Supporting information for:

Premutilin synthase: Ring rearrangement by a class II diterpene cyclase

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Methods

All reagents were purchased from Fisher Scientific unless noted otherwise. Draft genome sequencing and identification of the pleuromutilin biosynthetic gene cluster will be described in more detail elsewhere. Sequences of the *Cp*GGPS and *Cp*PS characterized here have been deposited in GenBank (MG764076 and MG764077, respectively). These were characterized in a previously described modular metabolic engineering system in *E. coli*.[1] Briefly, this enables co-expression with a GGPP synthase, using pGG or pGG-DEST constructs created via recombination into the DESTination cassette by the Gateway cloning system (Thermo-Fischer Scientific). Initial characterization was carried using the native gene for *Cp*PS co-expressed with *Cp*GGPS. These were cloned into pACYC-Duet (Novagen). *Cp*GGPS was cloned into the first multiple cloning site using the corresponding BamHI and NotI restriction sites, while *Cp*PS was cloned into the second multiple cloning site MSC2 using NdeI and PacI restriction sites. The resulting vector was used for isolation of **2** for NMR. For all other studies, a synthetic gene for *Cp*PS (s*Cp*PS, sequence given below) was cloned into pDONOR222 via a BP clonase reaction, which was required for construction of the site-directed mutations due to difficulties experienced with the native gene. Mutants were generated by whole-plasmid PCR amplification with overlapping mutagenic primers of this construct, each of which was verified by complete gene sequencing. All *Cp*PS constructs were then transferred by directional recombination to the pDEST17 expression vector. *Cp*PS:D311A also was transferred to pGG-DEST,[1] to enable co-expression with *Cp*PS:D649L. The resulting constructs were transformed into the C41 OverExpress strain of *E. coli* (Lucigen), and heterologously expressed. Briefly, the recombinant mutant clones were grown in liquid TB media (12 g casein, 24 g yeast extract, 8 mL 50% glycerol in 1 L H_2O, and pH adjusted to 7.0) with the appropriate antibiotics at 37 °C to OD_{600} ~ 0.6, then transferred to 16 °C for an hour and induced with IPTG (1 mM final concentration). At the time of induction, cultures were supplemented with phosphate buffer (pH 7.0) to 100 mM (final concentration). After 24 hr growth at 16 °C, dephosphorylated enzymatic products were extracted by addition of equal volume of hexanes and gentle swirling, the organic solvent was separated out and then dried under N_2, with the residue resuspended in fresh hexanes and analyzed by GC-MS. Note that dephosphorylation of the class II DTC product **3** to generate **3'** is mediated by the endogenous phosphatases in *E. coli*.

Compound analysis by GC-MS was carried out as previously described.[7] Briefly, using a 3900 GC with Saturn 2100T ion trap MS (Varian), equipped with a HP-5MS column (Agilent, 0.25 µm, 0.25 ID, 30 m) with a He flow rate of 1.2 mL/min, and the following oven temperature program: 50 °C for 3 min, 15 °C/min to 300 °C, hold 3 min. Samples (1 µL) were injected via splitless injection at 250 °C.

The final *Cp*PS product **2** and the dephosphorylated class II DTC product of the *Cp*PS:D649L mutant (**3'**) were purified much as previously described.[2-5] To obtain sufficient quantities of the compound, 3.5 L of the relevant bacterial cultures were grown and extracted as described above, but with growth at 16 °C after induction extended to 3 days to increase yield. After extraction, the phases were separated in a separatory funnel, and the pooled hexanes dried by rotary evaporation. The resulting extract was redissolved in 10 mL of fresh hexanes and fractionated over silica (4 g) using a Reveleris automated flash chromatography system (Grace, Deerfield, IL) with a 15 mL/min flow rate, 5 mL injections, and UV detection at 200 nm, with the following stepwise gradient: 0%, 10%, 20% acetone (in hexane) for 2 minute each, and a final wash with 100% acetone for 3 minutes. The resulting fractions were analyzed by GC-MS (as described above). Those containing the targeted product were dried under N_2 and dissolved in 5 mL of methanol. These compounds were then further purified via HPLC using an Agilent 1200 system equipped with an Agilent Poroshell 120 EC-C18 (4.6 x 100 mm, 4 µm) column at a flow rate of 1 mL/min. The column was pre-equilibrated, sample injected and washed with 50% acetonitrile/dH_2O (0 - 2 minutes), eluted with 50 - 100% acetonitrile (2 - 7 minutes), and followed by a 100% acetonitrile wash (7 - 23 minutes), with peak based fraction collection. Again, those containing the targeted product were identified by GC-MS analysis. The final yield of pure **2** was estimated to be ~4 mg, and of pure **3'** estimated to be ~2 mg, by GC-FID (flame ionization detection) analysis using an Agilent 6890N GC equipped with HP-1 column and the same temperature program described above, with comparison to a standard curve generated for the diterpene alcohol sclareol.

The HPLC fractions containing pure compound were pooled, dried under N_2 and dissolved in 0.5 mL $CDCl_3$ (Aldrich). NMR spectra were acquired on a Bruker AVIII-800 spectrometer equipped with a 5-mm HCN cryogenic probe, using TopSpin 3.2 software. Analysis was carried

out at 25 °C. Chemical shifts were calculated by reference to those known for $CDCl_3$ signals offset from TMS (^{13}C 77.23 ppm, ^{1}H 7.24 ppm). All spectra were acquired using standard programs from the TopSpin 3.2 software, with collection of 1D ^{1}H-NMR, and 2D double-quantum filtered correlation spectroscopy (DQF-COSY), heteronuclear single-quantum coherence (HSQC), heteronuclear multiple-bond correlation (HMBC), HMQC-COSY and NOESY (800 MHz), as well as 1D ^{13}C-NMR (201 MHz), spectra. Observed HMBC correlations were used to propose a partial structure, while COSY correlations between protonated carbons were used to complete the structure, which was further verified by HSQC correlations. Observed correlations from NOESY spectrum were used to assign relative configuration.

Optical rotation was measured in $CHCl_3$ solvent on an AP-300 automatic polarimeter (ATAGO) at 25 °C. These measurements were carried out according to the instruction manual, in particular using mode 1 with tube E (50 mm). The instrument was blanked with pure solvent, and 5 readings for each sample were recorded and the average value reported here. The specific optical rotation value for **2** measured here, $[\alpha]_D^{25}$ = +21 (*c* = 0.33, $CHCl_3$), closely resembles that previously reported (ref. 13). The specific optical rotation value of **3'** was determined to be $[\alpha]_D^{25}$ = +35 (*c* = 0.17, $CHCl_3$).

Infrared spectroscopy was measured on Bruker Tensor 37 FTIR (Billerica, MA). A transmittance spectrum was generated using "single-beam" measurements in the transmission mode (Figure S13). The scan range is from 4000 to 600 cm^{-1} with a resolution of 4 cm^{-1}. **3'** dissolved in $CHCl_3$ was deposited on a polished NaCl salt plate, which was scanned 16 times in total, with blank $CHCl_3$ solvent being measured as the reference sample [ν_{max} cm^{-1}: 3314 (br, s), 2959 (m), 2875 (m), 1450 (s), 1380 (m), 999 (br, s)].

High-resolution mass spectra were obtained using the Agilent 6540 QTOF (Agilent Santa Clara, CA) run in positive ion mode. 1 µL of **3'** dissolved in $CHCl_3$ was injected into the ESI ion source via loop injection. 20/80 H_2O/AcN solvent was delivered by the Agilent 1200 binary pump. Ion spray capillary voltage was 4000 V and the gas temperature is 325 °C. Data were measured for *m/z* from 100-1000. The calculated molecular weight for **3'** ($C_{20}H_{34}O$) was 290.2610, and the major observed ions were $[MH^+ - H_2O]^+$ at m/z 273.2590 and also $[M_2H^+ - H_2O]^+$ at 563.5207

(Figure S14). The observed loss of water is presumably due to the high gas temperature and/or high voltage applied here.

Quantum Chemical Calculations

Calculations were performed with GAUSSIAN03[8] and GAUSSIAN09.[9] Geometries were optimized using the B3LYP method with the basis set of 6-31+G(d,p).[10] All stationary points were characterized as minima or transition state structures using frequency calculations at the same level. All reported energies include zero-point energy corrections (unscaled) from the frequency calculations at the same level. Intrinsic reaction coordinate (IRC) calculations were used for further characterization of transition state structures.[11] mPW1PW91[12] single point energies are also shown, since it is known that B3LYP underestimates the relative energies of cyclic structures versus acyclic isomers.[12] The validity of this computational approach for examining terpene-forming carbocation rearrangements is well-established.[13] Structural images were created with *Ball&Stick*.[14]

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>s*Cp*PS (synthetic gene)

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Table S1: ^{1}H and ^{13}C NMR assignments for premutilin (**2**) in $CDCl_3$.

Position	Premutilin (**2**)	
	δ_H	δ_C
1 a	1.40 (1H, m)	33.8
b	1.21 (1H, m)	
2 a	1.60 (1H, m)	19.0
b	1.52 (1H, m)	
3 a	1.83 (1H, m)	27.0
b	1.75 (1H, m)	
4	1.83 (1H, m)	47.8
5		41.3
6	1.73 (1H, m)	35.0
7 a	1.49 (1H, m)	27.9
b	1.33 (1H, m)	
8 a	1.42 (1H, m)	28.6
b	1.30 (1H, m)	
9		45.9
10	1.79 (1H, m)	31.0
11a	1.51 (1H, m)	43.2
b	1.15 (1H, d, *J* = 15.0 Hz)	
12		40.5
13a	2.04 (1H, dd, *J* = 15.0, 8.0 Hz)	46.2
b	1.48 (1H, m)	
14	4.26 (1H, d, *J* = 7.8 Hz)	69.0
15	0.90 (3H, s)	17.2
16	1.00 (3H, d, *J* = 9.0 Hz)	18.5
17	0.85 (3H,d, *J* = 6.9 Hz)	21.2
18	1.00 (3H, s)	33.0
19	5.87 (1H, dd, *J* = 17.8, 11.0 Hz)	147.1
20*E*	5.25 (1H, d, *J* = 17.8 Hz)	112.8
Z	5.15 (1H, d, *J* = 11.0 Hz)	

Figure S1: Carbon numbering and correlations from COSY, HMBC and NOESY spectra for **2**.

