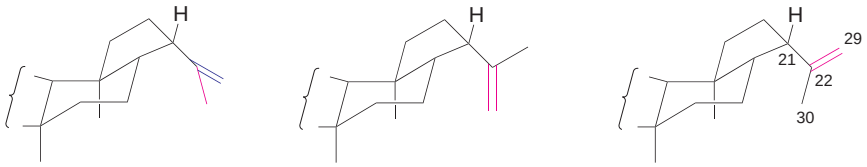
2. Energies in Table S7c were used to establish that the ZPE-corrected B3LYP/6-311+G(2d,p) energy for cyclization of squalene (extended conformer) to hopene is positive. This calculation requires consideration of the Boltzmann distribution of energies for hopene. There are three side-chain conformers for hopene, denoted as X, Y, and Z, with relative energies of 0.10, 0.12, and 0.00 kcal/mol (B3PW91/6-311G(2d,p)//B3LYP/6-31G*). On this scale, the Boltzmann distribution gives an energy of 0.069 kcal/mol. Thus, for cyclization of extended conformer 1 to hopene (Boltzmann average), the ZPE-corrected energy is –11.059 + 11.142 –0.069 = 0.014 kcal/mol. The crossover from exothermic to endothermic occurs at the B3LYP/6-311+G(2d,p) basis set level, the exact result depending on which squalene and

hopene conformers (for the Boltzmann average) are considered appropriate for the reaction environment. For larger basis sets, such as 6-311+G(2df,2p), the B3LYP prediction of endothermicity is unambiguous.

3. The exothermicity of cyclization energies decreases markedly as basis size increases. The magnitude of this effect slightly smaller in going from B3LYP to mPW1PW91 to MPW1K. The basis set dependence of the cyclization energies is especially strong for conversion of squalene to hopene. The effect is roughly halved for conversion of oxidosqualene to hopen-3β-ol, lupeol, or lanosterol (see Table S7a). The magnitude of the basis set dependence increases with the number of rings formed (Table S8). Similar data on basis set effects for $C_{10}H_{18}$ models are given in Table S2b.

4. Because of the strong basis set dependence of cyclization energies (discussed in comment #3), the choice of optimal DFT method for cyclization energies is rather arbitrary. Our choice of mPW1PW91 works well only for 6-311+G(2d,p) or a slightly larger basis set. Smaller or larger basis sets give substantial deviations from accuracy. Similarly, changing the amount of exact HF exchange would lead to inaccurate energy predictions (see Table S7e below). With more powerful computers that would allow use of a 6-311+G(2df,2p) or cc-pVTZ basis set, we might have chosen a different DFT method for cyclization energy calculations. However, mPW1PW91 does appear to be a robust method that performs well in many applications ranging from our geometry optimizations to NMR calculations (see K. B. Wiberg, *J. Comput. Chem.*, 1999, **20**, 1299-1303).

Table S7 Part d Relative electron energies for hopene side-chain conformers [a]



Conformer-X Conformer-Y Conformer-Z

	B3LYP/ 6-31G*	B3PW91/ 6-311G(2d,p)	Me-H torsion	CH_2-H torsion	Me orientation
Conformer X	0.12	0.10	35.3	-141.2	front
Conformer Y	0.18	0.12	-41.7	139.2	up/back
Conformer Z	0.00	0.00	-174.1	6.0	down

[a] The Me-H and CH_2-H torsion angles refer to C30-C22-C21-H21 and C29-C22-C21-H21. Magenta and blue bonds are directed toward and away from the viewer, respectively.

Comment: The hopene conformers have similar energies, corresponding to a Boltzmann distribution of about 3:3:4. This conformational heterogeneity has little effect on calculating the exothermicity of squalene cyclization to hopene.

Table S7 Part e mPWPW91 energies of β-pinene and adamantine relative to myrcene for various amounts of exact HF exchange[a]

	β-Pinene vs. Myrcene		Adamantane vs. Myrcene	
% HF	6-31G*	6-311+G(2d,p)	6-31G*	6-311+G(2d,p)
20	-13.8	-9.2	-62.8	-55.1
25	-14.9	-10.4	-65.0	-57.3
30	-16.1	-11.5	-67.2	-59.5
35	-17.3	-12.7	-69.4	-61.6
40	-18.5	-13.8	-71.6	-63.8
42.8	-19.2	-14.5	-72.9	-65.0
45	-19.7	-15.0	-73.8	-65.9
50	-20.9	-16.2	-76.0	-68.1
60	-23.2	-18.5	-80.4	-72.3

[a] Values of exact HF exchange (% HF) corresponding to MPW1PW91 and MPW1K are shown in red. Energies were calculated in Gaussian 03.

Comments for Table S7e:

1. This table illustrates how the cyclization energy can be increased by increasing the percentage of exact HF exchange.
2. For both basis sets, the β-pinene energies increased by 1.2 kcal/mol for each 5% increase in exact HF exchange. The increase for adamantane energies was 2.2 kcal/mol. Because cyclizations differ markedly in their sensitivity to the effect of % HF exchange on reaction energy, modifying the percentage of HF exchange in a DFT functional is only a crude tool for optimizing cyclization energies.
3. These $C_{10}H_{18}$ results are described here with the triterpene data because cyclization energies have a dependence on both HF exchange and basis set size (discussed immediately above).

Table S8 Relative electron energies for cationic species in the three major pathways for oxidosqualene cyclization (Corresponds to Table 5) [a]

	Hopen-3β-ol formation					Lupeol formation			Lanosterol formation				
Number of rings	1	2	3	4	5	3	4	5	2	3	4-C20	4-C9	4-C8
AM1	-32.0	-42.5	-47.3	-49.2	-48.5	-45.9	-53.5	-62.5	-37.2	-39.8	-41.0	-60.4	-52.8
HF/6-31G*	-19.7	-32.1	-35.7	-35.3	-36.2	-36.1	-42.7	-49.1	-23.9	-25.2	-25.9	-45.5	-40.0
B3LYP/6-31G*	-17.8	-31.5	-36.6	-38.6	-38.6	-36.3	-41.5	-47.8	-23.5	-26.9	-28.0	-40.6	-36.8
B3LYP/6-311+G(2d,p)	-16.9	-27.6	-30.0	-29.1	-27.1	-30.0	-32.5	-36.6	-19.8	-18.0	-16.4	-32.1	-28.4
MPW1K/6-31G*	-24.8	-47.1	-60.0	-71.1	-80.3	-59.7	-74.9	-90.4	-39.0	-49.6	-60.5	-75.8	-71.4
MPW1K/6-311+G(2d,p)	-23.8	-43.8	-54.2	-63.2	-70.4	-54.4	-67.3	-81.1	-35.9	-43.8	-51.4	-68.1	
mPW1/6-31G*	-22.4	-42.2	-53.0	-61.4	-67.5	-52.4	-64.3	-77.0	-34.2	-42.9	-50.7	-64.3	-60.3
mPW1/6-311+G(2d,p)	-21.5	-38.9	-47.2	-53.7	-57.7	-47.3	-57.2	-67.9	-30.7	-37.6	-43.6	-56.7	-53.2
ZPE increment	1.1	3.6	5.1	7.4	9.5	5.3	7.2	9.4	3.1	4.8	7.9	6.6	6.9
ΔH increment	0.3	1.7	2.5	3.7	4.9	3.1	4.1	5.2	1.8	2.8	4.5	3.5	3.9
ΔG increment	4.8	10.1	13.9	19.9	24.8	13.4	18.0	23.8	8.6	12.1	19.1	17.2	17.7
Relative entropy	-15.4	-28.0	-38.5	-54.2	-66.7	-34.5	-46.3	-62.3	-22.8	-31.0	-48.9	-45.9	-46.3

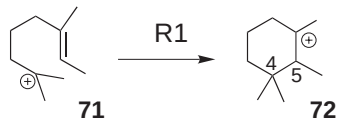
[a] Cyclization energies (kcal/mol) or entropy (cal/mol-K) relative to the protonated oxidosqualene conformer that is folded to form hopene or lupeol (also used for lanosterol formation). Geometries and frequencies are from B3LYP/6-31G* calculations. Energy differences of (protonated) oxidosqualene folded for lupeol and hopen-3β-ol synthesis were negligible. One bond was frozen at 3.8 Å for monocycles (C9-C10) and bicycles (C8-C14); other structures were energy minima. Lanosterol intermediates were modeled with the same non-extended side chain used for lanosterol calculations in Table 4. [b] For lanosterol formation, column headings 4-C8, 4-C9, and 4-C20 denote the lanosteryl C8, lanosteryl C9, and protosteryl cations, respectively.

Comments:

1. This table gives energies for the important C8 lanosteryl cation, which is the final cation before deprotonation in lanosterol synthesis (at least with the human enzyme). In cycloartenol and parkeol synthesis, the C9 lanosteryl cation is the final cation.

2. mPW1PW91/6-311+G(2d,p)//B3LYP/6-31G* calculations showed the flat C9 lanosteryl cation to be 3.9 kcal/mol lower in enthalpy than the slightly arced C8 cation because the 9β-hydrogen of the C8 cation enforces an unfavorable non-chair conformation for rings B and C. Cycloartenol can adopt a flat conformation in which ring C is a twist/boat or an arced shape in which ring C is a chair.[35] Although a recent NMR study[35] concluded that the arced C-chair conformer "does not exist," comparison of observed NMR shieldings in $CDCl_3$ solution with shieldings from empirically corrected GIAO predictions indicates that cycloartenol exists as a ca. 5:1 mixture of the C-boat and C-chair conformers (Guo, L.-W.; Wilson, W. K.; Shackleton, C. H. L., unpublished results). This result is consistent with the expected Boltzmann distribution, in which the arced conformer is about 1 kcal/mol higher in energy. If positions of C3 and C17 are fixed, arcing raises the position of C9 by roughly 1.5 Å in cycloartenol (ring-C chair vs. ring-C boat conformer) and roughly 1 Å in lanosterol species (C8 cation vs. C9 cation or neutral product). The active site cavity of lanosterol synthase[9a] can clearly accommodate the flat lanosterol structure and presumably its somewhat arced precursors with a 9β hydrogen. The later steps of enzymatic lanosterol and cycloartenol synthesis are probably governed by gas-phase energetics and proximity of the cation to a deprotonating moiety rather than by the ability of the enzyme to discriminate between flat and arced conformers.

Table S9 Relative energies and geometry changes during A-ring formation in a small model for hopene synthesis (conversion of **71** to **72**, corresponds to Fig. 2) [a]



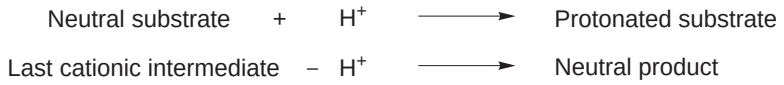
71 **72**

	Energy relative to cyclized product (kcal/mol)			Geometry changes during ring closure		
C4-C5 Distance (Å), frozen	HF 3-21G	B3LYP 6-31G*	mPW1 6-311+G(2d,p)	C4-C10 (Å)	C4-C5-C10 (°)	C4-C10-C5 (°)
1.685	0.0	0.0	0.0	2.462	103.1	41.8
1.8	2.7	0.7	1.3	2.485	99.8	45.5
2.0	7.7	3.1	4.5	2.520	93.8	52.4
2.2	11.4	4.9	6.9	2.563	88.1	59.1
2.4	14.1	6.3	8.8	2.626	83.4	65.2
2.6	16.3	7.4	10.4	2.697	78.9	71.1
2.8	18.2	8.7	12.0	2.771	74.6	77.0
3.0	19.7	10.1	13.7	2.859	70.8	82.4
3.2	21.1	11.7	15.3	2.955	67.3	87.5
3.28	21.6	12.2	15.9	2.999	66.1	89.4
3.4	22.2	13.1	16.6	3.066	64.3	92.1
3.6	23.3	14.4	17.8	3.191	61.8	96.2
3.8	24.5	15.6	19.0	3.310	58.9	100.5
4.0	25.0	16.8	20.3	3.429	55.9	105.0
4.2	24.1	17.1	20.3	3.876	66.9	94.4
4.4	23.5	15.0	18.2	4.157	70.8	91.2
4.6	22.9	14.6	18.2	4.258	67.0	96.0

[a] Energies, distances, and angles are from B3LYP/6-31G* geometries except for HF/3-21G//HF/3-21G energies.

Comments: This small model indicates no energy barrier for annulation to a 6-membered ring. However, energy minima have occasionally been reported for larger models. [7b,7o] Hess and Smentek[7o] modeled the cyclization of (oxido)squalene toward the protosteryl cation and found shallow minima on this path. However, they doubted any significant role for these minima, which may not survive at higher levels of theory. In our calculations, a $C_{30}H_{51}O^{+}$ conformer of protonated oxidosqualene folded for lupeol formation represented a local energy minimum, with a C4-C5 distance of 3.63 Å. At a C4-C5 distance of 3.24 Å (the separation in Hess and Smentek's transition state[7o]), the energy was 0.7 kcal/mol higher.

Table S10 Energetics for substrate protonation and deprotonation of the final cation for the following reactions [a]



	Protonation energy + Deprotonation energy				Protonation energy E(protonated substrate)-E(neutral substrate)		Deprotonation energy E(neutral product)-E(last cation)			
	Hopen-3β-ol	Lupeol	Lano-sterol	Cyclo-artenol	Oxidosqualene (for hopenol)	Oxidosqualene (for lupeol)	Hopen-3β-ol	Lupeol	Lano-sterol	Cyclo-artenol
HF/3-21G	-7.9	-6.9	-11.0	8.4	-227.2	-227.3	219.4	220.4	216.3	235.7
HF/6-31G*	5.1	7.6	1.5	16.3	-214.8	-214.5	219.9	222.1	216.0	230.9
B3LYP/6-31G*	7.4	8.4	0.9	14.8	-214.6	-214.5	222.1	222.9	215.4	229.3
B3LYP/6-311+G(2d,p)	4.2	4.4	-1.6	13.5	-214.8	-214.6	219.0	219.0	213.0	228.1
MPW1K/6-31G*	6.9	8.3	1.8	11.4	-212.8	-212.7	219.7	221.0	214.6	224.1
MPW1K/6-311+G(2d,p)	2.5	4.4	-0.9	9.5	-215.0	-214.8	217.5	219.2	214.0	224.3
mPW1/6-31G*	7.9	9.1	1.9	12.4	-213.6	-213.5	221.5	222.6	215.5	225.9
mPW1/6-311+G(2d,p)	**3.4**	**5.1**	**-1.4**	**10.3**	-214.8	-214.6	218.2	219.7	213.2	224.9
ZPE	1.0	1.0	0.7	2.0	7.3	7.3	-6.3	-6.3	-6.6	-5.3
ΔH increment	0.7	0.3	0.2	1.0	7.7	7.1	-6.9	-6.8	-6.9	-6.1
ΔG increment	2.0	2.7	2.2	4.2	7.7	8.4	-5.7	-5.7	-6.2	-4.2

[a] Energies ("E", kcal/mol) do not include the 5/2RT enthalpy of the proton (this cancels out for columns 2-5). Thermochemical increments do not include the effect of different number of particles in the reactions. The most reliable values are the mPW1PW91/6-311+G(2d,p) energies, which are shown in boldface.

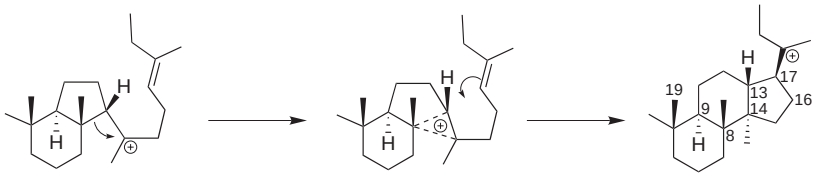
Comments:

1. These values are very rough because accurate proton affinities require large basis sets that include diffuse functions. These protonation and deprotonation energies should not be quoted as reliable proton affinities. Better estimates of substrate proton affinities will be published separately.[39] The net reaction values in columns 2-5 should benefit from cancellation of errors and have substantially higher accuracy.

2. The sum of the two reactions gives the net protonation/deprotonation energies for the conversion of neutral substrate to neutral product. These values mainly reflect the stability of the neutral product relative to the last cation. The last cations prior to lanosterol and cycloartenol are the C8 and C9 lanosteryl cations, respectively.

3. Our preliminary results for the protonation of squalene gave protonation energies within about 1 kcal/mol of energies for oxidosqualene. This gave the erroneous impression that squalene and oxidosqualene have essentially identical proton affinities. This matter was further investigated with small model compounds at higher levels of theory. As discussed in an unpublished manuscript,[39] the proton affinities for squalene and oxidosqualene differ by roughly 8 kcal/mol, oxidosqualene being easier to protonate.

Table S11 Comparison of interatomic distances (Å) between B3LYP/6-31G* and MPW1K/6-31G* geometries for models of C-ring expansion/D-ring formation (described in Table 1 of the Reference 10 of the main text)



	Reactant			Transition state			Product		
	MPW1K	B3LYP	difference	MPW1K	B3LYP	difference	MPW1K	B3LYP	difference
C8-C13	1.664	1.722	0.058	2.198	2.363	0.165			
C8-C14				1.916	1.970	0.054			
C13-C14	1.434	1.441	0.007	1.391	1.409	0.018			
C14-C15	1.458	1.466	0.008	1.507	1.523	0.016			
C15-C16	1.578	1.613	0.035	1.544	1.564	0.020			
C16-C17							1.539	1.560	0.021
C13-C17	3.314	3.377	0.063	2.830	2.782	-0.048	1.626	1.655	0.029
H9α-14αMe	2.143	2.245	0.102	1.922	1.965	0.043	1.886	1.933	0.047
H17α -14αMe	3.296	3.551	0.255	2.498	2.467	-0.031	2.116	2.141	0.025
H19 - 8βMe	1.959	1.990	0.031				1.895	1.945	0.050
H13 - 8βMe	2.220	2.241	0.021				1.963	2.030	0.067

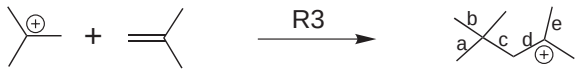
Comments:

1. This table illustrates how the B3LYP geometries are looser than MPW1K geometries.
2. Notably, the C8-C13 distance, corresponding to a long bond in the cyclopropane/carbionium ion transition state, is much longer (2.363 Å) for B3LYP relative to MPW1K (2.198 Å).
3. In cyclopropane/carbonium ions, the length of the long bonds (those to the pentacoordinate carbon) increases with the substitution level of the system. This trend is seen in Table 8 for B3LYP/6-31G* geometries (although **18** represents an exception to this pattern).

Entry	Substitution level*	Long bond lengths	
83B	CH_3; unsubstituted	1.824	1.724
85B	CH_2R; unsubstituted	1.890	1.741
20	CH_2R; trisubstituted	2.015	1.859
25	CHR_2; trisubstituted	2.187	1.961
18	CR_3; trisubstituted	2.192	1.907
23	CR_3; trisubstituted	2.361	1.992

*The substitution level entries are (respectively) for the pentacoordinate carbon and the other two carbons (considered as a substituted ethylene system).

Table S12 Comparison of interatomic distances (Å) for cation **77** among geometries from different theoretical methods (corresponds to Table 6, reaction R3)[a]



75 **76** **77**

Geometry	C-C (a) Me-Q	C-C (b) Me-Q	C-C (c) Hyperconj.	C-C (d) CH_2-C^+	C-C (e) Me-C^+	C-H Hyperconj.	C-H other
B3LYP/6-31G*	1.532	1.538	1.668	1.443	1.476	1.107	1.093
B3LYP/6-31+G**	1.533	1.539	1.664	1.445	1.474	1.107	1.092
MPW1/6-31G*	1.520	1.524	1.616	1.441	1.462	1.101	1.087
MP2/6-31G*	1.525	1.531	1.646	1.433	1.470	1.105	1.089
MP2/6-31+G**	1.525	1.531	1.645	1.433	1.470	1.101	1.087
MP4(SDQ)/6-31G*	1.530	1.535	1.624	1.450	1.474	1.107	1.093
CCSD/6-31G*	1.531	1.535	1.621	1.452	1.474	*1.107	*1.093
AM1	1.518	1.524	1.557	1.462	1.455	*1.130	*1.120

[a] Hyperconj., hyperconjugated bonds. Considerable variation was noted for the CCSD and AM1 C-H bond lengths, which are marked by an asterisk.

Comments: This table indicates that the looseness of the B3LYP geometry pertains mainly to the bonds involving hyperconjugation. Except for bonds involving the cationic center directly, the B3LYP geometry was similar to that of MP4 and CCSD geometries, all of which were modestly tighter than mPW1PW91 and MP2.

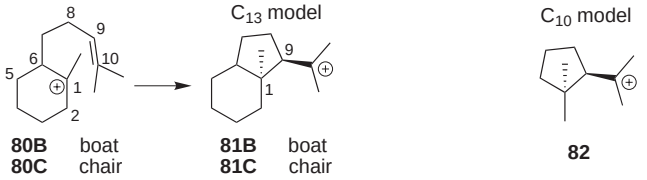
Table S13 Bond lengths in squalene from various sources: mol A, B, and C denote data from molecules A, B, and C from a crystal structure of 2-azasqualene; B3LYP and MPW1K denote data from 6-31G* optimizations; the last column represents a B3LYP/6-31G* optimization in which torsion angles beyond C5 were frozen to their values in the 2-azasqualene crystal structure (molecule C) [a]

Bond	mol A	mol B	mol C	B3LYP	MPW1K	B3LYP*
			Distances (Å)			
C1-N2	1.473	1.464	1.478	1.511	1.498	1.511
N2-C3	1.462	1.473	1.483	1.342	1.332	1.342
N2-C25	1.467	1.485	1.472	1.510	1.497	1.510
C3-C4	1.540	1.533	1.537	1.505	1.494	1.505
C4-C5	1.533	1.546	1.544	1.550	1.532	1.551
C5-C6	1.523	1.526	1.492	1.516	1.503	1.516
C6-C7	1.355	1.356	1.337	1.342	1.332	1.342
C6-C26	1.494	1.508	1.494	1.510	1.498	1.511
C7-C8	1.524	1.529	1.515	1.505	1.494	1.505
C8-C9	1.525	1.535	1.541	1.550	1.532	1.550
C9-C10	1.493	1.510	1.500	1.516	1.503	1.516
C10-C11	1.330	1.342	1.344	1.342	1.332	1.342
C10-C27	1.501	1.505	1.500	1.510	1.497	1.510
C11-C12	1.500	1.524	1.502	1.505	1.493	1.508
C12-C13	1.500	1.544	1.523	1.551	1.536	1.549
C13-C14	1.505	1.518	1.512	1.505	1.493	1.506
C14-C15	1.338	1.353	1.349	1.342	1.332	1.347
C15-C16	1.511	1.525	1.515	1.516	1.503	1.512
C15-C28	1.517	1.491	1.502	1.510	1.497	1.512
C16-C17	1.502	1.547	1.537	1.549	1.532	1.548
C17-C18	1.518	1.512	1.513	1.506	1.494	1.513
C18-C19	1.345	1.352	1.359	1.342	1.332	1.343
C19-C20	1.528	1.530	1.523	1.516	1.503	1.516
C19-C29	1.503	1.510	1.507	1.510	1.498	1.512
C20-C21	1.531	1.528	1.536	1.552	1.532	1.541
C21-C22	1.523	1.522	1.512	1.505	1.494	1.510
C22-C23	1.359	1.363	1.350	1.342	1.332	1.342
C23-C24	1.512	1.494	1.509	1.510	1.497	1.510
C23-C30	1.510	1.501	1.506	1.511	1.498	1.510

[a] Bond lengths are defined for the 2-azasqualene structure; for the B3LYP and other DFT structures (squalene), replace N2 by C2. Bonds to methyl are indicated in magenta. [b] Average deviations (X-ray crystal structure – B3LYP geometry) for B3LYP distances from molecules A, B, and C were 0.005, -0.003, and 0.004 Å, respectively. The same deviations for MPW1K distances were –0.008, -0.015, and –0.009.

Comment: These data show that the B3LYP/6-31G* geometry is very slightly loose and that the MPW1K geometry is somewhat tight. Freezing the torsion angles in the B3LYP optimization had almost no effect on bond lengths.

Table S14 Energy and geometries from a variety of theoretical methods for Hess's model of C-ring formation en route to the protosteryl cation.[a] (Corresponds to Table 7)



80B boat
80C chair

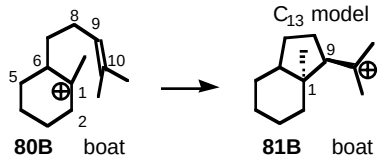
81B boat
81C chair

82

	HF 6-31G*	B3LYP 6-31G*	mPW1PW91 6-31G*	MPW1K 6-31G*	HCTH 6-31G*	HCTH 6-31G*	MP2 6-31G*
Geometry optimization method	-2.3	-3.5	-8.4	-11.0	0.8	-1.5	-15.0
MPW1PW91/6-311+G(2d,p)	-6.6	-4.1	-6.4	-6.2	-5.7		-6.3
B3LYP/6-311+G(2d,p)	0.4	-1.6	-0.2	0.2	-0.6		-0.3
HF/3-21G	-8.3	-3.6	-8.3	-8.2	-7.4		-7.3
ZPE increment	2.1	1.4	2.0	2.2	1.7		
ΔH increment	1.1	0.9	1.1	1.2	1.1		
ΔG increment	4.6	4.0	5.0	5.3	3.7		
Entropy (cal/mol-K)	-11.7	-10.3	-12.9	-13.9	-8.6		
C1-C9 distance (Å) in **81B**	1.645	2.396	1.755	1.705	1.850	2.808	1.893
C1-C10 distance (Å) in **81B**	2.502	2.716	2.444	2.411	2.590	3.140	2.303
C10-H2α distance (Å) in **81B**		2.731	2.438	2.384	2.594	3.105	2.424

[a] Electron energies for cyclization of **80B** to **81B**. The second entry for HCTH/6-31G* gives the distances for the second energy minimum.

Table S15 Relative energies and geometries in relaxed PES scans for the cyclization of **80B** to **81B** from optimizations with various DFT methods. Energies are presented relative to the energy at 1.7 Å. Frozen bonds are in boldface type (corresponds to Fig. 4)



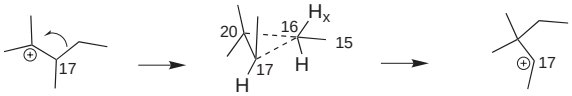
80B boat **81B** boat

C1-C9 Distance (Å)	Relative Energy (kcal/mol)	C1-C10 Distance (Å)	C8-C9-C10-MeA Torsion angle (°)	C8-C9-C10-MeB Torsion angle (°)	C10-H2α Distance (Å)
HF/3-21G//HF/3-21G					
1.7	0.0	2.478	27.5	-150.9	2.370
1.9	1.6	2.462	17.3	-160.9	2.466
2.1	3.2	2.452	6.4	-167.4	2.528
2.3	4.3	2.539	-0.5	-171.9	2.608
2.5	5.2	2.731	-2.2	-174.7	2.726
2.7	5.8	2.951	-2.2	-176.5	2.885
2.9	6.3	3.166	-2.1	-177.6	3.098
3.1	7.0	3.374	-1.8	-178.1	3.367
3.22	8.3	**3.8**	2.9	-175.1	3.835
B3LYP/6-31G*//B3LYP/6-31G*					
1.7	0.0	2.488	27.5	-152.6	2.449
1.9	-0.7	2.527	20.6	-159.9	2.536
2.1	-0.8	2.577	12.4	-165.9	2.602
2.3	-1.11	2.659	5.3	-171.1	2.684
2.396	-1.15	2.716	2.7	-173.2	2.731
2.5	-1.09	2.788	0.5	-175.0	2.785
2.7	-0.7	2.949	-1.9	-177.6	2.921
2.9	0.0	3.130	-3.1	-179.1	3.101
3.1	1.1	3.334	-3.0	-179.6	3.342
3.18	2.38	**3.8**	4.0	-174.3	3.861
BV5LYP/6-31G*//BV5LYP/6-31G*					
1.7	0.0	2.489	27.5	-152.6	2.450
1.9	-0.7	2.529	20.6	-159.8	2.538
2.1	-0.8	2.579	12.4	-165.8	2.604
2.3	-1.16	2.662	5.4	-171.0	2.686
2.402	-1.21	2.722	2.6	-173.2	2.735
2.5	-1.17	2.790	0.6	-174.9	2.787
2.7	-0.8	2.950	-1.9	-177.6	2.923
2.9	-0.1	3.131	-3.0	-179.1	3.102
3.1	1.0	3.335	-3.0	-179.6	3.343
3.18	2.25	**3.8**	4.0	-174.3	3.861
MPW1K/6-31G*//MPW1K/6-31G*					
1.7	0.0	2.410	24.0	-155.4	2.381
1.705	-.0012	2.411	23.8	-155.6	2.384
1.9	1.1	2.403	15.1	-162.9	2.456
2.1	2.6	2.425	5.3	-168.9	2.515
2.3	3.9	2.516	-1.5	-173.7	2.596
2.5	5.3	2.676	-4.6	-177.3	2.697
2.7	6.8	2.876	-4.9	-179.2	2.834
2.9	8.1	3.087	-4.6	-179.9	3.029
3.1	9.5	3.318	-3.4	-179.7	3.309
3.176	11.0	**3.8**	3.8	-174.4	3.840

mPW1PW91/6-31G*//mPW1PW91/6-31G*					
1.7	0.0	2.438	25.2	-154.7	2.410
1.755	-0.1	2.444	23.2	-157.0	2.438
1.9	0.3	2.458	17.6	-161.7	2.490
2.1	1.2	2.496	8.7	-167.7	2.551
2.3	2.0	2.578	1.4	-172.8	2.633
2.5	2.9	2.714	-3.0	-176.7	2.729
2.7	4.1	2.896	-4.2	-178.8	2.867
2.9	5.4	3.092	-4.5	-179.8	3.053
3.1	6.8	3.316	-3.7	-179.9	3.316
3.162	8.3	**3.8**	4.2	-174.1	3.842
HCTH/6-31G*//HCTH/6-31G*					
1.7	0.0	2.535	29.3	-151.5	2.525
1.850	-.51	2.590	24.5	-156.2	2.594
1.9	-.50	2.607	23.0	-157.5	2.613
2.1	-0.7	2.681	16.2	-163.0	2.683
2.3	-1.5	2.773	9.9	-167.9	2.767
2.5	-2.3	2.903	4.9	-172.2	2.877
2.7	-2.73				
2.808	-2.80	3.140	0.2	-176.9	3.104
2.9	-2.75	3.223	-0.6	-177.8	3.200
3.1	-2.3	3.404	-1.7		3.420
3.229	-1.3	**3.8**	3.6	-175.1	3.873
mPW1PW91/6-311+G(2d,p)//B3LYP/6-31G*					
1.7	0.0	2.488	27.5	-152.6	2.449
1.9	0.4	2.527	20.6	-159.9	2.536
2.1	1.2	2.577	12.4	-165.9	2.602
2.3	1.8	2.659	5.3	-171.1	2.684
2.5	2.5	2.788	0.5	-175.0	2.785
2.7	3.3	2.949	-1.9	-177.6	2.921
2.9	4.2	3.130	-3.1	-179.1	3.101
3.1	5.2	3.334	-3.0	-179.6	3.342
mPW1PW91/6-31G*//B3LYP/6-31G*					
1.7	0.0	2.488	27.5	-152.6	2.449
1.9	0.4	2.527	20.6	-159.9	2.536
2.1	1.2	2.577	12.4	-165.9	2.602
2.3	2.0	2.659	5.3	-171.1	2.684
2.5	2.9	2.788	0.5	-175.0	2.785
2.7	4.0	2.949	-1.9	-177.6	2.921
2.9	5.3	3.130	-3.1	-179.1	3.101
3.1	6.7	3.334	-3.0	-179.6	3.342
HF/6-31G*//HF/6-31G*					
1.7	0.0				
1.9	2.5				
2.1	3.7				
2.3	3.6				
2.5	2.9				
2.7	2.0				
2.9	1.4				
3.1	1.4				
3.22	1.3				

Comment: The relative mPW1PW91/6-31G* single-point energies for the B3LYP/6-31G* geometries were similar to those from mPW1PW91/6-31G* geometries (both shown in red).

Table S16. Relative energies and geometry parameters in relaxed B3LYP/6-31G* PES scans for formation of **89** from **87** (modeling ring-D enlargement in lupeol synthesis)[a] (Corresponds to Fig. 5)

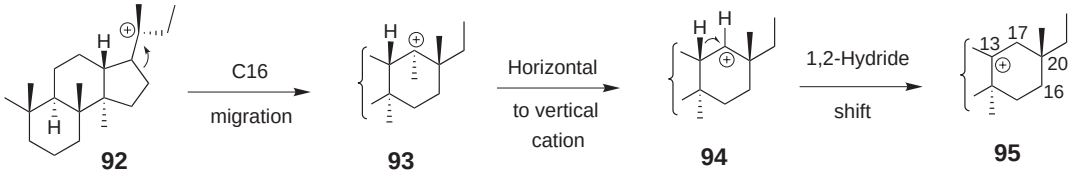


87 **88** **89**

C16-C17	C16-C20	B3LYP 6-31G*	MPW1PW91 6-311+G(2d,p)
Distance (Å)		*Energy (kcal/mol)*	
1.659	2.25	1.8	1.2
1.65	2.249	1.8	1.1
1.75	2.253	2.5	2.3
1.85	2.229	4.2	4.3
1.95	2.189	6.2	6.5
2.05	2.113	8.0	8.4
2.15	1.928	9.6	9.5
2.25	1.799	10.5	10.6
2.35	1.765	11.6	12.1
2.45	1.757	13.1	14.0
2.55	1.762	15.1	16.4
2.65	*1.784*	*17.7*	*19.3*
2.75	*1.839*	*20.8*	*22.9*
2.85	*1.972*	*24.3*	*27.1*
2.95	*2.258*	*27.4*	*31.1*

[a] The C16-C17 bond length was frozen in 0.1 Å increments from 1.65 to 2.95 Å; values above 2.6 Å represent unrealistic elongation of the C16-C20 bond (indicated by italics).

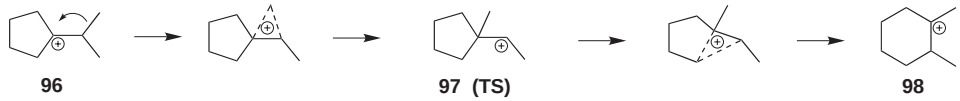
Table S17 PES scans modeling the conversion of the 17β-dammarenyl cation to the C13 cation en route to bacchar-12-en-3β-ol [a] (Corresponds to Fig. 7)



Comment	C16-C17	C16-C18	Me-14-13-18	Me-17-18-H	14-13-18-H	H-C18	H-C13	13-14	16-17-C-C	C-H-C	B3LYP	mPW1
Minimum (**92**)	**2.34**	1.66	-179	162	84	2.14	1.10	1.56	151		0.0	0.0
Frozen	**2.24**	1.66	-180	162	85	2.13	1.10	1.56	154		0.2	-0.2
Frozen	**2.10**	1.68	180	163	87	2.13	1.09	1.56	158		1.2	0.1
Frozen	**2.00**	1.70	180	163	87	2.12	1.09	1.56	160		2.6	0.9
Frozen	**1.90**	1.74	179	164	86	2.12	1.09	1.57	163		4.4	2.3
Frozen	**1.85**	1.82	179	164	85	2.11	1.09	1.57	165		5.4	3.4
Frozen	**1.80**	2.05	180	164	83	2.09	1.09	1.60	172		5.902	5.5
Transition state (**92A**)	1.78	2.11	180	162	83	2.09	1.09	1.61	174		5.935	5.9
Frozen	**1.75**	2.19	-180	159	85	2.09	1.09	1.64	176		5.866	6.4
Frozen	**1.70**	2.28	-178	154	88	2.09	1.09	1.68	178		5.6	6.7
Minimum (**93**)	1.63	2.34	-177	148	92	2.09	1.09	1.74	179		5.2	6.5
Frozen	1.62	2.38	-176	138	**100**	2.09	1.09	1.74	-179		5.5	6.9
Frozen	1.60	2.42	-175	127	**110**	2.08	1.09	1.73	-177		6.5	7.9
Frozen	1.59	2.46	-174	115	**120**	2.07	1.10	1.69	-175		7.7	9.1
Frozen	1.57	2.49	-173	102	**130**	2.04	1.10	1.65	-173		8.6	9.6
Transition state (**93A**)	1.56	2.50	-173	95	136	2.03	1.11	1.62	-173		8.711	9.4
Frozen	1.56	2.51	-173	91	**140**	2.02	1.11	1.60	-173		8.669	9.2
Minimum (**94**)	1.55	2.51	-176	81	153	1.98	1.12	1.58	-174	46	8.49	8.7
Transition state (**94A**)	1.55	2.51	-176	71	164	1.86	1.137	1.56	-173	51	8.57	8.5
Frozen	1.55	2.51	-174	65	171	1.76	**1.14**	1.55	-172	54	8.55	8.1
Frozen	1.55	2.50	-172	63	174	1.67	**1.15**	1.55	-172	57	8.46	7.6
Frozen	1.55	2.50	-169	63	177	1.53	**1.16**	1.54	-172	62	8.3	6.8
Frozen	1.55	2.50	-165	67	179	1.38	**1.20**	1.54	-172	66	7.3	5.0
Frozen	1.55	2.50	-162	71	179	1.26	**1.30**	1.52	-173	67	4.8	2.4
Frozen	1.55	2.51	-160	75	177	1.21	**1.40**	1.51	-173	65	2.8	0.6
Frozen	1.55	2.51	-158	78	175	1.17	**1.50**	1.50	-173	63	0.9	-0.9
Frozen	1.55	2.52	-155	81	173	1.15	**1.60**	1.50	-173	60	-1.0	-2.3
Frozen	1.55	2.54	-152	82	170	1.13	**1.70**	1.49	-173	57	-2.7	-3.6
Frozen	1.55	2.55	-149	83	168	1.12	**1.80**	1.48	-172	54	-4.1	-4.6
Frozen	1.55	2.55	-149	84	168	1.12	**1.90**	1.48	-172	50	-4.9	-4.9
Frozen	1.55	2.56	-162	78	-177	1.10	**2.00**	1.47	-174	46	-6.0	-5.1
Frozen	1.56	2.57	-161	75	-176	1.10	**2.07**	1.46	-175	43	-6.3	-5.1
Minimum-boat (**95**)	1.56	2.57	-160	75	-176	1.10	2.07	1.46	-175	43	-6.3	-5.1
Minimum-chair	1.54	2.49	-95	172	80	1.09	2.13	1.47	178		-5.6	-5.6

[a] Sequential PES scans were done with B3LYP/6-31G* optimization for the C16-C20 bond (**92** to **93**), the C14-C13-C17-H17 torsion angle (**93** to **94**), and the C13-H13 bond (**94** to **95**). Values in boxes represent frozen bond distance or torsion angles (except for stationary points). Frozen distances or angles are shown in boldface type. Geometries are B3LYP/6-31G*; energies are B3LYP/6-31G* or mPW1PW91/6-311+G(2d,p). Lupeol numbering was used.

