# Supporting Information

## Selective Hydrogenation of 5-(Hydroxymethyl)furfural to 5-Methylfurfural over Single Atomic Metals Anchored on $Nb_2O_5$

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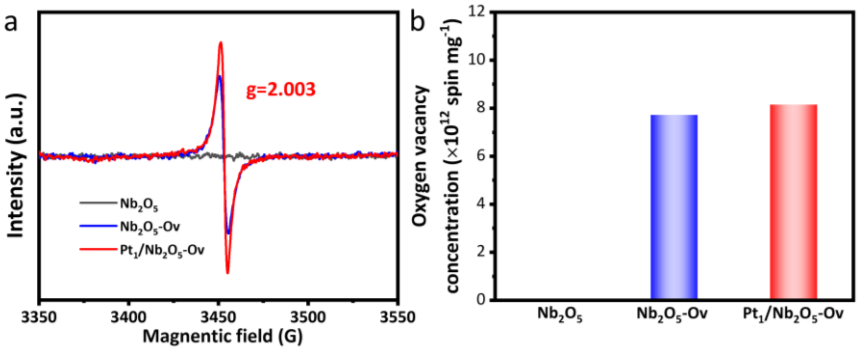
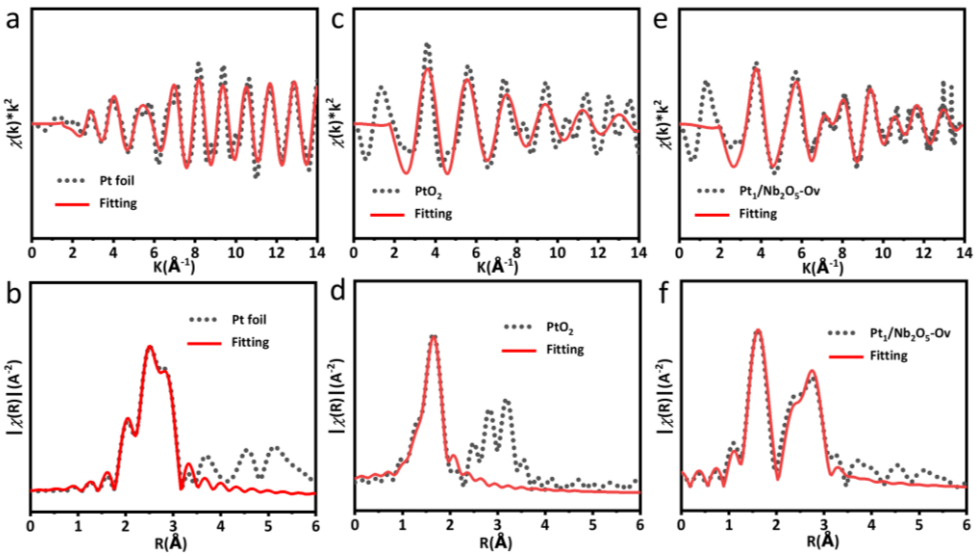
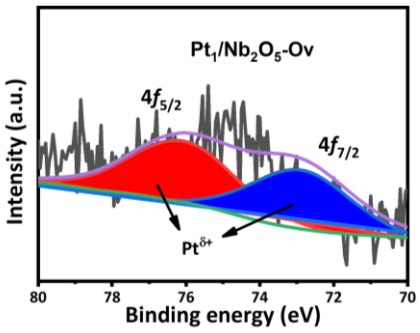
**Additional figures**



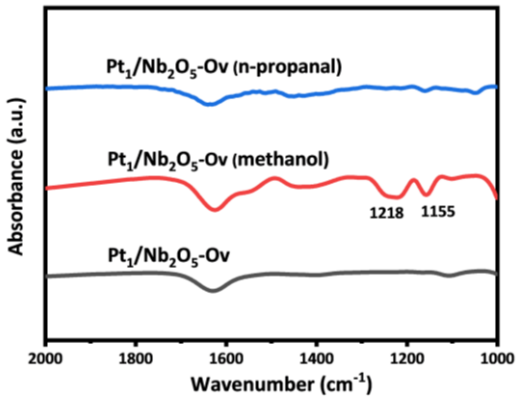

**Supplementary Fig. 1 Characterization results from electron-paramagnetic resonance spectra.** (a) EPR of $Nb_2O_5$, $Nb_2O_5$-Ov and $Pt_1/Nb_2O_5$-Ov. (b) Quantitative EPR analysis at room temperature. Data for the reduced samples were acquired under vacuum.



