Supporting Information

Chirality transition in the epoxidation of (-)-α-pinene and successive hydrolysis studied by Raman optical activity and DFT

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Synthesis of α-pinene oxide

Preparation of the catalyst ZnAl-[Salen(Mn)] and the catalytic epoxidation reaction were similar with the method of Anderson.[S1] Catalyst characterization was shown by XRD and IR spectra. 0.6mL (-)-α-pinene (dissolved in 20mL toluene), 1.05mL pivalaldehyde and 0.100 g of ZnAl-[Salen(Mn)] were stirred in a twin-necked round-bottom flask equipped with condenser at room temperature (298 K) while bubbling molecular oxygen at atmospheric pressure. After completion of the reaction, the catalyst was filtered off. Evaporation of the toluene solvent on a rotary evaporator gave an oily residue that was distilled through a vacuum-jacketed column, yielding α-pinene oxide as colorless oil, b.p. 89–90° (28 mm.).The purity of the product was confirmed by GC-MS (Agilent 6890N GC/5973 MS detector), and ^{1}H NMR (Bruker DRX-400).

Visualization of vibrational modes and atomic contributions to the ROA signals

The pyVib2 program[S2, S3] is used for the analysis of the vibrational modes of Raman as well as the ROA spectra from Gaussian outputs. For vibrational normal modes, the size and the direction of the nuclear motion for each vibrational mode in polyatomic chiral molecules are represented by a sphere centered on the nucleus. The radius of the sphere relies on the magnitude of the nuclear motion and the hemisphere shaded by yellow or blue color indicates the direction of the nuclear motion in the vibration. It is easy to find the contribution of single nuclei to the vibrational energy of a normal mode and powerful to ascertain affinities between vibrational modes for molecules

with similar structure. In particular, the analysis of scattering cross sections can be done using modules such as atomic contribution patterns (ACPs) as either 2D or 3D pictorial representations, respectively. One can read the Hessian, the gradients of the various polarizability tensors involved in Raman and ROA calculations which are capable of evaluating the contribution of each atom to the calculated Raman scattered intensities. Sphere in ACPs with yellow color on each nucleus represents negative contribution for the ROA intensity and red for positive. With this tool we can visualize the generation of ROA and analyze the vibrational spectra and hope to get practically understanding of the vibrational modes in these chiral molecules.

References

S1. Bhattacharjee, S., Dines, T. J. and Anderson, J. A., *J. Catal.,* 2004, **225**, 398-407.

S2. Hug, W., *Chem. Phys.,* 2001, **264**, 53-69.

S3. Zerara, M., *J. Comput. Chem.,* 2008, **29**, 306-311.

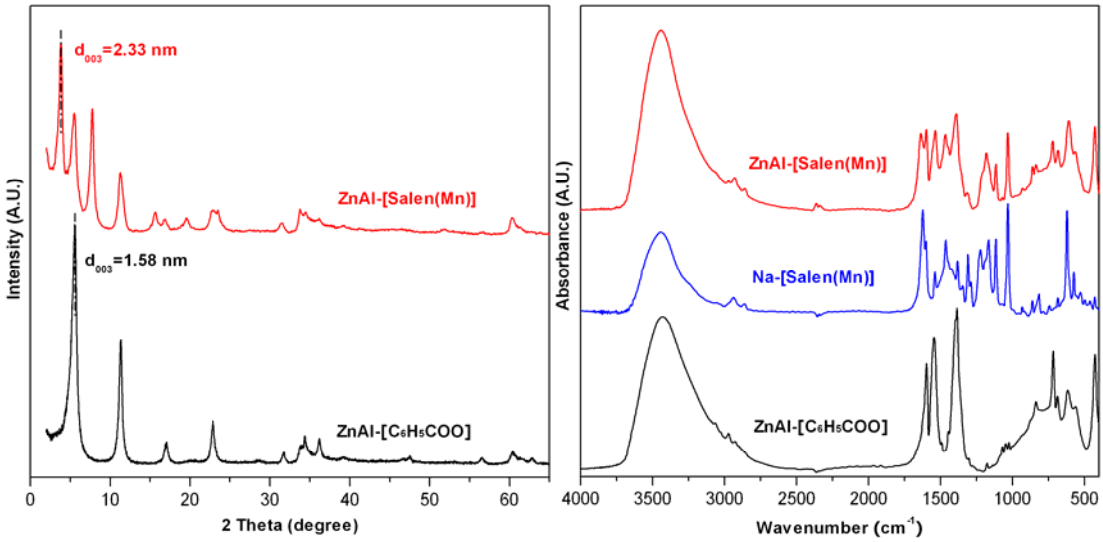

Figure S1. XRD (left) and IR (right) spectra of catalyst ZnAl-[Salen(Mn)] and its precursors

