Formation of β-Ga_2O_3 Nanorings from Metal-Organic Frameworks and High Catalytic Activity for Epoxidation of Alkenes †

Wei Ping Wang,[a] Le Xin Song,*[a,b] Yao Li,[a] Yue Teng,[c] Juan Xia[a], Fang Wang[a] and Nan Ning Liu[a]

[a] Department of Chemistry, University of Science and Technology of China, Jin Zhai Road 96, Hefei 230026, P. R. China E-mail: solexin@ustc.edu.cn; Fax: +86-551-63601592;
[b] National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei 230026, P. R. China
[c] State Grid Anhui Electric Power Research Institute, Zi Yun Road 299, Hefei 230601, P. R. China

A list of the contents for all the Supporting Information

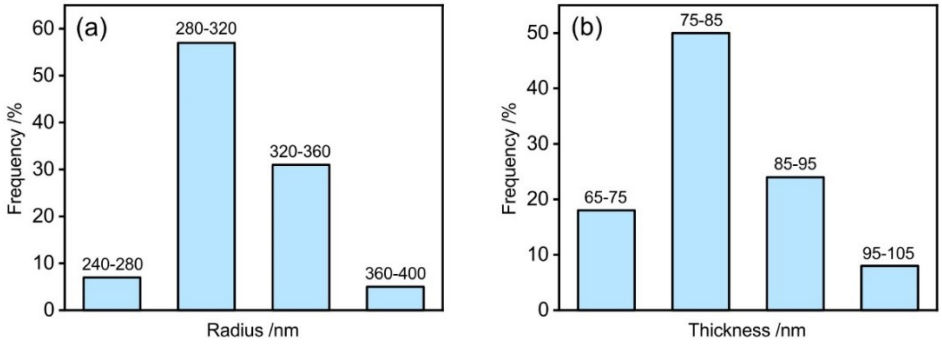

Figure S1. (a) The average diameter distribution of the Ga-MOF-nd. The diameter of the Ga-MOF-nd is about 300 nm; (b) the average thickness distribution of the Ga-MOF-nd. The thickness is about 80 nm.

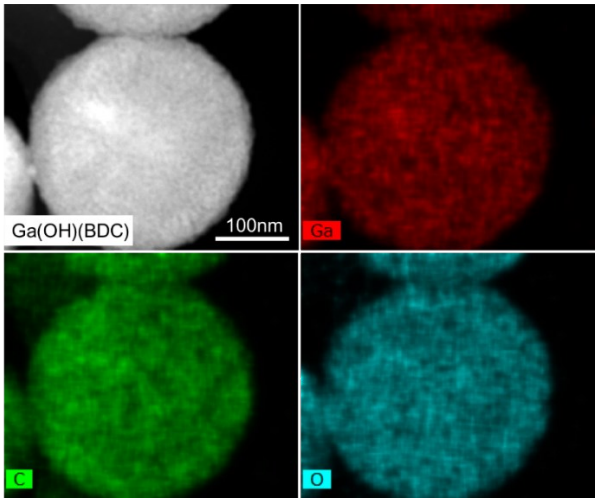

Figure S2. The EDS maps of the nanodisk-like Ga-MOF structure [molecular formula: Ga(OH)(BDC)]. The Ga (red), C (green) and O (aquamarine) elements in the Ga-MOF show a very uniform distribution.

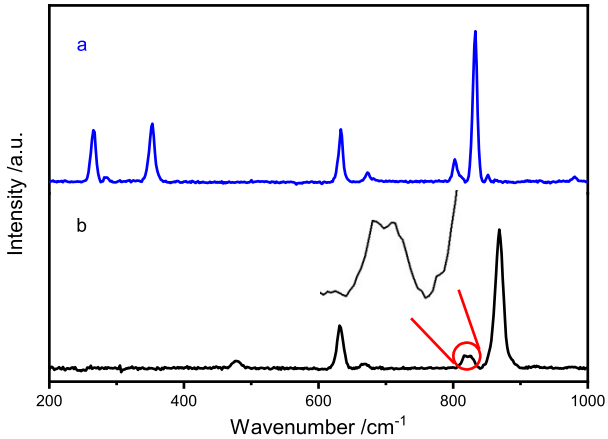

Figure S3. (a) The Raman spectrum (blue line) of the Ga-MOF-nd; (b) the Raman spectrum (black line) of the free H_2BDC. After coordination, the CCC bending vibrational band of the aromatic ring at 816 and 826 cm^{-1} in the free H_2BDC (see the red circle of figure b) became a single band at 802 cm^{-1} in the Ga-

MOF (see figure a).

