**Supplementary Information**

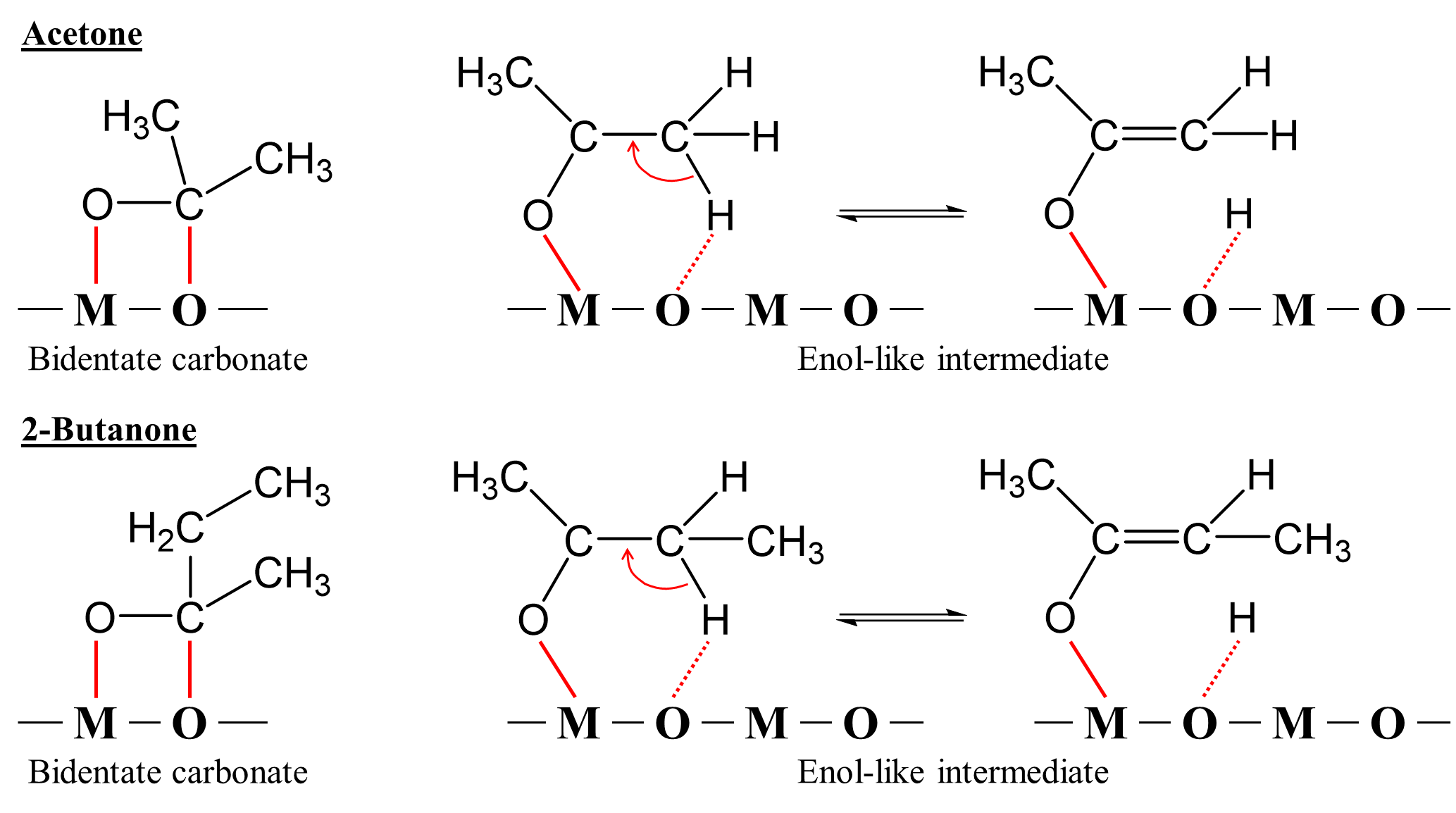


**Figure S1.** Representative chromatogram of reaction products obtained from.

aldol condensation of furfural and 2-butanone.