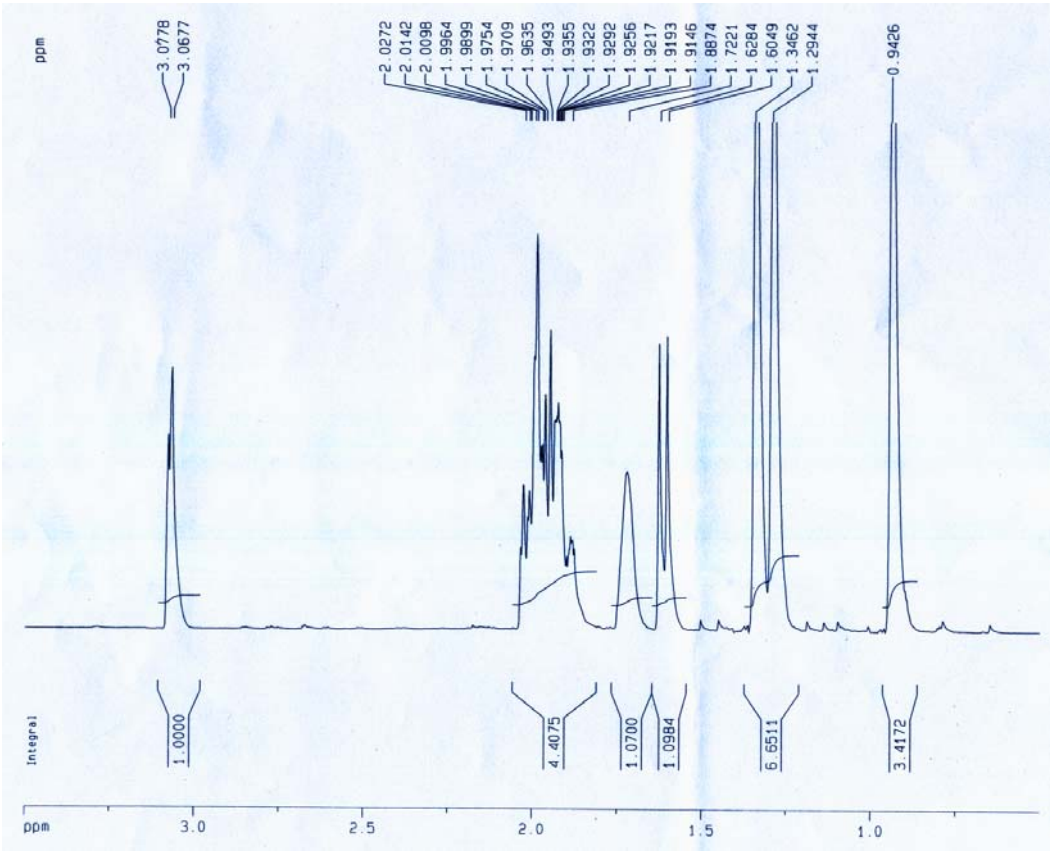

Figure S2. ^{1}H NMR spectrum of α-pinene oxide (in $CDCl_3$)

^{1}H NMR spectrum shows: δ 0.94, 1.29, and 1.35 (3 s, 9H, $3CH_3$), 1.60–2.03 (m, 6H, $2CH_2$ and 2CH), 3.07 (m, 1H, CHOC)

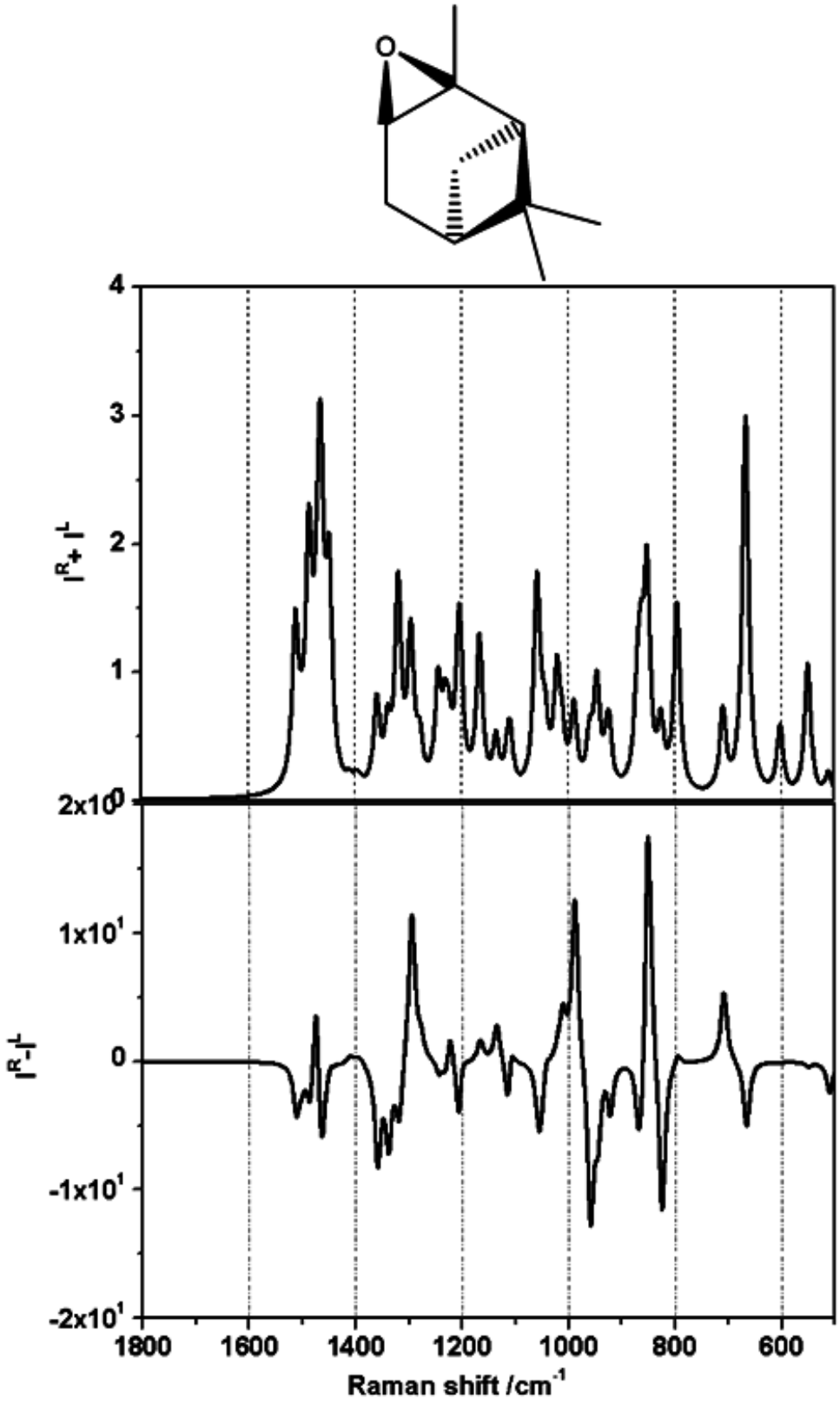

Figure S3. The computational simulation of Raman and ROA Spectra of cis -α-pinene oxide (The Raman and ROA Spectra were plotted with a Lorentzian band shape with a full width at half-maximum height of 7 cm^{-1})