Figure 4. (a) The time-dependent growth picture of Ga-MOFs from left to right at 15, 20, 25, 30 and 35 min; (b) the FE-SEM image of the Ga-MOF at 25 min.

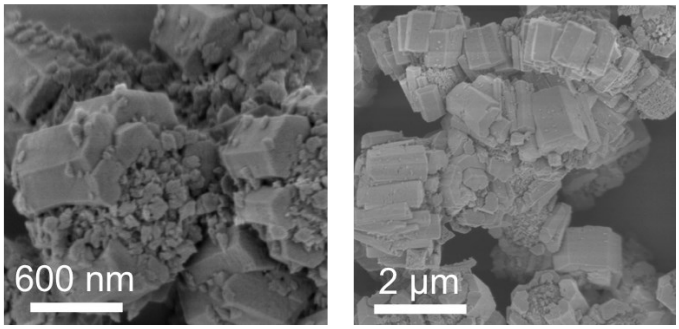

Figure S5. The FE-SEM images of the Ga-MOF samples synthesized at different crystallization times: (a) 10 h; (b) 24 h. It can be seen that cuboid structures with clear crystal faces begin to appear on the edge of the nanodisks after 10-hour crystallization. Extending to 24 h with crystallization time, the nanodisk structure totally disappeared leaving the irregular microcubes. This phenomenon is due to the Ostwald ripening-induced particle growth in the late crystallization stage.

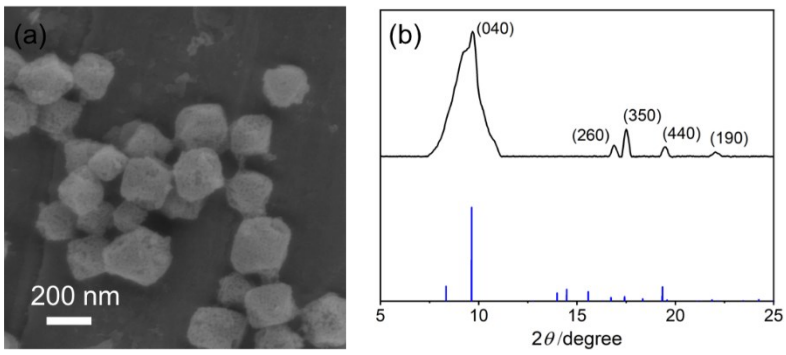

Figure 6. (a) The FE-SEM image of the Ga-MOF sample obtained under the same preparation conditions as the Ga-MOF-nd, but in the absence of β-CD; (b) the XRD pattern of the Ga-MOF (blank line) in the absence of β-CD.

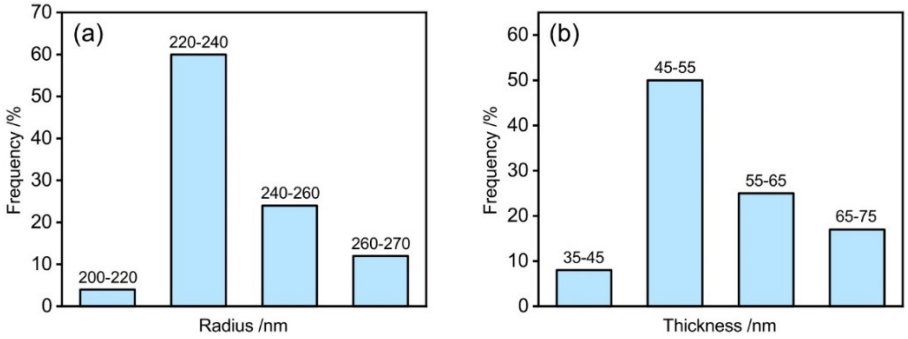

Figure S7. (a) The average outer diameter distribution of the β-Ga_2O_3-nr. The outer diameter of nanorings is about 230 nm; (b) the average height distribution of the rings. The height is about 50 nm.