Table S18 Energies and geometry parameters in the conversion of **96** to **98** [a] (Corresponds to Fig. 8)



96 **97 (TS)** **98**

C6-C7	C7-C1-C6-C8	C1-C2	C1-C7	C1-C5	B3LYP 6-31G*	MPW1PW91 6-311+G(2d,p)
Distance (Å)	*Torsion angle (°)*	*Distance (Å)*			*Energy (kcal/mol)*	
1.58					0.0	0.0
1.60	113	1.479	2.412	1.473	0.0	0.1
1.70	110	1.484	2.428	1.477	2.0	2.7
1.80	106	1.489	2.428	1.482	5.8	6.9
1.90	102	1.489	2.401	1.496	10.1	11.6
1.95					12.3	13.7
2.00	89	1.540	1.854	1.528	13.9	13.5
2.10	85	1.555	1.719	1.543	14.7	14.4
2.20	83	1.564	1.678	1.552	15.3	15.4
2.30	81	1.574	1.657	1.553	16.2	16.7
	70	1.620			16.5	16.7
2.363	62	1.619	1.596	1.547	17.2	17.7
	60	1.620			17.1	17.5
	50	1.620			15.1	14.9
	40	1.620			13.0	12.3
	30	1.620			11.5	10.4
N/A	21	**1.620**	1.531	N/A	11.0	9.6
N/A	20	**1.640**	1.530	N/A	10.5	9.1
N/A	17	**1.70**	1.525	N/A	9.1	7.8
N/A	10	**1.80**	1.515	N/A	7.5	6.1
N/A	1	**1.90**	1.503	N/A	5.5	4.1
N/A		**2.00**		N/A	3.0	2.0
N/A		**2.10**		N/A	0.6	0.1
N/A		**2.20**		N/A	-1.2	-1.2
N/A		**2.30**		N/A	-2.3	-1.8
N/A		**2.40**		N/A	-2.5	-1.7
N/A		**2.50**		N/A	-1.7	-.5
N/A		2.553		N/A	-2.1	-1.8

[a] First, the C6-C7 bond was frozen at values from 1.6-2.3 Å. A similar scan was obtained by freezing the C1-C2 bond length. These two PES scans were bridged by a third PES scan of the C7-C1-C6-C8 torsion angle in the vicinity of the transition state. Frozen parameters are indicated in boldface.

Recent claims for 6-6-6 tricyclic intermediates in triterpene synthesis

[References in the following sections correspond to references of the main text.]

Formation of ring C could proceed by anti-Markovnikov addition to generate a 6-6-6 secondary cation like **90** or by Markovnikov addition to produce a 6-6-5 tricycle like **12**. The passionate controversy over these two alternatives has generated much confusion. We review two recent claims[7n,p,54a] for the 6-6-6 tricycle as the intermediate in triterpene synthesis.

Nishizawa and coworkers[7n,p] proposed that the 6-6-5 and 6-6-6 tricycles are sequential intermediates in triterpene synthesis. The endothermic conversion of the 6-6-5 tricycle to the 6-6-6 tricycle was suggested to be aided by enzymatic stabilization through an aspartate or glutamate residue. These reasoning was based on biomimetic reactions that give different results depending on the counterion of the Lewis acid. The biomimetic results were rationalized by molecular modeling of this reaction at the HF/6-31G* level, which suggested that oxygen anions stabilize a specific orientation of the cation (horizontal *vs.* vertical cation). This hypothesis was supported by publications of Farcasiu and coworkers showing that the gas-phase geometry of cations can be markedly altered by the close proximity of anionic species (D. Farcasiu and D. Hancu, *J. Am. Chem. Soc.*, 2000, **122**, 668-676 and references therein).

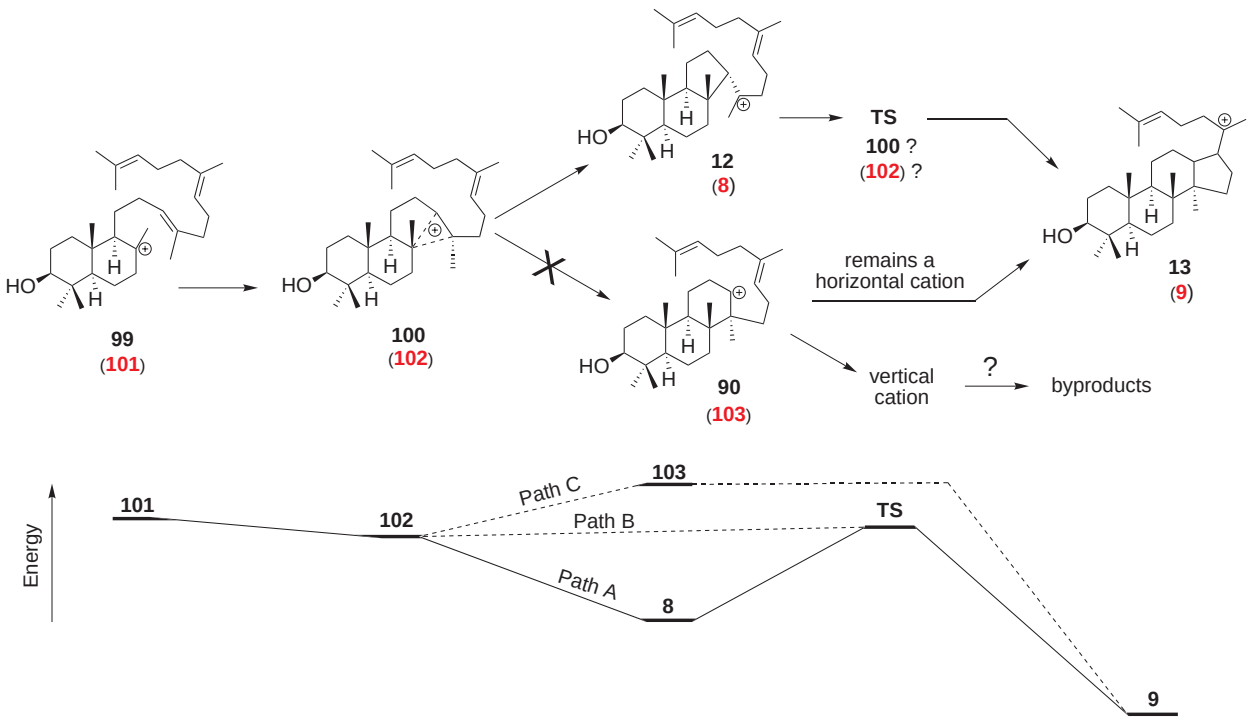
This logic is plausible as an explanation for the biomimetic results. However, we were unable to locate any aspartate or glutamate residues in the putative vicinity of ring C in crystal structures of SHC[8] or lanosterol synthase.[9a] Although electrostatic forces of anions are non-directional with a 1/R distance dependence (in classical mechanics), the nearest carboxylate residues seem to be too distant to affect the relative stabilities of **8** and **103**. Any remote electrostatic effect would be diminished by dielectric effects and by hydrogen bonding between carboxylate and ordered water molecules.

Seemann *et al.*[54a] also favored anti-Markovnikov addition in C-ring construction and questioned the existence of the 6-6-5 tricycle **8** as an intermediate in protosteryl cation formation. No calculations were performed, but electron energies from an earlier calculation[7a] (designated as ΔG) were used to argue that it would be disadvantageous for the reaction pathway to pass through a low-energy 6-6-5 intermediate like **8** because the ensuing step to form the anti-Markovnikov 6-6-6 product would be even more endothermic.

Cursory inspection would suggest that this argument is flawed. An intermediate species like **102** should fall into any energy well on its path, and the energy diagram in Scheme S1 indicates that the reaction path would be exposed to the energy well represented by **8**.[7d] Any cationic species following the minimum energy path (MEP) would go through intermediate **8** (path A). However, the MEP is not necessarily the predominant pathway at room temperature.

Scheme S1 illustrates three plausible pathways from the bicyclic cation **101** to the tetracyclic protosteryl cation **9**. The pathways diverge at the bridged species **102**. Formation of ring C is expected to involve **102** by analogy with the geometry changes shown in Fig. 2B. As in Fig. 2A, **102** is probably neither an intermediate nor saddle point. The different disposition of the methyl groups in Fig. 2 presumably affects the energies, and, in contrast to the situation in Fig. 2, **102** may not be near the energy midpoint of the reaction.

If the proximate olefin is near the cationic center, **102** may be similar in structure to the transition state (**TS**) for D-ring formation. If so, dynamics of the reaction may lead directly to D-



Scheme S1 Conversion of bicycle **99** to the 6-6-5 or 6-6-6 tricycle en route to the dammarenyl cation **13**. Compound numbers in magenta correspond to the analogous structures in protosteryl cation formation (lanosterol synthesis); these structures have inverted stereochemistry at C8, C9, and C13/C14. The energy diagram is estimated and includes three structures that are not stationary points (**101**, **102**, and **103**).

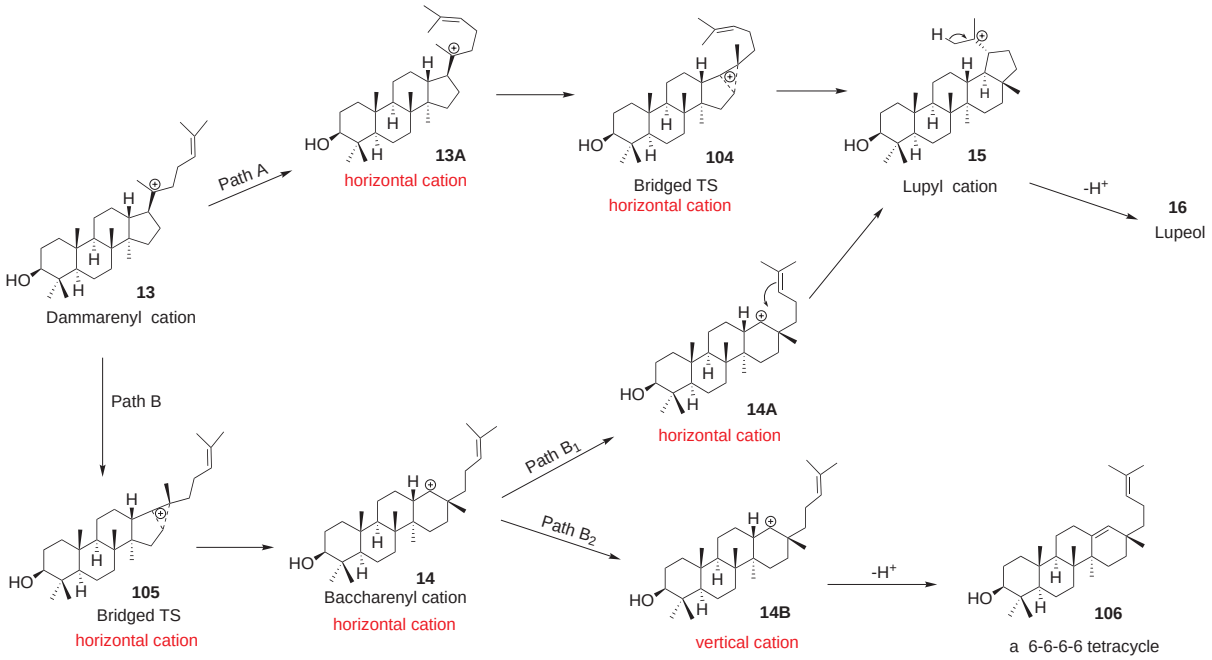
ring annulation via path B, without intermediacy of tricycle **8**. Path C through the 6-6-6 tricycle **103** is only moderately higher in energy than path B and then also becomes plausible.

We propose that enzymatic reactions generally follow path A, as depicted in Fig. 3. (1) The partially folded substrate needs to contract within the active site cavity as cyclization proceeds.[8,9a,40] Thus, the proximate olefin is remote from the cationic center when **102** forms. The time required for the side chain to become repositioned in the active site favors the MEP at this stage. (2) If path B were the major enzymatic pathway, path C would also be somewhat populated. This could lead readily to the vertical cation form of **103**, which would readily undergo 1,2-shifts to form enzymatic byproducts. Such byproducts have never been observed. (3) Many tricyclic triterpenes are known in nature[3] and as byproducts of enzyme mutants, whereas no 6-6-6 tricycles are generated from (oxido)squalene, even by mutant cyclases.

This matter is not fully settled. First, no rigorous study of the energetics of Scheme 1 has been made. Some cyclase mutants might access path C as a minor pathway, and some 6-6-6 enzymatic byproducts may eventually be discovered, at least in mutants. Whether enzymatic reactions mainly follow path A or path B may ultimately be resolved by NMR studies of ^{13}C isotopic effects (J. Hirschi, D. A. Singleton and A. I. Scott, Abstract of Papers, 229th ACS National Meeting, San Diego, CA, USA, 2005).

Evidence for 6-6-6-6 tetracyclic intermediates in triterpene synthesis

Unlike the hypothetical 6-6-6 tricyclic cation, the 6-6-6-6 tetracyclic cation is definitely an intermediate, at least in certain enzymatic reactions. Hoshino *et al.* provided experimental evidence for the 6-6-6-6 prohopanyl cation **4** by isolating 6-6-6-6 tetracyclic olefins from an SHC mutant.[57] Other groups later reported that the baccharenyl cation[3] (**14**) or its dihydro analog[11a] are also likely intermediates in plant triterpene synthesis.



Scheme S2 Possible mechanisms of lupeol formation from the dammarenyl cation (**13**). A pathway to 6-6-6-6 tetracycles is also shown.

We suggest that either the secondary cation **14** or the bridged cation **104** is an intermediate in lupeol synthesis depending on the relative rates of side-chain folding and D-ring expansion. It is assumed that the side chain of **13** is initially in an extended conformation in the active-site cavity (see main text). If side-chain folding is faster than D-ring expansion (Path A), the bridged transition state for D-ring expansion (**104**) directly collapses to the lupyl cation (**15**). Path B, in which D-ring expansion is faster, is only a few kcal/mol higher in energy than Path A. If side-chain folding is sufficiently slow, conversion of **14** to its vertical cation form can lead to elimination to generate 6-6-6-6 tetracycles like **106**. If side-chain folding is completely blocked, 6-6-6-6 tetracycles may be the sole enzymatic products.

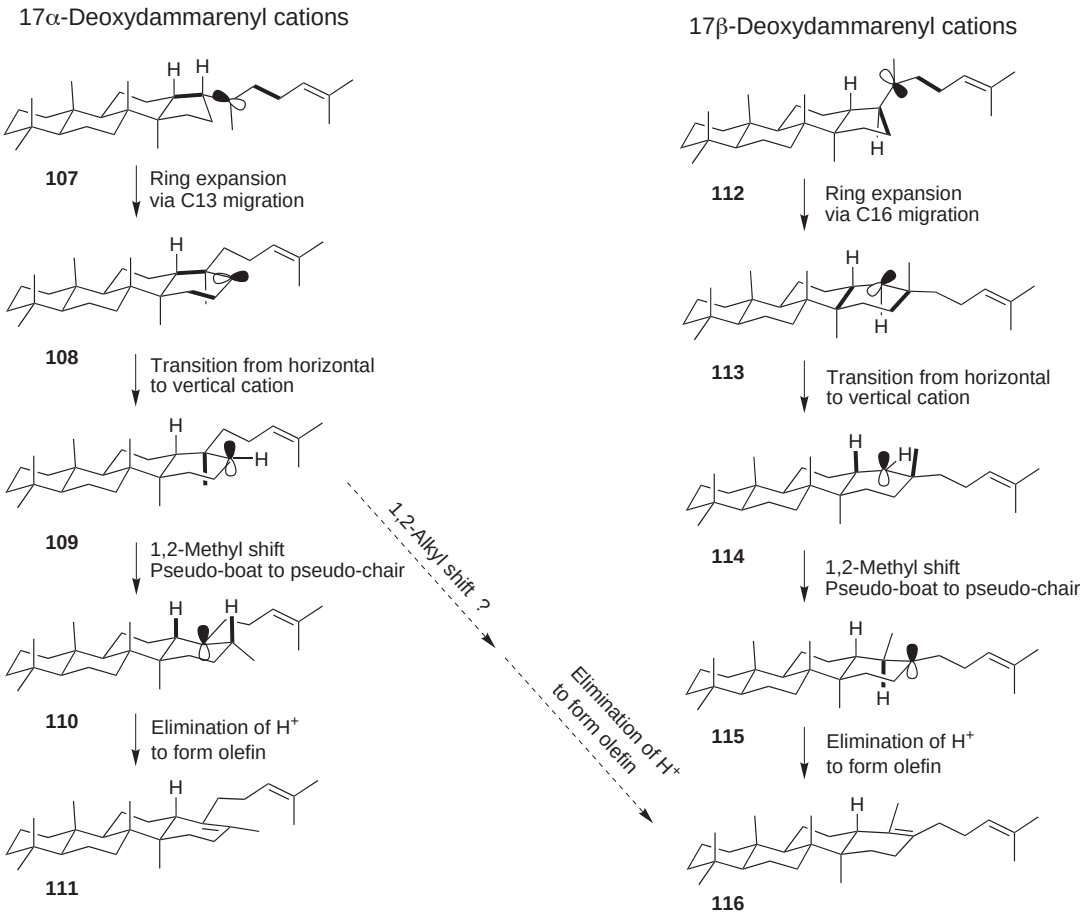
Mechanistically and energetically, the factors affecting the formation of anti-Markovnikov intermediates are similar for tricycles and tetracycles. Apparently, enzymatic effects are responsible for the lack of 6-6-6 tricycles in nature, contrasted with the presence of many 6-6-6-6 tetracycles.

In the mechanism proposed by Hoshino *et al.*[57] for the formation of the 6-6-6-6 tetracycles from the SHC mutant I261A, both **111** and **116** arise from the 17α-deoxydammarenyl cation **107**

(Scheme S3). The C16 cation (**108** or **109**) could undergo a 1,2-methyl shift to give **111** or a 1,2-alkyl shift of the side chain to give **116**. This formation of **116** would probably require the side chain to become axial in a D-ring twist/boat conformation in order to bring the migrating bond into hyperconjugation with the cationic *2p* orbital. This would entail a high-energy conformer that would probably not fit in the active site cavity.

We suggest that **116** might instead arise from the 17β-deoxydammarenyl cation **112**, as shown in Scheme S3. This pathway avoids the 1,2-migration of the equatorial alkyl side chain from **108**/**109** and is consistent with production of some 17β-deoxydammarenyl cation by this mutant. This proposal is compatible with the preference of C16 migration for 17β-dammarenyl cations and C13 migration for 17α-dammarenyl cations.

It is noteworthy that the SHC active site can apparently accommodate C16 migration but not a lupeol-type skeleton, i.e. the side chain cannot rotate into the appropriate position for annulation. Whereas most of the horizontal cation **108** undergoes E-ring formation, apparently none of the horizontal cation **113** does. We suggest that a bridged form of **108** may be a transient species in hopene synthesis but that the vertical cation **109** is not formed. If **109** were formed during hopene synthesis, some aberrant methyl migration to **111** would be expected, and this is apparently not observed.[39]



Scheme S3 Possible mechanisms of for the formation of 6-6-6-6 tetracycles **111** and **116**.

Computational strategies

Model size. One strategy for maximizing computational efficiency is to use model compounds small enough that the calculated integrals can be stored in memory. Such calculations are very fast but are limited by computer memory to about 10 first-row atoms with 2 GB of RAM (or about 8 atoms with 1 GB or RAM) for unsymmetrical molecules. Because of the N^4 scaling, doubling of RAM results in only a 19% increase in the size of the molecule that qualifies for this speed advantage. (These considerations apply to typical DFT geometry optimizations using a 6-31G* basis set.)

Use of small fragments of triterpenes to model cyclization can give misleading results. The difference in the C8-C13 bond length in the B3LYP/6-31G* geometries of the full C_{30} cation **8** and its small model **81B** (1.72 Å vs. 2.40 Å) is a notable example. In triterpene synthesis, steric interactions between angular methyl groups may affect conformations as well as energetics. Inclusion of such interactions usually requires models with two carbocyclic rings, resulting in a minimum of about 15 carbon atoms. Inclusion of cation stabilization by the proximate olefinic bond in the substrate results in model structures with over 20 carbon atoms. With a 6-31G* basis set and 1-2 GB of RAM, these geometry optimizations cannot be done in memory. When integrals are stored on disk rather than in memory, DFT computations are much slower, but substantial portions of the calculations can be done with the fast multipole method, which shows linear scaling for large molecules (L. Greengard, *Science*, 1994, **265**, 909-914; M. C. Strain, G. E. Scuseria and M. J. Frisch, *Science*, 1996, **271**, 51-53). For triterpene models, cpu time scaled roughly according to N^2, where N is the number of first-row atoms. Thus, increasing the model size from 15 to 30 carbon atoms resulted in only about a 4-fold increase in cpu time. The scaling was closer to linear for an increase from 30 to 99 first-row atoms.[40]

We have elected to use larger substrate models (15-31 first-row atoms), although structures were sometimes truncated in order to minimize conformational complexity or to increase generality, *e.g.* by deleting ring A so that the models applied to both squalene and oxidosqualene cyclizations. The main drawback of the large substrate models was the complexity and flatness of the PES in the open-chain portions of the molecules. For example, geometry optimization of lupeol intermediates prior to formation of rings D and E readily fell into energy wells corresponding to improperly folded conformers.

Limitations of addressable disk space. With the usual 32-bit computers currently available, Gaussian can address only 16 gigabytes of scratch disk space. This prevented many optimizations of medium-sized structures with G3 or CCSD methods. Notably, many of our CCSD optimizations and CCSD(T) energies were limited to the 6-31G* basis set, which is overly small for CCSD methods. As inexpensive 64-bit workstations become available (with matching Gaussian software), this restriction will be lifted.

Practical considerations. The many lengthy calculations for the large models were done by dividing the work among several inexpensive personal computers (Dell Optiplex, configured with Windows or Linux). Computers running Windows were simultaneously usable for simple word processing and other routine tasks. Linux provided more power and flexibility and allowed control from a central unix computer using a batch queue. For USD $900 computers with a 2.4

GHz processor, ≥400-MHz bus, and 7500 rpm disk drive (purchased in 2002), B3LYP/6-31G* geometry optimizations and frequency calculations and DFT/6-311+G(2d,p) single point energy calculations typically required 1-4 days for models of 15-30 carbons.

Path calculations vs. PES scans. Determining the reaction path connecting reactant and product is far more challenging than simple geometry optimization. Practical methods for exploring the PES have been reviewed recently: H. B. Schlegel, *J. Comput. Chem.* 2003, **24**, 1514-1527; see also D. J. Wales, *Energy Landscapes*, Cambridge University Press, Cambridge, UK, 2003. These studies can be conducted at 3 levels: locating the transition state (if any); elucidating the MEP; and determining the relative populations of all reaction paths by molecular dynamics.

Locating a transition state in triterpene synthesis is now relatively straightforward, albeit tedious. We determined the structures of transitions states by QST3 calculations in Gaussian, and this was routinely successful when we started with a transition state guess derived from a relaxed PES scan. Methods for improved interpolation between reactant and product (for QST2-type calculations) are under active development, e.g. S. A. Trygubenko and D. J. Wales, *J. Chem. Phys.* 2004, **120**, 2082-2094.

Elucidating the MEP was far more difficult. We tried to use path calculations to obtain structures connecting intermediates and transition states whenever possible (see Ref. 10). However, our Gaussian path calculations for triterpene synthesis usually failed to converge after an initially promising start. One alternative is an intrinsic reaction coordinate (IRC) calculation, a method that Hess has used to describe A-ring formation.[7h] The IRC calculations proceed well in the vicinity of the transition state but require new force constant calculations for major portions of the reaction path. Instead we constructed relaxed PES scans using a distance or angle that defined the pathway. The relaxed PES scans do not correspond to the MEP but do provide a rough estimate of this path.

In our experience with triterpene modeling, well-chosen relaxed PES scans usually pass through the transition state or at least provide a close guess for the transition-state structure. This occurred in the PES scans used in Figs. 7 and 8. PES scans are also useful in describing reaction paths that include multiple minima and transition states, as in Fig. 7.

The main drawback of using PES scans is that this is not a rigorous way to study reaction paths (M. J. S. Dewar, E. F. Healy and J. J. P. Stewart, *J. Chem. Soc., Faraday Trans. 2*, 1984, **80**, 227-233). Cramer has illustrated diagrammatically how relaxed PES scans can conceal major features of the PES (Ref. 44, pages 6-10; see also C. J. Cramer, S. E. Denmark, P. C. Miller, R. L. Dorow, K. A. Swiss and S. R. Wilson, *J. Am. Chem. Soc.*, 1994, **116**, 2437-2447). Despite these potential pitfalls, relaxed PES scans provide a more comprehensive picture than would be obtained by simply characterizing stationary points with limited IRC paths. We regarded this rough picture as adequate to understand the general nature of the chemical transformation. Because specific enzymatic effects cannot presently be modeled with good accuracy, a precise gas-phase MEP of the bare substrate would also be an imperfect model.

Molecular dynamics studies were not undertaken here. These studies normally require semi-empirical methods or primitive *ab initio* methods such as HF/3-21G. Use of these low-level methods by us (Tables 1-6) and by Rajamani and Gao[7b] gave results differing markedly from our

mPW1PW91/6-311+G(2d,p)//B3LYP/6-31G* energetics. These discrepancies indicated that validating molecular dynamics calculations in triterpene synthesis would be difficult.

Conformational heterogeneity. Squalene and oxidosqualene are populated by thousands of conformations in solution, and many triterpene products also can adopt a variety of conformations. Neglect of this matter could generate substantial errors when calculated reaction energies are compared. We limited such errors by using conformers consistent with likely constraints of the active site and by working with only one or two standard side-chain conformers. As in Ref. 10, we studied the energy differences among conformers and found them to be relatively small (see Tables S7, parts a-d). The following efforts were made to maintain conformational consistency:

Orientation of OH in 3β-hydroxy triterpenes: We generally oriented the OH of the 3β-hydroxyl to make H anti to C4. Because of hyperconjugation, this orientation is not necessarily the lowest energy conformer. In earlier studies of predicted NMR shieldings for lupeol (Guo, Wilson, and Shackleton, unpublished results), the OH groups had been given a different standard orientation. The lupeol structure used in those studies was slightly lower in energy than the lupeol structure used in the present calculations. Atomic coordinates are given below for both lupeol OH conformers.

Side-chain conformation of sterols: Before the lanosterol synthase crystal structure was published,[9a] we optimized a lanosterol structure with an arbitrarily chosen side chain. For consistency in comparisons, we optimized cycloartenol and all lanosteryl cations with the same side-chain conformation. Extended side chains were used only in optimizations for the NMR studies. The arbitrary side-chain conformation for lanosterol and cycloartenol used herein is about 3 kcal/mol higher than the extended conformation. The arbitrary side chain for the protosteryl cation had the following side-chain dihedral angles: ω1, 163°; ω2, 88°; ω3, 64°; ω4, 88° (ω1-4 defined in Scheme 4 of Ref. 10). Angles for the tricyclic intermediate, lanosterol, and cycloartenol were similar. Only after most of the calculations were completed did we recognize that the side-chain of tetracyclic intermediates are largely in an extended conformation.[8,9a,59]

Atomic coordinates for molecular modeling

Section I. Compounds **17**-**21**: (Fig. 1) Entries with C16 migration.

Section II. Compounds **22**-**26**: (Fig. 1) Entries with C13 migration.

Section III. Compounds **27**-**34**: $C_{10}H_{18}$ isomers: (Table 1)

Section IV. Compounds **71**-**74**, **78**, **79**: Models of oxidosqualene cyclization (Table 3)

Section V. Neutral triterpenes (Table 4)

Section VI. Triterpene cations, hopen-3b-ol precursors (Table 5)

Section VII. Triterpene cations, lupeol precursors (Table 5)

Section VIII. Triterpene cations, lanosterol precursors (Table 5)

Section IX. Compounds **80B**, **81B**, Hess's models of C-ring formation (Table 7)

Section X. Compounds **92-95**, models for baccharenyl cation (Fig. 7)

Section XI. Compounds **96-98** (Fig. 8)

All atomic coordinates below are from B3LYP/6-31G* geometry optimizations.

Frozen bonds are described by atom numbering from the figures in the text, not by atom numbering from the coordinate files.

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 "|" with the paragraph mark. If desired, commas can be replaced by spaces or the tab mark.

Section I. Compounds 17-21: Structures from Fig. 1: Lupeol precursors.

Compound **17**, reactant in Fig. 1, lupeol precursor

```
1\1\GINC-DFTB\FOpt\RB3LYP\6-31G(d)\C25H43(1+)\BILLW\11-Sep-2003\0\\# B
3LYP/6-31G* OPT=READFC GEOM=ALLCHECK GUESS=READ\\ERing lup SM open ok\
\1,1\C,-1.9999431763,0.0894407245,-1.578394824\C,-0.5567205541,-0.3887
872408,-1.3019938849\C,-0.3168288502,-0.3498785915,0.2295337176\C,0.05
07016204,-1.5306316966,0.9580325184\C,-1.8669178121,0.1266590302,0.876
9745489\C,-2.7567954033,-0.3156918299,-0.3129828258\C,-0.2800420451,-2
.8969138706,0.4849243958\C,3.1754813561,-1.1599900282,1.0889730655\C,0
.8018418283,-1.3956384192,2.2173614408\C,2.3167637075,-1.8875406647,2.
0853288968\C,3.829066355,0.0012869905,1.2846440842\C,3.7556426056,0.80
55570406,2.5591663092\C,4.7220302164,0.5879704629,0.2083720588\C,-1.66
04142379,1.6351667927,1.08697107\C,-4.28313185,0.002886154,-0.17445220
01\C,-2.3783745508,-0.5313916443,2.1701693201\C,-3.8658368268,-0.16969
44069,2.3880683837\C,-4.7433656731,-0.5716465728,1.1926141359\C,-4.649
7850194,1.4961121679,-0.3035057609\C,-5.0265045416,-0.7553960594,-1.29
71809989\C,4.020188772,1.6368956344,-0.7036398088\C,3.1758142834,0.993
6455834,-1.7728943035\C,3.1433238201,1.2703234585,-3.0872793479\C,2.27
31954052,0.4673911341,-4.0267428011\C,3.9373951356,2.3613491611,-3.762
0917112\H,-2.4069181809,-0.3769364088,-2.4790086672\H,-2.0304799328,1.
1720957104,-1.7373788714\H,-0.4140725241,-1.4002205662,-1.6949859605\H
,0.1926955736,0.2410388311,-1.7875482807\H,0.3403332496,0.4674941766,0
.5284076204\H,-2.7308525637,-1.4175371963,-0.2863591464\H,-1.228191458
9,-2.9359664224,-0.0587230715\H,0.494277705,-3.1858405792,-0.246465272
\H,-0.2678022845,-3.6378953179,1.2875435597\H,3.3095912651,-1.65959930
48,0.1298532322\H,0.8125389186,-0.3586075166,2.5607555202\H,0.34697184
33,-2.032254445,2.9865783981\H,2.7087394261,-1.7851849811,3.1017886586
\H,2.302986553,-2.958853442,1.8608144043\H,3.0482538513,0.4120794714,3
```

.2941754453\H,4.7435676508,0.8478592803,3.0360434428\H,3.4755417137,1.
84539139,2.3456124424\H,5.1269234279,-0.2095589988,-0.4241130184\H,5.5
781446565,1.071254147,0.6954283651\H,-1.3554148668,2.1505090784,0.1727
574432\H,-0.8919706723,1.809288195,1.8479284719\H,-2.5762323631,2.1062
002273,1.4469479943\H,-2.307440831,-1.6254264359,2.1027647513\H,-1.787
4797203,-0.2190944538,3.0396260863\H,-3.9664013714,0.900819961,2.59855
79927\H,-4.2165300825,-0.6845353608,3.289657984\H,-5.7807617675,-0.269
1115669,1.3800979851\H,-4.7540790891,-1.6691735873,1.1223596075\H,-4.3
625733872,2.0958889544,0.5632501539\H,-4.1994528917,1.9513899148,-1.19
2221565\H,-5.7360082314,1.5933224451,-0.4073763555\H,-4.7558419722,-1.
8181426341,-1.3182380035\H,-6.1087737234,-0.6926879481,-1.1387952524\H
,-4.8151160854,-0.3299895814,-2.2841074808\H,4.7909985351,2.2705457015
,-1.1511004552\H,3.4107152637,2.3048513067,-0.0746591461\H,2.546192046
9,0.1742249299,-1.4210984458\H,1.7215546539,-0.3231579138,-3.505795890
4\H,2.879058098,-0.0068544008,-4.8105856635\H,1.5476800799,1.108952461
2,-4.5457802586\H,4.5760533097,2.9253633866,-3.0791061856\H,4.57398817
57,1.9424018289,-4.5527723616\H,3.2648806119,3.0767578047,-4.254583078
7\\Version=x86-Linux-G98RevA.9\HF=-978.2764706\RMSD=4.881e-09\RMSF=6.6
16e-05\PG=C01 [X(C25H43)]\\@

Compound **18**, first transition state in Fig. 1, lupeol precursor

1\1\GINC-DFTC\FTS\RB3LYP\6-31G(d)\C25H43(1+)\BILLW\26-Sep-2003\0\\# B3
LYP/6-31G(D) OPT=QST3\\D ring formation TS open-TS guess\\1,1\C,-1.749
7008285,-0.2947343513,-0.9960397908\C,-0.3013384039,-0.9023481358,-1.1
306226969\C,0.4030603408,-0.4669353978,0.0852007537\C,0.2593290348,-1.
0652210768,1.3563463529\C,-1.4186628046,-0.1165191413,1.5355408189\C,-
2.3275514412,-0.6183335227,0.3862557108\C,0.0075031189,-2.5708966867,1
.4402950239\C,3.0558105768,-1.0826004954,0.5909403283\C,1.2851737241,-
0.5921333351,2.3820831447\C,2.6837642767,-1.199970586,2.0498682525\C,3
.741159711,-0.0789768088,-0.007336314\C,4.2516752951,1.1336992721,0.72
79078089\C,4.1214071243,-0.1853418011,-1.4706565815\C,-1.136381576,1.3
883976832,1.583719308\C,-3.8580564078,-0.2437931336,0.5644058513\C,-1.
9131645295,-0.6220457,2.8971618016\C,-3.3865250296,-0.1964585027,3.112
9343532\C,-4.2882185565,-0.6966507174,1.9828734169\C,-4.1840523304,1.2
468359313,0.3371817309\C,-4.6823920495,-1.0616528556,-0.4564087827\C,3
.9066472813,1.0802439951,-2.3397995236\C,2.4853475238,1.5735702011,-2.
4236089167\C,1.6887139062,1.641936509,-3.5051902643\C,0.3155940848,2.2
683637797,-3.4155437449\C,2.0645567055,1.1699378007,-4.8888284709\H,-2
.3563498059,-0.7264223405,-1.7956268154\H,-1.7030087372,0.7829345341,-
1.1779385696\H,-0.3700106841,-1.9903464683,-1.210927353\H,0.1829285133
,-0.498480425,-2.0237116176\H,0.8395829329,0.5267384496,0.0541049173\H
,-2.3403154465,-1.7111715365,0.4721795576\H,-0.873097898,-2.9134173471
,0.8972242256\H,0.8692533315,-3.101573761,1.0205187429\H,-0.0894353241
,-2.8885532788,2.4812152388\H,2.806518981,-1.9434141196,-0.0314306953\
H,1.3788843232,0.4972593636,2.3588071418\H,0.9904362939,-0.8778904722,
3.3966698973\H,3.4177455453,-0.7034124143,2.6920933155\H,2.6963121962,
-2.2568166636,2.3373318567\H,4.0847519658,1.086128466,1.8061192014\H,5
.3295923839,1.2540926551,0.5591334803\H,3.7812215806,2.0528844748,0.35
5735775\H,3.5966698258,-1.0335212933,-1.925932428\H,5.1951905127,-0.42
59888964,-1.5115743315\H,-1.0267248608,1.8496011461,0.6001789556\H,-0.
2427274988,1.6127672989,2.1699120637\H,-1.9603043845,1.8965828383,2.08
90246918\H,-1.87466772,-1.7141178902,2.9428547876\H,-1.2871926063,-0.2
315033929,3.7060004037\H,-3.4621615605,0.8911466079,3.2212989868\H,-3.
7169604256,-0.6182289935,4.0691225316\H,-5.3200810515,-0.3696024805,2.
1597636803\H,-4.3068665542,-1.7957457208,2.0086564999\H,-3.7753574196,

1.9095336252,1.1030625828\H,-3.8280230279,1.5993069795,-0.6369202669\H
,-5.271189884,1.3814250005,0.3466728443\H,-4.4289240605,-2.128140806,-
0.4232637908\H,-5.7492972998,-0.9701665717,-0.2253929769\H,-4.54589242
71,-0.7079832446,-1.4835136879\H,4.301792699,0.8613192008,-3.335679677
8\H,4.5355290718,1.8904074874,-1.9451825758\H,2.0883706577,1.987523528
1,-1.492765432\H,0.0811408149,2.6062261168,-2.3997460914\H,-0.46802636
79,1.5701441995,-3.7423632094\H,0.2419734697,3.1397324405,-4.079783882
9\H,3.0349224236,0.6716278396,-4.9319204385\H,1.3108631263,0.472566024
1,-5.2780032233\H,2.0907419166,2.0163122956,-5.5880817364\\Version=x86
-Linux-G98RevA.9\HF=-978.2682023\RMSD=3.437e-09\RMSF=4.278e-06\PG=C01
[X(C25H43)]\\@

Compound **19**, intermediate in Fig. 1, lupeol precursor

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 **20**. Second transition state of Fig. 1, lupeol precursor

```
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\H,0,1.832875,-3.304494,-0.454426\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\H,0,-3.784929,2.902558,-1.256345\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)]\\@
```

