

Supporting information

The thermal decomposition of furfural: molecular chemistry unraveled

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Contents

1	Comparison of quantum mechanical methods.....	3
2	Nomenclature	8
3	Thermodynamic data of molecules	9
4	Thermodynamic data of transition states.....	10
5	Theoretical calculation details.....	11

1 Comparison of quantum mechanical methods

The differences between the barriers for the initial decomposition pathways of furfural are small and within the uncertainty of the CBS-QB3 level of theory. These pathways include the ring opening with the formation of formylvinylketene and the carbene formation pathways. More accurate methods have been used to calculate these barriers or barriers for similar reactions in smaller species. All additional calculations have been done with the high-performance supercomputer at Ghent University with Gaussian 16 [1].

One potential short-coming of the CBS-QB3 method is the use of density functional theory for the geometry optimization and frequency calculation steps. To address this, CBS-QB3 calculations in which B3LYP/6-311G(2d,d,p) is replaced by QCISD/6-31G(d) were carried out. This method is further referred to as QCBS-QB3. A rather small basis set is used to allow frequency calculations to finish within acceptable times. The results are given in Figure 1 and Figure 2 for furan and furfural pathways respectively. In both figures, it can be seen that the barriers for the carbene chemistry do not notably change by applying the post-HF geometry optimization method. As for the ring opening pathway for furfural, the barrier calculated with the QCBS-QB3 approach is 4 kJ/mol higher. This is within the expected error of the CBS-QB3 level of theory, but when developing a kinetic model this difference could have a clear impact on model predictions.

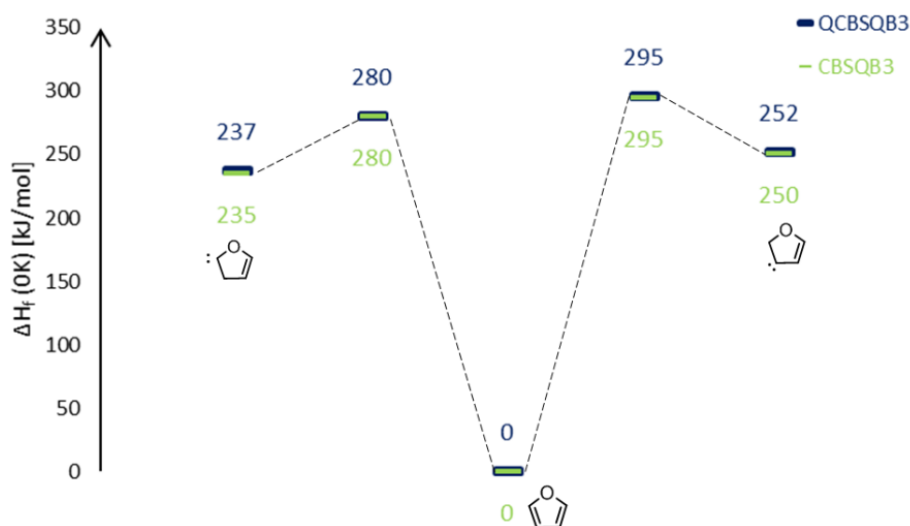


Figure 1. A comparison of the barriers for the furan initial decomposition pathways at CBS-QB3 and QCBS-QB3 level of theory

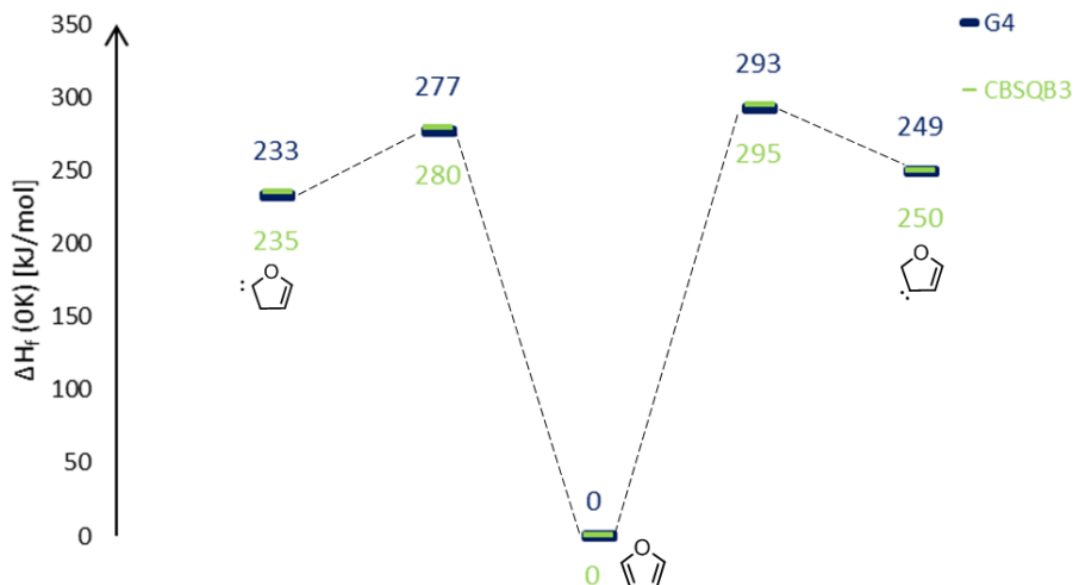


Figure 3. A comparison of the barriers for the furan initial decomposition pathways at CBS-QB3 and G4 level of theory

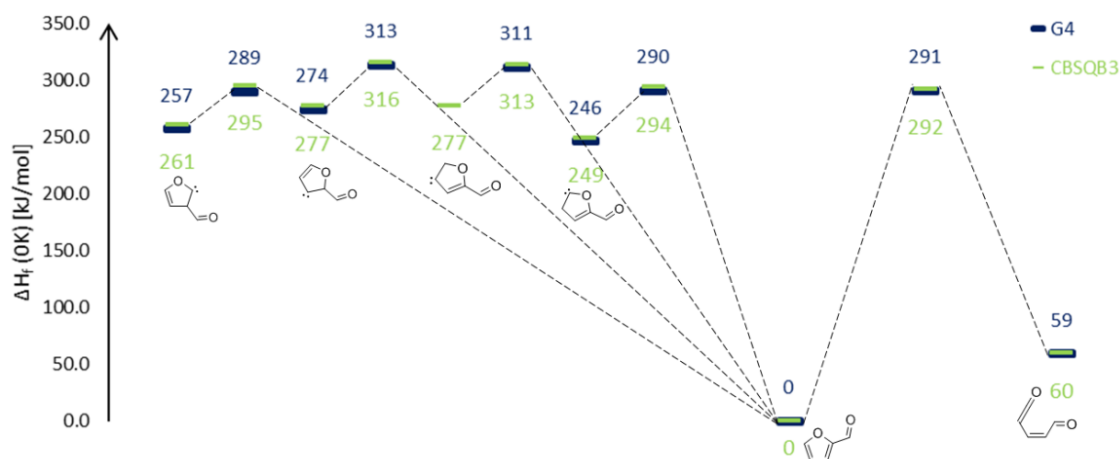


Figure 4. A comparison of the barriers for the furfural initial decomposition pathways at CBS-QB3 and G4 level of theory