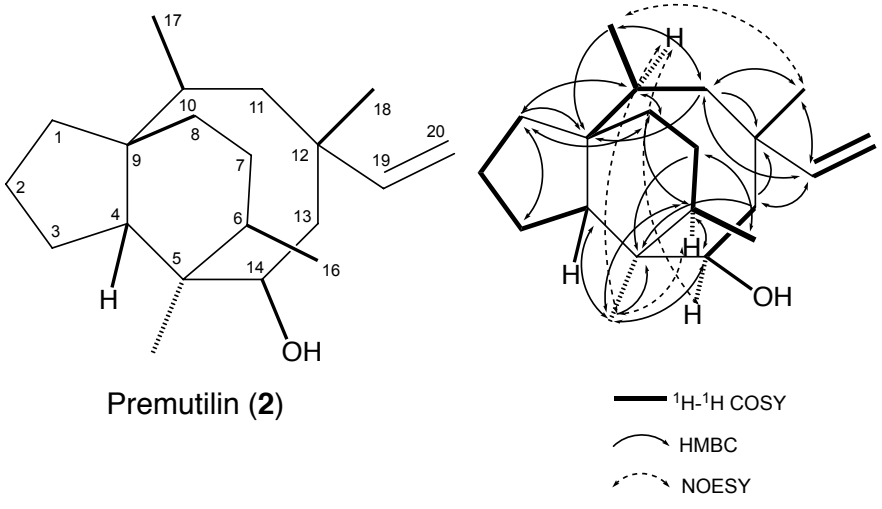


Table S2: ^{1}H and ^{13}C NMR assignments for mutildienol (**3'**) in $CDCl_3$.

	Mutildienol (**3'**)	
Position	δ_H	δ_C
1 a	1.82 (1H, m)	41.2
b	1.26 (1H, m)	
2 a	1.74 (1H, m)	22.0
b	1.59 (1H, m)	
3 a	1.80 (1H, m)	27.4
b	1.72 (1H, m)	
4	2.19 (1H, t, *J* = 9.4 Hz)	48.1
5		37.49
6	1.72 (1H, m)	37.54
7 a	1.54 (1H, m)	28.2
b	1.27 (1H, m)	
8 a	1.88 (1H, d, *J* = 13.8 Hz)	31.8
b	1.49 (1H, m)	
9		49.3
10		151.4
11a	4.93 (1H, s)	109.8
b	4.83 (1H, s)	
12		141.5
13a	2.01 (1H, td, *J* = 13.6, 3.8 Hz)	34.5
b	1.93 (1H, td, *J* = 13.6, 4.5 Hz)	
14a	1.69 (1H, m)	29.3
b	1.18 (1H, td, *J* = 13.2, 4.9 Hz)	
15	0.85 (3H, s)	25.7
16	0.83 (3H, d, *J* = 7.0 Hz)	16.1
17	1.83 (3H, s)	20.0
18	1.71 (3H, s)	16.8
19	5.43 (1H, t, *J* = 7.0 Hz)	122.7
20	4.19 (2H, d, *J* = 7.0 Hz)	59.7

Figure S2: Carbon numbering (based on **2**) and correlations from COSY, HMBC and NOESY spectra for **3'**.

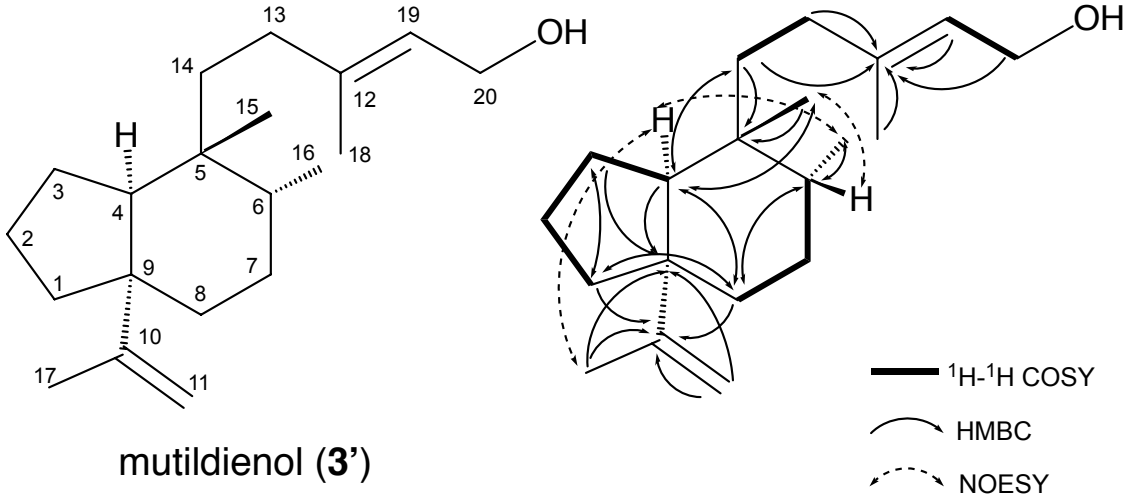


Figure S3: 1D ^{1}H spectrum of mutildienol (**3'**) in $CDCl_3$.

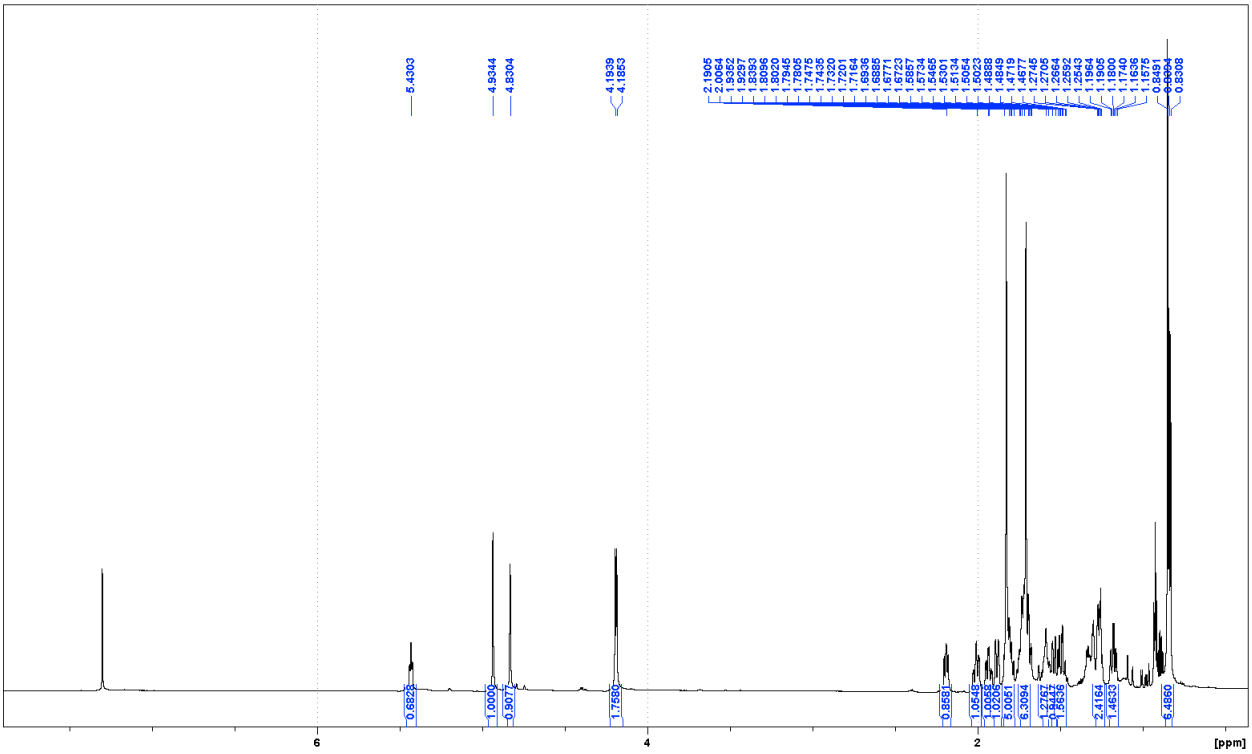


Figure S4: 1D ^{13}C spectrum of mutildienol (**3'**) in $CDCl_3$.

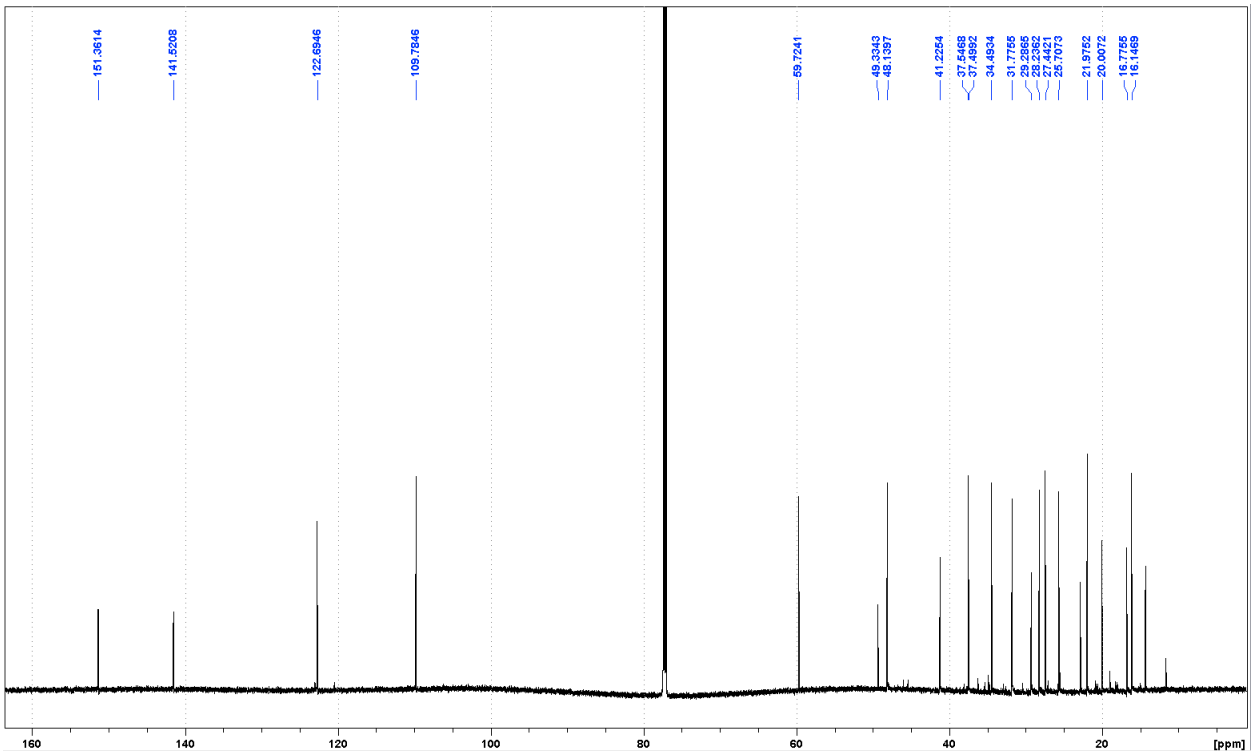


Figure S5: DEPT135 spectrum of mutildienol (**3'**).