Compound **21**, product in Fig. 1, lupyl cation

```
1|1|UNPC-UNK|FOpt|RB3LYP|6-31G(d)|C25H43(1+)|PCUSER|14-Aug-2003|0||# B
3LYP/6-31G* OPT=READFC GEOM=ALLCHECK 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,-1.252996264|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)]||@

Section II. Compounds 22-26: Structures from Fig. 1: Hopene precursors

Compound **22**, reactant in Fig. 1, hopene precursor.

1\1\GINC-DFTB\FOpt\RB3LYP\6-31G(d)\C25H43(1+)\BILLW\18-Aug-2003\0\\# B
3LYP/6-31G* OPT=READFC GEOM=ALLCHECK GUESS=READ\\E ring mod hopene OPE
N before D ring forms\\1,1\C,-2.1943340823,-0.4434329219,-2.6281637851
\C,-0.8400723829,-0.6841732909,-1.9060376225\C,-0.9717069213,-0.195519
628,-0.4322037602\C,-1.0190374096,-1.1785660291,0.6304174194\C,-2.4070
62211,0.6859332865,-0.4576723202\C,-3.1910587453,-0.1611003506,-1.4970
726453\C,-1.5527718017,-2.5525596083,0.4638064371\C,1.8717116499,0.096
8944438,1.4122909897\C,-0.5046088331,-0.8218493649,1.9557646796\C,1.09
34923199,-1.0463977874,1.969806965\C,2.7305300445,0.0840318485,0.36998
58388\C,3.0145535478,-1.1285765221,-0.4792760277\C,3.5154807618,1.3290
936851,0.0207053218\C,-1.9461963538,2.0824826861,-0.9140869942\C,-4.63
61508298,0.3236532181,-1.8375977313\C,-3.216570132,0.7886785984,0.8449
447094\C,-4.625851876,1.3505245932,0.5540216949\C,-5.3801021057,0.5071
496493,-0.4866172816\C,-4.7159185164,1.608560458,-2.6882881106\C,-5.33
77657272,-0.8000764253,-2.6335728711\C,5.0539310156,1.1712970097,0.157

2187861\C,5.4879133677,0.8329393622,1.5585579608\C,6.3247129944,-0.134
8170907,1.966033048\C,6.6601349836,-0.2960085793,3.4300293892\C,7.0243
050921,-1.1169673571,1.057669881\H,-2.488761707,-1.3074015481,-3.22963
85628\H,-2.1174906325,0.4060835851,-3.313325948\H,-0.5463739391,-1.736
721462,-1.9476276395\H,-0.0259070265,-0.1286544488,-2.3796102947\H,-0.
2003244553,0.5340175725,-0.1612512404\H,-3.3633671093,-1.1250403444,-0
.9923304882\H,-1.6445363775,-2.884028494,-0.5698277352\H,-0.9626450993
,-3.274156997,1.0421790887\H,-2.5575918875,-2.5707426165,0.9199662562\
H,1.7651756878,1.0288914317,1.9685116818\H,-0.6727884956,0.2319747161,
2.1942600604\H,-0.9360509025,-1.4542169557,2.7362393629\H,1.3119030473
,-1.1575987204,3.0385293293\H,1.3354810263,-2.0028937011,1.5001646177\
H,3.0671053239,-0.8547664823,-1.5398998957\H,3.9906449071,-1.555999554
9,-0.217174255\H,2.2722626489,-1.924349401,-0.3705733685\H,3.184396213
9,2.1609004395,0.6540058185\H,3.2940809479,1.6119909859,-1.0190983398\
H,-1.4114932056,2.0587422304,-1.8672852266\H,-1.2817460228,2.524501681
8,-0.1636422223\H,-2.7941024113,2.7588955099,-1.0280373043\H,-3.340454
5528,-0.2032546663,1.3021221868\H,-2.7057087779,1.4195729613,1.5832904
982\H,-4.5563310732,2.3944125475,0.2275590466\H,-5.193274315,1.3690407
078,1.4914269384\H,-6.3660830953,0.949308736,-0.6743242069\H,-5.569349
8929,-0.487328446,-0.0559907703\H,-4.4291839747,2.5128273341,-2.146868
7375\H,-4.0934860641,1.5430877661,-3.5871382096\H,-5.7486405679,1.7554
822301,-3.0230506665\H,-5.2749504575,-1.7645278656,-2.1146307344\H,-6.
399602069,-0.5638158966,-2.7645092041\H,-4.904144331,-0.9221661327,-3.
6322538211\H,5.4966007551,2.1313496447,-0.1457110132\H,5.4155661492,0.
4342911832,-0.5665928128\H,5.0710646657,1.4877756968,2.3266470311\H,6.
1353821942,0.432986667,4.0552674832\H,7.7383537184,-0.1750386771,3.601
2817743\H,6.4026292249,-1.3030080984,3.7868564369\H,6.7505087142,-1.01
49147547,0.0045030145\H,8.1133447757,-0.9924968158,1.1269387679\H,6.81
45413477,-2.1501748474,1.3666594794\\Version=x86-Linux-G98RevA.9\HF=-9
78.2803859\RMSD=3.566e-09\RMSF=4.469e-06\PG=C01 [X(C25H43)]\\@

Compound **23**, first transition state in Fig. 1, hopene precursor.

Frequency calculation: 1 imaginary frequency: -174.5 cm-1, IR intensity
275.1

1|1|UNPC-UNK|SP|RB3LYP|6-31G(d)|C25H43(1+)|PCUSER|19-Oct-2003|0||# B3L
YP/6-31G* SP GEOM=CHECK SCF=TIGHT||E ring hopene QST3 TS1 optimized fr
om QST3||1,1|C,2.4511646592,1.8389730898,-0.4568411202|C,0.9753303849,
1.8357611569,0.085718841|C,0.4523097842,0.4796972427,-0.1782338487|C,0
.7191653132,-0.65505446,0.6096258055|C,2.4865536658,-0.7116847875,-0.3
075329559|C,3.1988040863,0.6067849803,0.0647373854|C,0.9407452188,-0.4
93249681,2.1099280784|C,-2.1735757647,-0.4319412654,-0.000921661|C,-0.
112119853,-1.8846586614,0.2655310761|C,-1.6009200974,-1.6465383202,0.6
713995499|C,-2.647928345,0.7086074574,0.5557771706|C,-2.7134694309,0.9
792136869,2.0376504673|C,-3.2432782521,1.7881919159,-0.3232058658|C,2.
2629741779,-0.9909699858,-1.7942382616|C,4.7561854782,0.5957371996,-0.
2427925065|C,3.1240565708,-1.9137726259,0.3916728542|C,4.6299895938,-1
.9804323726,0.0320534956|C,5.3521895275,-0.6829425626,0.4008985785|C,5
.1103798193,0.6762202577,-1.7417081001|C,5.3992931054,1.8145318595,0.4
571418966|C,-4.799981707,1.7773642096,-0.3651551571|C,-5.363622786,0.5
81461078,-1.0833568421|C,-6.2033354726,-0.3584995714,-0.6207099736|C,-
6.6802036749,-1.4736812582,-1.5211837471|C,-6.7661662228,-0.4072393542
,0.778745583|H,2.9244532906,2.7648279369,-0.1215352589|H,2.4335309136,
1.8698557282,-1.5507340073|H,0.9771681921,2.0786686488,1.1515373488|H,
0.3924179942,2.5923809909,-0.4473238064|H,0.0744516123,0.3007548591,-1
.180233842|H,3.1738475091,0.662226056,1.1595887838|H,1.6915813516,0.24

93662814,2.3798909277|H,-0.0002869691,-0.1778619141,2.5727574776|H,1.2
202853749,-1.4453008325,2.5673188824|H,-2.2486915832,-0.5113801671,-1.
0869975291|H,-0.0874578845,-2.0900983043,-0.8090804847|H,0.2702127768,
-2.7727379557,0.7776046839|H,-2.1631130148,-2.5362121506,0.3596891589|
H,-1.6870813959,-1.5932701082,1.7597509372|H,-2.1345982374,1.876069745
1,2.2959556714|H,-3.7471606223,1.1894768167,2.3382078183|H,-2.35885819
18,0.1503486862,2.6540457379|H,-2.8711845823,1.6816055534,-1.349983212
8|H,-2.9166683886,2.7731935271,0.0380000105|H,2.0465213495,-0.09991931
96,-2.3865563706|H,1.459788384,-1.7134704283,-1.9544559934|H,3.1622218
946,-1.4482583235,-2.2141144386|H,3.048771276,-1.8176300148,1.47846390
08|H,2.6252278343,-2.8434492434,0.1001442017|H,4.7620141066,-2.2142183
443,-1.0300730804|H,5.066013113,-2.8215346088,0.5830862072|H,6.4107305
546,-0.7565483044,0.1236107747|H,5.3298239688,-0.5671083481,1.49407419
76|H,4.8349696032,-0.2164480773,-2.3073432265|H,4.6418236355,1.5391565
845,-2.2269229788|H,6.1935675671,0.7999709234,-1.8480910583|H,5.104471
5797,1.8805373314,1.5114520155|H,6.4904914487,1.7227446735,0.425595654
8|H,5.1435601261,2.7601538526,-0.0315376948|H,-5.1070496507,2.69254367
97,-0.890938036|H,-5.1978536492,1.8662343181,0.6502941423|H,-5.0474168
762,0.4981329408,-2.1255554771|H,-6.2482523803,-1.4059703135,-2.524448
6436|H,-7.7738411313,-1.456403191,-1.6217946621|H,-6.4247062367,-2.457
1372356,-1.1026500479|H,-6.4057882807,0.3960582226,1.4258281498|H,-7.8
623535987,-0.3461195423,0.753825625|H,-6.5228214575,-1.3645059981,1.25
96430855||Version=x86-Win32-G98RevA.11.2|HF=-978.2695756|RMSD=8.203e-0
09|PG=C01 [X(C25H43)]||@

Compound **24**, hopene intermediate in Fig. 1.

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 **25**. Transition state of Fig. 1, 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
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\\Ver
sion=x86-Linux-G98RevA.9\HF=-978.273353\RMSD=4.002e-09\RMSF=6.302e-06\
PG=C01 [X(C25H43)]\\@

Compound **26**, hopene product cation in Fig. 1.

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)]||@

Section III. $C_{10}H_{18}$ isomers (Table 1).

Compound **27**, dihydromyrcene.

1\1\GINC-LNX\FOpt\RB3LYP\6-31G(d)\C10H18\BILLW\02-Jan-2004\0\\# B3LYP/
6-31G* OPT=READFC GEOM=ALLCHECK FREQ\\dihydromyrcene\\0,1\C,-4.0342168
034,-0.7228139963,-0.2736960522\C,-2.7031328359,-0.1453012021,0.148004
3187\C,-1.5910621907,-0.896202898,0.1213718013\C,-0.1817306365,-0.5096
64676,0.4861487817\C,0.7578330654,-0.5446976036,-0.7382134508\C,2.2591
189077,-0.2687703067,-0.4587497334\C,2.4890948692,1.09974839,0.1369951
434\C,3.0893952367,2.1173836614,-0.4817279771\C,2.9028918203,-1.361649
8389,0.416582136\C,-2.7620718718,1.298935075,0.5836547626\H,-3.9475281
559,-1.7706998099,-0.5782043545\H,-4.4629642407,-0.1586853153,-1.11427
69368\H,-4.7681385029,-0.6659976072,0.542895743\H,-1.6960926635,-1.926
781919,-0.2248706421\H,0.1880593832,-1.2120771064,1.2474136629\H,-0.15
21072219,0.483945568,0.9444991013\H,0.6762614874,-1.529857977,-1.22014
75472\H,0.3986676034,0.1885512705,-1.4712932622\H,2.1354305272,1.24264
34361,1.159880794\H,3.4683602336,2.0253907723,-1.4981802918\H,3.227310
555,3.0819965478,0.0000821873\H,2.4955488481,-1.3605590094,1.434433609
4\H,3.9844496782,-1.207188038,0.4961454449\H,-1.7887692443,1.707610303
4,0.8645253836\H,-3.1697884633,1.9279785694,-0.2199640803\H,-3.4379078
352,1.4186138023,1.4422130048\H,2.7611853798,-0.2895827213,-1.43650786
74\H,2.731305267,-2.3571003954,-0.0108623309\\Version=x86-Linux-G98Rev
A.9\HF=-391.8727296\RMSD=8.960e-09\RMSF=4.533e-06\PG=C01 [X(C10H18)]\\
@

Compound **28**, *cis*-decalin, Table 1.

1\1\GINC-LNX\FOpt\RB3LYP\6-31G(d)\C10H18\BILLW\04-Jan-2004\0\\# B3LYP/
6-31G(D) OPT FREQ\\cisDecalinSP B3LYP coord\\0,1\C,0.6868739085,1.7398
651621,-0.8952021009\C,-0.4855631601,1.532644807,-1.8677219732\C,-1.79
68144301,1.280072919,-1.1092310992\C,-1.6592435777,0.1044194695,-0.129
4744613\C,-0.4925106831,0.3147065813,0.857797731\C,0.8458688306,0.5893
826491,0.1206566855\C,-0.3372416524,-0.8453087298,1.86333964\C,1.42910
93441,-0.6932325597,-0.5077710222\C,0.2573547956,-2.1165304354,1.23580
92808\C,1.587378768,-1.8159273392,0.529300338\H,1.6238713213,1.8759629
988,-1.4525355875\H,0.5180057987,2.674695282,-0.340435219\H,-0.2782728
811,0.6808551956,-2.5305900261\H,-0.5863002703,2.4101847492,-2.5194503
02\H,-2.0690523021,2.1869181342,-0.5483988747\H,-2.6167377616,1.092658
1891,-1.8146655515\H,-1.5159587253,-0.8222863282,-0.7013513519\H,-2.59
17366884,-0.0271261632,0.4364023541\H,-0.7336324217,1.2216618463,1.434
7751201\H,1.5703760476,0.9191999115,0.8821817073\H,0.3258012074,-0.515
7614238,2.676950649\H,-1.3081628682,-1.0682027217,2.3267375757\H,2.400
7594526,-0.4615013469,-0.965221587\H,0.784790886,-1.0484530702,-1.3232
643988\H,0.4027698658,-2.879759102,2.011251489\H,-0.4504791195,-2.5454
134919,0.5126638236\H,2.3329974362,-1.5115976201,1.2792674473\H,1.9796
88163,-2.7225901834,0.0506646217\\Version=x86-Linux-G98RevA.9\HF=-391.
9283673\RMSD=9.683e-09\RMSF=7.875e-06\PG=C01 [X(C10H18)]\\@

Compound **29**, *trans*-decalin, Table 1.

1|1|UNPC-UNK|FOpt|RB3LYP|6-31G(d)|C10H18|PCUSER|28-Apr-2003|0||# B3LYP

/6-31G(D) OPT||trans-decalin||0,1|C,-1.1078229614,0.9203849621,-1.3199
473287|C,-2.4724364136,0.7629790223,-0.6328335975|C,-2.594592846,-0.60
09731404,0.0626502507|C,-1.4292061078,-0.839338585,1.03441835|C,-0.061
1883459,-0.6881864935,0.3473836186|C,0.0611883459,0.6881864935,-0.3473
836186|C,1.4292061078,0.839338585,-1.03441835|C,2.594592846,0.60097314
04,-0.0626502507|C,2.4724364136,-0.7629790223,0.6328335975|C,1.1078229
614,-0.9203849621,1.3199473287|H,-1.0318220491,0.1983491362,-2.1477245
093|H,-1.0226162444,1.918256929,-1.7716518853|H,-3.2823553626,0.893468
94,-1.3622380795|H,-2.5947868745,1.5611814521,0.1143978775|H,-3.552677
5097,-0.674072096,0.5934534702|H,-2.5985840443,-1.3955326557,-0.698369
1345|H,-1.5096625449,-1.8374576021,1.4864597016|H,-1.4942051298,-0.117
8959524,1.8637185398|H,0.0027077658,-1.457192104,-0.4424284012|H,-0.00
27077658,1.457192104,0.4424284012|H,1.4942051298,0.1178959524,-1.86371
85398|H,1.5096625449,1.8374576021,-1.4864597016|H,2.5985840443,1.39553
26557,0.6983691345|H,3.5526775097,0.674072096,-0.5934534702|H,2.594786
8745,-1.5611814521,-0.1143978775|H,3.2823553626,-0.89346894,1.36223807
95|H,1.0226162444,-1.918256929,1.7716518853|H,1.0318220491,-0.19834913
62,2.1477245093||Version=x86-Win32-G98RevA.11.2|HF=-391.9336781|RMSD=1
.608e-009|RMSF=1.956e-005|PG=CI [X(C10H18)]||@
FIXED SPACES TO HERE-xxx

Compound **30**, spiro[4,5]decane, Table 1.

1\1\GINC-LNX\FOpt\RB3LYP\6-31G(d)\C10H18\BILLW\01-Jan-2004\0\\# B3LYP/
6-31G* OPT=READFC GEOM=ALLCHECK FREQ\\Spiro45decan\\0,1\C,-0.436302544
,0.1692617112,1.2055025892\C,-1.9405082124,-0.0556280821,0.9757981126\
C,-2.2245663289,-1.466105945,0.4397802752\C,-1.3988514887,-1.755908548
3,-0.8218733129\C,0.1012177835,-1.5320250049,-0.5703145072\C,0.4310525
352,-0.1187493047,-0.0468374718\C,0.2635827788,0.9863931054,-1.1238664
894\C,1.9345625436,0.0308041002,0.2907421032\C,1.1396297705,2.17103456
39,-0.6484799206\C,2.2208746003,1.5495326521,0.2841819053\H,-0.1021199
024,-0.4977496298,2.0144661285\H,-0.2647831812,1.1926827135,1.56323335
94\H,-2.4858313528,0.1122183531,1.9136304528\H,-2.3247968761,0.6866362
72,0.2619975833\H,-3.295650669,-1.5885071045,0.2331129155\H,-1.9687734
465,-2.2048323725,1.2142980876\H,-1.5703078228,-2.7858695886,-1.160774
2771\H,-1.7372029073,-1.1009444339,-1.6374089454\H,0.6727107395,-1.723
0946968,-1.4893629047\H,0.448225352,-2.2708174349,0.1685695716\H,0.642
7921065,0.6022243538,-2.0807460744\H,-0.777521727,1.2803059635,-1.2941
93609\H,2.5234126286,-0.4638102352,-0.4942783979\H,2.2008867625,-0.450
1146993,1.2399524994\H,1.5815259522,2.7053095216,-1.4963371714\H,0.536
3158181,2.9048647142,-0.1021847143\H,3.2384163803,1.7669606175,-0.0574
64757\H,2.1385535178,1.9628821989,1.2956905497\\Version=x86-Linux-G98R
evA.9\HF=-391.9202822\RMSD=3.302e-09\RMSF=3.671e-05\PG=C01 [X(C10H18)]
\\@

Compound **31**, delta-1-para-menthene, Table 1.

1\1\GINC-DFTC\FOpt\RB3LYP\6-31G(d)\C10H18\BILLW\31-Dec-2003\0\\# B3LYP
/6-31G* OPT=READFC FREQ GUESS=READ GEOM=ALLCHECK\\Cyclohexen1Me4iPr\\0
,1\C,-0.492080451,-0.9988513704,0.6426899274\C,-1.8149195557,-0.239065
4871,0.8149816434\C,-2.1227099154,0.683294391,-0.3441576505\C,-1.17436
33813,1.0153743246,-1.228974318\C,0.2634122618,0.5622344044,-1.1626961
897\C,0.6499412078,-0.0694691499,0.1913060725\C,-3.5342066748,1.201947
0972,-0.4373245978\C,2.0280324538,-0.7801651329,0.1402703158\C,3.13570
50941,0.1304763854,-0.4182100451\C,2.4622828813,-1.3182542633,1.514761
1809\H,-0.6233721456,-1.7880032358,-0.1124380151\H,-0.2437672043,-1.50
24983609,1.5826807106\H,-2.6398904316,-0.9553020812,0.9432644092\H,-1.

7935293718,0.3463253138,1.7488896992\H,-1.434515575,1.6691086199,-2.06
23715802\H,0.4598547089,-0.1592264212,-1.9745937755\H,0.9119558193,1.4
215739328,-1.3764837334\H,0.7262211454,0.7472478672,0.9286673325\H,-3.
6630857654,1.8814555526,-1.2861724043\H,-4.2550117923,0.379136146,-0.5
46166544\H,-3.8189534225,1.743923886,0.4760307097\H,1.9270826168,-1.63
99247283,-0.5419513343\H,3.2404129719,1.0390109711,0.1899978845\H,2.94
26650566,0.4391143568,-1.4501719262\H,4.1022093727,-0.3869539476,-0.40
54754559\H,2.5385231105,-0.5033802827,2.2470634933\H,3.4482233748,-1.7
931304592,1.4480197529\H,1.7684140088,-2.0636043233,1.915332744\\Versi
on=x86-Linux-G98RevA.9\HF=-391.9070932\RMSD=7.665e-09\RMSF=3.800e-06\P
G=C01 [X(C10H18)]\\@

Compound **32**, Δ1-para-menthene, Table 1.

1\1\GINC-DFT\FOpt\RB3LYP\6-31G(d)\C10H18\BILLW\01-Jan-2004\0\\# B3LYP/
6-31G* OPT=READFC FREQ GUESS=READ GEOM=ALLCHECK\\Dicyclopentyl\\0,1\C,
-1.7433331608,0.6473295498,0.7119298557\C,-2.7663391715,-0.2386863393,
1.4599014868\C,-1.9765833902,-1.5033398938,1.9167690582\C,-0.528591126
,-1.2978644391,1.4146481988\C,-0.6548207005,-0.3292392009,0.2205778604
\C,1.9765835096,1.503340228,-1.9167685122\C,0.5285911806,1.2978644836,
-1.4146481331\C,0.6548207098,0.3292391824,-0.220577862\C,1.743333127,-
0.6473296134,-0.7119299079\C,2.7663390041,0.238686069,-1.4599020554\H,
-1.2868908872,1.3682469659,1.4055291972\H,-2.1987969781,1.2272261421,-
0.0983187168\H,-3.2240811597,0.292044955,2.3016112497\H,-3.5852869104,
-0.5240855876,0.7894218325\H,-2.4109093829,-2.4046430627,1.4687906918\
H,-2.0133374235,-1.6467450315,3.0020168933\H,0.0800679357,-0.820694957
6,2.1963034558\H,-0.0336364926,-2.239894911,1.154208972\H,-1.059654176
9,-0.892092871,-0.6376484588\H,2.0133378721,1.6467465675,-3.0020161782
\H,2.4109095224,2.4046428286,-1.4687890077\H,-0.0800675701,0.820694924
7,-2.1963035911\H,0.0336362798,2.2398948372,-1.1542089699\H,1.05965419
49,0.8920928276,0.6376484696\H,1.2868907173,-1.368247222,-1.4055289534
\H,2.1987971452,-1.2272259916,0.0983187019\H,3.2240798849,-0.292045179
6,-2.3016124457\H,3.5852875377,0.5240846066,-0.7894230781\\Version=x86
-Linux-G98RevA.9\HF=-391.9134545\RMSD=4.997e-09\RMSF=3.326e-05\PG=C01
[X(C10H18)]\\@

Compound **33**, bicyclo[5.3.0]decane, Table 1.

1\1\GINC-LNX\FOpt\RB3LYP\6-31G(d)\C10H18\BILLW\04-Jan-2004\0\\# B3LYP/
6-31G(D) OPT=READFC GEOM=ALLCHECK GUESS=READ\\Bicyclo530decan\\0,1\C,-
1.4723300908,1.3342779812,-1.238177255\C,-2.4663994654,1.1368031968,-0
.0701287976\C,-2.0265736737,0.2784231412,1.1386906171\C,-0.554652007,0
.3751828149,1.584674866\C,0.3831084368,-0.4869924699,0.7308548483\C,0.
6527059422,0.0095689389,-0.7014028641\C,-0.5704590271,0.1433990182,-1.
6166659162\C,1.7536322109,-0.9554640281,-1.1814066163\C,1.8077532187,-
0.6860359386,1.2826698803\C,2.6350046796,-1.2145160507,0.0749228479\H,
-0.8159441673,2.1864349738,-1.0130253366\H,-2.0556496034,1.6411868071,
-2.1162439396\H,-2.7492169121,2.1361258703,0.2878564904\H,-3.392304361
6,0.6946000342,-0.4624825503\H,-2.2378502564,-0.7788919366,0.926194878
3\H,-2.6791808935,0.5411729322,1.9816153753\H,-0.2127284966,1.42102973
13,1.586581301\H,-0.486938657,0.0330744299,2.626880285\H,-0.0808436743
,-1.4848873961,0.6445063269\H,1.1060066001,1.0123732926,-0.6153572118\
H,-0.2177645646,0.2917346989,-2.6469175952\H,-1.1432825671,-0.79602235
41,-1.625137711\H,1.2935697045,-1.8914114051,-1.5265733809\H,2.3244143
105,-0.5529060493,-2.0259415815\H,1.8324341434,-1.3630525299,2.1441359
711\H,2.2043768934,0.2791513714,1.6260329721\H,2.8625771385,-2.2805191

```
224,0.1827780232\H,3.5975840192,-0.6970729726,0.0009080292\\Version=x8
6-Linux-G98RevA.9\HF=-391.9132245\RMSD=6.315e-09\RMSF=5.558e-06\PG=C01
[X(C10H18)]\\@
```

Compound **34**, 5-decyne, Table 1.

```
1|1|UNPC-UNK|FOpt|RB3LYP|6-31G(d)|C10H18|PCUSER|28-Jan-2004|0||# B3LYP
/6-31G* OPT=READFC FREQ GUESS=READ GEOM=ALLCHECK||Dec5yne||0,1|C,5.423
318199,0.2266703001,0.8778798788|C,4.389147289,0.1835054234,-0.2516154
048|C,2.9618745447,-0.0612341045,0.2514368496|C,1.9261446126,-0.107157
7577,-0.8919366534|C,0.5572516582,-0.3400258777,-0.425688527|C,-0.5626
475007,-0.5391772999,-0.0116141195|C,-1.9314592228,-0.757090887,0.4620
424085|C,-2.9610647992,0.1926590562,-0.1860600842|C,-4.3883136986,-0.0
468406185,0.3195761143|C,-5.4164515118,0.8901807691,-0.3223397848|H,6.
4323424389,0.4048616587,0.4890768552|H,5.1955612654,1.0262298193,1.593
4020418|H,5.442278152,-0.7186561267,1.4338727506|H,4.6619895752,-0.604
6147979,-0.9680226879|H,4.4195680954,1.1284688901,-0.8127951817|H,2.91
98763968,-1.0064590321,0.8084840485|H,2.6758467923,0.7272267019,0.9599
475467|H,2.211826941,-0.8935056035,-1.6059142284|H,1.9676873816,0.8372
295351,-1.4542733907|H,-2.2283472504,-1.798027515,0.2670298638|H,-1.96
6489119,-0.6354903054,1.5546549801|H,-2.925627428,0.0663181688,-1.2761
51506|H,-2.663823658,1.2305044002,0.0139201341|H,-4.67241237,-1.090904
3032,0.1245561821|H,-4.4121924375,0.0759203835,1.4118969535|H,-5.44198
5742,0.7635456166,-1.4115786333|H,-6.4255696979,0.6975333841,0.0592588
353|H,-5.1773267577,1.9408851035,-0.117448628||Version=x86-Win32-G98Re
vA.11.2|HF=-391.8616147|RMSD=7.999e-009|RMSF=6.458e-007|PG=C01 [X(C10H
18)]||@
```

Section IV. Models of oxidosqualene cyclization (Table 3).

Compound **71**, reactant in Table 3

```
This optimization was done with the C4-C5 distance frozen at 3.8 A.

1|1|UNPC-UNK|FOpt|RB3LYP|6-31G(d)|C10H19(1+)|PCUSER|11-Apr-2004|0||# B
3LYP/6-31G* OPT FREQ GEOM=MODREDUNDANT||Model 3.8 A freeze B3LYP geom|
|1,1|C,2.1851166886,-1.3478113549,-1.9686117166|C,1.8849357713,-0.7275
737592,-0.6397348611|C,0.9285821947,-1.0688569664,0.2597617794|C,0.885
7839028,-0.3744123649,1.6035573797|C,-0.4370441084,0.3210166053,1.9862
068873|C,-0.7493606871,1.5824909006,1.1134671189|C,-1.2667316888,1.357
7202082,-0.2415624329|C,-2.4458675134,0.4981523855,-0.4622448832|C,-0.
7137614286,2.1000846571,-1.3905247045|C,0.0048919605,-2.2522924545,0.0
856339068|H,1.4598513696,-2.1029050681,-2.279316799|H,3.1735205158,-1.
8268670742,-1.9401120631|H,2.2450441995,-0.5806091632,-2.7517041041|H,
2.5565048195,0.0859437812,-0.3596288763|H,1.7043508094,0.351030291,1.6
790478499|H,1.0659186835,-1.1207438809,2.3924169917|H,-1.2790499573,-0
.3778241975,1.9529083573|H,-0.3697753254,0.6734735963,3.019880707|H,0.
1044827494,2.2651535921,1.1087775091|H,-1.5862850205,2.0910416131,1.63
13329309|H,-3.001043727,0.2703180967,0.4497894199|H,-3.1071353409,0.92
255886,-1.2276802645|H,-2.085955575,-0.4560192045,-0.8851227017|H,0.34
34821577,2.3455726545,-1.2719591638|H,-1.2630645709,3.0617915948,-1.42
06902212|H,-0.9075671337,1.6094628699,-2.3489278117|H,-0.0487026757,-2
.6046955087,-0.9466618021|H,0.3537673908,-3.0949541365,0.6979803585|H,
-1.0176139178,-2.0428358559,0.4239788406||Version=x86-Win32-G98RevA.11
.2|HF=-392.2208933|RMSD=7.154e-009|RMSF=7.859e-004|PG=C01 [X(C10H19)]|
|@
```

Compound **72**, product in Table 3


```
1\1\GINC-DFT\FOpt\RB3LYP\6-31G(d)\C10H19(1+)\BILLW\21-Apr-2004\0\\# G3
MP2B3\\Model-Prod B3LYP coord\\1,1\C,0.6564953541,1.4030841229,-1.8273
613475\C,0.192782534,0.1071510268,-1.1549512964\C,-1.2272232518,-0.039
3515341,-0.8866842062\C,-1.7275633606,-1.3848308498,-0.5766503969\C,-1
.0991065953,-1.7414977643,0.8356745445\C,0.4170137153,-1.5760015361,0.
8004258503\C,0.8978800242,-0.1821721423,0.3482412637\C,0.5420996207,0.
9113934492,1.3661232352\C,2.4153365026,-0.1954474497,0.1076156875\C,-2
.1368065367,1.115135316,-0.7893643393\H,0.5196416348,2.2883806227,-1.2
0068749\H,0.1114898541,1.5640784246,-2.7633073841\H,1.7160405668,1.332
8086606,-2.0800705234\H,0.5408175926,-0.7643575508,-1.7209543002\H,-1.
3522244945,-2.1229027825,-1.2935053601\H,-2.817754458,-1.4336433977,-0
.5249462939\H,-1.560071807,-1.1151174857,1.6057146135\H,-1.3877541959,
-2.7752369539,1.0478152049\H,0.8553922532,-2.34057552,0.1463273189\H,0
.8172040474,-1.7615531529,1.8052627842\H,-0.5180788884,0.9314188834,1.
6384554981\H,1.1091998352,0.7344256234,2.2864903359\H,0.8210958313,1.9
075087122,1.0102649592\H,2.7025601283,-0.9086835638,-0.6720316075\H,2.
9108777514,-0.4973077521,1.0377280995\H,2.8010779977,0.7917510847,-0.1
581036668\H,-1.635999296,2.0550689824,-0.5495939654\H,-2.5577795602,1.
2400092714,-1.806508333\H,-2.9888196665,0.9299160399,-0.1287482927\\Ve
rsion=x86-Linux-G03RevB.02\State=1-A\HF=-392.2457722\RMSD=4.405e-09\RM
SF=8.917e-06\Dipole=-1.0084228,0.0927303,-0.3042017\PG=C01 [X(C10H19)]
\\@
```


Compound **73**, reactant in Table 3


