# SUPPORTING INFORMATION

#### Exploring 5-Hydroxymethylfurfural Hydrogenation Pathways using NHC-Stabilized Water-Soluble Nanoparticles of various Metals and Alloys

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# 1. Nanoparticle syntheses



**Scheme S1.** Schematic of (a) imidazolium salt preparation, (b) carbene synthesis (imidazolium deprotonation), and (c) NP syntheses.



**Figure S1.** <sup>1</sup>H-NMR spectrum of the imidazolium salt IMesPrSO<sub>3</sub>H in dmso-d<sub>6</sub> at 298 K. The asterisk denotes the residual signal of the dmso-d<sub>6</sub>. The square denotes the signal for the water.

# 2. Catalyst characterization

### 2.1 Metal content of the different water-soluble NPs

Table S1. Total amount of organic matter in each NPs.

NPs	<b>Organic wt.%</b> (Ligand) <sup>a</sup>
Ru@IMesPrSO <sub>3</sub>	33.6
Pd@IMesPrSO <sub>3</sub>	48.5
Ir@IMesPrSO <sub>3</sub>	29.7
RuIr2@IMesPrSO3 <sup>b</sup>	33.5

<sup>a</sup> Determined by TGA; <sup>b</sup> Ru:Ir mol ratio (1:2) estimated by ICP.

## 2.2 Additional BF-TEM images for the different water-soluble NPs



Figure S2. BF-TEM micrographs for different regions (a, b) of Ru@IMesPrSO<sub>3</sub> NPs (NPs size =  $2.0 \pm 0.7$  nm).



**Figure S3.** BF-TEM micrographs for different regions (a, b) of Pd@IMesPrSO<sub>3</sub> NPs (NPs size =  $2.1 \pm 0.3$  nm).



**Figure S4.** BF-TEM micrographs for different regions (a, b) of Ir@IMesPrSO<sub>3</sub> NPs (NPs size =  $2.0 \pm 0.5$  nm).



**Figure S5.** BF-TEM micrographs for different regions (a, b) of  $RuIr_2@IMesPrSO_3$  NPs (NPs size =  $1.7 \pm 0.3$  nm).



2.3 Dynamic Light Scattering (DLS) measurements for the different water-soluble NPs.

Figure S6. DLS measurements in water for a) Ru@IMesPrSO<sub>3</sub>, b) Pd@IMesPrSO<sub>3</sub>, c) Ir@IMesPrSO<sub>3</sub>, and d) RuIr<sub>2</sub>@IMesPrSO<sub>3</sub> NPs.

#### 2.4 Powder X-Ray Diffraction (XRD) measurements



Figure S7. XRD measurements for the different water-soluble NPs.

## 2.5 Methodology for Pair Distribution Function (PDF) refinement

After PDF extraction, the experimental PDF was compared against theoretical PDFs computed from structural models from the *ASE Python library*.

### 2.5.1 Refinement for Ru/Pd/Ir@IMesPrSO<sub>3</sub> NPs:

A .cif file corresponding to the metal (usually an fcc structure, space group Fm-3m) was selected as a first attempt, as if we had a bulk material. A form factor corresponding to a spherical shape for the nanoparticle is applied to reproduce the PDF envelope through the refinement of the particle diameter. In some instances, this model was further refined by rebuilding a structural model (xyz file) from the .cif file, such as a spherical particle (cluster) with a similar structure as the bulk. In these cases, the .xyz file was used for the fitting.

However, since these spherical NPs made of fcc structure may match with the experimental PDF, but they are physically inconsistent, as the surface energy of the particle is not minimized, we explored two possibilities:

*Option 1:* If the fcc model aligned well with the experimental PDF, a cuboctahedron model was constructed, since it corresponds to the fcc structure minimizing surface energy. The size of this model should be approximately equal to the previously optimized sphere diameter.