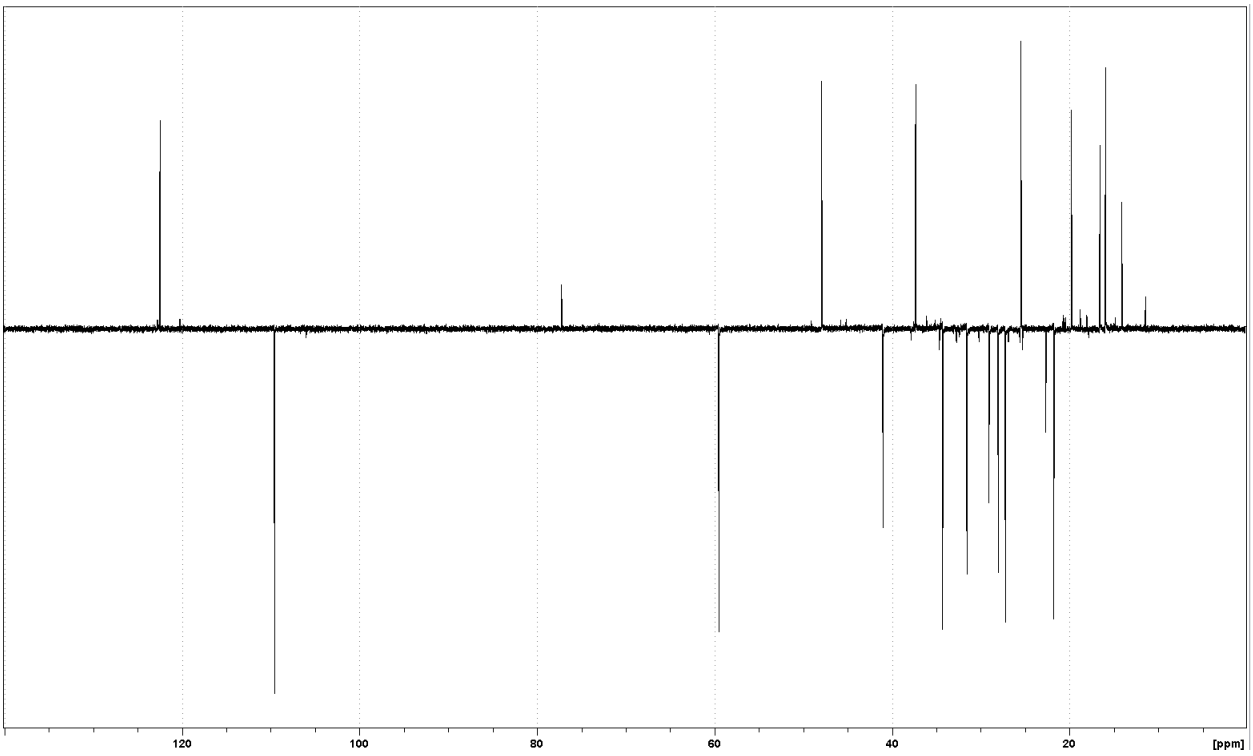


Figure S6: DEPT90 spectrum of mutildienol (**3'**).

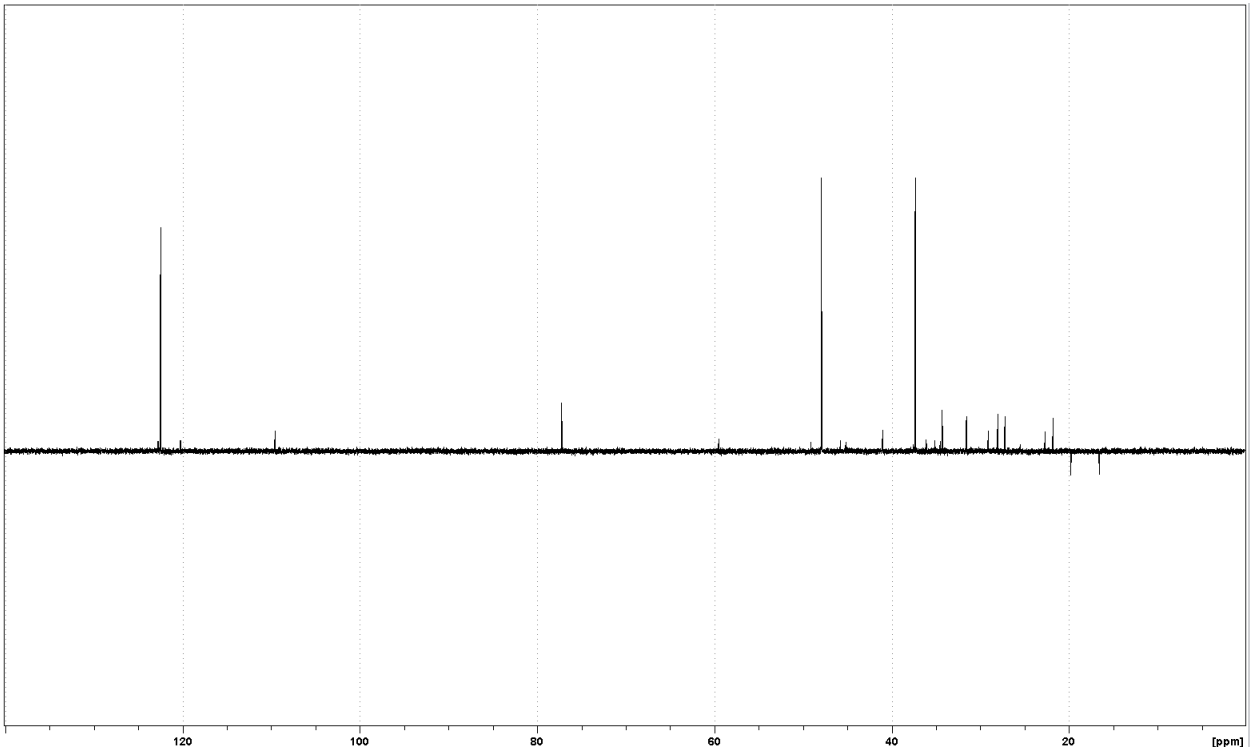


Figure S7: DEPT45 spectrum of mutildienol (**3'**).

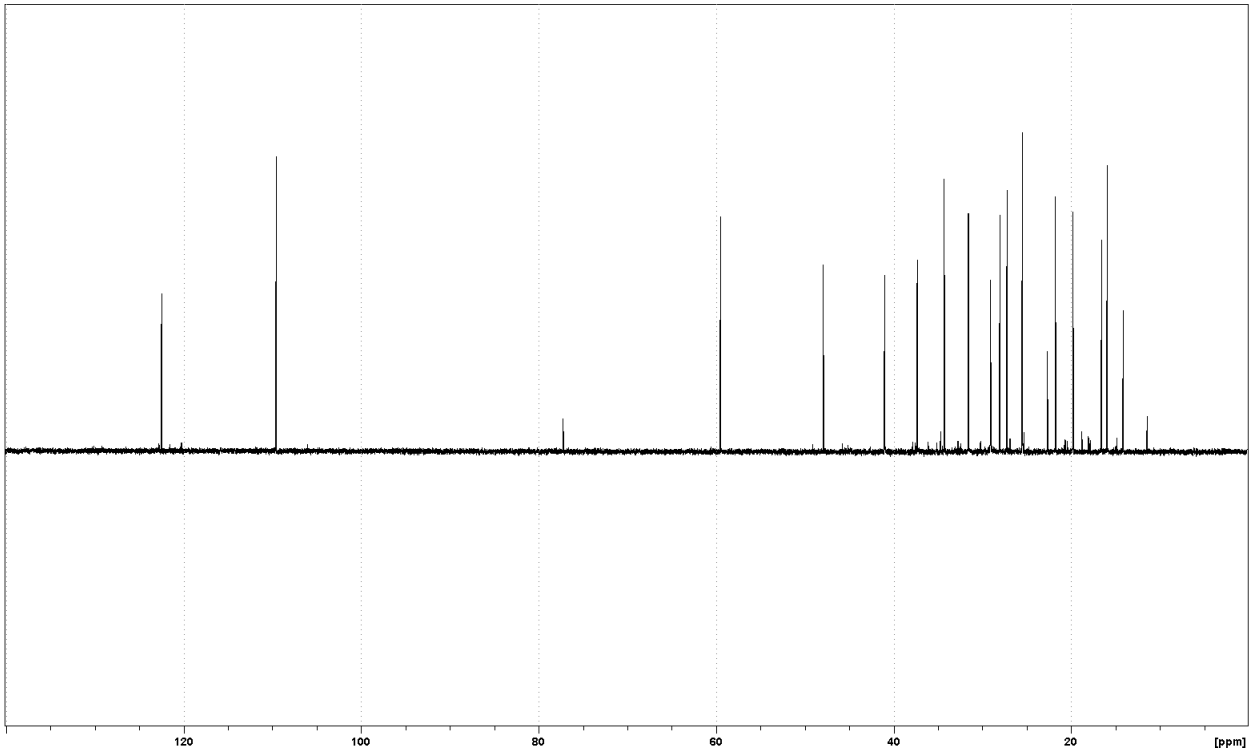


Figure S8: DFQ-COSY spectrum of mutildienol (**3'**).

