Supporting Information Available

Synthesis of C-17-Functionalized Spongiane Diterpenes: Diastereoselective Synthesis of (-)-Spongian-16-oxo-17-al, (-)-Acetyldendrillol-1and (-)-Aplyroseol-14

Manuel Arnó,[*] *Miguel A. González and Ramón J. Zaragozá*[*]

Departamento de Química Orgánica, Facultad de Química, Universidad de Valencia, C/ Dr. Moliner 50, E- 46100 Burjassot, Valencia, Spain

Table of contents:

- Representative data and experimental procedures for the preparation of **24**, **25**, **28** and **29**

- Representative data for **21** and **23**.

- ^{1}H NMR spectra for **2**, **3**, **15**, **16**, **21** and **23**.

- Cartesian coordinates for: **22a**, **22b-chair**, **22c-chair**, **2**, **23**, **TSa**, **TSb** and **TSc**

Methyl 15-acetoxy-17-oxo-ent-isocopal-14-en-16-oate (24). A suspension of dialdehyde **14** (2 mg, 0.0057 mmol) and approximately 2 mg of sodium acetate in acetic anhydride (50 μL) was heated at 60 °C for 16 h. The reaction mixture was then diluted with Et_2O, washed with 10% aqueous $NaHCO_3$, brine, filtered and concentrated. The resulting residue was filtered through a short silica gel column eluting with hexane-AcOEt (9:1), to give exclusively the enol acetate **24** in essentially quantitative yield as a colorless oil: IR (KBr) 3098, 2947, 1764, 1731, 1215 cm^{-1}; ^1H NMR (400 MHz) δ 9.76 (1H, s, H-17), 7.21 (1H, s, H-15), 3.92 (1H, br d, J = 6.0, H-13), 3.63 (3H, s, CO_2Me), 2.58-2.50 (2H, m), 2.15 (3H, s, COMe), 2.06 (1H, m), 0.85, 0.77, and 0.76 (3H each, each s, H-18, H-19 and H-20). NOE result: Irradiation of the proton H-15 (δ 7.21) showed a enhancement of a couple of signals (δ 2.53 and 1.30) assignable to protons H-7.

(-)-15α-Acetoxyspongian-16-oxo-17-al (25). To a stirred solution of dendrillol-1 **10** (R^1= H; R^2= β-OH) (15.0 mg, 0.045 mmol), 4-pyrrolidinopyridine (98%, 1.0 mg, 0.007 mmol) in dry Et_3N (0.4 mL) at 0 °C was added Ac_2O (25 μL, 0.26 mmol). The reaction mixture was then allowed to warm to room temperature, stirred for 70 min, and diluted with Et_2O. The organic phase was washed with 1.5 M HCl and brine, dried, filtered and concentrated. Purification of the residue by flash chromatography, using hexane-AcOEt (from 7:3 to 6:4) as eluent, provided spongiane **25** (15.2 mg, 90%) as a white solid: mp 161-162 °C (from hexane-AcOEt); $[\alpha]^{23}_D$ –9.0 (c 0.69, $CHCl_3$); IR (KBr) 2943, 2739, 1790, 1769, 1711, 1214 cm^{-1}; ^1H NMR (400 MHz) δ 9.93 (1H, d, *J* = 1.3, H-17), 6.18 (1H, s, H-15β), 2.97 (1H, dd, *J* = 7.9, 7.7, H-13), 2.72 (1H, ddd, *J* = 13.1, 3.2, 3.2, H-7β), 2.51 (1H, br d, *J* = 12.1, H-12β), 2.26 (1H, d, *J* = 7.9, H-14), 2.08 (3H, s, OCO*Me*), 0.86, 0.76 and 0.68 (3H each, each s, H-18, H-19 and H-20); ^{13}C NMR (75 MHz) δ_C 204.25 (d), 176.31 (s), 168.55 (s), 93.92 (d), 56.40 (d), 55.75 (d), 53.32 (d), 49.36 (s), 41.69 (t), 38.96 (t), 37.80 (s), 35.84 (t), 35.15 (d), 33.34 (q), 33.23 (s), 22.36 (t), 21.42

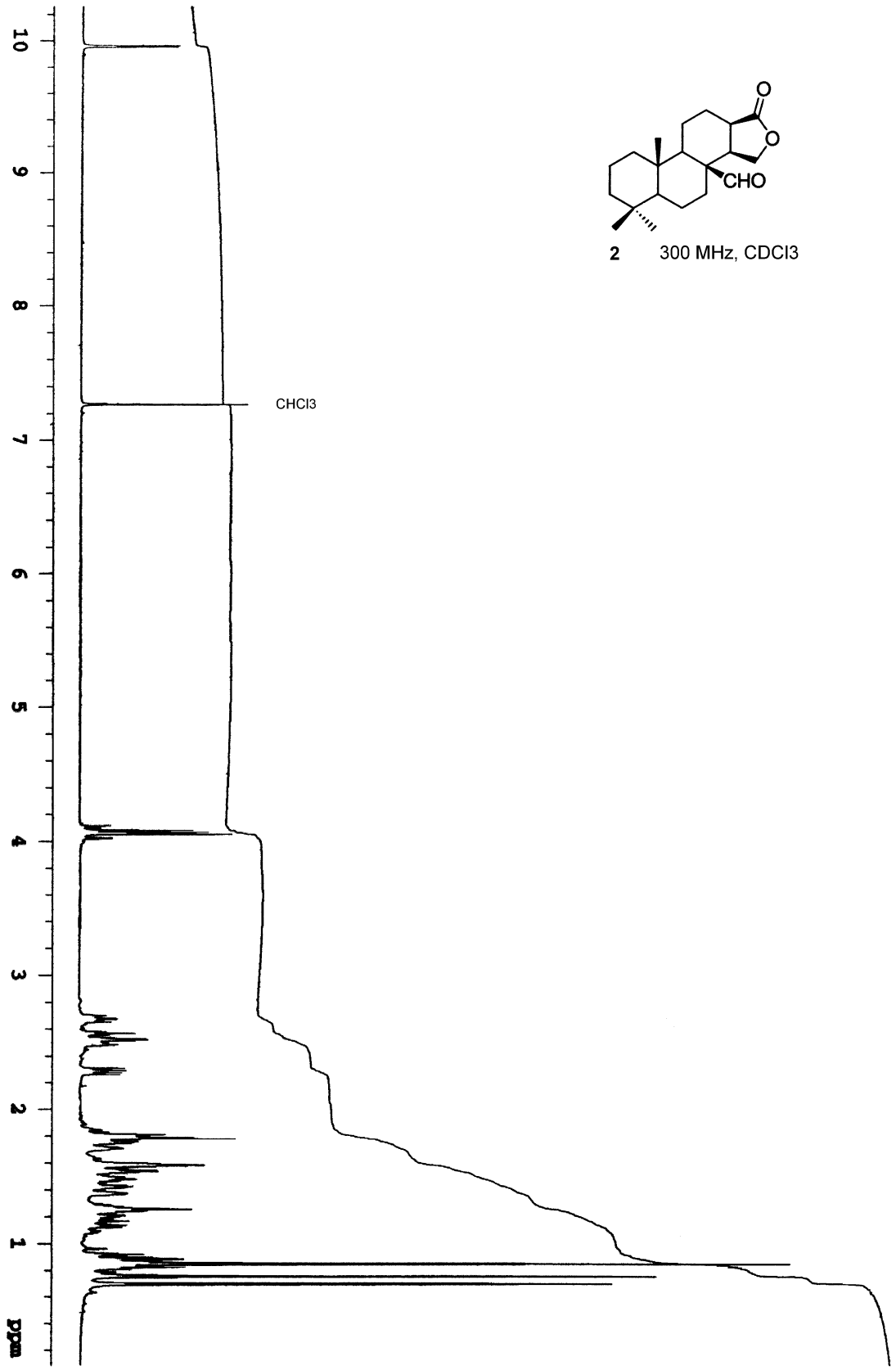
(q), 20.86 (q), 18.66 (t), 18.55 (t), 16.08 (t), 15.14 (q); MS (EI) *m/z* 376 (M^+, 4), 316 (58), 288 (78), 123 (44), 86 (100); HRMS $C_{22}H_{32}O_5$ requires 376.2250, found 376.2249.