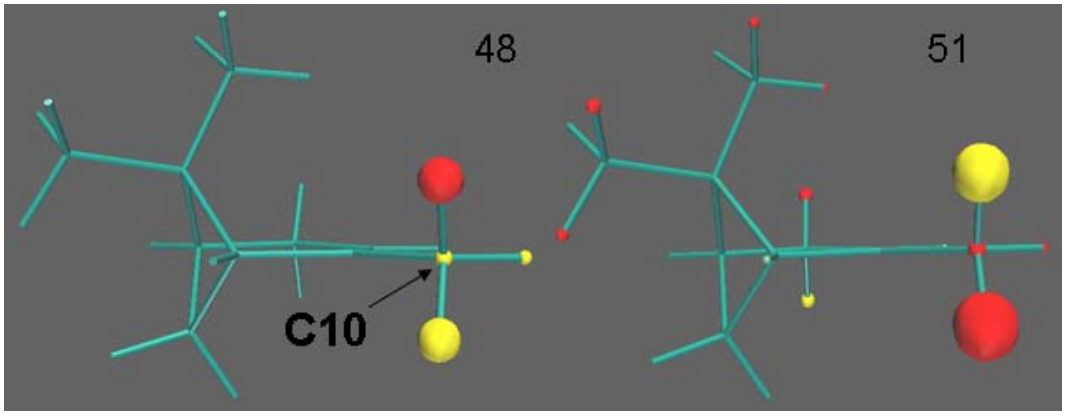

Figure S4. (-)-α-pinene ACP pictorial representation of mode 48 (left) and mode 51 (right) (the position of atoms C10 is labeled)

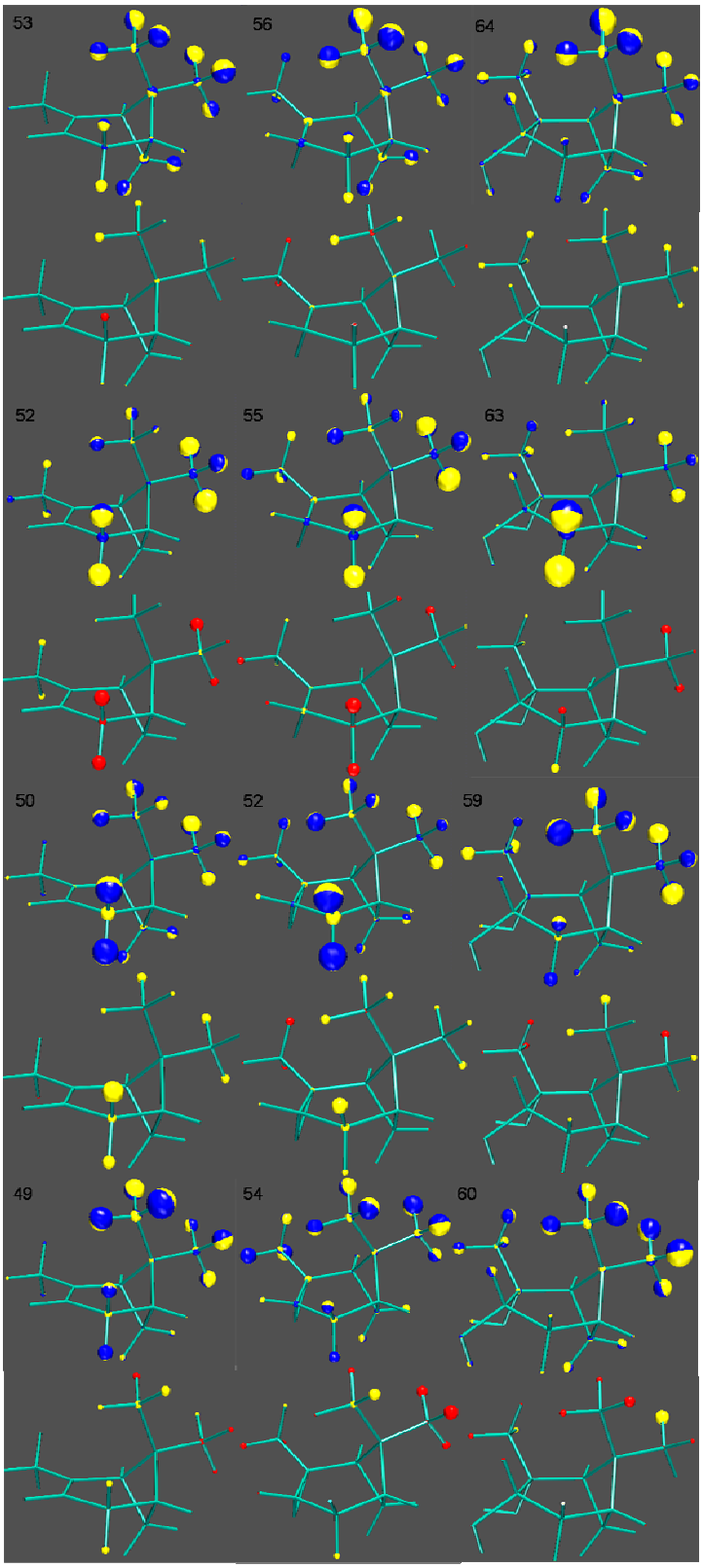

Figure S5a. Similar vibrational normal modes (upper) and their ACPs (bottom) for (-)-α-pinene (left column), α-pinene oxide (middle column) and (-)-pinanediol (right column)