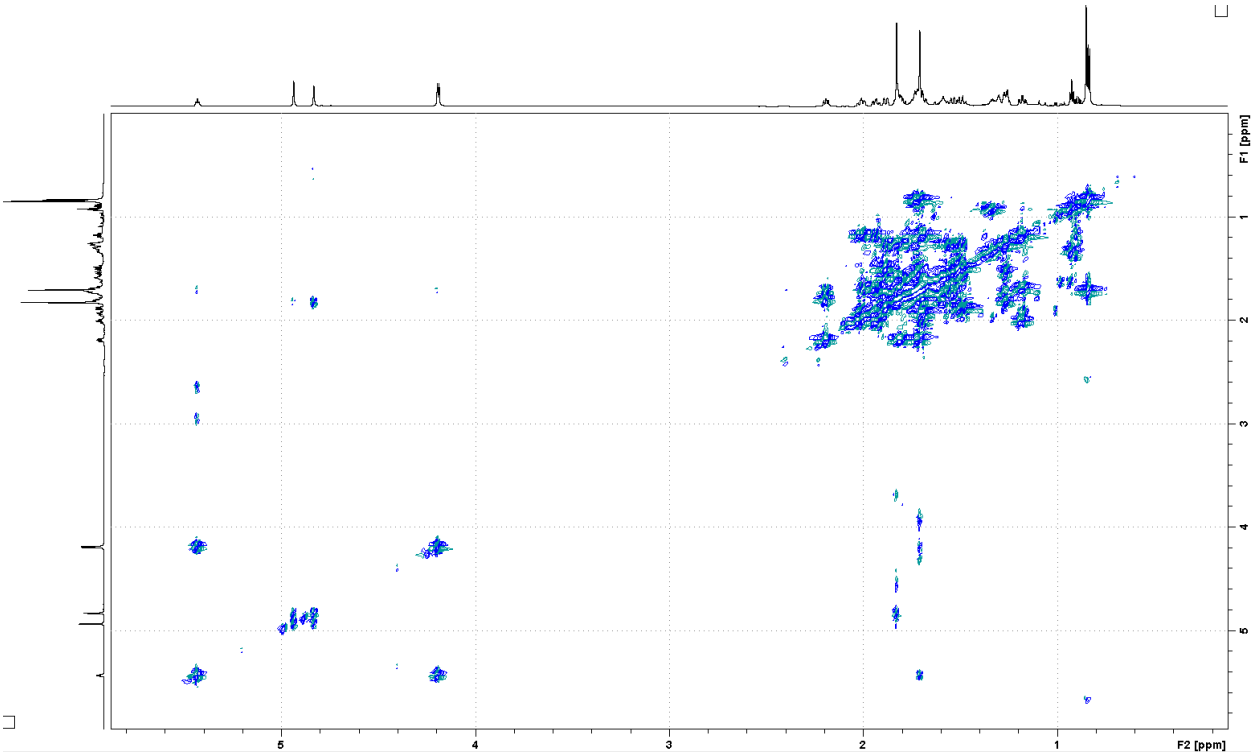


Figure S9: HSQC spectrum of mutildienol (**3'**).

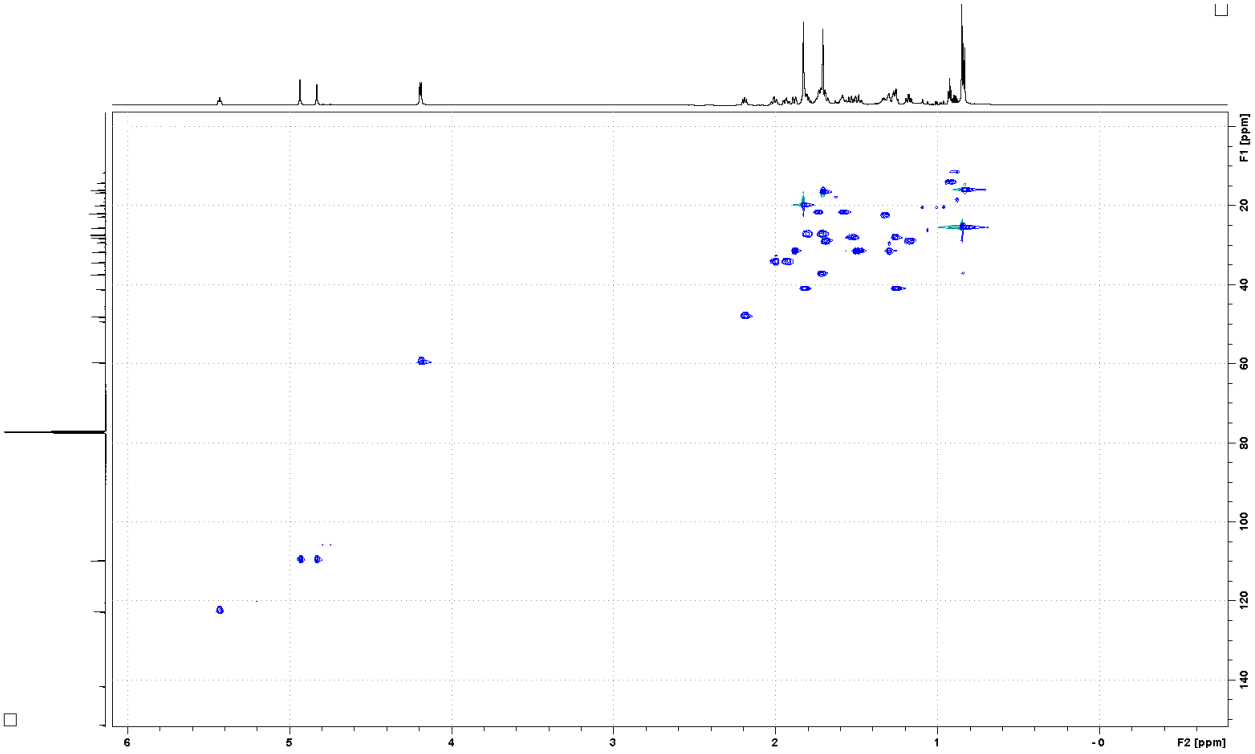


Figure S10: HMBC spectrum of mutildienol (**3'**).

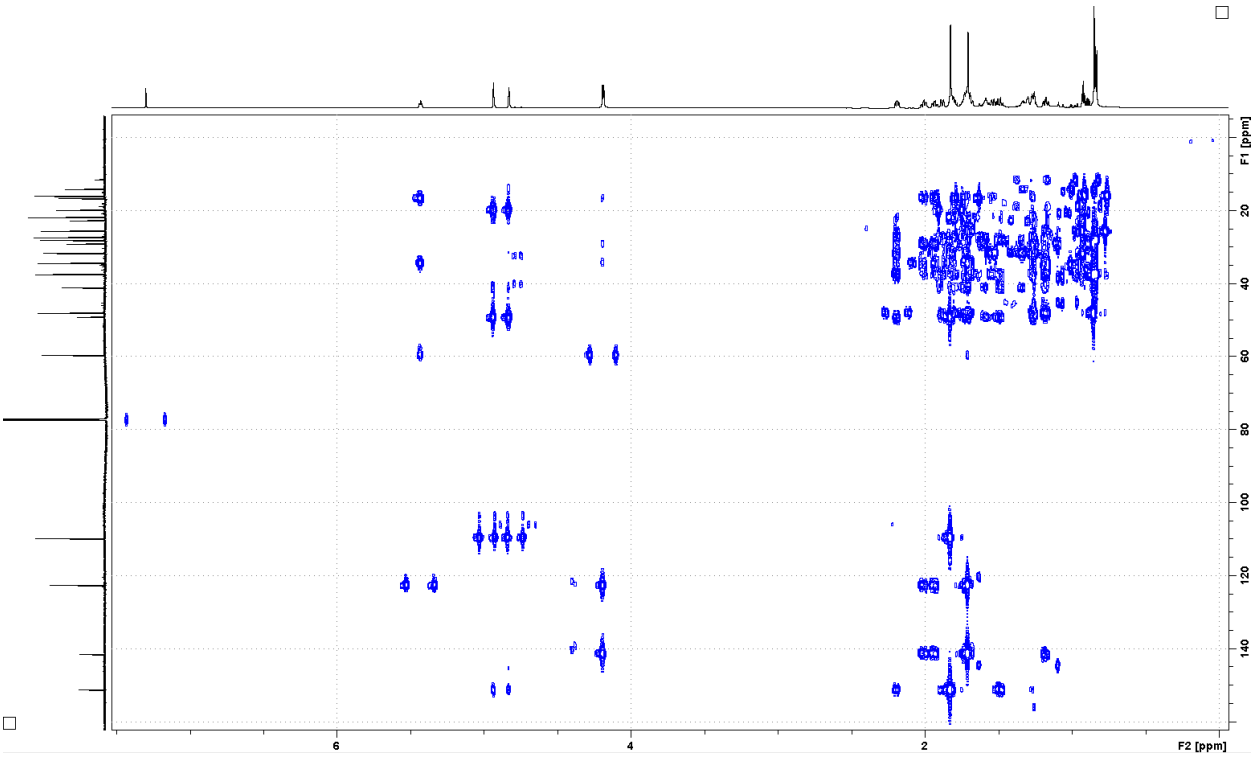


Figure S11: HMQC-COSY spectrum of mutildienol (**3'**).