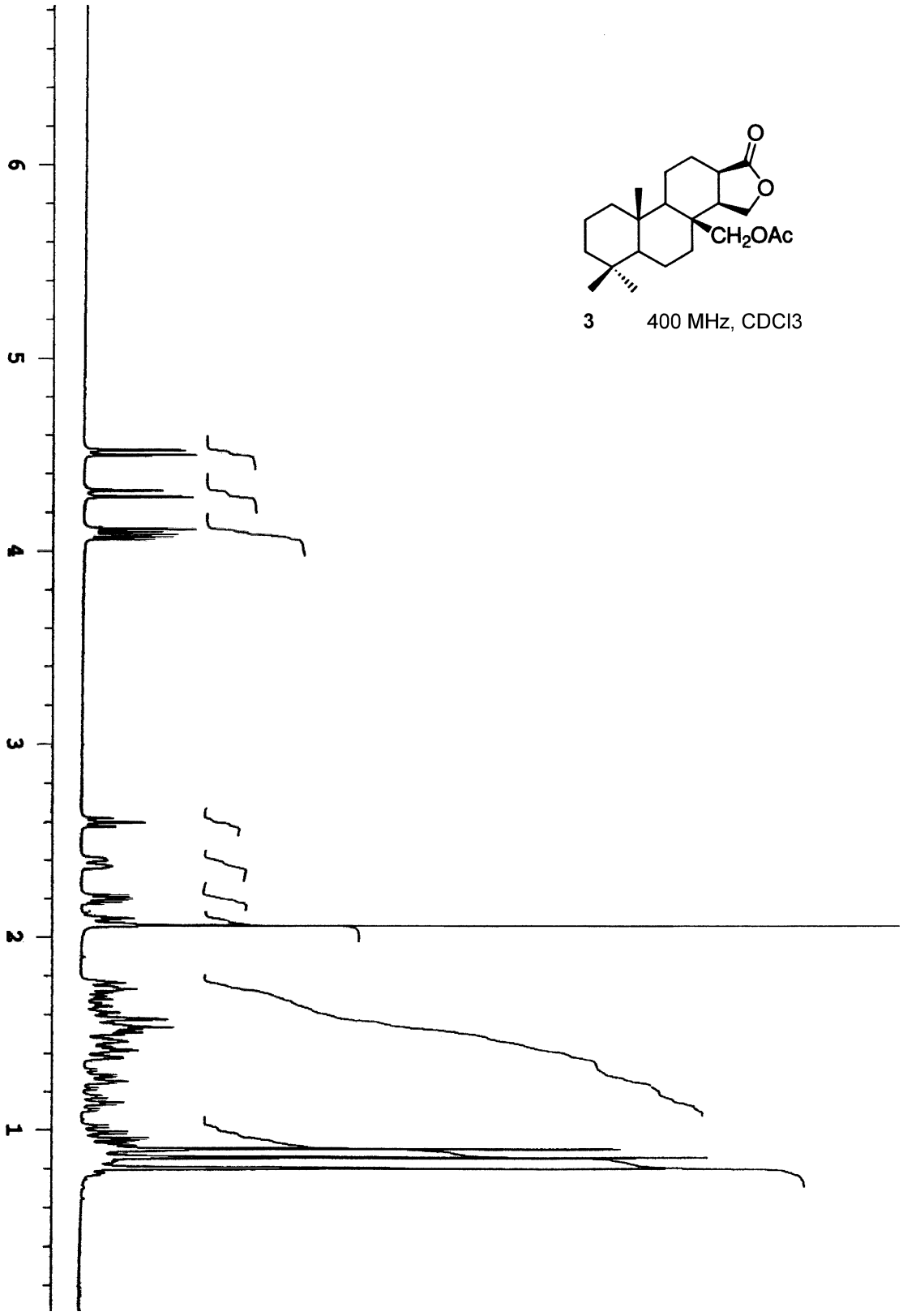
Preparation of acetates 28 and 29 from aldehyde 14. To a cooled solution of aldehyde **14** (11.0 mg, 0.034 mmol) in CH_2Cl_2 (0.21 mL) at –78 °C DIBALH (1 M in cyclohexane, 80 μL, 0.08 mmol, 2.3 equiv) was added dropwise. After 45 min, the reaction was treated sequentially with pyridine (13 μL, 0.16 mmol, 4.6 equiv), a solution of DMAP (12.7 mg, 0.10 mmol, 3.0 equiv) in CH_2Cl_2 (0.1 mL), and Ac_2O (30 μL, 0.31 mmol, 9.0 equiv). The mixture was stirred at – 78°C for 6 h and allowed to warm to 0 °C slowly (14 h), quenched with ammonium chloride and Rochelle's salt and warmed to room temperature. The resulting mixture was diluted with CH_2Cl_2 and stirred until layer separation occurred. The organic layer was separated and the aqueous one was reextracted with additional CH_2Cl_2. The combined CH_2Cl_2 extracts were washed with 10% aqueous $NaHCO_3$ and brine, dried, filtered and concentrated. The residue thus obtained was purified by column chromatography, using hexane-AcOEt (from 9:1 to 8:2), to afford **29** and **28**. Mixture of epimers **29** (7 mg, 50%): For major epimer: ^{1}H NMR (300 MHz) δ 5.94 (1H, br s, H-16), 4.42-4.17 (3H, m), 3.59 (1H, dd, *J* = 12.7, 1.5), 2.12 (3H, s, OCOMe), 2.06 (3H, s, OCOMe), 1.00, 0.84 and 0.80 (3H each, each s, H-18, H-19 and H-20); δ_C (75 MHz) 171.03 (s), 169.67 (s), 93.84 (d), 69.81 (t), 61.97 (t), 59.42 (d), 56.58 (d), 49.63 (d), 41.87 (t), 39.94 (t), 37.84 (s), 35.63 (s), 35.14 (t), 33.86 (d), 33.23 (q), 33.18 (s), 26.43 (t), 21.44 (q), 21.24 (q), 21.04 (q), 20.58 (t), 18.67 (t), 18.47 (t), 15.72 (q). For minor epimer: ^{1}H NMR (300 MHz) δ 5.93 (1H, br s, H-16), 4.41 (1H, dd, *J* = 11.2, 8.6), 4.27 (1H, dd, *J* = 11.2, 6.6), 4.12 (1H, d, *J* = 12.3), 3.67 (1H, d, *J* = 12.3), 2.05 (3H, s, OCOMe), 2.05 (3H, s, OCOMe), 1.01, 0.84 and 0.80 (3H each, each s, H-18, H-19 and H-20); δ_C (75 MHz) 171.13 (s), 169.91 (s), 96.07 (d), 65.49 (t), 63.85 (t), 59.26 (d), 56.68 (d), 46.35 (d), 41.88 (t), 39.93 (t), 37.81 (s), 35.86 (t), 35.48 (s), 33.74 (d), 33.25 (s), 33.17 (q), 30.06 (t), 21.44 (q), 21.35 (q), 21.08 (q), 19.62 (t), 18.48 (t), 18.44 (t), 15.73 (q). For