The W1 level of theory as implemented in the Gaussian software achieves superior accuracy compared to CBS-QB3 due to CBS extrapolation at the coupled cluster level. Since the coupled-cluster theory CCSD(T) incorporates substantial contributions from excited states, any multi-reference character should lead to substantially different features on the PES. A comparison for the furan and furfural initial chemistry is shown in Figure 5 and Figure 6. The barriers calculated with both levels of theory are very similar, hence it is expected that the influence of higher electronic levels is rather limited. For the furfural carbene with the carbenic center in alpha position to the carbon atom bearing the carbonyl group, the W1 method predicts a 16 kJ/mol lower energy compared to CBS-QB3. However, the barriers calculated by both

methods are still very similar and the initial chemistry predicted with the CBS-QB3 level of theory is confirmed by the W1 level of theory.

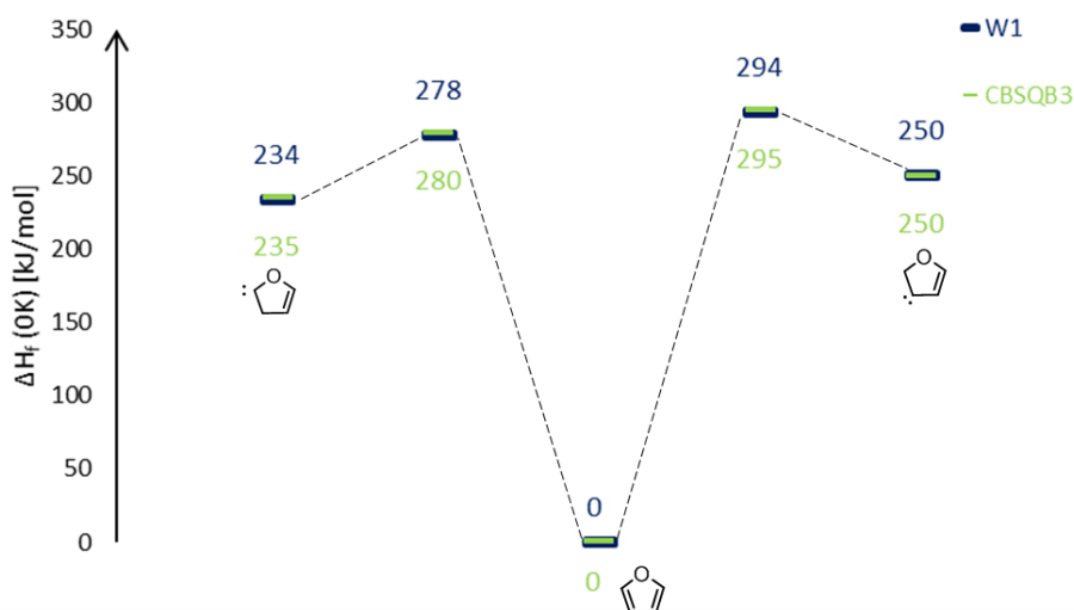


Figure 5. A comparison of the barriers for the furan initial decomposition pathways at CBSQB3 and W1 level of theory

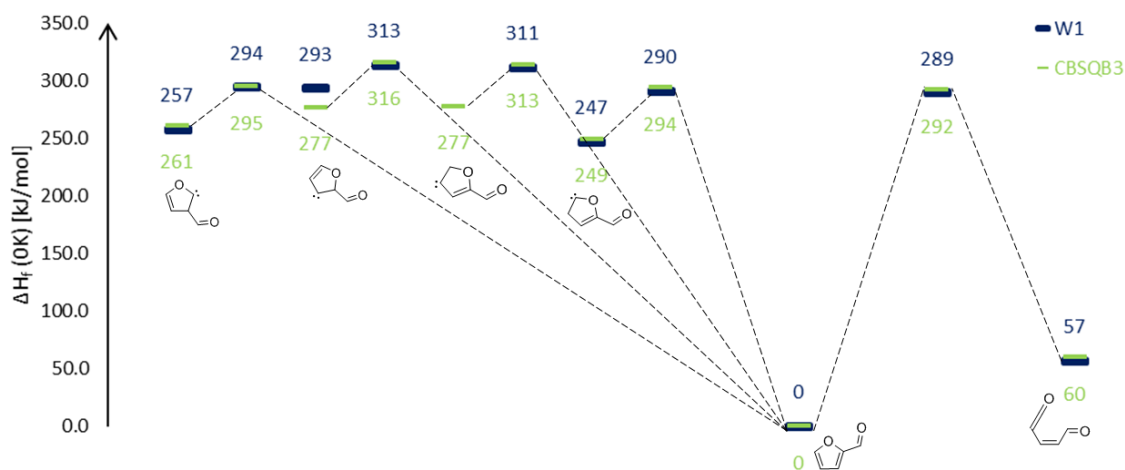


Figure 6. A comparison of the barriers for the furfural initial decomposition pathways at CBSQB3 and W1 level of theory

The barriers for the direct ring-opening channel from furfural are 4 kJ/mol (QCBS-QB3), 1 kJ/mol (G4) and 3 kJ/mol (W1) lower than the barrier calculated at the CBS-QB3 level of theory. These values are well within the uncertainty of the CBS-QB3 level of theory. The largest observed difference of a barrier for carbene formation is 6 kJ/mol at the G4 level of theory for 1 channel. It is expected that these small deviations have no significant impact on the

general mechanism. They indicate that the accuracy of the CBS-QB3 level of theory is sufficient to be used to study the decomposition chemistry of furans.



