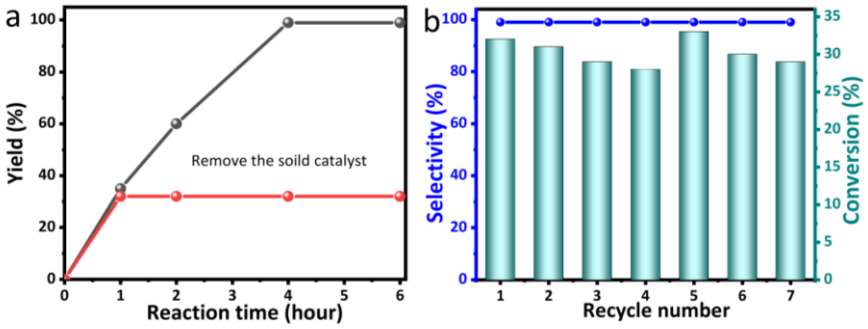

**Supplementary Fig. 2 Characterization results from EXAFS.** (a, c, e) EXAFS in k space of Pt foil, $PtO_2$, and $Pt_1/Nb_2O_5$-Ov. (b, d, f) The corresponding EXAFS fitting of Pt foil, $PtO_2$, and $Pt_1/Nb_2O_5$-Ov at R space.



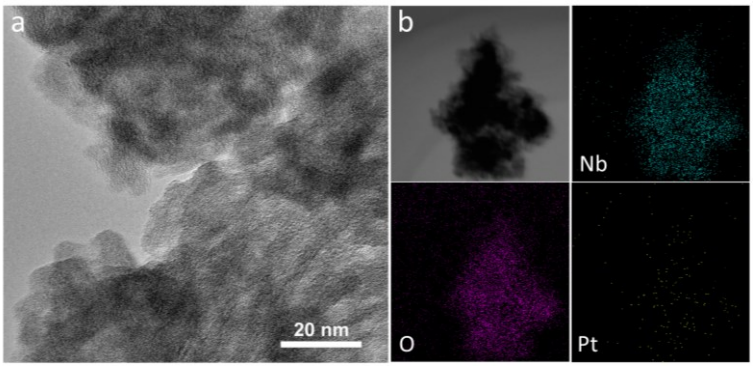

**Supplementary Fig. 3 Characterization results from XPS.** The Pt 4*f* of $Pt_1/Nb_2O_5$-Ov.



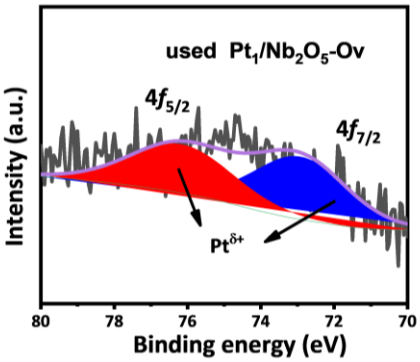

**Supplementary Fig. 4 Characterization results from FT-IR.** FT-IR spectra of methanol and n-propanal adsorbed on $Pt_1/Nb_2O_5$-Ov.