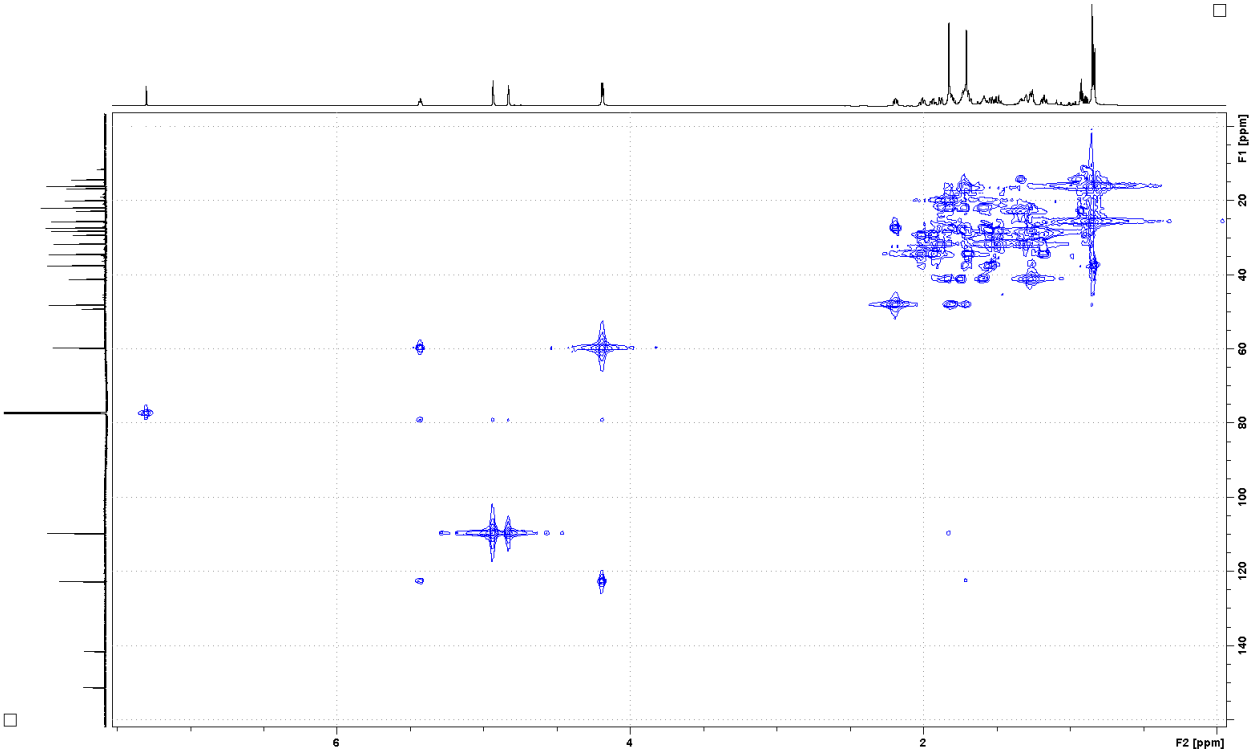


Figure S12: NOESY spectrum of mutildienol (**3'**).

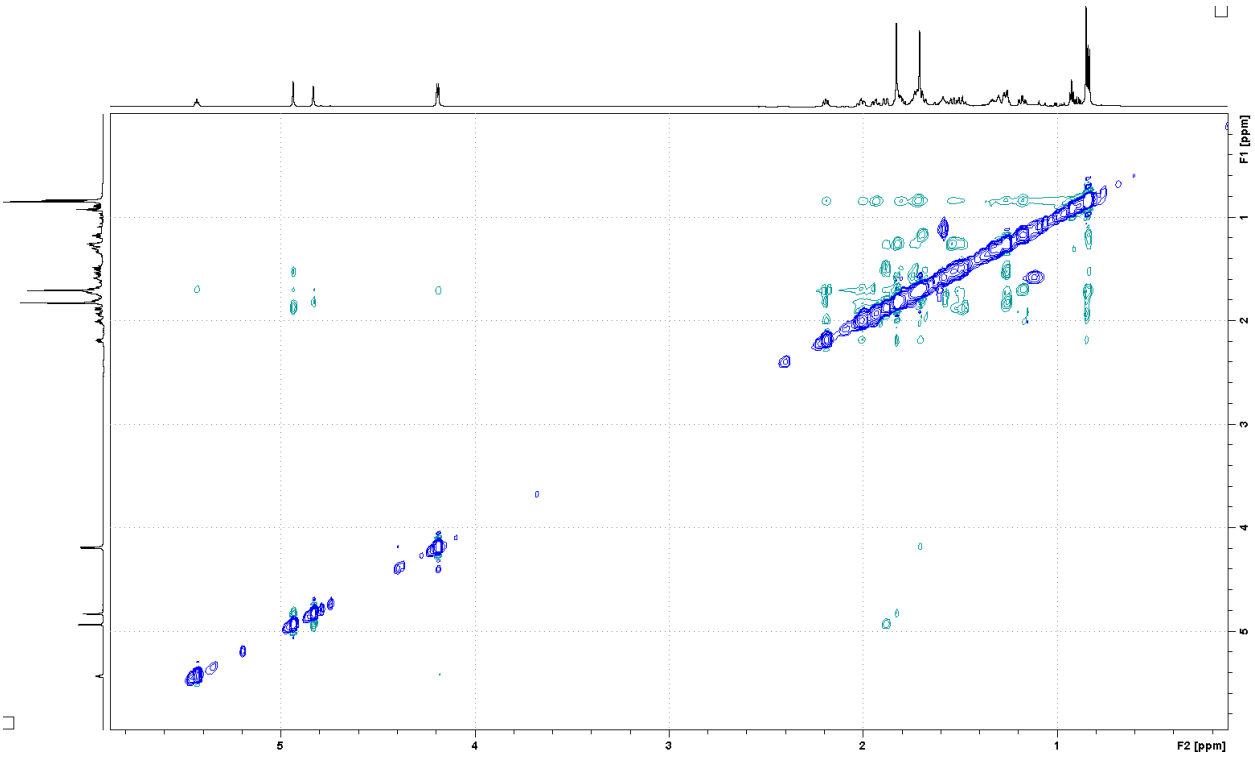


Figure S13: FTIR spectrum of mutildienol (**3'**).

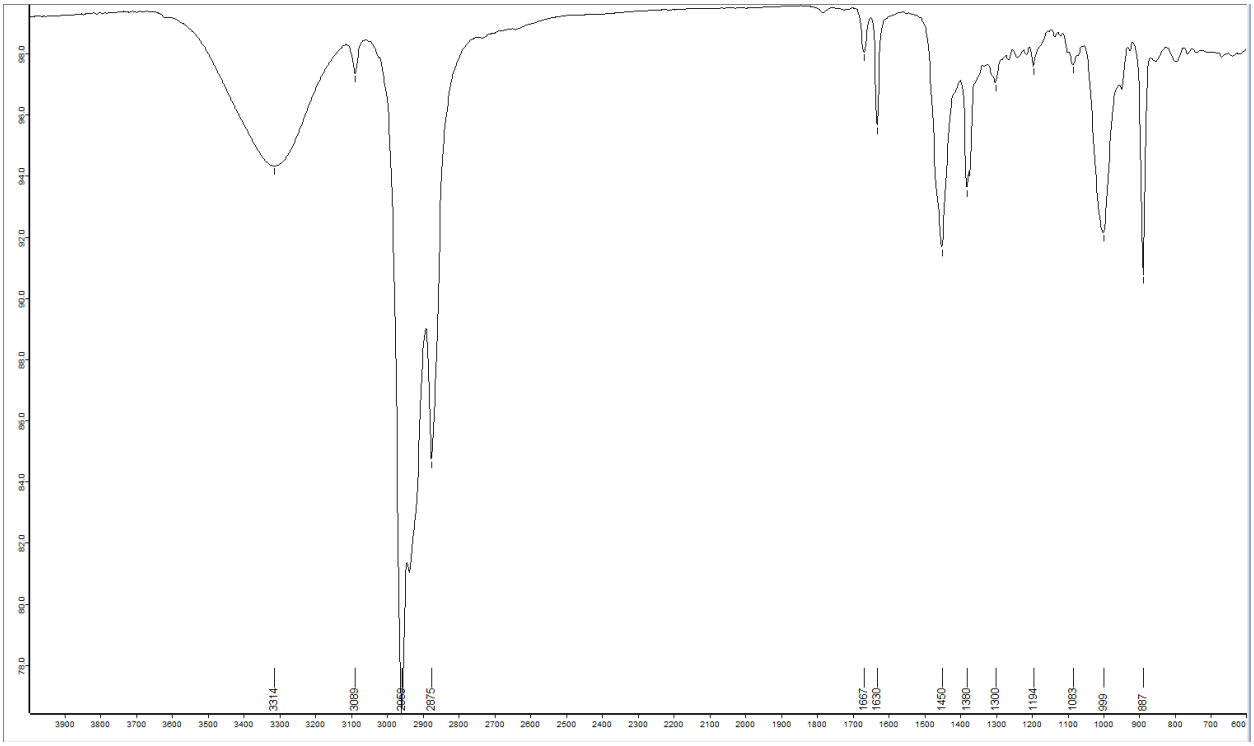
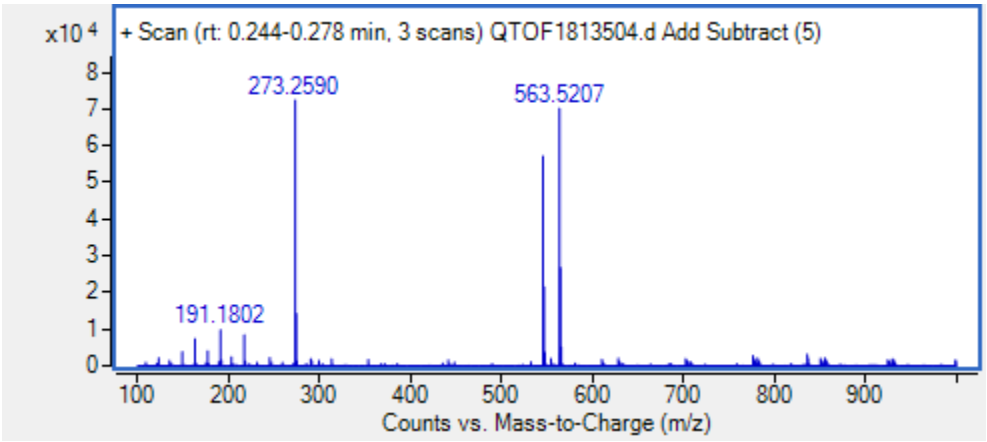
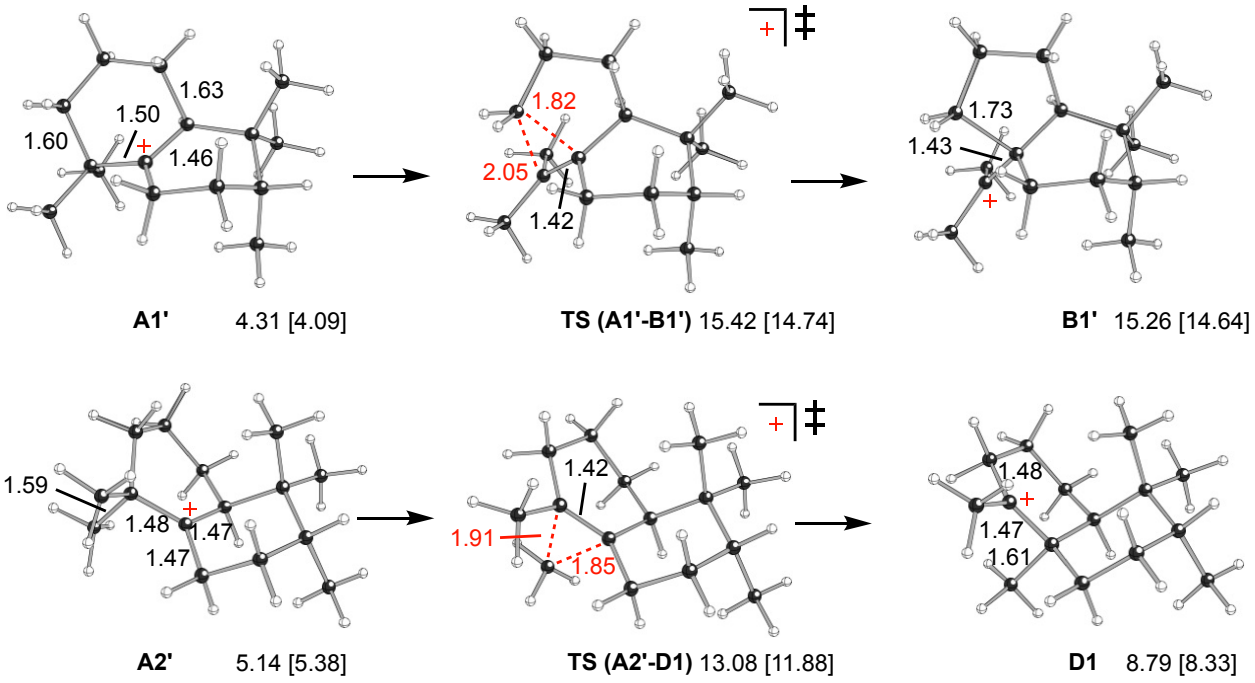


