# Development of 6-amyl-α-pyrone as a potential biomass-derived platform molecule

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## SUPPLIMENTARY INFORMATION

## 1. EXPERIMENTAL AND COMPUTATIONAL METHODS

### 1.1 Materials

6PP, γ-alumina, silica-alumina, 4-nonanone, 5-nonanone, HMF and furfural were obtained from Sigma Aldrich Chemicals Pvt. Ltd. (India). Sodium chloride, sodium sulphate, tetrahydrofuran, and ethyl acetate were procured from Sisco Research Laboratories Pvt. Ltd. (SRL, India). A 10% Pd/C catalyst, was obtained from Alpha Aeser (India). Magnesium nitrate, calcium nitrate, NaOH and $Na_2CO_3$ were procured from S.D. Fine Chemical Pvt. Ltd., India.

### 1.2 Preparation of CaO-MgO catalyst

The CaO-MgO catalyst was synthesized via a co-precipitation method.[1] In this method 23.61 gm $Ca(NO_3)_2.4H_2O$ and 12.80 gm of $Mg(NO_3)_2.6H_2O$ were dissolved in 500mL DI water. The solution was stirred rigorously for 1 h to achieve homogeneous mixing. A precipitate was obtained on drop-wise addition of the NaOH and $Na_2CO_3$ solution at a constant pH of 10. After

the completion of precipitation, the solution was filtered and washed with DI water until the pH of filtrate reached 7. The obtained slurry was dried at 393 K for 12 h and calcined at 1073 K for 6 h.

**1.3 Instrumentation**

The XRD patterns of CaO-MgO material (Figure 2a) were collected at room temperature using a Bruker D8 Advance and a Rigakuminiflex-(II) X-Ray diffractometer equipped with a monochromatized Cu-Kα radiation (λ = 1.54056 Å) source operated at 45 V and 40 mA. The XRD peaks were compared with pure phase of CaO (JCPDS File No. 00-037-1497), MgO (JCPDS file No. 00-004-0829), $CaCO_3$ (JCPDS File No. 00-047-1743) and $Ca(OH)_2$ (JCPDS File No. 00-084-1264)[2]. FT-IR spectra of CaO-MgO were recorded on a Perkin-Elmer spectrophotometer (model 1752X FTIR).

**1.4 Ring-opening, decarboxylation and hydrogenation reactions:**

Reactions were performed in a high pressure batch reactor (100 ml, Amar Equipment Pvt. Ltd., India) equipped with a multi-blade impeller and a heater. For ring-opening and decarboxylation reaction, mass ratio of the reactant and catalyst was kept at 2:1 in a solvent mixture of water and THF (1:3) at a specified temperature. On completion of the reaction, the organic phase was separated by adding sodium chloride (0.5 g) and the aqueous layer was extracted with ethyl acetate. The residual water in the combined organic solution was absorbed through sodium sulfate and the organic solvent was evaporated under reduced pressure in a rotary evaporator. Hydrogenation of obtained non-2-ene-4one was performed in 25 mL THF at temperature 373 K and 37 bar $H_2$ pressure for 5 hours using 10% Pd/C (50% wt% to the reactant).

**1.5 Product characterization and analysis**

Quantitative analysis of reaction mixture were performed on a 30 m x 0.250 mm x 0.50 μm DB-wax column (Agilent Technologies, India) placed in a gas chromatograph (GC) (Nucon, India Model: 6775) and integrated to a flame ionization detector (FID). The column was maintained at 333 K for 4 minutes, 403 K for 2 min and 513 K for 30 min with an intermediate ramping rate of 10° $min^{-1}$ between steps. The temperatures of injector and detector were set to 503 and 513 K respectively. Additionally, products in liquid phase were qualitatively analyzed using a GC-MS (Perkin Elmer, Clarus 600) equipped with a DB-wax column (Agilent Technologies, India) under similar conditions as of in GC analysis. The MS spectra (Figure S1, Scheme S1) of the reaction products were compared with the spectra of the standards obtained from the NIST MS library.

The conversion of 6PP on a carbon basis was calculated as follows,

$$\%\ \text{conversion} = \left( \frac{C_i - C_o}{C_i} \right) \times 100$$

where $C_i$ was the initial concentration of 6PP in the reaction mixture and $C_o$ was the final concentration in the product mixture. The selectivity to the product '*i*' was calculated based on the total number of carbon atoms in the product,

$$S_i = [(n_i M_i) / \sum n_j (C_i - C_o)] \times 100$$

where $n_i$ is the number of carbon atoms in the product, $n_j$ is the number of carbon atoms in the reactant and $M_i$ is the moles of product formed. Calibration curves for 6PP and 4-nonanone were plotted using the standards. Response factor of the product non-2-en-4-one on FID was assumed to be equal to 4-nonanone.[3]

Further confirmation of the identified products was obtained on utilizing a $^{1}H$ and $^{13}C$ NMR analysis performed on a JEOL JNM ECX-400P at 400 and 100 MHz respectively. The NMR spectral analyses were performed on a JEOL DELTA program version 4.3.6. The values for chemical shifts were reported with respect to the internal standard, teramethylsilane ($\delta$H 0.00). The NMR data was represented in following manner: chemical shift ($\delta$, ppm), multiplicity (s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet) and coupling constant. $^{1}H$ NMR (400 MHz, $CDCl_3$): $\delta$ 6.83-6.77 (m, 1H), 6.10-6.05 (m, 1H), 2.46 (t, $J$ = 7.6 Hz, 2H), 1.86-1.84 (m, 3H), 1.26-1.24 (m, 6H), 0.85-0.82 (m, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 200.8, 142.5, 131.8, 39.9, 31.4, 23.9, 22.4, 18.1, 13.8. The $^{1}H$ and $^{13}C$ NMR spectra are shown in Figure S2.

**1.6 Aldol condensation between nonanone and furanic aldehydes**

Aldol condensation of HMF or furfural with 5-nonanone was conducted under neat condition in a 10 mL round bottom flask placed in a pre-heated oil bath equipped with a magnetic stirrer. The flask was purged with nitrogen and the reaction was performed under the inert atmosphere. For a typical aldol reaction, HMF or furfural (8 mmol), 5-nonanone (16 mmol) and CaO-MgO catalyst (100 mg) were added in the flask and the mixture was continuously stirred at desired temperature (353-443 K) and reaction time (6-18 h). Upon completion of the reaction, the mixture was cooled down to room temperature and catalyst was separated by centrifugation. The yields (mol%) of products were determined by $^{1}H$ NMR spectroscopy using mesitylene as an internal standard. Details on the method are given in our earlier study[4]. NMR spectra of the products revealed the formation of 4-(furan-2-ylmethylene)nonan-5-one (F5N) and 4-((5-(hydroxymethyl)furan-2-yl)methylene)nonan-5-one (H5N). $^{1}H$ NMR of F5N (400 MHz, $CDCl_3$): $\delta$ 7.49 (d, $J$ = 1.3 Hz, 1H), 7.15 (s, 1H), 6.57 (d, 1H), 6.45 (dd, 1H), 2.70 – 2.66 (m, 2H), 2.60 – 2.57 (m, 2H), 1.21-1.52 (m, 6H), 0.91 – 0.81 (m, 6H) ppm (Figure S3). $^{1}H$ NMR of H5N (400 MHz, $CDCl_3$): $\delta$ 7.26

(s, 1H), 6.52 (d, 1H), 6.43 (dd, 1H), 4.67 (s, 1H), 2.77 – 2.67 (m, 2H), 2.60 – 2.64 (m, 2H), 1.29-1.62 (m, 6H), 0.98 – 0.81 (m, 6H) ppm (Figure S4).

To study catalyst stability, after the 1st cycle of reaction, the catalyst was separated by filtration, washed with distilled water, dried and reused for three consecutive cycles. Fresh catalyst was not added to replenish any loss of the catalyst mass during recovery.

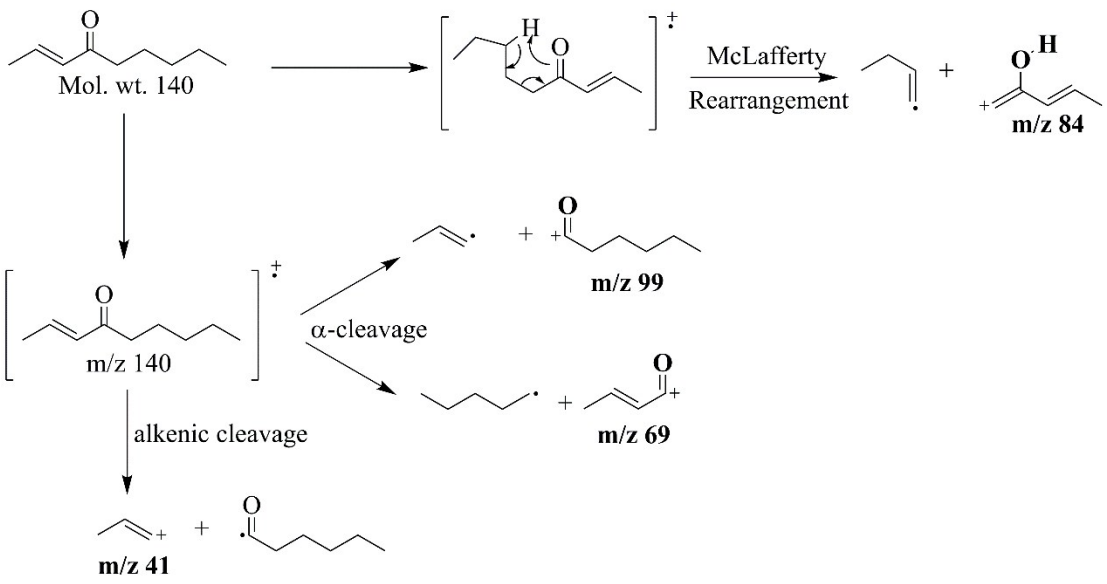
**1.7 Computation methods**

DFT calculations in non-catalytic water medium were performed using DMol$^3$ module available in Material Studio 8 (Biovia, San Diego, USA)[5] with DNP (Double Numerial plus Polarization) numerical basis set. GGA (Generalized gradient approximation) with PW91 (Perdew and Wang's) functional was utilized to explain exchange correlation energy and potential[6]. DMol$^3$ specified "Fine" convergence criteria for energy, force and atom displacement was set to 0.0001 eV, 0.05 eV/ Å and 0.005 Å respectively for geometry optimization and transition state search. The self-consistent field calculations of electron density were converged to $1\times10^{-6}$ value with a density mixing parameter set to 0.02.

The activation barriers were measured through a transition state (TS) search by linear synchronous transit/quadratic synchronous transit (LST/QST) method[7]. In LST, a set of single point calculations were performed on a set of linearly interpolated structures between the reactant and product. The first estimate of TS structure was provided by the maximum energy structure along this path. Subsequently, the structure was refined in orthogonal direction to the QST, which was further used as an intermediate for QST pathway. The method thus yields a refined transition state geometry. Transition state thus obtained is further refined with the 'TS Optimization' module in DMol$^3$. In this technique the optimization starts with the transition state

structure obtained from LST/QST method and is searched for energy maxima along a normal mode using the Newton-Raphson line search algorithm. The transition states obtained were verified by the presence of a single imaginary frequency vibrational mode along the reaction coordinate. Solvent environment was simulated using conductor-like screening model (COSMO) in which solvents were represented by their respective dielectric constant; for water $\varepsilon$=78.54[8,9]

Periodic plane-wave DFT code as implemented in Vienna Ab initio Simulation Package (VASP)[45] was utilized to study the water mediated ring opening reaction of 6PP over the $\gamma$-$Al_2O_3$ (110) surface[10].The $\gamma$-$Al_2O_3$ (110) surface was modeled using the bulk $\gamma$-$Al_2O_3$ geometry reported by *Digne et al.* [11]. The (110) surface is the most abundant surface in $\gamma$-$Al_2O_3$ consisting nearly 74% of the total surface. The cell parameters for the $\gamma$-$Al_2O_3$ (110) surface are a = 16.83 Å, b = 16.14 Å and $\alpha = \beta = \gamma = 90°$. Two neighboring slabs were separated by a vacuum of 15 Å. Two bottom layers of the $\gamma$-$Al_2O_3$ surface were fixed whereas the top-most two layer was allowed to relax. Adsorption and TS energy calculations were performed using the GGA-PW91 exchange-correlation functions as described by Perdew and Wang[12]. Ultra-soft pseudopotentials were used to describe the core electrons[13]. Basis sets were expanded to an energy cut-off value of 396 eV. The energy and force convergence criteria for all structural optimization were set to $1x10^{-4}$ eV and 0.05 eV/Å respectively. The surface Brillouin zone was sampled using a 1x1x1 Monkhorst-Pack grid. The activation barriers for 6PP ring opening and subsequent proton transfer steps was calculated using the Nudged Elastic Band (NEB) method with climbing images[14]. In the NEB simulation, a set of 8 images between the initial and the final states were optimized along the potential energy surface until the force on each atom was converged to 0.10 eV/Å. The activation energy was calculated as the difference in the energy between the TS and reactant state.