**Figure S2** 1H NMR spectrum of C9B-OH and C9B produced from aldol condensation of furfural and 2-butanone over LDO3 catalyst. From the GC analysis, this sample contained both C9 compounds more than 90%.



**Figure S3** Possible molecular configuration of acetone and 2-butanone adsorbed on a representative MgAl mixed oxide as deduced from *in situ* FTIR study.

**Table S1** Crystallite size and Mg/Al molar ratio of prepared MgAl LDH series

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Sample** | **Crystallite size of MgOa**  **(Å)** | **Mg/Al ratio obtained from WDS analysis** | | | | | | | | |
| **Theoretical** |  | **Actual** | | | | | | |
|  | **Mg** | |  | **Al** | |  | **Mg/Al** |
|  | (wt.%) | (mol) |  | (wt.%) | (mol) |  |
| LDH2 | 41.5 | 2 |  | 22.3 | 0.9 |  | 12.1 | 1.9 |  | 2.1 |
| LDH3 | 40.5 | 3 |  | 28.6 | 1.2 |  | 9.9 | 0.4 |  | 3.3 |
| LDH4 | 40.8 | 4 |  | 25.9 | 1.1 |  | 6.6 | 0.2 |  | 4.5 |

a Determined from XRD analysis using the calcined LDH samples

**Table S2** The result from GC-MS analysis and notation of unsaturated carbonyl compound as the obtained product of aldol condensation of furfural and 2-butanone

|  |  |  |  |
| --- | --- | --- | --- |
| **No.** | **Name** | **Notation** | **m/z** |
| 1 | 4-(Furan-2-yl)-4-hydroxy-3-methylbutan-2-one | C9B-OH | 43, 77, 96, 108, 121, 135, 150, 192, 207 |
| 2 | 1-(Furan-2-yl)pent-1-en-3-one | C9B | 43, 67, 79, 107, 135, 150 |
| 3 | 4-(Furan-2-yl)-3-methylbut-3-en-2-one | C9S | 43, 67, 93, 121, 135, 150 |
| 4 | 1,5-di(Furan-2-yl)-2-methylpenta-1,4-dien-3-one | C14 | 43, 73, 121, 150, 169, 182, 197, 239, 318 |
| 5 | 1-(Furan-2-yl)-4,5-dimethylhepta-1,4-dien-3-one | C13 | 43, 67, 68, 95, 121, 160, 175, 204 |
| 6 | 1-(Furan-2-yl)-2,5-dimethylhepta-1,4-dien-3-one | C13 | 43, 67, 92, 107, 109, 119, 148, 148, 175, 189, 204 |
| 7 | 7-(Furan-2-yl)-5,6-dimethylhepta-4,6-dien-3-one | C13 | 43, 67, 82, 107, 109, 147, 175, 189, 204 |
| 8 | 1,7-Di(furan-2-yl)-4,5,6-trimethylhepta-1,4,6-trien-3-one | C18BS | 43, 67, 81, 93, 108, 121, 135, 164, 178, 191,  205, 207, 220, 300 |
| 9 | 5-Ethyl-1,7-di(furan-2-yl)-4-methylhepta-1,4,6-trien-3-one | C18SS | 43, 67, 91, 117, 121, 131, 145, 159, 175, 188, 225, 253, 265, 282 |