Figure S14: HRM spectrum of mutildienol (**3'**).





Scheme S1: Effect of alternative carbocation **A** configuration on ring contraction versus additional methyl shift. From QCC analysis with selected distances (Å) and relative energies (kcal/mol; B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) in normal text and mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p) in brackets) shown.

Coordinates and Energies

Scheme 2
A1
B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p)
HF = -587.6525413 hartrees (-368757.846191163 kcal/mol)
Zero-point correction = 0.390238 (Hartree/Particle)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p)
HF = -587.526650672 hartrees

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.827701	-0.028987	1.884962
2	1	-1.488358	0.710425	2.618575
3	1	-2.881159	-0.229890	2.093454
4	6	-1.633854	0.508725	0.446696

5	6	-2.162139	-0.482428	-0.634146
6	6	-1.413736	-1.820975	-0.550021
7	6	-0.094990	0.717647	0.259961
8	6	0.718866	-0.489479	0.066265
9	1	0.279789	1.295029	1.110660
10	6	0.116527	-1.683899	-0.560091
11	1	0.613112	-2.584687	-0.180878
12	1	0.489871	-1.625989	-1.604188
13	6	0.350465	1.600071	-1.011468
14	1	0.068899	1.092396	-1.939635
15	1	-0.234424	2.519781	-0.948539
16	6	2.197461	-0.410351	0.265649
17	6	2.654770	0.583592	-0.906739
18	1	3.720648	0.768311	-0.737646
19	6	1.849998	1.877742	-0.964306
20	1	2.140772	2.436822	-1.862147
21	6	2.951544	-1.740161	0.081662
22	1	4.024619	-1.556050	0.177451
23	1	2.678836	-2.469721	0.851426
24	1	2.788806	-2.191858	-0.900439
25	6	2.581312	0.194776	1.645983
26	1	2.199977	-0.424918	2.463110
27	1	3.671644	0.209193	1.721777
28	1	2.224891	1.214620	1.792063
29	6	-2.354318	1.868636	0.349027
30	1	-1.841624	2.632645	0.945260
31	1	-2.431123	2.231165	-0.680926
32	1	-3.370770	1.789550	0.742178
33	6	-3.679449	-0.725755	-0.596120
34	1	-3.998071	-1.184345	0.345382
35	1	-4.245948	0.198106	-0.733635
36	1	-3.967525	-1.406124	-1.403666
37	1	-1.940053	-0.031142	-1.613066
38	1	-1.268603	-0.953448	2.072677
39	1	2.568741	0.042939	-1.856788
40	1	2.086336	2.523727	-0.112026
41	1	-1.710996	-2.355047	0.359471
42	1	-1.706809	-2.466425	-1.383792

TS (A1-B1)

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p)
HF = -587.6407456 hartrees (-368750.444271456 kcal/mol)
Imaginary Frequencies: 1 (-157.8272 1/cm)

Zero-point correction = 0.390001 (Hartree/Particle)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p)
HF = -587.515726535 hartrees

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.540469	-0.299338	1.889004
2	1	-1.177115	0.375180	2.672102
3	1	-2.549011	-0.606514	2.175200
4	6	-1.544502	0.418787	0.518621
5	6	-2.096976	-0.498955	-0.615656
6	6	-1.147673	-1.677103	-0.885309
7	6	-0.065869	0.858252	0.209819
8	6	0.851278	-0.299474	-0.196448
9	1	0.299567	1.295980	1.142362
10	6	0.263659	-1.199208	-1.275886
11	1	0.908006	-2.051411	-1.493678
12	1	0.170204	-0.625004	-2.204633
13	6	0.180935	1.934791	-0.877554
14	1	-0.240686	1.640528	-1.844362
15	1	-0.268926	2.891941	-0.606756
16	6	2.022317	-0.640238	0.517761
17	6	2.321284	0.637628	-0.966665
18	1	3.345778	0.618067	-0.588971
19	6	1.710850	2.037296	-0.950673
20	1	2.058299	2.562423	-1.848534
21	6	2.817496	-1.887695	0.205821
22	1	3.853925	-1.780700	0.533247
23	1	2.379675	-2.717487	0.775526
24	1	2.809938	-2.171689	-0.846105
25	6	2.432627	0.016998	1.813835
26	1	2.094095	-0.636322	2.628184
27	1	3.521073	0.080869	1.889596
28	1	2.006628	1.003633	1.982676
29	6	-2.402777	1.693995	0.655033
30	1	-1.930962	2.416434	1.330961
31	1	-2.567069	2.186583	-0.308749
32	1	-3.383155	1.457306	1.075766
33	6	-3.528918	-1.011059	-0.387185
34	1	-3.589762	-1.696289	0.464255

35	1	-4.237319	-0.196412	-0.218266
36	1	-3.871936	-1.559430	-1.270245
37	1	-2.120147	0.113334	-1.530083
38	1	-0.910061	-1.195522	1.904260
39	1	2.301042	0.115207	-1.921456
40	1	2.092411	2.597563	-0.091021
41	1	-1.101428	-2.343541	-0.015763
42	1	-1.532639	-2.282793	-1.712634

B1

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p)
HF = -587.6430066 hartrees (-368751.863071566 kcal/mol)
Zero-point correction = 0.389651 (Hartree/Particle)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p)
HF = -587.517507273 hartrees

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.336513	-0.744145	1.750033
2	1	-0.953558	-0.273241	2.662377
3	1	-2.317122	-1.159745	1.993473
4	6	-1.436247	0.290106	0.605636
5	6	-1.992792	-0.355471	-0.704780
6	6	-0.989330	-1.352899	-1.312161
7	6	-0.015538	0.903956	0.365853
8	6	0.996517	-0.064106	-0.336138
9	1	0.369384	1.157660	1.359797
10	6	0.366735	-0.696126	-1.596189
11	1	1.055513	-1.398388	-2.074503
12	1	0.212969	0.104868	-2.326587
13	6	0.109510	2.198224	-0.468242
14	1	-0.383341	2.104632	-1.440907
15	1	-0.339589	3.054153	0.039705
16	6	1.851691	-0.907313	0.475946
17	6	2.223677	0.950796	-0.817784
18	1	3.168048	0.843195	-0.275658
19	6	1.624850	2.365878	-0.629422
20	1	1.906482	2.996344	-1.479233
21	6	2.407123	-2.180549	-0.057568

22	1	3.087071	-2.667600	0.641490
23	1	1.584189	-2.862598	-0.308305
24	1	2.933823	-2.003919	-1.004424
25	6	2.282430	-0.549250	1.850519
26	1	1.765316	-1.248318	2.527771
27	1	3.350349	-0.751834	1.985179
28	1	2.040608	0.464458	2.162707
29	6	-2.364114	1.429448	1.085132
30	1	-1.907778	1.985626	1.912078
31	1	-2.589643	2.138950	0.283044
32	1	-3.313339	1.031281	1.451914
33	6	-3.374733	-1.014030	-0.558801
34	1	-3.344312	-1.895673	0.089722
35	1	-4.122887	-0.325006	-0.158989
36	1	-3.732668	-1.345358	-1.538797
37	1	-2.107616	0.463614	-1.430038
38	1	-0.685207	-1.593501	1.509387
39	1	2.418903	0.672778	-1.855402
40	1	2.048143	2.827799	0.268077
41	1	-0.873745	-2.223285	-0.651995
42	1	-1.389583	-1.743994	-2.254102

A2

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p)
HF = -587.6479641 hartrees (-368754.973952391 kcal/mol)
Zero-point correction = 0.390713 (Hartree/Particle)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p)
HF = -587.5218026 hartrees

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	3.003223	-1.139468	-1.070766
2	6	1.628824	0.617358	0.289243
3	6	2.295310	-0.792486	0.252320
4	1	3.842201	-0.470994	-1.272359
5	6	2.591013	1.675129	-0.286695
6	6	0.270980	0.592939	-0.621073
7	1	2.729497	1.582659	-1.366942
8	1	3.071969	-0.764862	1.029429