**Scheme S1.** Fragmentation pattern of nonane-2-en-4-one showing characteristic peaks of m/z values 41, 69 and 84.

Scheme S1 shows the fragmentation pattern of non-2-en-4-one MS acquired under the ionization condition. The m/z value at 140 indicates the base peak of the non-2-en-4-one. α-cleavage of non-2-en-4-one resulting into the loss of prop-2-ene and hexane radicals was attributed to the peaks at 99 and 69 respectively. A second type of fragmentation occurred due to McLafferty rearrangement of the molecular ion, which involves transfer of gamma hydrogen to carbonyl-oxygen with concurrent formation of the alcohol showing distinct peak at m/z value of 84. A peak at 41 indicates the α-cleavage of the base peak into propene.

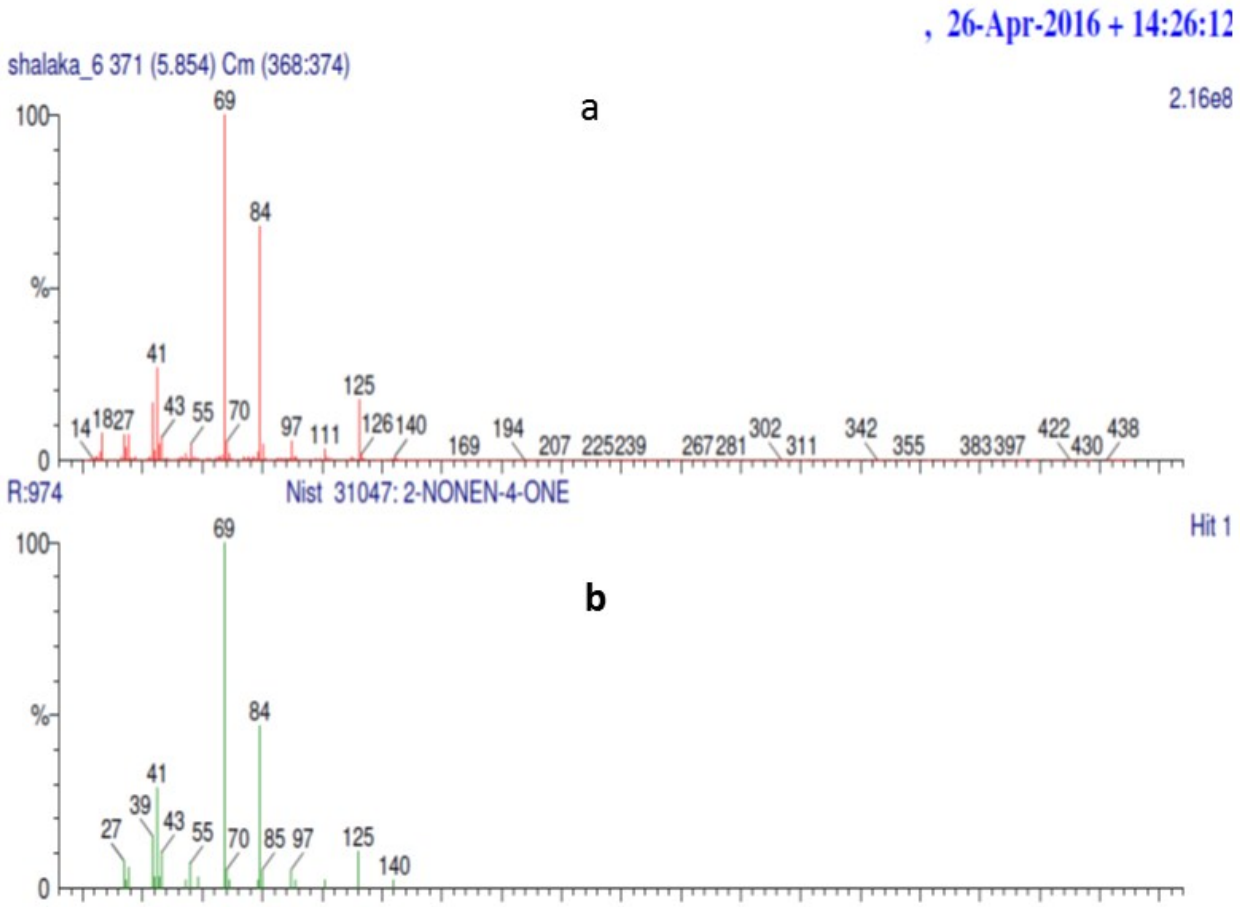



**Figure S1.** Fragmentation pattern obtained from the GCMS of (a) 6PP derived non-2-en-4-one and (b) Nist library

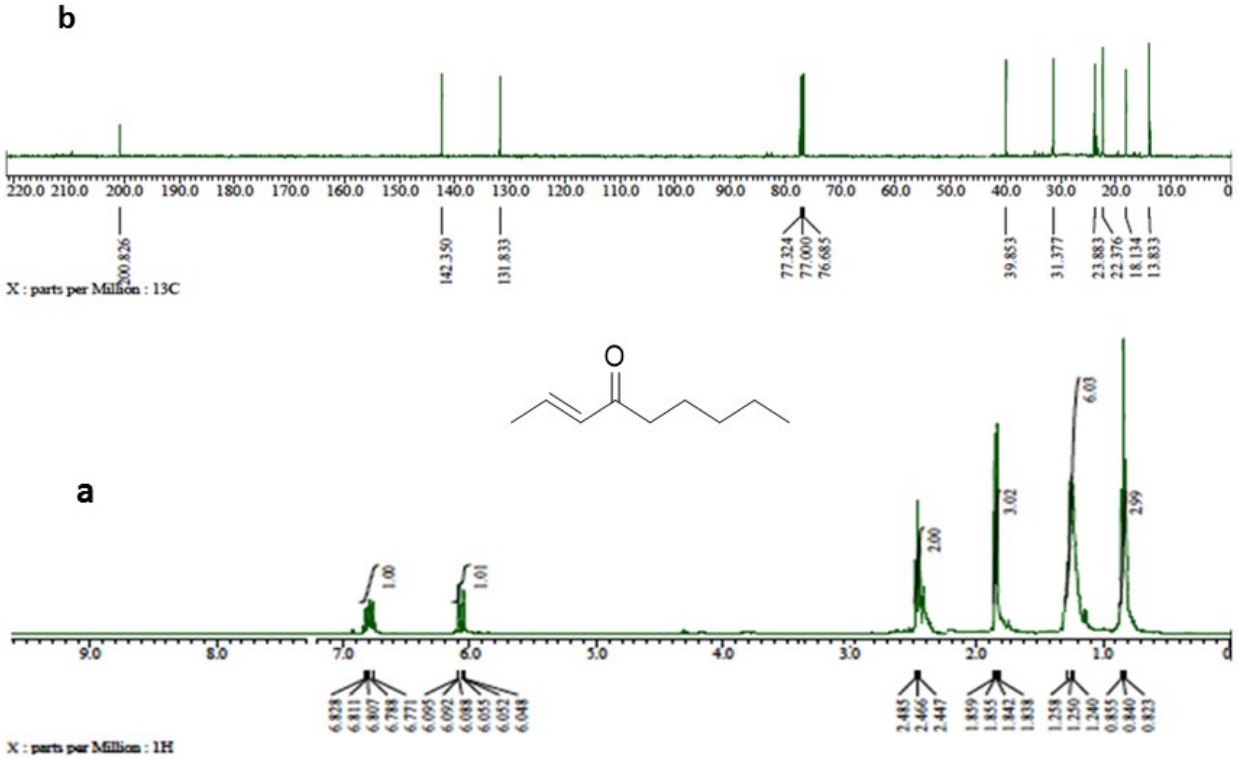



**Figure S2** (a) $^{1}H$ NMR spectra and (b) $^{13}C$ NMR spectra of silica-alumina catalyzed reaction mixture showing the formation of non-2-en-4-one

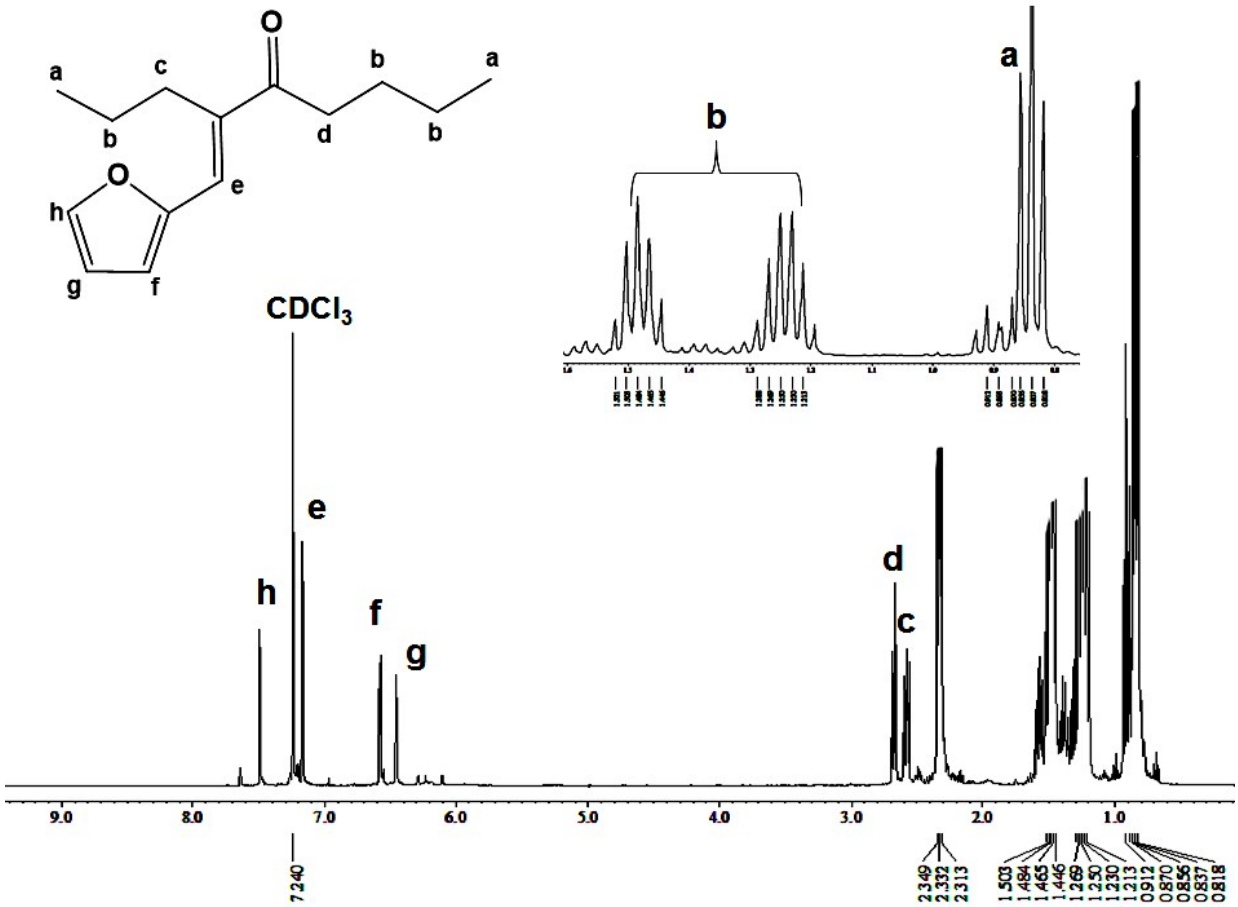



**Figure S3.** [1]H NMR spectrum of **F5N** produced from aldol condensation of furfural with 5-nonanone at 443K for 12 h over the CaO-MgO catalyst.