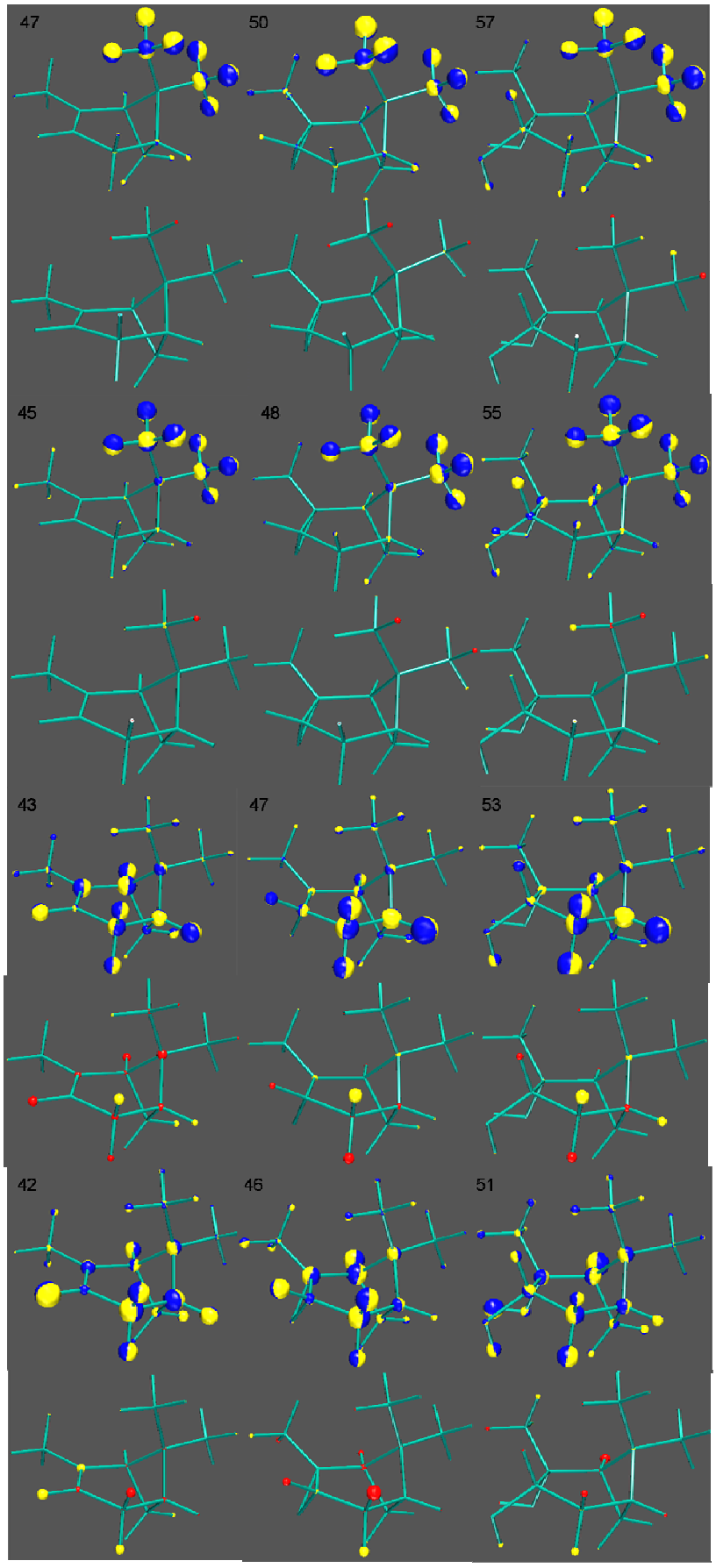

Figure S5b. (Continued)