2 Nomenclature

Table S 1. Nomenclature

Name	Identifier	Structure
2-keto,3,4-pentadienal	InChI=1S/C5H4O2/c1-2-3-5(7)4-6/h3-4H,1H2	
3-furaldehyde	InChI=1S/C5H4O2/c6-3-5-1-2-7-4-5/h1-4H	
formylacetylene	InChI=1S/C3H2O/c1-2-3-4/h1,3H	
formylvinylketene	InChI=1S/C5H4O2/c6-4-2-1-3-5-7/h1-4H/b2-1-	
furan	InChI=1S/C4H4O/c1-2-4-5-3-1/h1-4H	
furfural	InChI=1S/C5H4O2/c6-4-5-2-1-3-7-5/h1-4H	
furfural-3-carbene	InChI=1S/C5H4O2/c6-4-5-2-1-3-7-5/h1,3-5H	
furfural-4-carbene	InChI=1S/C5H4O2/c6-4-5-2-1-3-7-5/h2,4H,3H2	
furfural-5-carbene	InChI=1S/C5H4O2/c6-4-5-2-1-3-7-5/h2,4H,1H2	
penta-2,3-dienedial	InChI=1S/C5H4O2/c6-4-2-1-3-5-7/h2-5H	
vinylacetylene	InChI=1S/C4H4/c1-3-4-2/h1,4H,2H2	
vinylketene	InChI=1S/C4H4O/c1-2-3-4-5/h2-3H,1H2	
α -pyrone	InChI=1S/C5H4O2/c6-5-3-1-2-4-7-5/h1-4H	

3 Thermodynamic data of molecules

Table S 2. Thermodynamic data for the molecules included in the potential energy surface. Enthalpy of formation at 0 K and 298 K, total entropy at 298 K and heat capacity at three different temperatures (500 K, 1000 K and 1500 K) are given.

N°	Structure	$\Delta H_f(0K)$ [kJ mol ⁻¹]	$\Delta H_f(298K)^a$ [kJ mol ⁻¹]	$S^\circ_{tot}(298K)$ [J mol ⁻¹ K ⁻¹]	$C_p(500K)$ [J mol ⁻¹ K ⁻¹]	$C_p(600K)$ [J mol ⁻¹ K ⁻¹]	$C_p(800K)$ [J mol ⁻¹ K ⁻¹]	$C_p(1000K)$ [J mol ⁻¹ K ⁻¹]	$C_p(1500K)$ [J mol ⁻¹ K ⁻¹]
M1		-146.2	-153.1	322.8	141.0	158.9	184.5	201.8	226.2
M2		-188.3	-196.0	310.6	141.1	158.8	184.1	201.3	225.8
M3		-143.0	-149.2	322.3	142.2	159.9	185.4	202.5	226.1
M4		-86.5	-99.9	352.9	146.5	162.3	185.9	202.4	226.5
M5		-30.0	-42.5	340.3	156.8	172.2	194.0	208.4	227.7
M6		-17.4	-28.7	355.1	154.3	170.1	193.4	208.7	228.2
M7		130.5	126.4	336.4	145.6	162.4	186.3	202.3	224.8
M8		131.0	127.8	334.1	149.5	165.2	187.7	203.0	225.0
M9		102.9	99.2	330.0	148.1	164.8	189.0	205.1	227.3
M10		114.4	110.2	333.0	151.1	166.9	189.0	204.0	225.4
M11		-21.0	-29.0	266.8	107.0	122.0	143.4	157.9	179.0
M12		38.3	25.2	301.3	119.4	130.5	147.3	159.5	178.0
M13		106.1	95.1	313.5	115.4	126.6	143.9	156.7	176.4
M14		-166.4	-171.1	301.5	95.6	104.4	117.6	127.0	140.7
M15		136.2	132.5	274.6	81.2	87.8	98.1	105.6	117.1
M16		-45.8	-50.5	241.3	65.1	70.1	78.1	84.1	93.9
M17		17.7	19.0	325.9	134.6	150.2	172.2	186.5	206.0
M18		66.8	60.6	341.5	132.9	146.0	165.5	179.3	200.4

^a $\Delta H_f(298 K)$ from quantum mechanical calculations corrected with spin-orbit and bond additive corrections.

4 Thermodynamic data of transition states

Table S 3. Thermodynamic data for the transition states included in the potential energy surface. Enthalpy of formation at 0 K and 298 K, total entropy at 298 K and heat capacity at three different temperatures (500 K, 1000 K and 1500 K) are given.

N°	N° reactant	N° product(s)	ΔH_f (0K) [kJ mol ⁻¹]	ΔH_f (298K) [kJ mol ⁻¹]	S°_{tot} (298K) [J mol ⁻¹ K ⁻¹]	C_p (500K) [J mol ⁻¹ K ⁻¹]	C_p (600K) [J mol ⁻¹ K ⁻¹]	C_p (800K) [J mol ⁻¹ K ⁻¹]	C_p (1000K) [J mol ⁻¹ K ⁻¹]	C_p (1500K) [J mol ⁻¹ K ⁻¹]
TS1	M1	M11+CO	226.0	215.3	355.8	144.2	159.8	182.3	197.7	219.8
TS2	M1	M4	145.4	133.8	335.5	143.0	158.8	182.1	198.2	220.9
TS3	M4	M2	-41.7	-52.5	344.1	140.7	155.8	178.6	194.8	218.5
TS4	M2	M11+CO	128.1	116.3	347.1	142.6	158.2	180.9	196.6	219.3
TS5	M1	M7	169.6	156.1	324.1	143.4	160.5	184.3	199.8	220.6
TS6	M1	M8	167.2	154.3	330.2	139.5	156.8	181.6	197.9	219.8
TS7	M1	M9	147.4	134.2	326.2	143.0	160.0	184.1	199.9	221.0
TS8	M1	M10	148.5	134.2	323.7	139.0	156.0	180.1	196.3	219.3
TS9	M7	M5	141.3	128.4	339.2	138.1	154.9	179.3	195.9	219.4
TS10	M7	M3	159.1	144.5	320.7	137.4	154.7	179.3	195.8	219.1
TS11	M8	M6	132.7	120.1	334.0	139.0	155.5	179.6	196.1	219.4
TS12	M9	M15+M16	202.7	193.6	360.9	148.1	161.8	182.5	197.3	218.8
TS13	M10	M3	151.6	138.0	323.6	144.0	162.4	187.2	202.3	221.5
TS14	M10	M14+C ₂ H ₂	226.0	216.3	348.7	155.3	169.1	188.5	201.4	220.1
TS15	M4	M5	187.7	177.0	341.6	145.0	160.6	183.7	199.6	221.8
TS16	M4	M12+CO	169.1	158.4	349.6	145.4	160.6	183.2	198.9	221.2
TS17	M5	M13+CO	161.1	153.5	371.2	154.8	167.4	186.3	199.8	219.6
TS18	M6	M12+CO	125.1	113.7	333.5	148.2	163.3	185.4	200.6	222.1

5 Theoretical calculation details

Table S 4. SCF energy, zero-point corrected electronic energy, frequencies and geometry of molecules and transition states included in the potential energy surface, calculated at the CBS-Q3 level of theory.