compound **28** (2.1 mg, 15%): ^{1}H NMR (300 MHz) δ 6.04 (1H, d, *J* = 5.6, H-16), 4.42 (1H, d, *J* = 12.0, H-17), 4.17 (1H, dd, *J* = 9.0, 2.2, H-15), 4.04 (1H, d, *J* = 12.0, H-17'), 3.96 (1H, dd, *J* = 9.0, 6.0, H-15'), 2.19 (1 H, m), 2.08 (3H, s, OCOMe), 2.05 (3H, s, OCOMe), 0.92, 0.86 and 0.80 (3H each, each s, H-18, H-19 and H-20).

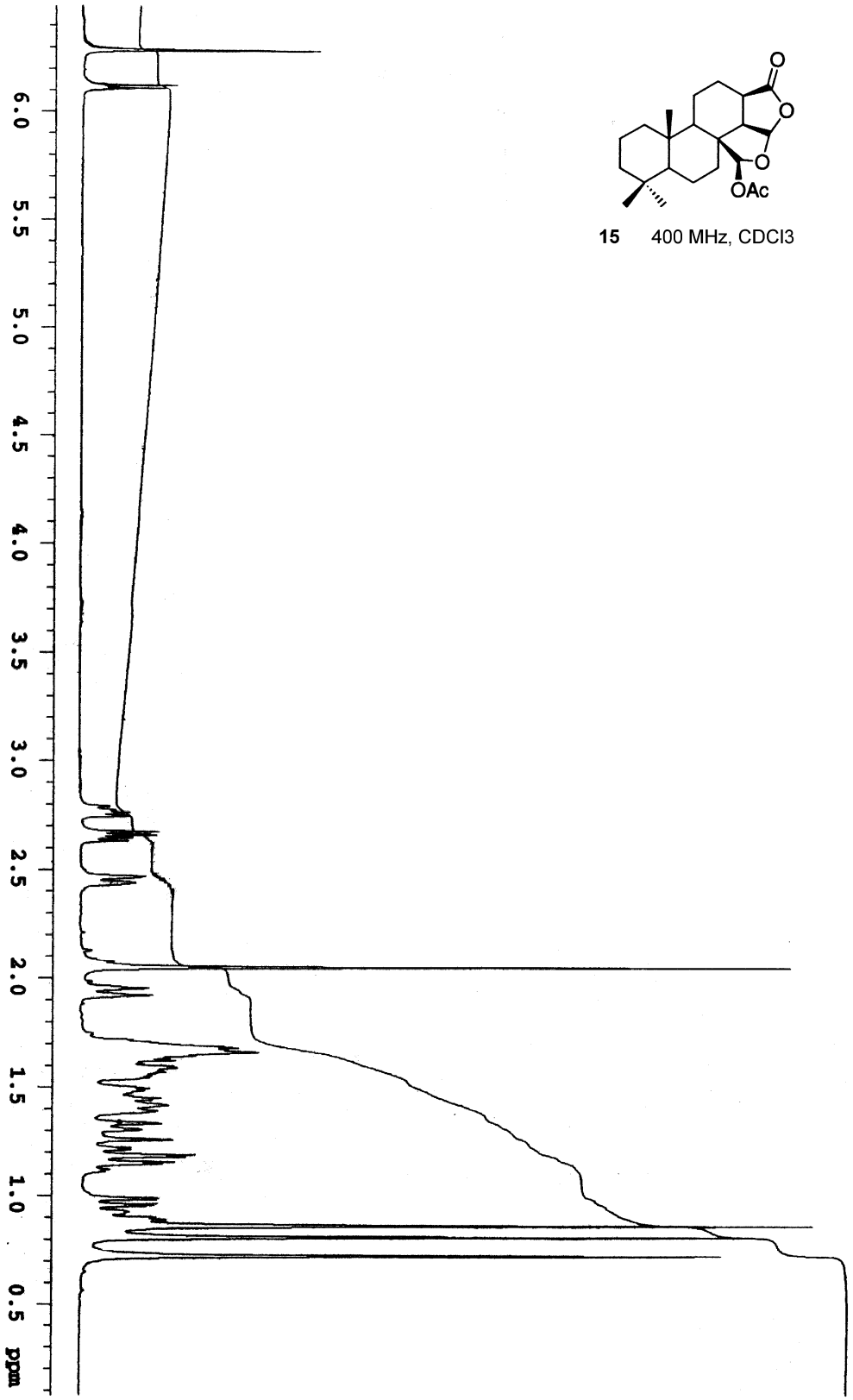
(-)-17β-methoxy-15,17-epoxyspongian-16-one (21). Representative data: mp 205-26 °C (from MeOH); $[\alpha]^{25}_{D}$ –44.8 (*c* 1.25, $CHCl_3$); IR (KBr) 2924, 1770, 1112, 1072 cm^{-1}; ^{1}H NMR (400 MHz) δ 6.05 (1 H, d, *J* = 6.0, H-15), 4.92 (1 H, s, H-17), 3.28 (3 H, s, OMe), 2.67 (1 H, dd, *J* = 11.0, 7.7, H-13), 2.52 (1 H, dd, *J* = 11.0, 6.0, H-14), 2.36 (1 H, m, H-12β), 1.92-1.78 (2 H, m), 0.85, 0.82 and 0.82 (3H each, each s, H-18, H-19 and H-20); δ_C (75 MHz) 176.94 (s), 109.99 (d), 104.08 (d), 56.78 (d), 55.43 (d), 53.88 (d), 49.24 (d), 46.76 (s), 41.95 (t), 41.41 (t), 39.09 (t), 38.11 (s), 37.69 (d), 33.35 (s), 33.35 (q), 23.70 (t), 21.36 (q), 20.11 (t), 18.77 (t), 16.69 (t), 15.53 (q); MS (EI) *m/z* 348 (M^+, 30), 317 (20), 288 (100), 137 (23); HRMS $C_{21}H_{32}O_4$ requires 348.2301, found 348.2308.