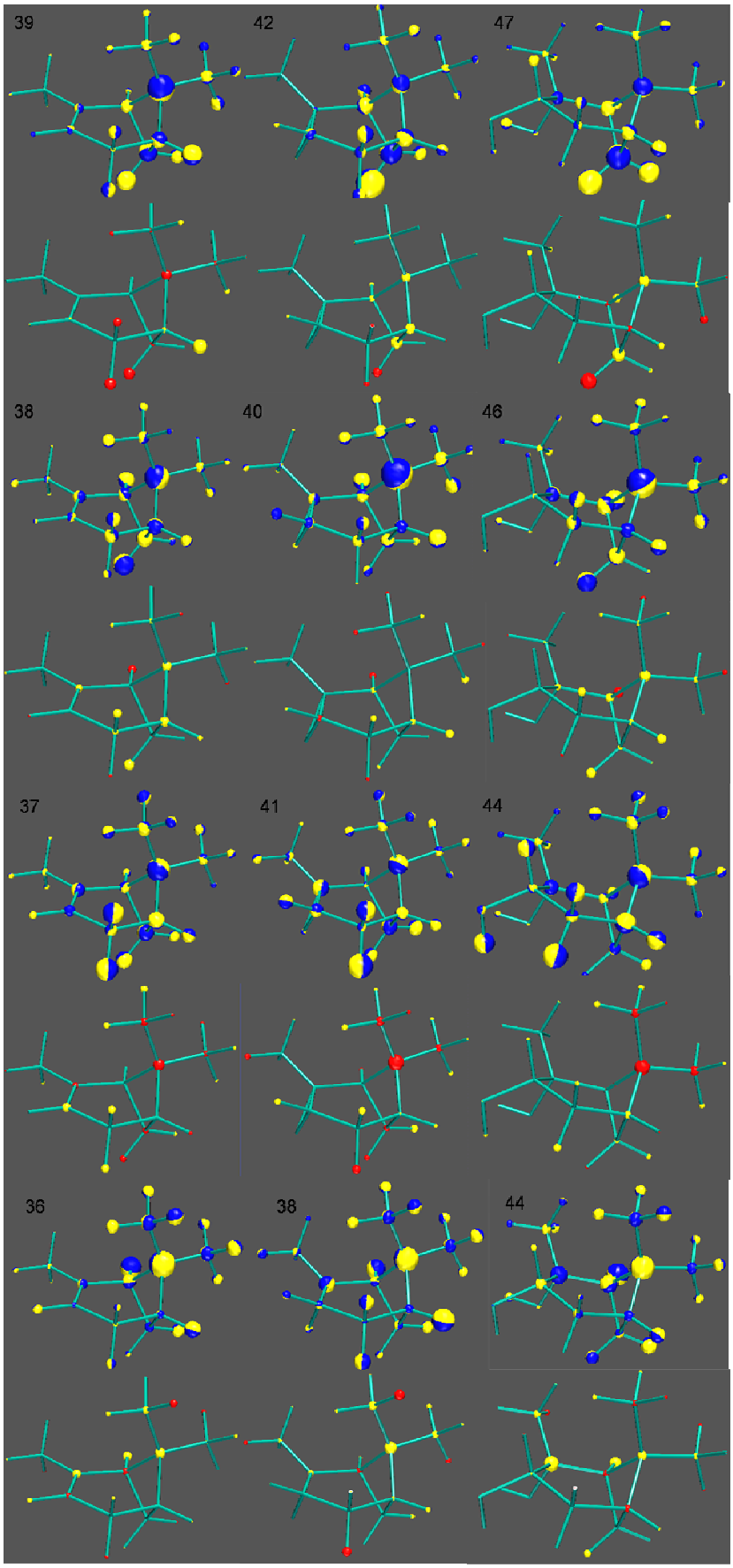

Figure S5c. (Continued)

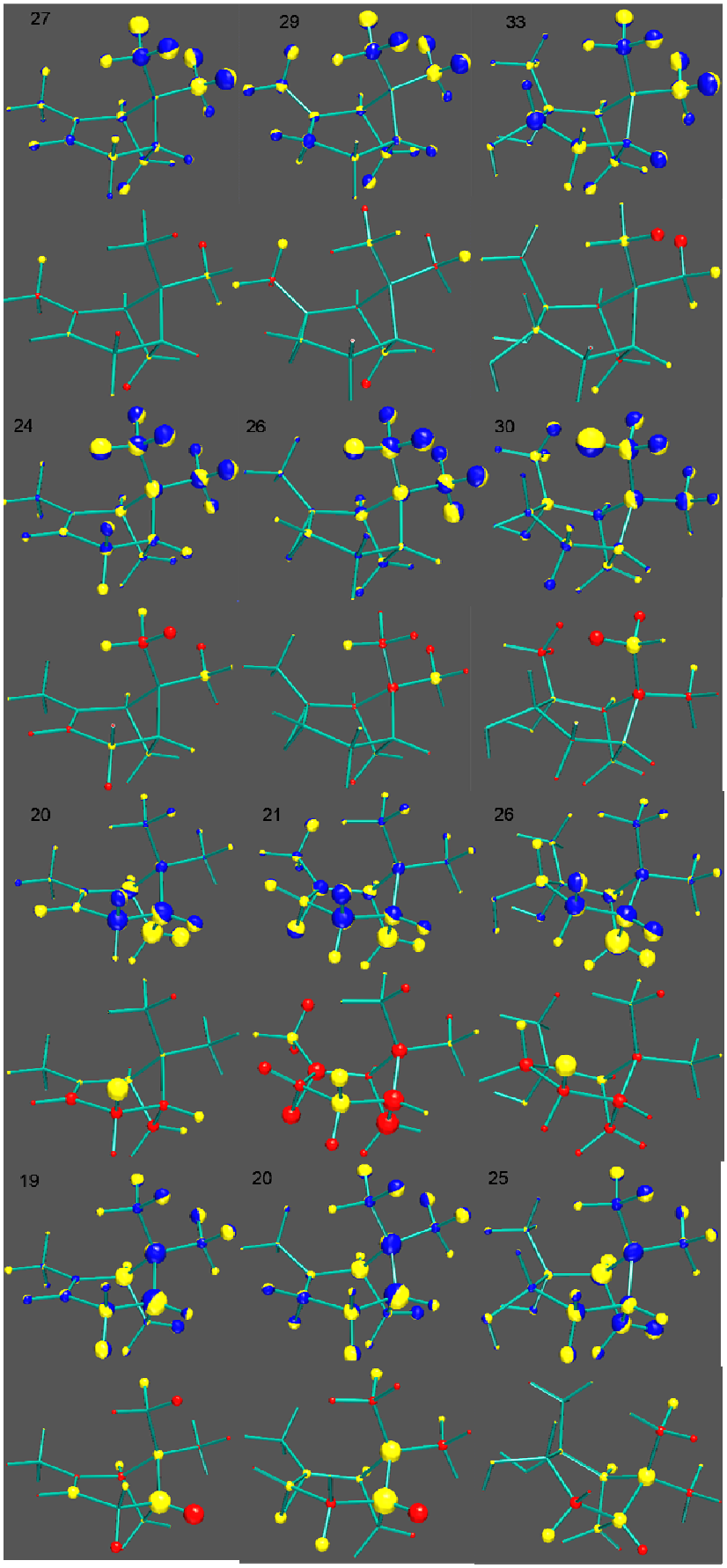

Figure S5d. (Continued)