N°	E(SCF) [Hartrees]	CBSQB3 (0K) [Hartrees]	Frequencies [cm ⁻¹]			Geometry		
						N°	Atom N°	XYZ Coordinates [Angstroms]
M1	-341.467416	-342.828727	160.1	206.8	257.9	1	8	-0.650642 -1.103193 -0.000006
						2	6	-1.869532 -0.521299 -0.000041
						3	6	-1.758994 0.839889 -0.000052
						4	6	-0.365899 1.121315 -0.000021
						5	6	0.275088 -0.089226 0.000006
						6	6	1.681190 -0.467361 0.000044
						7	1	0.121144 2.083032 -0.000019
						8	1	-2.572999 1.546918 -0.000078
						9	1	-2.712636 -1.192108 -0.000055
						10	8	2.592797 0.331378 0.000058
						11	1	1.855339 -1.562762 0.000058
M2	-341.489094	-342.844746	147.6	366.5	459.6	1	8	0.324115 0.063668 -0.165787
						2	6	0.172515 0.023140 1.167210
						3	6	1.211033 -0.019147 2.027667
						4	6	2.531951 -0.020302 1.478261
						5	6	2.720208 0.020010 0.136016
						6	6	1.603858 0.065431 -0.787955
						7	1	3.387337 -0.053785 2.144329
						8	1	1.034361 -0.050745 3.093220
						9	1	-0.871090 0.028720 1.456094
						10	8	1.633213 0.103343 -1.985256
						11	1	3.703286 0.020488 -0.314917
M3	-341.468340	-342.827515	139.5	196.8	288.4	1	6	0.007477 0.000000 -0.005541
						2	8	-0.014749 0.000000 1.342979
						3	6	1.292666 0.000000 1.765076

			889.5	890.9	989.9	4	6	2.132911	0.000000	0.706116
			1024.8	1027.6	1102.7	5	6	1.296005	0.000000	-0.465321
			1179.4	1250.9	1299.9	6	6	1.718914	0.000000	-1.865504
			1398.6	1434.4	1540.0	7	1	3.210302	0.000000	0.718772
			1605.8	1775.5	2882.3	8	1	1.432731	0.000000	2.832314
			3260.2	3265.7	3285.5	9	1	-0.950679	0.000000	-0.499025
						10	8	2.873960	0.000000	-2.228730
						11	1	0.888247	0.000000	-2.603348
M4	-341.453750	-342.805998	111.7	124.7	213.1	1	6	0.032442	0.000000	-0.040761
			236.6	390.0	416.0	2	6	0.006000	0.000000	1.283362
			557.3	634.0	724.4	3	6	1.192903	0.000000	2.093421
			783.2	826.3	963.2	4	6	1.213260	0.000000	3.450476
			993.1	1028.9	1075.7	5	6	0.030133	0.000000	4.304989
			1137.5	1261.8	1334.2	6	8	-1.130130	0.000000	3.924284
			1428.9	1478.3	1603.8	7	8	0.031010	0.000000	-1.196484
			1740.1	2216.9	2896.0	8	1	-0.967449	0.000000	1.765490
			3141.8	3153.4	3177.5	9	1	2.144681	0.000000	1.569989
						10	1	2.172777	0.000000	3.955467
						11	1	0.248732	0.000000	5.392908
M5	-341.433934	-342.784446	72.5	102.4	184.7	1	8	0.055988	0.133616	0.074968
			201.7	268.6	433.8	2	6	0.103079	0.394234	1.250905
			490.1	527.1	637.3	3	6	1.012090	-0.304803	2.197725
			756.1	919.1	1015.1	4	6	1.045323	-0.001930	3.469530
			1022.2	1054.9	1062.7	5	6	1.018362	0.301164	4.741430
			1114.9	1223.2	1347.9	6	6	0.107349	-0.391265	5.691177
			1411.9	1445.1	1770.4	7	8	0.065919	-0.130311	6.867252
			1787.4	2008.8	2916.4	8	1	-0.536458	-1.169977	5.236788
			2919.9	3152.0	3153.2	9	1	1.666699	1.068117	5.156654
						10	1	1.653512	-1.076430	1.780428
						11	1	-0.533603	1.177584	1.707355
M6	-341.42683	-342.779656	77.2	124.6	133.9	1	6	-0.013275	0.040834	0.004829
			236.2	369.1	422.9	2	6	0.006321	-0.032199	1.298845

