

Evaluation of the Katsuki-Sharpless Epoxidation Precatalysts by ESI-FTMS, CID and IRMPD Spectroscopy

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This supplementary information file contains :

Figure S1. Mass spectrum in positive mode of a ~2.5 mM methanol solution of Ti(O <i>i</i> Pr) ₄ and DMT (to this solution, 1 μL of formic acid was added prior to the analysis). The base peak (<i>m/z</i> 579) is [Ti(HDMT) ₃] ⁺	S2
Figure S2. Mass spectrum in negative mode of a ~2.5 mM methanol solution of Ti(O <i>i</i> Pr) ₄ and DMT. It shows the dimeric species [(MMT)(DMT)Ti ₂ (OMe) ₄] ⁻ (<i>m/z</i> 557) and a signal 28 Da higher at <i>m/z</i> 585 related to the retention of one of the initial isopropoxide ligands.	S2
Figure S3. Spectrum in negative mode of a ~2.5 mM methanol solution of Ti(O <i>i</i> Pr) ₄ and DIPT.	S2
Figure S4. Mass spectrum in negative mode of ~0.5 mM CH ₂ Cl ₂ /EtOH (1:1) solution of Ti(OEt) ₄ and DET. It shows the dimeric species [(MET)(DET)Ti ₂ (OEt) ₄] ⁻ (<i>m/z</i> 655). ..	S3
Figure S5. MS ² (IRMPD at the 1080-1100 cm ⁻¹ range) spectrum in negative mode of of the mass-selected dimer [(MIPT)(DIPT)Ti ₂ (OMe) ₄] ⁻ (<i>m/z</i> 641) from a ~2.5 mM methanol solution of Ti(O <i>i</i> Pr) ₄ and DIPT.	S3
Figure S6. MS ² (IRMPD at 1290 cm ⁻¹) spectrum in negative mode of the mass-selected monomer [(MMT)(DMT)Ti] ⁻ (<i>m/z</i> 385) from a ~2.5 mM methanol solution of Ti(O <i>i</i> Pr) ₄ and DMT.	S3
Figure S7. MS ² (IRMPD at the 1155-1190 cm ⁻¹ range) spectrum in negative mode of the mass-selected dimer [(MMT)(DMT)Ti ₂ (OMe) ₄] ⁻ (<i>m/z</i> 557) from a ~2.5 mM methanol solution of Ti(O <i>i</i> Pr) ₄ and DMT	S4
Figure S8. Comparison between the IRMPD spectra of the analog species [(MMT)(DMT)Ti(OMe) ₄] ⁻ <i>m/z</i> 557 (blue) and [(MIPT)(DIPT)Ti(OMe) ₄] ⁻ <i>m/z</i> 641 (red).	S4
Table S1. Atomic coordinates for the optimized geometries.....	S5

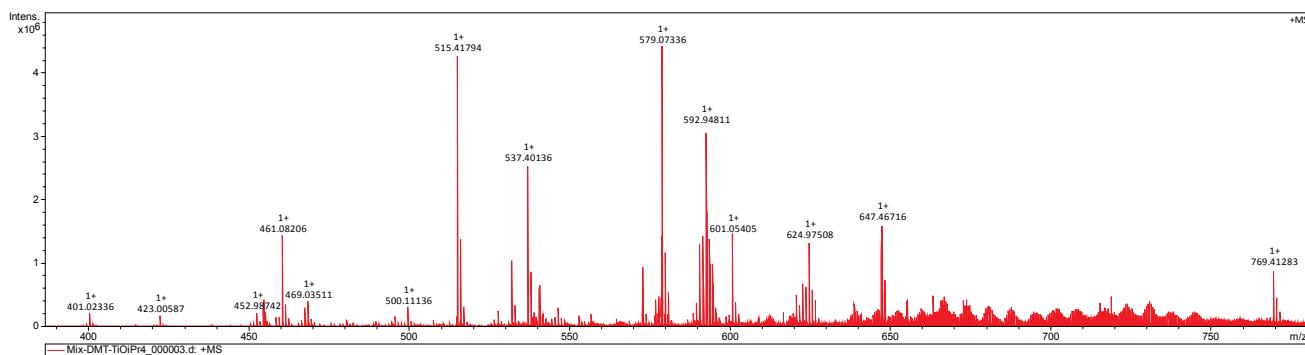


Figure S1. Mass spectrum in positive mode of a ~2.5 mM methanol solution of $Ti(OiPr)_4$ and DMT (to this solution, 1 μ L of formic acid was added prior to the analysis). The base peak (m/z 579) is $[Ti(HDMT)_3]^+$.