(-)-15,16-dideoxy-15,17-oxido-16,17-oxidospongian-16-one (23). Representative data: mp 241-243°C (from Et_2O-CH_2Cl_2); $[\alpha]^{24}_{D}$ –65.0 (c 2.0, $CHCl_3$); IR (KBr) 1742, 1120 cm^{-1}; ^{1}H NMR (400 MHz) δ5.65 (1H, d, *J* = 1.2, H-17), 4.08 (1H, dd, *J* = 8.8, 4.7, H-15), 3.77 (1H, d, *J* = 8.8, H-15'), 2.80 (1H, m, H-13), 0.96, 0.87 and 0.84 (3H each, each s, H-18, H-19 and H-20); ^{13}C NMR (100 MHz) δ_C 173.77 (s), 104.50 (d), 70.07 (t), 56.56 (d), 53.81 (d), 46.31 (d), 45.90 (d), 45.71 (s), 41.77 (t), 38.74 (t), 37.86 (s), 34.73 (t), 33.30 (s), 33.08 (q), 29.59 (t), 21.29 (q), 19.38 (t), 19.22 (t), 18.70 (t), 15.33 (q); MS (EI) *m/z* 318 (M^+, 5), 274 (12), 218 (100); HRMS $C_{20}H_{30}O_3$ requires 318.2195, found 318.2200.