*Option 2:* If the fcc model does not match the experimental PDF, other structural models are explored, such as icosahedron, decahedron, etc. In all cases, the size of the modelled particle is chosen to match the observed NP size in the PDF. The model showing the best agreement is selected.



**Figure S8.** PDF obtained from WAXS measurement of Ru@IMesPrSO<sub>3</sub> NPs and comparison against a) a P63mmc spherical, b) an Fm3m cluster, and c) an octahedron models.



**Figure S9.** PDF obtained from WAXS measurement of Pd@IMesPrSO<sub>3</sub> NPs and comparison against a) an Fm3m spherical, b) a cuboctahedron, and c) an icosahedron models.

![](_page_8_Figure_0.jpeg)

**Figure S10.** PDF obtained from WAXS measurement of Ir@IMesPrSO<sub>3</sub> NPs and comparison against a) an Fm3m spherical, b) decahedron 5-1-0, and c) an icosahedron models.

#### 2.5.2 Refinement for RuIr<sub>2</sub>@IMesPrSO<sub>3</sub> NPs:

Instead of using the model of the fcc sphere, a model of the Ir icosahedron (length=7, diameter = 21.0 angströms) was built. In this model, Ir was substituted by Ru atoms to attain the RuIr<sub>2</sub> stoichiometry determined by ICP in 2 manners, randomly and 1 out of 3, in order of appearance in the original file. Both structures give similar results and improve the refinement compared to the spherical fcc case previously considered in the cases mentioned above.

![](_page_9_Figure_0.jpeg)

**Figure S11.** PDF obtained from WAXS measurement of RuIr<sub>2</sub>@IMesPrSO<sub>3</sub> NPs and comparison against a) an Fm3m spherical, b) a cuboctahedron and, c) pure Ir icosahedron models.

# 3. Reaction analytics

### 3.1 NMR signals for the corresponding HMF valorization products

### 5-(Hydroxymethyl)furfural (5-HMF)

![](_page_9_Figure_5.jpeg)

<sup>1</sup>H-NMR (500 MHz, D<sub>2</sub>O, 298 K):  $\delta = 9.46$  (s, 1H, CHO), 7.54 (d, <sup>3</sup>J<sub>H-H</sub>=3.6 Hz, 1H, H<sup>3</sup>), 6.68 (d, <sup>3</sup>J<sub>H-H</sub>=3.6 Hz, 1H, H<sup>4</sup>), 4.70 (s, 2H, CH<sub>2</sub>OH). (Figure S12)

### 2,5-Bis(hydroxymethyl)furan (2,5-BHMF)

![](_page_9_Figure_8.jpeg)

<sup>1</sup>H-NMR (500 MHz, D<sub>2</sub>O, 298 K):  $\delta = 6.37$  (s, 2H, H<sup>3</sup>), 4.57 (s, 4H, CH<sub>2</sub>OH). <sup>13</sup>C{<sup>1</sup>H}-NMR (125 MHz, D<sub>2</sub>O, 298 K):  $\delta = 153.7$  (C<sup>2</sup>), 109.1 (C<sup>3</sup>), 55.8 (CH<sub>2</sub>OH). (Figure S13)

#### 1-Hydroxyhexane-2,5-dione (HHD)

$$HO = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 4 & 5 \\ 0 & 4 & 5 \\ 0 & 4 & 5 & 6 \end{bmatrix}$$
<sup>1</sup>H-NMR (500 MHz, D<sub>2</sub>O, 298 K):  $\delta = 4.41$  (s, 2H, H<sup>1</sup>), 2.90 (t, <sup>3</sup>J<sub>H-H</sub>  
= 6.0 Hz, 2H, H<sup>3</sup>), 2.71 (t, <sup>3</sup>J<sub>H-H</sub> = 6.0 Hz, 2H, H<sup>4</sup>), 2.24 (s, 3H, H<sup>6</sup>).  
<sup>13</sup>C{<sup>1</sup>H}-NMR (125 MHz, D<sub>2</sub>O, 298 K):  $\delta = 214.0$  (C<sup>5</sup>), 212.7 (C<sup>2</sup>),  
67.0 (C<sup>1</sup>), 36.7 (C<sup>3</sup>), 31.8 (C<sup>4</sup>), 29.2 (C<sup>6</sup>). (Figures S14, S18, S19, S21,

and S32-S34)