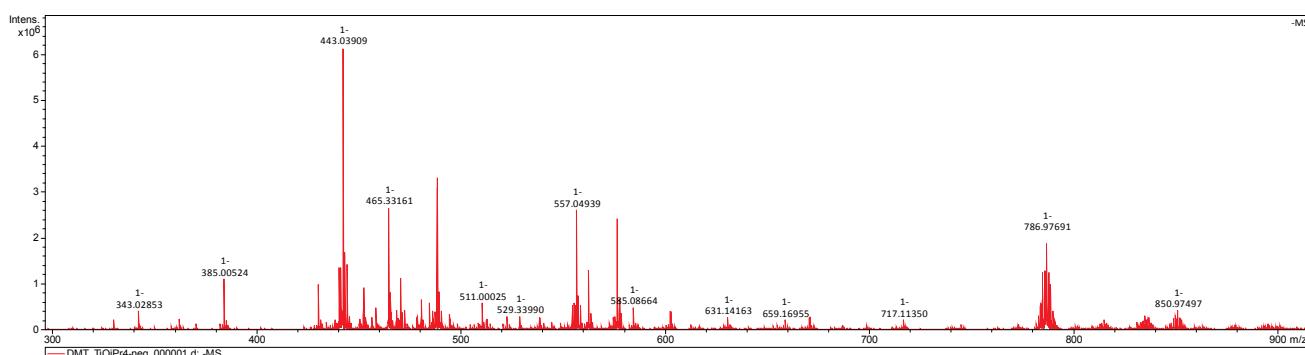


Figure S2. Mass spectrum in negative mode of a ~2.5 mM methanol solution of $Ti(OiPr)_4$ and DMT. It shows the dimeric species $[(MMT)(DMT)Ti_2(OMe)_4]^-$ (m/z 557) and a signal 28 Da higher at m/z 585 related to the retention of one of the initial isopropoxide ligands.

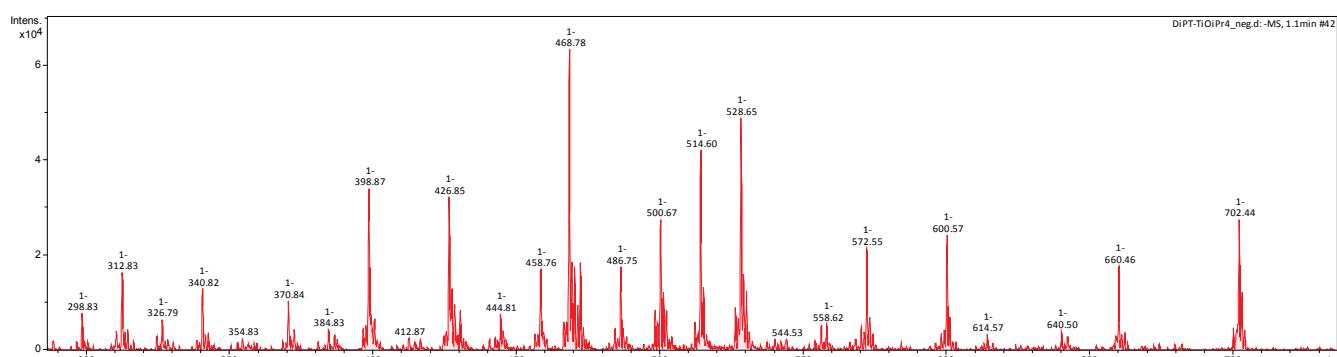


Figure S3. Spectrum in negative mode of a ~2.5 mM methanol solution of $Ti(OiPr)_4$ and DIPT.