9	1	3.403906	-2.156517	-1.026163
10	1	2.259065	2.693418	-0.074140
11	6	1.305804	-1.890414	0.655948
12	1	0.995796	-1.785680	1.699675
13	1	1.766018	-2.878642	0.566541
14	6	0.036103	-1.882321	-0.244138
15	1	-0.659993	-2.663931	0.056520
16	1	0.354968	-2.118663	-1.272473
17	6	-0.607222	-0.548803	-0.304554
18	1	0.696207	0.281314	-1.593671
19	6	-0.419876	1.967051	-0.797538
20	1	0.268826	2.764352	-0.517257
21	1	-0.625181	2.114828	-1.864589
22	6	-2.073656	-0.436728	-0.046943
23	6	-2.663568	0.951553	-0.390950
24	1	-2.873208	0.988087	-1.467761
25	1	-3.630723	1.044120	0.113435
26	6	-1.733214	2.104161	-0.025652
27	1	-1.548429	2.125977	1.055505
28	1	-2.205410	3.059474	-0.274174
29	6	1.275424	1.021637	1.734194
30	1	0.640419	0.291860	2.244099
31	1	2.195019	1.125441	2.319288
32	6	-2.228253	-0.708522	1.501659
33	1	-1.775994	0.079464	2.106134
34	1	-3.303215	-0.723100	1.703931
35	1	-1.813001	-1.672600	1.802238
36	6	-2.875025	-1.531996	-0.809382
37	1	-3.938208	-1.340549	-0.638697
38	1	-2.696757	-1.479014	-1.887487
39	1	-2.663666	-2.545848	-0.465485
40	1	2.337002	-1.092586	-1.942618
41	1	0.766499	1.989000	1.765376
42	1	3.571196	1.558443	0.187603

TS (A2-C1)

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p)
HF = -587.6307066 hartrees (-368744.144698566 kcal/mol)
Imaginary Frequencies: 1 (-292.7880 1/cm)
Zero-point correction = 0.390529 (Hartree/Particle)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p)
HF = -587.5073554 hartrees

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.736703	-1.110082	-1.407316
2	6	1.627805	0.621648	0.220498
3	6	2.293145	-0.784726	0.033078
4	1	3.515131	-0.427921	-1.755303
5	6	2.467435	1.699591	-0.503964
6	6	0.180458	0.624737	-0.406029
7	1	2.404345	1.617951	-1.593145
8	1	3.205814	-0.772104	0.643134
9	1	3.153985	-2.121342	-1.447430
10	1	2.156664	2.710615	-0.226732
11	6	1.389025	-1.897794	0.596343
12	1	1.278689	-1.795560	1.681432
13	1	1.858888	-2.873644	0.435339
14	6	0.004323	-1.915688	-0.060084
15	1	-0.607837	-2.709990	0.370314
16	1	0.105215	-2.158636	-1.126863
17	6	-0.713401	-0.568683	-0.023159
18	1	0.345279	0.381596	-1.467861
19	6	-0.496513	2.029493	-0.391123
20	1	-0.025398	2.662536	0.363261
21	1	-0.280478	2.508289	-1.350357
22	6	-2.109931	-0.492124	-0.249607
23	6	-2.724287	0.814537	-0.695150
24	1	-2.658449	0.788848	-1.794648
25	1	-3.792586	0.825654	-0.456614
26	6	-2.016939	2.054837	-0.151523
27	1	-2.236563	2.146214	0.918332
28	1	-2.449477	2.945658	-0.614956
29	6	1.636659	0.977723	1.727345
30	1	1.202847	0.203078	2.365579
31	1	2.671145	1.108738	2.059902
32	6	-1.572494	-0.413421	1.571954
33	1	-0.875075	0.300504	2.001303
34	1	-2.574779	-0.008172	1.729899
35	1	-1.502222	-1.406554	2.004490
36	6	-2.995053	-1.702156	-0.405421
37	1	-4.001340	-1.501828	-0.029259
38	1	-3.085248	-1.895394	-1.482452

39	1	-2.611908	-2.609016	0.059208
40	1	1.919457	-1.068569	-2.136954
41	1	1.121358	1.920384	1.938226
42	1	3.520929	1.601311	-0.222904

C1

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p)
HF = -587.6360043 hartrees (-368747.469058293 kcal/mol)
Zero-point correction = 0.390041 (Hartree/Particle)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p)
HF = -587.5104434 hartrees (-368668.678337934 kcal/mol)

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.419277	-1.104785	-1.673738
2	6	1.641998	0.588189	0.175026
3	6	2.209735	-0.832682	-0.170502
4	1	3.167518	-0.436679	-2.105233
5	6	2.395266	1.665904	-0.642948
6	6	0.117208	0.654151	-0.215150
7	1	2.126136	1.655443	-1.703897
8	1	3.202935	-0.882568	0.294911
9	1	2.779923	-2.128274	-1.819657
10	1	2.204153	2.671219	-0.256588
11	6	1.354732	-1.938351	0.477256
12	1	1.404299	-1.874377	1.569229
13	1	1.766522	-2.920757	0.219989
14	6	-0.110102	-1.912727	0.022326
15	1	-0.662296	-2.705926	0.533698
16	1	-0.161506	-2.129193	-1.051082
17	6	-0.784274	-0.525940	0.283377
18	1	0.124479	0.534426	-1.308627
19	6	-0.535565	2.030633	0.062161
20	1	-0.398127	2.311493	1.109481
21	1	-0.008013	2.784324	-0.524594
22	6	-2.127790	-0.449749	-0.319638
23	6	-2.548262	0.792473	-0.981929
24	1	-2.044266	0.719964	-1.968422
25	1	-3.622282	0.811786	-1.185832

26	6	-2.044081	2.079584	-0.284058
27	1	-2.651218	2.225486	0.614856
28	1	-2.272038	2.919568	-0.944412
29	6	1.936869	0.895466	1.664715
30	1	1.624998	0.107708	2.353961
31	1	3.017214	1.012307	1.796383
32	6	-1.192096	-0.421442	1.822550
33	1	-1.698252	0.512961	2.070597
34	1	-1.819409	-1.261443	2.126263
35	1	-0.264715	-0.462239	2.392940
36	6	-3.089745	-1.569924	-0.287827
37	1	-4.025551	-1.230294	0.178097
38	1	-3.371705	-1.796990	-1.328329
39	1	-2.734172	-2.477118	0.194418
40	1	1.505072	-0.996260	-2.268111
41	1	1.476298	1.831318	1.992985
42	1	3.474976	1.499315	-0.572751

Scheme S1

A1'

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p)
HF = -587.6462016 hartrees (-368753.867966016 kcal/mol)
Zero-point correction = 0.390771 (Hartree/Particle)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p)
HF = -587.5206643 hartrees

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	2.314486	-0.737138	1.707519
2	1	2.111471	-1.757279	2.051498
3	1	3.396490	-0.582552	1.766917
4	6	1.820824	-0.546347	0.256086
5	6	2.210241	0.863202	-0.302264
6	6	1.365663	1.172432	-1.551226
7	6	0.239279	-0.707767	0.297360
8	6	-0.604816	0.402615	-0.137252
9	1	-0.056997	-1.048822	1.290223
10	6	-0.107443	1.334410	-1.172072
11	1	-0.319761	2.344676	-0.786376

12	1	-0.777510	1.270291	-2.044378
13	6	-0.392460	-1.850813	-0.673990
14	1	-0.242777	-1.584943	-1.725233
15	1	0.201398	-2.744436	-0.475560
16	6	-2.033529	0.459004	0.297062
17	6	-2.665997	-0.774085	-0.509854
18	1	-3.692972	-0.874026	-0.143794
19	6	-1.868639	-2.065250	-0.354618
20	1	-2.273697	-2.820617	-1.039046
21	6	-2.782107	1.739910	-0.119774
22	1	-3.832379	1.648208	0.168289
23	1	-2.380895	2.621830	0.390697
24	1	-2.758004	1.921711	-1.197117
25	6	-2.223134	0.242809	1.822334
26	1	-1.707330	1.020629	2.393557
27	1	-3.289100	0.315879	2.052586
28	1	-1.876887	-0.728867	2.175502
29	6	2.514712	-1.627346	-0.604195
30	1	2.324066	-2.636632	-0.227815
31	1	2.227163	-1.599010	-1.658935
32	1	3.596872	-1.475090	-0.558313
33	6	2.121919	2.011326	0.721803
34	1	1.148025	2.075820	1.224195
35	1	2.874518	1.907105	1.505905
36	1	2.296850	2.972559	0.226936
37	1	3.257288	0.797910	-0.619074
38	1	1.837996	-0.046077	2.408489
39	1	-2.726623	-0.492776	-1.567694
40	1	-1.978193	-2.475978	0.654749
41	1	1.710489	2.092208	-2.032945
42	1	1.476512	0.376507	-2.294773

TS (A1'-B1')

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p)
HF = -587.6281885 hartrees (-368742.564565635 kcal/mol)
Imaginary Frequencies: 1 (-84.4875 1/cm)
Zero-point correction = 0.390451 (Hartree/Particle)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p)
HF = -587.503375323 hartrees

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.927905	-0.105925	1.938627
2	1	-1.817779	0.757703	2.603793
3	1	-2.938231	-0.499859	2.084460
4	6	-1.704102	0.315095	0.469624
5	6	-1.996391	-0.867531	-0.523203
6	6	-1.182625	-0.668757	-1.810953
7	6	-0.216244	0.854832	0.341550
8	6	0.801553	-0.134263	-0.269637
9	1	0.097391	1.083954	1.362549
10	6	0.322063	-0.853095	-1.553640
11	1	0.525942	-1.921644	-1.452173
12	1	0.884578	-0.521742	-2.431323
13	6	0.041030	2.163561	-0.450439
14	1	-0.283382	2.079546	-1.492591
15	1	-0.480042	3.017688	-0.014923
16	6	1.862834	-0.702910	0.484125
17	6	2.198756	0.969416	-0.658815
18	1	3.165762	0.851699	-0.162612
19	6	1.561137	2.328397	-0.372179
20	1	1.955786	3.049521	-1.097445
21	6	2.698252	-1.818281	-0.080301
22	1	3.708376	-1.813240	0.334567
23	1	2.227519	-2.763686	0.226065
24	1	2.750068	-1.821039	-1.168900
25	6	2.150240	-0.376794	1.922100
26	1	1.708640	-1.186235	2.520262
27	1	3.224106	-0.385415	2.124143
28	1	1.721240	0.559645	2.271807
29	6	-2.703059	1.455955	0.167559
30	1	-2.532385	2.328103	0.806795
31	1	-2.664007	1.786489	-0.874919
32	1	-3.721864	1.107553	0.362484
33	6	-1.793364	-2.287252	0.041344
34	1	-0.786465	-2.458079	0.440881
35	1	-2.497854	-2.507317	0.846202
36	1	-1.960865	-3.028797	-0.747209
37	1	-3.057134	-0.793637	-0.790581
38	1	-1.223140	-0.875813	2.269564
39	1	2.335712	0.715653	-1.707907
40	1	1.856024	2.680778	0.621595
41	1	-1.486355	-1.395669	-2.571617