**Table S3** Assignment of FTIR bands observed in acetone and 2-butanone adsorption on a representative MgAl mixed oxide

|  |  |  |
| --- | --- | --- |
| **Ketone** | **Wavenumber**  **(cm-1)** | **Assignment** |
| Acetone | 3750–3723 | O–H stretching of surface hydroxyl groups of metal oxides |
|  | 3650–3500 | O–H stretching of H-bonded surface hydroxyl groups |
|  | 3015 | C–H stretching of C=C–H in enol-like intermediate |
|  | 2960–2878 | C–H stretching of adsorbed acetone |
|  | 1735 | C=O stretching of free acetone |
|  | 1708–1701 | C=O stretching of adsorbed acetone |
|  | 1650 | OCO stretching of carbonate species |
|  | 1630 | OCO stretching of bidentate carbonate |
|  | 1602 | C=C stretching of enol-like intermediate |
|  | 1425 | C–H bending of adsorbed acetone |
|  | 1370 | C–H bending of adsorbed acetone |
|  | 1310 | OCO stretching of bidentate carbonate |
|  | 1237 | C–C stretching of adsorbed acetone |
| 2-Butanone | 3760–3720 | O–H stretching of surface hydroxyl groups of metal oxides |
|  | 3650–3500 | O–H stretching of H-bonded surface hydroxyl groups |
|  | 3069 | C–H stretching of C=C–H in enol-like intermediate |
|  | 2975–2890 | C–H stretching of adsorbed 2-butanone |
|  | 1734 | C=O stretching of free 2-butanone |
|  | 1703–1700 | C=O stretching of adsorbed 2-butanone |
|  | 1648 | OCO stretching of carbonate species |
|  | 1637 | OCO stretching of bidentate carbonate |
|  | 1601 | C=C stretching of enol-like intermediate |
|  | 1463 | C–H bending of adsorbed 2-butanone |
|  | 1420 | C–H bending of adsorbed 2-butanone |
|  | 1375 | C–H bending of adsorbed 2-butanone |
|  | 1305 | OCO stretching of bidentate carbonate |

**Table S4** The fitting parameters of CO2- and NH3-TPD profile of LDO2, LDO3 and LDO4

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Catalyst** | **Peak Index** | **Center Max** | **Area Fit** | **Max Height** | **FWHM** |
| **CO2-TPD** | | | | | |
| LDO4C | 1 | 100 | 0.35 | 0.00413 | 80 |
| LDO4C | 2 | 174 | 0.39 | 0.00369 | 98 |
| LDO4C | 3 | 255 | 0.26 | 0.00249 | 98 |
| LDO4C | 4 | 335 | 0.09 | 0.00090 | 91 |
| LDO3C | 1 | 118 | 0.41 | 0.00387 | 80 |
| LDO3C | 2 | 207 | 0.57 | 0.00351 | 110 |
| LDO3C | 3 | 300 | 0.12 | 0.00126 | 87 |
| LDO3C | 4 | 400 | 0.03 | 0.00032 | 76 |
| LDO2C | 1 | 95 | 0.23 | 0.00374 | 57 |
| LDO2C | 2 | 141 | 0.24 | 0.00284 | 80 |
| LDO2C | 3 | 198 | 0.30 | 0.00239 | 119 |
| LDO2C | 4 | 300 | 0.20 | 0.00124 | 149 |
| **NH3-TPD** | | | | | |
| LDO4C | 1 | 116 | 0.39 | 0.00460 | 80 |
| LDO4C | 2 | 176 | 0.13 | 0.00186 | 64 |
| LDO4C | 3 | 227 | 0.03 | 0.00054 | 57 |
| LDO3C | 1 | 112 | 0.42 | 0.00435 | 90 |
| LDO3C | 2 | 180 | 0.18 | 0.00239 | 71 |
| LDO3C | 3 | 238 | 0.09 | 0.00125 | 68 |
| LDO3C | 4 | 445 | 0.00 | 0.00012 | 40 |
| LDO2C | 1 | 113 | 0.28 | 0.00331 | 79 |
| LDO2C | 2 | 173 | 0.10 | 0.00156 | 61 |
| LDO2C | 3 | 219 | 0.04 | 0.00074 | 47 |
| LDO2C | 4 | 404 | 0.01 | 0.00014 | 72 |