Table S1. Mulliken atomic charges distribution (in electron units, e) for three molecules and their comparison respectively

entry	α-pinene (1)	α-pinene oxide (2)	2,3-(-)-pinanediol (3)	△(2-1)	△(3-1)	△(3-2)
1C	2.377816	2.113743	2.175336	-0.26407	-0.20248	0.06159
2C	-0.681953	-0.700664	-0.548981	-0.01871	0.13297	0.15168
3C	0.773799	1.443122	1.723701	0.66932	0.9499	0.28058
4C	0.74696	0.63749	0.65663	-0.10947	-0.09034	0.01913
5C	1.96839	1.69201	1.81204	-0.27638	-0.15635	0.12003
6C	0.78291	1.13273	0.99365	0.34982	0.21074	-0.13909
7C	-2.57139	-2.54765	-2.48239	0.02374	0.089	0.06526
8C	1.72635	1.8703	1.90032	0.14395	0.17396	0.03001
9C	1.5734	1.70218	1.6234	0.12878	0.05001	-0.07877
10C	0.96658	1.09053	1.26016	0.12395	0.29358	0.16963
11H	-1.16447	-1.08006	-1.05241	0.08441	0.11206	0.02765
12H	-0.95957	-0.85091	-0.78838	0.10867	0.17119	0.06253
13H	-0.41934	-0.39172	-0.43389	0.02763	-0.01454	-0.04217
14H	-0.40022	-0.47927	-0.49096	-0.07905	-0.09074	-0.01169
15H	-0.89939	-0.94474	-0.95837	-0.04536	-0.05898	-0.01363
16H	-0.70916	-0.69231	-0.75392	0.01685	-0.04476	-0.06162
17H	-0.75066	-0.70629	-0.70102	0.04437	0.04964	0.00527
18H	-0.38116	-0.35617	-0.61246	0.02498	-0.2313	-0.25629
19H	-0.25308	-0.2584	-0.1483	-0.00532	0.10478	0.1101
20H	-0.15243	-0.25206	-0.32848	-0.09964	-0.17605	-0.07641
21H	-0.27502	-0.28039	-0.28871	-0.00536	-0.01369	-0.00833
22H	-0.266	-0.29597	-0.27759	-0.02997	-0.01159	0.01838
23H	-0.38722	-0.38205	-0.39846	0.00516	-0.01125	-0.01641
24H	-0.14577	-0.20349	-0.29834	-0.05772	-0.15257	-0.09485
25H	-0.13039	-0.13318	-0.3031	-0.00279	-0.1727	-0.16992
26H	-0.36899	-0.28929	-0.18218	0.0797	0.18681	0.10711
27O	--	-0.8375	-0.64835	-0.26407	-0.20248	0.18915
28H	--	--	0.07355	-0.01871	0.13297	0.06159
29O	--	--	-0.58439	0.66932	0.9499	0.15168
30H	--	--	0.06188	-0.10947	-0.09034	0.28058

Table S2. Raman vibrational analysis of (-)-α-pinene

Mode	$\omega_{cal.}$,cm^{-1}	$\omega_{exp.}$,cm^{-1}	Mode description
56	1717	1666	C2=C3 stretch
55	1502	1477	C(4,6,)-H scissor; C(8,9)-H antisymmetric deformation
53	1483	1477	C(8,9)-H antisymmetric deformation; C6-H scissor
52	1475	1452	C4-H scissor; C(8,9)-H antisymmetric deformation
51	1469	——	C10 antisymmetric deformation
50	1467	1438	C4-H scissor; C(8,9)-H antisymmetric deformation
49	1464	1428	C(8,9)-H antisymmetic deformation; C4-H scissor
48	1455	——	C(10)-H antisymmetric deformation
47	1407	——	C(8,9)-H symmetric deformation
46	1397	1379	C10-H symmetric deformation
45	1388	——	C(8,9)-H symmetric deformation
44	1356	1346	six member ring C-C stretch; C(1,3,4,5,6)-H wag; C10-H symmetric deformation
43	1347	1331	C(1,3,4,5)-H wag; six member ring C-C stretch; four member ring breath
42	1326	1311	C(1,3,4,5)-H wag; C4-C5 stretch
41	1286	1270	C7-C(1,5) stretch; C(1,5)-H wag; C4-H twist
40	1264	1252	C(1,3,5,6)-H in-plane wag; C4-C(3,5) stretch
39	1238	1232	four member ring breath; C(5,6)-H wag; C4-H twist
38	1232	1216	C(1,4,6)-H wag; six and four member ring deformation
37	1222	——	C4-H twist; C6-H wag; six four member ring deformation
36	1195	1187	C(1,3,4,5,6,8,9)-H wag; four member ring deformation
35	1180	1170	C2-C10 stretch; C(1,3,4,5,6)-H wag
34	1141	1130	C2-C10, C7-C9 stretch; C(1,3,4,5,6,8)-H deformation
33	1115	1107	four member ring deformation; C(1,4,5,6,8,9)-H twist
32	1097	1091	six member ring deformation; C(1,5,6,10)-H twist
31	1071	1069	C(3,4,5,6,10)-H wag
30	1055	——	six and four member ring breath
29	1050	1043	C10-H twist
28	1027	1018	C(1,3,4,6,10)-H out-plane wag
27	1011	1018	C(8,9)-H out-plane wag
26	972	——	six member ring deformation, four member ring breath; C(8,9)-H out-plane wag
25	964	956	all C-H deformation
24	950	——	C(8,9)-H out-of plane wag
23	937	931	six member ring deformation; C10-H out-of plane wag
22	914	909	six and four member ring deformation; all C-H deformation
21	895	890	six member ring breath; C(4,6)-H in-plane wag