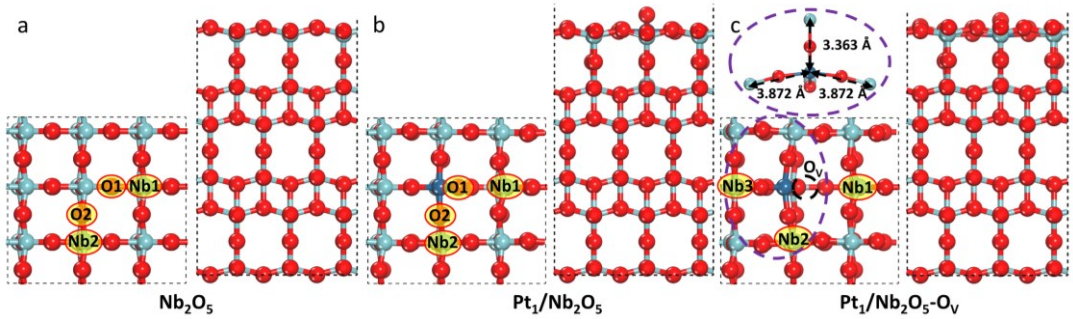

**Supplementary Fig. 5 Recycling test of the $Pt_1/Nb_2O_5$-Ov catalyst.** (a) Time-yield plots for MF from selective hydrodeoxygenation of HMF over $Pt_1/Nb_2O_5$-Ov (black line) or removing $Pt_1/Nb_2O_5$-Ov after 1 h (red line); (b) Reusability of the $Pt_1/Nb_2O_5$-Ov. Reaction conditions: HMF (0.3 mmol), catalyst (20 mg), solvent (THF 2 mL), reaction temperature (160°C), $H_2$ pressure (4.0 MPa), reaction time (1 h), stirring speed (600 rpm).



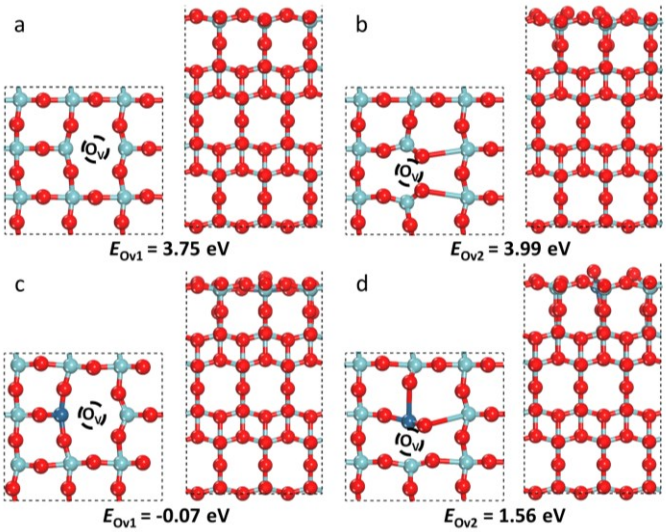

**Supplementary Fig. 6 The HR-TEM image and corresponding EDS pattern of $Pt_1/Nb_2O_5$-Ov.** (a) TEM images of the used $Pt_1/Nb_2O_5$-Ov. (b) EDS mapping images of the used $Pt_1/Nb_2O_5$-Ov.