42	1	-1.384680	0.319145	-2.237546

B1'

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p)
HF = -587.6281821 hartrees (-368742.560549571 kcal/mol)
Zero-point correction = 0.390194 (Hartree/Particle)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p)
HF = -587.503274476 hartrees

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-1.870717	-0.343574	1.914769
2	1	-1.814693	0.464044	2.653067
3	1	-2.852189	-0.815110	2.023734
4	6	-1.681196	0.217585	0.487991
5	6	-1.901106	-0.891886	-0.602963
6	6	-1.128739	-0.518132	-1.876104
7	6	-0.237560	0.861195	0.397769
8	6	0.847476	-0.012435	-0.292065
9	1	0.070711	1.044159	1.430880
10	6	0.395860	-0.587470	-1.666637
11	1	0.704453	-1.632059	-1.741806
12	1	0.893249	-0.065752	-2.488977
13	6	-0.056329	2.230194	-0.304016
14	1	-0.382653	2.201446	-1.348111
15	1	-0.615508	3.026430	0.190228
16	6	1.811077	-0.756262	0.465992
17	6	2.144575	1.115828	-0.514021
18	1	3.044902	0.988551	0.095716
19	6	1.455021	2.459941	-0.215270
20	1	1.826039	3.207832	-0.924565
21	6	2.676717	-1.785381	-0.190865
22	1	3.623732	-1.918665	0.335199
23	1	2.135085	-2.742427	-0.134327
24	1	2.860672	-1.590929	-1.247990
25	6	2.008987	-0.617957	1.940025
26	1	1.549904	-1.511742	2.390004
27	1	3.068141	-0.649997	2.208408
28	1	1.534325	0.252314	2.386710

29	6	-2.754344	1.313209	0.289277
30	1	-2.630074	2.135943	1.000721
31	1	-2.744563	1.734705	-0.720306
32	1	-3.747822	0.886393	0.457632
33	6	-1.585811	-2.337503	-0.171060
34	1	-0.560872	-2.470578	0.196594
35	1	-2.254929	-2.679948	0.621142
36	1	-1.715623	-3.015948	-1.021046
37	1	-2.969133	-0.875869	-0.851189
38	1	-1.117153	-1.092298	2.179994
39	1	2.435703	0.951850	-1.550710
40	1	1.727228	2.802752	0.787847
41	1	-1.387678	-1.199643	-2.693526
42	1	-1.424726	0.480435	-2.212248

A2'

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p)
HF = -587.6457584 hartrees (-368753.589853584 kcal/mol)
Zero-point correction = 0.391644 (Hartree/Particle)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p)
HF = -587.5194857 hartrees

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	3.143479	-0.952422	-0.927041
2	6	1.506946	0.645420	0.350779
3	6	2.267980	-0.719019	0.318365
4	1	3.943012	-0.213115	-1.005717
5	6	2.416865	1.802852	-0.096407
6	6	0.256621	0.551077	-0.731389
7	1	2.673004	1.760581	-1.157874
8	1	2.949407	-0.685232	1.180358
9	1	3.619650	-1.935612	-0.868211
10	1	1.964221	2.775741	0.108136
11	6	1.320027	-1.900479	0.568503
12	1	0.906521	-1.877508	1.580239
13	1	1.843949	-2.855045	0.465092
14	6	0.133909	-1.923396	-0.471545
15	1	-0.519019	-2.772017	-0.275891

16	1	0.581086	-2.035757	-1.466020
17	6	-0.547340	-0.621410	-0.374280
18	1	0.810109	0.298146	-1.644659
19	6	-0.544064	1.840510	-0.990203
20	1	0.136189	2.693262	-1.013006
21	1	-0.927147	1.757851	-2.013124
22	6	-1.955504	-0.494639	0.075448
23	6	-2.249925	0.882530	0.723119
24	1	-3.333773	0.955437	0.855465
25	1	-1.828820	0.856367	1.732572
26	6	-1.726885	2.122244	-0.032977
27	1	-1.443303	2.878989	0.704190
28	1	-2.535892	2.570943	-0.616591
29	6	1.005649	0.950989	1.774992
30	1	0.376648	0.161856	2.195956
31	1	1.867375	1.072060	2.439433
32	6	-2.438053	-1.620562	1.016712
33	1	-1.832473	-1.672720	1.926554
34	1	-3.466342	-1.404263	1.318626
35	1	-2.441789	-2.604316	0.542196
36	6	-2.733841	-0.636329	-1.300190
37	1	-3.796019	-0.547549	-1.050623
38	1	-2.483843	0.145766	-2.018233
39	1	2.579026	-0.921794	-1.867110
40	1	0.442734	1.886765	1.808566
41	1	-2.569138	-1.613321	-1.760782
42	1	3.349449	1.760288	0.477132

TS (A2'-D1)

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p)
HF = -587.6324391 hartrees (-368745.231859641 kcal/mol)
Imaginary Frequencies: 1 (-267.9007 1/cm)
Zero-point correction = 0.390975 (Hartree/Particle)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p)
HF = -587.5084585 hartrees

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	3.068026	-1.012831	-0.854134

2	6	1.439598	0.677625	0.331061
3	6	2.223967	-0.681695	0.392479
4	1	3.851341	-0.270500	-1.021306
5	6	2.383617	1.805821	-0.136350
6	6	0.252239	0.532311	-0.714985
7	1	2.661634	1.710748	-1.189952
8	1	2.932431	-0.579048	1.224518
9	1	3.565726	-1.978107	-0.716644
10	1	1.935894	2.793333	0.004916
11	6	1.278669	-1.844394	0.752492
12	1	0.891581	-1.726517	1.769955
13	1	1.827122	-2.791933	0.742490
14	6	0.098801	-1.968321	-0.235356
15	1	-0.552600	-2.792007	0.060749
16	1	0.489365	-2.209287	-1.230393
17	6	-0.642101	-0.646264	-0.323488
18	1	0.751542	0.235056	-1.645547
19	6	-0.565912	1.799483	-1.040491
20	1	0.108064	2.645073	-1.191342
21	1	-1.055704	1.650675	-2.011491
22	6	-1.916001	-0.428570	0.254123
23	6	-2.485508	0.965664	0.457741
24	1	-3.481489	0.987592	-0.001075
25	1	-2.684993	1.032034	1.534889
26	6	-1.625866	2.164315	0.007922
27	1	-1.144484	2.602371	0.883347
28	1	-2.280473	2.942796	-0.394524
29	6	0.954356	1.033584	1.757045
30	1	0.171656	0.369021	2.137069
31	1	1.794039	0.968105	2.456409
32	6	-2.695958	-1.500354	0.979225
33	1	-2.447981	-1.421321	2.044766
34	1	-3.771051	-1.325411	0.884627
35	1	-2.473169	-2.517670	0.661456
36	6	-1.960324	-0.920452	-1.593029
37	1	-2.869323	-0.333210	-1.708717
38	1	-1.273119	-0.622785	-2.384466
39	1	2.481866	-1.081622	-1.777455
40	1	0.579012	2.057456	1.812456
41	1	-2.157803	-1.987588	-1.605014
42	1	3.305296	1.787210	0.454752

D1

B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p)
HF = -587.63859 hartrees (-368749.0916109 kcal/mol)
Zero-point correction = 0.390300 (Hartree/Particle)

mPW1PW91/6-31+G(d,p)//B3LYP/6-31+G(d,p)
HF = -587.5134376 hartrees

Coordinates (from last standard orientation):

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	-3.092013	-0.831059	0.744916
2	6	-1.299353	0.745035	-0.355429
3	6	-2.160785	-0.564019	-0.454253
4	1	-3.846794	-0.048854	0.851611
5	6	-2.216567	1.932911	0.017676
6	6	-0.198422	0.573932	0.760602
7	1	-2.575308	1.872240	1.049119
8	1	-2.815887	-0.426105	-1.324119
9	1	-3.627435	-1.773924	0.592908
10	1	-1.708571	2.893717	-0.103649
11	6	-1.264715	-1.783000	-0.750161
12	1	-0.807505	-1.685192	-1.742211
13	1	-1.875488	-2.691356	-0.793242
14	6	-0.187936	-1.968841	0.323303
15	1	0.428246	-2.847268	0.108392
16	1	-0.673185	-2.182708	1.281197
17	6	0.687552	-0.710331	0.546618
18	1	-0.753328	0.373677	1.684450
19	6	0.685488	1.807126	1.050934
20	1	0.061594	2.700328	1.129264
21	1	1.132032	1.687205	2.043717
22	6	1.801621	-0.503604	-0.389095
23	6	2.520189	0.788890	-0.445996
24	1	3.404338	0.578524	0.191281
25	1	2.969180	0.902026	-1.441180
26	6	1.797393	2.064267	0.021733
27	1	1.393293	2.558396	-0.863611
28	1	2.536589	2.755143	0.437683
29	6	-0.709252	1.040448	-1.754702
30	1	0.103227	0.361215	-2.044977
31	1	-1.483592	0.928808	-2.520605
32	6	2.361133	-1.606712	-1.200835

33	1	1.693872	-1.732196	-2.069873
34	1	3.361994	-1.388783	-1.577619
35	1	2.341770	-2.567693	-0.680314
36	6	1.543827	-1.003747	1.876945
37	1	2.253845	-0.219553	2.134759
38	1	0.801400	-1.080233	2.675866
39	1	-2.566327	-0.909670	1.702471
40	1	-0.332953	2.062047	-1.834909
41	1	2.069071	-1.958308	1.798785
42	1	-3.093036	1.950743	-0.638727