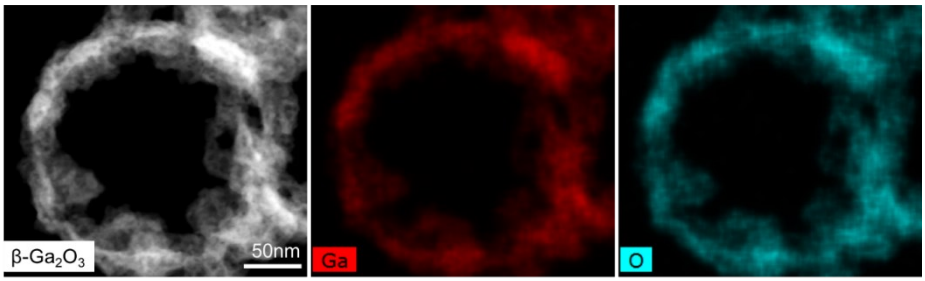

Figure S8. The EDS maps of the β-Ga_2O_3-nr. Both Ga (red) and O (aquamarine) elements have a uniform distribution, which is indicative of a single-phase microstructure.

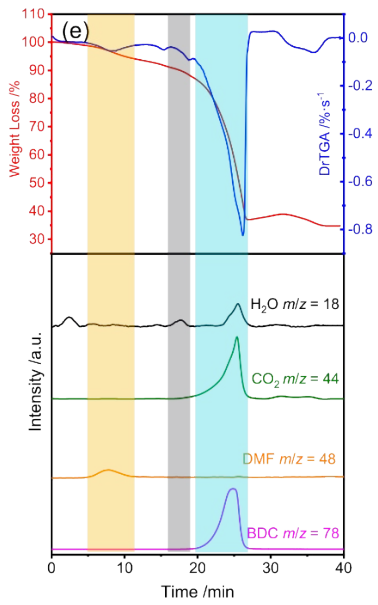

Figure S9. The thermogravimetric analysis and mass spectrometry curves of Ga-MOF. Color scheme of MS signals: black, water (*m/z*=18); red, CO_2 (*m/z*=44); blue, DMF (*m/z*=48); purple, BDC ligands (*m/z*=78), recorded during pyrolysis/oxidation of the Ga-MOF-nd. The heating rate is 20 K/min starting from 298 K. The weight loss at the orange zone is corresponding to the pyrolysis of DMF. At the gray zone, a small amount of H_2O and CO_2 released, corresponding to the pyrolysis of free H_2BDC (Figure S6

ESI). No other signal was detected, indicating the integrity of the Ga-MOF at this zone. When the time reached the ultramarine zone, three sharp peaks appeared, corresponding to H_2O, CO_2 and benzene.

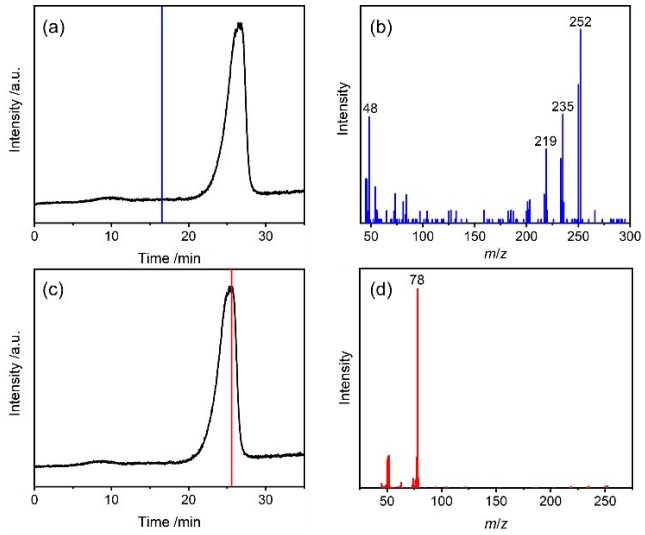

Figure S10. (a and c) The thermogravimetric analysis of the Ga-MOF-nd. (b and d)The mass spectra at different times correspond to the blue and red lines in (a and c). The mass spectra at different times show different pyrolysis processes. The blue line in (a) represents a dimer formed by free H_2BDC pyrolysis, corresponding to *m/z* = 252 in (b). Instead, the pyrolysis of the Ga-MOF-nd produced benzene (*m/z* = 78) and CO_2 (*m/z* = 44) as shown in the red lines of (c) and (d). During the pyrolysis of the Ga-MOF-md, no signal of *m/z* at 252 was detected. These results indicate that, the pyrolysis process of the MOF framework occurred after free H_2BDC pyrolysis. In other words, before the Ga-MOF started pyrolysis, free H_2BDC were pyrolyzed.