			429.3	533.1	650.9	3	6	0.047383	-0.097836	2.608895
			653.8	866.4	879.7	4	6	1.237438	0.320370	3.379971
			920.6	990.0	1016.1	5	6	1.118237	0.178468	4.907257
			1104.5	1147.1	1352.1	6	8	0.140446	-0.239619	5.467890
			1371.6	1458.3	1752.3	7	8	2.275796	0.755260	2.929628
			1808.0	2032.1	2928.0	8	1	0.319195	-0.790092	-0.609578
			3123.2	3162.8	3198.5	9	1	-0.357601	0.937031	-0.501865
						10	1	-0.798412	-0.464987	3.181851
						11	1	2.035646	0.504907	5.437332
M7	-341.371784	-342.723334	68.8	178.7	270.9	1	6	-0.158242	-0.036319	0.038459
			423.6	502.3	581.7	2	6	-0.005981	0.006929	1.434890
			724.2	781.5	863.8	3	6	1.343611	-0.003716	1.769432
			883.3	908.8	961.5	4	8	2.160760	-0.066150	0.754226
			1009.6	1011.0	1102.6	5	6	1.232296	-0.057592	-0.428872
			1145.1	1176.9	1231.4	6	1	-0.801648	0.052058	2.166962
			1282.3	1391.3	1416.1	7	6	1.505880	1.194479	-1.279473
			1499.8	1831.1	2948.1	8	1	1.818762	0.030076	2.744545
			3073.1	3186.2	3204.8	9	1	1.480627	-0.951284	-1.010463
						10	8	2.133693	2.141618	-0.907967
						11	1	1.027881	1.135211	-2.274724
M8	-341.368039	-342.723142	75.8	197.7	209.2	1	6	0.009063	-0.000439	0.073466
			347.0	364.8	522.1	2	8	-0.061972	-0.001758	1.373692
			613.4	732.8	771.9	3	6	1.450704	-0.006630	1.780626
			804.6	903.1	978.3	4	6	2.250065	-0.007519	0.574946
			1012.8	1028.6	1125.7	5	6	1.298816	-0.003538	-0.461106
			1156.5	1212.0	1289.6	6	6	-1.301299	0.004197	-0.660063
			1377.3	1382.6	1465.1	7	8	-1.362352	0.005774	-1.861227
			1492.8	1803.5	2949.0	8	1	1.489900	-0.002837	-1.525416
			3074.7	3127.4	3213.6	9	1	1.553444	-0.901795	2.398396
						10	1	-2.197843	0.006026	-0.012145
						11	1	1.558647	0.886444	2.400533

M9	-341.381123	-342.733853	136.3	203.5	211.0	1	6	0.021265	0.002210	-0.068243
			301.5	455.5	584.4	2	8	0.074158	-0.006246	1.366565
			732.2	743.4	826.1	3	6	1.306271	-0.000739	1.838176
			852.7	885.4	926.4	4	6	2.190135	0.012873	0.603871
			948.5	1030.8	1078.8	5	6	1.255744	0.013693	-0.567390
			1105.1	1200.4	1257.0	6	6	-1.315880	-0.003135	-0.681393
			1272.6	1375.0	1418.9	7	8	-1.492854	0.003007	-1.876507
			1673.6	1785.4	2938.9	8	1	1.504614	0.021840	-1.617130
			3022.9	3044.6	3253.5	9	1	2.862939	-0.854647	0.639576
						10	1	-2.152368	-0.013296	0.043616
						11	1	2.851038	0.888991	0.650282
M10	-341.377122	-342.729502	81.4	178.6	235.6	1	6	0.019314	0.082900	0.043770
			431.7	535.2	676.4	2	6	0.038879	0.039383	1.541797
			725.6	778.5	834.9	3	6	1.308011	-0.082013	1.893472
			859.2	875.9	898.0	4	8	2.151104	-0.102398	0.735320
			915.7	986.4	1040.6	5	6	1.482442	0.017398	-0.390931
			1120.3	1138.7	1191.5	6	1	-0.813240	0.105654	2.198237
			1264.1	1331.4	1403.5	7	6	-0.743202	1.220548	-0.629487
			1654.0	1815.1	2936.7	8	1	1.830465	-0.157736	2.833081
			2956.0	3252.3	3278.1	9	1	-0.405902	-0.839730	-0.393736
						10	8	-1.428602	2.008067	-0.037299
						11	1	-0.616175	1.254608	-1.728208
M11	-228.701207	-229.643080	615.2	623.0	734.4	1	6	0.032115	0.000000	-0.048583
			758.3	850.5	884.3	2	8	-0.006666	0.000000	1.313397
			888.6	894.8	1014.0	3	6	1.285831	0.000000	1.744622
			1058.0	1087.2	1164.2	4	6	2.139005	0.000000	0.688491
			1198.7	1285.2	1412.6	5	6	1.316982	0.000000	-0.487260
			1510.2	1593.6	3240.2	6	1	1.644071	0.000000	-1.514707
			3250.9	3275.2	3281.7	7	1	3.216296	0.000000	0.734066
						8	1	1.423634	0.000000	2.812394
						9	1	-0.923431	0.000000	-0.544626

M12	-228.687522	-229.620531	128.7	170.4	414.3	1	6	-0.024032	0.000000	0.015622
			520.6	564.4	638.8	2	6	0.013059	0.000000	1.351795
			711.6	891.9	927.0	3	1	0.909727	0.000000	-0.539619
			1012.6	1118.2	1185.8	4	1	0.956955	0.000000	1.881379
			1323.4	1361.5	1471.2	5	1	-0.890892	0.000000	1.951314
			1678.4	2214.3	3138.1	6	6	-1.245552	0.000000	-0.779494
			3146.8	3169.2	3228.0	7	6	-1.262166	0.000000	-2.098787
						8	1	-2.218040	0.000000	-0.298533
						9	8	-1.284694	0.000000	-3.259478
M13	-228.662626	-229.594676	58.6	176.2	329.4	1	6	-0.040060	-0.032361	0.029419
			463.4	505.1	674.8	2	6	-0.081847	0.034467	1.227650
			693.4	729.6	976.8	3	1	-0.124203	0.082918	2.288198
			1027.8	1043.8	1218.7	4	6	0.025830	-0.062286	-1.425235
			1290.4	1408.6	1441.9	5	6	0.679229	1.189437	-2.018464
			1823.8	2227.6	2901.3	6	1	0.632351	-0.918666	-1.752444
			3003.4	3077.5	3476.6	7	1	-0.961939	-0.178627	-1.878892
						8	8	0.345948	1.669714	-3.066395
						9	1	1.506101	1.615534	-1.413053
M14	-264.548933	-265.559678	154.1	170.6	497.7	1	8	-0.042230	0.000000	0.132267
			577.9	616.1	642.0	2	6	0.011361	0.000000	1.285072
			1003.3	1086.0	1115.9	3	6	0.031423	0.000000	2.607858
			1332.1	1449.6	1765.9	4	1	0.988384	0.000000	3.114224
			2226.2	2900.0	3199.5	5	6	-1.208405	0.000000	3.394575
						6	8	-1.228668	0.000000	4.602350
						7	1	-2.142756	0.000000	2.797867
M15	-189.606476	-190.362793	212.3	275.4	634.4	1	6	-0.021564	0.000000	0.037848
			687.0	744.3	952.9	2	8	0.046558	0.000000	1.243176
			1016.2	1414.5	1763.6	3	1	0.884412	0.000000	-0.597472
			2197.8	2932.7	3468.1	4	6	-1.267842	0.000000	-0.701072
						5	6	-2.284996	0.000000	-1.344254
						6	1	-3.191072	0.000000	-1.901366