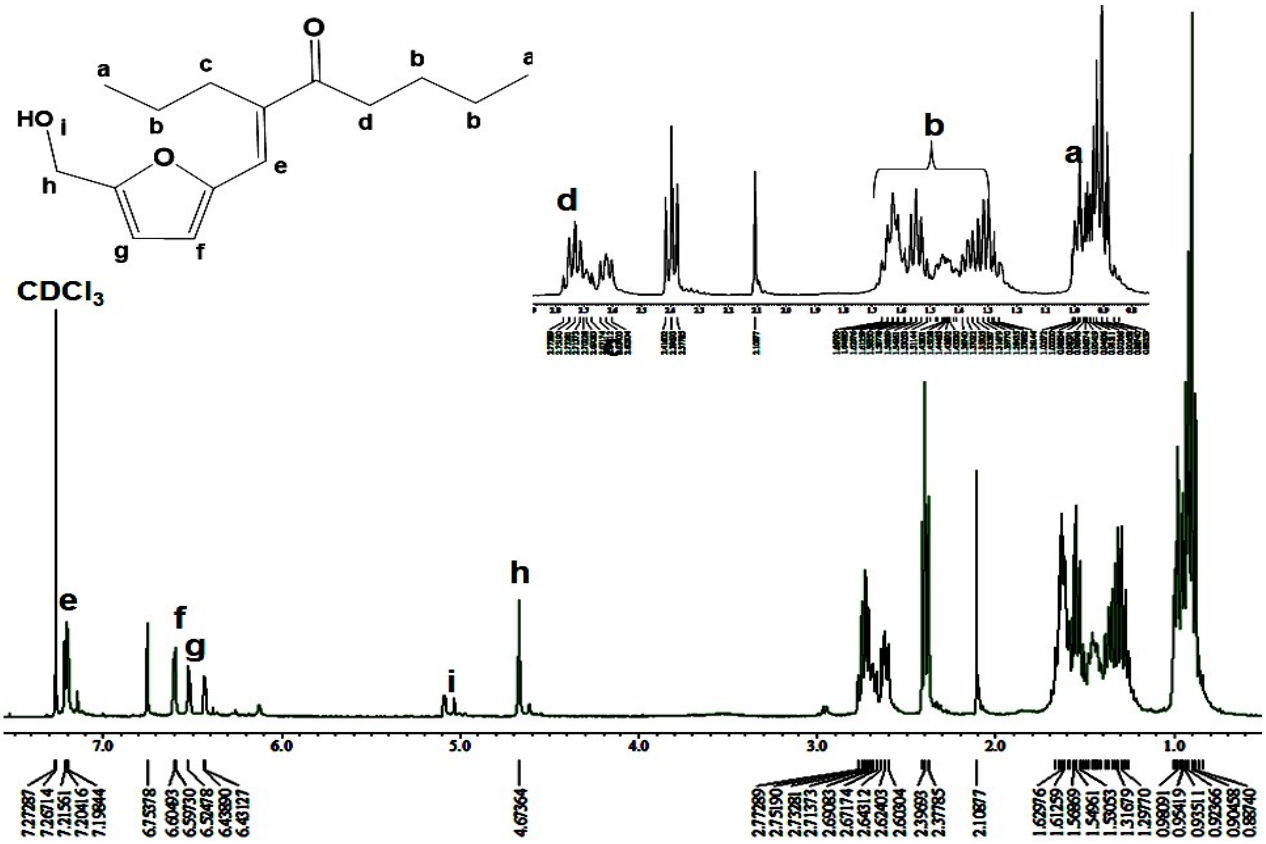
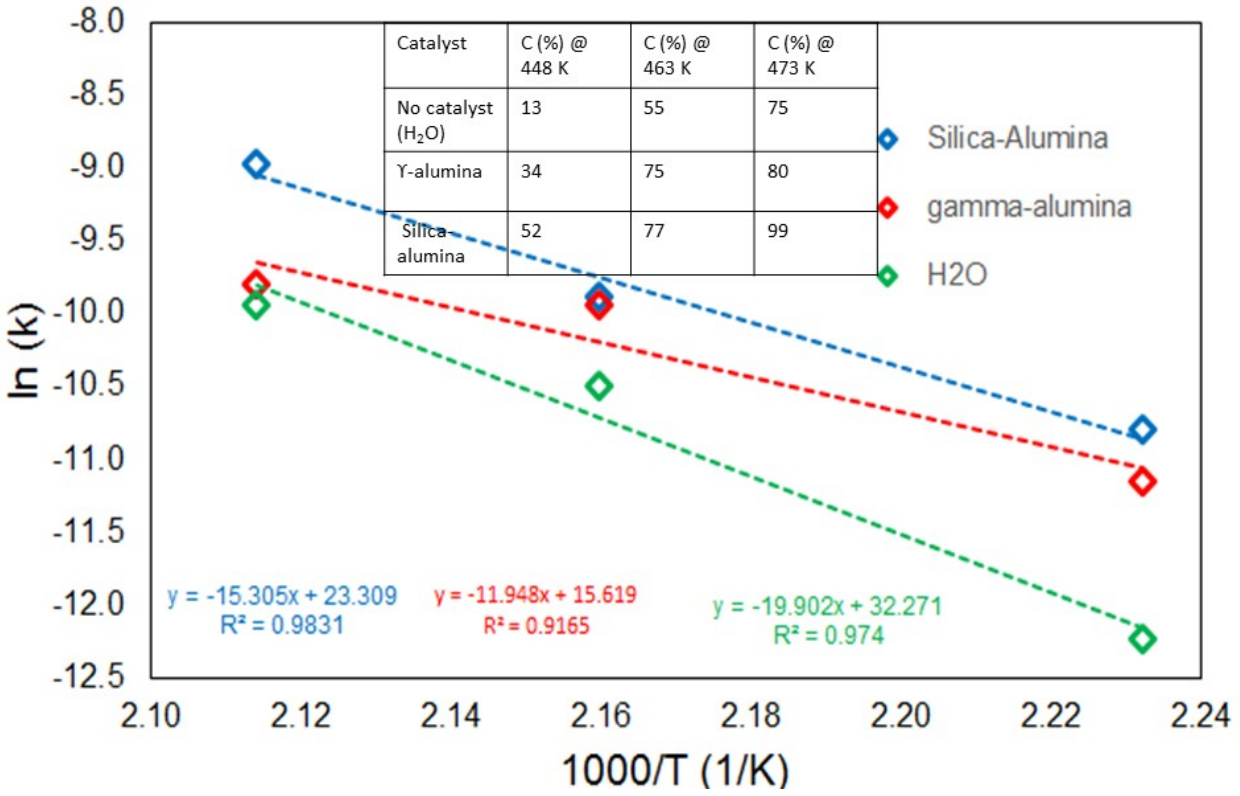



**Figure S4.** [1]H NMR spectrum of H5N produced from aldol condensation of HMF with 5-nonanone at 393 K for 12 h over the CaO-MgO catalyst.




| Catalyst | C (%) @ 448 K | C (%) @ 463 K | C (%) @ 473 K |
|---|---|---|---|
| No catalyst ($H_2O$) | 13 | 55 | 75 |
| ϒ-alumina | 34 | 75 | 80 |
| Silica-alumina | 52 | 77 | 99 |

**Figure S5.** Arrhenius plot for ring opening and decarboxylation of 6pp in non catalytic water, silica-alumina and ϒ-alumina catalyzed system. *C* (%) indicates 6PP conversion (%)

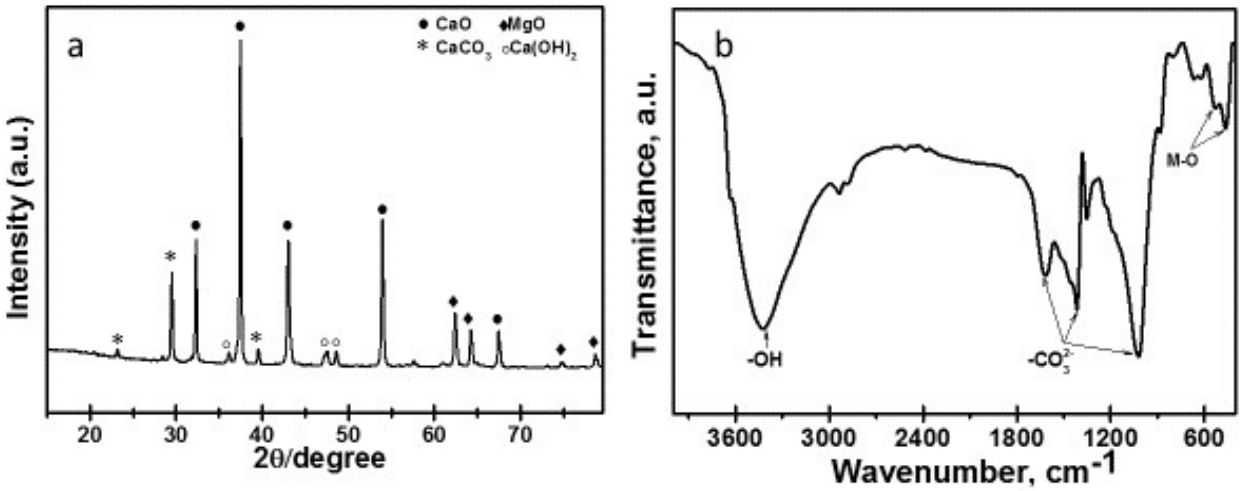



**Figure 6. (a)** XRD pattern and **(b)** FT-IR spectrum of the mixed oxide CaO-MgO Catalyst.

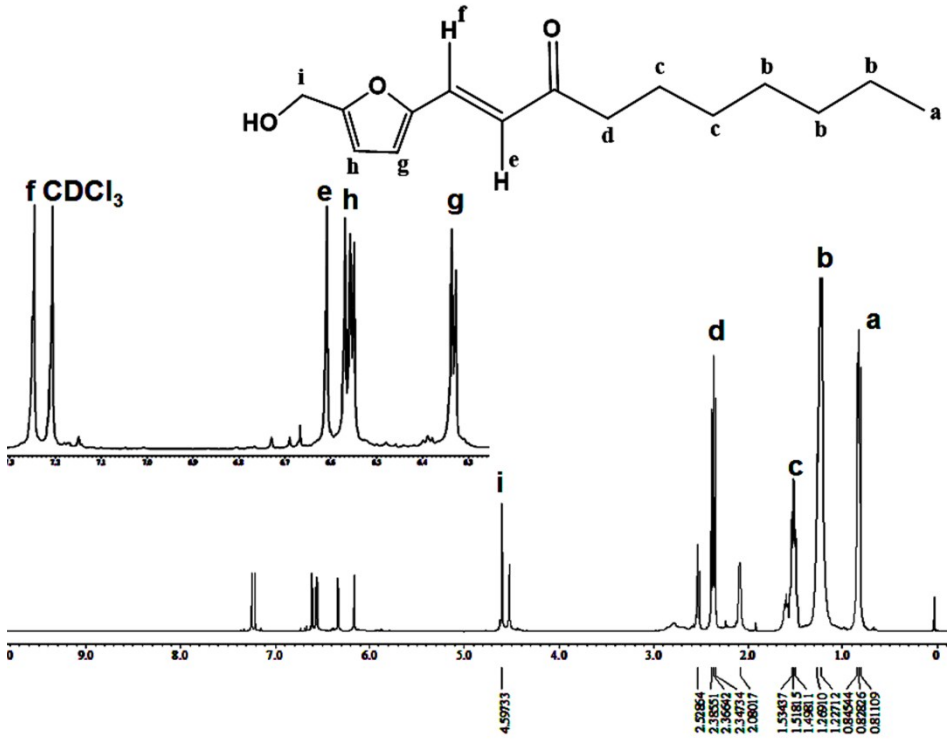



**Figure S7.** $^{1}$H NMR spectrum of aldol product obtained from the reaction of HMF with 2-nonanone.$^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.24 (s, 1H), 6.41 (d, 1H), 6.57 (dd, 1H), 4.59 (s, 1H), 2.34 – 2.38 (m, 2H), 11.49 – 1.53 (m, 4H), 1.22-1.26 (m, 4H), 0.81 – 0.84 (m, 3H) ppm.