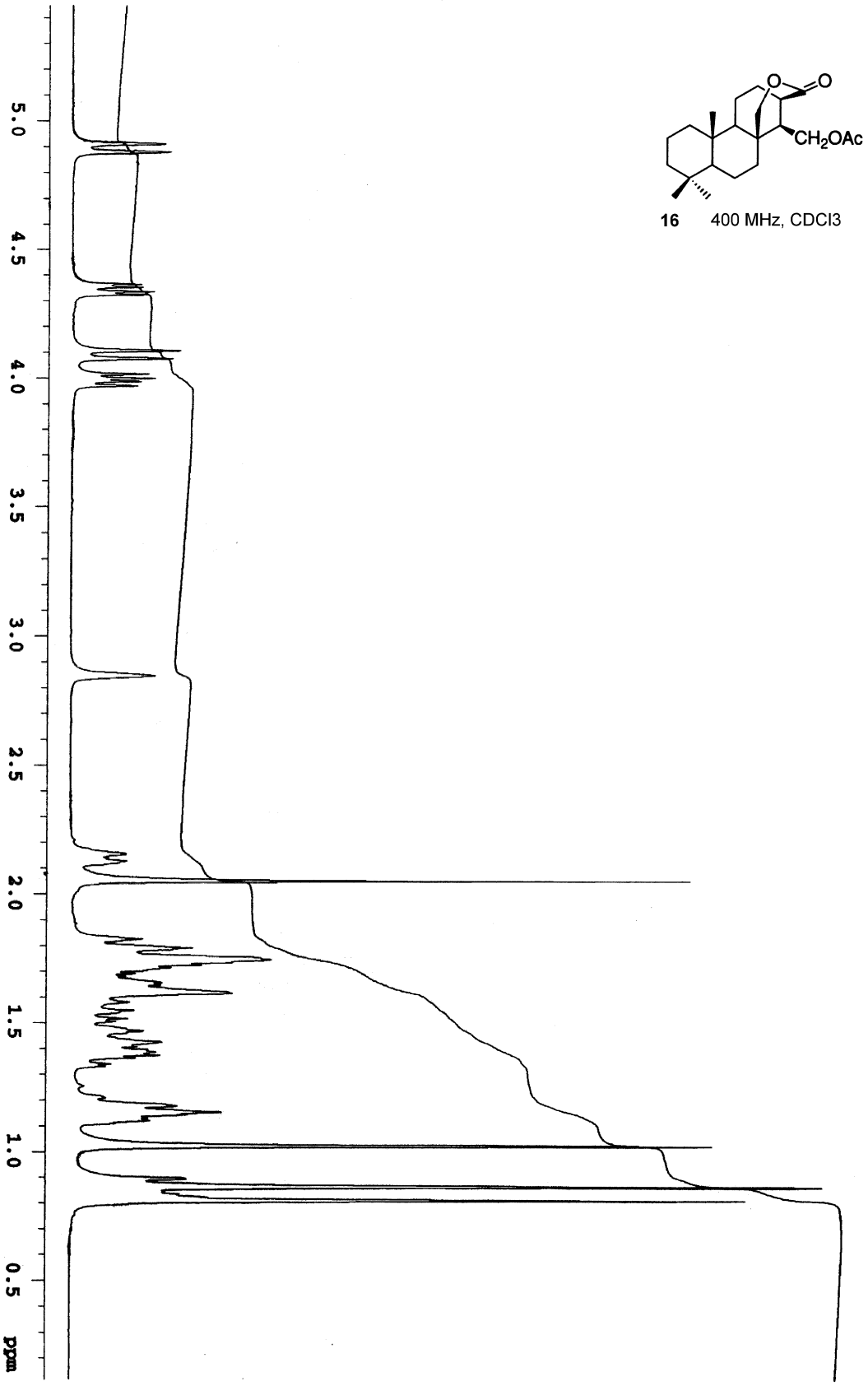

O
O
CHO
2 300 MHz, CDCl3
CHCl3
10
9
8
7
6
5
4
3
2
1
ppm



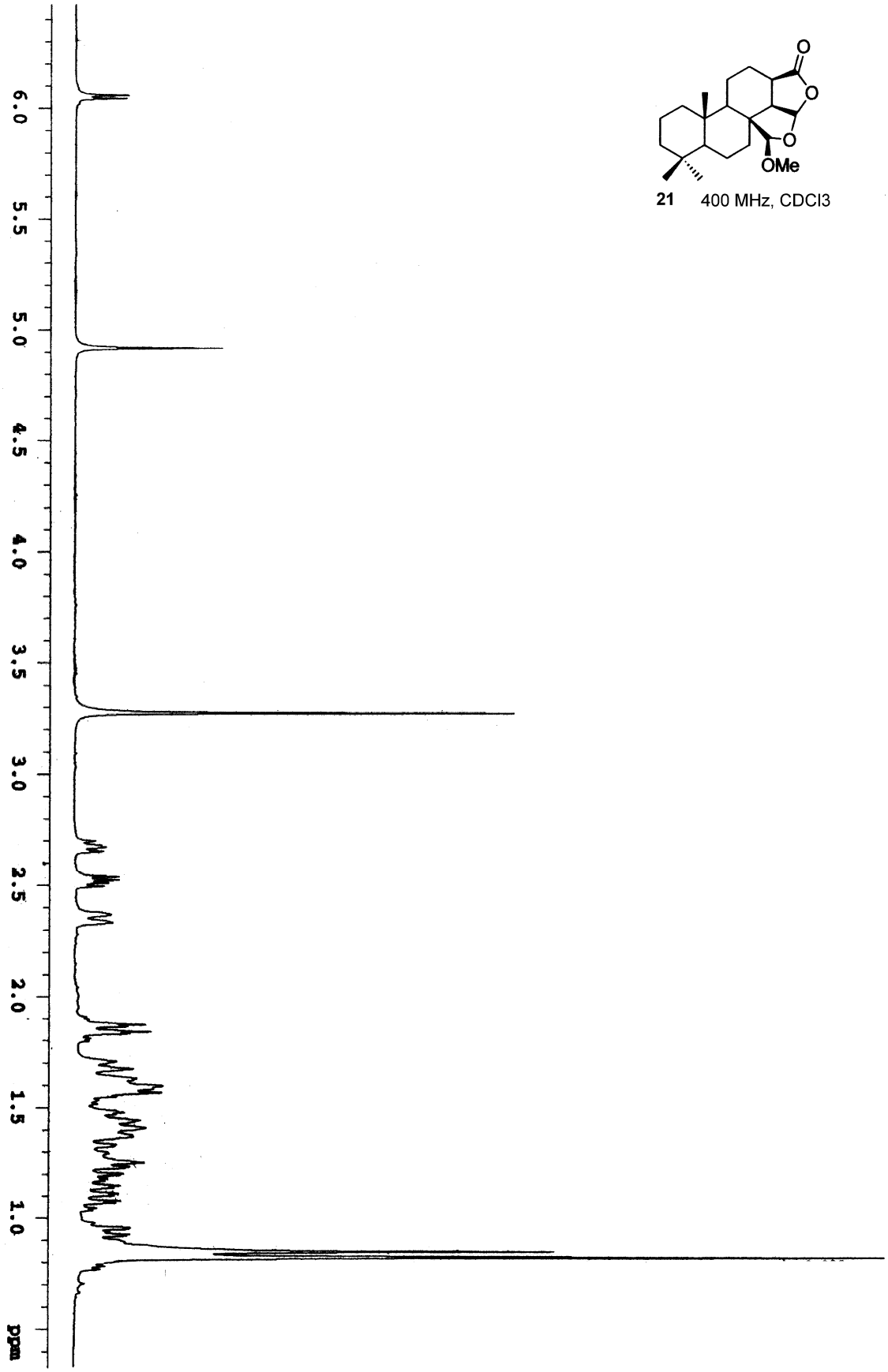
3 400 MHz, CDCl3



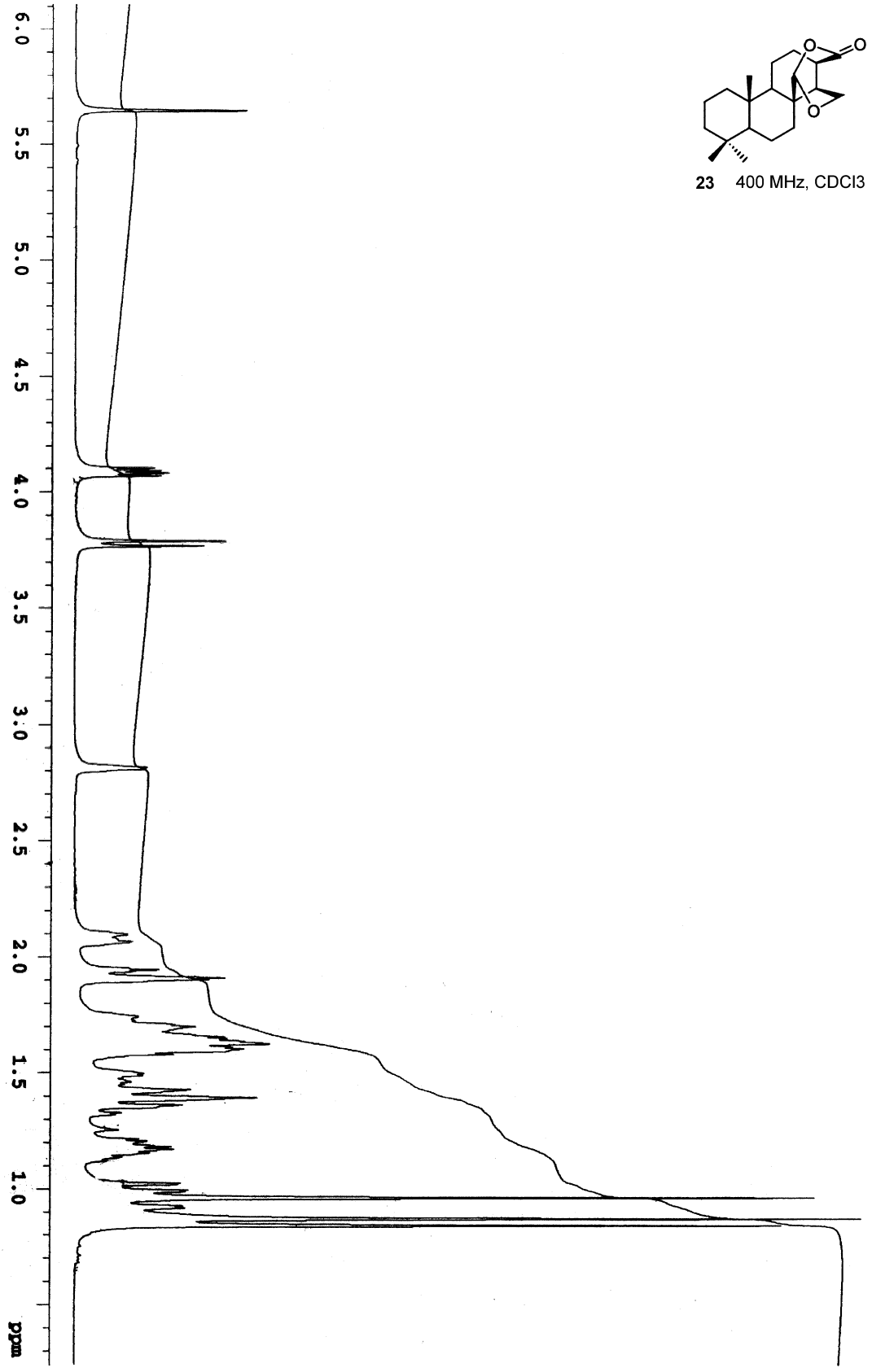
15 400 MHz, CDCl3



16 400 MHz, CDCl3



21 400 MHz, CDCl3



23 400 MHz, CDCl3

22a

HF/6-31G*

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.516759
C	1.446986	0.000000	2.039464
C	2.109928	-1.377417	2.004844
C	1.277215	-2.404783	2.793990
C	-0.152188	-2.559274	2.178653
C	2.018207	-3.749578	3.142233
C	-0.827337	-1.136754	2.165094
C	-0.140109	-3.169820	0.773826
C	-0.991805	-3.485860	3.085476
C	1.068285	-4.536103	4.108367
C	3.315275	-3.411824	3.917269
C	2.417823	-4.525623	1.868214
C	-0.289410	-4.794744	3.443795
C	1.666708	-5.766377	4.864488
C	-2.292711	-1.067034	1.697931
O	-2.472430	-1.129195	0.312838
C	3.958608	-4.619544	4.602469
C	0.706434	-6.183057	5.997876
C	1.893609	-7.015865	3.993531
C	2.983238	-5.326632	5.537641
O	0.471751	-0.860252	-0.680321
O	-0.511359	1.109228	-0.494237
C	-0.624991	1.192084	-1.903961
H	-0.467400	0.930472	1.814809
H	1.427052	0.355097	3.067071
H	2.042797	0.716105	1.480338
H	2.256050	-1.680370	0.976485
H	3.095202	-1.279560	2.442200
H	1.099356	-1.945302	3.765343
H	0.869267	-3.825592	4.911397
H	-0.940095	-5.342389	4.114815
H	-0.186867	-5.413415	2.558947
H	-2.331444	-2.020301	0.017512
H	-0.864433	-0.868143	3.219314
H	-2.681968	-0.102553	2.001405
H	-2.890271	-1.819584	2.198578
H	-1.258259	0.398139	-2.270532
H	0.347782	1.124990	-2.369062
H	-1.072277	2.152694	-2.106160
O	-1.110642	-3.675686	0.290853
H	0.781856	-3.142724	0.210417
H	-1.215323	-2.951914	4.006615
H	-1.935131	-3.710929	2.609428
H	4.043962	-2.963460	3.250732
H	3.090280	-2.665702	4.678128
H	3.154933	-5.285365	2.078813
H	2.869048	-3.857503	1.143526
H	1.588324	-5.024761	1.384503
H	4.821507	-4.281793	5.170722

H	4.346253	-5.314650	3.864592
H	1.201059	-6.887271	6.660670
H	0.400010	-5.329888	6.596484
H	-0.187614	-6.670603	5.626613
H	2.171490	-7.853714	4.626810
H	0.990862	-7.300110	3.463140
H	2.679995	-6.896165	3.262343
H	2.740477	-4.648279	6.354385
H	3.462118	-6.190690	5.992371

22b-chair

HF/6-31G*

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.527528
C	1.444188	0.000000	2.032052
C	2.090712	-1.382094	1.922148
C	1.336324	-2.388072	2.805009
C	-0.186099	-2.463463	2.480729
C	2.040606	-3.771881	3.039320
C	1.294974	-4.432181	4.249784
C	3.506019	-3.524343	3.470851
C	2.062347	-4.613395	1.744002