M16	-151.781439	-152.375835	447.3	563.0	597.0	1	8	-0.007598	0.000000	0.065882
			990.9	1171.6	1408.3	2	6	0.001604	0.000000	2.536584
			2233.4	3178.0	3270.4	3	1	0.941524	0.000000	3.068476
						4	1	-0.934320	0.000000	3.075475
						5	6	-0.003279	0.000000	1.227203
M17	-340.846727	-342.184216	141.1	188.9	340.7	1	6	0.012165	0.000000	0.035139
			501.8	607.0	651.4	2	6	0.042955	0.000000	1.406367
			717.2	783.6	866.3	3	8	1.358503	0.000000	1.833587
			900.6	914.6	925.2	4	6	2.123767	0.000000	0.726116
			1035.2	1103.8	1167.6	5	6	1.360780	0.000000	-0.407402
			1201.5	1255.5	1420.3	6	6	-1.042799	0.000000	2.349653
			1481.6	1598.7	1883.1	7	8	-1.039982	0.000000	3.538470
			3246.8	3257.4	3270.2	8	1	-0.883183	0.000000	-0.565832
						9	1	1.721801	0.000000	-1.422967
						10	1	3.189438	0.000000	0.889872
M18	-340.836053	-342.165521	93.8	108.0	217.2	1	6	-0.002326	0.000287	0.014083
			221.1	402.2	414.0	2	6	0.002276	-0.000285	1.337688
			548.5	598.4	688.5	3	6	1.204795	-0.000482	2.127178
			689.8	764.5	948.5	4	6	1.239814	-0.001063	3.481044
			994.4	1081.6	1147.3	5	6	0.025193	-0.001555	4.276977
			1236.7	1333.9	1436.9	6	8	-0.119589	-0.002082	5.457158
			1624.1	1876.9	2221.8	7	8	-0.026031	0.000784	-1.141619
			3121.8	3150.8	3168.3	8	1	-0.966108	-0.000614	1.829815
						9	1	2.148206	-0.000137	1.590167
						10	1	2.193318	-0.001175	4.004648
TS1	-341.296659	-342.686944	-1697.7	50.8	69.7	1	6	0.091004	-0.299755	0.025822
			108.1	259.6	566.5	2	8	0.056364	0.164900	1.320307
			608.5	628.0	751.4	3	6	1.342345	0.340141	1.733330
			814.5	874.6	892.2	4	6	2.210402	0.007522	0.741116
			897.1	940.0	1010.8	5	6	1.401533	-0.399879	-0.368752
			1051.5	1102.2	1151.6	6	6	-1.785587	0.020998	-0.945072
			1212.6	1380.3	1429.8	7	8	-2.183366	1.097044	-0.840250

			1566.4	1936.7	3008.9	8	1	1.752198	-0.729688	-1.335142
			3225.9	3238.5	3265.2	9	1	3.287431	0.049067	0.792330
						10	1	1.472914	0.696692	2.741977
						11	1	-1.272173	-0.947040	-0.813671
TS2	-341.342192	-342.717690	-934.2	71.9	152.1	1	6	0.043024	0.000163	0.008704
			275.2	317.6	439.9	2	6	-0.078466	-0.002259	1.397221
			519.0	541.7	672.9	3	6	1.038869	-0.000478	2.186703
			751.2	781.1	882.3	4	6	2.264517	0.003673	1.443614
			929.9	1008.7	1035.7	5	8	2.224968	0.005528	0.209145
			1072.4	1157.3	1340.4	6	6	-0.276357	-0.000465	-1.253199
			1403.4	1486.4	1563.4	7	8	-0.256232	0.000170	-2.443687
			1668.5	1959.7	2177.4	8	1	-1.341962	-0.004325	-0.556811
			3001.0	3195.9	3227.7	9	1	-1.070528	-0.005141	1.830800
						10	1	0.994157	-0.002487	3.265970
						11	1	3.232601	0.005620	1.966997
TS3	-341.436226	-342.788910	-257.7	69.8	122.1	1	6	-0.066912	-0.008411	0.042971
			177.4	264.6	395.6	2	6	0.031540	-0.051025	1.349311
			473.5	565.6	633.6	3	8	0.131408	-0.087413	2.506512
			744.3	868.7	898.6	4	6	-0.411439	1.227896	-0.706707
			990.4	1023.0	1040.0	5	6	-1.644692	1.659895	-1.003469
			1130.1	1244.9	1388.7	6	6	-2.929674	1.000737	-0.654409
			1424.1	1441.6	1659.5	7	8	-3.058286	-0.081215	-0.132418
			1791.8	2232.4	2875.7	8	1	0.079959	-0.943980	-0.486493
			3102.1	3146.5	3161.1	9	1	0.426562	1.825469	-1.064371
						10	1	-1.743719	2.584659	-1.566900
						11	1	-3.823636	1.599539	-0.933730
TS4	-341.339247	-342.724235	-785.6	74.2	102.7	1	6	0.036014	-0.053765	0.062621
			304.5	372.9	435.2	2	6	0.278366	-0.018212	1.424637
			540.4	621.4	680.7	3	6	1.608736	0.299250	1.811658
			771.5	853.6	889.2	4	8	2.225164	0.524929	0.112137
			943.8	953.8	1083.4	5	6	1.234472	0.199770	-0.616100
			1118.0	1173.5	1232.9	6	6	1.937665	-0.465940	3.317194