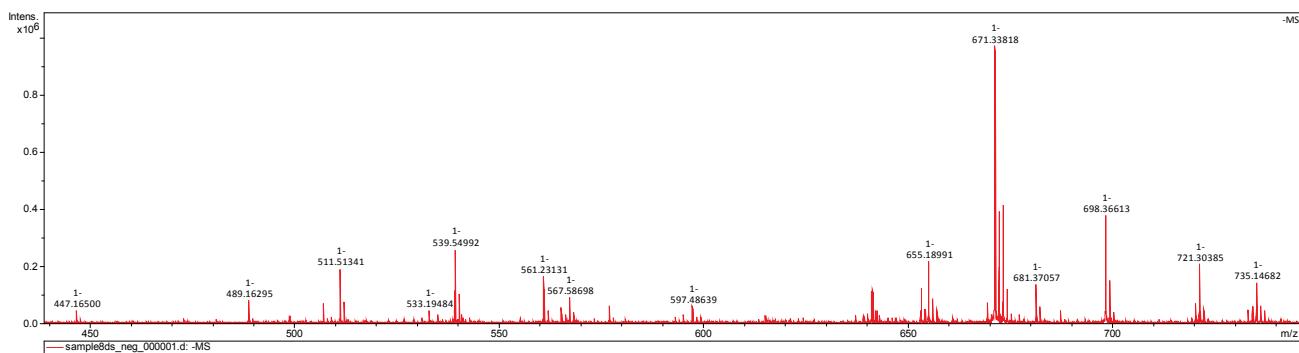


Figure S4. Mass spectrum in negative mode of $\sim 0.5\text{ mM}$ $\text{CH}_2\text{Cl}_2/\text{EtOH}$ (1:1) solution of $\text{Ti}(\text{OEt})_4$ and DET. It shows the dimeric species $[(\text{MET})(\text{DET})\text{Ti}_2(\text{OEt})_4]^-$ (m/z 655).

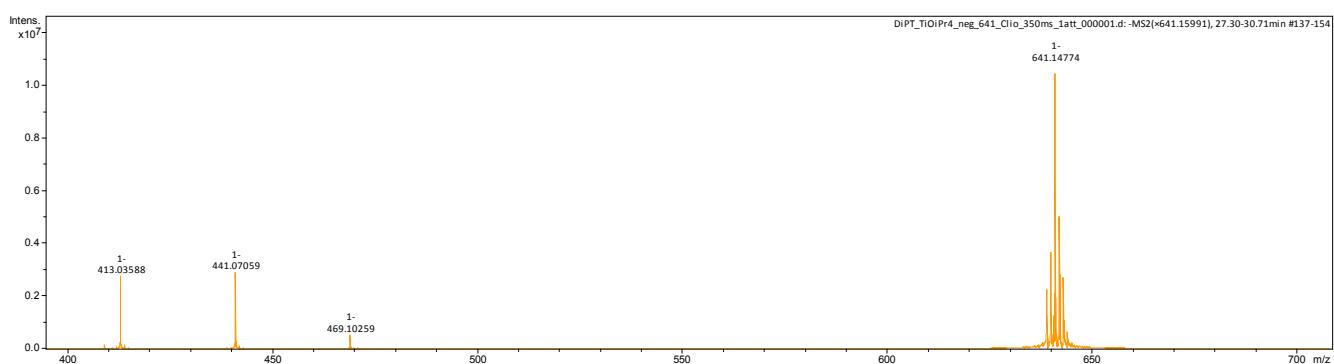


Figure S5. MS² (IRMPD at the 1080-1100 cm^{-1} range) spectrum in negative mode of the mass-selected dimer $[(\text{MIPT})(\text{DIPT})\text{Ti}_2(\text{OMe})_4]^-$ (m/z 641) from a $\sim 2.5\text{ mM}$ methanol solution of $\text{Ti}(\text{O}i\text{Pr})_4$ and DIPT.