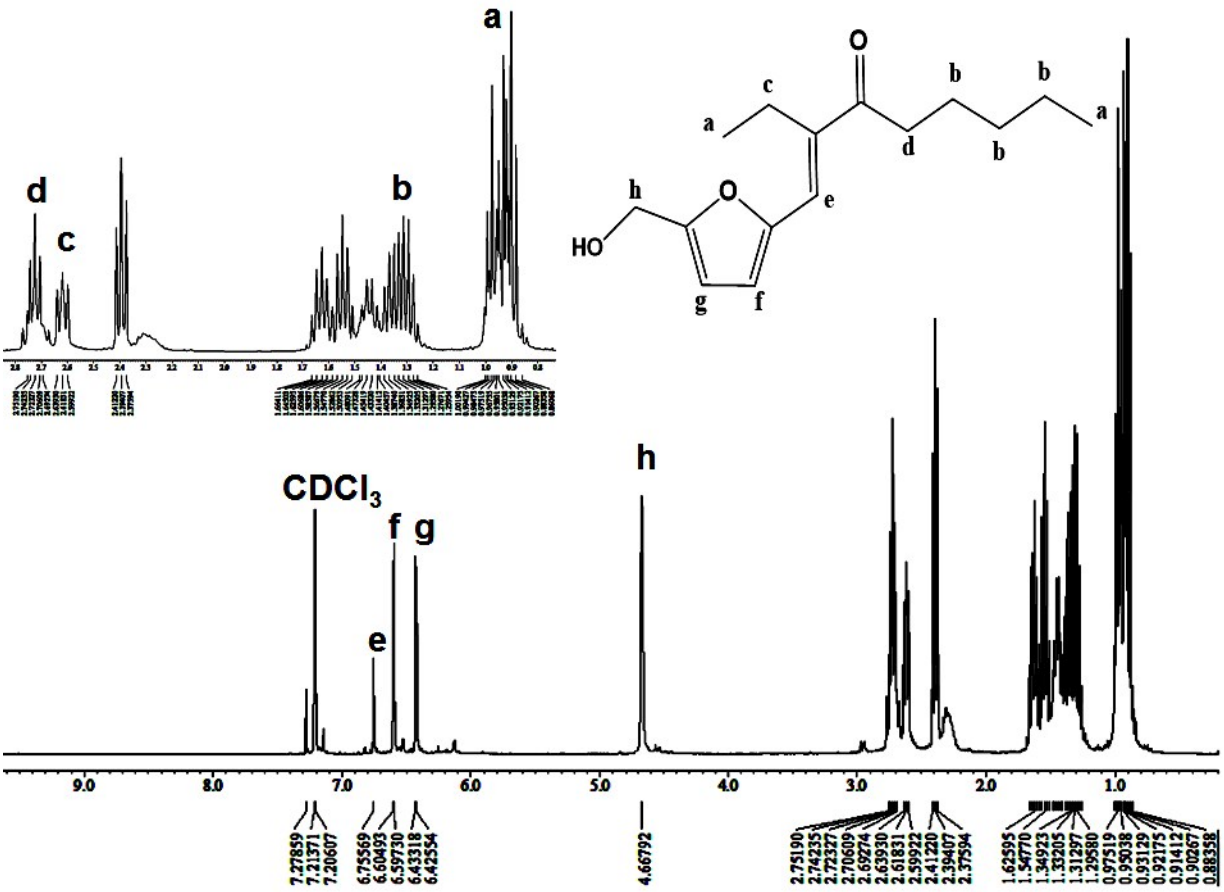



**Figure S8.** $^{1}$H NMR spectrum of aldol product obtained from the reaction of HMF with 4-nonanone.$^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.27 (s, 1H), 6.60 (d, 1H), 6.43 (dd, 1H), 4.66 (s, 1H), 2.69 – 2.75 (m, 2H), 2.59 – 2.63 (m, 2H), 1.25- 1.48 (m, 6H), 0.88-0.97(m, 3H) ppm.

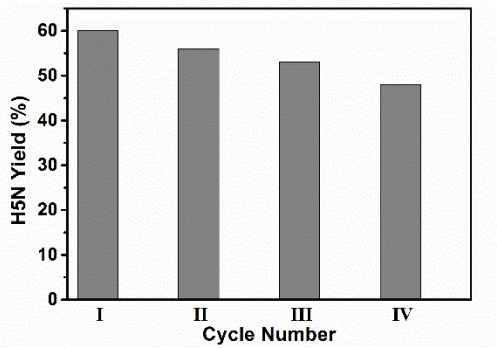



**Figure S9.** Recyclability of CaO-MgO catalyst for aldol condensation of HMF with 5-nonanone Reaction conditions: HMF (8 mmol), 5-nonanone (16 mmol), catalyst (100 mg), 393 K and 12 h.

**Table S1** Measured basicity of the fresh and recovered CaO-MgO catalyst

| Entry | Cycle Number | Amount of basic site /mmolg$^{-1}$ |
|---|---|---|
| 1 | 1 | 3.0 |
| 2 | 2 | 2.84 |
| 3 | 3 | 2.78 |
| 4 | 4 | 2.51 |

**Table S2.** Structural co-ordinates of reactant, product and TS in ring-opening reaction of 6PP in non-catalytic water

1a

| Atom# | X | Y | Z |
|---|---|---|---|
| C1 | -2.07581 | 2.785815 | 0.012918 |
| C2 | -1.59585 | 1.456974 | -0.11319 |
| C3 | -0.29962 | 1.252444 | -0.4845 |
| C4 | 0.105868 | 3.654378 | -0.60076 |
| C5 | -1.25519 | 3.856431 | -0.22648 |
| C6 | 0.40587 | -0.04785 | -0.66799 |
| C7 | -0.33919 | -1.27751 | -0.15095 |
| C8 | 0.503912 | -2.54801 | -0.27045 |
| C9 | -0.18464 | -3.78638 | 0.305506 |
| C10 | 0.67804 | -5.04378 | 0.21468 |
| O11 | 0.521215 | 2.315408 | -0.72862 |
| O12 | 1.933046 | 5.645009 | 1.616418 |
| O13 | 0.972367 | 4.506765 | -0.82402 |
| H14 | -3.11076 | 2.953093 | 0.307352 |
| H15 | -2.24175 | 0.607411 | 0.084619 |
| H16 | -1.59541 | 4.884021 | -0.13072 |
| H17 | 2.471143 | 4.923583 | 1.983973 |
| H18 | 1.383881 | 0.035927 | -0.16992 |
| H19 | 0.63434 | -0.16407 | -1.73997 |
| H20 | -1.28089 | -1.40922 | -0.70435 |
| H21 | -0.61113 | -1.12077 | 0.903702 |
| H22 | 1.463311 | -2.3944 | 0.249371 |
| H23 | 0.753826 | -2.72559 | -1.32873 |
| H24 | -1.1381 | -3.94948 | -0.22082 |
| H25 | -0.44561 | -3.59349 | 1.357921 |
| H26 | 0.912254 | -5.28912 | -0.83071 |
| H27 | 0.173821 | -5.9124 | 0.658981 |
| H28 | 1.63163 | -4.90397 | 0.743492 |
| H29 | 1.629411 | 5.288784 | 0.75326 |

$TS_{1a}$

| Atom# | X | Y | Z |
|---|---|---|---|
| C1 | -1.96774 | 2.899685 | 0.19241 |
| C2 | -1.43484 | 1.57885 | 0.208516 |
| C3 | -0.15239 | 1.365968 | -0.18249 |

| | | | |
|---|---|---|---|
| C4 | 0.190781 | 3.731945 | -0.48133 |
| C5 | -1.18354 | 3.955627 | -0.17008 |
| O6 | 0.630203 | 2.434142 | -0.5656 |
| O7 | 1.124334 | 4.629728 | 1.04489 |
| C8 | 0.56842 | 0.069306 | -0.34054 |
| C9 | -0.24735 | -1.18039 | -0.0069 |
| C10 | 0.580939 | -2.46011 | -0.14611 |
| C11 | -0.20348 | -3.72532 | 0.205539 |
| C12 | 0.639464 | -4.99682 | 0.107595 |
| O13 | 0.919088 | 4.560854 | -1.24403 |
| H14 | -3.00981 | 3.06005 | 0.462382 |
| H15 | -2.05843 | 0.731062 | 0.475585 |
| H16 | -1.5402 | 4.98161 | -0.19065 |
| H17 | 1.754224 | 3.991362 | 1.427334 |
| H18 | 1.477408 | 0.102153 | 0.280176 |
| H19 | 0.927687 | 0.017252 | -1.3809 |
| H20 | -1.12526 | -1.24127 | -0.66741 |
| H21 | -0.63049 | -1.11108 | 1.022187 |
| H22 | 1.467126 | -2.39179 | 0.50476 |
| H23 | 0.961622 | -2.54222 | -1.17684 |
| H24 | -1.07707 | -3.80772 | -0.45988 |
| H25 | -0.60508 | -3.62795 | 1.226325 |
| H26 | 1.026878 | -5.1377 | -0.91129 |
| H27 | 0.054705 | -5.88899 | 0.36959 |
| H28 | 1.503057 | -4.9509 | 0.786212 |
| H29 | 1.40974 | 4.952676 | -0.38946 |

1b

| Atom# | X | Y | Z |
|---|---|---|---|
| C1 | -2.02535 | 2.481406 | -0.38409 |
| C2 | -1.45192 | 1.162231 | -0.39675 |
| C3 | -0.10279 | 1.02646 | -0.33663 |
| C4 | 0.230923 | 3.479942 | -0.61772 |
| C5 | -1.24786 | 3.584811 | -0.45057 |
| C6 | 0.674513 | -0.24971 | -0.24679 |
| C7 | -0.15728 | -1.5295 | -0.2019 |
| C8 | 0.709216 | -2.78828 | -0.14292 |
| C9 | -0.1086 | -4.08015 | -0.10606 |
| C10 | 0.757799 | -5.3376 | -0.06489 |
| O11 | 0.724924 | 2.113331 | -0.29944 |

| | | | |
|---|---|---|---|
| O12 | 0.966013 | 4.334326 | 0.198913 |
| O13 | 0.576591 | 3.760923 | -1.9465 |
| O14 | 0.109919 | 3.931182 | 2.724736 |
| H15 | -3.1075 | 2.584124 | -0.3007 |
| H16 | -2.0871 | 0.281656 | -0.3998 |
| H17 | -1.64975 | 4.595948 | -0.42479 |
| H18 | 0.666115 | 4.180646 | 1.143291 |
| H19 | 1.320348 | -0.19039 | 0.644468 |
| H20 | 1.367679 | -0.28591 | -1.10269 |
| H21 | -0.80489 | -1.57982 | -1.0902 |
| H22 | -0.8261 | -1.5056 | 0.671318 |
| H23 | 1.36081 | -2.74384 | 0.744819 |
| H24 | 1.381685 | -2.8091 | -1.01548 |
| H25 | -0.76684 | -4.11431 | -0.98835 |
| H26 | -0.77476 | -4.06027 | 0.770478 |
| H27 | 1.40994 | -5.39623 | -0.94781 |
| H28 | 0.144352 | -6.24764 | -0.03954 |
| H29 | 1.404179 | -5.34337 | 0.823901 |
| H30 | 1.534682 | 3.956408 | -1.9584 |
| H31 | 0.580975 | 3.168299 | 3.105134 |
| H32 | -0.80992 | 3.620015 | 2.634956 |

$TS_{1b}$

| Atom# | X | Y | Z |
|---|---|---|---|
| C1 | -1.87043 | 2.447131 | -0.25849 |
| C2 | -1.1337 | 1.248999 | -0.15244 |
| C3 | 0.182991 | 1.036134 | 0.285227 |
| C4 | -0.08242 | 4.110816 | -0.76362 |
| C5 | -1.42284 | 3.748284 | -0.41883 |
| O6 | 0.973326 | 1.920523 | 0.818351 |
| O7 | 0.618193 | 4.984598 | -0.13125 |
| C8 | 0.783094 | -0.37056 | 0.1688 |
| C9 | -0.12333 | -1.57988 | -0.10503 |
| C10 | 0.667647 | -2.89393 | -0.11119 |
| C11 | -0.19914 | -4.14059 | -0.32059 |
| C12 | 0.608725 | -5.4439 | -0.31405 |
| O13 | 0.442125 | 3.558429 | -1.86997 |
| H14 | -2.95238 | 2.345621 | -0.11534 |
| H15 | -1.73747 | 0.346195 | -0.21021 |
| H16 | -2.0868 | 4.55454 | -0.10382 |

| | | | |
|---|---|---|---|
| H17 | 0.469677 | 4.693977 | 1.130704 |
| H18 | 1.368858 | -0.55754 | 1.083181 |
| H19 | 1.537807 | -0.31747 | -0.63976 |
| H20 | -0.63811 | -1.46859 | -1.07243 |
| H21 | -0.90967 | -1.64461 | 0.664209 |
| H22 | 1.210886 | -2.99915 | 0.844963 |
| H23 | 1.440865 | -2.86263 | -0.8995 |
| H24 | -0.74322 | -4.05554 | -1.27803 |
| H25 | -0.97036 | -4.18559 | 0.4685 |
| H26 | 1.368242 | -5.44079 | -1.11386 |
| H27 | -0.03796 | -6.32448 | -0.46969 |
| H28 | 1.135585 | -5.57997 | 0.645661 |
| H29 | 1.408944 | 3.773472 | -1.85222 |
| O30 | 0.494316 | 4.015301 | 2.072597 |
| H31 | 0.59771 | 3.031844 | 1.554389 |
| H32 | -0.40117 | 4.04936 | 2.463729 |