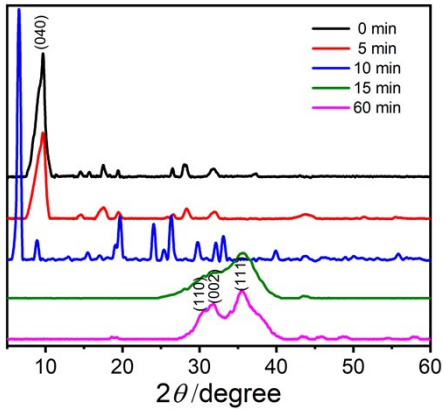

Figure 11. The evolution of XRD patterns of the Ga-MOF-nd during the calcination process from 0 to 60 min.

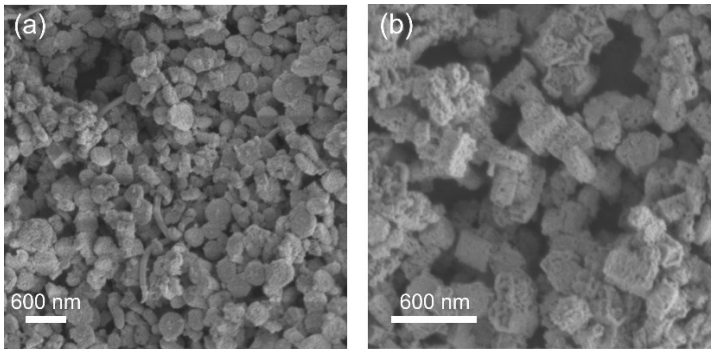

Figure S12. The FE-SEM images of the β-Ga_2O_3 samples obtained at different crystallization times: (a) 10 h; (b) 24 h. These results show the integrity of the two samples without producing hollow structures. The gas release caused by the pyrolysis of organic ligands led to the generation of porous structures.

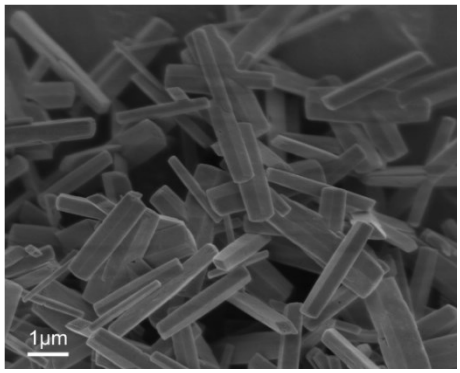

Figure S13. The FE-SEM image of the β-Ga_2O_3-mr. The length of the microrods is about 5 μm, and the width and height are about 0.5 μm. The microrods show a smooth surface.

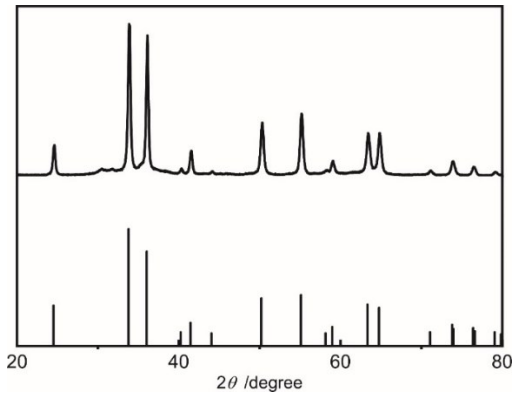

Figure S14. The XRD pattern of the β-Ga_2O_3-mr. The peaks are in good agreement with those of pure β-Ga_2O_3 (JCPDS card No: 43-1013).

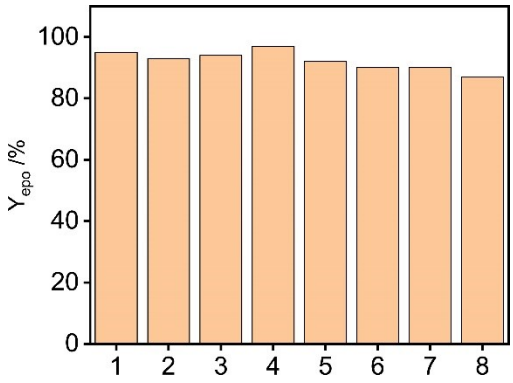

Figure S15. The epoxidation recycling test of the β-Ga_2O_3-nr. After eight cycles, the catalyst still shows a good catalytic performance.