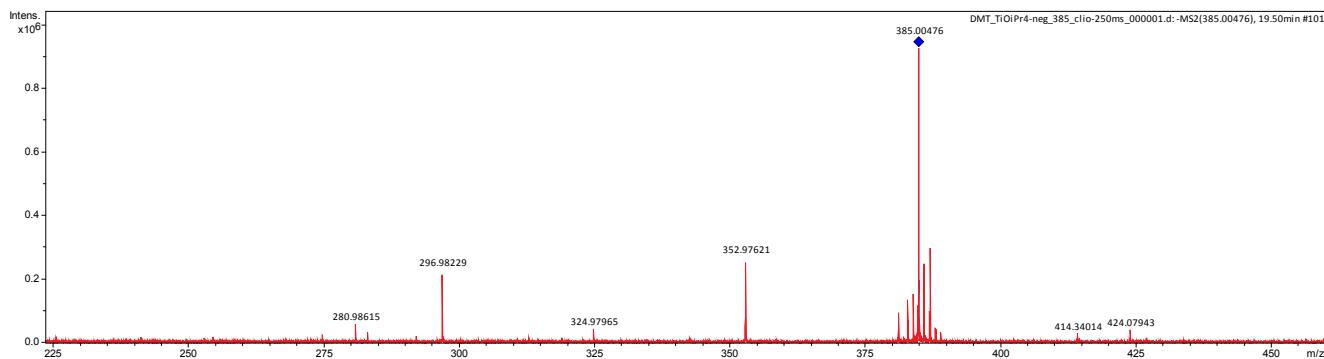


Figure S6. MS² (IRMPD at 1290 cm^{-1}) spectrum in negative mode of the mass-selected monomer $[(\text{MMT})(\text{DMT})\text{Ti}]^-$ (m/z 385) from a $\sim 2.5\text{ mM}$ methanol solution of $\text{Ti}(\text{O}i\text{Pr})_4$ and DMT.

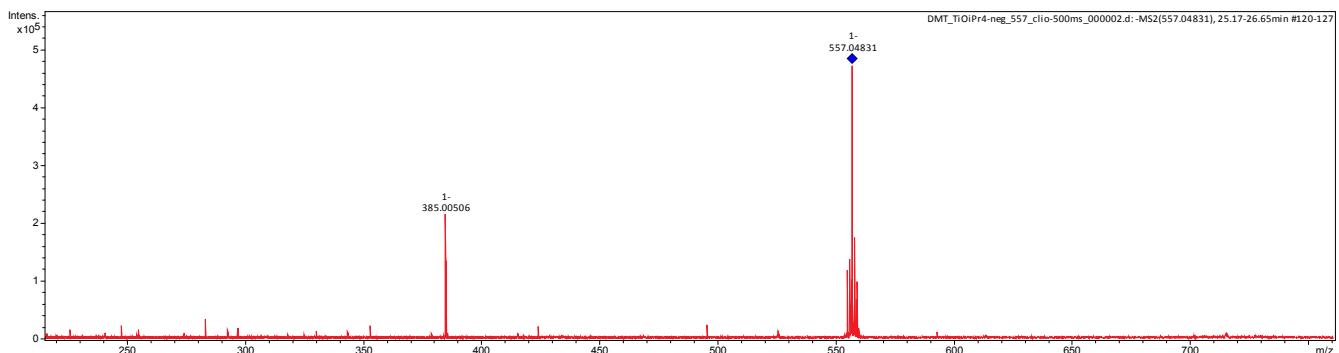


Figure S7. MS^2 (IRMPD at the 1155-1190 cm^{-1} range) spectrum in negative mode of the mass-selected dimer $[(MMT)(DMT)Ti_2(OMe)_4]^-$ (m/z 557) from a ~ 2.5 mM methanol solution of $Ti(OiPr)_4$ and DMT