			1308.1	1395.6	1468.0	7	8	2.756505	-1.200594	3.660643
			1556.2	2006.5	3101.2	8	1	-0.447133	-0.352510	2.152457
			3180.3	3217.5	3235.8	9	1	-0.886278	-0.374286	-0.398230
						10	1	1.390331	0.059557	-1.687242
						11	1	2.013887	1.269972	2.069836
TS5	-341.343958	-342.708474	-994.2	124.3	208.3	1	6	-0.000241	-0.010479	-0.002421
			296.4	486.1	569.8	2	6	-0.000898	0.007894	1.358160
			676.4	734.7	846.0	3	8	1.245178	0.021411	1.874485
			871.7	896.7	950.3	4	6	2.077534	0.028106	0.750626
			982.5	1064.0	1107.3	5	6	1.362827	0.081804	-0.487376
			1116.0	1179.9	1218.3	6	6	3.511625	0.383495	0.975965
			1306.1	1379.8	1405.8	7	8	3.957490	0.743390	2.031390
			1522.8	1814.2	2189.3	8	1	2.088384	-0.994145	0.052496
			2946.8	3220.3	3243.1	9	1	-0.883640	-0.038515	-0.623356
						10	1	-0.795239	-0.008313	2.090838
						11	1	4.116426	0.303733	0.052978
TS6	-341.343867	-342.709366	-971.0	126.7	209.7	1	6	-0.013693	0.010058	-0.003895
			231.2	486.4	591.4	2	8	-0.044735	0.076758	1.354521
			606.2	749.3	824.1	3	6	1.307568	0.112857	1.720382
			887.1	898.3	972.3	4	6	2.208732	-0.002527	0.629281
			993.6	1028.6	1053.0	5	6	1.261060	0.019054	-0.483459
			1149.4	1203.1	1260.7	6	6	-1.326060	-0.028075	-0.687855
			1293.2	1367.8	1428.3	7	8	-1.434448	-0.095570	-1.886897
			1563.8	1793.6	2229.4	8	1	1.518247	-0.008739	-1.531664
			2932.9	3223.5	3237.9	9	1	1.911236	1.140301	1.419069
						10	1	1.471415	-0.036881	2.779380
						11	1	-2.202310	0.009090	-0.011738
TS7	-341.348953	-342.716920	-1085.5	137.7	206.1	1	6	-0.018249	0.023926	-0.006910
			239.4	479.7	599.7	2	6	-0.047824	0.044668	1.345068
			630.6	757.2	807.9	3	6	1.348826	0.080173	1.732886
			860.5	904.9	979.9	4	6	2.189121	0.030929	0.558114
			999.6	1016.1	1030.0	5	1	1.971065	1.122239	1.337487

			1075.2	1158.0	1276.4	6	8	1.268709	0.073880	-0.476155
			1289.2	1370.1	1423.6	7	1	1.743960	-0.046325	2.732761
			1620.9	1789.2	2102.3	8	1	-0.926774	0.028582	1.968245
			2942.2	3213.3	3265.4	9	6	-1.101924	-0.038361	-1.007509
						10	8	-2.272002	-0.029587	-0.710805
						11	1	-0.751346	-0.093797	-2.055891
TS8	-341.345362	-342.716482	-367.1	166.6	242.3	1	6	0.011314	-0.113230	0.072869
			382.6	534.9	561.8	2	6	-0.011263	0.027429	1.408524
			652.6	791.0	847.6	3	6	1.393847	0.190264	1.783696
			878.4	909.0	929.2	4	6	2.198798	0.258401	0.581511
			971.1	979.4	1029.1	5	6	2.154999	-1.376950	1.759121
			1075.1	1095.8	1148.9	6	8	1.306400	-0.016366	-0.411397
			1307.0	1340.3	1350.5	7	8	2.906008	-1.685514	2.620135
			1583.5	1835.0	2945.9	8	1	1.735243	0.604072	2.723039
			3211.4	3246.0	3268.9	9	1	-0.874535	-0.010240	2.053308
						10	1	-0.755288	-0.273748	-0.668655
						11	1	1.657442	-2.050661	1.038327
TS9	-341.355206	-342.719226	-413.8	66.3	158.2	1	6	-0.150806	0.077539	0.046944
			245.3	406.7	543.2	2	6	0.002206	0.086503	1.445760
			669.9	738.9	850.5	3	6	1.348176	0.061828	1.735648
			865.5	875.7	992.8	4	6	2.104777	-0.001051	0.531512
			1008.6	1043.3	1063.1	5	8	1.472566	-0.020497	-0.566335
			1080.3	1229.3	1282.6	6	6	-0.737914	1.367846	-0.532091
			1343.4	1394.8	1412.9	7	8	-0.096714	2.316457	-0.875963
			1551.8	1829.5	2916.1	8	1	1.809828	0.080667	2.714481
			3102.2	3145.4	3196.8	9	1	3.191306	-0.044675	0.470078
						10	1	-0.579408	-0.819744	-0.404804
						11	1	-1.845262	1.348554	-0.574201
TS10	-341.340424	-342.712447	-418.4	164.7	272.6	1	6	-0.168551	0.095637	0.013227
			411.7	545.4	637.2	2	6	-0.096993	0.086709	1.379350
			668.3	777.4	835.8	3	8	1.162918	0.009604	1.834708
			853.1	897.7	950.1	4	6	1.940967	-0.074355	0.658744

			979.2	998.2	1074.9	5	6	1.159643	0.026372	-0.515241
			1129.8	1143.7	1231.3	6	6	2.090819	-1.604714	-0.056808
			1318.7	1342.7	1401.5	7	8	1.426708	-2.548668	0.248842
			1506.1	1772.4	3013.6	8	1	2.965041	0.241653	0.818303
			3195.4	3219.4	3239.9	9	1	-0.860690	0.099000	2.144570
						10	1	-1.085917	0.096871	-0.556870
						11	1	3.038740	-1.626414	-0.610986
TS11	-341.362813	-342.722510				1	6	0.030938	0.002792	-0.041413
			-294.5	68.5	203.0	2	6	0.064763	-0.001027	1.366119
			226.3	368.2	503.1	3	8	1.226963	-0.002051	1.919347
			626.4	726.6	771.0	4	6	2.198288	0.001998	0.576288
			774.7	905.7	970.8	5	6	1.328814	0.004687	-0.550816
			1028.8	1046.6	1074.8	6	6	-1.120373	-0.003997	2.295490
			1128.2	1219.3	1324.4	7	8	-2.252424	-0.003550	1.890353
			1377.3	1391.0	1437.4	8	1	-0.896038	0.003927	-0.598217
			1518.0	1804.3	2951.1	9	1	2.793616	-0.899105	0.731162
			3087.2	3148.1	3212.9	10	1	-0.865980	-0.006593	3.371824
						11	1	2.792829	0.902772	0.736036
TS12	-341.300086	-342.695874				1	6	0.071107	-0.081572	0.010046
			-433.0	77.2	95.2	2	6	0.053780	-0.295118	1.382756
			153.9	200.1	260.7	3	8	0.724411	-0.342280	2.323738
			369.6	460.3	588.7	4	6	1.842616	0.242231	-0.379412
			609.0	669.8	742.2	5	6	2.743288	0.138469	0.483596
			943.6	975.2	983.7	6	6	3.752839	0.028140	1.469650
			1040.7	1094.5	1140.2	7	1	1.774485	0.480438	-1.429831
			1403.6	1428.8	1681.0	8	1	-0.220348	-0.964705	-0.558633
			1952.5	2089.9	2881.9	9	1	-0.493793	0.800819	-0.290412
			3096.7	3161.4	3227.1	10	8	4.397749	-0.980945	1.713498
						11	1	3.934213	0.974641	2.020726
TS13	-341.349026	-342.715288				1	6	0.102609	0.122998	-0.066632
			-1029.3	125.9	201.5	2	6	0.195702	0.403648	1.357047
			297.6	474.8	592.2	3	6	1.564330	0.204687	1.805693
			656.7	735.6	804.6					