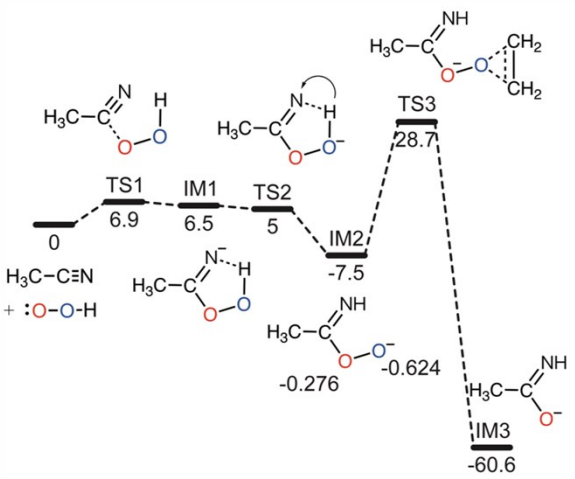

Figure S16. Calculated Gibbs free-energy profiles (kcal·mol^{-1}) for proposed Payne route.[1] With the addition of alkali, H^+ ions produced by initial dissociation will be combined with OH^- ions. As a result, H^+ ions do not bind to C=N bonds in the IM1. Instead, it will go through a process of transferring hydrogen from the OOH to the N in C=N bond through forming the TS2. From the calculated results, the bond length of the N···H bond is 1.67 Å. Considering the negative charge of N atoms, therefore, strong hydrogen bonds can be formed between them. Additionally, on the basis of the fact that the free energy barrier and electron energy barrier of TS2 are −1.5 and 0.06 kcal/mol, respectively, the hydrogen transfer process is extremely prone to occur and ultimately exposes the β-O for nucleophilic epoxidation.

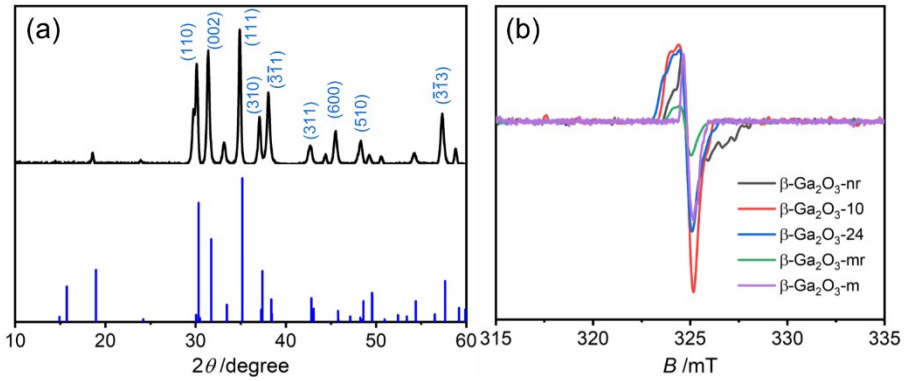

Figure 17. (a) The XRD pattern of the β-Ga_2O_3-m and (b) EPR spectra of β-Ga_2O_3-nr, -10, -24, -mr and -m. The β-Ga_2O_3-m was synthesized via a simple chemical route followed by calcination, according to the literature[2]: Typically 0.1 M of $Ga(NO_3)_3$ was dissolved into 100 mL water with continuous stirring. The temperature of the solution gradually increased from room temperature to 365 K. After reaching the final temperature, ammonia was added drop by drop to the solution until the pH of the solution reached about 9. Subsequently, the solution was kept for 4 h at that temperature and then cooled down naturally to the room temperature. The collected white precipitate was dried overnight at 333 K and calcined at 1273 K for 3 h.

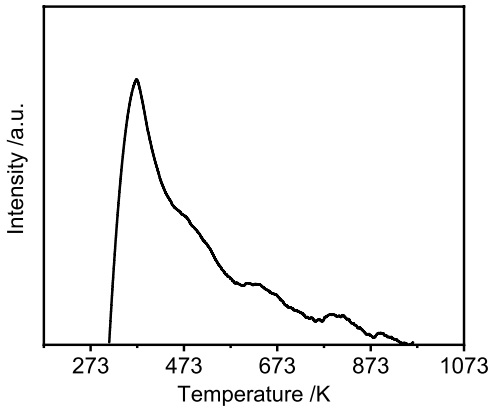

Figure S18. The NH_3 temperature programmed desorption (NH_3-TPD) curve of the β-Ga_2O_3-nr. The peak at 373 K shows the weak acid properties of Ga^{3+} sites in the β-Ga_2O_3.