```
1|1|UNPC-UNK|FOpt|RB3LYP|6-31G(d)|C15H26|PCUSER|05-Dec-2003|0||# B3LYP
/6-31G* OPT=READFC GEOM=ALLCHECK GUESS=READ FREQ||polypodatetraene mod
el OPEN||0,1|C,5.2370405576,0.6558020546,-0.3200137237|C,3.3153654832,
0.3144499306,1.3470543393|C,4.1783441642,-0.1183466623,0.4145564561|C,
3.2542164917,1.7332990424,1.8605050643|C,-0.3085334397,0.6193012039,-0
.3682123444|C,2.3217417786,-0.6460963864,1.9713130281|C,0.8314788743,-
0.2833931734,1.7522757743|C,0.4332813677,-0.2777240339,0.3002882202|C,
-0.9050111461,1.8633676132,0.2471237552|C,-0.601567115,0.4219543909,-1
.842607258|C,-2.0985739138,0.2169313808,-2.1922884542|C,-2.6737777001,
-1.0410342327,-1.5990652382|C,-3.7948581485,-1.2012491998,-0.879388997
2|C,-4.2015016782,-2.5679247736,-0.3794567644|C,-4.7495633229,-0.09367
7281,-0.5038492056|H,5.3034075614,1.7016485293,-0.0085359126|H,5.04632
49345,0.6452631704,-1.40224683|H,6.2264193518,0.2003789087,-0.17475463
3|H,4.1179925289,-1.1712846324,0.1334562493|H,4.0784142213,2.353422886
3,1.5006996605|H,3.2779829807,1.750021144,2.9590091036|H,2.3191208574,
2.2239056816,1.5594695359|H,2.4997666926,-1.6566658468,1.5817639626|H,
2.4975772343,-0.6954498343,3.0572642255|H,0.6076801161,0.6751473463,2.
2321520351|H,0.229849169,-1.0330108524,2.2898720036|H,0.8009415688,-1.
1371841085,-0.2643066824|H,-0.5295415029,2.0635514804,1.2536578306|H,-
1.9983636457,1.7871732906,0.3181520376|H,-0.6922359484,2.7445748229,-0
.373644525|H,-0.2438844198,1.2991728942,-2.4036754485|H,-0.0322548844,
-0.4391603246,-2.2151860446|H,-2.1727210077,0.164459275,-3.2897229512|
H,-2.6739411221,1.0999019242,-1.8956152864|H,-2.0806587196,-1.93640253
92,-1.7978656392|H,-3.4841868224,-3.3405225383,-0.6738740159|H,-5.1893
509208,-2.8558261402,-0.7669902603|H,-4.2836624767,-2.5803590736,0.716
7610731|H,-4.4309065675,0.8909483223,-0.8540428288|H,-5.7492680775,-0.
286719086,-0.9181665531|H,-4.8729946198,-0.0409439397,0.5869619827||Ve
rsion=x86-Win32-G98RevA.11.2|HF=-587.2195143|RMSD=3.993e-009|RMSF=1.87
```

0e-006|PG=C01 [X(C15H26)]||@

Compound **74**, product in Table 3

1|1|UNPC-UNK|FOpt|RB3LYP|6-31G(d)|C15H26|PCUSER|06-Dec-2003|0||# B3LYP
/6-31G* OPT||polypodatetraen model C15H26||0,1|C,2.3974679118,1.563124
4721,-1.5266619791|C,2.3896667794,0.4264699106,0.7643948498|C,1.764432
2151,0.4958578529,-0.6220355408|C,3.2771647884,1.3041258857,1.24421840
52|C,0.1858618892,0.5678734199,-0.5104424564|C,1.9018773747,-0.7376869
049,1.5952163401|C,0.3648258098,-0.7849600335,1.6698097476|C,-0.266341
9737,-0.7288797201,0.264691939|C,-0.2090782213,1.889869179,0.184138101
8|C,-0.4284385887,0.5332062761,-1.9321695745|C,-1.9427438586,0.2913886
564,-1.9403653147|C,-2.2977967275,-1.0143984196,-1.2260389321|C,-1.796
239136,-1.0895881009,0.2381523986|C,-1.9794328628,-2.5534960952,0.7033
78825|C,-2.6809656434,-0.2115579231,1.1498970634|H,3.4793836718,1.4049
414826,-1.5891644923|H,2.0004625772,1.5103366152,-2.5440014491|H,2.236
2683812,2.5807930557,-1.1559402933|H,1.9708262303,-0.4763843957,-1.100
6675035|H,3.641319763,2.1490360611,0.6685044125|H,3.6795575428,1.20071
05379,2.249464544|H,2.3340639568,-0.699570767,2.6020808598|H,2.2514681
337,-1.6760030764,1.1353049755|H,0.0672043187,-1.7039870848,2.18615282
32|H,0.0056670872,0.0463510188,2.2881618103|H,0.1985605164,-1.55133336
35,-0.3057313634|H,-1.2902968211,2.0342620195,0.2208718479|H,0.2041596
119,2.7421968056,-0.3662210948|H,0.1725537499,1.9535311332,1.206504238
9|H,-0.2069748801,1.4693081496,-2.458265454|H,0.055603883,-0.270389371
1,-2.5087848177|H,-2.3000852979,0.2533558014,-2.9777737816|H,-2.465593
7064,1.1363453827,-1.4742885542|H,-3.3842164057,-1.1781356352,-1.24384
61212|H,-1.8521982775,-1.8487054665,-1.7889218095|H,-3.0070881903,-2.8
83475426,0.5071579483|H,-1.3046486976,-3.2326642653,0.1675154416|H,-1.
80082251,-2.6770520375,1.7767554654|H,-3.6968007125,-0.6248667897,1.18
47917618|H,-2.3039622314,-0.1881693561,2.1780670512|H,-2.7659702317,0.
8214782392,0.8051703159||Version=x86-Win32-G98RevA.11.2|HF=-587.250736
5|RMSD=9.680e-009|RMSF=4.095e-006|PG=C01 [X(C15H26)]||@

Compound **78**, reactant in Table 3

1\1\GINC-DFT\FOpt\RB3LYP\6-31G(d)\C23H36O1\BILLW\28-Dec-2003\0\\# B3LY
P/6-31G* OPT=READFC GEOM=ALLCHECK GUESS=READ\\DesMeSqualenHopen\\0,1\C
,-1.3288076485,0.7080384497,-0.9204654118\C,0.112082708,0.9962915298,-
1.4118928787\C,1.1226212847,1.0915104479,-0.301727843\C,2.2119538423,0
.3297519383,-0.176765085\C,-1.9224966121,-0.8878624557,0.9455865011\C,
-1.4943583157,-0.6505852406,-0.2965551434\C,4.8450355569,2.0420489072,
-0.2028351966\C,3.222300538,0.4245984077,0.9335976001\C,4.6662603004,0
.6945277975,0.4413692205\C,5.2815052542,2.2554405983,-1.4463976912\C,5
.4605454761,3.6027770206,-2.0908636933\C,-5.6346238584,-1.8552277492,0
.8601830759\C,-2.0852345005,-2.2476561649,1.568058451\C,-3.5229024622,
-2.5370461166,2.0676393304\C,-4.5414750639,-2.6154560896,0.9634429543\
C,-6.650894389,-1.9312144573,-0.2483360051\C,6.9025831635,3.8684141853
,-2.5909657282\C,7.9199935905,3.9565306217,-1.486412086\C,9.0059234252
,3.188307177,-1.3697401896\C,10.0221521309,3.2829203318,-0.2673924002\
C,-8.0797931922,-2.2566133716,0.2377989144\C,-8.207277461,-3.645965699
8,0.8199447633\C,-8.1777289692,-3.9079635251,2.2646662604\O,-9.4151399
682,-3.9326304431,1.5410229237\H,-2.0034948217,0.7973839915,-1.7853480
204\H,-1.6346768371,1.4844465404,-0.2063416619\H,0.4173861989,0.219705
5409,-2.1260643749\H,0.0931112238,1.9436110888,-1.9716260308\H,0.92487
90642,1.8538063206,0.4559806594\H,2.4096658133,-0.432410162,-0.9346266
364\H,-2.1846433354,-0.0393937008,1.5824494586\H,-1.2312052263,-1.4996

449112,-0.9323624212\H,4.5868083523,2.9032940401,0.4183648329\H,2.9233
399705,1.2098963337,1.6409227648\H,3.2314781482,-0.5182568348,1.501256
0495\H,5.3381155952,0.6120221526,1.3091262809\H,4.967412937,-0.0949223
379,-0.2604132971\H,5.5397205305,1.3940909924,-2.0674615534\H,5.165442
9444,4.3927623923,-1.3871172903\H,4.7843225674,3.6877735261,-2.9550291
841\H,-5.8296325516,-1.1068540154,1.6323897311\H,-1.4062067953,-2.3403
130192,2.4290569604\H,-1.7840485412,-3.0227703843,0.850549581\H,-3.502
8449398,-3.4912642857,2.615684987\H,-3.8206717849,-1.7679683831,2.7929
856043\H,-4.3446250193,-3.3600851944,0.1880406303\H,-6.6865031093,-0.9
677600132,-0.7774537686\H,-6.3347743117,-2.6778050289,-0.9895665301\H,
6.8930246576,4.8120169156,-3.1574647737\H,7.194156122,3.0830668617,-3.
3014033476\H,7.7321863193,4.7193186543,-0.7265486655\H,9.1898207162,2.
4232245399,-2.1269486808\H,9.7644375761,4.0693565118,0.4503581086\H,10
.1029820457,2.3355564315,0.2830716543\H,11.0236897205,3.5007947189,-0.
6633095842\H,-8.7771845725,-2.165471026,-0.6059007654\H,-8.402211844,-
1.5256134985,0.9905061369\H,-7.8906210143,-4.4568877975,0.1576493739\H
,-8.0584538012,-3.0743859344,2.9577998503\H,-7.8332510387,-4.872676735
2,2.6389842162\\Version=x86-Linux-G98RevA.9\HF=-973.2222149\RMSD=7.501
e-09\RMSF=1.901e-06\PG=C01 [X(C23H36O1)]\\@

Compound **79**, product in Table 3

1\1\GINC-LNX\FOpt\RB3LYP\6-31G(d)\C23H36O1\BILLW\28-Dec-2003\0\\# B3LY
P/6-31G* OPT=READFC GEOM=ALLCHECK GUESS=READ\\desmethyl hopene\\0,1\C,
-0.2305193097,1.1852164752,-1.4876786935\C,1.1834285908,0.596320127,-1
.4849455962\C,1.7081980831,0.3604852157,-0.0637650634\C,0.7276645615,-
0.5387434738,0.7368292814\C,-0.7051117625,0.0629180556,0.7444864388\C,
-1.229228379,0.3208411357,-0.6968931002\C,3.6300286729,-0.4649056568,1
.3855056287\C,1.2692688252,-0.8222133204,2.1570939392\C,2.6998742762,-
1.3937695467,2.1607583867\C,3.1212647511,-0.2380249585,-0.0456411792\C
,4.2598113158,0.572764484,-0.7013830956\C,-2.6599700233,0.9240364611,-
0.6904994013\C,-1.7065159094,-0.8010389826,1.5336981151\C,-3.118065908
5,-0.2068888002,1.5323539569\C,-3.640399561,0.0369747964,0.1129547492\
C,-3.2206680384,1.1757924908,-2.1061811542\C,5.5556147813,0.157582855,
0.0643694322\C,5.1271211225,-0.8406531817,1.1780111656\C,5.3176548232,
-2.3061659804,0.8589759638\C,5.6322542325,-2.8598657585,-0.314024997\C
,-4.6457846363,1.7498060278,-2.0755663681\C,-5.0600017103,0.6273144959
,0.1294529392\C,-5.6028521984,0.8616362298,-1.2764498079\O,-6.89655021
89,1.4513361926,-1.1398267146\H,-7.2362064105,1.6183961565,-2.03312843
74\H,-0.5647807794,1.3063849327,-2.5238740281\H,-0.2060146065,2.195183
709,-1.0491660484\H,1.1818254062,-0.3606059369,-2.0295222859\H,1.86328
55842,1.2619414642,-2.0323261298\H,1.7528422033,1.3392291205,0.4460938
141\H,0.6729322012,-1.5063237751,0.2076902229\H,-0.6437723471,1.043524
8418,1.2485754931\H,-1.291424402,-0.6603590046,-1.1998390858\H,3.62529
61009,0.5135873216,1.8952627841\H,1.2528417328,0.1129288907,2.73832404
32\H,0.610347031,-1.5224793611,2.6810222062\H,3.0420141648,-1.53091102
77,3.195897937\H,2.694357558,-2.3886077109,1.6945566363\H,3.0755713058
,-1.2232120209,-0.5363666961\H,4.0750860496,1.6485007967,-0.581375401\
H,4.3373744382,0.385508931,-1.7775015766\H,-2.6045502434,1.8999578088,
-0.177148952\H,-1.3738046808,-0.9235824729,2.569747729\H,-1.7333528902
,-1.8105049816,1.0941811866\H,-3.8055958835,-0.8700711428,2.0746809902
\H,-3.1127959723,0.7474572603,2.0808114726\H,-3.6870419713,-0.94027990
19,-0.3982779273\H,-2.5765983465,1.8642276063,-2.6627301655\H,-3.21744
35745,0.227689211,-2.6661364035\H,6.0166386771,1.0361279402,0.52843546
53\H,6.3138116128,-0.2704983281,-0.5975076873\H,5.6844361137,-0.642248
3208,2.1044143838\H,5.1600957368,-2.9732191522,1.7084642851\H,5.807295

3657,-2.274380934,-1.2129969516\H,5.7327700999,-3.9370304365,-0.418752
0972\H,-5.0204174094,1.8803193239,-3.10170767\H,-4.6402500781,2.745609
569,-1.6107904191\H,-5.7423805401,-0.034787957,0.6772939508\H,-5.05899
97593,1.5898041164,0.6611087313\H,-5.6893893309,-0.1144812201,-1.78756
88941\\Version=x86-Linux-G98RevA.9\HF=-973.3593845\RMSD=9.369e-09\RMSF
=5.488e-06\PG=C01 [X(C23H36O1)]\\@

Section V. Neutral triterpenes (Table 4)

Squalene fully folded for cyclization to hopene:

1\1\GINC-DFT\FOpt\RB3LYP\6-31G(d)\C30H50\BILLW\24-Feb-2004\0\\# B3LYP/
6-31G* OPT\\HopSqualNoOXFull\\0,1\C,0.4991993926,0.8147935933,-1.68441
595\C,-0.9429468807,1.109702019,-1.1954158411\C,-1.5998387327,-0.07816
15238,-0.5455353951\C,-2.0689424602,-0.2087850208,0.7051719404\C,2.250
3334215,-0.4408095773,-0.277710352\C,1.4751078417,0.6190542807,-0.5556
805792\C,-2.0230591201,0.8764388481,1.7543701175\C,-5.0885248944,-0.99
49490886,0.4914847461\C,-2.6838121366,-1.5196733544,1.1555157029\C,-4.
1668582578,-1.4343539333,1.5975484039\C,-6.0618133664,-0.0709392486,0.
5194806109\C,-6.4275563942,0.7498091746,1.7335257528\C,-6.8823268683,0
.2114582871,-0.723966621\C,2.2886792361,-1.7112898386,-1.0931371347\C,
6.0212899405,0.5367188765,-1.2819409995\C,3.1629270098,-0.4194488164,0
.9333113985\C,4.6746551799,-0.5493700307,0.6202748115\C,5.2017007697,0
.5831801948,-0.2200122467\C,6.5856034391,-0.7343582962,-1.8711190002\C
,6.4440940822,1.8159775135,-1.9775233175\C,-8.4009038678,-0.0681564532
,-0.5869398539\C,-8.7099021776,-1.5144867525,-0.3068402515\C,-9.511933
2839,-2.0401061523,0.6317646917\C,-9.6935957286,-3.5361444475,0.741986
0217\C,-10.3036200134,-1.2430643791,1.6404312511\C,7.9566398248,2.1472
936044,-1.8792256107\C,8.4081896135,2.428076743,-0.4714613298\C,9.4246
103727,1.8845584833,0.2151844442\C,9.715917322,2.316360555,1.633499908
8\C,10.3666515863,0.8318349182,-0.3178355377\H,0.8289311788,1.66702103
88,-2.2981717489\H,0.480713554,-0.0522379639,-2.3540701708\H,-0.926233
2006,1.9763981395,-0.5251210241\H,-1.5401592064,1.4118688843,-2.069131
8315\H,-1.6892081519,-0.947054326,-1.2016925217\H,1.5407071257,1.47216
60524,0.1236042731\H,-1.4352203383,1.743562605,1.4451503907\H,-1.58726
92285,0.4925916966,2.6871448181\H,-3.0317040614,1.2330259725,2.0024952
998\H,-4.93010623,-1.5205793814,-0.4526799087\H,-2.105577508,-1.917318
4434,2.0041033278\H,-2.5983121694,-2.257940224,0.3479125366\H,-4.25676
76538,-0.7855808441,2.4750420179\H,-4.4641950158,-2.4387304482,1.93774
03216\H,-5.70835968,0.6482839316,2.5499551277\H,-7.4100323023,0.457008
2151,2.12754143\H,-6.4974662752,1.8158316972,1.4767206745\H,-6.7617981
507,1.2692174248,-1.0054419408\H,-6.4891575995,-0.3796692492,-1.560829
2721\H,1.5100517267,-1.7505202355,-1.8581697518\H,2.1661803409,-2.5901
715753,-0.4452336421\H,3.2552140494,-1.8281777174,-1.6014055753\H,2.99
81880204,0.5091346119,1.4948792392\H,2.8886128816,-1.2449604633,1.6084
379047\H,4.87595596,-1.5196875798,0.154244527\H,5.2084243468,-0.565117
4695,1.5835638775\H,4.8667174708,1.5703687136,0.1053790945\H,6.1607124
864,-1.6372768189,-1.4258401158\H,7.6741702675,-0.7862230439,-1.734602
2229\H,6.4043593986,-0.7747074091,-2.9542222426\H,6.1850963527,1.75154
78674,-3.0456096741\H,5.8721376598,2.6588906532,-1.5690613652\H,-8.873
1134146,0.2257572,-1.5374308452\H,-8.8325019,0.5878865126,0.1760709607
\H,-8.2031343557,-2.2149110956,-0.9742707974\H,-9.1066205391,-4.075371
3844,-0.0082263435\H,-10.7485638338,-3.8191137607,0.6161514178\H,-9.39
20960814,-3.8997330136,1.7347593198\H,-10.142613807,-0.1650598989,1.56
46411091\H,-11.3806702053,-1.4273121748,1.5202734479\H,-10.0508401579,

-1.5518799702,2.66446112\H,8.1349608801,3.0397835954,-2.498927995\H,8.
5435299354,1.3437720338,-2.3359193834\H,7.8115086845,3.1848285405,0.04
26925181\H,9.6667740471,1.4635028872,2.3256916463\H,10.7309405542,2.72
91556083,1.7228331\H,9.0093175581,3.0759676042,1.9826271746\H,10.35264
09413,-0.0612649454,0.3224974017\H,10.1335037521,0.5166706349,-1.33763
61855\H,11.4025827959,1.1993962476,-0.3116582081\\Version=x86-Linux-G9
8RevA.9\HF=-1173.2344737\RMSD=6.028e-09\RMSF=6.019e-05\PG=C01 [X(C30H5
0)]\\@

SqualeneX (Table 4), crystal structure carbon coordinates were frozen beyond C5

1|1|UNPC-UNK|FOpt|RB3LYP|6-31G(d)|C30H50|PCUSER|27-Feb-2004|0||# B3LYP
/6-31G* OPT GEOM=ALLCHECK||C2-azasqualene-xray-fix torsions reopt afte
r went astray in ring A||0,1|C,-7.7375608521,-5.6246483271,1.740681276
5|C,-7.9813238053,-4.1341732203,1.7896603193|C,-7.3437329768,-3.308053
6621,0.9461026151|C,-7.4487770205,-1.8114754813,0.8247117013|C,-6.0684
182087,-1.1052365294,0.8136309041|C,-5.2529475534,-1.2714927362,2.0807
920622|C,-4.0700856673,-1.9050167343,2.0457262253|C,-3.1196021188,-2.1
955817431,3.1764376722|C,-1.6343294776,-1.9609719512,2.8003165725|C,-1
.3033787044,-0.5459562567,2.3684663026|C,-0.9427833026,-0.2884473746,1
.1018819421|C,-0.6104197786,1.0412322299,0.4738135747|C,0.5230166219,0
.9521619342,-0.5778778056|C,1.8796866915,0.7307531683,0.0385123563|C,2
.7087645565,-0.3282428526,-0.0332060302|C,4.0394008354,-0.2964586235,0
.6842787294|C,5.2792288514,-0.3852817883,-0.2385942525|C,5.4588255925,
0.8465724375,-1.0983228047|C,6.5792326958,1.2549393678,-1.7158290517|C
,6.6554818903,2.5223270894,-2.5436618873|C,5.4128351181,3.4329683356,-
2.5533402221|C,5.6219294764,4.6872645268,-3.3683044488|C,5.4147133935,
4.8516662221,-4.6840352344|C,4.8964397141,3.7725330243,-5.6038993861|C
,-8.9798877806,-3.7028570399,2.8366841491|C,-5.8690246406,-0.680231011
5,3.3269391973|C,-1.4935785275,0.5090830436,3.4320792262|C,2.342471154
4,-1.5421875022,-0.8568579595|C,7.8630278824,0.4598830296,-1.636814998
1|C,5.7029039296,6.1713905134,-5.3590782199|H,-7.0127202035,-5.8944627
636,0.9661667291|H,-8.668828977,-6.1740159958,1.5410848888|H,-7.359780
8243,-5.9959714115,2.7040613266|H,-6.6493903089,-3.7638246693,0.236790
2973|H,-8.0765544301,-1.3887461891,1.6157856758|H,-7.950766658,-1.5604
4198,-0.122770331|H,-5.4906979717,-1.4763797194,-0.0425795732|H,-6.243
0453342,-0.0334209461,0.6316855662|H,-3.7416548,-2.2898419726,1.078058
1087|H,-3.3721545009,-1.6124142694,4.0688673572|H,-3.2192932305,-3.251
4348218,3.4735299025|H,-1.3623435536,-2.6572883076,1.9964432991|H,-1.0
183703619,-2.2337743758,3.6707144702|H,-0.884482785,-1.1373535871,0.41
77135208|H,-0.3425707816,1.785370636,1.233230387|H,-1.5061027329,1.436
0754621,-0.0323419041|H,0.2702098885,0.1806125687,-1.3129104863|H,0.54
66485594,1.9019850242,-1.1318018137|H,2.2084005204,1.5703153182,0.6569
693034|H,4.1056742304,0.6161771038,1.2880666945|H,4.0872176907,-1.1435
175249,1.3863081085|H,5.1951271134,-1.2871821944,-0.8636197388|H,6.160
6796401,-0.5471224992,0.3942688558|H,4.5573523445,1.4464090638,-1.2111
036481|H,6.9022584952,2.255112346,-3.5830682675|H,7.5210915144,3.11070
13761,-2.1991561728|H,4.5547259001,2.8663526771,-2.933766067|H,5.16340
02104,3.7093332716,-1.5214223044|H,6.024658858,5.5382137876,-2.8165512
439|H,4.660065293,2.8412355061,-5.0832257981|H,3.9900933348,4.10693851
38,-6.1280989708|H,5.6357149393,3.5411094672,-6.3836910965|H,-9.962829
5781,-4.1561838715,2.6450494983|H,-9.1184206461,-2.6201496012,2.884249
8902|H,-8.6705853725,-4.0479734751,3.8331976915|H,-5.1812075459,-0.662
7751047,4.1759650047|H,-6.2046228287,0.3497860388,3.1433234669|H,-6.75
61476057,-1.2472489507,3.6396814891|H,-1.0836952615,1.4811641625,3.146
1847483|H,-1.019173639,0.2070230262,4.3757587932|H,-2.560393961,0.6566

382236,3.6482932462|H,1.3183474666,-1.503173309,-1.2280496907|H,3.0068
608341,-1.6579425428,-1.7245176549|H,2.447234703,-2.4631397524,-0.2654
580867|H,7.7614320871,-0.4524046695,-1.0457835164|H,8.6748367352,1.059
1001629,-1.1998103414|H,8.2045329184,0.1681068083,-2.6404555834|H,6.08
26760596,6.9166906074,-4.6529572749|H,6.4451524209,6.0540848834,-6.161
6112621|H,4.798794202,6.5808759402,-5.832052646||Version=x86-Win32-G98
RevA.11.2|HF=-1173.231276|RMSD=3.235e-009|RMSF=1.543e-003|PG=C01 [X(C3
0H50)]||@

Squalene, extended conformer 1 (some adjacent methyls are on the same side of the chain):

1\1\GINC-DFTB\FOpt\RB3LYP\6-31G(d)\C30H50\BILLW\17-Jan-2005\0\\# B3LYP
/6-31G* OPT\\squalene stretch (almost) from ox-squal stretch model res
tart from apsara\\0,1\C,-0.4944739974,0.3125047684,0.0002359749\C,0.43
68000737,-0.5423377668,-0.8967326982\C,1.8845206345,-0.1568605616,-0.7
529573716\C,2.9175853241,-0.8972953923,-0.3191199005\C,-2.8686322001,-
0.4755485614,0.5986327759\C,-1.9512163323,0.025309384,-0.2446675089\C,
2.8111300334,-2.337092749,0.1265939753\C,6.6398154452,-0.201510227,-1.
24871444\C,4.3094376106,-0.2976873627,-0.2554355997\C,5.3011804764,-0.
8883776685,-1.292014058\C,7.8355781324,-0.7015715607,-0.8964133245\C,8
.0772559599,-2.1355308198,-0.4852078212\C,9.0632446075,0.1890780258,-0
.8983911179\C,-2.5922310131,-0.8652147368,2.0320434605\C,-7.5398914676
,0.8402084634,-0.4085571279\C,-4.2963999501,-0.6821162052,0.1300661379
\C,-5.3175823702,0.2974594261,0.7651808568\C,-6.7221714896,0.037049662
2,0.2916373225\C,-7.1817977132,2.233204119,-0.871496124\C,-8.930042301
9,0.3653262349,-0.7863015942\C,9.639013019,0.4789491357,0.5125961214\C
,10.7876932637,1.450426882,0.4680128815\C,12.0756138221,1.2466239671,0
.7864065138\C,13.0877039546,2.3613467355,0.6595830828\C,12.6471615114,
-0.0564174472,1.290880409\C,-10.0734645349,1.0819295512,-0.0214920105\
C,-11.4336179975,0.6231208955,-0.4736274774\C,-12.3747077688,-0.033707
9042,0.2224368113\C,-13.6846858707,-0.4186894615,-0.4247919513\C,-12.2
505055877,-0.4459559327,1.6692750802\H,-0.2971826841,1.3747337702,-0.2
121322073\H,-0.2175803298,0.1576036462,1.0481365318\H,0.2721738156,-1.
6009949156,-0.6720398922\H,0.1297049075,-0.4024983129,-1.9448552469\H,
2.0982221901,0.8776501081,-1.032283045\H,-2.2827506722,0.2482961577,-1
.2616423607\H,1.7819174874,-2.7021915419,0.1517294771\H,3.2353077326,-
2.4600528125,1.1327703713\H,3.3805283886,-3.0048613978,-0.5336339408\H
,6.6070285361,0.8540793933,-1.5282656086\H,4.7349435723,-0.4488877551,
0.7477936675\H,4.2486678423,0.787283562,-0.4076186475\H,4.859770321,-0
.7625236389,-2.291647447\H,5.4032143831,-1.9662535136,-1.1324794307\H,
7.1880031083,-2.7634185302,-0.5756697508\H,8.4207440061,-2.200131693,0
.5558019976\H,8.8683838223,-2.584563211,-1.1015858864\H,9.8582451376,-
0.2730873058,-1.5024206549\H,8.82192564,1.1443911871,-1.38125977\H,-1.
5403848038,-0.7628976807,2.3084659484\H,-2.8853981283,-1.9095343215,2.
2083661354\H,-3.1776416934,-0.256703111,2.7340835912\H,-4.3483606111,-
0.5754178654,-0.9598757158\H,-4.614649311,-1.7110829209,0.3591630806\H
,-5.0001228656,1.3233125521,0.5514386655\H,-5.2863301923,0.1876990401,
1.8591102675\H,-7.1018663548,-0.9546856851,0.54878743\H,-6.1489356355,
2.5075826182,-0.6454161123\H,-7.8312146451,2.9893870154,-0.4106927708\
H,-7.3224492045,2.3242548968,-1.9575232452\H,-9.088300002,0.5148246749
,-1.8656185926\H,-9.0168587435,-0.7125331321,-0.6055305632\H,9.9334755
661,-0.4593177736,0.9930948743\H,8.8304562065,0.9010076722,1.127635355
5\H,10.5168491617,2.4459767155,0.1096095163\H,12.6323886505,3.28762915
54,0.2950557376\H,13.8972397308,2.0855299682,-0.0312177517\H,13.565592
0093,2.5751262301,1.6262916435\H,11.9062877855,-0.8557398444,1.3652362
176\H,13.4527799259,-0.4063593436,0.6302596864\H,13.0988925559,0.07630

8172,2.2840669594\H,-9.9920141785,2.1656980889,-0.1893170251\H,-9.9286
224163,0.925811062,1.0525836206\H,-11.6575402002,0.8517725018,-1.51802
99766\H,-13.8378477743,-1.5069302609,-0.3938655674\H,-14.5366530763,0.
0284956453,0.1070929138\H,-13.7335055688,-0.0993981852,-1.4707001122\H
,-12.3715349317,-1.5334087671,1.772703399\H,-11.2923318906,-0.17245201
57,2.1166993212\H,-13.0465462094,0.0117343415,2.2733772454\\Version=x8
6-Linux-G98RevA.9\HF=-1173.2391443\RMSD=5.937e-09\RMSF=1.550e-06\PG=C0
1 [X(C30H50)]\\@

Squalene, extended conformer 2 (adjacent methyls are on opposite sides of the chain):

1|1|UNPC-UNK|FOpt|RB3LYP|6-31G(d)|C30H50|PCUSER|17-Jan-2005|0||# B3LYP
/6-31G(D) OPT GEOM=ALLCHECK||squalene stretch2--more stretched than st
retch1 done earlier||0,1|C,-0.2001647655,0.0839871422,0.2493464963|C,1
.0301071555,0.8096550269,-0.3539355367|C,2.2655697579,-0.0497341557,-0
.3560664393|C,3.4320802883,0.1441579689,0.2807556502|C,-2.589308524,0.
7809942987,-0.4028422517|C,-1.4305275862,0.9508094149,0.2546265374|C,3
.7369302519,1.3250171198,1.1725753769|C,6.8726700516,-1.3305268952,-0.
8095208551|C,4.559451192,-0.8589355937,0.1229359421|C,5.7340688189,-0.
3481741514,-0.7523983228|C,7.3584890798,-2.003090212,-1.8657558926|C,6
.8381997535,-1.8730473658,-3.2780574258|C,8.5189475327,-2.9632381123,-
1.6833359115|C,-2.8928610986,-0.382107777,-1.3182075506|C,-6.562524252
5,2.9011334291,1.6869989513|C,-3.7030352262,1.7998299194,-0.2512792572
|C,-4.9378571391,1.2781210663,0.5284528576|C,-6.0349889102,2.305416932
6,0.6050032283|C,-6.1290088636,2.6333396091,3.1093265864|C,-7.67588780
27,3.9186486686,1.524878902|C,8.1423985372,-4.4572373016,-1.8605671958
|C,9.336048137,-5.3626753555,-1.7183459921|C,9.5609121933,-6.323790330
9,-0.8088324733|C,10.8434050759,-7.1223375332,-0.8321084069|C,8.605680
6485,-6.7127522927,0.2933836332|C,-9.0591090763,3.4268358978,2.0255725
89|C,-10.1217572851,4.4833305805,1.8869273448|C,-11.227991555,4.469651
7121,1.1268926124|C,-12.1733665192,5.6482357113,1.1186210218|C,-11.649
2513254,3.3286951445,0.2326561478|H,0.0460756235,-0.203985304,1.281927
3567|H,-0.3677898546,-0.8522685796,-0.2943607181|H,0.783639895,1.09365
59157,-1.3876872899|H,1.1933584413,1.7484407814,0.186646089|H,2.174882
929,-0.9581273572,-0.9564996957|H,-1.3391198029,1.8477495924,0.8717479
41|H,2.8900593509,2.0051130717,1.2886157425|H,4.5806117452,1.912574277
9,0.7868042115|H,4.030879755,0.9822888562,2.1744815282|H,7.3485155557,
-1.515123406,0.1564960222|H,4.175584287,-1.7851730877,-0.3206362241|H,
4.955950821,-1.127546749,1.1142303055|H,6.1056779045,0.5979906308,-0.3
327287756|H,5.3492424475,-0.1118424784,-1.7497268781|H,6.0291186725,-1
.1451822102,-3.3708822478|H,6.4630493279,-2.8333601672,-3.6554916427|H
,7.6447903266,-1.566439288,-3.9587049209|H,9.3141333125,-2.7192806699,
-2.405000826|H,8.9539693214,-2.8324964293,-0.6855734813|H,-2.042935688
2,-1.0552696714,-1.4515677609|H,-3.1924787091,-0.020321939,-2.31168091
2|H,-3.7318349255,-0.9820519949,-0.9412029394|H,-3.3226972672,2.691591
6321,0.2605824211|H,-4.0371952324,2.1300169853,-1.2472525199|H,-4.6152
481022,0.9522697857,1.5227388377|H,-5.3274723044,0.3825494015,0.022782
2953|H,-6.4319088026,2.6043715409,-0.3680842544|H,-5.2830270955,1.9456
438791,3.176887589|H,-6.9474308433,2.2078589401,3.7051471454|H,-5.8398
810609,3.5705453274,3.6048812175|H,-7.4166892558,4.8388386929,2.071318
4721|H,-7.7710624936,4.1999131877,0.4694944443|H,7.7069639703,-4.60069
03242,-2.8602472868|H,7.3544107843,-4.7086921521,-1.1430810256|H,10.11
99781252,-5.1864902978,-2.4584237777|H,11.5041223557,-6.8111008863,-1.
6475221158|H,10.6404403584,-8.1963619872,-0.9504530941|H,11.3950143893
,-7.0144342381,0.1127585342|H,7.6936750438,-6.1118022604,0.308621221|H
,8.3112362397,-7.7674213518,0.1973731852|H,9.0887133923,-6.6156787487,

1.2757829803|H,-8.9764414693,3.144689297,3.0852980956|H,-9.3229187444,
2.5122940719,1.4842391414|H,-9.9396486292,5.3806766544,2.4826103295|H,
-12.2794540019,6.064229381,0.1065243702|H,-13.1823892887,5.3500407471,
1.4374670254|H,-11.8326704751,6.4506382965,1.7806778748|H,-11.7578541049,3.6715760636,-0.8058858399|H,-10.9467821763,2.4921773199,0.2362508366|H,-12.633075314,2.942131852,0.5341068177||Version=x86-Win32-G98RevA.11.2|HF=-1173.2391343|RMSD=3.389e-009|RMSF=1.479e-006|PG=C01 [X(C30H50)]||@

Hopene, side chain conformer 1

1\1\GINC-DFTC\FOpt\RB3LYP\6-31G(d)\C30H50\BILLW\22-Feb-2004\0\\# B3LYP/6-31G* OPT GEOM=CHECK\\HopProdNoOX-Full\\0,1\C,-0.8249378066,2.0611454926,0.2263684706\C,0.6439273087,2.0775133653,-0.2361650207\C,1.4439228796,0.8522025373,0.2411700541\C,0.7237482212,-0.4891768368,-0.1648850853\C,-0.724494597,-0.48161881,0.5548513827\C,-1.5410791353,0.7202602861,-0.0549703207\C,0.5731375958,-0.6152578919,-1.7109674801\C,3.6241178903,-0.3403298184,0.5649485224\C,1.5604418065,-1.7247473137,0.2896268735\C,3.0766926463,-1.6471548521,-0.0025321079\C,2.9692100472,0.9099769982,-0.0821805387\C,3.2812817804,1.0807458036,-1.5863497792\C,3.7262712112,2.0213337957,0.6890984411\C,-0.5852848184,-0.3509697134,2.0985720691\C,-3.0992840672,0.7489508262,0.2335199893\C,-1.4644222847,-1.8236545095,0.3017423279\C,-2.9744665053,-1.780497398,0.5804878798\C,-3.6542067781,-0.6530040379,-0.2139856536\C,-3.4249395011,1.1245302339,1.701220044\C,-3.738980012,1.8314733729,-0.6833426145\C,5.1958596815,1.5285268203,0.7462878636\C,5.1621064071,-0.035435881,0.6890811341\C,6.1037042177,-0.7136553773,-0.3061137938\C,6.4865700746,-2.1354666093,0.0488517328\C,6.6437562665,-0.1405760468,-1.3877465032\C,-5.2693018544,1.7492205579,-0.7691253533\C,-5.2103741904,-0.8008789454,-0.3563842656\C,-5.7338419921,0.3662665844,-1.2306169357\C,-5.9697625859,-0.8546490226,0.9869235685\C,-5.5337172291,-2.1091412794,-1.1157446105\H,-1.3520639106,2.8787764885,-0.276716754\H,-0.8602723855,2.3000143122,1.2956196836\H,0.6698313854,2.1538926292,-1.3294699323\H,1.1242893543,2.9918327486,0.1361454958\H,1.4181687923,0.879898459,1.3384658261\H,-1.4979417652,0.5776211031,-1.1426097166\H,0.4399564184,0.3407217652,-2.2205355957\H,1.4558420083,-1.0871710766,-2.1486573158\H,-0.2753228881,-1.2457072267,-1.9885932183\H,3.2735966624,-0.3137433405,1.6097500802\H,1.4603423321,-1.8774595237,1.3696443929\H,1.149731449,-2.6265713521,-0.1810999746\H,3.5505345438,-2.5142864122,0.473630708\H,3.2903258122,-1.7332553714,-1.0749419813\H,3.0660945273,0.1937052491,-2.1834140293\H,4.3338982809,1.3185781496,-1.7476572183\H,2.7002256319,1.9098207298,-2.0039281896\H,3.6441598432,3.009114898,0.2210490627\H,3.3150019859,2.1095917423,1.7040137398\H,-0.3966858816,0.6668850881,2.4440497981\H,-1.4963624301,-0.6877602013,2.5971169084\H,0.2236580212,-0.9768474763,2.4847598251\H,-1.0046396767,-2.6091970162,0.9151030954\H,-1.3409928003,-2.1439569372,-0.7381205096\H,-3.3959782453,-2.7525651722,0.3024672406\H,-3.1695596076,-1.6701535845,1.6536207876\H,-3.2930184048,-0.7611031096,-1.2513811689\H,-3.3449253377,0.2868967205,2.3964948755\H,-4.4384712264,1.5211889041,1.7977489681\H,-2.7515328981,1.9092963069,2.0587873303\H,-3.4545224056,2.8328096223,-0.3391036053\H,-3.3294788918,1.7240409153,-1.6990488888\H,5.7006426909,1.8774521545,1.6533602203\H,5.7662527534,1.9387572287,-0.0904666244\H,5.4710998126,-0.4231792995,1.6693735476\H,7.1801767767,-2.5603495889,-0.6833281185\H,5.6143651082,-2.7963457125,0.1081166285\H,6.9704086306,-2.1701731435,1.0351794553\H,6.4491198948,0.8849005936,-1.6834573189\H,7.325435105,-0.6928129905,-2.0298955678\H,-5.6322790647,2.5128795792,-1.4695543242\H,-5.722442465,1.99657424,0.19924

67186\H,-5.3831613593,0.2085335846,-2.2618979358\H,-5.9293585946,0.085
0031801,1.5413854887\H,-5.5746990137,-1.6418069411,1.6390168908\H,-7.0
279055814,-1.0821351412,0.8061132559\H,-4.9510752724,-2.1894781407,-2.
0418975026\H,-6.5960538697,-2.1311081672,-1.3890200854\H,-5.3370227976
,-3.0030688054,-0.5144352691\H,-6.8313191083,0.325855352,-1.2708709231
\\Version=x86-Linux-G98RevA.9\HF=-1173.2806672\RMSD=7.680e-09\RMSF=3.0
99e-06\PG=C01 [X(C30H50)]\\@

Hopene, side chain conformer 2

1|1|UNPC-UNK|FOpt|RB3LYP|6-31G(d)|C30H50|PCUSER|16-Jul-2004|0||# B3LYP
/6-31G* OPT||AbeBoatUpConfYMeUp||0,1|C,-4.1136935674,0.5722416017,-0.7
668043034|C,-5.5874458822,0.4479555746,-0.3563098779|C,-5.828044246,-0
.7872526488,0.5139530727|C,-4.9365949552,-0.8544623126,1.7792531369|C,
-3.4426003907,-0.6462815739,1.3443086453|C,-2.4220733557,-0.7534971194
,2.4892899083|C,-1.0036864021,-0.9873724376,1.9481039082|C,-0.52379228
3,0.0714388701,0.9174366701|C,-1.6611442129,0.3678558158,-0.1335697776
|C,-3.123381653,0.5954915678,0.4337057325|C,-1.2026280762,1.4482419289
,-1.1399174827|C,0.1326140425,1.1118650096,-1.8278618096|C,1.237212513
,0.7051243319,-0.8373195788|C,0.7589015193,-0.4738870047,0.0954266004|
C,1.8994353649,-0.9078386429,1.0699060989|C,3.2818191793,-1.0972396805
,0.4067757675|C,3.6384121691,0.1841997834,-0.3446491958|C,2.6455391585
,0.5272597948,-1.4853377986|C,3.2704663576,1.8622270064,-1.9710497988|
C,4.8008240143,1.6171043281,-1.9561508662|C,5.0748628119,0.5225950222,
-0.8531269023|C,6.0423575606,-0.5444980725,-1.3433014955|C,-5.10565667
65,-2.2736938621,2.3705530965|C,-5.4326870256,0.1441771549,2.847378326
2|C,-3.2783688724,1.9626243963,1.1469347749|C,-0.1649717184,1.34023379
65,1.7417372959|C,0.3893777208,-1.7443874204,-0.7266598648|C,2.6737060
465,-0.4628043735,-2.6706688152|C,5.737091363,-1.789584638,-1.72604054
25|C,7.4792487688,-0.0691996396,-1.3946284038|H,-1.9643805058,1.584572
7301,-1.9149488344|H,-1.1067499742,2.42133869,-0.6440431592|H,-0.03509
78265,0.318163477,-2.5653141315|H,0.4661104178,1.9849528966,-2.4042519
716|H,1.3786653223,1.5641698563,-0.168728541|H,-1.7670791277,-0.557848
6919,-0.7140038407|H,-0.0619154788,-1.5287573358,-1.6968234229|H,1.275
4799759,-2.3538732086,-0.9188004309|H,-0.3083553136,-2.3895939066,-0.1
86965375|H,3.4607239729,0.9836564279,0.3939617238|H,2.0266038341,-0.16
64794506,1.8663013165|H,1.6060073116,-1.8403362708,1.5680106182|H,4.02
55950422,-1.3129406846,1.1848021871|H,3.2761046878,-1.9709236962,-0.25
16892133|H,2.4328785686,-1.4886023094,-2.386551133|H,3.6586391569,-0.4
83511901,-3.1444638118|H,1.9522691837,-0.1587322851,-3.4371494934|H,2.
9192085689,2.1724152507,-2.9618725163|H,3.0101073217,2.6661488276,-1.2
692266903|H,-0.1095073518,2.2542911439,1.1481426127|H,-0.9092224982,1.
5164489266,2.5207374549|H,0.7947455117,1.2291251031,2.2537047114|H,-0.
2965535777,-1.0195048738,2.7867474128|H,-0.9927419486,-1.9900131102,1.
507608979|H,-2.6733949231,-1.5918226752,3.148117075|H,-2.4553770513,0.
139699502,3.1240863005|H,-3.2459888912,-1.512679194,0.6893332951|H,-2.
9180740524,1.9609008516,2.1771630588|H,-4.3225620474,2.2825117767,1.17
77600699|H,-2.7315960906,2.74520445,0.6125798332|H,-3.9886925619,1.474
2110196,-1.3774674937|H,-3.862531212,-0.2798495391,-1.4165620457|H,5.3
550474364,2.5415983042,-1.7630337543|H,5.1354749199,1.2504086004,-2.93
24955373|H,5.5952415709,1.0103039142,-0.0168733221|H,8.1488436102,-0.8
40308525,-1.7876941146|H,7.8353227654,0.2158384113,-0.3947707113|H,7.5
821045425,0.8233092017,-2.0267891841|H,4.7291052152,-2.1838607737,-1.7
1847509|H,6.5121226205,-2.4690476781,-2.0737069199|H,-6.2089454796,0.3
890389381,-1.2595373344|H,-5.9169754503,1.3524569974,0.1706800673|H,-5
.6311326249,-1.6837390764,-0.0934779217|H,-5.4950014844,1.1716559346,2

.4825806326|H,-4.7796638428,0.1438023336,3.7274970462|H,-6.4359569855,
-0.1429257293,3.1870051787|H,-4.6816818252,-3.0378740149,1.7071272664|
H,-6.1711293171,-2.500983075,2.4999948041|H,-4.6322376732,-2.378765734
8,3.3524717601|H,-6.8844520801,-0.8450691638,0.8111034646||Version=IA3
2W-G03RevC.02|HF=-1173.2805832|RMSD=7.079e-009|RMSF=9.405e-007|Dipole=
-0.0449456,0.1697271,-0.106543|PG=C01 [X(C30H50)]||@

Hopene, side chain conformer 3

1|1|UNPC-UNK|FOpt|RB3LYP|6-31G(d)|C30H50|PCUSER|20-Jul-2004|0||# B3LYP
/6-31G* OPT||Hopen-NMR-ConfC C30H50 CH2= eclipses H||0,1|C,-3.31780800
1,-0.9374616334,-2.4475615918|C,-4.75638013,-1.4497174585,-2.602747653
|C,-5.0954632178,-2.505439628,-1.5482728445|C,-4.8788093529,-2.0337505
2,-0.0884355841|C,-3.4305625267,-1.4395013294,0.0293359522|C,-3.040198
176,-0.9820398847,1.4444710592|C,-1.5166457834,-0.8440267866,1.5831652
04|C,-0.8569472438,0.0877147551,0.5301696297|C,-1.4281681402,-0.217639
5727,-0.9064252671|C,-3.0010936045,-0.3648671081,-1.0358527964|C,-0.79
76583814,0.7268995708,-1.9557875421|C,0.7425568501,0.7208212274,-1.938
7070915|C,1.3314064499,0.9037942735,-0.5286926072|C,0.7396655458,-0.16
25071763,0.4753577749|C,1.3698003452,-0.0194023699,1.8994039616|C,2.90
31088969,0.1750971979,1.9250001293|C,3.2477025907,1.3379160969,1.00139
57924|C,2.8838890182,1.0627939818,-0.4820136218|C,3.4165781413,2.37286
17193,-1.1216157859|C,4.7810903102,2.6141025821,-0.4254944938|C,4.6355
425705,2.0712117741,1.0369187436|C,5.8326914325,1.3231916358,1.6061794
047|C,-4.9921907746,-3.2885864031,0.8089583762|C,-6.0015666584,-1.0644
58704,0.3401892252|C,-3.7360670107,0.992589273,-0.9033410039|C,-1.1801
670433,1.5428099928,0.9762921717|C,1.0560917535,-1.6181045322,0.016510
6007|C,3.6406377362,-0.1137760936,-1.1389287705|C,6.371157119,1.728225
4552,2.7643196717|C,6.4177628434,0.1303830479,0.8852652863|H,-1.130757
7267,0.4441750459,-2.9600672354|H,-1.1464704342,1.7554591313,-1.807114
5492|H,1.098638684,-0.2122232478,-2.3909214224|H,1.1087205157,1.524850
2336,-2.590818207|H,0.9687948693,1.8771920587,-0.174097214|H,-1.068368
3703,-1.2251316625,-1.1527965261|H,1.0970848186,-1.7416215484,-1.06711
19844|H,2.020662651,-1.9472076177,0.4102182811|H,0.3186920281,-2.33254
29716,0.3911704742|H,2.5463342594,2.1364398227,1.2918150901|H,0.938094
0115,0.8385410813,2.4260111473|H,1.1037988829,-0.902386597,2.493445412
1|H,3.2197502942,0.3849747493,2.9545977879|H,3.4260997554,-0.742680614
2,1.629779459|H,3.5800154619,-1.0467972055,-0.5768322704|H,4.700776565
9,0.1147996976,-1.2670333817|H,3.2392920156,-0.3086882826,-2.139019350
5|H,3.5157508303,2.3182736585,-2.2120212058|H,2.7285514829,3.200362759
9,-0.8991896677|H,-1.1105822338,2.2795969556,0.1741745065|H,-2.1945149
635,1.6084272779,1.3753504207|H,-0.5147999941,1.8764160241,1.776997200
9|H,-1.2756055134,-0.4775591262,2.5892058302|H,-1.0980322363,-1.854208
0466,1.5230502356|H,-3.3814890949,-1.7087516891,2.1896314969|H,-3.5410
531213,-0.0406163061,1.6989401317|H,-2.7827008615,-2.3051216998,-0.192
6126754|H,-3.8734068373,1.3173982613,0.1296525359|H,-4.7280561226,0.95
80651085,-1.360138062|H,-3.1855508382,1.783005734,-1.4223506752|H,-3.1
254150994,-0.1776430172,-3.2142099242|H,-2.6297140771,-1.7705419284,-2
.6559217329|H,5.0632660427,3.6721142228,-0.4319765292|H,5.5761668523,2
.0846998452,-0.9608693536|H,4.5057465762,2.9329608242,1.7008016962|H,7
.2818129556,-0.2645090921,1.4285902758|H,6.753901685,0.3874445951,-0.1
272072348|H,5.6889527198,-0.6807647731,0.7775489083|H,5.9822638805,2.5
850789742,3.3096461344|H,7.2216902464,1.2187799393,3.2112936207|H,-4.8
798895758,-1.8779766639,-3.6061789829|H,-5.468834381,-0.6169532659,-2.
5466596167|H,-4.4603657669,-3.3871785095,-1.7232458251|H,-6.1080110263

,-0.207884425,-0.3283186456|H,-5.8322615167,-0.6772155487,1.3512583643
|H,-6.9635482718,-1.5922644709,0.3504551492|H,-4.1648156417,-3.9862285
742,0.6286895579|H,-5.9274684975,-3.8201288552,0.5935204468|H,-4.99981
02631,-3.0423896161,1.8760450283|H,-6.133068972,-2.8466409429,-1.66951
48982||Version=IA32W-G03RevC.02|HF=-1173.2808629|RMSD=9.914e-009|RMSF=
3.445e-006|Dipole=0.0800567,0.1622402,0.1184359|PG=C01 [X(C30H50)]||@

Oxidosqualene fully folded for cyclization to lupeol:

1|1|UNPC-UNK|FOpt|RB3LYP|6-31G(d)|C30H50O1|PCUSER|17-Nov-2003|0||# B3L
YP/6-31G(D) OPT=READFC GEOM=ALLCHECK GUESS=READ||squalene LUP||0,1|C,0
.3361131216,-0.5609906737,-1.3002411719|C,1.7309453088,-1.2002472163,-
1.0649449481|C,2.469965815,-0.5908237784,0.0958637632|C,2.8598208308,-
1.1605136898,1.2476687019|C,-1.3002534539,-0.1157898737,0.6338670232|C
,-0.6652432052,-0.9179510733,-0.2349913123|C,2.6072165527,-2.603905956
9,1.616040356|C,5.9439895227,-0.5186871647,1.3207315654|C,3.5922562576
,-0.342958272,2.29563063|C,5.0744889962,-0.7449095354,2.5280010028|C,7
.0842258225,0.185504327,1.2239202392|C,7.7542536351,0.8984224801,2.375
8625119|C,7.8099367777,0.2851083225,-0.1057098409|C,-1.112169592,1.380
5734533,0.7104055465|C,-5.0502288069,0.3216867384,-0.619097946|C,-2.27
22304941,-0.7007052765,1.6401528543|C,-3.7269437143,-0.1765529418,1.53
07549454|C,-4.3658461065,-0.4894358133,0.20363509|C,-5.3101603153,1.78
74619297,-0.3611744797|C,-5.6135699623,-0.2105337452,-1.9247236378|C,7
.8136542382,1.6982086574,-0.7506570067|C,6.4412673818,2.1746013104,-1.
1421717534|C,6.0178618484,2.61910708,-2.3359843372|C,4.583195496,3.051
6529331,-2.5319668125|C,6.8767116796,2.7460738933,-3.5712278757|C,-7.1
502618267,-0.3822595664,-1.9532973432|C,-7.630941616,-1.5058930865,-1.
0610656516|C,-8.286840976,-1.3770039084,0.2574421576|C,-8.1719693753,-
2.526651525,1.2400283732|C,-8.5927369444,-0.0345247836,0.8884565575|O,
-9.0523565157,-1.6876979128,-0.92961275|H,-0.0390408389,-0.9175630196,
-2.2712881187|H,0.4505169206,0.5242243996,-1.398944584|H,1.6138510139,
-2.2829184166,-0.9447597624|H,2.326625008,-1.0556797612,-1.9785174512|
H,2.7035873641,0.4681488479,-0.0357489903|H,-0.8840953266,-1.986688381
8,-0.1749784974|H,2.0143853702,-3.1371809758,0.8699439729|H,2.07268001
6,-2.666437596,2.5740201738|H,3.5469102595,-3.1565827741,1.7481731618|
H,5.5746154979,-0.9925226626,0.4105692552|H,3.0656974982,-0.4427007271
,3.2571833998|H,3.5585591625,0.718842889,2.0240899929|H,5.1121501242,-
1.8080177548,2.8106872695|H,5.4453513358,-0.1909108793,3.3964722845|H,
7.2146701075,0.7930295203,3.3197086779|H,7.861155479,1.972727328,2.175
4784874|H,8.7711524889,0.5102388362,2.5290388883|H,8.8584018662,-0.018
9980395,0.0359665013|H,7.3689701613,-0.4207864009,-0.8193861921|H,-0.2
928271627,1.7388458965,0.0835595326|H,-0.9017198143,1.6899075671,1.743
4724568|H,-2.0218143592,1.9127983197,0.4018465223|H,-2.2826996885,-1.7
937580049,1.5421372925|H,-1.9155927048,-0.482143571,2.6587212788|H,-3.
7517401609,0.8971231009,1.7432264332|H,-4.306425723,-0.655371698,2.335
4967652|H,-4.2378807371,-1.52596937,-0.1162390495|H,-4.8739996957,2.14
28990467,0.5752088049|H,-6.3859920905,2.0021045524,-0.3224365649|H,-4.
9017020266,2.3994826585,-1.1775214231|H,-5.3354309651,0.4708816169,-2.
7416626|H,-5.1479319511,-1.1769669492,-2.15751778|H,8.4870822842,1.677
4120199,-1.6138370144|H,8.2590464906,2.4108366738,-0.0399552769|H,5.70
74061581,2.1353831302,-0.3363426968|H,3.9955403569,2.9432870454,-1.614
6567387|H,4.0949052005,2.4616093631,-3.3208186363|H,4.5241248333,4.102
2387897,-2.8510179516|H,7.9033582633,2.4027688853,-3.4242645962|H,6.44
56952453,2.1721395542,-4.403576475|H,6.9195926979,3.7917748109,-3.9075
469224|H,-7.4567673007,-0.6226382373,-2.9807789223|H,-7.6535585718,0.5
562346995,-1.6998411237|H,-7.094383228,-2.4455772523,-1.2328028513|H,-

7.3502351778,-2.3553347945,1.9459814029|H,-9.0977744584,-2.6310390855,
1.8188016938|H,-7.9900804537,-3.4699338601,0.7164108645|H,-7.780194749
4,0.2742610018,1.5567485043|H,-8.7434406777,0.7433625391,0.1367123861|
H,-9.5108925915,-0.1036390432,1.4844430098||Version=x86-Win32-G98RevA.
11.2|HF=-1248.440333|RMSD=3.220e-009|RMSF=1.472e-006|PG=C01 [X(C30H50O
1)]||@

Oxidosqualene, extended conformer (some adjacent methyls on the same side of the chain):

1|1|UNPC-UNK|FOpt|RB3LYP|6-31G(d)|C30H50O1|PCUSER|08-Feb-2004|0||# B3L
YP/6-31G* OPT=READFC GEOM=ALLCHECK||Squalen-stretch C30H50O||0,1|C,-0.
0183538917,-0.3406951785,-0.0480103247|C,0.8168732158,0.6582096705,0.7
927421109|C,2.2509720417,0.728808483,0.3415563933|C,2.9342490447,1.778
6345685,-0.1428565997|C,-2.5878097819,-0.2366547306,-0.0998548358|C,-1
.4133604739,-0.5180221125,0.4876277205|C,2.3571446202,3.1623230624,-0.
3309450105|C,6.8162140739,2.1120791016,0.0025753139|C,4.3895350989,1.6
209381278,-0.5403760853|C,5.3835444454,2.3719011183,0.3841376539|C,7.7
346817816,2.9711117846,-0.4691201771|C,7.4956517482,4.4474157382,-0.68
61488988|C,9.1262491342,2.4801991278,-0.819861303|C,-2.7347873128,0.34
38178286,-1.4870605578|C,-6.4039701051,-2.9620176083,1.5029851822|C,-3
.8866537397,-0.5039669927,0.6365464651|C,-4.7110202299,-1.6814193016,0
.0537104986|C,-6.0019774321,-1.8923807447,0.7975905835|C,-5.5916578941
,-4.2227681075,1.6863192865|C,-7.7592683306,-2.9553493228,2.1850343798
|C,9.445934263,2.5115042276,-2.3374976138|C,10.7938596788,1.9171326618
,-2.6457783307|C,11.8825550095,2.5167953829,-3.1525266882|C,13.1575711
547,1.7382371222,-3.3787994689|C,11.965764736,3.9720455378,-3.54546896
56|C,-8.7788166611,-3.9380362977,1.5689460447|C,-10.0945489543,-3.9290
759153,2.3154380962|C,-11.2956153419,-3.1427213305,1.9559225007|C,-12.
2773019522,-2.7698793207,3.0506071552|C,-11.3493367359,-2.2570371333,0
.7274050912|O,-11.2237161975,-4.5622775353,1.6896571679|H,0.496390389,
-1.3139994279,-0.0376828176|H,-0.0199759996,-0.0111796691,-1.092109597
6|H,0.3314848063,1.6390074496,0.7644780757|H,0.7861741792,0.3337918232
,1.8445505758|H,2.7862031299,-0.2210122785,0.4139550319|H,-1.451078458
3,-0.9192520665,1.5032695036|H,1.2851865159,3.2102140671,-0.1263414664
|H,2.5177666073,3.5088103301,-1.3612425169|H,2.8493245146,3.8947215224
,0.3228184796|H,7.1240785597,1.0699414243,0.1151641488|H,4.5369313032,
1.9865738169,-1.5675078266|H,4.654257715,0.5561030728,-0.5479522817|H,
5.212997488,2.0270711965,1.4146900606|H,5.1587345718,3.4429003756,0.37
51444304|H,6.5104795332,4.776755885,-0.3482653435|H,7.5856907595,4.714
9781605,-1.7473431502|H,8.2491429678,5.041918179,-0.1511187059|H,9.879
3091503,3.0912359567,-0.3002693142|H,9.2548620627,1.4530327518,-0.4559
795471|H,-1.777168203,0.5871095675,-1.952844885|H,-3.3358463538,1.2632
521938,-1.4559305886|H,-3.2609586449,-0.3474415906,-2.1587932541|H,-3.
6779411307,-0.7178852379,1.691419804|H,-4.5139794448,0.4008641259,0.61
88357495|H,-4.0884822779,-2.582027768,0.0565649402|H,-4.9410269775,-1.
470425287,-1.0008371351|H,-6.6828707174,-1.0387679393,0.7580118782|H,-
4.5850608036,-4.14568675,1.2695833875|H,-6.0773145328,-5.0872478622,1.
2144438276|H,-5.4943031171,-4.4654266412,2.7535822471|H,-7.631095841,-
3.2064672995,3.24994998|H,-8.1807133712,-1.9430333588,2.1532957599|H,9
.3717065549,3.5375481596,-2.7112022639|H,8.6673365015,1.9352953501,-2.
8589977504|H,10.8804403432,0.8561454569,-2.4013478417|H,13.053530325,0
.6888218051,-3.0853829749|H,13.992428605,2.1697358029,-2.8083230454|H,
13.4577842732,1.7673199749,-4.435976383|H,11.041251883,4.524670486,-3.
3632069659|H,12.7718077675,4.475668002,-2.9936147235|H,12.2126580531,4
.0728792343,-4.6117596704|H,-8.3836446758,-4.9620363713,1.5977872189|H
,-8.9344364095,-3.6971352185,0.5126907481|H,-9.9925802729,-4.183396096

1,3.3760019246|H,-12.0860523501,-1.7554690367,3.4214970914|H,-13.30511
02974,-2.7994837106,2.6689107896|H,-12.207151022,-3.4670705359,3.89086
90016|H,-11.1084995001,-1.2184380809,0.9852534831|H,-10.6596327975,-2.
5928683102,-0.0496461949|H,-12.3612330373,-2.269172035,0.3046130655||V
ersion=x86-Win32-G98RevA.11.2|HF=-1248.4442211|RMSD=9.996e-009|RMSF=3.
006e-006|PG=C01 [X(C30H50O1)]||@

Oxidosqualene, hairpin conformer (one gauche dihedral, chain folds back on itself):

1|1|UNPC-UNK|FOpt|RB3LYP|6-31G(d)|C30H50O1|PCUSER|16-Jan-2005|0||# B3L
YP/6-31G(D) OPT||OxSqualen-"Lowest" energy conf, almost opt in B3LYP o
n H2||0,1|C,5.872404951,-1.2378972137,0.623700937|C,5.5647869216,-2.13
41832036,-0.610710063|C,4.1336809062,-2.6009151567,-0.622914063|C,3.16
22359157,-2.3131251248,-1.503565063|C,4.0954950022,0.3232778446,1.6221
02937|C,4.9723929906,-0.0311951842,0.670148937|C,3.3550359418,-1.51867
11311,-2.773397063|C,-0.5373150705,-1.8924990034,-0.363018063|C,1.7302
439019,-2.7327680778,-1.223857063|C,0.9375269388,-1.6092960518,-0.4984
29063|C,-1.192781086,-2.3651389819,0.710201937|C,-0.5229380976,-2.7191
570038,2.018852937|C,-2.6921190941,-2.6102799327,0.718986937|C,3.92260
49783,-0.4048781497,2.935820937|C,1.1453581014,3.3471409414,-1.0484820
63|C,3.1291670403,1.4840618763,1.463029937|C,3.1448280656,2.2554898758
,0.131310937|C,1.9422930952,3.1585249153,0.015997937|C,1.377396081,2.7
239389338,-2.406096063|C,-0.0741118691,4.2454529814,-0.945405063|C,-3.
4964920789,-2.1494259063,-0.510667063|C,-4.9503710913,-2.5259968586,-0
.396016063|C,-6.027479065,-1.7260538232,-0.360171063|C,-7.4146920843,-
2.3140657777,-0.239655063|C,-5.9947310156,-0.2189488243,-0.439992063|C
,-1.4225938923,3.5373630257,-1.219320063|C,-1.6853919307,2.3694480343,
-0.293983063|C,-2.5015309295,2.4030590611,0.940231937|C,-2.2094679628,
1.3882950515,2.028766937|C,-3.2159938885,3.6531010845,1.412500937|O,-3
.0216379485,1.8264080781,-0.281797063|H,6.9256889612,-0.9255662483,0.5
63008937|H,5.7806149312,-1.8407482107,1.533180937|H,5.8082619398,-1.57
84562116,-1.522951063|H,6.2459018932,-2.997516226,-0.583687063|H,3.850
9448867,-3.1966421474,0.248725937|H,5.0189110106,0.5784138143,-0.23185
1063|H,4.3701229544,-1.1335601644,-2.894729063|H,2.6666189698,-0.66351
21085,-2.815248063|H,3.1271009214,-2.1399361236,-3.651006063|H,-1.1149
15064,-1.6952859844,-1.264611063|H,1.7065358724,-3.632590077,-0.597589
063|H,1.2149928936,-2.9876600609,-2.160732063|H,1.0608509695,-0.673888
0558,-1.062008063|H,1.4108699444,-1.4373570673,0.473611937|H,0.5590999
073,-2.5680910394,2.005300937|H,-0.7081461322,-3.7720739978,2.27328493
7|H,-0.9378420781,-2.1250319902,2.845034937|H,-2.8647961294,-3.6869759
27,0.881265937|H,-3.1165670781,-2.1242479187,1.610829937|H,4.622880951
2,-1.2320301727,3.069333937|H,2.9041599651,-0.8080571163,3.029469937|H
,4.060387001,0.2850958458,3.780010937|H,2.1137910272,1.0848439096,1.61
5910937|H,3.2761180636,2.1951858715,2.291878937|H,3.1632790422,1.54239
38752,-0.697857063|H,4.0759780847,2.8387528452,0.062098937|H,1.6850521
128,3.6942479237,0.932444937|H,2.3221140631,2.1795239028,-2.468151063|
H,1.3903831064,3.4993779334,-3.184601063|H,0.5728200581,2.0273789602,-
2.678068063|H,-0.1061978541,4.7029139825,0.051093937|H,0.017624158,5.0
708559784,-1.667549063|H,-3.0809160947,-2.6313469199,-1.408382063|H,-3
.3670800435,-1.0708029105,-0.644549063|H,-5.1288871266,-3.6018698527,-
0.327617063|H,-7.3944911202,-3.4077637784,-0.193545063|H,-8.0447250747
,-2.021559757,-1.091933063|H,-7.9248080722,-1.944606761,0.661582937|H,
-4.9889140017,0.2033391427,-0.482370063|H,-6.5440080041,0.1304581937,-
1.326288063|H,-6.5076920012,0.2201771925,0.427861937|H,-1.4469559046,3
.1632280265,-2.251572063|H,-2.2346148684,4.2674460523,-1.146666063|H,-
0.913617956,1.596933009,-0.325705063|H,-1.5560669487,1.8189160301,2.79

7562937|H,-3.1399029732,1.073955082,2.517564937|H,-1.7225649919,0.5015
940355,1.612095937|H,-2.612117871,4.1884910647,2.155271937|H,-3.441955
8662,4.3344980919,0.589462937|H,-4.1648668975,3.3799421157,1.889895937
||Version=x86-Win32-G98RevA.11.2|HF=-1248.4412406|RMSD=6.963e-009|RMSF
=1.964e-006|PG=C01 [X(C30H50O1)]||@

Hopen-3β-ol

1\1\GINC-DFTC\FOpt\RB3LYP\6-31G(d)\C30H50O1\BILLW\13-Nov-2003\0\\# B3L
YP/6-31G* OPT=READFC GEOM=ALLCHECK GUESS=READ\\hopene-full\\0,1\C,-0.6
688856027,1.5500782796,-1.3272524852\C,0.705214291,1.0892231579,-1.848
2889874\C,1.6491736043,0.6152910512,-0.7284334834\C,0.9649344037,-0.49
46941579,0.1566381403\C,-0.3491603048,0.1769249234,0.8178713742\C,-1.3
294840811,0.5405873262,-0.3602732247\C,0.5823170628,-1.747737981,-0.68
71379702\C,3.9263151748,-0.064502619,0.0666977141\C,1.9416127216,-1.00
18163348,1.2623147314\C,3.3856848016,-1.2929974909,0.793380847\C,3.099
9062769,0.2880993569,-1.1998286068\C,3.1669149934,-0.7787651638,-2.315
9042546\C,3.8914570418,1.5303667598,-1.6827474683\C,0.0228509522,1.432
2052935,1.6579698179\C,-2.818738608,0.9099206282,0.03552191\C,-1.03077
72951,-0.8138348294,1.8004048544\C,-2.4756044992,-0.4483054421,2.17297
76943\C,-3.3482170255,-0.2780238144,0.918437496\C,-2.9279666316,2.3027
036389,0.7053334902\C,-3.6672217667,0.9441158303,-1.2672474877\C,5.381
6193144,1.148231891,-1.485393142\C,5.4420385514,0.109852724,-0.3156526
141\C,6.2656947781,-1.1558795438,-0.5533344374\C,6.7891573129,-1.81925
05727,0.7036910735\C,6.5992092639,-1.6594457392,-1.7471463464\C,-5.179
9629789,0.9397857878,-1.0134037708\C,-4.8934116509,-0.3489328944,1.196
131531\C,-5.6152079257,-0.2599993863,-0.1731837139\O,-7.0261317393,-0.
24098838,0.0641104254\H,-7.464329944,-0.2125172493,-0.8002928729\C,-5.
4189152276,0.7243671988,2.1735754835\C,-5.2437086747,-1.7320405177,1.7
981626667\H,-1.321991027,1.7238590943,-2.1893696643\H,-0.5518589793,2.
5267048336,-0.8434302465\H,0.5554909142,0.2954687937,-2.5895470369\H,1
.1752377133,1.9185806948,-2.3928558175\H,1.7893788621,1.4774261953,-0.
0632402829\H,-1.4516521945,-0.3889216375,-0.9315840258\H,0.3017528591,
-1.5175742695,-1.716520167\H,1.4166604743,-2.4511772545,-0.736221557\H
,-0.2511951269,-2.298971373,-0.2445844764\H,3.7373379564,0.7785216588,
0.7513216755\H,2.0205718838,-0.2657088319,2.0695057241\H,1.5231181925,
-1.9066003904,1.7202259679\H,3.9835038659,-1.5211018396,1.6842356168\H
,3.4354652801,-2.1838854835,0.155547872\H,2.9086616515,-1.7837245574,-
1.9797493183\H,4.1683007791,-0.8401024084,-2.7448840836\H,2.4856892508
,-0.5178177721,-3.1328652944\H,3.674509235,1.8081294967,-2.7207026663\
H,3.6345982382,2.3957914861,-1.0565769945\H,0.185070453,2.3332516601,1
.0639915708\H,-0.768203074,1.6660409981,2.3733269457\H,0.9286262573,1.
2690639513,2.2478815049\H,-0.4283125913,-0.8853765667,2.7150363331\H,-
1.0558510705,-1.8236219102,1.3775118772\H,-2.8719804004,-1.247315368,2
.8081315903\H,-2.501579473,0.4589704919,2.7874704812\H,-3.1557922538,-
1.1727767692,0.3013107386\H,-2.6876023718,2.2957629526,1.7699459335\H,
-3.9351017893,2.715607364,0.6109956516\H,-2.2546873195,3.0179561295,0.
2236730177\H,-3.4116803441,1.8259573408,-1.8656926165\H,-3.4131728412,
0.0682636161,-1.8824970626\H,5.9947998886,2.0276390396,-1.2618837896\H
,5.7896665414,0.7250302329,-2.4063666049\H,5.919909651,0.591503596,0.5
483089027\H,7.3924251911,-2.7023163408,0.4714556551\H,5.9806539317,-2.
1318611919,1.3742070926\H,7.4155675658,-1.1209640585,1.2765096314\H,6.
2964030155,-1.2170940162,-2.6903812814\H,7.2114717185,-2.5545791798,-1
.8237007861\H,-5.7072998996,0.9117879417,-1.9789408279\H,-5.5063376372
,1.8614832911,-0.5180094608\H,-5.3526516684,-1.1768703464,-0.732345839
9\H,-5.3478937782,1.7395446158,1.7790289426\H,-4.8614546749,0.69353186

23,3.1161606136\H,-6.4720352097,0.5353624747,2.3989625192\H,-4.7784440
446,-2.5461386112,1.2275923482\H,-6.3274152806,-1.8776184261,1.7742471
249\H,-4.9183240954,-1.8218610795,2.8394890492\\Version=x86-Linux-G98R
evA.9\HF=-1248.4895033\RMSD=6.928e-09\RMSF=4.547e-06\PG=C01 [X(C30H50O
1)]\\@

Lupeol, OH hydrogen *anti* to C4; side-chain methyl *anti* to H19

1\1\GINC-APSARA\FOpt\RB3LYP\6-31G(d)\C30H50O1\BILLW\19-Dec-2004\0\\# B
3LYP/6-31G* OPT\\lupeol-128 B3LYP coord--confirming\\0,1\C,-3.19929622
41,-1.1368607677,-1.2192828179\C,-4.5378786548,-0.9166219706,-1.935452
8026\C,-5.0961365406,0.4853835656,-1.6950383786\C,-4.1237637568,1.6192
226622,-2.1112793335\C,-2.7484849154,1.3358586388,-1.407056869\C,-1.69
28792782,2.4334504124,-1.6178282409\C,-0.5622650845,2.3213762277,-0.58
42019394\C,0.1476695734,0.9417228503,-0.5583240492\C,-0.9376745132,-0.
2021513318,-0.5435528193\C,-2.1139522508,-0.0893937838,-1.6000100257\C
,-0.2689356994,-1.593670244,-0.4893110887\C,0.7320640634,-1.7459831879
,0.6696785373\C,1.7702865626,-0.6113768197,0.711523118\C,1.0533056966,
0.7929922192,0.7693977344\C,2.1059087595,1.9419845988,0.8694045754\C,3
.2002118084,1.7278264712,1.9380640957\C,2.8267139549,-0.7525427716,1.8
250174104\C,-1.6515283128,-0.3936892099,-3.0484462858\O,-6.3315937672,
0.6756152787,-2.3916544823\H,-6.938608768,-0.0216355473,-2.0994529705\
C,-4.0431608188,1.7511298958,-3.6470122573\C,-4.7187707418,2.940497687
1,-1.5652476733\C,1.0338446278,0.867072444,-1.8318819295\C,0.194267357
8,0.9025687805,2.0609300771\C,3.9025732131,0.3725714279,1.7692282839\C
,3.6677567273,-2.0552246797,1.9480733871\C,4.7397800826,0.3725723019,0
.4678690193\C,4.8196934965,-0.0539923872,2.9337958358\C,4.9035208133,-
1.5979286506,2.8122389566\C,3.0008127824,-3.2857240045,2.5379184996\C,
2.2225687781,-3.1319746925,3.8243645465\C,3.1479725653,-4.4862636365,1
.9637991357\H,-2.8453749186,-2.1508013972,-1.4375092713\H,-3.370179303
,-1.0955357663,-0.1331617651\H,-4.4461319413,-1.0842930399,-3.01474706
4\H,-5.2655609,-1.6591809781,-1.5747322519\H,-5.2699042363,0.598270674
8,-0.6089813553\H,-2.9965593738,1.3715629773,-0.3319972305\H,-2.147659
6507,3.4240631812,-1.5131068617\H,-1.2928923376,2.3979009271,-2.637879
9794\H,0.176922103,3.1110826864,-0.7696591797\H,-1.0016999698,2.537258
4177,0.3961124163\H,-1.466681557,-0.0865907762,0.4106803128\H,-1.03153
36449,-2.3734378286,-0.3890213551\H,0.2530671861,-1.8083474183,-1.4299
047673\H,1.2423657173,-2.7097351942,0.5732551071\H,0.1859727536,-1.793
6438533,1.6211366811\H,2.3162112506,-0.6590994552,-0.2388832339\H,1.58
71126028,2.884123714,1.0849154513\H,2.6046102676,2.0933243994,-0.09167
44394\H,3.9257588898,2.5508378251,1.8731494851\H,2.7670721643,1.784511
3504,2.9457339998\H,2.3198978142,-0.6239389214,2.7922166481\H,-2.46948
4678,-0.7901746598,-3.6552866759\H,-0.8639976068,-1.1526345488,-3.0574
605706\H,-1.2672274064,0.4820034443,-3.5746731652\H,-3.7645520619,0.82
19309172,-4.1478157403\H,-5.0159533065,2.0558537066,-4.0426088965\H,-3
.3102297091,2.5152037313,-3.9292726258\H,-4.6727606095,2.9773826561,-0
.4690999647\H,-4.1948360026,3.8193827436,-1.9540510764\H,-5.768041115,
3.0201195628,-1.8632006901\H,0.4857395216,1.2076027095,-2.7113377809\H
,1.9086453095,1.5170062927,-1.7488961442\H,1.3968932248,-0.1379848152,
-2.056092764\H,-0.5792584886,0.1385305003,2.1505241998\H,0.8190294124,
0.817396251,2.9537611135\H,-0.2989631371,1.8766203431,2.1262290352\H,4
.0259022424,-2.3323855549,0.9492145747\H,4.1385939722,0.5242793958,-0.
4325746802\H,5.2976336359,-0.5595451751,0.3324820938\H,5.4747480963,1.
1860775886,0.5106947772\H,5.8051586028,0.4257514499,2.9003242393\H,4.3
567149707,0.2283596045,3.8885951545\H,5.8324360686,-1.9153402757,2.327
0647964\H,4.8981863862,-2.0750280212,3.7975313318\H,1.3020530547,-2.55

53429605,3.669372327\H,1.9407085039,-4.106308868,4.2349575783\H,2.8012
531848,-2.5975907727,4.5890655316\H,3.7020007522,-4.6129206815,1.03635
37777\H,2.7208087421,-5.3868550448,2.3986875159\\Version=x86-Linux-G98
RevA.9\HF=-1248.5031327\RMSD=5.898e-09\RMSF=3.223e-06\PG=C01 [X(C30H50
O1)]\\@

Lupeol, OH hydrogen *anti* to H3; side-chain methyl *anti* to H19

1|1|UNPC-UNK|FOpt|RB3LYP|6-31G(d)|C30H50O1|PCUSER|16-Feb-2003|0||#T B3
LYP/6-31G* OPT=READFC GEOM=CHECK GUESS=READ||C30H50O lupeol 128 deg ro
tamer||0,1|C,-3.3713456551,0.9008070159,-0.9110667625|C,-4.8821276616,
0.9689544966,-0.6521336082|C,-5.3979046826,-0.2459034175,0.1182584041|
C,-4.6568839887,-0.4866411095,1.4680492379|C,-3.1156080168,-0.49726073
6,1.1688243161|C,-2.237697071,-0.8429118711,2.382857226|C,-0.823642241
4,-1.2545064238,1.9471188725|C,-0.0877017501,-0.1974866612,1.081742095
2|C,-1.0555268594,0.3086370661,-0.0556709603|C,-2.5216305432,0.7251302
957,0.3802065186|C,-0.3483229227,1.342962922,-0.9593342285|C,0.9884417
494,0.8407145781,-1.5330225385|C,1.9313295032,0.2907375384,-0.44881535
02|C,1.2159917278,-0.8433800981,0.382881145|C,2.1911651259,-1.44177337
98,1.4455118666|C,3.588246056,-1.8172384997,0.9046847013|C,3.305007269
7,-0.1732204079,-0.9718274634|C,-2.5582150128,2.0657748927,1.158294879
|O,-6.8193074539,-0.1925778521,0.2699569036|H,-7.0314380513,0.65272350
26,0.6963961083|C,-5.0934196962,0.5431258764,2.5325598737|C,-5.0963618
901,-1.8815705808,1.9725919801|C,0.3228408745,0.9589088736,2.034157280
3|C,0.835336482,-2.0300876569,-0.547104379|C,4.2506881806,-0.639620234
3,0.1747303286|C,4.1935121981,0.7924334344,-1.8069908551|C,4.602426055
,0.4762144219,1.1874848792|C,5.522493703,-0.9817905621,-0.6281852143|C
,5.6267069509,0.1490131278,-1.6845803421|C,3.8160806634,1.0394375908,-
3.2573144388|C,3.509161043,-0.1546803219,-4.1314213269|C,3.8127500379,
2.2793097978,-3.7625600169|H,-3.0657090452,1.8051532995,-1.4494595054|
H,-3.1718967546,0.0562044889,-1.587044045|H,-5.1361913156,1.8859661985
,-0.1010052542|H,-5.421889458,1.0303729429,-1.6048627886|H,-5.23308128
11,-1.1370579941,-0.5026625062|H,-2.997064235,-1.3447115833,0.47149888
16|H,-2.6745682459,-1.6769936856,2.9421901358|H,-2.1982181615,-0.00275
33727,3.0863132293|H,-0.2233312127,-1.4835710039,2.8367870514|H,-0.920
1163143,-2.194428692,1.3922519437|H,-1.2391272958,-0.5675394747,-0.689
9179672|H,-0.9992367106,1.6182823263,-1.7960017211|H,-0.1624097498,2.2
736008436,-0.4090939759|H,1.4774339263,1.6632831844,-2.064753798|H,0.7
949866358,0.0708431812,-2.291657268|H,2.1284866217,1.1230736233,0.2382
014723|H,1.7349102951,-2.3371273268,1.8852755766|H,2.3323364738,-0.744
7334094,2.2758826551|H,4.2141630496,-2.1551997833,1.7425272283|H,3.515
5152499,-2.6706408609,0.2172526278|H,3.1468282643,-1.0620266061,-1.599
3830449|H,-3.5144335777,2.5796202357,1.0282380757|H,-1.788525151,2.752
1501049,0.7942298806|H,-2.4081877942,1.9484767499,2.2332566259|H,-4.97
87077424,1.5813724053,2.2105151578|H,-6.1461020452,0.3863305822,2.7959
428871|H,-4.5144669847,0.4212190878,3.4540708421|H,-4.6783804329,-2.68
18910447,1.3487387857|H,-4.7885239182,-2.0654130776,3.0070752032|H,-6.
1871067773,-1.9561138845,1.9290799433|H,-0.5019634593,1.2376861944,2.6
914189225|H,1.1464408181,0.663988187,2.6892855858|H,0.6322602124,1.867
4617472,1.5135970688|H,0.1677402607,-1.7607145815,-1.3667719247|H,1.72
58449307,-2.4690014661,-1.0042811791|H,0.3540276295,-2.8349995434,0.01
57510215|H,4.2075492882,1.7692191919,-1.3084828049|H,3.7282814948,0.88
3626659,1.7024589278|H,5.1223070722,1.3164484997,0.7162357156|H,5.2733
930203,0.0699617338,1.9546631167|H,6.4182012817,-1.0558807201,0.000000
5485|H,5.3947367652,-1.954055632,-1.1222274413|H,6.3518778412,0.913874
059,-1.3877065026|H,5.9724507373,-0.2381980637,-2.6484017359|H,2.56674

98555,-0.6341989896,-3.8385257233|H,3.422563398,0.1364609967,-5.182633
0534|H,4.2880768859,-0.9247274419,-4.057087848|H,4.0282828778,3.149025
5545,-3.1458754903|H,3.5949526882,2.4716356674,-4.810511587||Version=x
86-Win32-G98RevA.11.2|HF=-1248.5037991|RMSD=8.016e-009|RMSF=3.435e-006
|PG=C01 [X(C30H50O1)]||@

Lanosterol, non-extended side chain, arbitrarily chosen

1\1\GINC-LNX\FOpt\RB3LYP\6-31G(d)\C30H50O1\BILLW\16-Apr-2004\0\\# B3LY
P/6-31G* OPT GEOM=CHECK\\lanosterol kinked SC restart\\0,1\C,-3.216399
1135,1.1482290781,-1.6212846682\C,-4.6391947024,1.7091887077,-1.509170
8426\C,-5.5973567741,0.7041903688,-0.8701568892\C,-5.1499627529,0.2316
797768,0.5367001689\C,-3.6594436738,-0.2497590706,0.4253291445\C,-3.07
43292207,-0.8000953084,1.7322787004\C,-1.8265124721,-1.6413191113,1.44
23223921\C,-0.9439244736,-1.0922040795,0.3429621248\C,-1.2939427359,-0
.0531991478,-0.4453880701\C,-2.6247548772,0.7188491478,-0.2502363763\C
,-0.363093072,0.493422186,-1.5292545543\C,1.0267202996,-0.1822234675,-
1.6927020741\C,1.4784711286,-0.8557157727,-0.3950140131\C,0.3496741928
,-1.8511963898,0.054409456\C,1.0542101281,-2.6102896744,1.2091099997\C
,2.5361045702,-2.7505603585,0.7380999779\C,2.7066581545,-1.8081459563,
-0.4983870813\C,1.7211049587,0.2446401281,0.6664570533\C,-2.2962135186
,1.9938119955,0.573171979\C,4.1161888713,-1.1816201792,-0.7343978944\C
,4.9663097072,-2.1330502208,-1.5996782557\C,4.8955770126,-0.7834571191
,0.5408733236\C,6.0829215005,0.1868518331,0.3148063835\C,5.692972937,1
.5260337127,-0.2598213932\C,5.5567658573,2.6978051746,0.3827074723\C,5
.1569554399,3.9483082804,-0.3651000493\C,5.7816535622,2.9011538085,1.8
615381843\O,-6.9186768511,1.2421490061,-0.7611487331\C,-6.0439589945,-
0.9762070519,0.9110670861\C,-5.3963433636,1.3275446425,1.5963619667\C,
-0.0195919209,-2.9179716709,-1.0207341427\H,-7.2005454414,1.4995160449
,-1.6524054031\H,-2.5734036203,1.8945167343,-2.1011728987\H,-3.2339567
481,0.2753439898,-2.2900448018\H,-4.6561793279,2.6424856999,-0.9342654
393\H,-5.0072725864,1.9642578432,-2.5143901568\H,-5.6220385905,-0.1927
119678,-1.5160290591\H,-3.7066468428,-1.1057768357,-0.2681235756\H,-3.
8052553556,-1.4172189259,2.264191804\H,-2.8191047621,0.0214295724,2.41
1128219\H,-1.2383821727,-1.7601768916,2.362150621\H,-2.133172405,-2.66
39908504,1.1675855468\H,-0.2140336822,1.5650242391,-1.3337691211\H,-0.
873737859,0.4601826776,-2.4996112912\H,0.9868645072,-0.9253328173,-2.4
970619287\H,1.7535784027,0.5739831331,-2.0171304201\H,0.5916029994,-3.
583256069,1.4079051701\H,1.0055585129,-2.0444416487,2.1452474764\H,3.2
155816295,-2.4781232102,1.5503326108\H,2.7750704073,-3.7868027717,0.47
47241669\H,2.5251736525,-2.414791518,-1.3938031298\H,2.5106209736,0.92
40717731,0.3276262059\H,2.0321602331,-0.1620412719,1.6329813502\H,0.82
18100145,0.8394138187,0.8418656614\H,-3.1300353102,2.6979712559,0.6167
844508\H,-1.4547051847,2.5265680084,0.1163729534\H,-2.0059482532,1.754
2219065,1.5996884812\H,3.9541343904,-0.2676422069,-1.3232568333\H,5.11
09544957,-3.0965974792,-1.0936439901\H,4.4808258671,-2.3332436414,-2.5
620665475\H,5.9589339552,-1.7208548396,-1.8128370662\H,5.2870790071,-1
.6927523495,1.0186536942\H,4.2243364173,-0.3176432309,1.2681839589\H,6
.5975325683,0.3149327895,1.2738132537\H,6.8168849563,-0.2818555999,-0.
3548870431\H,5.4965461375,1.5303304164,-1.3328633194\H,5.0014421504,3.
7547510466,-1.4312628757\H,4.2296674941,4.3759171015,0.041948718\H,5.9
251384915,4.7290848047,-0.2700341467\H,6.0845990904,1.9900252344,2.382
7559388\H,4.8667712514,3.2729065673,2.3437342992\H,6.5540870225,3.6632
974454,2.0363345761\H,-5.826278097,-1.8467315627,0.2789881985\H,-5.912
06185,-1.277359647,1.9553715787\H,-7.0957522552,-0.7105155065,0.771575
3811\H,-4.9572627527,2.2922540669,1.3339346777\H,-6.4709401086,1.48668

09492,1.7202637282\H,-4.9854136628,1.0262851227,2.5661432031\H,-0.3860
564199,-2.4670137286,-1.946597769\H,0.8131048355,-3.5848231962,-1.2676
070297\H,-0.826061296,-3.5491120957,-0.6294468661\\Version=x86-Linux-G
98RevA.9\HF=-1248.4975991\RMSD=7.229e-09\RMSF=1.798e-06\PG=C01 [X(C30H
50O1)]\\@

Cycloartenol, ring-C boat, non-extended side chain, arbitrarily chosen

1|1|UNPC-UNK|FOpt|RB3LYP|6-31G(d)|C30H50O1|PCUSER|20-Apr-2004|0||# B3L
YP/6-31G* OPT GEOM=CHECK||cycloartenol C-boat C30H51O||0,1|C,3.3752944
547,0.919856443,1.7941450759|C,4.6278286395,1.7650128633,1.5207808401|
C,5.6720792391,0.998137528,0.7045290013|C,5.1221868832,0.4426010881,-0
.6373006906|C,3.8461201477,-0.4035135816,-0.2921991619|C,3.2548364024,
-1.1933874675,-1.4704231016|C,2.0624256492,-2.0292484225,-0.9957312701
|C,0.8833952853,-1.133773231,-0.5860183265|C,1.2990741882,-0.012387540
4,0.4233120095|C,2.784183363,0.3949872366,0.4864236386|C,0.4910073092,
0.10098182,1.7347718143|C,-1.0342897342,-0.2383827005,1.6784069424|C,-
1.471847093,-0.8784506484,0.3490889455|C,-0.3777487436,-1.9071761121,-
0.1173827603|C,-1.1209194431,-2.6777585496,-1.2427281494|C,-2.61997973
,-2.7094008731,-0.8145633069|C,-2.7427671028,-1.7819941432,0.432570051
|C,-1.6803392469,0.2601841818,-0.6795664293|C,1.7801551524,1.277605609
2,-0.2197366045|C,-4.1236574569,-1.1010358879,0.6866908437|C,-5.000852
6331,-2.0194032438,1.560810482|C,-4.9007175441,-0.6729992191,-0.580498
6774|C,-6.0485880488,0.3401761913,-0.341073871|C,-5.6044657964,1.66051
16753,0.2376508959|C,-5.4463124262,2.8347309429,-0.3953345751|C,-4.993
2933816,4.0640756919,0.3571906615|C,-5.6965086129,3.0618937998,-1.8665
968218|O,6.8064094356,1.8214336485,0.4167964434|C,6.2130178517,-0.4644
754713,-1.2467829709|C,4.838634763,1.5928361299,-1.6253024119|C,-0.010
6557214,-2.9372848276,0.983641256|H,7.1496028456,2.1474130553,1.262907
0841|H,2.6530374472,1.5202915616,2.3541214552|H,3.6423739642,0.0708256
416,2.4421191877|H,4.3543990838,2.680347263,0.981927787|H,5.0782859488
,2.0834327046,2.4730181035|H,5.9984401736,0.1268185689,1.3014293481|H,
4.2004237391,-1.1729245654,0.4167681323|H,4.0213794046,-1.8522750989,-
1.8920536332|H,2.9396718921,-0.5241177119,-2.2829574686|H,1.7371323083
,-2.7123061389,-1.7916238755|H,2.3911147977,-2.6560074819,-0.156736106
6|H,0.5830769039,-0.6226119087,-1.5100977772|H,0.9602548601,-0.5443079
961,2.4879460779|H,0.6001154257,1.1176837228,2.1233791097|H,-1.6210724
994,0.6710336625,1.8577824962|H,-1.2696016186,-0.9147590175,2.50920857
59|H,-1.0102515979,-2.1574920765,-2.201487548|H,-0.7138582903,-3.68433
09222,-1.3881241078|H,-2.9537494312,-3.726832107,-0.5823757019|H,-3.25
09807829,-2.3611337436,-1.63720316|H,-2.5864950146,-2.4124971734,1.315
3545447|H,-0.806204296,0.9123785565,-0.7454372639|H,-1.8986445118,-0.1
083702385,-1.6873652778|H,-2.5208945902,0.8890359697,-0.3689836269|H,1
.7891483335,1.3265412041,-1.3062735879|H,1.521381467,2.2237780201,0.25
48317243|H,-3.9204120129,-0.1953668968,1.2754699261|H,-5.1882410741,-2
.9767683867,1.0571142861|H,-4.5133692694,-2.2380255567,2.5181561512|H,
-5.9744165959,-1.569007957,1.784387608|H,-5.3300963086,-1.5671801574,-
1.0543159041|H,-4.2199533905,-0.2333017551,-1.3157173814|H,-6.56573194
41,0.4921379494,-1.2951313684|H,-6.7941442927,-0.1043773277,0.33239058
81|H,-5.3853008715,1.6471548082,1.3062498022|H,-4.8205202207,3.8536400
214,1.4174881643|H,-4.0627340012,4.468913726,-0.0653658446|H,-5.739866
0735,4.8681509566,0.2875979598|H,-6.0316367832,2.1649288663,-2.3926010
69|H,-4.7830432921,3.4182482296,-2.3628576917|H,-6.4539806761,3.844186
5032,-2.0160385504|H,6.3674844507,-1.3657027922,-0.6387885653|H,5.9545
569494,-0.7836965794,-2.2616506423|H,7.162046083,0.0766427199,-1.29574
54874|H,4.0922191881,2.2970843803,-1.2486995524|H,5.7584949019,2.15169

16413,-1.8187233057|H,4.474386959,1.2017381629,-2.5817551535|H,0.52237
27401,-2.4952732662,1.8296747171|H,-0.8894367874,-3.4532208586,1.38004
21942|H,0.6381811932,-3.7111950568,0.5617331105||Version=x86-Win32-G98
RevA.11.2|HF=-1248.4813127|RMSD=2.835e-009|RMSF=2.246e-006|PG=C01 [X(C
30H50O1)]||@

Section VI. Triterpene cations, hopen-3β-ol precursors (Table 5)

Hopen-3β-ol precursor, monocycle, cation (Table 5), C9-C10 bond frozen at 3.8 A

1\1\GINC-DFTC\FTS\RB3LYP\6-31G(d)\C25H43(1+)\BILLW\26-Sep-2003\0\\# B3
LYP/6-31G(D) OPT=QST3\\D ring formation TS open-TS guess\\1,1\C,-1.749
7008285,-0.2947343513,-0.9960397908\C,-0.3013384039,-0.9023481358,-1.1
306226969\C,0.4030603408,-0.4669353978,0.0852007537\C,0.2593290348,-1.
0652210768,1.3563463529\C,-1.4186628046,-0.1165191413,1.5355408189\C,-
2.3275514412,-0.6183335227,0.3862557108\C,0.0075031189,-2.5708966867,1
.4402950239\C,3.0558105768,-1.0826004954,0.5909403283\C,1.2851737241,-
0.5921333351,2.3820831447\C,2.6837642767,-1.199970586,2.0498682525\C,3
.741159711,-0.0789768088,-0.007336314\C,4.2516752951,1.1336992721,0.72
79078089\C,4.1214071243,-0.1853418011,-1.4706565815\C,-1.136381576,1.3
883976832,1.583719308\C,-3.8580564078,-0.2437931336,0.5644058513\C,-1.
9131645295,-0.6220457,2.8971618016\C,-3.3865250296,-0.1964585027,3.112
9343532\C,-4.2882185565,-0.6966507174,1.9828734169\C,-4.1840523304,1.2
468359313,0.3371817309\C,-4.6823920495,-1.0616528556,-0.4564087827\C,3
.9066472813,1.0802439951,-2.3397995236\C,2.4853475238,1.5735702011,-2.
4236089167\C,1.6887139062,1.641936509,-3.5051902643\C,0.3155940848,2.2
683637797,-3.4155437449\C,2.0645567055,1.1699378007,-4.8888284709\H,-2
.3563498059,-0.7264223405,-1.7956268154\H,-1.7030087372,0.7829345341,-
1.1779385696\H,-0.3700106841,-1.9903464683,-1.210927353\H,0.1829285133
,-0.498480425,-2.0237116176\H,0.8395829329,0.5267384496,0.0541049173\H
,-2.3403154465,-1.7111715365,0.4721795576\H,-0.873097898,-2.9134173471
,0.8972242256\H,0.8692533315,-3.101573761,1.0205187429\H,-0.0894353241
,-2.8885532788,2.4812152388\H,2.806518981,-1.9434141196,-0.0314306953\
H,1.3788843232,0.4972593636,2.3588071418\H,0.9904362939,-0.8778904722,
3.3966698973\H,3.4177455453,-0.7034124143,2.6920933155\H,2.6963121962,
-2.2568166636,2.3373318567\H,4.0847519658,1.086128466,1.8061192014\H,5
.3295923839,1.2540926551,0.5591334803\H,3.7812215806,2.0528844748,0.35
5735775\H,3.5966698258,-1.0335212933,-1.925932428\H,5.1951905127,-0.42
59888964,-1.5115743315\H,-1.0267248608,1.8496011461,0.6001789556\H,-0.
2427274988,1.6127672989,2.1699120637\H,-1.9603043845,1.8965828383,2.08
90246918\H,-1.87466772,-1.7141178902,2.9428547876\H,-1.2871926063,-0.2
315033929,3.7060004037\H,-3.4621615605,0.8911466079,3.2212989868\H,-3.
7169604256,-0.6182289935,4.0691225316\H,-5.3200810515,-0.3696024805,2.
1597636803\H,-4.3068665542,-1.7957457208,2.0086564999\H,-3.7753574196,
1.9095336252,1.1030625828\H,-3.8280230279,1.5993069795,-0.6369202669\H
,-5.271189884,1.3814250005,0.3466728443\H,-4.4289240605,-2.128140806,-
0.4232637908\H,-5.7492972998,-0.9701665717,-0.2253929769\H,-4.54589242
71,-0.7079832446,-1.4835136879\H,4.301792699,0.8613192008,-3.335679677
8\H,4.5355290718,1.8904074874,-1.9451825758\H,2.0883706577,1.987523528
1,-1.492765432\H,0.0811408149,2.6062261168,-2.3997460914\H,-0.46802636
79,1.5701441995,-3.7423632094\H,0.2419734697,3.1397324405,-4.079783882
9\H,3.0349224236,0.6716278396,-4.9319204385\H,1.3108631263,0.472566024
1,-5.2780032233\H,2.0907419166,2.0163122956,-5.5880817364\\Version=x86
-Linux-G98RevA.9\HF=-978.2682023\RMSD=3.437e-09\RMSF=4.278e-06\PG=C01
[X(C25H43)]\\@

Hopen-3β-ol precursor, bicycle, cation (Table 5), C8-C14 bond frozen at 3.8 A