1c

| Atom# | X | Y | Z |
|---|---|---|---|
| C1 | -1.79 | 2.45 | 0.00 |
| C2 | -1.06 | 1.21 | 0.07 |
| C3 | 0.23 | 0.92 | 0.44 |
| C4 | -0.28 | 4.25 | -1.02 |
| C5 | -1.48 | 3.72 | -0.38 |
| C6 | 0.80 | -0.46 | 0.41 |
| C7 | -0.10 | -1.61 | -0.05 |
| C8 | 0.64 | -2.94 | -0.07 |
| C9 | -0.23 | -4.12 | -0.48 |
| C10 | 0.52 | -5.45 | -0.51 |
| O11 | 1.14 | 1.79 | 0.92 |
| O12 | -0.09 | 5.45 | -1.21 |
| O13 | 0.62 | 3.31 | -1.44 |
| O14 | 0.71 | 4.22 | 2.04 |
| H15 | -2.85 | 2.33 | 0.28 |
| H16 | -1.69 | 0.33 | -0.08 |
| H17 | -2.25 | 4.48 | -0.27 |
| H18 | 0.78 | 5.03 | 1.50 |
| H19 | 1.20 | -0.68 | 1.41 |
| H20 | 1.69 | -0.42 | -0.24 |
| H21 | -0.50 | -1.40 | -1.05 |

| | | | |
|---|---|---|---|
| H22 | -0.97 | -1.68 | 0.62 |
| H23 | 1.07 | -3.14 | 0.93 |
| H24 | 1.50 | -2.87 | -0.75 |
| H25 | -0.66 | -3.93 | -1.48 |
| H26 | -1.09 | -4.20 | 0.21 |
| H27 | 1.36 | -5.41 | -1.22 |
| H28 | -0.13 | -6.28 | -0.80 |
| H29 | 0.94 | -5.69 | 0.48 |
| H30 | 1.35 | 3.81 | -1.86 |
| H31 | 0.78 | 2.70 | 1.13 |
| H32 | -0.16 | 4.29 | 2.46 |

**Table S3.** Structural co-ordinates of reactant, product and TS in ring-opening reaction of 6PP in γ-alumina

2a

| Atom# | X | Y | Z |
|---|---|---|---|
| Al1 | 2.31 | 5.03 | 1.37 |
| Al2 | 6.55 | 7.01 | 0.03 |
| Al3 | 6.55 | 3.18 | 3.00 |
| Al4 | 2.36 | 0.88 | 3.67 |
| Al5 | 1.04 | 3.19 | 3.02 |
| Al6 | 5.23 | 0.87 | 3.66 |
| Al7 | 5.26 | 5.03 | 1.36 |
| Al8 | 1.02 | 7.01 | 0.03 |
| Al9 | 7.99 | 1.07 | 1.14 |
| Al10 | 8.01 | 0.96 | 3.91 |
| Al11 | 7.97 | 6.11 | 2.97 |
| Al12 | 3.77 | 6.79 | 5.00 |
| Al13 | 3.79 | 7.11 | 0.08 |
| Al14 | 3.78 | 2.18 | 1.27 |
| Al15 | 3.80 | 3.48 | 4.63 |
| Al16 | 7.99 | 4.10 | 0.12 |
| Al17 | 2.34 | 13.16 | 1.44 |
| Al18 | 6.55 | 15.07 | 0.03 |
| Al19 | 6.56 | 11.27 | 3.05 |
| Al20 | 2.34 | 9.05 | 3.77 |
| Al21 | 0.98 | 11.27 | 3.04 |
| Al22 | 5.19 | 9.05 | 3.77 |
| Al23 | 5.22 | 13.16 | 1.43 |
| Al24 | 1.02 | 15.07 | 0.03 |

| | | | |
|---|---|---|---|
| Al25 | 7.99 | 9.13 | 1.14 |
| Al26 | 7.96 | 8.97 | 3.90 |
| Al27 | 7.98 | 14.22 | 2.98 |
| Al28 | 3.78 | 14.70 | 4.14 |
| Al29 | 3.79 | 15.18 | 0.08 |
| Al30 | 3.78 | 10.23 | 1.18 |
| Al31 | 3.77 | 11.50 | 3.47 |
| Al32 | 7.99 | 12.17 | 0.12 |
| Al33 | 10.72 | 5.03 | 1.37 |
| Al34 | 14.97 | 7.01 | 0.03 |
| Al35 | 14.92 | 3.19 | 3.02 |
| Al36 | 10.79 | 0.92 | 3.69 |
| Al37 | 9.50 | 3.20 | 3.05 |
| Al38 | 13.63 | 0.90 | 3.65 |
| Al39 | 13.68 | 5.03 | 1.36 |
| Al40 | 9.43 | 7.01 | 0.03 |
| Al41 | 16.41 | 1.07 | 1.14 |
| Al42 | 16.40 | 0.95 | 3.90 |
| Al43 | 16.41 | 6.12 | 2.98 |
| Al44 | 12.13 | 6.70 | 4.70 |
| Al45 | 12.20 | 7.11 | 0.08 |
| Al46 | 12.20 | 2.18 | 1.27 |
| Al47 | 12.23 | 3.59 | 4.66 |
| Al48 | 16.41 | 4.10 | 0.12 |
| Al49 | 10.76 | 13.16 | 1.44 |
| Al50 | 14.97 | 15.07 | 0.03 |
| Al51 | 14.98 | 11.27 | 3.05 |
| Al52 | 10.74 | 9.03 | 3.66 |
| Al53 | 9.37 | 11.27 | 3.03 |
| Al54 | 13.61 | 9.04 | 3.72 |
| Al55 | 13.64 | 13.16 | 1.43 |
| Al56 | 9.43 | 15.07 | 0.03 |
| Al57 | 16.41 | 9.13 | 1.14 |
| Al58 | 16.39 | 8.98 | 3.91 |
| Al59 | 16.39 | 14.22 | 2.98 |
| Al60 | 12.19 | 14.73 | 4.12 |
| Al61 | 12.20 | 15.18 | 0.08 |
| Al62 | 12.19 | 10.23 | 1.18 |
| Al63 | 12.18 | 11.50 | 3.47 |
| Al64 | 16.41 | 12.17 | 0.12 |
| O1 | 5.14 | 7.76 | 4.86 |

| | | | |
|---|---|---|---|
| O2 | 1.06 | 5.04 | 2.85 |
| O3 | 5.18 | 6.90 | 1.14 |
| O4 | 0.98 | 5.19 | 0.15 |
| O5 | 0.89 | 0.87 | 22.42 |
| O6 | 5.14 | 3.28 | 1.70 |
| O7 | 0.92 | 1.20 | 2.73 |
| O8 | 5.25 | 2.57 | 4.40 |
| O9 | 6.68 | 0.87 | 22.42 |
| O10 | 2.44 | 3.28 | 1.72 |
| O11 | 6.67 | 1.20 | 2.72 |
| O12 | 2.34 | 2.58 | 4.40 |
| O13 | 2.39 | 7.75 | 4.86 |
| O14 | 6.51 | 5.02 | 2.84 |
| O15 | 2.39 | 6.90 | 1.14 |
| O16 | 6.60 | 5.19 | 0.15 |
| O17 | 7.96 | 7.31 | 4.22 |
| O18 | 7.99 | 7.08 | 1.30 |
| O19 | 3.79 | 1.07 | 0.04 |
| O20 | 3.79 | 1.03 | 2.70 |
| O21 | 3.78 | 5.10 | 5.01 |
| O22 | 3.79 | 5.11 | 0.12 |
| O23 | 7.99 | 2.96 | 1.39 |
| O24 | 8.00 | 2.81 | 4.13 |
| O25 | 5.17 | 15.55 | 4.53 |
| O26 | 0.96 | 13.08 | 2.81 |
| O27 | 5.19 | 14.99 | 1.13 |
| O28 | 0.98 | 13.26 | 0.15 |
| O29 | 0.89 | 8.93 | 22.42 |
| O30 | 5.06 | 11.37 | 1.79 |
| O31 | 0.91 | 9.24 | 2.75 |
| O32 | 5.20 | 10.83 | 4.29 |
| O33 | 6.68 | 8.93 | 22.42 |
| O34 | 2.50 | 11.36 | 1.78 |
| O35 | 6.62 | 9.25 | 2.75 |
| O36 | 2.32 | 10.82 | 4.28 |
| O37 | 2.40 | 15.57 | 4.55 |
| O38 | 6.58 | 13.08 | 2.82 |
| O39 | 2.38 | 14.99 | 1.14 |
| O40 | 6.60 | 13.26 | 0.15 |
| O41 | 7.98 | 15.43 | 4.23 |
| O42 | 7.99 | 15.15 | 1.30 |

| | | | |
|---|---|---|---|
| O43 | 3.79 | 9.14 | 0.04 |
| O44 | 3.76 | 9.22 | 2.76 |
| O45 | 3.76 | 13.28 | 3.10 |
| O46 | 3.79 | 13.18 | 0.12 |
| O47 | 7.98 | 11.03 | 1.41 |
| O48 | 7.97 | 10.83 | 4.16 |
| O49 | 13.51 | 7.73 | 4.80 |
| O50 | 9.39 | 5.01 | 2.82 |
| O51 | 13.60 | 6.90 | 1.14 |
| O52 | 9.39 | 5.19 | 0.15 |
| O53 | 9.30 | 0.87 | 22.42 |
| O54 | 13.55 | 3.28 | 1.70 |
| O55 | 9.34 | 1.21 | 2.73 |
| O56 | 13.66 | 2.60 | 4.36 |
| O57 | 15.09 | 0.87 | 22.42 |
| O58 | 10.85 | 3.28 | 1.72 |
| O59 | 15.08 | 1.19 | 2.71 |
| O60 | 10.77 | 2.62 | 4.38 |
| O61 | 10.77 | 7.71 | 4.70 |
| O62 | 15.00 | 5.01 | 2.81 |
| O63 | 10.80 | 6.90 | 1.14 |
| O64 | 15.01 | 5.19 | 0.15 |
| O65 | 16.38 | 7.31 | 4.25 |
| O66 | 16.41 | 7.08 | 1.30 |
| O67 | 12.20 | 1.07 | 0.04 |
| O68 | 12.19 | 1.01 | 2.68 |
| O69 | 12.19 | 5.17 | 3.95 |
| O70 | 12.20 | 5.11 | 0.12 |
| O71 | 16.40 | 2.96 | 1.39 |
| O72 | 16.40 | 2.80 | 4.12 |
| O73 | 13.58 | 15.57 | 4.51 |
| O74 | 9.38 | 13.08 | 2.81 |
| O75 | 13.60 | 14.99 | 1.13 |
| O76 | 9.39 | 13.26 | 0.15 |
| O77 | 9.30 | 8.93 | 22.42 |
| O78 | 13.47 | 11.37 | 1.79 |
| O79 | 9.29 | 9.25 | 2.71 |
| O80 | 13.61 | 10.80 | 4.27 |
| O81 | 15.09 | 8.93 | 22.42 |
| O82 | 10.91 | 11.36 | 1.78 |
| O83 | 15.06 | 9.24 | 2.75 |