Figure 19. (a) The photo of the acetonitrile solutions with the β-Ga_2O_3-nr catalyst on the left and without the β-Ga_2O_3-nr catalyst on the right; (b) the photo of the same solutions after half an hour of placement at room temperature. The two solutions on the left sides of (a) and (b) in the figure are both turbid, while the two solutions on the right sides are transparent. From these photos, especially from those of the same solutions after half an hour, we conclude that the β-Ga_2O_3 catalyst can be well dispersed in acetonitrile solution.

Reference:

1. Payne G. B., Williams P. H., Reactions of hydrogen peroxide. VII. *J. Org. Chem.* 1961, 26, 651-659.
2. B. Das, B. Das, N. Sankar Das, S. Pal, B. Kumar Das, S. Sarkar, K. K. Chattopadhyay, *Appl. Surf. Sci* . 2020, 515, 145958.

Cartesian coordinates for all the structures

Blank route

TS1

C	-0.49578059	0.33755274	0.00000000
N	-0.86074259	1.45482774	0.00082600
C	0.31784441	-0.86179626	0.00029900
H	0.89216941	-0.96203026	0.93702200
H	-0.28939359	-1.78659126	-0.09826300
H	1.03644241	-0.86280726	-0.83700500
O	-2.11971259	-0.87353526	-0.01113900
O	-3.35438659	-0.23988726	0.01227000
H	-3.07817859	0.71919174	-0.07095600

IM1

C	-0.52429218	0.47218354	-0.00001669
N	-0.16886118	1.64088354	-0.00000069
C	-1.87238518	-0.22653646	0.00002831
H	-1.98478818	-0.86954446	-0.88194969
H	-1.98429118	-0.87080946	0.88115831
H	-2.66311218	0.52584254	0.00080231
O	0.42766696	-0.62076392	-0.00001669
O	1.71968296	0.02862408	0.00002631
H	1.31422412	1.02865405	0.00005577

IM2

C	-1.36075948	0.40080953	-0.00524688
N	-0.71395948	-0.39135546	-0.79741186
C	-2.90075948	0.40080953	-0.00524688
H	-3.25742583	0.87441504	0.88547582
H	-3.25742583	0.93539504	-0.86076278
H	-3.25742634	-0.60738154	-0.04045369
O	-0.64575948	1.27650211	0.87044570
O	0.65213699	1.10640694	0.70035054
H	1.02760500	1.89092756	0.29396259
H	0.28604052	-0.39135546	-0.79741186

TS2

C	-1.65434381	0.32347504	0.00000000
N	-1.51176281	1.57144704	0.00955700
C	-2.97395081	-0.39122796	0.00414800
H	-3.08658181	-0.98520696	-0.90589300
H	-3.04447481	-1.07028396	0.85713100
H	-3.76676281	0.35164404	0.05777100
O	0.65400519	-0.02615596	-0.09577400
H	1.03216819	-0.34596796	0.73555200
H	-0.52209581	1.81955704	-0.01508900
C	1.49439409	-2.43202879	-0.64031259

H	1.35228353	-4.53471100	-0.64031259
C	0.81911978	-3.60700608	-0.64031259
H	-0.25088022	-3.60700608	-0.64031259
H	2.56439409	-2.43202879	-0.64031259
H	0.96123035	-1.50432387	-0.64031259
O	-0.65125181	-0.64259796	-0.02896900

Payne route

TS1

C	-0.49578059	0.33755274	0.00000000
N	-0.86074259	1.45482774	0.00082600
C	0.31784441	-0.86179626	0.00029900
H	0.89216941	-0.96203026	0.93702200
H	-0.28939359	-1.78659126	-0.09826300
H	1.03644241	-0.86280726	-0.83700500
O	-2.11971259	-0.87353526	-0.01113900
O	-3.35438659	-0.23988726	0.01227000
H	-3.07817859	0.71919174	-0.07095600

IM1

C	-0.52429218	0.47218354	-0.00001669
N	-0.16886118	1.64088354	-0.00000069
C	-1.87238518	-0.22653646	0.00002831
H	-1.98478818	-0.86954446	-0.88194969
H	-1.98429118	-0.87080946	0.88115831
H	-2.66311218	0.52584254	0.00080231
O	0.42766696	-0.62076392	-0.00001669
O	1.71968296	0.02862408	0.00002631
H	1.31422412	1.02865405	0.00005577