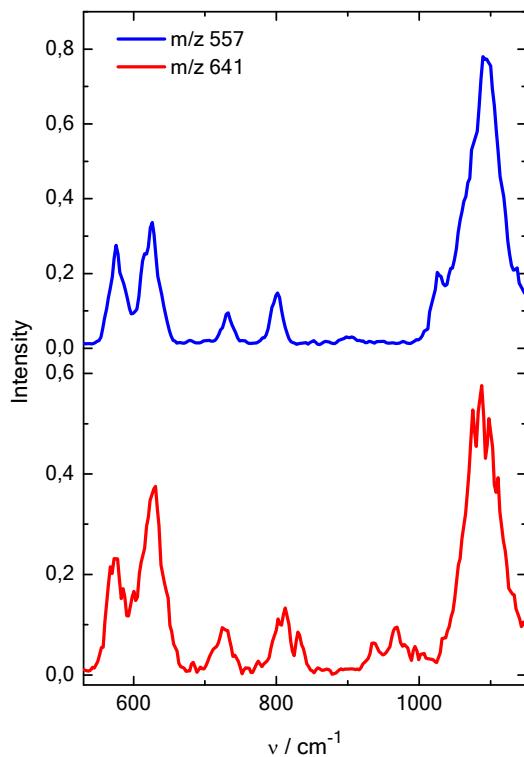


Figure S8. Comparison between the IRMPD spectra of the analog species $[(MMT)(DMT)Ti(OMe)_4]^-$ m/z 557 (blue) and $[(MIPT)(DIPT)Ti(OMe)_4]$ m/z 641 (red).

Table S1. Coordinates of the optimized geometries.

Theory – m/z 385 – Figure 1 c) no carboxylate interaction			
6	-0.517292000	-0.314716000	0.516743000
6	1.029722000	-0.363870000	0.616435000
8	-0.849399000	-0.646722000	-0.865139000
8	1.587424000	0.104476000	-0.643609000
22	0.407423000	-0.111109000	-2.010130000
6	0.981722000	-0.379526000	-4.693771000
6	0.152815000	0.931964000	-4.545141000
8	0.777753000	-1.150263000	-3.518717000
8	0.174252000	1.321071000	-3.189065000
6	-1.154365000	-1.226779000	1.615664000
8	-2.082090000	-1.994049000	1.313731000
8	-0.581263000	-0.999069000	2.720338000
6	0.668257000	2.016957000	-5.485625000
8	1.260438000	1.777538000	-6.523717000
8	0.360155000	3.256431000	-5.074223000
6	0.785444000	4.326059000	-5.935600000
1	1.872236000	4.314458000	-6.051479000
1	0.319515000	4.233684000	-6.920375000
1	0.461594000	5.241071000	-5.439881000
6	0.534918000	-1.214859000	-5.896596000
8	-0.591866000	-1.246142000	-6.347902000
8	1.551171000	-1.960237000	-6.373028000
6	1.220157000	-2.851053000	-7.452151000
1	0.449742000	-3.559406000	-7.137134000
1	0.858214000	-2.285567000	-8.314742000
1	2.146888000	-3.371775000	-7.693423000
6	1.638234000	0.463191000	1.745239000
8	2.598395000	0.118635000	2.402986000
8	1.055252000	1.677521000	1.860699000
6	1.546921000	2.496971000	2.927872000
1	1.395392000	1.993078000	3.886216000
1	2.612121000	2.708276000	2.795415000
1	0.963919000	3.417940000	2.882568000
1	1.368475000	-1.391152000	0.777403000
1	-0.879530000	0.718714000	-4.866120000
1	2.046912000	-0.145529000	-4.813388000
1	-0.865628000	0.708241000	0.695415000
Theory – m/z 385 – Figure 1 b) carboxylate interaction			
22	-0.101476000	-0.496140000	-3.098752000
6	0.991151000	-0.839685000	-5.711021000
6	-0.078655000	0.331179000	-5.823459000
8	1.221677000	-1.044037000	-4.365758000
8	-0.875935000	0.220079000	-4.699270000
6	0.673689000	1.664333000	-5.905965000
8	1.031137000	2.188526000	-6.947776000
8	0.934469000	2.165567000	-4.689573000
6	1.674325000	3.392422000	-4.633889000
1	2.666363000	3.261021000	-5.075707000
1	1.143482000	4.181936000	-5.173003000
1	1.750299000	3.632366000	-3.573705000
6	0.447137000	-2.095305000	-6.402613000
8	-0.0003037000	-3.083125000	-5.869371000
8	0.524502000	-1.955688000	-7.758304000
6	-0.007496000	-3.044136000	-8.525319000
1	0.537916000	-3.968356000	-8.313189000
1	-1.065394000	-3.198349000	-8.294557000
1	0.118714000	-2.756769000	-9.570085000
1	-0.650151000	0.254048000	-6.758223000
1	1.911920000	-0.563141000	-6.248595000
6	0.118692000	-0.914868000	-0.586075000
6	-1.199100000	-1.708740000	-0.925159000
8	0.984068000	-1.175555000	-1.665047000
8	-1.464309000	-1.474678000	-2.288949000
6	-0.999062000	-3.185471000	-0.587137000