**Table S5** Input: Optimization of the adsorption of 2-butanone on MgO(100) (methylene enolate route)

%chk=B2L\_1.chk

%mem=4GB

%nprocshared=16

# opt 6-31g geom=connectivity m062x

butanone2-MgO4

0 1

Mg

Mg 1 2.91656771

O 1 2.05368059 2 44.79599578

O 2 2.04297720 1 44.47955064 3 179.91362989 0

Mg 3 7.35235399 1 145.78815581 4 -179.64632885 0

Mg 5 2.89387882 3 100.97176695 1 179.95351124 0

O 5 2.03691042 3 145.84748374 1 179.92839086 0

Mg 1 4.06098171 4 179.55423647 2 -22.12262344 0

Mg 3 2.04259692 1 89.52523413 4 -179.98887835 0

O 9 2.04108637 3 179.55170318 1 131.93306867 0

Mg 10 2.03665677 9 90.54076875 3 48.06532855 0

O 5 2.03319600 3 34.04300174 1 -0.08701395 0

Mg 6 2.89377320 5 90.30750700 3 0.04297829 0

Mg 13 2.88658600 6 90.25894159 5 -179.85799395 0

O 13 2.03736426 6 44.85353347 5 -179.94186988 0

Mg 3 2.03764605 1 179.88716251 4 89.25148293 0

Mg 13 2.90181323 6 179.51592916 5 -161.58821761 0

O 13 2.03188443 6 135.04916004 5 0.09839423 0

O 2 2.03351355 1 135.84251914 4 -179.93222011 0

O 14 2.03256653 13 46.01580531 6 179.89366456 0

O 1 2.03034158 4 179.69010826 2 -152.85890681 0

Mg 18 2.05812189 13 89.82489444 6 -0.09234365 0

O 22 2.03411013 18 89.93373768 13 179.90074057 0

O 22 2.03511917 18 89.97523134 13 0.02456168 0

Mg 15 2.05441581 13 179.93721637 6 141.21066417 0

O 14 2.04053597 13 134.36777002 6 -0.07094420 0

Mg 7 2.05435193 5 179.89611956 3 -141.64792007 0

O 25 2.03333354 15 90.83349432 13 -141.24481650 0

Mg 4 1.98985436 2 88.49363607 1 88.45367464 0

Mg 3 2.06924464 1 89.90251189 21 -90.14751168 0

O 29 1.99105556 4 93.30543093 2 1.85289771 0

O 29 1.99037595 4 93.31389177 2 -92.93408224 0

Mg 7 2.06871849 5 90.22044500 3 90.17053621 0

Mg 10 2.07426349 9 89.97063666 3 138.11679859 0

Mg 32 2.03916294 29 176.55520222 4 54.38577632 0

O 35 2.03766219 32 178.92364430 29 -155.05715400 0

Mg 23 2.12456509 22 90.06969297 18 -89.53835868 0

Mg 12 2.07040840 5 90.04773925 3 -90.28874614 0

O 38 2.02841301 12 90.87163335 5 179.73214732 0

O 38 2.03806948 12 90.54591480 5 0.12479437 0

Mg 15 2.07156944 13 90.20181635 6 -90.22961774 0

Mg 31 2.03606718 29 176.64049742 4 -52.83688572 0

Mg 20 2.04956606 14 89.96008305 13 89.39139428 0

O 43 2.03167772 20 90.38612948 14 0.80726157 0

Mg 18 2.10775088 13 90.36001853 6 90.53259682 0

O 43 2.03760077 20 90.66202379 14 179.92776287 0

O 45 2.02738448 18 89.64193851 13 -179.98213016 0

O 41 2.04366336 15 90.63518616 13 -0.14903780 0

Mg 40 2.05844372 38 90.37522426 12 89.60755353 0

O 49 2.04054559 40 90.04887988 38 -179.52739443 0

O 35 2.02610164 32 90.48841782 29 38.27736303 0

O 49 2.03281000 40 89.98088182 38 0.36186271 0

Mg 26 1.99014672 14 88.70057117 13 -88.31686103 0

O 53 1.99548392 26 93.68658668 14 92.56808520 0

Mg 54 2.03191672 53 176.50979789 26 -43.94367862 0

O 55 2.03072863 54 178.88553006 53 179.63668087 0