C	-0.207351	-4.563659	3.969242
C	1.949589	-5.699650	4.886962
C	4.197705	-4.763477	4.044546
C	1.258709	-6.017335	6.228953
C	1.863975	-6.974817	4.028536
C	3.419784	-5.362557	5.212084
O	0.052797	-2.751068	0.091439
O	0.974772	0.111806	-0.670989
O	-1.219037	0.019045	-0.524813
C	-0.831396	-1.052634	2.323639
C	-0.719267	-3.112876	1.189329
C	-1.306675	0.107619	-1.933372
C	-2.206602	-1.419357	1.759861
C	-0.855800	-3.210390	3.659546
O	-2.019152	-2.630889	1.048129
H	-0.451758	0.963442	1.762857
H	1.444537	0.314003	3.074317
H	2.024193	0.728000	1.480846
H	2.124764	-1.687951	0.887293
H	3.113391	-1.293817	2.266607
H	-0.407199	-3.014577	-0.695243
H	-0.949470	-0.612646	3.308600
H	-2.625387	-0.680232	1.100561
H	-2.912445	-1.602106	2.561376
H	-0.798010	-4.188310	1.237930
H	1.343410	-1.925161	3.792124
H	-0.789846	-2.584370	4.546530
H	-1.910665	-3.366742	3.467305
H	-0.714042	-4.977416	4.833238
H	-0.390719	-5.260297	3.158221

H	1.376617	-3.687369	5.042003
H	-0.863614	1.027882	-2.285596
H	-0.802927	-0.726936	-2.399516
H	-2.360248	0.085531	-2.165772
H	4.084963	-3.160940	2.628755
H	3.528118	-2.738959	4.225262
H	2.842727	-5.360591	1.765097
H	2.252876	-3.979884	0.888500
H	1.134254	-5.135504	1.556382
H	5.193431	-4.485911	4.381268
H	4.346595	-5.509099	3.270125
H	1.841347	-6.749527	6.780811
H	1.170083	-5.132069	6.852466
H	0.266949	-6.434755	6.096548
H	2.238702	-7.821454	4.597280
H	0.838574	-7.201643	3.755135
H	2.442115	-6.919879	3.117698
H	3.432521	-4.648676	6.034531
H	3.923081	-6.255276	5.576637

22c-chair

HF/6-31G*

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.525928
C	1.439152	0.000000	2.047781
C	2.100547	-1.375545	1.975295
C	1.301559	-2.393971	2.800727
C	-0.174540	-2.527918	2.306802
C	2.045425	-3.740417	3.116131
C	1.201073	-4.443328	4.233088
C	3.438711	-3.421223	3.710422
C	2.251779	-4.563737	1.827871
C	-0.241353	-4.672069	3.769032
C	1.845406	-5.670271	4.956307
C	4.122093	-4.626701	4.359833
C	1.024059	-6.011578	6.216731
C	1.918696	-6.955947	4.112149
C	3.251516	-5.259953	5.439943
C	-0.460960	-3.061170	0.867826
O	0.849703	-0.462044	-0.694211
O	-1.041189	0.656073	-0.492482
C	-0.853163	-1.124424	2.195059
O	-0.837760	-4.398190	0.866766
C	-1.176478	0.674621	-1.902679
C	-2.074828	-1.469043	1.358762
C	-0.933975	-3.367538	3.363918
O	-1.525096	-2.294660	0.357182
H	-0.475627	0.936042	1.799285
H	1.423820	0.329931	3.084538
H	2.027721	0.727633	1.498738
H	2.206061	-1.675051	0.942356
H	3.100337	-1.278310	2.377327