TS2

C	0.45854400	0.29006900	-0.00002800
N	0.06500100	1.44935000	-0.00006300

C	1.80730200	-0.39026400	0.00006900
H	1.92445900	-1.03047200	0.88030800
H	1.92515400	-1.02921000	-0.88100100
H	2.59824600	0.36032200	0.00090900
O	-0.54506000	-0.86095900	-0.00011700
O	-1.83652600	-0.21246600	0.00007500
H	-1.32286974	1.04118474	0.00039532

IM2

C	0.37800688	0.77319586	0.00000000
N	0.67632388	2.01745586	-0.00000100
C	-1.03940512	0.25960086	0.00000000
H	-1.22540212	-0.36153814	-0.88092600
H	-1.22540712	-0.36152414	0.88093500
H	-1.73484312	1.09785086	-0.00000800
O	1.26195688	-0.23563214	0.00000000
O	2.64784788	0.23432786	0.00000000
H	1.70867388	2.00461586	0.00000000

TS3

C	1.05104668	-0.11168649	-0.00001498
N	0.83355568	1.14938251	-0.00006998
C	2.43261268	-0.71524549	-0.00000498
H	2.57839168	-1.34679649	0.88104002
H	2.57829268	-1.34705349	-0.88087998
H	3.18078468	0.07634751	-0.00015898
O	0.10485368	-1.06250349	0.00004802
O	-1.62695264	-0.35408125	0.00004291
H	-0.19716132	1.20303951	-0.00004898
C	-3.44468653	-0.60153580	0.00004469
H	-3.73003036	-1.14961102	0.87359632
H	-3.73007934	-1.14926763	-0.87370630
C	-2.76108076	1.11054812	0.00003234

H	-2.58197633	1.70033921	0.87465687
H	-2.57929510	1.70240280	-0.87264286

IM3

C	-0.29106031	0.09355509	0.00000000
N	-0.50855131	1.35462409	-0.00005500
C	1.09050569	-0.51000391	0.00001000
H	1.23628469	-1.14155491	0.88105500
H	1.23618569	-1.14181191	-0.88086500
H	1.83867769	0.28158909	-0.00014400
O	-1.23725331	-0.85726191	0.00006300
H	-1.53926831	1.40828109	-0.00003400

Ga_2O_3 route

TS1

C	-0.49578059	0.33755274	0.00000000
N	-0.86074259	1.45482774	0.00082600
C	0.31784441	-0.86179626	0.00029900
H	0.89216941	-0.96203026	0.93702200
H	-0.28939359	-1.78659126	-0.09826300
H	1.03644241	-0.86280726	-0.83700500
O	-2.11971259	-0.87353526	-0.01113900
O	-3.35438659	-0.23988726	0.01227000
H	-3.07817859	0.71919174	-0.07095600

IM1

C	-0.52429218	0.47218354	-0.00001669
N	-0.16886118	1.64088354	-0.00000069
C	-1.87238518	-0.22653646	0.00002831
H	-1.98478818	-0.86954446	-0.88194969
H	-1.98429118	-0.87080946	0.88115831
H	-2.66311218	0.52584254	0.00080231
O	0.42766696	-0.62076392	-0.00001669

O	1.71968296	0.02862408	0.00002631
H	1.31422412	1.02865405	0.00005577

IM2

Ga	-1.72552600	-4.49768300	0.01568300
Ga	-1.64387100	-1.38381000	-0.02293500
Ga	-1.55801400	1.57968900	0.07410300
Ga	-1.47466100	4.61844400	0.10345800
Ga	4.42170400	-3.14918900	0.32666200
Ga	4.50532200	-0.11048100	0.35593100
Ga	4.58894000	2.92822900	0.38520100
Ga	1.51867500	-4.58254300	-0.44234800
Ga	1.60229300	-1.54383800	-0.41308000
Ga	1.68591000	1.49485800	-0.38380800
Ga	1.76952800	4.53358300	-0.35453800
Ga	-4.54493500	-2.89232600	-0.72407400
Ga	-4.46132500	0.14638000	-0.69476900
Ga	-4.37770300	3.18508900	-0.66551700
O	-5.04504100	-4.41044200	0.44185000
O	-4.96142400	-1.37173400	0.47112000
O	-4.87780600	1.66697500	0.50039000
O	-4.79418800	4.70568500	0.52966100
O	1.10219300	-3.06194900	0.75281600
O	1.18571600	-0.02321800	0.78214400
O	1.26942800	3.01546800	0.81135700
O	3.41068700	-4.63869800	-0.01763700
O	3.49430500	-1.59998800	0.01163200
O	3.57792300	1.43872100	0.04090300
O	3.66154100	4.47742900	0.07017200
O	-2.65293200	-2.94850300	-0.29923100
O	-2.56935000	0.09027000	-0.27000200
O	-2.48582300	3.12888400	-0.24066500
O	-0.34690600	-4.52369400	-1.22228300