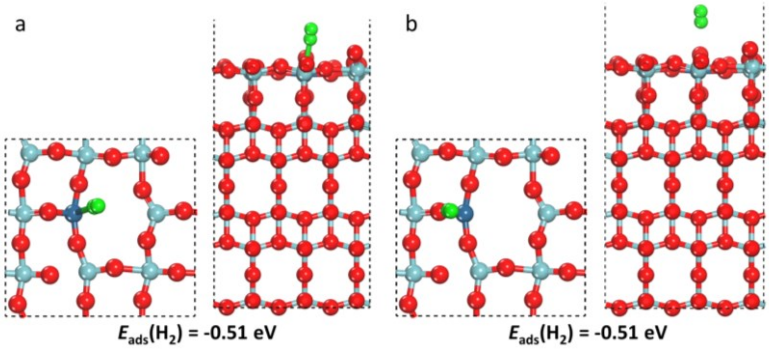

**Supplementary Fig. 7 Characterization results from XPS.** The Pt 4*f* of the used $Pt_1/Nb_2O_5$-Ov.



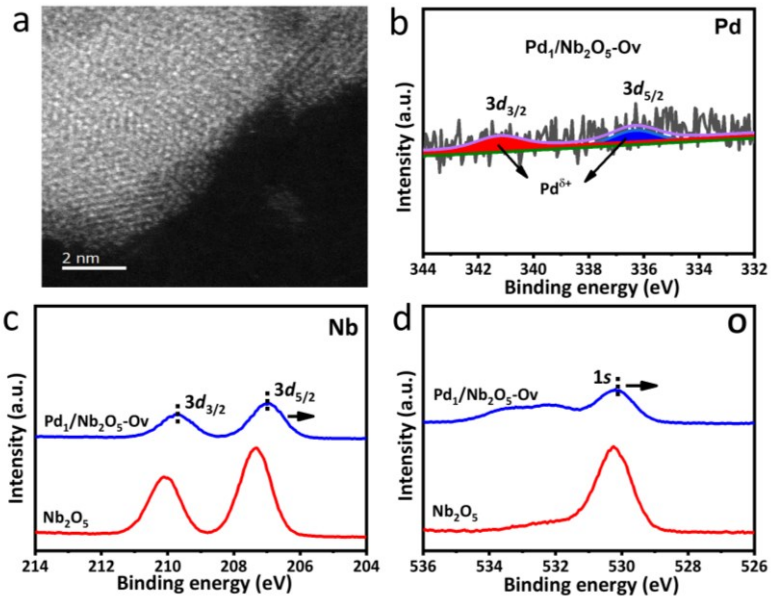

**Supplementary Fig. 8 Calculated structures of the stoichiometric.** (a) $Nb_2O_5$, (b) $Pt_1/Nb_2O_5$, (c) $Pt_1/Nb_2O_5$-Ov surfaces (Left: top view; Right: side view). Red: O, light blue: Nb, blue: Pt; the dotted circles label the missing oxygens (vacancies). These notations are used throughout the paper.



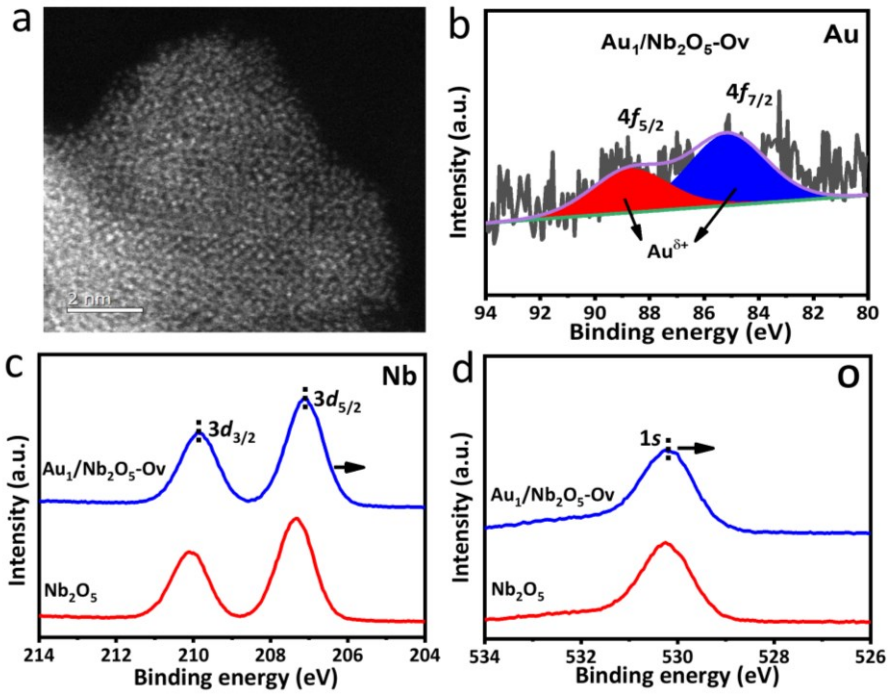

**Supplementary Fig. 9 Calculated structures and the oxygen vacancy energies**. (a, b) $Nb_2O_5$ and (c, d) $Pt_1/Nb_2O_5$ surfaces. The dotted circles label the missing oxygens (vacancies). (Left: top view; Right: side view). Red: O, light blue: Nb, blue: Pt.




**Supplementary Fig. 10 Calculated adsorption energy and structures of $H_2$ on $Pt_1/Nb_2O_5$-$O_V$ surfaces.** (a) Pt site, (b) O site. (Left: top view; Right: side view). Red: O, light blue: Nb, blue: Pt, green: H.




**Supplementary Fig. 11 AC–HAADF–STEM image and XPS pattern of $Pd_1/Nb_2O_5$-Ov.** (a) AC–HAADF–STEM image of $Pd_1/Nb_2O_5$-Ov. The XPS spectra of Pd 3*d* (b), Nb 3*d* (c) and O 1*s* (d) of $Nb_2O_5$ and $Pd_1/Nb_2O_5$-Ov.