#### 1-Hydroxyhex-3-ene-2,5-dione (HHED)

![](_page_10_Figure_4.jpeg)

<sup>1</sup>H-NMR (500 MHz, D<sub>2</sub>O, 298 K):  $\delta = 7.13$  (d,  ${}^{3}J_{\text{H-H}} = 10.4$  Hz, 1H, H<sup>3</sup>), 6.17 (d,  ${}^{3}J_{\text{H-H}} = 10.4$  Hz, 1H, H<sup>4</sup>), 4.58 (d,  ${}^{2}J_{\text{H-H}} = 17.5$  Hz, 1H, H<sup>1</sup>), 4.25 (d,  ${}^{2}J_{\text{H-H}} = 17.5$  Hz, 1H, H<sup>1</sup>), 2.27 (s, 3H, H<sup>6</sup>). <sup>13</sup>C{<sup>1</sup>H}-NMR (125 MHz, D<sub>2</sub>O, 298 K):  $\delta = 213.0$  (C<sup>5</sup>), 210.0 (C<sup>2</sup>), 125.5 (C<sup>4</sup>), 66.0 (C<sup>1</sup>), 25.3 (C<sup>6</sup>). C<sup>3</sup> was not observed. (Figures S29 and S30)

#### 3-(Hydroxymethyl)cyclopent-2-en-1-one (HCPEN)

![](_page_10_Figure_7.jpeg)

<sup>1</sup>H-NMR (500 MHz, D<sub>2</sub>O, 298 K):  $\delta = 6.19$  (q, <sup>4</sup>*J*<sub>H-H</sub> = 1.7 Hz, 1H, H<sup>2</sup>), 4.53 (m, 2H, CH<sub>2</sub>OH), 2.69 (m, 2H, H<sup>5</sup>), 2.54 (m, 2H, H<sup>4</sup>). <sup>13</sup>C{<sup>1</sup>H}-NMR (125 MHz, D<sub>2</sub>O, 298 K):  $\delta = 215.4$  (C<sup>1</sup>), 187.2 (C<sup>3</sup>), 126.6 (C<sup>2</sup>), 61.8 (CH<sub>2</sub>OH), 35.1 (C<sup>4</sup>), 28.2 (C<sup>5</sup>). (Figures S14 – S17)

#### 3-(Hydroxymethyl)cyclopentan-1-one (HCPN)

![](_page_10_Figure_10.jpeg)

<sup>1</sup>H-NMR (500 MHz, D<sub>2</sub>O, 298 K):  $\delta = 3.64$  (d,  ${}^{3}J_{\text{H-H}} = 6.3$  Hz, 2H, CH<sub>2</sub>OH), 2.48 (m, 1H, H<sup>3</sup>), 2.43 (m, 1H, H<sup>2</sup>), 2.38 – 2.26 (m, 2H, H<sup>5</sup>), 2.16 (m, 1H, H<sup>4</sup>), 2.05 (m, 1H, H<sup>2</sup>), 1.68 (ddt,  ${}^{2}J_{\text{H-H}} = 12.8$  Hz,  ${}^{3}J_{\text{H-H}} = 9.8$  Hz,  ${}^{3}J_{\text{H-H}} = 8.9$  Hz, 1H, H<sup>4</sup>). <sup>13</sup>C{<sup>1</sup>H}-NMR (125 MHz, D<sub>2</sub>O, 298 K):  $\delta = 227.0$  (C<sup>1</sup>), 65.0 (CH<sub>2</sub>OH), 41.6 (C<sup>2</sup>), 38.4 (C<sup>3</sup>), 37.9 (C<sup>5</sup>), 25.2 (C<sup>4</sup>). (Figures S14, S31 – S33)