| | | | |
|---|---|---|---|
| O84 | 10.74 | 10.79 | 4.25 |
| O85 | 10.81 | 15.58 | 4.55 |
| O86 | 14.99 | 13.08 | 2.82 |
| O87 | 10.80 | 14.99 | 1.14 |
| O88 | 15.01 | 13.26 | 0.15 |
| O89 | 16.40 | 15.43 | 4.23 |
| O90 | 16.41 | 15.15 | 1.30 |
| O91 | 12.20 | 9.14 | 0.04 |
| O92 | 12.19 | 9.20 | 2.71 |
| O93 | 12.18 | 13.28 | 3.10 |
| O94 | 12.20 | 13.18 | 0.12 |
| O95 | 16.40 | 11.03 | 1.41 |
| O96 | 16.38 | 10.84 | 4.16 |
| O97 | 11.86 | 6.22 | 7.04 |
| O98 | 12.24 | 4.06 | 6.46 |
| O99 | 14.46 | 5.47 | 7.99 |
| O100 | 14.46 | 5.82 | 10.87 |
| O101 | 15.10 | 8.01 | 6.96 |
| C1 | 11.29 | 5.45 | 9.61 |
| C2 | 11.31 | 6.81 | 9.27 |
| C3 | 11.62 | 7.20 | 8.00 |
| C4 | 11.96 | 4.86 | 7.38 |
| C5 | 11.63 | 4.49 | 8.70 |
| C6 | 11.71 | 8.60 | 7.52 |
| C7 | 11.13 | 9.67 | 8.45 |
| C8 | 11.15 | 11.05 | 7.79 |
| C9 | 10.51 | 12.16 | 8.64 |
| C10 | 10.53 | 13.51 | 7.93 |
| H1 | 11.00 | 5.16 | 10.62 |
| H2 | 11.10 | 7.58 | 10.00 |
| H3 | 11.66 | 3.44 | 8.92 |
| H4 | 11.23 | 8.64 | 6.53 |
| H5 | 12.78 | 8.81 | 7.33 |
| H6 | 11.69 | 9.70 | 9.39 |
| H7 | 10.09 | 9.40 | 8.70 |
| H8 | 10.63 | 11.00 | 6.83 |
| H9 | 12.19 | 11.33 | 7.56 |
| H10 | 11.04 | 12.23 | 9.60 |
| H11 | 9.47 | 11.89 | 8.88 |
| H12 | 11.55 | 13.84 | 7.72 |
| H13 | 10.06 | 14.29 | 8.55 |

| | | | |
|---|---|---|---|
| H14 | 9.97 | 13.47 | 6.98 |
| H15 | 14.49 | 5.56 | 8.96 |
| H16 | 14.72 | 6.36 | 7.64 |
| H17 | 15.35 | 6.18 | 11.04 |
| H18 | 14.45 | 4.95 | 11.29 |
| H19 | 16.00 | 7.78 | 6.67 |
| H20 | 14.55 | 7.87 | 6.14 |

$TS_{2a}$

| Atom# | X | Y | Z |
|---|---|---|---|
| Al1 | 2.31 | 5.03 | 1.37 |
| Al2 | 6.55 | 7.01 | 0.03 |
| Al3 | 6.56 | 3.18 | 2.99 |
| Al4 | 2.36 | 0.88 | 3.67 |
| Al5 | 1.03 | 3.19 | 3.02 |
| Al6 | 5.23 | 0.87 | 3.64 |
| Al7 | 5.26 | 5.03 | 1.36 |
| Al8 | 1.02 | 7.01 | 0.03 |
| Al9 | 7.99 | 1.07 | 1.14 |
| Al10 | 8.02 | 0.96 | 3.91 |
| Al11 | 7.98 | 6.11 | 2.97 |
| Al12 | 3.78 | 6.78 | 5.00 |
| Al13 | 3.79 | 7.11 | 0.08 |
| Al14 | 3.78 | 2.18 | 1.27 |
| Al15 | 3.80 | 3.48 | 4.62 |
| Al16 | 7.99 | 4.10 | 0.12 |
| Al17 | 2.34 | 13.16 | 1.44 |
| Al18 | 6.55 | 15.07 | 0.03 |
| Al19 | 6.58 | 11.26 | 3.05 |
| Al20 | 2.36 | 9.05 | 3.77 |
| Al21 | 0.99 | 11.27 | 3.05 |
| Al22 | 5.21 | 9.05 | 3.77 |
| Al23 | 5.22 | 13.16 | 1.43 |
| Al24 | 1.02 | 15.07 | 0.03 |
| Al25 | 7.99 | 9.13 | 1.14 |
| Al26 | 7.99 | 8.97 | 3.90 |
| Al27 | 7.99 | 14.22 | 2.98 |
| Al28 | 3.78 | 14.70 | 4.13 |
| Al29 | 3.79 | 15.18 | 0.08 |
| Al30 | 3.78 | 10.23 | 1.18 |

| | | | |
|---|---|---|---|
| Al31 | 3.79 | 11.49 | 3.47 |
| Al32 | 7.99 | 12.17 | 0.12 |
| Al33 | 10.72 | 5.03 | 1.37 |
| Al34 | 14.97 | 7.01 | 0.03 |
| Al35 | 14.91 | 3.19 | 3.02 |
| Al36 | 10.80 | 0.92 | 3.71 |
| Al37 | 9.53 | 3.20 | 3.08 |
| Al38 | 13.63 | 0.89 | 3.65 |
| Al39 | 13.68 | 5.03 | 1.36 |
| Al40 | 9.43 | 7.01 | 0.03 |
| Al41 | 16.41 | 1.07 | 1.14 |
| Al42 | 16.40 | 0.96 | 3.90 |
| Al43 | 16.41 | 6.12 | 2.97 |
| Al44 | 12.10 | 6.71 | 4.95 |
| Al45 | 12.20 | 7.11 | 0.08 |
| Al46 | 12.20 | 2.18 | 1.27 |
| Al47 | 12.27 | 3.57 | 4.81 |
| Al48 | 16.41 | 4.10 | 0.12 |
| Al49 | 10.76 | 13.16 | 1.44 |
| Al50 | 14.97 | 15.07 | 0.03 |
| Al51 | 14.99 | 11.27 | 3.05 |
| Al52 | 10.75 | 9.01 | 3.68 |
| Al53 | 9.40 | 11.26 | 3.04 |
| Al54 | 13.61 | 9.04 | 3.75 |
| Al55 | 13.64 | 13.16 | 1.43 |
| Al56 | 9.43 | 15.07 | 0.03 |
| Al57 | 16.41 | 9.13 | 1.14 |
| Al58 | 16.41 | 8.98 | 3.89 |
| Al59 | 16.40 | 14.22 | 2.98 |
| Al60 | 12.19 | 14.72 | 4.11 |
| Al61 | 12.20 | 15.18 | 0.08 |
| Al62 | 12.19 | 10.23 | 1.18 |
| Al63 | 12.19 | 11.49 | 3.47 |
| Al64 | 16.41 | 12.17 | 0.12 |
| O1 | 5.15 | 7.76 | 4.87 |
| O2 | 1.05 | 5.04 | 2.85 |
| O3 | 5.18 | 6.90 | 1.14 |
| O4 | 0.98 | 5.19 | 0.15 |
| O5 | 0.89 | 0.87 | 22.42 |
| O6 | 5.14 | 3.28 | 1.70 |
| O7 | 0.92 | 1.21 | 2.73 |

| | | | |
|---|---|---|---|
| O8 | 5.26 | 2.58 | 4.37 |
| O9 | 6.68 | 0.87 | 22.42 |
| O10 | 2.44 | 3.28 | 1.72 |
| O11 | 6.68 | 1.20 | 2.72 |
| O12 | 2.34 | 2.58 | 4.40 |
| O13 | 2.39 | 7.75 | 4.86 |
| O14 | 6.52 | 5.02 | 2.84 |
| O15 | 2.39 | 6.90 | 1.14 |
| O16 | 6.60 | 5.19 | 0.15 |
| O17 | 7.97 | 7.31 | 4.22 |
| O18 | 7.99 | 7.08 | 1.30 |
| O19 | 3.79 | 1.07 | 0.04 |
| O20 | 3.79 | 1.03 | 2.69 |
| O21 | 3.78 | 5.10 | 5.01 |
| O22 | 3.79 | 5.11 | 0.12 |
| O23 | 7.99 | 2.96 | 1.39 |
| O24 | 8.01 | 2.81 | 4.13 |
| O25 | 5.17 | 15.55 | 4.52 |
| O26 | 0.97 | 13.08 | 2.81 |
| O27 | 5.19 | 14.99 | 1.13 |
| O28 | 0.98 | 13.26 | 0.15 |
| O29 | 0.89 | 8.93 | 22.42 |
| O30 | 5.06 | 11.37 | 1.79 |
| O31 | 0.93 | 9.23 | 2.75 |
| O32 | 5.22 | 10.83 | 4.29 |
| O33 | 6.68 | 8.93 | 22.42 |
| O34 | 2.50 | 11.36 | 1.78 |
| O35 | 6.64 | 9.25 | 2.75 |
| O36 | 2.34 | 10.82 | 4.29 |
| O37 | 2.41 | 15.56 | 4.55 |
| O38 | 6.58 | 13.08 | 2.82 |
| O39 | 2.38 | 14.99 | 1.14 |
| O40 | 6.60 | 13.26 | 0.15 |
| O41 | 7.98 | 15.43 | 4.23 |
| O42 | 7.99 | 15.15 | 1.30 |
| O43 | 3.79 | 9.14 | 0.04 |
| O44 | 3.78 | 9.22 | 2.76 |
| O45 | 3.77 | 13.28 | 3.10 |
| O46 | 3.79 | 13.18 | 0.12 |
| O47 | 7.98 | 11.03 | 1.41 |
| O48 | 8.00 | 10.83 | 4.16 |

| | | | |
|---|---|---|---|
| O49 | 13.49 | 7.78 | 4.91 |
| O50 | 9.41 | 5.02 | 2.83 |
| O51 | 13.60 | 6.90 | 1.14 |
| O52 | 9.39 | 5.19 | 0.15 |
| O53 | 9.30 | 0.87 | 22.42 |
| O54 | 13.55 | 3.28 | 1.70 |
| O55 | 9.35 | 1.21 | 2.75 |
| O56 | 13.67 | 2.58 | 4.36 |
| O57 | 15.09 | 0.87 | 22.42 |
| O58 | 10.85 | 3.28 | 1.72 |
| O59 | 15.08 | 1.19 | 2.71 |
| O60 | 10.80 | 2.61 | 4.43 |
| O61 | 10.77 | 7.76 | 4.79 |
| O62 | 14.99 | 5.02 | 2.81 |
| O63 | 10.80 | 6.90 | 1.14 |
| O64 | 15.01 | 5.19 | 0.15 |
| O65 | 16.37 | 7.31 | 4.26 |
| O66 | 16.41 | 7.08 | 1.30 |
| O67 | 12.20 | 1.07 | 0.04 |
| O68 | 12.19 | 1.00 | 2.68 |
| O69 | 12.20 | 5.19 | 4.21 |
| O70 | 12.20 | 5.11 | 0.12 |
| O71 | 16.40 | 2.96 | 1.39 |
| O72 | 16.40 | 2.81 | 4.12 |
| O73 | 13.59 | 15.56 | 4.51 |
| O74 | 9.38 | 13.08 | 2.81 |
| O75 | 13.60 | 14.99 | 1.13 |
| O76 | 9.39 | 13.26 | 0.15 |
| O77 | 9.30 | 8.93 | 22.42 |
| O78 | 13.47 | 11.37 | 1.79 |
| O79 | 9.31 | 9.24 | 2.72 |
| O80 | 13.63 | 10.81 | 4.28 |
| O81 | 15.09 | 8.93 | 22.42 |
| O82 | 10.91 | 11.36 | 1.78 |
| O83 | 15.06 | 9.23 | 2.75 |
| O84 | 10.76 | 10.78 | 4.26 |
| O85 | 10.82 | 15.58 | 4.55 |
| O86 | 15.00 | 13.08 | 2.82 |
| O87 | 10.80 | 14.99 | 1.14 |
| O88 | 15.01 | 13.26 | 0.15 |
| O89 | 16.41 | 15.43 | 4.23 |

| | | | |
|---|---|---|---|
| O90 | 16.41 | 15.15 | 1.30 |
| O91 | 12.20 | 9.14 | 0.04 |
| O92 | 12.20 | 9.20 | 2.73 |
| O93 | 12.18 | 13.28 | 3.10 |
| O94 | 12.20 | 13.18 | 0.12 |
| O95 | 16.40 | 11.03 | 1.41 |
| O96 | 16.40 | 10.83 | 4.15 |
| O97 | 11.94 | 6.25 | 7.01 |
| O98 | 12.46 | 4.00 | 6.59 |
| O99 | 14.14 | 5.38 | 7.87 |
| O100 | 14.48 | 5.77 | 10.67 |
| O101 | 14.96 | 7.62 | 6.97 |
| C1 | 11.26 | 5.47 | 9.60 |
| C2 | 11.38 | 6.84 | 9.26 |
| C3 | 11.69 | 7.24 | 8.01 |
| C4 | 12.30 | 4.89 | 7.47 |
| C5 | 11.71 | 4.52 | 8.74 |
| C6 | 11.74 | 8.67 | 7.57 |
| C7 | 11.11 | 9.70 | 8.51 |
| C8 | 11.12 | 11.11 | 7.88 |
| C9 | 10.46 | 12.22 | 8.71 |
| C10 | 10.48 | 13.57 | 7.99 |
| H1 | 10.78 | 5.19 | 10.53 |
| H2 | 11.14 | 7.62 | 9.98 |
| H3 | 11.61 | 3.45 | 8.92 |
| H4 | 11.25 | 8.73 | 6.59 |
| H5 | 12.79 | 8.94 | 7.38 |
| H6 | 11.63 | 9.73 | 9.48 |
| H7 | 10.07 | 9.42 | 8.73 |
| H8 | 10.63 | 11.06 | 6.90 |
| H9 | 12.17 | 11.40 | 7.68 |
| H10 | 10.96 | 12.31 | 9.69 |
| H11 | 9.42 | 11.94 | 8.92 |
| H12 | 11.50 | 13.90 | 7.79 |
| H13 | 10.00 | 14.35 | 8.59 |
| H14 | 9.94 | 13.53 | 7.04 |
| H15 | 14.29 | 5.44 | 8.85 |
| H16 | 14.46 | 6.29 | 7.49 |
| H17 | 15.35 | 6.14 | 10.91 |
| H18 | 14.31 | 5.06 | 11.30 |
| H19 | 15.87 | 7.49 | 6.66 |