20	847	842	six and four member ring deformation; C6-H wag
19	823	822	six and four member ring deformation; C(4,6,8,9)-H out-of plane wag
18	795	794	C(3,4,6,10)-H wag
17	777	774	six member ring breath
16	672	668	six member ring breath; C6-H in-plane wag
15	623	628	six member ring deformation, four member ring breath
14	571	566	C2=C3 twist; C10-H twist

Table S3. Raman vibrational analysis of α-pinene oxide

Mode	$\omega_{cal.}$,cm^{-1}	$\omega_{exp.}$,cm^{-1}	Mode description
59	1503	1472	C6-H scissor; C(8,9,10)-H antisymmetric deformation
57	1488	1472	C2-C3 stretch; C(8,9,10)-H antisymmetric deformation; C4-H scissor
55	1474	1440	C4-H scissor; C(8,9,10)-H antisymmetric deformation
54	1469	1440	C(8,9,10)-H antisymmetric deformation
53	1468	——	C(10,8,9)-H antisymmetric deformation
52	1463	——	C4-H scissor; C(8,9,10)-H antisymmetric deformation
51	1451	——	C2-C3 strech; C10-H antisymmetric deformation
49	1399	1396	C10-H symmetric deformation
48	1389	1396	C(8,9)-H symmetric deformation
47	1359	1361	C3-C4 stretch; C(1,3,4,5)-H out-of plane wag
46	1339	1329	C1-C2, C4-C5 stretch; C(1,3,4,5)-H wag
45	1321	1309	C1-C2 stretch; C(1,3,4,6)-H out-of plane wag
44	1293	1283	C(1,5)-H wag; C4-H twist; C7-C(5,1) stretch
43	1285	1268	C(1,3,4,5,6)-H wag
42	1250	1240	C(1,6)-H wag, C4-H twist; four member ring deformation
41	1238	1227	all C-H wag; four member ring deformation
40	1229	1191	four member ring breath; C(1,3,4,5,6,9)-H wag
39	1212	1191	C2-C10 stretch; six and four member ring deformation; all C-H wag
38	1199	1191	six and four member ring deformation; C(1,4,5,8,9,10)-H wag
37	1172	1159	C7-C9 stretch; C(1,3,4,5,8)-H wag
36	1140	1144	four member ring deformation; all C-H wag
35	1110	1107	six member ring deformation; C(3,5,6,10)-H wag
34	1096	1086	C(1,3,4,5,6)-H twist
33	1081	——	six member ring deformation; C(1,3,6,10)-H in-plane wag
32	1066	1064	six, four and three member ring deformation; C(4,5,6,10)-H wag
31	1056	1045	C(1,3,4,5,6,10)-H wag; C-O stretch
30	1017	1013	C(1,3,4,8,9,10)-H wag
29	1005	——	C(5,6,8,9,10)-H in-plane wag
28	975	945	four member ring breath; C(4,6,8,9,10)-H wag
27	954	945	C7-C(1,5) stretch; C(3,4,8,9)-H wag
26	948	945	C(8,9)-H out-of plane wag
25	940	945	six and four member ring deformation; C(3,6,8,10)-H wag
24	907	——	C1-C(6,7) stretch; C(4,6,10)-H in-plane wag

23	897	901	skeletal C-C, C-O deformation; C(1,4,5)-H wag
22	865	865	C3-O stretch; six and four member ring deformation; C(1,4,6,10)-H wag
21	847	845	C2-O stretch; six and four member ring deformation; C(3,4,8,9,10)-H in plane wag
20	821	820	C-O, six and four member ring deformation; C(6,8,9)-H twist
19	772	772	C-O, six member ring breath; C(1,5,6,10)-H wag
18	707	700	C-O, six member ring deformation; C6-H in plane wag
17	650	657	skeletal breath
16	628	628	C-O, six and four member ring deformation;C7-C8 stretch
15	522	572	six member ring deformation
14	507	516	skeletal deformation

Table S4. Raman vibrational analysis of (-)-pinanediol

Mode	$\omega_{cal.}$,cm^{-1}	$\omega_{exp.}$,cm^{-1}	Mode description
64	1493	1476	C(8,9,10)-H antisymmetric deformation
63	1486	——	C4-H scissor, C9-H antisymmetric deformation
62	1480	1461	C(9,10)-H antisymmetric deformation
58	1440	——	C3-H, O29 -H wag; C8-H scissor
56	1395	——	C10-H symmetric deformation
52	1342	1312	C(1,3,4,5)-H, O27-H wag; C10-H scissor; six member ring deformation
50	1306	1237	six and four member ring deformation; O(27,29)-H wag; C(1,3,5) - H wag; C4-H twist
49	1293	1224	C(1,3,5,6)-H, O(27,29)- H wag;C4-H twist; six and four member ring deformation;
48	1278	1224	C(1,3,5)-H, O29-H wag; C4-H twist; C7-C(5,1) stretch six and four member ring deformation
46	1233	1196	C(1,4,5,6)-H wag; four member ring breath; six ring deformation;
44	1209	1170	four member ring deformation; C(1,5)-H wag;C6-H twist
43	1192	——	six and four member ring deformation; all C-H, O-H wag
41	1139	1136	all C-H, O-H wag; six and four member ring deformation
39	1115	1114	six member ring deformation; C(1,4,5,6,10)-H, O(27,29)-H wag
38	1093	1088	six member ring deformation; C2-C10 stretch; C(1,4,5,6,10)-H, O-H wag
37	1066	1052	six member ring breath; C-O29 stretch; C(4,5,6,10)-H wag
36	1053	1052	six member ring deformation; C2-C10 stretch; O27-H wag; C6-H twist
32	973	965	C(8,9,10)-H wag; six and four member ring deformation; C(8,9,10)-H out-of plane wag
30	947	944	C(8,10)-H wag; C7-C9 stretch
29	928	930	six member ring deformation; C(4,5,6,10)-H, O28-H wag
28	919	911	six and four member ring deformation; C(4,6,10)-H wag
27	904	——	six member ring breath; C(4,6,10)-H wag
26	867	867	six and four member ring deformation
25	835	834	six and four member ring deformation; C(4,6,8,9)-H wag
24	828	——	six and four member ring deformation; C(1,8,9,10)-H wag
23	716	——	six member ring breath