```
1|1|UNPC-UNK|FOpt|RB3LYP|6-31G(d)|C30H51O1(1+)|PCUSER|19-Feb-2004|0||#
 B3LYP/6-31G* OPT GEOM=CHECK||HopenBicycl frozen bond 3.8 C30H51O+ res
tart||1,1|C,-1.4731779812,-1.3497084797,-1.0881379974|C,-0.1089714327,
-1.4689734601,-0.3639043489|C,0.7173271922,-0.212468757,-0.3849949943|
C,1.340747653,0.4012410625,0.6476786545|C,-2.128799144,1.102331671,-0.
7346081389|C,-2.3650798918,-0.2977200978,-0.4130936567|C,1.2514036931,
-0.0534114908,2.0823385816|C,4.3846421432,0.3431525336,-0.020957669|C,
2.2126187724,1.6132550545,0.3996596873|C,3.70536279,1.4217046189,0.779
6952159|C,5.1533907777,-0.6679153399,0.4149364027|C,5.487535233,-0.927
9609806,1.86450231|C,5.7664178319,-1.6390095586,-0.5749601857|C,-1.668
1447642,1.6004822764,-2.0531173976|C,-4.0270846228,-0.4544822263,-0.66
7865654|C,-2.6427582478,2.0974904912,0.2200336625|C,-4.2165278788,1.98
78354377,0.1034727366|C,-4.685254922,0.5487049955,0.3364865806|C,-4.34
00142407,-0.2453262933,-2.1592480439|C,-4.3980552963,-1.8954689543,-0.
2476270873|C,7.3163016818,-1.6751981106,-0.5809349638|C,7.9370776374,-
0.354327469,-0.9497641975|C,8.9261315829,0.3115544414,-0.3334940975|C,
9.4257229356,1.6284706548,-0.8798587508|C,9.6433562591,-0.1557094818,0
.910123325|C,-6.2454348835,0.420324803,0.5227544519|C,-5.9218961068,-2
.0621269078,-0.1162998035|C,-6.5379901265,-1.0669902299,0.8711098702|O
,-7.9499236098,-1.2160754732,0.9340076593|H,-8.1529490089,-2.088089999
3,1.3062964473|C,-6.6754171446,1.2672675369,1.7446849978|C,-7.08125764
55,0.8884956242,-0.6867329764|H,-1.9649761729,-2.3243187087,-1.0532006
243|H,-1.3136373664,-1.1243400474,-2.1477766503|H,-0.2795445916,-1.816
9198735,0.6605796359|H,0.449578977,-2.2732355832,-0.8642490215|H,0.913
8746573,0.1816273873,-1.3840962408|H,-2.3035768923,-0.4272625591,0.672
4562915|H,0.4371599311,-0.7584796303,2.2670214157|H,1.1238150903,0.803
10367,2.7560217872|H,2.183708534,-0.5497083986,2.3807864095|H,4.239303
6666,0.4296416735,-1.0999002264|H,1.8228192973,2.4604519026,0.98428925
31|H,2.1532004432,1.8996992988,-0.6584392325|H,3.7923127306,1.24237551
44,1.8557928298|H,4.2044239089,2.3848562138,0.5970794785|H,4.893024176
,-0.3305257392,2.560844412|H,6.5427154013,-0.7040374348,2.0661778745|H
,5.3390885763,-1.9869771378,2.1142957187|H,5.4080519556,-2.6556856696,
-0.3512623121|H,5.4142676498,-1.3984029352,-1.5861906712|H,-2.31734942
49,2.4154878016,-2.3989856171|H,-0.6799913447,2.0597691668,-1.90230816
77|H,-1.5774415381,0.8361566236,-2.8234940667|H,-2.3252723667,3.116314
2296,-0.017034572|H,-2.3608708311,1.8533630148,1.2484863222|H,-4.61872
24216,2.6689082696,0.8566172613|H,-4.5320766637,2.3698557112,-0.872400
1225|H,-4.2851500827,0.2554991189,1.3198179738|H,-4.3363510272,0.80396
24364,-2.4667337455|H,-5.3219521052,-0.6474766107,-2.4104481038|H,-3.6
168928947,-0.7830938088,-2.7812498551|H,-4.02013737,-2.6201138466,-0.9
750281339|H,-3.9269560465,-2.1297400569,0.7165706514|H,7.6170599854,-2
.4379336143,-1.3153283056|H,7.6821022028,-2.0341176899,0.386393585|H,7
.5194224715,0.0993249879,-1.8512939783|H,8.8850313395,1.9291815432,-1.
7828154966|H,10.4950721678,1.5739371128,-1.1270218751|H,9.3214672556,2
.4307956199,-0.1358335218|H,9.2464845999,-1.087741254,1.3201343264|H,1
0.7105438927,-0.314438525,0.7021993703|H,9.5946018441,0.6093615355,1.6
972713825|H,-6.1243557894,-3.0853457928,0.2265606115|H,-6.4200919935,-
1.9649021976,-1.0868203496|H,-6.0949423827,-1.2550438585,1.8658762518|
H,-6.021476236,1.0967197835,2.6094184924|H,-7.6918074083,0.9871045224,
2.0318179501|H,-6.6798637312,2.3395195199,1.5237663348|H,-6.9611031077
,0.2647251813,-1.5744799928|H,-6.8350079778,1.9197964982,-0.9626143117
|H,-8.1402762268,0.8619162345,-0.4208872287||Version=x86-Win32-G98RevA
.11.2|HF=-1248.832061|RMSD=8.317e-009|RMSF=3.353e-004|PG=C01 [X(C30H51
O1)]||@
```

Hopen-3β-ol precursor, tricycle, cation (Table 5)