H	-1.151557	-4.608416	-0.003122
H	-1.117177	-0.764184	3.183127
H	-2.542976	-0.624374	0.879869
H	-2.827429	-1.998526	1.930572
H	0.372488	-2.917848	0.196439
H	1.187891	-1.923719	3.777739
H	-1.040699	-2.750495	4.254272
H	-1.934089	-3.604068	3.026551
H	-0.824106	-5.103081	4.575662
H	-0.280906	-5.374165	2.950234
H	1.144609	-3.693323	5.023344
H	-0.323795	1.155526	-2.359105
H	-1.268568	-0.332551	-2.281476
H	-2.075571	1.235959	-2.104560
H	4.093279	-3.028381	2.940067
H	3.337301	-2.638475	4.461568
H	2.987961	-5.343235	1.960194
H	2.628095	-3.922225	1.037426
H	1.345300	-5.027124	1.471221
H	5.062791	-4.303506	4.798953
H	4.385713	-5.363585	3.607842
H	1.575969	-6.709437	6.840280
H	0.822769	-5.126817	6.814283
H	0.075090	-6.478414	5.979170
H	2.259722	-7.779450	4.733881
H	0.945016	-7.230144	3.720620
H	2.599352	-6.883946	3.276307
H	3.138907	-4.543234	6.252382
H	3.754651	-6.125427	5.865527

2

HF/6-31G*

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.571738
C	1.381908	0.000000	2.240125
C	2.475216	-0.828507	1.579817
C	1.674436	1.481957	2.381261
O	0.517436	2.145934	2.373763
C	-0.590430	1.265121	2.209891
C	1.054027	-1.038573	-0.505467
C	-1.404554	-0.413438	-0.471232
C	0.296241	1.419599	-0.489389
C	-1.484026	-0.711439	-1.966992
C	-0.467293	-1.790992	-2.364873
C	2.457054	-0.727151	0.055274
C	-0.730873	-2.439512	-3.763067
C	0.997957	-1.329391	-2.050413
C	1.950973	-2.507781	-2.365457
C	1.471023	-0.101547	-2.859275
C	1.757512	-3.102713	-3.761593
C	0.317333	-3.548012	-3.990635
C	-2.110611	-3.129881	-3.751564

C	-0.738652	-1.451152	-4.943913
H	1.794492	-3.297398	-1.631594
H	2.983595	-2.191995	-2.264616
H	2.421287	-3.955980	-3.874344
H	2.059851	-2.391531	-4.523586
H	0.205792	-3.948657	-4.995378
H	0.101256	-4.369896	-3.309426
H	-0.631631	-2.618204	-1.672991
H	0.756225	-1.976153	-0.036384
H	-2.123034	0.353963	-0.210284
H	-1.689340	-1.313367	0.068839
H	-1.342647	0.199412	-2.534336
H	-2.490917	-1.048196	-2.181979
H	-2.930180	-2.420967	-3.772609
H	-2.234709	-3.761596	-2.876485
H	-2.214116	-3.762003	-4.628737
H	-1.428241	-0.631562	-4.772380
H	-1.066397	-1.964244	-5.843626
H	0.230991	-1.024828	-5.157056
H	0.746646	0.700355	-2.895550
H	1.699519	-0.360330	-3.881892
H	2.386539	0.299270	-2.438329
H	2.807349	0.253457	-0.244897
H	3.179907	-1.431965	-0.332657
H	-0.563723	-0.871952	1.878416
H	3.437746	-0.518882	1.970254
H	2.334641	-1.868050	1.863647
H	1.249385	-0.345679	3.265229
O	-0.539779	2.165273	-0.891403
H	1.329092	1.762048	-0.431074
H	-1.325999	1.778843	1.613151
H	-1.010433	1.052984	3.186047
O	2.725027	2.011985	2.489653

23

HF/6-31G*

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.547729
C	1.459079	0.000000	2.020404
C	2.158718	-1.290261	1.574058
C	2.254378	1.156343	1.424599
C	2.220339	-1.374959	0.047577
O	1.831968	1.631135	0.245964
C	0.835068	-1.175921	-0.598893
C	0.476599	1.462044	-0.122239
C	-1.433326	-0.116658	-0.557374
C	-0.666796	1.340559	1.861087
O	-0.327204	2.166915	0.759001
C	0.840970	-1.239207	-2.169259
C	-1.496162	-0.216761	-2.082625
C	-0.654262	-1.384544	-2.611462
C	-0.920142	-1.752684	-4.106363

C	-0.075351	-2.997122	-4.449451
C	-2.398800	-2.154299	-4.281310
C	-0.641544	-0.619210	-5.110316
C	1.595895	-2.515434	-2.611761
C	1.566124	-0.010384	-2.770497
C	1.400798	-2.867649	-4.087905
H	-0.533581	-0.839385	1.980165
H	1.517564	0.101001	3.097554
H	3.158446	-1.329645	1.991194
H	1.607976	-2.137861	1.975077
O	3.257446	1.558932	1.904769
H	-0.299180	1.793662	2.774383
H	-1.744487	1.270513	1.928363
H	0.265318	-2.051875	-0.288412
H	-2.039197	0.720776	-0.236535
H	-1.885245	-1.010335	-0.131516
H	0.395345	1.920713	-1.088105
H	-1.187498	0.723048	-2.528254
H	-2.535332	-0.347510	-2.359811
H	-1.004801	-2.264213	-2.070536
H	2.599322	-2.352462	-0.220942
H	2.942851	-0.657824	-0.322722
H	2.657265	-2.406731	-2.415022
H	1.252523	-3.357216	-2.011742
H	2.004540	-0.237472	-3.731907
H	2.376180	0.316984	-2.132051
H	0.913850	0.838406	-2.921338
H	1.906379	-3.807404	-4.294369
H	1.880462	-2.129677	-4.722736
H	-0.487179	-3.850143	-3.911927
H	-0.181244	-3.224417	-5.507579
H	-2.544762	-2.612894	-5.255024
H	-3.068991	-1.303933	-4.226990
H	-2.708974	-2.875278	-3.530121
H	-0.954581	-0.929249	-6.103339
H	0.402295	-0.347704	-5.173902
H	-1.201327	0.277145	-4.864033

TSa

HF/6-31G*

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.528059
C	1.418723	0.000000	2.102633
C	2.172081	-1.299856	1.819362
C	1.385954	-2.532676	2.299426
C	-0.126598	-2.525853	1.911517
C	2.119142	-3.906490	2.085427
C	1.352782	-4.955931	2.958305
C	3.560928	-3.789537	2.635605
C	2.204983	-4.262908	0.582553
C	-0.128760	-5.014980	2.568533
C	2.029767	-6.350399	3.153636