Table S5. Calculated values of $\beta(G')^2$ and $\beta(A)^2/3$ of (-)-α-pinene, α-pinene oxide and (-)-pinanediol (unit: $10^4A^5/AMU$)

	(-)-α-pinene		α-pinene oxide		(-)-pinanediol	
mode	$\beta(G')^2$	$\beta(A)^2/3$	$\beta(G')^2$	$\beta(A)^2/3$	$\beta(G')^2$	$\beta(A)^2/3$
14	-0.7063	-0.14923	0.3061	0.04527	0.0359	-0.05223
15	0.9063	0.22437	-0.1774	-0.08137	0.0631	0.01957
16	0.6194	0.07463	-0.4981	-0.1	-0.1070	0.03747
17	2.3960	-0.00523	0.9693	0.20097	-0.3729	-0.10097
18	-2.3547	-0.42717	-2.0615	-0.19217	0.3942	0.02297
19	-0.9808	0.122	2.5236	0.21747	-1.0960	-0.20257
20	-0.4049	0.093	-3.0722	-0.39987	0.3089	0.09717
21	-1.7565	-0.07843	5.2903	1.15337	-0.3287	-0.0138
22	-0.0208	0.1098	-2.8888	-0.51467	-0.2958	-0.08203
23	1.7599	-0.01907	0.2619	-0.02993	-0.6843	-0.20903
24	-0.1376	0.1639	-0.2487	-0.0167	1.6664	0.22143
25	1.4387	0.23347	0.6808	-0.18487	-2.1804	-0.4136
26	0.2127	-0.26727	0.6427	0.23447	1.2173	0.0735
27	0.2122	-0.03437	0.1645	0.02407	0.6546	0.10547
28	0.6903	0.01617	0.4862	0.16283	2.0263	0.35803
29	-0.5472	0.14783	-0.2551	-0.17197	-1.5930	-0.38543
30	0.2576	-0.07923	0.7115	0.1247	1.3086	0.3542
31	-0.8913	-0.34477	-1.3279	-0.17617	0.2179	0.21357
32	1.0530	0.25897	1.0408	-0.11517	-2.8911	-0.76767

33	-0.7280	0.0487	-0.0949	-0.04187	-0.4575	-0.07953
34	-1.4749	0.0414	-0.6165	-0.13627	-0.3407	0.03067
35	1.9579	0.34557	1.7209	0.14217	-1.1053	0.19923
36	-1.3467	-0.06117	0.4107	0.0806	2.3390	-0.05693
37	0.4591	0.14797	1.2845	0.15183	1.4811	0.1897
38	-1.7884	-0.26673	-1.1034	-0.16837	0.8852	0.1058
39	1.5427	-0.10793	-0.7647	-0.1421	-2.5505	-0.40783
40	0.3439	0.0786	-0.6790	0.00157	0.5907	0.15427
41	1.3283	0.01223	1.4802	0.32637	4.4360	0.50953
42	-0.2871	-0.39183	-1.2451	-0.44003	-0.1899	-0.21457
43	1.8749	0.26873	-3.5269	-0.60377	1.3517	0.3918
44	-0.8369	-0.13477	5.7683	0.91013	-1.8276	-0.65987
45	0.0552	-0.00623	-0.1772	-0.60367	0.3654	0.1641
46	0.5137	0.099	1.2260	0.22063	-2.5180	-0.1124
47	0.0106	0.00197	0.1210	-0.20703	-0.6083	-0.17583
48	-0.1565	0.0737	0.0675	0.00857	1.0253	0.60403
49	-0.4758	-0.3874	0.0661	0.02793	2.5730	0.5527
50	-4.4490	-1.09647	0.0370	0.00217	-2.1332	-0.42703
51	0.5351	0.0692	2.0720	0.13583	0.2836	-0.1872
52	3.1185	0.84727	-2.2558	-0.5424	2.6137	0.64733
53	-0.7315	0.05397	-1.4701	-0.2869	-0.4765	-0.0505
54	0.0118	-0.1162	2.3379	0.108	-0.0001	-0.26513

55	-0.8363	0.06107	2.0542	0.488	0.1296	0.00907
56	-1.0720	-0.10123	-0.4142	0.26767	0.0414	0.03027
57			-0.8972	-0.48353	-0.0673	0.0105
58			-0.2131	-0.0181	-1.2808	-0.2184
59			-1.5720	-0.05427	0.1730	-0.2129
60					0.0983	0.00503
61					0.0768	0.29993
62					1.9782	0.22283
63					1.1210	0.16097
64					-2.6918	-0.5361
65					0.5614	0.1019
66					-0.5740	-0.0274