| | | | |
|---|---|---|---|
| H20 | 14.41 | 7.65 | 6.10 |

2b

| Atom# | X | Y | Z |
|---|---|---|---|
| Al1 | 2.31 | 5.03 | 1.37 |
| Al2 | 6.55 | 7.01 | 0.03 |
| Al3 | 6.59 | 3.18 | 2.98 |
| Al4 | 2.36 | 0.88 | 3.67 |
| Al5 | 1.03 | 3.19 | 3.01 |
| Al6 | 5.24 | 0.87 | 3.64 |
| Al7 | 5.26 | 5.03 | 1.36 |
| Al8 | 1.02 | 7.01 | 0.03 |
| Al9 | 7.99 | 1.07 | 1.14 |
| Al10 | 8.03 | 0.96 | 3.91 |
| Al11 | 7.99 | 6.11 | 2.97 |
| Al12 | 3.78 | 6.78 | 5.00 |
| Al13 | 3.79 | 7.11 | 0.08 |
| Al14 | 3.78 | 2.18 | 1.27 |
| Al15 | 3.81 | 3.47 | 4.61 |
| Al16 | 7.99 | 4.10 | 0.12 |
| Al17 | 2.34 | 13.16 | 1.44 |
| Al18 | 6.55 | 15.07 | 0.03 |
| Al19 | 6.59 | 11.26 | 3.05 |
| Al20 | 2.38 | 9.04 | 3.77 |
| Al21 | 1.01 | 11.28 | 3.06 |
| Al22 | 5.23 | 9.04 | 3.77 |
| Al23 | 5.22 | 13.16 | 1.43 |
| Al24 | 1.02 | 15.07 | 0.03 |
| Al25 | 7.99 | 9.13 | 1.14 |
| Al26 | 8.00 | 8.96 | 3.91 |
| Al27 | 7.99 | 14.22 | 2.98 |
| Al28 | 3.78 | 14.70 | 4.13 |
| Al29 | 3.79 | 15.18 | 0.08 |
| Al30 | 3.78 | 10.23 | 1.18 |
| Al31 | 3.81 | 11.49 | 3.48 |
| Al32 | 7.99 | 12.17 | 0.12 |
| Al33 | 10.72 | 5.03 | 1.37 |
| Al34 | 14.97 | 7.01 | 0.03 |
| Al35 | 14.90 | 3.19 | 3.04 |
| Al36 | 10.81 | 0.92 | 3.72 |

| | | | |
|---|---|---|---|
| Al37 | 9.56 | 3.22 | 3.12 |
| Al38 | 13.63 | 0.89 | 3.64 |
| Al39 | 13.68 | 5.03 | 1.36 |
| Al40 | 9.43 | 7.01 | 0.03 |
| Al41 | 16.41 | 1.07 | 1.14 |
| Al42 | 16.40 | 0.96 | 3.90 |
| Al43 | 16.40 | 6.12 | 2.97 |
| Al44 | 12.00 | 6.69 | 5.20 |
| Al45 | 12.20 | 7.11 | 0.08 |
| Al46 | 12.20 | 2.18 | 1.27 |
| Al47 | 12.28 | 3.50 | 4.94 |
| Al48 | 16.41 | 4.10 | 0.12 |
| Al49 | 10.76 | 13.16 | 1.44 |
| Al50 | 14.97 | 15.07 | 0.03 |
| Al51 | 15.01 | 11.28 | 3.04 |
| Al52 | 10.76 | 9.03 | 3.68 |
| Al53 | 9.40 | 11.27 | 3.03 |
| Al54 | 13.62 | 9.07 | 3.69 |
| Al55 | 13.64 | 13.16 | 1.43 |
| Al56 | 9.43 | 15.07 | 0.03 |
| Al57 | 16.41 | 9.13 | 1.14 |
| Al58 | 16.43 | 8.99 | 3.90 |
| Al59 | 16.40 | 14.23 | 2.99 |
| Al60 | 12.19 | 14.73 | 4.11 |
| Al61 | 12.20 | 15.18 | 0.08 |
| Al62 | 12.19 | 10.23 | 1.18 |
| Al63 | 12.20 | 11.52 | 3.47 |
| Al64 | 16.41 | 12.17 | 0.12 |
| O1 | 5.14 | 7.76 | 4.87 |
| O2 | 1.05 | 5.04 | 2.85 |
| O3 | 5.18 | 6.90 | 1.14 |
| O4 | 0.98 | 5.19 | 0.15 |
| O5 | 0.89 | 0.87 | 22.42 |
| O6 | 5.14 | 3.28 | 1.70 |
| O7 | 0.92 | 1.21 | 2.73 |
| O8 | 5.26 | 2.58 | 4.36 |
| O9 | 6.68 | 0.87 | 22.42 |
| O10 | 2.44 | 3.28 | 1.72 |
| O11 | 6.69 | 1.20 | 2.72 |
| O12 | 2.34 | 2.58 | 4.40 |
| O13 | 2.39 | 7.74 | 4.86 |

| | | | |
|---|---|---|---|
| O14 | 6.53 | 5.02 | 2.83 |
| O15 | 2.39 | 6.90 | 1.14 |
| O16 | 6.60 | 5.19 | 0.15 |
| O17 | 7.96 | 7.30 | 4.22 |
| O18 | 7.99 | 7.08 | 1.30 |
| O19 | 3.79 | 1.07 | 0.04 |
| O20 | 3.79 | 1.03 | 2.69 |
| O21 | 3.78 | 5.10 | 5.00 |
| O22 | 3.79 | 5.11 | 0.12 |
| O23 | 7.99 | 2.96 | 1.39 |
| O24 | 8.02 | 2.82 | 4.13 |
| O25 | 5.17 | 15.56 | 4.51 |
| O26 | 0.97 | 13.08 | 2.82 |
| O27 | 5.19 | 14.99 | 1.13 |
| O28 | 0.98 | 13.26 | 0.15 |
| O29 | 0.89 | 8.93 | 22.42 |
| O30 | 5.06 | 11.37 | 1.79 |
| O31 | 0.95 | 9.23 | 2.75 |
| O32 | 5.25 | 10.82 | 4.29 |
| O33 | 6.68 | 8.93 | 22.42 |
| O34 | 2.50 | 11.36 | 1.78 |
| O35 | 6.65 | 9.24 | 2.75 |
| O36 | 2.36 | 10.82 | 4.29 |
| O37 | 2.40 | 15.57 | 4.55 |
| O38 | 6.59 | 13.08 | 2.81 |
| O39 | 2.38 | 14.99 | 1.14 |
| O40 | 6.60 | 13.26 | 0.15 |
| O41 | 7.98 | 15.43 | 4.23 |
| O42 | 7.99 | 15.15 | 1.30 |
| O43 | 3.79 | 9.14 | 0.04 |
| O44 | 3.80 | 9.22 | 2.76 |
| O45 | 3.77 | 13.28 | 3.10 |
| O46 | 3.79 | 13.18 | 0.12 |
| O47 | 7.98 | 11.03 | 1.41 |
| O48 | 8.01 | 10.83 | 4.16 |
| O49 | 13.50 | 7.79 | 4.88 |
| O50 | 9.44 | 5.03 | 2.84 |
| O51 | 13.60 | 6.90 | 1.14 |
| O52 | 9.39 | 5.19 | 0.15 |
| O53 | 9.30 | 0.87 | 22.42 |
| O54 | 13.55 | 3.28 | 1.70 |

| | | | |
|---|---|---|---|
| O55 | 9.37 | 1.22 | 2.76 |
| O56 | 13.67 | 2.57 | 4.35 |
| O57 | 15.09 | 0.87 | 22.42 |
| O58 | 10.85 | 3.28 | 1.72 |
| O59 | 15.09 | 1.19 | 2.70 |
| O60 | 10.81 | 2.59 | 4.45 |
| O61 | 10.77 | 7.77 | 4.75 |
| O62 | 14.98 | 5.03 | 2.82 |
| O63 | 10.80 | 6.90 | 1.14 |
| O64 | 15.01 | 5.19 | 0.15 |
| O65 | 16.33 | 7.32 | 4.27 |
| O66 | 16.41 | 7.08 | 1.30 |
| O67 | 12.20 | 1.07 | 0.04 |
| O68 | 12.20 | 1.00 | 2.68 |
| O69 | 12.18 | 5.15 | 4.50 |
| O70 | 12.20 | 5.11 | 0.12 |
| O71 | 16.40 | 2.96 | 1.39 |
| O72 | 16.40 | 2.81 | 4.12 |
| O73 | 13.59 | 15.56 | 4.51 |
| O74 | 9.38 | 13.08 | 2.81 |
| O75 | 13.60 | 14.99 | 1.13 |
| O76 | 9.39 | 13.26 | 0.15 |
| O77 | 9.30 | 8.93 | 22.42 |
| O78 | 13.47 | 11.37 | 1.79 |
| O79 | 9.31 | 9.25 | 2.71 |
| O80 | 13.64 | 10.81 | 4.27 |
| O81 | 15.09 | 8.93 | 22.42 |
| O82 | 10.91 | 11.36 | 1.78 |
| O83 | 15.08 | 9.23 | 2.75 |
| O84 | 10.77 | 10.80 | 4.25 |
| O85 | 10.82 | 15.58 | 4.57 |
| O86 | 15.00 | 13.08 | 2.82 |
| O87 | 10.80 | 14.99 | 1.14 |
| O88 | 15.01 | 13.26 | 0.15 |
| O89 | 16.40 | 15.44 | 4.23 |
| O90 | 16.41 | 15.15 | 1.30 |
| O91 | 12.20 | 9.14 | 0.04 |
| O92 | 12.21 | 9.15 | 2.70 |
| O93 | 12.19 | 13.29 | 3.09 |
| O94 | 12.20 | 13.18 | 0.12 |
| O95 | 16.40 | 11.03 | 1.41 |

| | | | |
|---|---|---|---|
| O96 | 16.42 | 10.83 | 4.15 |
| O97 | 12.11 | 6.56 | 6.98 |
| O98 | 12.56 | 3.49 | 6.77 |
| O99 | 13.91 | 4.79 | 7.97 |
| O100 | 14.50 | 5.66 | 10.47 |
| O101 | 15.03 | 7.76 | 7.04 |
| C1 | 11.29 | 5.44 | 9.49 |
| C2 | 11.45 | 6.82 | 9.20 |
| C3 | 11.77 | 7.36 | 7.97 |
| C4 | 12.72 | 4.21 | 7.80 |
| C5 | 11.72 | 4.31 | 8.84 |
| C6 | 11.74 | 8.83 | 7.66 |
| C7 | 11.08 | 9.82 | 8.59 |
| C8 | 11.09 | 11.21 | 7.96 |
| C9 | 10.40 | 12.31 | 8.77 |
| C10 | 10.42 | 13.65 | 8.03 |
| H1 | 10.62 | 5.24 | 10.32 |
| H2 | 11.13 | 7.53 | 9.97 |
| H3 | 11.22 | 3.36 | 9.05 |
| H4 | 11.27 | 8.91 | 6.67 |
| H5 | 12.78 | 9.13 | 7.48 |
| H6 | 11.59 | 9.84 | 9.57 |
| H7 | 10.04 | 9.51 | 8.78 |
| H8 | 10.60 | 11.16 | 6.97 |
| H9 | 12.13 | 11.50 | 7.76 |
| H10 | 10.89 | 12.41 | 9.75 |
| H11 | 9.36 | 12.02 | 8.97 |
| H12 | 11.45 | 13.99 | 7.84 |
| H13 | 9.92 | 14.44 | 8.61 |
| H14 | 9.90 | 13.58 | 7.06 |
| H15 | 14.02 | 5.13 | 8.90 |
| H16 | 14.56 | 7.03 | 7.50 |
| H17 | 15.30 | 6.11 | 10.79 |
| H18 | 14.13 | 5.18 | 11.23 |
| H19 | 15.90 | 7.41 | 6.79 |
| H20 | 14.18 | 7.73 | 5.62 |