O	-0.26327600	-1.48495500	-1.19299700
O	-0.17967900	1.55377500	-1.16375300
O	-0.09605200	4.59243300	-1.13447300
O	5.80032800	-3.17520100	-0.91131600
O	5.88394600	-0.13649100	-0.88204600
O	5.96756400	2.90221700	-0.85277500
N	-1.55090800	-1.55909400	1.86477600
C	-1.88323000	-0.78545300	2.78180600
C	-2.36178100	-1.15567800	4.16518100
H	-3.24271500	-0.56825600	4.43467400
H	-2.60740100	-2.21527100	4.19358800
H	-1.58326300	-0.93924800	4.90155900
O	-1.89002600	0.63026500	2.74531300
O	-0.95279500	1.17320500	1.79185000
H	0.35664900	0.16105300	1.27954200

TS2

Ga	-1.53650600	-4.56740200	-0.06739900
Ga	-1.45249800	-1.51206300	-0.10880600
Ga	-1.49543100	1.50263600	-0.16098900
Ga	-1.57552500	4.55251300	-0.03293800
Ga	4.55772100	-3.02288100	0.35569500
Ga	4.54474100	0.01706900	0.36709600
Ga	4.53171200	3.05701900	0.37869200
Ga	1.71726800	-4.55196800	-0.46103000
Ga	1.70422100	-1.51147200	-0.44944400
Ga	1.69111800	1.52732100	-0.43808600
Ga	1.67826500	4.56788300	-0.42654900
Ga	-4.38995100	-3.05654400	-0.87261100
Ga	-4.40299000	-0.01656600	-0.86097700
Ga	-4.41592400	3.02338200	-0.84976200
O	-4.86488300	-4.58297300	0.29289500
O	-4.87788500	-1.54301700	0.30438100

O	-4.89089200	1.49694400	0.31589100
O	-4.90389100	4.53688400	0.32736700
O	1.22926500	-3.03849100	0.71593900
O	1.58031300	0.00990400	0.39683900
O	1.20330600	3.04142500	0.73895300
O	3.60128800	-4.54565700	0.00111900
O	3.58826600	-1.50582800	0.01269000
O	3.57526800	1.53446700	0.02415600
O	3.56227800	4.57419600	0.03559500
O	-2.50573100	-3.04994100	-0.41039600
O	-2.51852800	-0.01014700	-0.39930000
O	-2.53179500	3.02940200	-0.38714600
O	-0.13341200	-4.55679000	-1.27783200
O	-0.14667600	-1.51708200	-1.26631500
O	-0.15976800	1.52329200	-1.25488700
O	-0.17242600	4.56305200	-1.24336000
O	5.96077200	-3.01230300	-0.85476300
O	5.94776800	0.02764800	-0.84327100
O	5.93476500	3.06759700	-0.83177800
N	-1.10113300	-1.46140700	1.75475300
C	-1.17530000	-0.63280100	2.67994300
C	-0.36904000	-0.66714300	3.95505600
O	-2.03584400	0.55301500	2.63847600
O	-1.03719200	1.82261500	1.64127300
H	-0.06398800	1.89914400	1.76487000
C	-4.03436700	-0.07018600	2.86910600
C	-3.64287600	-0.11543900	4.17602300
H	-4.41025600	0.83705400	2.40543700
H	-4.10033700	-0.96050700	2.24866300
H	-3.63041900	0.77552000	4.79507700
H	-3.34530700	-1.04912900	4.64344900
H	0.22775000	0.24888800	4.02648700
H	-1.01263700	-0.69839100	4.84047400

H	0.29483800	-1.53171100	3.93962400