8	-0.904870000	-3.593611000	0.558987000
8	-0.927146000	-3.978609000	-1.665519000
6	-0.668087000	-5.364612000	-1.408583000
1	0.283717000	-5.484347000	-0.883626000
1	-1.467059000	-5.801864000	-0.802207000
1	-0.626060000	-5.836132000	-2.390672000
6	-0.223078000	0.601155000	-0.623082000
8	-0.246560000	1.039628000	-1.873752000
8	-0.457980000	1.272857000	0.370752000
1	-2.031455000	-1.360062000	-0.296878000
1	0.534380000	-1.200048000	0.387048000
Theory – m/z 557 – Figure 2 c) symmetric			
22	-0.032950000	6.214580000	1.685167000
22	-2.414458000	5.986558000	4.067910000
8	-0.598015000	6.807635000	3.581481000
8	-2.168004000	5.649756000	2.129942000
8	-0.533499000	5.115666000	0.219737000
6	-1.236410000	4.000379000	0.701993000
6	-2.553045000	4.549835000	1.345444000
6	-0.434235000	3.376553000	1.866810000
8	0.235492000	4.295056000	2.493967000
8	-0.515421000	2.180179000	2.152577000
6	-3.574147000	4.959513000	0.285910000
8	-4.065401000	6.056163000	0.122489000
8	-3.913518000	3.884663000	-0.476176000
1	-1.444615000	3.265735000	-0.082304000
1	-3.022811000	3.763684000	1.954510000
6	0.102312000	7.536379000	4.536491000
6	-0.444671000	7.045219000	5.946856000
8	-1.706414000	6.532086000	5.744307000
6	-0.096945000	9.049493000	4.420506000
8	0.632884000	9.853554000	4.981719000
8	-1.159573000	9.388088000	3.689761000
6	0.503375000	5.990923000	6.558839000
8	0.280943000	4.805902000	6.553754000
8	1.670227000	6.428009000	7.123289000
1	-0.489341000	7.900801000	6.636768000
1	1.181455000	7.366897000	4.439153000
6	-4.875963000	4.131530000	-1.509471000
1	-5.818221000	4.488002000	-1.083123000
1	-4.501045000	4.878598000	-2.214530000
6	1.931615000	7.817442000	7.385768000
1	1.864903000	8.441499000	6.492167000
1	2.951134000	7.843301000	7.774985000
6	-1.408096000	10.793588000	3.535646000
1	-2.304918000	10.860212000	2.920575000
1	-1.569863000	11.263078000	4.509839000
1	1.247893000	8.202215000	8.151257000
1	-0.561967000	11.273926000	3.037597000
1	-5.020776000	3.172843000	-2.009187000
8	1.772150000	6.454080000	1.855946000
6	2.893565000	5.658599000	2.146773000
1	3.449844000	5.440044000	1.222805000
1	2.593672000	4.711186000	2.612325000
8	-0.432190000	7.753297000	0.787319000
6	-1.314052000	8.172741000	-0.213861000
1	-2.284866000	8.458137000	0.214202000
1	-1.488546000	7.361729000	-0.935058000
8	-3.904632000	7.012878000	4.009090000
6	-5.135016000	6.980712000	3.325801000
1	-4.977890000	6.980145000	2.240549000
8	-2.921082000	4.310787000	4.465062000
6	-2.424394000	3.154913000	5.122660000
1	-1.845994000	2.544762000	4.419389000
1	-5.713335000	6.086575000	3.604046000
1	-1.778158000	3.447106000	5.956922000
1	-0.891045000	9.039464000	-0.745652000
1	3.566910000	6.200143000	2.828308000