```
1\1\GINC-DFT\FOpt\RB3LYP\6-31G(d)\C30H51O1(1+)\BILLW\22-Dec-2003\0\\#
B3LYP/6-31G* OPT\\Tricycl-HOP-FULL\\1,1\C,-0.9006142623,-0.6148848937,
-2.208513486\C,0.4547609462,-0.969087787,-1.5574888563\C,0.494803955,-
0.2981626062,-0.1572265036\C,0.7707886489,-1.0907915852,1.0152362821\C
,-1.0707964968,0.3780292816,0.0313802829\C,-1.8318943998,-0.499438729,
-0.9992695051\C,0.500094992,-2.5500546441,1.0761795366\C,3.506422546,0
.643571874,1.1052529753\C,1.3996092242,-0.4490794957,2.1759310561\C,2.
9991493833,-0.4511281565,1.9844495583\C,4.1986504751,0.5284591595,-0.0
475830712\C,4.5456719973,-0.7846721132,-0.701913229\C,4.715327436,1.76
57766846,-0.7491778595\C,-0.8453610262,1.8568660823,-0.3245038446\C,-3
.3501258644,-0.1551476453,-1.1831715401\C,-1.7647734743,0.2633328696,1
.3995774994\C,-3.2694088508,0.599563512,1.2769975029\C,-3.9817843933,-
0.3047621229,0.2498651094\C,-3.5584501077,1.2234210417,-1.8578520998\C
,-3.9744305168,-1.2481427175,-2.0925032486\C,6.2612381252,1.8366074369
,-0.8670015341\C,6.9533501395,1.8601301786,0.4698904119\C,7.9869530216
,1.1143315391,0.89202971\C,8.5621016092,1.3113549452,2.274887585\C,8.6
877262154,0.0573024514,0.0729315691\C,-5.5478708912,-0.2813289262,0.33
71545668\C,-5.5086194912,-1.2220347233,-2.0731048981\C,-6.0734349665,-
1.3572768816,-0.6551832315\O,-7.4953589744,-1.2815647049,-0.6597450313
\H,-7.8362117394,-2.010360334,-1.2009042075\C,-5.9885684678,-0.7213665
104,1.7539145399\C,-6.1871026409,1.0952119057,0.0583370457\H,-1.217181
6255,-1.3872206653,-2.9141777552\H,-0.8353003842,0.3239626156,-2.76742
87264\H,0.546554465,-2.0560557712,-1.4728518037\H,1.3113108676,-0.6298
316802,-2.1475885946\H,1.157968007,0.5712119258,-0.1369941957\H,-1.848
9932573,-1.5064773066,-0.5512979016\H,-0.376623135,-2.8350305375,0.487
0409728\H,0.4046062103,-2.9157919141,2.1009823026\H,1.3520940839,-3.07
70642187,0.6140660918\H,3.3345752054,1.6482964859,1.4933336088\H,1.170
9827508,-0.9814388828,3.1020846192\H,1.1030437689,0.5998063039,2.26991
29365\H,3.3299704279,-1.4444333084,1.6724385305\H,3.3672007268,-0.3045
641034,3.0068445236\H,3.9856866886,-1.6351297064,-0.3035186321\H,5.612
11006,-1.006252842,-0.5701676754\H,4.367955578,-0.7371462505,-1.783427
7528\H,4.296262058,1.8006038564,-1.7659209231\H,4.3557994965,2.6605349
992,-0.2268553014\H,-1.7763921949,2.4220259004,-0.2720244309\H,-0.1544
65309,2.3122805597,0.3939225879\H,-0.4256790366,1.9911335412,-1.324905
068\H,-1.2973301775,0.9251887897,2.1394683717\H,-1.6850480153,-0.76077
51028,1.7895941615\H,-3.7144164878,0.4672333359,2.2671206904\H,-3.4022
609531,1.6585773265,1.0294212006\H,-3.7243508382,-1.3369552416,0.54539
7787\H,-3.5987432718,2.0531616226,-1.1495487232\H,-4.4940035326,1.2513
049188,-2.4190789044\H,-2.7605916895,1.4364153316,-2.5769158407\H,-3.6
154454824,-1.1326659244,-3.1225783907\H,-3.6343279477,-2.2375761008,-1
.7517164144\H,6.492860471,2.7591592272,-1.4191298363\H,6.6220257,1.015
2789858,-1.4938679365\H,6.5602321239,2.6053055207,1.1646969998\H,8.028
6821398,2.0858252904,2.8346195568\H,9.6209004155,1.59912022,2.22301816
01\H,8.5238779613,0.3795300655,2.8562244075\H,8.2445062199,-0.10155746
36,-0.9135060948\H,9.7408616192,0.3286854612,-0.0806736991\H,8.6942246
838,-0.9047755586,0.6033975268\H,-5.8873574117,-2.0487988482,-2.689859
7069\H,-5.8992098514,-0.3046754725,-2.5271536431\H,-5.7549809875,-2.33
85182513,-0.2569815936\H,-5.4547080951,-1.6233392184,2.0808080839\H,-7
.0579775935,-0.9467213831,1.7465523121\H,-5.8219061595,0.0619062927,2.
5006057396\H,-6.0601765094,1.4339397943,-0.9715019421\H,-5.7666648973,
1.8615123585,0.7194343407\H,-7.2615505392,1.0440764493,0.250416489\\Ve
rsion=x86-Linux-G98RevA.9\HF=-1248.8402702\RMSD=4.471e-09\RMSF=6.246e-
06\PG=C01 [X(C30H51O1)]\\@
```

Hopen-3β-ol precursor, tetracycle, cation (Table 5)


```
1|1|UNPC-UNK|FOpt|RB3LYP|6-31G(d)|C30H51O1(1+)|PCUSER|22-Dec-2004|0||#
 B3LYP/6-31G* OPT||HopFULLTetracycle restart last file was corrupted||
1,1|C,0.3663415188,1.4402712807,-0.863952197|C,-1.0059379141,1.5784855
851,-0.159882872|C,-1.6090054407,0.1886627706,-0.0344915376|C,-0.73490
68489,-0.7939553661,0.7847508258|C,0.6447548348,-0.9874932183,-0.01491
48694|C,1.3113573671,0.4350333647,-0.1670937072|C,-0.5035370561,-0.282
5128612,2.2296627836|C,-3.1502094601,-0.0763946176,0.5527121173|C,-1.6
643477345,-2.0273039848,0.8810336347|C,-3.0397288671,-1.4439858493,1.2
74089405|C,-3.726614584,1.0746906474,1.2196284145|C,-3.8577402551,1.24
1445849,2.6893270022|C,-4.2934818125,2.1496981798,0.3932632833|C,0.387
0065816,-1.6787651512,-1.3779579276|C,2.8010353292,0.4574513542,-0.708
5690192|C,1.5970994791,-1.9043926149,0.7949577485|C,3.0388591925,-1.90
80647914,0.2630339962|C,3.6255840609,-0.4859762998,0.2430477156|C,2.89
74049081,0.0976225059,-2.2146928454|C,3.3577033739,1.8993483,-0.525277
1306|C,-5.7965846085,1.7508334232,-0.0250709795|C,-5.8721409513,0.8258
328211,-1.1934449943|C,-6.4322492762,-0.4026270436,-1.2462395453|C,-6.
5032460198,-1.1513215331,-2.5531209728|C,-7.0619756734,-1.114116965,-0
.0766165214|C,5.1902778389,-0.4403184265,0.1227379209|C,4.8811234439,1
.9874342029,-0.6832952753|C,5.620419911,1.0436444808,0.2663875999|O,7.
0306622497,1.1133183231,0.0660236731|H,7.3142793166,2.0230138206,0.245
0898097|C,5.817633818,-1.2056236602,1.3138778617|C,5.7540937626,-1.061
3753353,-1.1732032877|H,0.8259226142,2.4318773908,-0.8937216153|H,0.19
00514773,1.1561349922,-1.9084121776|H,-0.8840340255,2.0534129318,0.822
5418239|H,-1.6347751648,2.2455200185,-0.7620016|H,-1.7048925825,-0.210
9549174,-1.0458814719|H,1.429982962,0.8121504137,0.8560918767|H,-1.427
6766082,0.0987468183,2.6730832743|H,-0.1645299615,-1.096849333,2.87558
15721|H,0.2311092702,0.5200362756,2.3032069053|H,-3.7254820796,-0.1688
313472,-0.383569162|H,-1.7523439672,-2.5303433766,-0.0857266309|H,-1.3
192795612,-2.771249821,1.6048398969|H,-3.8671765571,-2.0944181212,0.97
33685119|H,-3.107906169,-1.3381764097,2.3587818949|H,-3.0728582756,1.9
451315603,3.0138828702|H,-4.8055357218,1.7330217896,2.9399588071|H,-3.
7488007924,0.3238021005,3.2658666239|H,-3.7409315715,2.2932429783,-0.5
383521567|H,-4.341889827,3.0927661331,0.9441804984|H,1.3252485286,-1.9
31247692,-1.8679397754|H,-0.1788495223,-1.0713616749,-2.0899563842|H,-
0.1484955312,-2.623027559,-1.2458412398|H,1.6388786826,-1.5736542991,1
.8384620959|H,1.1986068901,-2.9276694727,0.8077025596|H,3.0875858514,-
2.3692788449,-0.7296915163|H,3.6337501503,-2.5510814501,0.9181551142|H
,3.4330673825,-0.0779890687,1.2506886121|H,3.0418340651,-0.968605824,-
2.3983061237|H,1.9998970454,0.4066605864,-2.7594581093|H,3.7364347716,
0.6097289388,-2.69041408|H,3.0868088226,2.265456652,0.4767724141|H,2.8
913082036,2.5842979854,-1.2433261483|H,-6.3384366574,1.3845814575,0.85
02611921|H,-6.2414511045,2.717528393,-0.2892034524|H,-5.471610887,1.23
6422243,-2.1210769545|H,-6.0285913047,-0.6037206216,-3.372003282|H,-6.
0249027772,-2.1359490175,-2.4687308065|H,-7.5486782446,-1.3398635638,-
2.8302559677|H,-6.9453844367,-0.5952055326,0.877927875|H,-6.6440966716
,-2.1235962827,0.0280226543|H,-8.1378060437,-1.2468204308,-0.251156161
2|H,5.1897819256,1.7713128716,-1.7123210815|H,5.2006298186,3.020416087
5,-0.4846677594|H,5.3792580514,1.3470182693,1.3019902995|H,5.35109301,
-0.9215388145,2.2662017286|H,5.7261517417,-2.2907634423,1.2025039984|H
,6.8829614084,-0.96855751,1.3759859394|H,5.4932352992,-0.502403456,-2.
0740715153|H,6.8450165097,-1.0943171892,-1.1183492546|H,5.3942907409,-
2.0887145038,-1.2990235683||Version=x86-Win32-G98RevA.11.2|HF=-1248.84
33872|RMSD=6.608e-009|RMSF=4.000e-005|PG=C01 [X(C30H51O1)]||@
```

Hopen-3β-ol precursor, pentacycle, cation (Table 5)


```
 1\1\GINC-DFT\FOpt\RB3LYP\6-31G(d)\C30H51O1(1+)\BILLW\22-Nov-2003\0\\#
 B3LYP/6-31G* OPT=READFC FREQ GEOM=ALLCHECK GUESS=READ\\Hopen-FULL-cat\
\1,1\C,-0.7742732592,1.2110731669,-1.5905108682\C,0.6204265776,0.74056
96377,-2.0467538121\C,1.5860392941,0.5324473134,-0.8629819813\C,0.9761
122848,-0.4390938498,0.2133955469\C,-0.3779306749,0.2612730565,0.76057
38301\C,-1.3776305133,0.3569344291,-0.4527582423\C,0.6854747773,-1.844
6691052,-0.3845996949\C,3.8392029196,0.1729595543,0.0184129868\C,1.978
5245358,-0.6651178016,1.385527362\C,3.4471271714,-0.9447205023,0.96312
60121\C,3.0641705822,0.2086379113,-1.3128462505\C,3.1917119093,-1.0624
551391,-2.1858708268\C,3.7501095448,1.3829705442,-2.0487446519\C,-0.07
94548859,1.6620542398,1.3648510843\C,-2.8835626793,0.7161216134,-0.112
3621051\C,-1.0015794715,-0.5834542644,1.9048211607\C,-2.4611527428,-0.
228235858,2.2265571289\C,-3.347826869,-0.3209051198,0.9739149849\C,-3.
0666251356,2.1990597382,0.2997877437\C,-3.7334729422,0.4695825941,-1.3
914937525\C,5.2673730723,1.1443117784,-1.8594856886\C,5.466820044,0.57
1966845,-0.4396509008\C,6.2460833437,-0.5948018242,-0.1737582821\C,6.7
72565202,-0.8267337495,1.1938635496\C,6.5823103388,-1.6223780944,-1.18
91737483\C,-5.2434793311,0.437601852,-1.1228396723\C,-4.8853122841,-0.
4102510469,1.2831860832\C,-5.6193014083,-0.6055042837,-0.069841374\O,-
7.023083594,-0.5984558961,0.1858402454\H,-7.4786492304,-0.7876915241,-
0.6488440674\C,-5.4558739755,0.7970190094,2.0575182593\C,-5.1637524794
,-1.6764489829,2.1300660471\H,-1.4338000096,1.1892619602,-2.4634745298
\H,-0.7101036166,2.2635340375,-1.2938569962\H,0.5140591898,-0.18318843
8,-2.6264131652\H,1.0385503083,1.4836554772,-2.7373070293\H,1.67712147
39,1.5097715714,-0.3729841671\H,-1.45508606,-0.6645531239,-0.846722717
6\H,0.2683282547,-1.8187705936,-1.3917778995\H,1.5931067694,-2.4514318
634,-0.4326896313\H,-0.0166531008,-2.4036330628,0.2368504446\H,3.63613
6676,1.112420586,0.5429172661\H,2.0054960982,0.2063632796,2.0459487467
\H,1.6394256706,-1.503769379,2.002501953\H,4.0590381302,-0.9460598037,
1.8726566311\H,3.5517479623,-1.9319078043,0.5001988625\H,3.2469059859,
-1.9907906864,-1.6147022028\H,4.0710193016,-1.0168451003,-2.8349438436
\H,2.3330274458,-1.1510939063,-2.8543844049\H,3.4869385528,1.439668810
5,-3.1087640413\H,3.460555934,2.336823673,-1.5901654192\H,0.093986334,
2.4438370916,0.622842886\H,-0.9172547256,1.9971735725,1.9763313031\H,0
.7883792291,1.6470936763,2.0311058333\H,-0.3932823432,-0.4725332497,2.
8123537324\H,-0.9831104037,-1.6494778593,1.6552484199\H,-2.8115930591,
-0.9257861641,2.9932461016\H,-2.5290569748,0.7670125788,2.6794843059\H
,-3.1183208717,-1.3012466556,0.5210003824\H,-2.8696241756,2.3876634816
,1.356717899\H,-4.085103761,2.541577026,0.1065864363\H,-2.408606147,2.
8544651134,-0.278657338\H,-3.5257317173,1.2399953721,-2.1432539969\H,-
3.4371990606,-0.4907901,-1.8395073343\H,5.8462348585,2.0672910464,-1.9
624070665\H,5.6476195332,0.4545451198,-2.6176360861\H,5.7111057688,1.3
435634441,0.2937011668\H,6.3585527586,-1.7639470515,1.5944842132\H,6.5
719306342,-0.008843306,1.8871591697\H,7.8583332685,-0.9968344301,1.135
5996649\H,5.8563956068,-1.6953272562,-1.9977768565\H,6.7618529573,-2.6
0429341,-0.742796172\H,-5.768569789,0.206919929,-2.060924708\H,-5.6146
449898,1.4180748431,-0.8038423221\H,-5.3199355229,-1.5979305352,-0.454
77326\H,-5.4397256025,1.7262270381,1.4852919541\H,-4.8953428918,0.9639
294995,2.9840234834\H,-6.4967238411,0.6010600901,2.3269695875\H,-4.660
3322601,-2.5582417777,1.7126983589\H,-6.2385947869,-1.8757288774,2.142
6744538\H,-4.8368528538,-1.5595478632,3.1682481896\H,7.535780171,-1.30
28992991,-1.6465377207\\Version=x86-Linux-G03RevB.02\HF=-1248.8433774\
RMSD=5.398e-09\RMSF=3.457e-06\Dipole=8.5704376,-1.4239473,-0.8576605\P
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G=C01 [X(C30H51O1)]\\@
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Section VII. Triterpene cations, lupeol precursors (Table 5)

Lupeol precursor, tricyclic cation (folded side chain)

```
1|1|UNPC-UNK|FOpt|RB3LYP|6-31G(d)|C30H51O1(1+)|PCUSER|04-Dec-2003|0||#
 B3LYP/6-31G* OPT=RCFC GEOM=ALLCHECK GUESS=READ||Lup-FULL-tricyle||1,1
|C,0.0484234233,0.2423444844,-2.0092763712|C,0.8282469676,-0.997907155
,-1.5270669688|C,0.6814106696,-1.0694349392,0.0130753777|C,0.224374284
2,-2.2644867895,0.6595976539|C,-0.536842909,0.1300656433,0.3800008725|
C,-1.1371863529,0.2826337936,-1.0423683785|C,-0.6470616109,-3.25542689
33,-0.0217574077|C,3.099397782,-3.1847569289,1.316961482|C,0.662728896
1,-2.5541010389,2.0329541874|C,1.8526927763,-3.6281034536,2.017325644|
C,4.2511667356,-2.7652945016,1.8774600577|C,4.470579475,-2.6090730154,
3.3614169556|C,5.45243927,-2.4751037532,1.0009117633|C,0.3146188747,1.
2834224498,0.9304062963|C,-2.2485371829,1.3816871188,-1.1795403534|C,-
1.6660082532,-0.2073384704,1.3694120465|C,-2.7923796608,0.851136475,1.
2815645004|C,-3.362203083,0.9753544285,-0.146731814|C,-1.675963551,2.8
107704371,-1.0129247764|C,-2.8560309673,1.2576540603,-2.6035582562|C,6
.0409731488,-1.0420149712,1.0995471284|C,5.1028104348,0.0505825365,0.6
606602772|C,5.2046658571,0.8441601744,-0.418919366|C,4.1937088288,1.93
82408115,-0.672022857|C,6.3029524793,0.7691809752,-1.4514541574|C,-4.1
704547741,2.0364575059,-2.7506184607|C,-4.7235542227,1.7487401639,-0.2
398839429|C,-5.2152503404,1.6208441432,-1.709526111|O,-6.4017918161,2.
3977621596,-1.8360360178|C,-4.6575673376,3.2272909478,0.1984969402|H,-
6.7737669289,2.2429159768,-2.7179606812|C,-5.7752577505,1.0460859485,0
.6521783399|H,-0.2594689261,0.1374496311,-3.0527389049|H,0.6664860807,
1.1438495202,-1.944330267|H,0.4163726518,-1.8941424248,-2.0012591387|H
,1.8912877206,-0.9626916038,-1.7837086395|H,1.5692520184,-0.6970067447
,0.5263034553|H,-1.6845673972,-0.657110817,-1.22033677|H,-1.3118800491
,-2.7946605824,-0.7570111894|H,-1.2196968811,-3.8654831378,0.680870504
9|H,0.0071678944,-3.936099561,-0.5929624928|H,3.0738112019,-3.25722534
74,0.2287171222|H,-0.1505156244,-2.9967555981,2.6178585697|H,1.0401917
108,-1.6587640341,2.5329184848|H,1.4613543598,-4.5461163617,1.56378264
63|H,2.0286334411,-3.8466101517,3.0732503778|H,3.6196121009,-2.9260130
566,3.9688974323|H,4.6867385474,-1.5642641977,3.6165829602|H,5.3444260
257,-3.1911153148,3.6807021083|H,6.2496480436,-3.1794253537,1.28176290
98|H,5.2030036874,-2.6825637522,-0.0459290197|H,-0.3101568308,2.139767
0643,1.1871638252|H,0.819327253,0.9704247362,1.8513229814|H,1.07765678
23,1.6216274941,0.2257762156|H,-1.2895893436,-0.2608205581,2.398486694
7|H,-2.113435685,-1.1822153003,1.1352875708|H,-3.5801522841,0.54226476
39,1.974162484|H,-2.4340483786,1.8182833371,1.6500417167|H,-3.63213770
65,-0.054294737,-0.4393630589|H,-1.6635685895,3.1581767004,0.022001985
|H,-2.2620539198,3.5382495551,-1.5768006867|H,-0.6533716119,2.87138681
04,-1.399048282|H,-2.1357175886,1.6058156076,-3.3540217833|H,-3.046944
0529,0.1964270657,-2.8227516369|H,6.9604011106,-1.0273999124,0.5074889
867|H,6.3532156912,-0.8526097939,2.1359231946|H,4.2566881761,0.2257181
204,1.3291055217|H,3.4350345079,1.9844148775,0.1165749538|H,3.68798315
35,1.8011154871,-1.6389623194|H,4.6830099346,2.9203187918,-0.720783992
3|H,7.0051883901,-0.0502235908,-1.2854835793|H,5.8785368667,0.64774824
48,-2.4573301017|H,6.8777787198,1.7048349724,-1.471092762|H,-4.5777113
313,1.8613327259,-3.7558960016|H,-4.0044546125,3.1172221634,-2.6777990
95|H,-5.4509559071,0.5529784395,-1.8729062185|H,-4.0624515408,3.853632
5996,-0.4685686601|H,-4.2410431305,3.3182012671,1.2080685979|H,-5.6664
602416,3.6461872545,0.2166825912|H,-5.7738512127,-0.0415142682,0.50149
```