Mg 10 2.05438257 9 179.89279320 3 -125.11508815 0

O 8 2.04201150 1 179.55453235 21 154.06898400 0

Mg 7 2.05622131 5 89.66956424 3 -179.93570382 0

Mg 12 2.06538192 5 90.20143069 3 179.94835914 0

O 57 2.03172734 10 91.08297375 9 173.07696903 0

O 59 2.03281356 7 90.90834464 5 -0.01491614 0

O 59 2.04101905 7 89.46531385 5 179.96603470 0

Mg 36 1.99165272 35 176.53187165 32 153.13275154 0

O 64 1.99103546 36 94.56600142 35 41.10638371 0

Mg 39 2.03474834 38 90.01114119 12 88.94067048 0

Mg 40 2.04806079 38 89.73792304 12 -89.01128771 0

O 67 2.03088634 40 90.04614624 38 179.77071877 0

O 67 2.03414190 40 90.80242191 38 -1.32734838 0

Mg 63 1.99217162 59 88.67073596 7 88.29263173 0

C 49 3.80221652 40 99.43225188 38 76.95431376 0

C 71 1.57798524 49 51.04188332 40 -91.90243531 0

C 72 1.52370688 71 120.22873698 49 165.25191549 0

C 73 1.53533662 72 122.15029173 71 13.56750140 0

O 73 1.32181267 72 116.50682865 71 -177.76404726 0

H 71 1.09703269 49 165.94749480 40 -97.33871170 0

H 71 1.09761282 49 81.74726250 40 33.27066756 0

H 71 1.09833520 49 80.31183511 40 142.62213989 0

H 72 1.09477168 71 106.27915810 49 56.39400213 0

H 72 1.11260695 71 108.25432989 49 -62.58528614 0

H 74 1.09024311 73 107.20383495 72 164.91140666 0

H 74 1.10201784 73 110.08683138 72 44.96337827 0

H 74 1.10248582 73 112.93684631 72 -74.64612894 0

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3 9 1.0 16 1.0 30 1.0

4 29 1.0

5 7 1.0 12 1.0 24 1.0 40 1.0 62 1.0

6 7 1.0 15 1.0 24 1.0 28 1.0 50 1.0

7 27 1.0 33 1.0 59 1.0

8 10 1.0 21 1.0 36 1.0 58 1.0 64 1.0

9 10 1.0 21 1.0 23 1.0 51 1.0

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11 12 1.0 23 1.0 39 1.0 57 1.0 61 1.0

12 22 1.0 38 1.0 60 1.0

13 15 1.0 18 1.0 20 1.0 24 1.0 48 1.0

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15 25 1.0 41 1.0

16 18 1.0 19 1.0 23 1.0 47 1.0

17 18 1.0 19 1.0 20 1.0 46 1.0

18 22 1.0 45 1.0

19 42 1.0

20 43 1.0

21 35 1.0

22 23 1.0 24 1.0 52 1.0

23 37 1.0

24 49 1.0

25 26 1.0 28 1.0 53 1.0 54 1.0

26 53 1.0

27 28 1.0 56 1.0 63 1.0 70 1.0

28 55 1.0

29 30 1.0 31 1.0 32 1.0

30 31 1.0 32 1.0 47 1.0 51 1.0

31 42 1.0

32 35 1.0

33 40 1.0 50 1.0 56 1.0 68 1.0 70 1.0

34 36 1.0 39 1.0 51 1.0 64 1.0 65 1.0

35 36 1.0 51 1.0

36 64 1.0

37 39 1.0 47 1.0 51 1.0 52 1.0 75 0.5

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39 66 1.0

40 49 1.0 67 1.0

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65 66 1.0

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67 68 1.0 69 1.0

68 70 1.0

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72 73 1.0 79 1.0 80 1.0

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74 81 1.0 82 1.0 83 1.0

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**Table S6** Input: Optimization of the adsorption of 2-butanone on MgO(100) (methyl enolate route)