**Supplementary Fig. 12 AC–HAADF–STEM image and XPS pattern of $Au_1/Nb_2O_5$-Ov.** (a) AC–HAADF–STEM image of $Au_1/Nb_2O_5$-Ov. The XPS spectra of Au 4*f* (b), Nb 3*d* (c) and (d) O 1*s* of $Nb_2O_5$ and $Au_1/Nb_2O_5$-Ov.

**Supplementary Table 1. Structural parameters extracted from quantitative EXAFS curve-fitting.**

| Sample | Shell | C. N. | $\sigma^2/10^{-3}(Å^2)$ | $E_0$/eV | R/ Å | R-factor |
|---|---|---|---|---|---|---|
| Pt foil | Pt-Pt | 12 | 4.63 | 8.576 | 2.76 | 0.002 |
| $PtO_2$ | Pt-O 1 | 2 | 3.10 | 11.98 | 1.92 | 0.017 |
| | Pt-O 2 | 4 | 0.87 | 11.98 | 2.02 | |
| | Pt-Pt | 2 | 3.80 | 14.55 | 3.14 | |
| $Pt_1/Nb_2O_5$-Ov | Pt-O | 2.11 | 2.93 | 14.10 | 2.00 | 0.019 |
| | Pt-Nb | 3.24 | 5.66 | 12.15 | 2.92 | |

EXAFS fitting details of Pt foil, $PtO_2$ and $Pt_1/Nb_2O_5$-Ov, catalyst. The EXAFS data (k-range: -12.5 $Å^{-1}$ and R-range: 1-3.3 Å) were fitted in 1,2 and3 k-weighted R-space. Amplitude reduction factors were evaluated for reference spectra.

**Supplementary Table 2. Catalytic Performances of Pt-Based Catalysts for the Conversion of HMF.**

| Entry | Catalyst | T(°C) | P(MPa) | Product | Conv. (%) | Yield (%) | TOF ($h^{-1}$) | Refrences |
|---|---|---|---|---|---|---|---|---|
| 1 | Pt/C | 120 | 6.2 | BHMF | 11 | 2 | 21.3 | 1 |
| 2 | Pt/MCM-41 | 35 | 0.8 | BHMF | 100 | 98.9 | 386.3 | 2 |
| 3 | $Pt_3Sn/SnO_2/rGO$ | 70 | 2 | BHMF | >99 | >99 | 1308.0 | 3 |
| 4 | Pt/AC | 120 | 3 | DMF | 67.4 | 32.6 | 33.7 | 4 |
| 5 | Pt/rGO | 120 | 2 | DMF | 100 | 73.2 | 50.0 | 4 |
| 6 | Pt/NaY | 220 | 1.5 | DMF | 100 | 30.4 | 195.1 | 5 |
| 7 | PtCo@HCS[a] | 180 | 2 | DMF | 100 | 98 | 32.5 | 6 |
| 8 | $Pt_1/Nb_2O_5$-Ov | 160 | 4 | MF | >99 | >99 | 1875.3 | This work |

[a]HCS, hollow carbon spheres.

**Supplementary Table 3. Calculated the entropy and energy of each compound at the 413.15 K.**

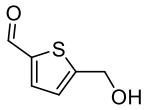
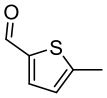
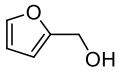
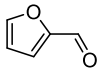
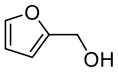
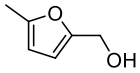
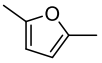
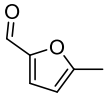
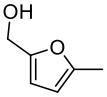
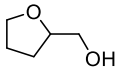
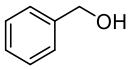
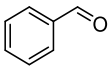
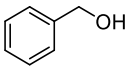
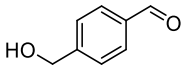
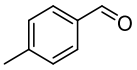
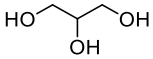
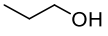
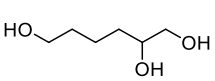
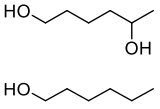
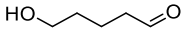
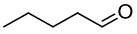
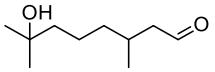
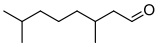
| | $H_2O$ | $H_2$ | HMF | MF | DMF |
|---|---|---|---|---|---|
| S/cal/mol/K | 45.08 | 31.13 | 90.51 | 84.18 | 81.81 |
| E/eV | -14.22 | -88.7 | -6.76 | -94.95 | -89.97 |