1	-5.721495000	7.868160000	3.603809000
1	-3.276573000	2.572078000	5.497284000
Theory – m/z 557 – Figure 2 b) asymmetric			
6	0.538838000	-1.338312000	0.417057000
6	1.553355000	-0.205450000	0.754208000
8	-0.558529000	-0.686800000	-0.198357000
8	1.721790000	0.559705000	-0.424500000
22	0.007940000	0.279952000	-1.684568000
6	-0.386007000	0.466385000	-4.430968000
6	1.156729000	0.636656000	-4.310794000
8	-0.830889000	-0.218212000	-3.290392000
8	1.470384000	0.827789000	-2.950806000
6	1.207885000	-2.230139000	-0.646970000
8	1.609948000	-3.364993000	-0.413160000
8	1.303581000	-1.584400000	-1.789141000
6	1.635601000	1.766289000	-5.214368000
8	1.186863000	1.949809000	-6.335324000
8	2.607416000	2.511933000	-4.673776000
6	3.131460000	3.559209000	-5.501395000
1	3.559172000	3.146136000	-6.419350000
1	2.344459000	4.271793000	-5.764329000
1	3.903272000	4.040429000	-4.900642000
6	-0.776478000	-0.347448000	-5.668793000
8	-0.145788000	-1.269232000	-6.142649000
8	-1.971341000	0.059441000	-6.157447000
6	-2.468058000	-0.686593000	-7.278075000
1	-1.775773000	-0.615751000	-8.121598000
1	-2.598246000	-1.738836000	-7.010618000
1	-3.427535000	-0.232727000	-7.529270000
6	1.072282000	0.601980000	1.956421000
8	0.794966000	0.092362000	3.028164000
8	1.033929000	1.932624000	1.747319000
6	0.630156000	2.721451000	2.875261000
1	-0.378688000	2.447473000	3.195964000
1	1.318772000	2.578153000	3.712974000
1	0.655451000	3.755796000	2.530269000
1	2.513061000	-0.644645000	1.061027000
22	3.097280000	-0.072415000	-1.880319000
8	4.134647000	1.425915000	-1.844283000
6	4.623850000	2.170066000	-0.761442000
1	5.259981000	2.986529000	-1.134845000
1	5.225310000	1.536857000	-0.090107000
8	3.667534000	-0.961646000	-3.360401000
6	3.472539000	-2.190740000	-4.022231000
1	2.583460000	-2.703577000	-3.637909000
1	4.350111000	-2.836453000	-3.875908000
8	3.978712000	-1.055463000	-0.597622000
6	4.751176000	-2.231357000	-0.581003000
1	4.101958000	-3.115804000	-0.599757000
1	5.356076000	-2.258683000	0.337529000
8	-0.886494000	1.828048000	-1.350179000
6	-1.587913000	2.487359000	-0.338307000
1	-1.850040000	1.795251000	0.475621000
1	-0.979891000	3.302507000	0.079680000
1	0.234956000	-1.906022000	1.300408000
1	1.631849000	-0.278066000	-4.688396000
1	-0.870732000	1.451077000	-4.500992000
1	-2.515631000	2.919377000	-0.743638000
1	5.432062000	-2.265259000	-1.444138000
1	3.799214000	2.605790000	-0.178992000
1	3.350779000	-2.017835000	-5.100647000