37228|H,-6.7711431018,1.4187005819,0.3994319367|H,-5.610680106,1.24232
40083,1.716752062||Version=x86-Win32-G98RevA.11.2|HF=-1248.8399357|RMS
D=4.454e-009|RMSF=2.907e-006|PG=C01 [X(C30H51O1)]||@

Lupeol precursor, tetracyclic cation (folded side chain)

1\1\GINC-APSARA\FOpt\RB3LYP\6-31G(d)\C30H51O1(1+)\BILLW\30-Mar-2004\0\
\# B3LYP/6-31G* OPT GEOM=CHECK GUESS=READ\\LupFULLTetracycl C25H43(1+)
 restart again\\1,1\C,0.1745990344,0.5558845434,-1.4423029991\C,-1.285
2038877,0.5779686748,-0.9429825458\C,-1.6441050983,-0.7925514809,-0.37
0778107\C,-0.6908497519,-1.2491148995,0.7751180948\C,0.7949608349,-1.3
511877685,0.2029318966\C,1.1780168034,0.0752977933,-0.3658892961\C,-0.
7901879399,-0.3032925387,2.0028963184\C,-3.0635844178,-0.9868021943,0.
1999559266\C,-1.3820231149,-2.5756133716,1.1808582354\C,-2.9069143068,
-2.2957418518,1.1657811279\C,-4.1717884867,-1.3531216361,-0.6665880207
\C,-3.9550873719,-2.0396666157,-1.9637976599\C,-5.5354000071,-1.009934
0795,-0.2701214021\C,0.8804594887,-2.4593487711,-0.877297558\C,2.69920
65365,0.2932081835,-0.7587144477\C,1.7926494144,-1.7294044233,1.326768
354\C,3.2656887755,-1.5528275976,0.9308661937\C,3.5459780103,-0.100065
9497,0.5072754884\C,3.0983561564,-0.4590996358,-2.056012128\C,2.914988
7494,1.8147150751,-1.0056499339\C,-5.959877269,0.3882516114,-0.9717797
336\C,-5.2366111413,1.5929852923,-0.4658101218\C,-5.6686735381,2.45219
43507,0.4803035135\C,-4.850243891,3.6662263276,0.8390102462\C,-6.96411
24695,2.3188121247,1.2385522939\C,4.3938627222,2.2199608394,-1.0582321
298\C,5.0674661264,0.2891404402,0.5073875836\C,5.154183075,1.807843899
,0.2025864641\C,5.9406127708,-0.5264866853,-0.4702684308\C,5.647975454
3,0.0833438404,1.9281398652\O,6.5336311281,2.1587098443,0.1092899299\H
,6.591559454,3.1210614787,0.0064499944\H,0.4375511491,1.5644427081,-1.
7728045797\H,0.2276276569,-0.0781123813,-2.3358449399\H,-1.4143196277,
1.35534996,-0.1786297659\H,-1.9513021292,0.846910326,-1.7755987665\H,-
1.5218846881,-1.523125076,-1.1786475608\H,1.0506937003,0.7642372243,0.
4786027015\H,-0.3574362036,0.6834789506,1.8316404195\H,-1.8278581662,-
0.1409988694,2.3126523171\H,-0.2807752321,-0.738663739,2.8659460308\H,
-3.3756559023,-0.1543852412,0.8389827835\H,-1.1617596459,-3.3745761755
,0.4700653438\H,-1.0858396767,-2.93290084,2.1732767058\H,-3.4707674942
,-3.1644577165,0.8108442925\H,-3.3187647991,-2.0255010921,2.1400239898
\H,-3.2270645405,-2.8537879946,-1.8672041337\H,-4.8782314484,-2.417887
185,-2.4060566511\H,-3.492705645,-1.3236505915,-2.662234553\H,-5.62872
09776,-0.8597419744,0.8078191259\H,-6.2524444976,-1.758477179,-0.61945
13945\H,0.2737175085,-2.2656608755,-1.7667476267\H,0.581625303,-3.4311
259157,-0.4720784355\H,1.903407387,-2.5826915084,-1.2266075338\H,1.623
502888,-1.0991114529,2.2063546486\H,1.609600966,-2.7647452195,1.646606
2493\H,3.5475619755,-2.2571644129,0.1401681543\H,3.8792259531,-1.81834
48917,1.7965891531\H,3.1210093615,0.5238004913,1.3129366337\H,3.457880
7617,-1.4743014794,-1.8773790502\H,2.2586904704,-0.5236186642,-2.75515
35529\H,3.8990139522,0.0623054364,-2.5846283888\H,2.4234053667,2.38258
78955,-0.2012016257\H,2.4348632593,2.1233502918,-1.9417499813\H,-5.832
5296163,0.2724153384,-2.0528936458\H,-7.033963131,0.4422184923,-0.7802
815142\H,-4.2784457506,1.8061040937,-0.9391266552\H,-3.915200335,3.718
238588,0.2739994331\H,-5.4190062489,4.5844810964,0.6429624088\H,-4.610
7024222,3.6746584504,1.9104769548\H,-7.5439960927,1.4284713235,0.98323
74266\H,-7.5999446001,3.1952369727,1.0585842258\H,-6.7714781101,2.2970
202327,2.318950233\H,4.89512964,1.7905627166,-1.9329891469\H,4.4606765
748,3.310738962,-1.1786007254\H,4.697208673,2.3322917385,1.0620595565\
H,5.7163568192,-0.3321514372,-1.5209939089\H,5.8200038259,-1.601296973
6,-0.2944930427\H,6.9936591056,-0.279256952,-0.3141232195\H,4.99128222

37,0.5095312555,2.697791672\H,6.618260255,0.581871356,1.9985039647\H,5
.8021861644,-0.9747492753,2.162434014\\Version=x86-Linux-G98RevA.9\HF=
-1248.8482862\RMSD=7.926e-09\RMSF=2.102e-06\PG=C01 [X(C30H51O1)]\\@

Lupeol precursor, pentacyclic cation (lupyl cation)

1|1|UNPC-UNK|FOpt|RB3LYP|6-31G(d)|C30H51O1(1+)|PCUSER|26-Nov-2003|0||#
 B3LYP/6-31G(D) OPT=READFC FREQ GEOM=ALLCHECK GUESS=READ||Lup-FULL-cat
128 C30H50O||1,1|C,-2.1259013543,1.1708929166,-2.6617077667|C,-3.49516
56896,1.3897997763,-3.3182301138|C,-4.4644793125,0.2415784239,-3.03309
99811|C,-4.6786831432,-0.0258460569,-1.5196751371|C,-3.2589007973,-0.1
938343748,-0.869812752|C,-3.2885808143,-0.5865095915,0.6157812251|C,-1
.9327946977,-1.1445151063,1.073380711|C,-0.7377418519,-0.1814075473,0.
8346313572|C,-0.8112646977,0.373942115,-0.6392776135|C,-2.2078077758,0
.9477116265,-1.1241330598|C,0.3837350891,1.3081373202,-0.9449993425|C,
1.739730246,0.6475807546,-0.647670964|C,1.8180843311,0.0791257175,0.77
37141635|C,0.6567732637,-0.9743522798,1.0134248822|C,0.7986440366,-1.5
992010528,2.4359052933|C,2.2078616902,-2.1317412739,2.7741230481|C,3.1
68961718,-0.5335402417,1.1298696627|C,-2.5620937315,2.3052880715,-0.46
44940204|O,-5.7403339439,0.4880572106,-3.6216127948|H,-5.6173388063,0.
5674739588,-4.5800243571|C,-5.554545161,1.0705816741,-0.8773145066|C,-
5.4530291017,-1.3620231636,-1.4070482219|C,-0.8541392264,0.9579060396,
1.8828320158|C,0.7820299115,-2.1562544975,0.0121907922|C,3.2877002794,
-1.0449230929,2.5934338264|C,4.4591664824,0.3865486306,0.9897258328|C,
3.1174383782,0.0564669033,3.6643408473|C,4.7447235992,-1.5362693893,2.
6013870467|C,5.5456173484,-0.4588952792,1.8221774352|C,4.9367030914,0.
6228335292,-0.3559173944|C,5.1915590232,-0.4813004679,-1.3092035627|C,
5.2859078611,1.9923241084,-0.7991997624|H,-1.4861821455,2.0314321815,-
2.8915174951|H,-1.6497809362,0.2940761644,-3.126509514|H,-3.9499694678
,2.3307456542,-2.9890359897|H,-3.359172769,1.4846854653,-4.4050997527|
H,-4.032269661,-0.6815153194,-3.4618133326|H,-2.8358218648,-1.06711461
23,-1.3961642652|H,-4.040669735,-1.3624858159,0.787097043|H,-3.5921741
758,0.2616336055,1.2393953978|H,-1.986256363,-1.404929618,2.1379402141
|H,-1.7735663579,-2.0838470121,0.5327153687|H,-0.6789111041,-0.5002599
699,-1.2880564255|H,0.3663716761,1.6058426828,-1.9974311131|H,0.312652
5741,2.2361299078,-0.3666393787|H,2.5348805274,1.4017107618,-0.7847647
584|H,1.9363591507,-0.1431783964,-1.3841726447|H,1.6484084749,0.911988
801,1.4649680174|H,0.0872627328,-2.4265287854,2.5310854869|H,0.5162674
913,-0.8776166217,3.2058627526|H,2.216180923,-2.494448781,3.809399909|
H,2.4558146424,-2.9967175005,2.1461306008|H,3.3504101925,-1.3994753182
,0.4818669333|H,-3.2059751633,2.9041795511,-1.1118715254|H,-1.66627114
03,2.9069475197,-0.2821367968|H,-3.0866762768,2.2032595912,0.487037496
6|H,-5.1697032226,2.080705737,-1.0299544811|H,-6.5574121691,1.03810426
29,-1.3103946437|H,-5.6503056837,0.9069521065,0.2018328178|H,-4.830689
7309,-2.2150736619,-1.7073631196|H,-5.8123048914,-1.5465133806,-0.3897
967319|H,-6.3255204846,-1.3321726677,-2.064977534|H,-1.8751303261,1.33
44081602,1.9328662044|H,-0.6142705873,0.6065347556,2.8895076397|H,-0.2
162245726,1.820823935,1.6756590913|H,0.6862362695,-1.869823816,-1.0357
182718|H,1.7416224642,-2.6719911179,0.1113970384|H,0.0165750571,-2.910
141412,0.2103212691|H,4.2786061293,1.3397952201,1.4909663282|H,2.15759
25198,0.5738080783,3.5987106119|H,3.9039458949,0.8179219589,3.62368190
23|H,3.1725981039,-0.401235346,4.6580064433|H,5.1538152282,-1.66380813
1,3.6092462012|H,4.8221385582,-2.5038235296,2.0922863396|H,6.058953005
6,0.2505849808,2.4761230807|H,6.3089702801,-0.9053985651,1.1788465289|
H,4.422038244,-0.4165803125,-2.0954803137|H,6.1467966437,-0.3322734349
,-1.8290842744|H,5.1489607954,-1.4762732551,-0.8663673776|H,4.69697003

96,2.7648464241,-0.2988743042|H,5.2604852055,2.1143279984,-1.885838832
5|H,6.3373023944,2.1492240837,-0.491764769||Version=x86-Win32-G98RevA.
11.2|HF=-1248.8583556|RMSD=6.313e-009|RMSF=6.358e-006|PG=C01 [X(C30H51
O1)]||@

Section VIII. Triterpene cations, lanosterol precursors (Table 5)

Lanosterol precursor, tricycle, cation

1\1\GINC-DFTC\FOpt\RB3LYP\6-31G(d)\C30H51O1(1+)\BILLW\06-Sep-2003\0\\#
 B3LYP/6-31G* OPT GEOM=CHECK\\protosteryl cat SM from HF geom\\1,1\C,-
2.8366116762,1.8785404444,-0.7644487408\C,-4.3568657801,2.0802300469,-
0.9142684286\C,-5.1820001315,0.8462192858,-0.5158960003\C,-4.873717150
4,0.2847046314,0.9041864883\C,-3.3170297702,0.1376819782,0.9702002126\
C,-2.7302794643,-0.6063205205,2.1828208511\C,-1.3322235173,-1.22446976
15,1.8658745863\C,-0.5606351635,-0.4311186058,0.7672402294\C,-0.948967
6554,1.0662961307,0.8676262487\C,-2.4734481863,1.4252599174,0.66798442
98\C,0.1171106677,1.8330401406,0.083954172\C,1.4246437605,1.2254201607
,0.627264816\C,1.1402250187,-0.2722157213,0.9154442236\C,1.547153609,-
0.8497233522,2.1756205084\C,-2.7080889545,2.6067033607,1.6457354517\O,
-6.576477306,1.1285235677,-0.5720815731\C,-5.5157447533,-1.1220875519,
0.9802122109\C,-5.5199666369,1.1380410171,2.0157909861\H,-6.8015031946
,1.3720172985,-1.4833430796\C,-0.712744761,-1.0984903865,-0.6114370627
\C,1.8343422808,-2.2852585508,2.2415661908\C,1.738274358,-0.0299450841
,3.3992882826\C,3.3714970999,-2.5281587458,1.809317176\C,3.5757434235,
-2.6401662818,0.3362977339\C,4.3945392299,-1.9064317113,-0.4495026647\
C,5.2443821248,-0.7602521107,0.034749921\C,4.5428698979,-2.2636813728,
-1.9149831887\C,3.6001279305,-1.4922926864,-2.8887897528\C,3.774253519
7,0.0041365123,-2.9287835222\C,4.4653696062,0.7292403781,-3.8252687346
\C,4.5219515481,2.2346842154,-3.7243800543\C,5.2301024496,0.1507594965
,-4.9899910485\H,-2.3181340183,2.8112900109,-1.0194969345\H,-2.4998391
213,1.126521946,-1.4914690315\H,-4.6964212855,2.9353974649,-0.32071200
22\H,-4.5835829251,2.3305797627,-1.9598191792\H,-4.9385683599,0.037348
0073,-1.2294099342\H,-3.1306344281,-0.5194923585,0.1132360606\H,-3.389
4674314,-1.4148000194,2.5079120451\H,-2.6438639201,0.0742597434,3.0382
753103\H,-0.7723661439,-1.2712128039,2.8062450636\H,-1.4554103774,-2.2
633256322,1.5376880887\H,-0.7573725859,1.3062675728,1.9255804388\H,0.0
217247234,1.6699537418,-0.9944366607\H,0.0769414938,2.9133946656,0.250
1448467\H,1.7143653594,1.754999116,1.5398218959\H,2.2644889609,1.31601
42279,-0.0685351138\H,1.5283808565,-0.9166994625,0.1201935787\H,-3.641
1590815,3.1359026189,1.4605172971\H,-2.7166119954,2.2793023436,2.69105
3706\H,-1.9015021461,3.3418052478,1.5375834106\H,-5.0041624122,-1.8397
993562,0.325486056\H,-6.559932234,-1.0611189761,0.6621777344\H,-5.5038
068036,-1.5241759279,1.9989055929\H,-5.3509158361,2.2094243905,1.90269
61083\H,-5.1474966807,0.8374707081,3.0021897725\H,-6.6024056969,0.9882
290322,2.008257085\H,-1.7621981331,-1.2247128503,-0.8845569883\H,-0.26
95240481,-2.101189111,-0.5960399384\H,-0.224664548,-0.528498015,-1.407
6477992\H,1.7049393377,-2.6738458113,3.2540824273\H,1.2229293743,-2.86
22760152,1.542201491\H,0.9546805542,0.7306908595,3.4952157899\H,1.7899
214016,-0.6318801813,4.3085326984\H,2.6796782202,0.5352933152,3.306488
2985\H,3.6057220438,-3.4861229155,2.2888865045\H,4.0136283007,-1.77911
22218,2.2784091067\H,3.0443007146,-3.4725538214,-0.1279755485\H,6.3001
547868,-1.0630144745,0.053153921\H,4.9867025132,-0.4067720914,1.037156
3297\H,5.1807191305,0.0834697066,-0.6612259705\H,5.5793075238,-2.08349
25397,-2.2258385205\H,4.3503581642,-3.3345968087,-2.0479550166\H,2.562
8424724,-1.7286421699,-2.6123790386\H,3.7535438961,-1.9240984311,-3.88

30580082\H,3.2653994567,0.5556492067,-2.1353919864\H,3.9571766703,2.61
24302504,-2.865748129\H,4.1164684569,2.7036471521,-4.6309910779\H,5.55
86187356,2.5857068109,-3.6326380917\H,5.1700338321,-0.9379304907,-5.05
61137514\H,4.8630101204,0.5681602986,-5.9369726147\H,6.2917472108,0.42
38768096,-4.9242367838\\Version=x86-Linux-G98RevA.9\HF=-1248.8250445\R
MSD=6.991e-09\RMSF=2.319e-05\PG=C01 [X(C30H51O1)]\\@

Lanosterol precursor, tetracycle, C20 cation (protosteryl cation)

1\1\GINC-DFTC\FOpt\RB3LYP\6-31G(d)\C30H51O1(1+)\BILLW\09-Sep-2003\0\\#
 B3LYP/6-31G* OPT GEOM=CHECK\\protosteryl cat 17b 180 deg\\1,1\C,0.264
1190074,2.2245482808,-2.838800531\C,-0.1015463083,3.0463683086,-4.0819
40057\C,-1.2429183501,2.4049120568,-4.8724584295\C,-2.5299549997,2.208
8640265,-4.0293941537\C,-2.1175418543,1.426195725,-2.7236154805\C,-3.3
371458398,1.0314268875,-1.8606332726\C,-2.9785134878,0.3956124217,-0.4
946708261\C,-1.5591505667,-0.2140315827,-0.4574001818\C,-0.5560734259,
0.984560018,-0.6783597073\C,-0.9307883798,1.9997199947,-1.8740345617\C
,0.9223217796,0.5286545649,-0.6119352532\C,1.25970496,-0.1857240881,0.
7184935672\C,0.2502872325,-1.3155778588,0.9255154404\C,-1.2271355109,-
0.8324153636,0.9782485961\C,-1.2693325482,3.3434836635,-1.1829045795\O
,-1.5820810747,3.1807465566,-6.020040265\C,-3.4888289891,1.3165217696,
-4.8561606581\C,-3.2476817962,3.5611108609,-3.8163740632\H,-0.79451115
82,3.2424173108,-6.5821482491\C,-1.4400637406,-1.3195458501,-1.5598564
973\C,-1.9538005983,-2.1443231313,1.3730929783\C,-1.5085628949,0.16880
33803,2.1287363069\C,-1.0714683334,-2.7898770384,2.4671471828\C,0.4397
8074,-2.441611844,2.0128247395\C,1.2209511156,-2.2503360544,3.23179611
15\C,1.2882737857,-0.9961420056,3.9999019095\C,2.052987452,-3.35387874
7,3.7155474582\C,3.5174788249,-3.2639316259,3.0271493951\C,4.33363509,
-2.0578600851,3.363601615\C,5.1761212557,-1.9228707586,4.4121195991\C,
5.9954385883,-0.6699984395,4.5812678544\C,5.3946223979,-2.9742635408,5
.4681316321\H,1.0891928675,2.7226946322,-2.3156311366\H,0.6503105259,1
.2526482383,-3.1752756692\H,-0.3755125887,4.0730066089,-3.8160595109\H
,0.783573469,3.1264111002,-4.7292498227\H,-0.9098753768,1.399897126,-5
.192558571\H,-1.7167964976,0.4923246681,-3.1338726757\H,-3.9545165797,
0.3348912051,-2.4356948089\H,-3.9738101589,1.9030024628,-1.675215001\H
,-3.0503925899,1.1683336084,0.276664835\H,-3.7264239451,-0.3657068895,
-0.2353880605\H,-0.6840442118,1.6017231915,0.2147134602\H,1.1718263876
,-0.144501029,-1.4415530065\H,1.585630567,1.3925361598,-0.7124353467\H
,1.2392653717,0.5428150643,1.5375395913\H,2.2849150222,-0.5785647706,0
.6688741491\H,0.3257227273,-1.9164012697,0.0124358087\H,-1.4284336643,
4.160191578,-1.8865243005\H,-2.1706916634,3.2661940889,-0.5645192891\H
,-0.443626854,3.6437388486,-0.5249479923\H,-3.1103099779,0.2897143652,
-4.9458214869\H,-3.5899371253,1.7270928466,-5.8642882218\H,-4.48855525
94,1.2714618989,-4.412389303\H,-2.5905348737,4.3571633763,-3.461296781
6\H,-4.0749822103,3.4658409913,-3.1058336896\H,-3.6653350646,3.9006327
914,-4.7673907977\H,-2.352996665,-1.3850338764,-2.156226503\H,-1.27688
3778,-2.3233598205,-1.1582171079\H,-0.6168019084,-1.1330150046,-2.2542
223009\H,-2.964835155,-1.9746622073,1.7579438598\H,-2.0369311831,-2.83
71524154,0.5320193946\H,-0.9182019972,1.0859369376,2.0824103159\H,-2.5
612757596,0.4607034846,2.1288724064\H,-1.3252049653,-0.281751851,3.108
1117197\H,-1.184747454,-3.8738222309,2.5427915424\H,-1.2953511006,-2.3
696733781,3.4511757457\H,0.817615697,-3.3455814774,1.5230488077\H,1.00
15867614,-1.1790904828,5.0451056737\H,0.7178182597,-0.1683080749,3.589
9552157\H,2.3630313362,-0.7303203453,4.0628747459\H,2.205418586,-3.318
1788996,4.7967498891\H,1.6437132144,-4.3242952596,3.419443729\H,3.3775
170502,-3.3491675132,1.9455665806\H,3.9966939337,-4.1869167102,3.36415

09363\H,4.2718526428,-1.2290574394,2.6586351833\H,5.7938474366,0.06756
1258,3.799359305\H,7.0667263844,-0.9086676077,4.5583450922\H,5.8045662
833,-0.2047528284,5.5571350358\H,4.8022678736,-3.880943273,5.322895528
\H,6.4524935591,-3.265322483,5.4978710108\H,5.161294774,-2.5710228276,
6.4621753886\\Version=x86-Linux-G98RevA.9\HF=-1248.826763\RMSD=3.967e-
09\RMSF=1.788e-06\PG=C01 [X(C30H51O1)]\\@

Lanosterol precursor, tetracycle, C9 cation (lanosteryl cation)

1\1\GINC-APSARA\FOpt\RB3LYP\6-31G(d)\C30H51O1(1+)\BILLW\17-Apr-2004\0\
\# B3LYP/6-31G* OPT\\lanosterol cation restart again\\1,1\C,-3.4364260
917,0.2698925805,-1.2396143942\C,-4.900787284,0.6217848693,-0.95227853
03\C,-5.6230685715,-0.4882860091,-0.1853085178\C,-4.9489816342,-0.8346
6731,1.1687802043\C,-3.4310339912,-1.1387722665,0.8997851118\C,-2.6403
089129,-1.5592099712,2.1463627919\C,-1.2927828346,-2.1536350927,1.7509
18568\C,-0.4471470235,-1.1788922142,0.8785981055\C,-1.2350842017,-0.54
02237412,-0.213262557\C,-2.6357784361,-0.0586246395,0.0494958269\C,-0.
6335467767,-0.3069565971,-1.5454873632\C,0.8928435109,-0.4825021103,-1
.7761560257\C,1.6525478388,-0.6117733066,-0.4502453306\C,0.9319954905,
-1.708123777,0.416664425\C,1.9595383379,-1.9550605868,1.5488041012\C,3
.3523564084,-1.7937525239,0.8676791154\C,3.0992354087,-1.1911309812,-0
.5505294179\C,1.6627721122,0.7796834744,0.2299992064\C,-2.3475423377,1
.2973901287,0.8140740496\C,4.2167836314,-0.282616558,-1.1502590564\C,5
.2176733459,-1.1514468386,-1.9371413965\C,4.9724035239,0.6093933971,-0
.135333495\C,5.7023907295,1.8245528536,-0.7584193583\C,4.7896269246,2.
8281306162,-1.4209395983\C,4.365242507,4.0071128766,-0.9339319171\C,3.
4727951151,4.9075079753,-1.7559748983\C,4.7356182813,4.5636389556,0.41
95955741\O,-6.9693865288,-0.1251612273,0.0864187637\C,-5.6192017044,-2
.1304286004,1.6891650756\C,-5.2025066245,0.2721576139,2.2150534991\C,0
.7190258418,-3.0421113526,-0.3477548651\H,-7.456423907,-0.0876239528,-
0.7511807631\H,-2.9767641612,1.1001342161,-1.7876939796\H,-3.411119251
7,-0.6016311803,-1.9087527952\H,-4.9880203849,1.5622191876,-0.39728776
06\H,-5.4072003848,0.7914120433,-1.9109960354\H,-5.5964529267,-1.40401
32791,-0.803520451\H,-3.4472257309,-2.0218684208,0.2393592783\H,-3.203
5605162,-2.3169249566,2.697693165\H,-2.5034969222,-0.7191257472,2.8370
656925\H,-0.6953620928,-2.4092977626,2.6313261512\H,-1.4562020225,-3.0
826333477,1.1959510183\H,-0.267441763,-0.3125281498,1.5448713724\H,-1.
2024094294,-1.0193717362,-2.1797907074\H,-1.0008513828,0.6558625318,-1
.9221383969\H,1.2463232273,0.3798049349,-2.3518013211\H,1.0635419903,-
1.3613899432,-2.4049591978\H,1.8380246816,-1.2186766266,2.3522633384\H
,1.8353299479,-2.9403700681,2.0086121097\H,3.8726438751,-2.75334177,0.
7946913844\H,3.9895664173,-1.1445189715,1.472280537\H,3.0246516134,-2.
0311732186,-1.2505365072\H,0.6728148229,1.2492160347,0.2702168477\H,2.
0456328101,0.7482779487,1.2543111265\H,2.2981812563,1.4669445364,-0.33
50104504\H,-3.2624884217,1.8887205985,0.8236175265\H,-2.0250594047,1.1
331462277,1.8428477085\H,-1.5852561884,1.8935459597,0.3009832167\H,3.7
249239424,0.3791263727,-1.8780189046\H,5.694216198,-1.8918737858,-1.28
24583132\H,6.0140823834,-0.5471735382,-2.3828768216\H,4.7233996468,-1.
6940258296,-2.7515532803\H,4.2926351114,0.9921316816,0.6331343736\H,5.
7140278518,-0.0062264706,0.3921273119\H,6.4330803724,1.4713540298,-1.4
978987528\H,6.2902441486,2.3016017511,0.0325885334\H,4.4558806358,2.56
32559955,-2.4255480185\H,3.2223302017,4.4639796511,-2.7250612818\H,3.9
583839125,5.874902098,-1.9437093655\H,2.5358482336,5.1326553604,-1.226
9036867\H,5.3731112787,3.897410411,1.0052821108\H,5.2607823178,5.52231
64267,0.3116073114\H,3.8343568782,4.7734466683,1.0122562575\H,-5.35867
78363,-2.9999413639,1.0723956012\H,-6.7043079514,-2.0069736884,1.65532

22879\H,-5.3438938941,-2.3516034533,2.7247594761\H,-4.9048150183,1.270
1265677,1.8850254692\H,-4.6787157965,0.0560492509,3.1517801921\H,-6.27
10695439,0.3186436304,2.4360159949\H,-0.0314602095,-2.9716493964,-1.14
44006961\H,0.3855465171,-3.8234005401,0.3408168632\H,1.6418916001,-3.4
058222855,-0.8024884776\\Version=x86-Linux-G98RevA.9\HF=-1248.846787\R
MSD=4.112e-09\RMSF=2.637e-06\PG=C01 [X(C30H51O1)]\\@

Lanosterol precursor, tetracycle, C8 cation (lanosteryl cation)

1\1\GINC-ULTRASCAN\FOpt\RB3LYP\6-31G(d)\C30H51O1(1+)\BILLW\01-May-2004
\0\\# B3LYP/6-31G* OPT\\LanostCatC8-OptSP C30H51O(1+) B3LYP restart fr
om DFT5\\1,1\C,-3.5484513316,0.7499053875,-0.9850131023\C,-5.072553801
5,0.7027540492,-0.8330594155\C,-5.5071197315,-0.6564865498,-0.28153118
92\C,-4.9245801406,-0.9501669978,1.128028033\C,-3.3614257608,-0.755464
2603,1.0685879776\C,-2.7131795681,-0.9475017287,2.4514920942\C,-1.1833
652969,-0.6694146953,2.4695121337\C,-0.5621670896,-0.525123193,1.14233
67725\C,-1.2451252125,0.2819620598,0.1046042329\C,-2.8037688202,0.5304
321518,0.3572936135\C,-0.7877826244,-0.0435642537,-1.3505727087\C,0.73
27501383,-0.3233975682,-1.575323704\C,1.5526187974,-0.4213046035,-0.27
41607063\C,0.7202613502,-1.1549949226,0.8316002265\C,1.7546530009,-1.4
734395487,1.9408969283\C,3.0846063981,-1.70715901,1.1569929428\C,2.815
0422304,-1.3375807942,-0.3357205924\C,1.9428815417,1.0049604595,0.1896
541415\C,-2.9418846601,1.825324451,1.1974610138\C,4.031160749,-0.84389
67547,-1.1789991566\C,4.7244876249,-2.0537110266,-1.8355437731\C,5.069
6294356,0.0173179316,-0.4203816839\C,5.9630133768,0.8974867071,-1.3297
833944\C,5.210681603,1.9508207419,-2.107574842\C,5.0888476332,3.258743
6238,-1.8206151041\C,4.3188592634,4.1834617227,-2.7341184832\C,5.70375
95277,3.9366636277,-0.6200913987\O,-6.9217354836,-0.7641087728,-0.1915
055524\C,-5.2260732147,-2.433701897,1.4523777461\C,-5.6438639922,-0.08
90332454,2.1913038342\C,0.1124735026,-2.5616542013,0.3507657158\H,-7.2
906845731,-0.7026959424,-1.0859846875\H,-3.2406353747,1.7039175333,-1.
4303502448\H,-3.2744347321,-0.0322964341,-1.7006341857\H,-5.4521707246
,1.5057082513,-0.1925988514\H,-5.5288205953,0.8565413549,-1.8197955049
\H,-5.1181042169,-1.4355777112,-0.9631403029\H,-3.0050270904,-1.586247
5259,0.4343239574\H,-2.8615440892,-1.9775685137,2.7859026208\H,-3.1902
118076,-0.3081687204,3.1966137865\H,-0.9981058047,0.3183841635,2.93184
95926\H,-0.6326429423,-1.3801116834,3.0899331826\H,-0.7601598959,1.252
5483413,0.34458713\H,-1.3657177122,-0.9077489111,-1.6915762095\H,-1.10
33542878,0.7883106059,-1.9817787146\H,1.1566959328,0.4615107365,-2.208
6221814\H,0.8314644862,-1.2535133511,-2.1454741443\H,1.8499168155,-0.6
302128019,2.6319870818\H,1.4673959897,-2.3434064025,2.5383625425\H,3.4
231376797,-2.7429152452,1.2513348386\H,3.8731434906,-1.0848611096,1.58
50173639\H,2.4824595472,-2.2506302043,-0.8441252757\H,1.0896977633,1.6
871219948,0.257642604\H,2.446921509,1.013424454,1.1602017683\H,2.62733
31903,1.4490125949,-0.5382455232\H,-3.9849075899,2.1028760022,1.349652
3477\H,-2.4852905672,1.7536323539,2.1901227677\H,-2.4633401785,2.66229
24202,0.6749857767\H,3.6145369641,-0.2308104168,-1.9902420717\H,5.0952
01187,-2.7545905599,-1.0769396263\H,5.5814164793,-1.7447527908,-2.4418
214056\H,4.039140625,-2.6017096002,-2.4927523648\H,4.5791818515,0.6817
293189,0.2983321768\H,5.7182714005,-0.6468400219,0.1676853454\H,6.5072
1865,0.2575434771,-2.0366573946\H,6.7295071375,1.3581149079,-0.6980052
104\H,4.7288794981,1.6014628667,-3.0220232452\H,3.8868897813,3.6523224
555,-3.5883649361\H,4.9689893493,4.97788993,-3.1252041943\H,3.50542887
28,4.6901680404,-2.1958875384\H,6.2502290961,3.2530757033,0.0336092923
\H,6.3983593277,4.7259927788,-0.9376933055\H,4.9310046567,4.43346695,-
0.0173094099\H,-4.6908686817,-3.1112549415,0.7745385513\H,-6.296002746

4,-2.6212344521,1.3347290612\H,-4.9555387414,-2.696216744,2.4805633499
\H,-5.4969380207,0.9860577988,2.0630666565\H,-5.3235090808,-0.35250022
26,3.2041624181\H,-6.7178477451,-0.276355596,2.1303710443\H,-0.5202770
369,-2.5006684736,-0.5338121963\H,-0.4464188372,-3.0406103113,1.159014
646\H,0.9677060883,-3.2001621401,0.1199843287\\Version=x86-Linux-G98Re
vA.9\HF=-1248.8408266\RMSD=4.356e-09\RMSF=4.121e-06\PG=C01 [X(C30H51O1
)]\\@

Section IX. Compounds 80B, 81B, Hess's models of C-ring formation (Table 7)

Compound **80B**, reactant in Table 7. The C1-C10 bond was frozen at 3.8 A

1\1\GINC-DFTC\FOpt\RB3LYP\6-31G(d)\C13H23(1+)\BILLW\24-Mar-2004\0\\# B
3LYP/6-31G* OPT FREQ GEOM=CHECK\\HessC13Mod-boat C13H23(1+) B3LYP rest
art\\1,1\C,3.4312772645,-0.2097588786,-0.4675078243\C,2.5845715596,1.0
485030145,-0.1709108694\C,0.9859451622,0.7708781523,-0.1809540066\C,0.
9243377287,-0.4385675707,0.6271207206\C,1.4280298589,-1.6751935053,-0.
0242209215\C,2.5731257985,-1.3554944391,-1.0303347879\C,0.1609347325,1
.9990662142,0.2010572464\C,-2.7845562652,-0.2615015724,-0.1808105655\C
,-1.3171031505,1.8525464487,-0.2349473667\C,-2.0371463354,0.7006221291
,0.410500876\C,-2.9764417978,-0.4118460376,-1.6676665303\C,-3.53568599
04,-1.2663598092,0.6562520833\C,0.6802407482,-0.4635171658,2.083949953
6\H,4.2304082502,0.0394128352,-1.1722326137\H,3.9221300261,-0.55444705
74,0.4507574161\H,2.8512075202,1.5100138441,0.7839476048\H,2.701809639
3,1.8081999936,-0.9494480343\H,0.7843036056,0.5020434665,-1.225153647\
H,0.5770187023,-2.1211471574,-0.5669404396\H,1.7310225146,-2.409644888
9,0.7298227419\H,3.1663536588,-2.261412312,-1.1819311718\H,2.162486127
7,-1.0837923718,-2.0082133071\H,0.2293234915,2.2014504774,1.2761514296
\H,0.5926376203,2.8733441477,-0.2988209825\H,-1.3609825483,1.789440273
9,-1.3273577505\H,-1.8261935903,2.7892047172,0.0330938292\H,-2.0384568
022,0.7201349039,1.5019056324\H,-4.0283125479,-0.2358764362,-1.9294174
562\H,-2.3698439571,0.2719577816,-2.2652159452\H,-2.7537335966,-1.4390
782493,-1.9855049903\H,-4.6157321316,-1.1822203168,0.4768421625\H,-3.2
617922289,-2.2950822355,0.3854879571\H,-3.3625759735,-1.1285670785,1.7
277122233\H,0.210897447,0.432274433,2.4850347049\H,0.0955624999,-1.352
516041,2.3529542663\H,1.6572863908,-0.6099546104,2.5773583251\\Version
=x86-Linux-G98RevA.9\HF=-508.9590119\RMSD=6.919e-09\RMSF=4.550e-04\PG=
C01 [X(C13H23)]\\@

Compound **81B**, product in Table 7

1\1\GINC-DFTC\FOpt\RB3LYP\6-31G(d)\C13H23(1+)\BILLW\23-Mar-2004\0\\# B
3LYP/6-31G* OPT GUESS=READ GEOM=(CHECK,MODREDUNDANT)\\HessC13Mod-boat
C13H23(1+) unfreezing torsion angle and then reopt\\1,1\C,3.0461904447
,-0.5909922435,-0.1539777837\C,2.4842335869,0.8534641545,-0.1952219767
\C,0.9170203759,0.8861135863,-0.357971274\C,0.4073853076,-0.22254319,0
.5063397387\C,0.6678770649,-1.59508246,-0.0546410177\C,2.0706794098,-1
.6026186943,-0.7706800134\C,0.2616622731,2.2373502283,-0.0899584184\C,
-2.2290971525,-0.3338986391,-0.1366288024\C,-1.2584539612,2.05815669,-
0.3292638344\C,-1.7407302423,0.8334368743,0.3965082688\C,-2.3144588168
,-0.612109793,-1.6083469357\C,-2.8076564858,-1.3955201503,0.7547701385
\C,0.4720289792,-0.1182871872,2.0007764925\H,4.002149697,-0.6330796375
,-0.6850253275\H,3.2652377104,-0.8814760054,0.8810820638\H,2.769404162
,1.4094723114,0.7039823565\H,2.883837159,1.4058044146,-1.0520136002\H,
0.7132258958,0.6090618935,-1.4001821559\H,-0.0777614484,-1.8773992805,

-0.8041347658\H,0.6292269282,-2.3428777179,0.7432814045\H,2.4706268344
,-2.6192646437,-0.7137527851\H,1.9307414407,-1.380486525,-1.8340135431
\H,0.455943409,2.5738270169,0.9349294764\H,0.6691383605,3.0047337376,-
0.755613189\H,-1.4551845544,1.9937998246,-1.4030628473\H,-1.802785727,
2.9341751098,0.0423347477\H,-1.8450341981,0.9474127528,1.4736855795\H,
-3.3641374207,-0.5255949822,-1.9231476077\H,-1.727505565,0.0692936511,
-2.2259634026\H,-2.0202748251,-1.6443843822,-1.8348973363\H,-3.8695746
708,-1.5382182038,0.5133430376\H,-2.3255258152,-2.3663556141,0.5798607
614\H,-2.7361336966,-1.144146672,1.8160282678\H,-0.227666489,-0.809105
2588,2.4812791652\H,1.4764893694,-0.4582931666,2.2989749187\H,0.325478
7414,0.8882863213,2.3927972881\\Version=x86-Linux-G98RevA.9\HF=-508.96
46349\RMSD=7.529e-09\RMSF=5.124e-06\PG=C01 [X(C13H23)]\\@