C	4.272497	-5.136544	2.782524
C	1.298632	-7.119339	4.272698
C	2.021453	-7.254899	1.907652
C	3.473662	-6.111381	3.641999
O	0.196783	-1.654316	-0.328019
O	1.087878	0.480702	-0.585723
O	-1.152268	0.366580	-0.515497
C	-0.819181	-1.156224	2.159836
C	-0.587296	-2.647702	0.456257
C	-1.497289	0.172183	-1.888853
C	-2.181848	-1.388548	1.509118
C	-0.815653	-3.654848	2.715214
O	-1.889693	-2.269957	0.412205
H	-0.486203	0.941091	1.768858
H	1.323716	0.138594	3.175588
H	1.978017	0.848153	1.730013
H	2.428020	-1.357743	0.770533
H	3.108838	-1.253904	2.356951
H	0.286057	-1.874534	-1.252365
H	0.886192	1.077944	-1.297454
H	-0.918642	-0.938628	3.215564
H	-2.654170	-0.503124	1.120227
H	-2.870548	-1.887694	2.172322
H	-0.448761	-3.578830	-0.057789
H	1.339178	-2.413675	3.380377
H	-0.804398	-3.365305	3.762325
H	-1.855625	-3.759561	2.434452
H	-0.657239	-5.710837	3.206876
H	-0.256607	-5.390835	1.558006
H	1.371973	-4.526189	3.959758
H	-2.221562	0.933917	-2.121357
H	-0.640683	0.277396	-2.542262
H	-1.940347	-0.805792	-1.995651
H	4.155192	-3.147031	1.993927
H	3.529284	-3.311120	3.613155
H	3.033052	-4.923202	0.376697
H	2.373616	-3.374249	-0.015528
H	1.320543	-4.760216	0.205644
H	5.244011	-4.967806	3.237213
H	4.475966	-5.569702	1.808607
H	1.883673	-7.984565	4.567175
H	1.158301	-6.504411	5.157048
H	0.327724	-7.486465	3.959715
H	2.400474	-8.236743	2.172498
H	1.016830	-7.396621	1.521967
H	2.637213	-6.885581	1.099801
H	3.432850	-5.721004	4.657397
H	3.994367	-7.062772	3.703395

TSb

HF/6-31G*

C	0.000000	0.000000	0.000000

C	0.000000	0.000000	1.505578
C	1.439473	0.000000	2.150631
C	2.253301	1.265306	1.831075
C	2.231316	-1.347722	1.985866
C	1.435920	2.543466	2.007649
C	1.353764	-2.466031	2.640396
C	3.550041	-1.233804	2.788529
C	2.587030	-1.605939	0.502626
C	0.117234	2.496074	1.231438
C	-0.018497	-2.544137	1.962461
C	2.030946	-3.852492	2.888278
C	-0.742773	1.334264	1.773718
C	0.331728	2.363741	-0.285704
C	-0.777416	-1.218687	2.049357
C	-2.102371	1.183025	1.090200
O	-1.849757	0.406465	-0.100565
O	0.499249	0.974285	-0.682531
O	1.445018	3.012148	-0.674160
O	-0.777338	2.722944	-1.024833
C	-1.005899	4.105717	-1.275744
C	4.263752	-2.572421	2.987786
C	1.134260	-4.696386	3.816748
C	2.276693	-4.688143	1.618596
C	3.354533	-3.607635	3.641747
H	-0.042234	-0.911709	-0.560788
H	1.203378	0.066510	3.210162
H	2.664641	1.238256	0.830920
H	3.097800	1.312977	2.503917
H	1.192859	2.685008	3.057102
H	2.019420	3.400863	1.702024
H	1.162178	-2.095515	3.647482
H	-0.413464	3.428997	1.381603
H	-0.634602	-3.292946	2.442374
H	0.069206	-2.860532	0.927861
H	-1.971199	0.947298	-0.878034
H	-0.884176	1.484310	2.837204
H	-0.996632	-1.010046	3.092725
H	-1.730661	-1.328299	1.548714
H	-2.800159	0.623369	1.689652
H	-2.550737	2.123378	0.812090
H	1.595195	2.888163	-1.606644
H	-1.957464	4.155561	-1.779865
H	-1.052437	4.672055	-0.355677
H	-0.236809	4.514906	-1.912628
H	4.227638	-0.544230	2.296521
H	3.332910	-0.812779	3.768902
H	3.443049	-2.255395	0.407890
H	2.853515	-0.686245	-0.005164
H	1.790828	-2.078404	-0.059368
H	5.135130	-2.409837	3.614611
H	4.646786	-2.945809	2.043753
H	1.682037	-5.565423	4.165999
H	0.821567	-4.135002	4.692526
H	0.245489	-5.064377	3.316545

H 2.640856 -5.670916 1.899711
H 1.362076 -4.839464 1.054156
H 3.009958 -4.258243 0.951125
H 3.120058 -3.271798 4.650396
H 3.884265 -4.549482 3.750978

TSc

HF/6-31G*

C 0.000000 0.000000 0.000000
C 0.000000 0.000000 1.508681
C 1.419691 0.000000 2.106336
C 2.031874 -1.392917 2.273838
C 1.080154 -2.332189 3.040375
C -0.234415 -2.547375 2.228755
C 1.742399 -3.634500 3.629159
C -0.899972 -1.142952 2.024937
C -0.015291 -3.241303 0.878946
C -1.221287 -3.412386 3.045987
C 0.633002 -4.351390 4.471973
C 2.876798 -3.207578 4.593104
C 2.365714 -4.511636 2.521546
C -0.586242 -4.685814 3.601360
C 1.087532 -5.505767 5.423217
C -2.144122 -1.100223 1.126735
O -1.676968 -0.593928 -0.157553
C 3.388016 -4.343693 5.482004
C -0.062157 -5.840607 6.396005
C 1.468194 -6.818780 4.714468
C 2.260305 -4.987959 6.281547
O 0.670932 -0.967640 -0.567514
O -0.056905 1.166846 -0.569941
C 0.276352 1.355302 -1.951557
H -0.480036 0.937454 1.765149
H 1.341654 0.467521 3.081978
H 2.069803 0.639641 1.517256
H 2.302502 -1.797124 1.306457
H 2.958281 -1.269951 2.817048
H 0.766953 -1.775088 3.922244
H 0.292825 -3.580505 5.164319
H -1.339737 -5.197525 4.185373
H -0.328611 -5.360764 2.792195
H -2.291112 0.027065 -0.538563
H 0.514368 -1.078020 -1.500765
H -1.211822 -0.843730 3.017957
H -2.869507 -0.394285 1.504011
H -2.599917 -2.054189 0.944240
H 0.136043 2.406285 -2.132826
H -0.390939 0.784469 -2.584931
H 1.307038 1.084334 -2.124238
O -0.920174 -3.599657 0.191719
H 1.004596 -3.402326 0.546825
H -1.582723 -2.820745 3.883533

H	-2.081123	-3.665235	2.437821
H	3.713643	-2.802476	4.033688
H	2.514775	-2.406818	5.236344
H	3.054051	-5.232687	2.931712
H	2.942810	-3.906358	1.830638
H	1.639754	-5.072550	1.947221
H	4.130637	-3.942614	6.165400
H	3.907231	-5.088665	4.888369
H	0.306360	-6.475680	7.195133
H	-0.474317	-4.946095	6.854390
H	-0.872173	-6.376970	5.915181
H	1.619897	-7.597145	5.455526
H	0.679018	-7.159245	4.052007
H	2.378540	-6.752602	4.136149
H	1.873451	-4.250752	6.983268
H	2.651792	-5.803216	6.883450