2c

| Atom# | X | Y | Z |
|---|---|---|---|

| | | | |
|---|---|---|---|
| Al1 | 2.31 | 5.03 | 1.37 |
| Al2 | 6.55 | 7.01 | 0.03 |
| Al3 | 6.58 | 3.18 | 2.98 |
| Al4 | 2.36 | 0.87 | 3.66 |
| Al5 | 1.03 | 3.19 | 3.01 |
| Al6 | 5.24 | 0.88 | 3.65 |
| Al7 | 5.26 | 5.03 | 1.36 |
| Al8 | 1.02 | 7.01 | 0.03 |
| Al9 | 7.99 | 1.07 | 1.14 |
| Al10 | 8.03 | 0.97 | 3.90 |
| Al11 | 8.00 | 6.12 | 2.97 |
| Al12 | 3.80 | 6.78 | 4.99 |
| Al13 | 3.79 | 7.11 | 0.08 |
| Al14 | 3.78 | 2.18 | 1.27 |
| Al15 | 3.80 | 3.47 | 4.62 |
| Al16 | 7.99 | 4.10 | 0.12 |
| Al17 | 2.34 | 13.16 | 1.44 |
| Al18 | 6.55 | 15.07 | 0.03 |
| Al19 | 6.59 | 11.27 | 3.05 |
| Al20 | 2.37 | 9.05 | 3.78 |
| Al21 | 1.00 | 11.27 | 3.06 |
| Al22 | 5.23 | 9.04 | 3.76 |
| Al23 | 5.22 | 13.16 | 1.43 |
| Al24 | 1.02 | 15.07 | 0.03 |
| Al25 | 7.99 | 9.13 | 1.14 |
| Al26 | 8.01 | 8.97 | 3.91 |
| Al27 | 8.00 | 14.22 | 2.98 |
| Al28 | 3.80 | 14.70 | 4.12 |
| Al29 | 3.79 | 15.18 | 0.08 |
| Al30 | 3.78 | 10.23 | 1.18 |
| Al31 | 3.80 | 11.50 | 3.47 |
| Al32 | 7.99 | 12.17 | 0.12 |
| Al33 | 10.72 | 5.03 | 1.37 |
| Al34 | 14.97 | 7.01 | 0.03 |
| Al35 | 14.90 | 3.20 | 3.05 |
| Al36 | 10.81 | 0.91 | 3.71 |
| Al37 | 9.55 | 3.21 | 3.11 |
| Al38 | 13.64 | 0.90 | 3.66 |
| Al39 | 13.68 | 5.03 | 1.36 |
| Al40 | 9.43 | 7.01 | 0.03 |
| Al41 | 16.41 | 1.07 | 1.14 |

| | | | |
|---|---|---|---|
| Al42 | 16.40 | 0.97 | 3.90 |
| Al43 | 16.41 | 6.12 | 2.97 |
| Al44 | 12.24 | 6.80 | 5.23 |
| Al45 | 12.20 | 7.11 | 0.08 |
| Al46 | 12.20 | 2.18 | 1.27 |
| Al47 | 12.27 | 3.48 | 5.01 |
| Al48 | 16.41 | 4.10 | 0.12 |
| Al49 | 10.76 | 13.16 | 1.44 |
| Al50 | 14.97 | 15.07 | 0.03 |
| Al51 | 15.01 | 11.27 | 3.04 |
| Al52 | 10.79 | 9.04 | 3.79 |
| Al53 | 9.42 | 11.26 | 3.05 |
| Al54 | 13.63 | 9.04 | 3.67 |
| Al55 | 13.64 | 13.16 | 1.43 |
| Al56 | 9.43 | 15.07 | 0.03 |
| Al57 | 16.41 | 9.13 | 1.14 |
| Al58 | 16.42 | 8.98 | 3.90 |
| Al59 | 16.41 | 14.22 | 2.98 |
| Al60 | 12.21 | 14.72 | 4.11 |
| Al61 | 12.20 | 15.18 | 0.08 |
| Al62 | 12.19 | 10.23 | 1.18 |
| Al63 | 12.21 | 11.51 | 3.47 |
| Al64 | 16.41 | 12.17 | 0.12 |
| O1 | 5.18 | 7.74 | 4.84 |
| O2 | 1.04 | 5.03 | 2.84 |
| O3 | 5.18 | 6.90 | 1.14 |
| O4 | 0.98 | 5.19 | 0.15 |
| O5 | 0.89 | 0.87 | 22.42 |
| O6 | 5.14 | 3.28 | 1.70 |
| O7 | 0.92 | 1.21 | 2.72 |
| O8 | 5.26 | 2.58 | 4.38 |
| O9 | 6.68 | 0.87 | 22.42 |
| O10 | 2.44 | 3.28 | 1.72 |
| O11 | 6.69 | 1.21 | 2.72 |
| O12 | 2.34 | 2.58 | 4.39 |
| O13 | 2.43 | 7.76 | 4.88 |
| O14 | 6.54 | 5.03 | 2.82 |
| O15 | 2.39 | 6.90 | 1.14 |
| O16 | 6.60 | 5.19 | 0.15 |
| O17 | 8.03 | 7.30 | 4.23 |
| O18 | 7.99 | 7.08 | 1.30 |

| | | | |
|---|---|---|---|
| O19 | 3.79 | 1.07 | 0.04 |
| O20 | 3.80 | 1.03 | 2.69 |
| O21 | 3.79 | 5.10 | 5.00 |
| O22 | 3.79 | 5.11 | 0.12 |
| O23 | 7.99 | 2.96 | 1.39 |
| O24 | 8.02 | 2.82 | 4.13 |
| O25 | 5.19 | 15.56 | 4.52 |
| O26 | 0.98 | 13.09 | 2.81 |
| O27 | 5.19 | 14.99 | 1.13 |
| O28 | 0.98 | 13.26 | 0.15 |
| O29 | 0.89 | 8.93 | 22.42 |
| O30 | 5.06 | 11.37 | 1.79 |
| O31 | 0.94 | 9.24 | 2.76 |
| O32 | 5.24 | 10.82 | 4.28 |
| O33 | 6.68 | 8.93 | 22.42 |
| O34 | 2.50 | 11.36 | 1.78 |
| O35 | 6.66 | 9.24 | 2.75 |
| O36 | 2.36 | 10.83 | 4.29 |
| O37 | 2.42 | 15.56 | 4.54 |
| O38 | 6.60 | 13.08 | 2.81 |
| O39 | 2.38 | 14.99 | 1.14 |
| O40 | 6.60 | 13.26 | 0.15 |
| O41 | 8.01 | 15.44 | 4.22 |
| O42 | 7.99 | 15.15 | 1.30 |
| O43 | 3.79 | 9.14 | 0.04 |
| O44 | 3.79 | 9.22 | 2.76 |
| O45 | 3.79 | 13.28 | 3.09 |
| O46 | 3.79 | 13.18 | 0.12 |
| O47 | 7.98 | 11.03 | 1.41 |
| O48 | 8.00 | 10.83 | 4.17 |
| O49 | 13.64 | 7.78 | 4.80 |
| O50 | 9.45 | 5.03 | 2.84 |
| O51 | 13.60 | 6.90 | 1.14 |
| O52 | 9.39 | 5.19 | 0.15 |
| O53 | 9.30 | 0.87 | 22.42 |
| O54 | 13.55 | 3.28 | 1.70 |
| O55 | 9.37 | 1.23 | 2.75 |
| O56 | 13.67 | 2.58 | 4.39 |
| O57 | 15.09 | 0.87 | 22.42 |
| O58 | 10.85 | 3.28 | 1.72 |
| O59 | 15.08 | 1.20 | 2.72 |

| | | | |
|---|---|---|---|
| O60 | 10.81 | 2.60 | 4.45 |
| O61 | 10.91 | 7.86 | 4.98 |
| O62 | 14.96 | 5.03 | 2.83 |
| O63 | 10.80 | 6.90 | 1.14 |
| O64 | 15.01 | 5.19 | 0.15 |
| O65 | 16.41 | 7.31 | 4.25 |
| O66 | 16.41 | 7.08 | 1.30 |
| O67 | 12.20 | 1.07 | 0.04 |
| O68 | 12.21 | 1.01 | 2.69 |
| O69 | 12.22 | 5.16 | 4.80 |
| O70 | 12.20 | 5.11 | 0.12 |
| O71 | 16.40 | 2.96 | 1.39 |
| O72 | 16.41 | 2.82 | 4.12 |
| O73 | 13.61 | 15.56 | 4.52 |
| O74 | 9.39 | 13.08 | 2.81 |
| O75 | 13.60 | 14.99 | 1.13 |
| O76 | 9.39 | 13.26 | 0.15 |
| O77 | 9.30 | 8.93 | 22.42 |
| O78 | 13.47 | 11.37 | 1.79 |
| O79 | 9.36 | 9.25 | 2.77 |
| O80 | 13.65 | 10.80 | 4.26 |
| O81 | 15.09 | 8.93 | 22.42 |
| O82 | 10.91 | 11.36 | 1.78 |
| O83 | 15.09 | 9.24 | 2.72 |
| O84 | 10.78 | 10.84 | 4.29 |
| O85 | 10.84 | 15.57 | 4.56 |
| O86 | 15.01 | 13.08 | 2.81 |
| O87 | 10.80 | 14.99 | 1.14 |
| O88 | 15.01 | 13.26 | 0.15 |
| O89 | 16.43 | 15.44 | 4.22 |
| O90 | 16.41 | 15.15 | 1.30 |
| O91 | 12.20 | 9.14 | 0.04 |
| O92 | 12.18 | 9.20 | 2.73 |
| O93 | 12.21 | 13.29 | 3.08 |
| O94 | 12.20 | 13.18 | 0.12 |
| O95 | 16.40 | 11.03 | 1.41 |
| O96 | 16.41 | 10.83 | 4.16 |
| O97 | 12.70 | 6.87 | 7.21 |
| O98 | 12.45 | 3.36 | 6.89 |
| O99 | 13.91 | 4.46 | 8.15 |
| O100 | 14.43 | 5.82 | 10.76 |

| | | | |
|---|---|---|---|
| O101 | 14.89 | 8.14 | 6.93 |
| C1 | 11.12 | 5.47 | 9.39 |
| C2 | 11.30 | 6.87 | 9.14 |
| C3 | 11.94 | 7.55 | 8.16 |
| C4 | 12.67 | 4.06 | 7.91 |
| C5 | 11.60 | 4.31 | 8.87 |
| C6 | 11.89 | 9.01 | 7.90 |
| C7 | 11.06 | 9.94 | 8.78 |
| C8 | 11.03 | 11.32 | 8.13 |
| C9 | 10.29 | 12.40 | 8.91 |
| C10 | 10.30 | 13.74 | 8.17 |
| H1 | 10.32 | 5.30 | 10.12 |
| H2 | 10.73 | 7.51 | 9.81 |
| H3 | 11.06 | 3.40 | 9.11 |
| H4 | 11.52 | 9.09 | 6.86 |
| H5 | 12.93 | 9.38 | 7.84 |
| H6 | 11.49 | 10.00 | 9.79 |
| H7 | 10.04 | 9.55 | 8.88 |
| H8 | 10.58 | 11.23 | 7.13 |
| H9 | 12.07 | 11.66 | 7.96 |
| H10 | 10.75 | 12.52 | 9.90 |
| H11 | 9.25 | 12.08 | 9.09 |
| H12 | 11.32 | 14.08 | 7.99 |
| H13 | 9.79 | 14.52 | 8.74 |
| H14 | 9.80 | 13.66 | 7.19 |
| H15 | 13.97 | 4.93 | 9.02 |
| H16 | 13.68 | 7.33 | 7.20 |
| H17 | 15.37 | 6.02 | 10.95 |
| H18 | 14.09 | 5.39 | 11.56 |
| H19 | 15.70 | 7.60 | 6.94 |
| H20 | 14.54 | 8.05 | 5.95 |

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