			887.2	923.4	950.5	4	6	2.212043	-0.219446	0.708207
			979.1	1018.9	1042.2	5	8	1.367575	-0.323012	-0.369871
			1093.0	1180.4	1214.1	6	6	-0.885829	1.127276	2.089715
			1295.6	1405.8	1413.1	7	8	-0.703940	1.682080	3.142549
			1595.0	1806.0	2085.6	8	1	1.958001	0.374797	2.793734
			2943.5	3248.5	3274.1	9	1	3.240226	-0.491558	0.525858
						10	1	-0.383452	-0.651726	0.949679
						11	1	-1.864645	1.133009	1.573737
TS14	-341.279641	-342.686955	-539.9	96.0	122.2	1	6	0.000483	0.020044	0.007361
			216.3	248.0	317.9	2	6	-0.013903	0.058493	1.417859
			475.1	501.5	549.6	3	8	0.882712	0.050034	2.182802
			564.6	689.6	725.6	4	6	1.836096	-0.029905	-0.350725
			747.8	875.0	963.9	5	6	2.581808	-0.018609	0.648421
			1022.6	1063.3	1092.0	6	1	3.437617	-0.007273	1.282222
			1281.0	1425.4	1775.4	7	1	1.863410	-0.063918	-1.427290
			1803.5	1914.5	2937.0	8	6	-0.570717	-1.211950	-0.643821
			3126.6	3253.3	3435.2	9	1	-0.350650	0.940209	-0.459755
						10	8	-0.803077	-1.261743	-1.825208
						11	1	-0.687463	-2.092950	0.014360
TS15	-341.314947	-342.701581	-1461.4	89.3	114.8	1	6	0.116147	-0.081686	-0.143829
			223.2	257.6	345.5	2	8	0.075963	-0.127030	1.032100
			462.2	561.8	635.6	3	6	0.867288	0.087272	-1.320955
			726.1	778.1	860.3	4	6	-0.028805	-0.523847	-2.157492
			992.1	1008.6	1034.5	5	6	-0.488418	-0.816251	-3.377705
			1098.7	1117.3	1246.7	6	6	-0.417081	0.176149	-4.463151
			1333.9	1425.7	1731.0	7	8	-0.796729	-0.041167	-5.591244
			1752.4	1790.8	1982.0	8	1	0.019461	1.153650	-4.174207
			2898.3	3187.4	3198.5	9	1	-0.984984	-1.754682	-3.593757
						10	1	1.849844	0.506406	-1.499579
						11	1	-0.876922	-0.654130	-0.971634
TS16	-341.279681	-342.708655	-546.9	84.9	115.5	1	6	-0.060075	0.140428	0.300635
			181.7	303.1	404.7	2	6	0.094652	-0.308622	1.771362

			464.7	531.6	621.1	3	6	1.488390	-0.309139	2.262434
			737.5	806.1	871.0	4	6	1.666900	0.092286	3.547829
			909.8	934.9	1002.3	5	6	0.435684	0.399109	4.201748
			1070.7	1135.7	1188.7	6	8	-0.049962	0.484618	5.270897
			1362.0	1417.6	1565.9	7	8	-0.688396	0.998715	-0.187208
			1896.0	1974.1	2166.3	8	1	-0.404240	-1.281977	1.782128
			3065.4	3133.0	3207.9	9	1	2.314089	-0.587081	1.620416
						10	1	2.629228	0.267988	4.022688
						11	1	-0.420701	0.351136	2.608562
TS17	-341.322159	-342.711661	-1351.0	70.5	98.8	1	6	-0.019265	-0.033584	-0.023733
			142.8	164.2	261.8	2	6	0.044008	-0.064479	1.363703
			381.9	471.9	481.6	3	6	0.908893	-0.029639	2.267746
			548.9	713.2	763.1	4	6	2.458858	0.048140	0.989038
			861.1	913.0	1037.1	5	8	3.577618	0.065055	1.236139
			1064.1	1137.4	1238.8	6	1	1.411198	0.036073	-0.001046
			1326.7	1425.9	1453.7	7	1	1.152527	-0.035421	3.310918
			1792.7	1946.3	2073.5	8	1	-0.276338	-0.947870	-0.557609
			2894.1	3119.8	3358.3	9	6	-0.482436	1.207869	-0.720943
						10	8	-0.865832	1.226101	-1.863190
						11	1	-0.412731	2.134500	-0.113514
TS18	-341.328820	-342.725408	-1102.5	141.2	182.6	1	6	-0.033181	-0.009779	-0.022432
			234.2	303.6	440.9	2	6	-0.072275	-0.005454	1.301532
			509.7	581.3	642.6	3	6	0.580345	0.003819	2.507515
			653.4	703.3	757.0	4	6	-0.192343	0.354490	3.658224
			800.1	847.5	972.0	5	6	-1.676650	0.278541	3.113298
			1038.5	1117.0	1217.1	6	8	-2.738556	0.094688	3.551546
			1282.3	1438.6	1646.7	7	8	0.034175	0.638292	4.807740
			1773.6	1830.0	1988.2	8	1	-0.874705	-0.324232	-0.626179
			3128.5	3202.3	3217.1	9	1	0.849435	0.353927	-0.540154
						10	1	1.542634	-0.471530	2.647492
						11	1	-1.358744	0.255151	1.832691