**Supplementary Table 4. The hydrodeoxygenation of MF to DMF over $Pt_1/Nb_2O_5$-Ov.**

| Entry | Catalyst | Temperature (°C) | Time (h) | Conversion (%) | Yield (%) |
|---|---|---|---|---|---|
| 1 | $Pt_1/Nb_2O_5$-Ov | 160 | 2 | trace | - |

Reaction conditions: MF (0.3 mmol), catalyst (20 mg), solvent (THF 2 mL), $H_2$ pressure (4 MPa), stirring speed (600 rpm).

**Supplementary Table 5. Hydrodeoxygenation of different substrates over the $Pt_1/Nb_2O_5$-Ov catalyst[a].**

| Entry | Substrate | Temperature / °C | Time / h | Product | Conversion / % | Yield. / % |
|---|---|---|---|---|---|---|
| 1 |  | 160 | 4 |  | >99 | 98 |
| 2 |  | 160 | 4 |  | >99 | >99 |
| 3 |  | 160 | 4 |  | trace | trace |
| 4 |  | 160 | 4 |  | >99 | >99 |
| 5 |  | 160 | 4 |  | trace | - |
| 6 |  | 160 | 6 |  | trace | - |
| 7[b] |  | 160 | 1 |  | 24 | 24 |
| 8[b] |  | 160 | 1 |  | 55 | 45 |
| 9[b] |  | 160 | 1 |  | >99 | 23 |
| 10[c] |  | 200 | 6 |  | 11 | 9 |
| 11[c] |  | 200 | 6 |  | 26 | 14.6<br>11.4 |
| 12[b] |  | 160 | 2 |  | trace | trace |
| 13[b] |  | 160 | 4 |  | trace | trace |

[a] Reaction conditions: substrate (0.3 mmol), catalyst (20 mg), solvent (THF 2 mL), $H_2$ pressure (2.0 MPa), stirring speed (600 rpm). [b] solvent (ethanol 2 mL). [c] 10wt% solution (2 mL).

**Supplementary Table 6. The imaginary frequency of TS.**

| Structure | Frequency ($cm^{-1}$) |
|---|---|
| TS1 | 971.15 |
| TS2 | 319.98 |

**Fractional coordinates for optimized DFT structures**

Fractional coordinates are provided in CIF-format and are labeled according to the nomenclature introduced in Supplementary Fig. 8c. The structures with CIF-format can be found in the Supplementary Data 1.

**AutoCreatByScript: O Nb Pt**

1.00000000000000

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0.0000000000000000 11.4381599999999999 0.0000000000000000

0.0000000000000000 0.0000000000000000 32.7415599999999998

a=12.25551; b=11.43816; c=32.74156

alpha=90.00; beta=90.00; gamma=90.00

O Nb Pt

134 53 1

**Selective dynamics**

**Direct**

| | | |
|---|---|---|
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| 0.4380080000000035 | 0.1250980000000013 | 0.0005060000000014 |
| 0.7713419999999971 | 0.1250980000000013 | 0.0005060000000014 |
| 0.1046750000000003 | 0.4584309999999974 | 0.0005060000000014 |
| 0.4380080000000035 | 0.4584309999999974 | 0.0005060000000014 |
| 0.7713419999999971 | 0.4584309999999974 | 0.0005060000000014 |
| 0.1046750000000003 | 0.7917649999999981 | 0.0005060000000014 |
| 0.4380080000000035 | 0.7917649999999981 | 0.0005060000000014 |
| 0.7713419999999971 | 0.7917649999999981 | 0.0005060000000014 |
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| 0.9356790000000004 | 0.2918859999999981 | 0.0153400000000019 |
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| 0.4352879999999999 | 0.6250769999999974 | 0.0736300000000014 |
| 0.7686210000000031 | 0.6250769999999974 | 0.0736300000000014 |
| 0.1019549999999967 | 0.9584100000000007 | 0.0736300000000014 |
| 0.4352879999999999 | 0.9584100000000007 | 0.0736300000000014 |
| 0.7686210000000031 | 0.9584100000000007 | 0.0736300000000014 |

| | | |
|---|---|---|
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