Section X. Compounds 92-95, models for baccharenyl cation (Fig. 7)

Compound **92**, reactant, in models for baccharenyl cation (Fig. 7)
Frequency calculation: no imaginary frequency (see below for thermochemistry data)

1\1\GINC-DFTC\FOpt\RB3LYP\6-31G(d)\C21H37(1+)\BILLW\04-Aug-2004\0\\# B
3LYP/6-31G* OPT\\Abe04-D-ring exp sec cat, NOfreeze 16-17 hyperconjuga
tion B3LYP opt\\1,1\C,-0.8411170338,1.5151278168,-0.9750802771\C,0.389
5769002,0.776151595,-1.5427296771\C,1.0541980048,-0.0056150627,-0.4103
986237\C,0.1019922324,-1.0243083235,0.2859642671\C,-1.1206259076,-0.23
07376578,0.9308695825\C,-1.821660837,0.5726887679,-0.2400197456\C,-0.3
683255361,-2.1308908499,-0.6973042326\C,2.3184953937,-0.8156354438,-0.
7572177012\C,1.1031131994,-1.6910856486,1.2625375703\C,2.396579458,-1.
9453694142,0.4518678665\C,3.645464169,-0.2767784088,-0.6023324907\C,3.
9500020605,0.814176686,0.3565622249\C,4.748943762,-0.805241483,-1.4386
62246\C,-0.6180707826,0.6917537158,2.0697495538\C,-3.212845337,1.23894
8005,0.0903364459\C,-2.1509681729,-1.2132344286,1.5483309546\C,-3.4548
811678,-0.5266369657,1.9786590337\C,-4.1104157905,0.1859224577,0.79138
30119\C,-3.1470842105,2.5335271497,0.9331913655\C,-3.910177577,1.60981
18643,-1.2413455267\C,4.9969272435,0.2017868058,-2.6115638201\H,-1.354
7447562,2.0136494347,-1.8019972447\H,-0.4969550724,2.3141816618,-0.306
1132722\H,0.0874130227,0.0982381552,-2.3515348821\H,1.0869036852,1.500
7092253,-1.9852116493\H,1.3408461403,0.7235320712,0.3543122561\H,-2.10
06767645,-0.1921218669,-0.9761689811\H,-1.102658187,-1.7834605531,-1.4
249982354\H,0.4603346362,-2.5567824931,-1.2730037943\H,-0.8197582555,-
2.9622424818,-0.1497872054\H,2.2291800059,-1.3622967311,-1.698666666\H
,1.3340184222,-1.0397968235,2.1088316237\H,0.7491823768,-2.6437031178,
1.673367574\H,2.4357173564,-2.9118675695,-0.0533748709\H,3.2909343098,
-1.8790751232,1.0809691649\H,3.3271752304,0.7753464175,1.2540277606\H,
5.007476519,0.8570540612,0.6257777143\H,3.6912475951,1.7625379276,-0.1
447539263\H,0.1042220393,1.4480055329,1.7480327043\H,-0.1606324768,0.1
096776464,2.876235248\H,-1.4422999474,1.2372943004,2.5234933551\H,-2.4
170839011,-1.9827328945,0.8148401778\H,-1.6971786505,-1.7370519656,2.4
011096277\H,-3.276624681,0.1744208464,2.8026791236\H,-4.1427845002,-1.
2829994185,2.3751361957\H,-4.3974524889,-0.5741910517,0.0494707787\H,-
5.0437622273,0.6687900583,1.1078089469\H,-2.9128312437,2.3615897598,1.
986340139\H,-2.4138960266,3.2454587142,0.5383199836\H,-4.1231707154,3.
0312374525,0.9066537926\H,-3.9033990689,0.7725924789,-1.9502970167\H,-
4.95727411,1.8715562633,-1.0514725173\H,-3.4497957556,2.4746989537,-1.
7308147292\H,5.7826654605,-0.2165032193,-3.2457427778\H,4.0986463906,0
.3378954459,-3.2201189875\H,5.3317337618,1.1743039388,-2.2423955092\H,
5.6723946833,-0.8939656816,-0.8569081191\H,4.48816677,-1.7801464182,-1

```
.8608309963\\Version=x86-Linux-G03RevB.02\HF=-822.2578135\RMSD=5.003e-
09\RMSF=3.767e-06\Dipole=4.4692591,-1.7560381,-1.2497356\PG=C01 [X(C21
H37)]\\@
```

Compound **92A**, transition state between **92** and **93** in models for baccharenyl cation (Fig. 7)

```
Frequency calculation:  1 imaginary frequency:  -122.7 cm-1, IR intensity
117.2 (see below for thermochemistry data)

1|1|UNPC-UNK|FTS|RB3LYP|6-31G(d)|C21H37(1+)|PCUSER|17-Aug-2004|0||# B3
 LYP/6-31G* OPT=QST3 FREQ||Abe prod for TS-X= PES-178 part opt||1,1|C,-
 1.1389153036,1.9146928456,0.0936967265|C,0.2929730791,1.9458123984,-0.
 4668396542|C,1.0560940921,0.6952182729,0.0137068367|C,0.3200333458,-0.
 660283029,-0.4598846813|C,-1.1352380673,-0.6715507398,0.1998126643|C,-
 1.9019374156,0.626734136,-0.2773033572|C,0.2687366584,-0.7565378527,-2
 .0073319288|C,2.4418558794,0.5732978911,-0.44757558|C,1.2800244969,-1.
 7681887264,0.0517740536|C,2.7164244473,-1.5207524771,-0.3828476229|C,3
 .5019411304,-0.0536330269,0.249959734|C,3.5131913673,-0.1273112344,1.7
 727182003|C,4.8927215018,0.0194698068,-0.3907984038|C,-1.024616074,-0.
 7639049277,1.7419478466|C,-3.4487869985,0.6945497222,0.0305613844|C,-1
 .9234969416,-1.9196779229,-0.2908656734|C,-3.3994864422,-1.8973327656,
 0.1319822234|C,-4.1000808214,-0.6444074721,-0.402029807|C,-3.824796482
 9,1.025717418,1.4932667273|C,-4.0713850871,1.8050281921,-0.8507108097|
 C,5.6413167015,1.3207524,-0.0590759444|H,-1.6707395344,2.7871515806,-0
 .296100096|H,-1.0985524178,2.0455385451,1.1818731166|H,0.2791790687,1.
 9863057509,-1.5628187888|H,0.8080278882,2.8496342487,-0.1220514159|H,1
 .0449103699,0.682690156,1.1046592326|H,-1.8873608323,0.5757954686,-1.3
 732658525|H,-0.4363362801,-0.0601404321,-2.4609166482|H,1.2374130031,-
 0.5632267282,-2.4771389369|H,-0.0281373444,-1.7629991452,-2.312132504|
 H,2.6488227582,0.8495457234,-1.4833589071|H,1.2429760959,-1.8596420188
 ,1.1388059374|H,0.9836929017,-2.7450240393,-0.3511745019|H,2.881891002
 6,-1.5844021469,-1.458429069|H,3.4335306383,-2.1874524014,0.1068996928
 |H,2.5441183005,-0.3692118773,2.2104777328|H,4.2366264945,-0.877522377
 2,2.1055022078|H,3.8295517235,0.8398010198,2.1761349942|H,-0.481535880
 1,0.0664985494,2.2025898987|H,-0.5443187585,-1.6964052112,2.0547670405
 |H,-2.0097599979,-0.768147769,2.2019802387|H,-1.9017158306,-1.96985308
 7,-1.3851301989|H,-1.43860442,-2.8332981803,0.078102063|H,-3.496232690
 8,-1.9650111228,1.2216680448|H,-3.8937307074,-2.7908741475,-0.26744051
 41|H,-4.1014643483,-0.6927778054,-1.5011746137|H,-5.1540702309,-0.6419
 265016,-0.0971615864|H,-3.6736623525,0.1948204191,2.1865400333|H,-3.27
 08491785,1.8891532696,1.8775644046|H,-4.8890932269,1.2820605514,1.5414
 496626|H,-3.7747741478,1.7050879773,-1.9021115383|H,-5.1644082674,1.74
 04640821,-0.8105787336|H,-3.7998671763,2.8112821905,-0.5139728008|H,6.
 6036446,1.3320123134,-0.578630583|H,5.0777341885,2.2034933045,-0.38251
 13722|H,5.8452586894,1.4171168868,1.0113707528|H,5.4816457074,-0.84011
 13601,-0.0497666232|H,4.7967517976,-0.0765831361,-1.479497377||Version
 =IA32W-G03RevC.02|HF=-822.248356|RMSD=5.606e-009|RMSF=3.955e-006|Dipol
 e=3.3412017,-0.3066234,-0.1952958|PG=C01 [X(C21H37)]||@
```

Compound **93**, first minimum, in models for baccharenyl cation (Fig. 7)

```
Frequency calculation:  no imaginary frequency (see below for thermochemistry
data)

1\1\GINC-APSARA\FOpt\RB3LYP\6-31G(d)\C21H37(1+)\BILLW\12-Aug-2004\0\\#
 B3LYP/6-31G(D) OPT\\Abe04-mimumum A near PES163=starting coord\\1,1\C
,-0.8219225994,-0.9339394906,-1.9253464738\C,0.6882059757,-1.019311243
6,-1.6800168091\C,1.1753592862,0.0848963187,-0.734385153\C,0.312906849
```

1,0.0215818245,0.7696962067\C,-1.2271496842,0.1825801307,0.3550622261\
C,-1.6416108428,-0.9854251943,-0.6226069672\C,0.6196381598,-1.30893670
27,1.4918809078\C,2.5071284595,0.0194906783,-0.2445221468\C,0.87244227
13,1.2038330462,1.589384153\C,2.3840026841,1.1735267115,1.7895865048\C
,3.2218158327,1.1223303471,0.3923219903\C,3.0928779105,2.4891631668,-0
.3157123476\C,4.6920446136,0.7722155745,0.7238904392\C,-1.4910808354,1
.582889377,-0.2482737405\C,-3.1860000108,-1.2124570001,-0.8659755242\C
,-2.0811932876,0.0723681135,1.6617852362\C,-3.5882351065,0.004843571,1
.3784382372\C,-3.9185145134,-1.2021913379,0.4988887114\C,-3.8606728737
,-0.2161579188,-1.8373162097\C,-3.3750697955,-2.6242883407,-1.47242229
69\C,5.6149831805,0.6685268908,-0.4969159364\H,-1.1025951513,-1.766144
8837,-2.5768251846\H,-1.0448121843,-0.0209351636,-2.4897318861\H,0.959
7318225,-2.003968397,-1.2800991389\H,1.2220016491,-0.9125248114,-2.631
8930533\H,0.9204706586,1.0783143139,-1.1028026136\H,-1.3453640848,-1.9
080899719,-0.1073793623\H,0.3248764322,-2.1893927848,0.9203649808\H,1.
6793053603,-1.4228199607,1.7306087567\H,0.0839914744,-1.3450840952,2.4
429364531\H,2.955833014,-0.9731481699,-0.1532628912\H,0.5835105813,2.1
550153456,1.1391653314\H,0.4029927874,1.181238535,2.5814109103\H,2.697
6762959,0.3339897602,2.4149640361\H,2.7390395249,2.0888652118,2.276577
7942\H,2.0605006663,2.8365408336,-0.3908035006\H,3.6556905558,3.236988
9127,0.2513541181\H,3.5106473673,2.4492288101,-1.3253723596\H,-0.89460
61971,1.8097320643,-1.1361953698\H,-1.3199777091,2.3771568401,0.483874
1994\H,-2.529867978,1.6740602657,-0.5569087174\H,-1.8200480644,-0.8374
2373,2.2111914908\H,-1.8573598752,0.9206334283,2.3198602731\H,-3.94521
49247,0.9350841852,0.9225513389\H,-4.1145179381,-0.0814832601,2.336668
942\H,-3.6499707385,-2.1155489745,1.0502891491\H,-4.9997722115,-1.2591
994608,0.3233703466\H,-4.0085312303,0.7813486438,-1.4155954646\H,-3.30
23875154,-0.1057438084,-2.7728936775\H,-4.855120244,-0.5923991769,-2.1
019338518\H,-2.8498236912,-3.3911965339,-0.8901179002\H,-4.4388198638,
-2.8861316811,-1.4756120956\H,-3.0291875171,-2.6872532476,-2.509688010
1\H,6.6175049024,0.3634344347,-0.1831621312\H,5.2554264205,-0.07843256
75,-1.2167301106\H,5.713448348,1.6229648681,-1.0226690628\H,5.07506622
21,1.5350469493,1.4120827288\H,4.7105289959,-0.1759538559,1.2777594902
\\Version=x86-Linux-G03RevB.05\State=1-A\HF=-822.2495044\RMSD=2.497e-0
9\RMSF=2.806e-05\Dipole=2.3914332,0.0185811,0.2784052\PG=C01 [X(C21H37
)]\\@

Compound **93A**, transition state between **93** and **94** in models for baccharenyl cation (Fig. 7)

```
Frequency calculation:  1 imaginary frequency:  -220.2 cm-1, IR intensity
209.1 (see below for thermochemistry data)
```

1|1|UNPC-UNK|FTS|RB3LYP|6-31G(d)|C21H37(1+)|PCUSER|11-Aug-2004|0||# B3
LYP/6-31G* OPT=QST3 FREQ||Abe prod for TS1=flat sec cation partly opt
with QST3||1,1|C,-1.249895136,1.8898991159,0.4242843026|C,0.2109920471
,2.0556465084,-0.0102774509|C,1.0216836784,0.7896262147,0.2974497223|C
,0.3942201859,-0.5818067548,-0.2907992747|C,-1.1227056679,-0.671992330
8,0.2090159664|C,-1.8952173866,0.6418459923,-0.2073891538|C,0.52720263
15,-0.5507408571,-1.8353643552|C,2.4296182421,0.8642083701,-0.02717002
27|C,1.2812148398,-1.7196910342,0.2702453302|C,2.7596610417,-1.6158451
924,-0.1258356795|C,3.3970945889,-0.2126910184,0.1190690676|C,3.782936
3938,-0.070392764,1.6631127288|C,4.6678555162,-0.0208985303,-0.7595324
209|C,-1.151802814,-0.9104035178,1.7379103011|C,-3.4710083608,0.624761
0741,-0.0931860501|C,-1.8084558164,-1.8870346844,-0.4828040426|C,-3.31
55993643,-1.953709896,-0.204650179|C,-4.0102947513,-0.6887173916,-0.71
27196341|C,-4.0360474527,0.8047604897,1.3354879212|C,-4.0284513445,1.7
912835879,-0.9449479499|C,5.5139852889,1.232806516,-0.5146303789|H,-1.

7985934122,2.7898820398,0.1343420253|H,-1.2985765959,1.8439245614,1.51
9259417|H,0.2583749635,2.2668009154,-1.0862711663|H,0.6651607182,2.914
970498,0.4995079956|H,0.9960195206,0.6025831731,1.3892076777|H,-1.7361
10462,0.7345541281,-1.290261031|H,-0.1297646387,0.1795899492,-2.310421
6039|H,1.5494181012,-0.303611974,-2.1472562183|H,0.2942447812,-1.52941
12601,-2.262636347|H,2.811027126,1.8237982302,-0.392035285|H,1.2016521
462,-1.7550052816,1.360591088|H,0.903132859,-2.6821561968,-0.092394415
3|H,2.8864450152,-1.8455408514,-1.1892949421|H,3.3472339975,-2.3615159
481,0.4201641669|H,2.9728573246,-0.4344964227,2.2974530912|H,4.6687907
267,-0.6991252021,1.7996721536|H,4.0404746621,0.9494733424,1.959323846
1|H,-0.517079457,-0.2196107284,2.3066200383|H,-0.8350776961,-1.9269378
279,1.9890963023|H,-2.1552465854,-0.7851260924,2.1377999822|H,-1.68202
51372,-1.8181725404,-1.5691327726|H,-1.3251916589,-2.8190843165,-0.165
1011198|H,-3.5082791685,-2.1074425008,0.8638175223|H,-3.7296443834,-2.
8313716373,-0.7150616268|H,-3.8843744215,-0.6415284315,-1.8046545496|H
,-5.0909412804,-0.7485366197,-0.5333973764|H,-3.9360232662,-0.08490984
99,1.9629614269|H,-3.5721749268,1.6446007913,1.8639736298|H,-5.1085358
624,1.0205852311,1.2728253438|H,-3.6111694354,1.7886785987,-1.95936152
76|H,-5.115959342,1.6953275649,-1.0373098553|H,-3.8325648689,2.7720268
068,-0.4982181287|H,6.3484293707,1.250426864,-1.2219320863|H,4.9553485
71,2.1644572364,-0.6676723488|H,5.9419166178,1.2564927743,0.4922282354
|H,5.286574348,-0.9123441072,-0.5981427924|H,4.3583135908,-0.057728301
1,-1.8119012368||Version=IA32W-G03RevC.02|HF=-822.243931|RMSD=3.984e-0
09|RMSF=3.747e-006|Dipole=3.0913865,0.277362,0.2211225|PG=C01 [X(C21H3
7)]||@

Compound **94**, second minimum, in models for baccharenyl cation (Fig. 7)

```
Frequency calculation:  no imaginary frequency (see below for thermochemistry
data)
```

1|1|UNPC-UNK|FOpt|RB3LYP|6-31G(d)|C21H37(1+)|PCUSER|27-Jul-2004|0||# B
3LYP/6-31G* OPT||Abe04ProdBoat from PES207 coord||1,1|C,1.0585856673,-
1.9170269592,-0.1992063608|C,-0.4335141099,-1.8099535401,-0.7150438292
|C,-1.0186437592,-0.5672582999,-0.1840102749|C,-0.4487024913,0.7214875
562,-0.5650314881|C,1.0983497635,0.6058922711,0.212344619|C,1.83288396
26,-0.6148107626,-0.4241692602|C,-0.2871102772,0.888106635,-2.10184228
21|C,-2.0856039432,-0.5833391095,0.8227951883|C,-1.3113800897,1.890708
3421,-0.0312894585|C,-2.8072429353,1.6167376092,-0.2843594444|C,-3.331
7472989,0.324652189,0.4096322534|C,-4.0762668872,0.6800314694,1.708923
4748|C,-4.2521571401,-0.4479482608,-0.5726299105|C,0.9126427441,0.4842
708333,1.7370969929|C,3.3801586925,-0.7298263502,-0.0964454561|C,1.844
498097,1.9199834357,-0.1034257428|C,3.3312283704,1.833498239,0.2989688
725|C,4.0253177589,0.6509438364,-0.3804179166|C,3.7154559439,-1.207455
9075,1.3326853407|C,4.0089012147,-1.7465266263,-1.078109061|C,-4.96057
50696,-1.6989489544,-0.041494523|H,1.5081479384,-2.7496692049,-0.74474
79316|H,1.0387197864,-2.2039572627,0.8553910344|H,-0.3957253066,-1.779
9511663,-1.8097390973|H,-0.999458537,-2.6919909796,-0.4070974503|H,-1.
6799789136,-0.1038462068,1.7259735446|H,1.8394018649,-0.4310047269,-1.
5038886044|H,0.3074728809,0.1129309584,-2.5823401551|H,-1.2747712674,0
.8827366287,-2.5725724723|H,0.1682839761,1.8542872258,-2.3254159268|H,
-2.3969955589,-1.5947706813,1.0893107936|H,-1.1561846024,2.056962063,1
.0380901609|H,-1.013546328,2.8178505561,-0.5292110656|H,-2.9778421594,
1.5462897786,-1.3651717724|H,-3.3928226925,2.4766052496,0.0571548438|H
,-3.4751196016,1.344547771,2.3409972921|H,-5.0118090721,1.1999931102,1
.4746014956|H,-4.326179802,-0.207599768,2.2988031868|H,0.60379967,-0.5
098110755,2.0698189004|H,0.190944695,1.2086317555,2.1230770795|H,1.850

```
1149809,0.7079671061,2.244956539|H,1.8087798352,2.129416586,-1.1767161
051|H,1.3625636169,2.7609691664,0.4074491149|H,3.4395723607,1.77628933
6,1.3878770913|H,3.8170754533,2.7693398359,-0.0006484133|H,4.023825769
7,0.8214044206,-1.4668868877|H,5.0796846987,0.6140657402,-0.0798018334
|H,3.4687229907,-0.4828396489,2.1113474064|H,3.2149531777,-2.150146386
5,1.5796822036|H,4.7929274287,-1.3926884332,1.4026498616|H,3.739101540
9,-1.5294180215,-2.1187964361|H,5.101002259,-1.7013774204,-1.006281778
8|H,3.7182178031,-2.7787987319,-0.8559033069|H,-5.5641262702,-2.146984
6912,-0.8371111767|H,-4.2614721869,-2.4703392221,0.3027663838|H,-5.637
1493142,-1.4667728053,0.786642092|H,-5.0129030334,0.2650042996,-0.9176
108399|H,-3.6676973601,-0.7126310305,-1.4664781697||Version=IA32W-G03R
evC.02|HF=-822.2678366|RMSD=5.732e-009|RMSF=4.123e-006|Dipole=0.677996
4,0.1931991,-0.1441851|PG=C01 [X(C21H37)]||@
```

Compound **94A**, transition state between **94** and **95** in models for baccharenyl cation (Fig. 7)

```
Frequency calculation:  1 imaginary frequency:  -60.6 cm-1, IR intensity 9.6
(see below for thermochemistry data)

1\1\GINC-APSARA\FTS\RB3LYP\6-31G(d)\C21H37(1+)\BILLW\16-Aug-2004\0\\#
B3LYP/6-31G* OPT=QST3\\coordinates for TS from PESb114\\1,1\C,-1.81251
52341,1.0854560149,-0.9062232337\C,-0.5444946097,0.935770527,-1.756183
6737\C,0.6767295354,0.6709276692,-0.8541195424\C,0.5406001697,-0.52005
79172,0.1474720997\C,-0.7907250958,-0.3041987506,1.0120004894\C,-2.017
6789714,-0.1203399206,0.0330729855\C,0.5100612188,-1.8320742546,-0.686
3061864\C,1.9760200517,0.8718639334,-1.4403992434\C,1.8259515206,-0.53
23108183,1.018900218\C,3.1186730031,-0.6475665802,0.1952370848\C,3.257
9980015,0.4442919365,-0.8940191492\C,3.8271029779,1.78292407,-0.259137
0529\C,4.2280094157,-0.0263045664,-2.042050539\C,-0.6002060131,0.91787
67729,1.9443426205\C,-3.4647897629,-0.1865352924,0.6621257434\C,-1.047
6438359,-1.5537215586,1.8970572896\C,-2.402803334,-1.510082993,2.61466
84995\C,-3.5463170732,-1.4158214873,1.6018092479\C,-3.9243958011,1.084
9990099,1.413496563\C,-4.480507416,-0.4203852881,-0.4826300362\C,4.612
838861,0.9863037453,-3.1234432591\H,-2.6650954141,1.189559918,-1.58259
68555\H,-1.7581459985,2.021673397,-0.3368346535\H,-0.6525130189,0.0938
638424,-2.4506021895\H,-0.3742359865,1.8320362975,-2.3661512564\H,0.77
80939188,1.6092839965,-0.2209831196\H,-2.0021489892,-1.0076819391,-0.6
132810536\H,-0.4385824039,-1.9995370037,-1.1978896382\H,1.2883935756,-
1.8319388464,-1.4584817375\H,0.6937162085,-2.6981515308,-0.044871021\H
,2.0167800675,1.513660645,-2.3258800806\H,1.8738775295,0.3735439133,1.
6326591192\H,1.7864691077,-1.3709900428,1.7205754405\H,3.1751852946,-1
.6292206058,-0.2868475869\H,3.9871732474,-0.588915791,0.8601989352\H,3
.2858396196,2.0341745485,0.6562518247\H,4.8746691038,1.5837465021,-0.0
110686596\H,3.7915463623,2.6380090769,-0.9384185225\H,-0.235898778,1.8
168162907,1.4285234914\H,0.1052136177,0.6978970199,2.7509810033\H,-1.5
356251618,1.2102455049,2.4158895424\H,-1.034596782,-2.4565000229,1.274
6325467\H,-0.2402861424,-1.6656412115,2.6313021483\H,-2.4392304808,-0.
6756713064,3.3255807542\H,-2.5176017863,-2.4203741632,3.214757731\H,-3
.5394529733,-2.3286912789,0.9877561388\H,-4.5138933872,-1.40417432,2.1
18859922\H,-3.4583209149,1.2082954095,2.394641619\H,-3.7424753159,1.99
81560955,0.8362620939\H,-5.0046267385,1.0282560004,1.5884352518\H,-4.1
819880453,-1.2570178935,-1.1261654209\H,-5.4622679963,-0.6645309243,-0
.0620163732\H,-4.6168657351,0.4641588949,-1.1143543501\H,5.2942786147,
0.5059907145,-3.8323849575\H,3.755303004,1.3418184274,-3.7065958725\H,
5.1338526028,1.8569445216,-2.7146967917\H,5.1301262677,-0.3650555002,-
1.5174029611\H,3.7918882557,-0.9201241469,-2.5038100151\\Version=x86-L
inux-G03RevB.05\HF=-822.2441591\RMSD=5.117e-09\RMSF=3.786e-06\Dipole=2
```

.2574663,-0.328604,-2.3766164\PG=C01 [X(C21H37)]\\@

Compound **95**, product (boat form), in models for baccharenyl cation (Fig. 7)
Frequency calculation: no imaginary frequency (see below for thermochemistry data)

1|1|UNPC-UNK|FOpt|RB3LYP|6-31G(d)|C21H37(1+)|PCUSER|27-Jul-2004|0||# B
3LYP/6-31G* OPT||Abe04ProdBoat from PES207 coord||1,1|C,1.0585856673,-
1.9170269592,-0.1992063608|C,-0.4335141099,-1.8099535401,-0.7150438292
|C,-1.0186437592,-0.5672582999,-0.1840102749|C,-0.4487024913,0.7214875
562,-0.5650314881|C,1.0983497635,0.6058922711,0.212344619|C,1.83288396
26,-0.6148107626,-0.4241692602|C,-0.2871102772,0.888106635,-2.10184228
21|C,-2.0856039432,-0.5833391095,0.8227951883|C,-1.3113800897,1.890708
3421,-0.0312894585|C,-2.8072429353,1.6167376092,-0.2843594444|C,-3.331
7472989,0.324652189,0.4096322534|C,-4.0762668872,0.6800314694,1.708923
4748|C,-4.2521571401,-0.4479482608,-0.5726299105|C,0.9126427441,0.4842
708333,1.7370969929|C,3.3801586925,-0.7298263502,-0.0964454561|C,1.844
498097,1.9199834357,-0.1034257428|C,3.3312283704,1.833498239,0.2989688
725|C,4.0253177589,0.6509438364,-0.3804179166|C,3.7154559439,-1.207455
9075,1.3326853407|C,4.0089012147,-1.7465266263,-1.078109061|C,-4.96057
50696,-1.6989489544,-0.041494523|H,1.5081479384,-2.7496692049,-0.74474
79316|H,1.0387197864,-2.2039572627,0.8553910344|H,-0.3957253066,-1.779
9511663,-1.8097390973|H,-0.999458537,-2.6919909796,-0.4070974503|H,-1.
6799789136,-0.1038462068,1.7259735446|H,1.8394018649,-0.4310047269,-1.
5038886044|H,0.3074728809,0.1129309584,-2.5823401551|H,-1.2747712674,0
.8827366287,-2.5725724723|H,0.1682839761,1.8542872258,-2.3254159268|H,
-2.3969955589,-1.5947706813,1.0893107936|H,-1.1561846024,2.056962063,1
.0380901609|H,-1.013546328,2.8178505561,-0.5292110656|H,-2.9778421594,
1.5462897786,-1.3651717724|H,-3.3928226925,2.4766052496,0.0571548438|H
,-3.4751196016,1.344547771,2.3409972921|H,-5.0118090721,1.1999931102,1
.4746014956|H,-4.326179802,-0.207599768,2.2988031868|H,0.60379967,-0.5
098110755,2.0698189004|H,0.190944695,1.2086317555,2.1230770795|H,1.850
1149809,0.7079671061,2.244956539|H,1.8087798352,2.129416586,-1.1767161
051|H,1.3625636169,2.7609691664,0.4074491149|H,3.4395723607,1.77628933
6,1.3878770913|H,3.8170754533,2.7693398359,-0.0006484133|H,4.023825769
7,0.8214044206,-1.4668868877|H,5.0796846987,0.6140657402,-0.0798018334
|H,3.4687229907,-0.4828396489,2.1113474064|H,3.2149531777,-2.150146386
5,1.5796822036|H,4.7929274287,-1.3926884332,1.4026498616|H,3.739101540
9,-1.5294180215,-2.1187964361|H,5.101002259,-1.7013774204,-1.006281778
8|H,3.7182178031,-2.7787987319,-0.8559033069|H,-5.5641262702,-2.146984
6912,-0.8371111767|H,-4.2614721869,-2.4703392221,0.3027663838|H,-5.637
1493142,-1.4667728053,0.786642092|H,-5.0129030334,0.2650042996,-0.9176
108399|H,-3.6676973601,-0.7126310305,-1.4664781697||Version=IA32W-G03R
evC.02|HF=-822.2678366|RMSD=5.732e-009|RMSF=4.123e-006|Dipole=0.677996
4,0.1931991,-0.1441851|PG=C01 [X(C21H37)]||@

Thermochemistry data for compounds 92-95:

Compound 92

Zero-point correction=	0.543855 (Hartree/Particle)
Thermal correction to Energy=	0.566492
Thermal correction to Enthalpy=	0.567437
Thermal correction to Gibbs Free Energy=	0.494719
Sum of electronic and zero-point Energies=	-821.713959
Sum of electronic and thermal Energies=	-821.691321
Sum of electronic and thermal Enthalpies=	-821.690377

Sum of electronic and thermal Free Energies= -821.763094

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	355.479	92.311	153.047

Compound 92A

Zero-point correction= 0.543534 (Hartree/Particle)
Thermal correction to Energy= 0.565363
Thermal correction to Enthalpy= 0.566307
Thermal correction to Gibbs Free Energy= 0.496576
Sum of electronic and zero-point Energies= -821.704822
Sum of electronic and thermal Energies= -821.682993
Sum of electronic and thermal Enthalpies= -821.682049
Sum of electronic and thermal Free Energies= -821.751780

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	354.770	91.227	146.761

Compound 93

Zero-point correction= 0.543639 (Hartree/Particle)
Thermal correction to Energy= 0.566113
Thermal correction to Enthalpy= 0.567057
Thermal correction to Gibbs Free Energy= 0.495752
Sum of electronic and zero-point Energies= -821.705865
Sum of electronic and thermal Energies= -821.683391
Sum of electronic and thermal Enthalpies= -821.682447
Sum of electronic and thermal Free Energies= -821.753753

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	355.241	93.288	150.075

Compound 93A

Zero-point correction= 0.542572 (Hartree/Particle)
Thermal correction to Energy= 0.564302
Thermal correction to Enthalpy= 0.565246
Thermal correction to Gibbs Free Energy= 0.495783
Sum of electronic and zero-point Energies= -821.701359
Sum of electronic and thermal Energies= -821.679629
Sum of electronic and thermal Enthalpies= -821.678685
Sum of electronic and thermal Free Energies= -821.748148

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	354.105	90.999	146.198

Compound 94

Zero-point correction= 0.542733 (Hartree/Particle)
Thermal correction to Energy= 0.565101
Thermal correction to Enthalpy= 0.566045
Thermal correction to Gibbs Free Energy= 0.495093
Sum of electronic and zero-point Energies= -821.701551
Sum of electronic and thermal Energies= -821.679183
Sum of electronic and thermal Enthalpies= -821.678239

```
Sum of electronic and thermal Free Energies=         -821.749191

                    E (Thermal)             CV                S
                     KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total                  354.606             92.798            149.331
```

Compound 94A

```
Zero-point correction=                           0.542101 (Hartree/Particle)
Thermal correction to Energy=                    0.563650
Thermal correction to Enthalpy=                  0.564594
Thermal correction to Gibbs Free Energy=         0.495617
Sum of electronic and zero-point Energies=          -821.702059
Sum of electronic and thermal Energies=             -821.680510
Sum of electronic and thermal Enthalpies=           -821.679565
Sum of electronic and thermal Free Energies=        -821.748542

                    E (Thermal)             CV                S
                     KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total                  353.695             90.837            145.174
```

Compound 95

```
Zero-point correction=                           0.544198 (Hartree/Particle)
Thermal correction to Energy=                    0.566391
Thermal correction to Enthalpy=                  0.567336
Thermal correction to Gibbs Free Energy=         0.496369
Sum of electronic and zero-point Energies=          -821.723639
Sum of electronic and thermal Energies=             -821.701445
Sum of electronic and thermal Enthalpies=           -821.700501
Sum of electronic and thermal Free Energies=        -821.771467

                    E (Thermal)             CV                S
                     KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
Total                  355.416             92.624            149.361
```

Section XI. Compounds 96-98, tandem methyl migration / ring expansion described by Vrcek *et al., J. Org. Chem.* 2003, 68, 1859 (Fig. 8)

Compound **96**, reactant (C6-C7 distance 1.58 Å) in the tandem methyl migration / ring expansion described in Fig. 8

```
1\1\GINC-DFT\FOpt\RB3LYP\6-31G(d)\C8H15(1+)\BILLW\02-May-2004\0\\# B3L
YP/6-31G* OPT\\Vrcek 1A JOC 68, 1859 SM for path restart B3LYP\\1,1\C,
-1.0068480552,-1.0990050017,-0.5549840009\C,-2.3683527957,-0.382237270
5,-0.404865066\C,-2.0796474304,0.7004272561,0.6534786673\C,-0.61871433
77,1.0992625921,0.3496877334\C,0.0264245133,-0.1010584794,-0.208278748
3\C,1.4695826891,-0.306999341,-0.3512164223\C,1.9169489206,-0.91953010
71,1.0389576337\C,2.2853641119,0.9610955154,-0.665689067\H,-0.89961695
77,-1.8783549594,0.2285881066\H,-0.8054616005,-1.6223915282,-1.4977641
854\H,-3.1668359823,-1.0677880034,-0.1152283831\H,-2.6513882198,0.0722
909899,-1.360880188\H,-2.760109984,1.5522079446,0.5986279188\H,-2.1439
491091,0.2870657541,1.6663599024\H,-0.5976144661,1.7981044292,-0.51732
24377\H,-0.0454372752,1.6092520055,1.1315486354\H,1.6520051926,-1.0816
278077,-1.1048118062\H,1.4056657724,-1.8585469176,1.2645324607\H,1.761
6807051,-0.2105415177,1.8565098693\H,2.9882739375,-1.121450773,0.95010
63686\H,3.3396600827,0.6869554521,-0.7592654278\H,1.9709611108,1.41308
```

```
26449,-1.6114517478\H,2.2036210988,1.7100113034,0.1279065352\\Version=
x86-Linux-G03RevB.02\HF=-313.6124026\RMSD=7.104e-09\RMSF=1.716e-05\Dip
ole=0.0841268,-0.1621346,-0.0902872\PG=C01 [X(C8H15)]\\@
```

Compound **97**, transition state in the tandem methyl migration / ring expansion described in Fig. 8. The coordinates below were keyed in from *J. Org. Chem.* 2003, **68**, 1859, page S8, TS-II. This printout lacked a minus sign for the z coordinate of atom 12 (shown below in magenta). After this correction, the coordinates gave the expected energy and frequency data for the transition state: `one imaginary frequency at -189.4 cm-1, IR intensity 6.1`

```
C -0.7499080935 1.4038505936 -1.4267335532
C -1.0165986888 1.1013944182 0.0623297898
C 0.7259488116 1.0491856828 -1.6613222804
H -0.9860954491 2.4485495423 -1.6524606288
H -1.3912991913 0.7781185442 -2.0575635452
C 0.0848024122 -0.0292001687 0.4234100013
C 0.8984374944 -0.2593427992 -0.872150878
C -0.5581477813 -1.1506771312 1.0438067988
H -0.8329745056 1.9670248631 0.7037484219
H -2.0432737212 0.7705520397 0.244232963
H 0.972988845 0.92980596 -2.7191837763
H 1.3811191813 1.8324251628 -1.2611925498
C 0.9914725594 0.5425579372 1.6053497315
C -0.4558830221 -2.5660398004 0.719885296
H 0.4667044757 -1.08312864 -1.4527952437
H 1.9415067087 -0.515128748 -0.6621647479
H -1.1993705456 -0.9127002754 1.8978650372
H 1.4812256725 1.4288789178 1.1910086735
H 1.7591149477 -0.1734726521 1.9089072727
H 0.3981821638 0.841540379 2.472931789
H -0.2348520837 -3.134447059 1.6390105152
H -1.4748930308 -2.9146364101 0.459420533
H 0.2411743818 -2.813754018 -0.079214147
```

Compound **98**, product (C1-C2 distance 2.553 Å) in the tandem methyl migration / ring expansion described in Fig. 8

```
1\1\GINC-ULTRASCAN\FOpt\RB3LYP\6-31G(d)\C8H15(1+)\BILLW\04-May-2004\0\
\# B3LYP/6-31G* OPT\\Vrcek JOC 68, 1859 product opt for PES calc\\1,1\
C,-1.248620174,0.0327594341,-0.882607238\C,-1.8755362587,0.2997111038,
0.4910967659\C,-1.276202351,-0.6239381487,1.5557783528\C,0.2679902706,
-0.5190023826,1.6004704922\C,0.9368846293,-0.5138168148,0.2875062879\C
,0.2977763496,0.1230959497,-0.8699213268\C,2.2697214314,-1.1182166586,
0.1544664887\C,0.8010688197,1.6276011033,-0.8035242238\H,-1.5275342381
,-0.9712539571,-1.2256197151\H,-1.6269887684,0.7340679698,-1.633090401
4\H,-2.9567743791,0.1382079726,0.432626918\H,-1.7391705427,1.349088993
1,0.7821972952\H,-1.6656045719,-0.3918173601,2.5509404643\H,-1.5431171
553,-1.6672187171,1.3478468338\H,0.5462614953,0.4722024772,2.019587158
3\H,0.7363040118,-1.2456486899,2.2741560843\H,0.7309874014,-0.28702294
46,-1.7906134108\H,2.0713822543,-2.1962488558,-0.013613183\H,2.8593077
091,-1.0663993879,1.0758033997\H,2.8309050538,-0.7609860914,-0.7126174
101\H,1.8907735596,1.7049988,-0.7639431255\H,0.4556933028,2.0997666111
,-1.727336138\H,0.3689947438,2.1546453244,0.0494158092\\Version=x86-Li
```

nux-G03RevB.05\State=1-A\HF=-313.6157532\RMSD=9.613e-09\RMSF=1.929e-05
\Dipole=1.0578567,-0.3799444,0.0376888\PG=C01 [X(C8H15)]\\@