%chk=S2L\_1.chk

%mem=4GB

%nprocshared=12

# opt 6-31g geom=connectivity m062x

butanone2-MgO4

0 1

Mg 0.00000000 0.00000000 0.00000000

Mg 0.00000000 0.00000000 2.91656771

O 1.44699176 0.00000000 1.45733278

O -1.43141986 0.00215779 1.45890232

Mg 8.66441579 0.02115261 2.85927861

Mg 8.66339654 0.01302075 5.75314583

O 10.10108243 0.02259257 4.30322838

Mg 2.86493709 0.00757938 -2.87813315

Mg 2.88448378 -0.00176009 0.00618987

O 4.32845789 0.00836146 -1.43633220

Mg 5.78140161 0.00847739 -0.00912328

O 7.22761775 0.01939338 1.42070491

Mg 5.76968557 0.00074984 5.76762305

Mg 5.77108533 -0.00019701 8.65420855

O 7.22116634 0.00432703 7.19732368

Mg 2.88264283 -0.00401251 2.90332424

Mg 2.86812223 -0.00387640 5.80542244

O 4.32453667 -0.00381185 4.33930999

O 1.41661235 -0.00045963 4.37546681

O 4.30790973 -0.00321930 7.24338087

O 1.41496370 0.00287652 -1.45607568

Mg 5.77572543 0.00724368 2.87992838

O 4.33173346 -0.00082611 1.44729930

O 7.21818031 0.01090211 4.31555387

Mg 8.68355699 0.00933696 8.64024183

O 7.23048058 0.00371227 10.08037028

Mg 11.55211123 0.02636788 5.75748525

O 10.13255341 0.01683654 7.21377822

Mg -1.35946737 -1.98639524 1.45861523

Mg 1.44281131 -2.06924026 1.45652204

O -0.01057547 -2.05267576 2.92162576

O -0.01103455 -2.05252442 -0.00390051

Mg 10.11807965 -2.04605293 4.29960771

Mg 4.33368075 -2.06588071 -1.44415400

Mg 1.44143499 -2.04622487 -1.43515103

O 2.86634118 -2.04804155 -2.89175882

Mg 4.33185714 -2.12537547 1.45547265

Mg 7.24069918 -2.05093305 1.40773329

O 5.80093819 -2.08193805 -0.02075763

O 8.67786575 -2.07032487 2.85269122

Mg 7.22930487 -2.06721350 7.20464241

Mg 1.43658818 -2.04578735 4.35384065

Mg 4.32893244 -2.05262002 7.22802554

O 5.77155016 -2.06223316 8.65857651

Mg 4.31027086 -2.11151317 4.34163487

O 2.86070478 -2.08064211 5.81546078

O 2.86893870 -2.09066011 2.91600709

O 5.76980887 -2.10065624 5.77449804

Mg 7.22790869 -2.07467061 4.31378540

O 8.67507782 -2.07723070 5.75236847

O 2.87559821 -2.08511701 -0.00450393

O 5.78548181 -2.06819340 2.88141700

Mg 7.24501442 -1.98500529 10.00637573

O 8.69940458 -2.05200155 8.64174507

Mg 10.12245725 -2.02919931 7.19154276

O 11.56386627 -2.03529459 5.76110170

Mg 5.77913677 0.01900533 -2.89094735

O 4.31540803 0.01886161 -4.31542844

Mg 11.55030855 0.03328616 2.84457305

Mg 8.68380213 0.02921775 -0.04395649

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Mg 12.91918303 -1.95519014 4.29990896

C 6.71223383 -7.52056476 4.15791593

C 7.08846518 -6.04714044 4.57923304

C 6.68277687 -4.87061255 3.70009607

C 5.65760799 -5.01334595 2.56611437

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H 7.59536913 -8.05397461 3.78334967

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36 64 1.0

37 39 1.0 47 1.0 51 1.0 52 1.0

38 39 1.0 40 1.0 52 1.0 66 1.0 67 1.0 69 1.0

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40 49 1.0 67 1.0

41 44 1.0 48 1.0 50 1.0 53 1.0 54 1.0

42 45 1.0 46 1.0 47 1.0

43 44 1.0 46 1.0 48 1.0

44 53 1.0

45 46 1.0 47 1.0 48 1.0 52 1.0

46

47

48 49 1.0

49 50 1.0 52 1.0 75 0.5

50 55 1.0

51

52 81 0.5

53 54 1.0

54 55 1.0

55 56 1.0

56 70 1.0

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58 64 1.0

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61 66 1.0

62 67 1.0

63 70 1.0

64 65 1.0

65 66 1.0

66 69 1.0

67 68 1.0 69 1.0

68 70 1.0

69

70

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72 73 1.0 79 1.0 80 1.0

73 74 1.0 75 2.0

74 81 1.0 82 1.0 83 1.0

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