### 4-Hydroxy-4-(hydroxymethyl)cyclopent-2-en-1-one (4-HHCPEN)

![](_page_10_Figure_13.jpeg)

<sup>1</sup>H-NMR (500 MHz, D<sub>2</sub>O, 298 K):  $\delta = 7.66$  (d, <sup>3</sup>*J*<sub>H-H</sub> = 5.7 Hz, 1H, H<sup>3</sup>), 6.34 (d, <sup>3</sup>*J*<sub>H-H</sub>=5.7 Hz, 1H, H<sup>2</sup>), 3.74 (d, <sup>2</sup>*J*<sub>H-H</sub> = 11.5 Hz, 1H, C*H*<sub>2</sub>OH), 3.69 (d, <sup>2</sup>*J*<sub>H-H</sub> = 11.5 Hz, 1H, C*H*<sub>2</sub>OH), 2.68 (d, <sup>2</sup>*J*<sub>H-H</sub> = 18.6 Hz, 1H, H<sup>5</sup>), 2.47 (d, <sup>2</sup>*J*<sub>H-H</sub> = 18.6 Hz, 1H, H<sup>5</sup>). <sup>13</sup>C{<sup>1</sup>H}-NMR (125 MHz, D<sub>2</sub>O, 298 K):  $\delta = 211.1$  (C<sup>1</sup>), 165.8 (C<sup>3</sup>), 134,6 (C<sup>2</sup>), 79.4 (C<sup>4</sup>), 66.0 (CH<sub>2</sub>OH), 45.6 (C<sup>5</sup>). (Figures S17 – )

S19, and S21)

#### 4-hydroxy-3-(hydroxymethyl)cyclopent-2-en-1-one (4-H-3-HCPEN)

![](_page_10_Picture_17.jpeg)

<sup>1</sup>**H-NMR (500 MHz, D<sub>2</sub>O, 298 K):**  $\delta = 6.24$  (s, 1H, H<sup>2</sup>), 5.00 (d, <sup>3</sup>*J*<sub>H-H</sub> = 5.8 Hz, 1H, H<sup>4</sup>), 4.68 (d, <sup>2</sup>*J*<sub>H-H</sub> = 18.9 Hz, 1H, CH<sub>2</sub>OH), 4.54 (d, <sup>2</sup>*J*<sub>H-H</sub> = 18.9 Hz, 1H, CH<sub>2</sub>OH), 2.95 (dd, <sup>2</sup>*J*<sub>H-H</sub> = 18.6 Hz, <sup>3</sup>*J*<sub>H-H</sub> = 6.1 Hz, 1H, H<sup>5</sup>), 2.40 (d, <sup>2</sup>*J*<sub>H-H</sub> = 18.8 Hz, 1H, H<sup>5</sup>). <sup>13</sup>C{<sup>1</sup>H}-NMR (125 MHz, D<sub>2</sub>O, 298 K):  $\delta = 209.9$  (C<sup>1</sup>), 182.5 (C<sup>3</sup>), 127.9 (C<sup>2</sup>), 69.2 (C<sup>4</sup>), 59.5 (CH<sub>2</sub>OH), 44.2 (C<sup>5</sup>). (Figures S17, S20, S21)

#### 2.5-Hexanedione (2.5-HD)

![](_page_11_Figure_1.jpeg)

<sup>1</sup>H-NMR (500 MHz, D<sub>2</sub>O, 298 K):  $\delta = 2.82$  (s, 4H, H<sup>3</sup>), 2.24 (s, 6H, H<sup>1</sup>). <sup>13</sup>C{<sup>1</sup>H}-NMR (125 MHz, D<sub>2</sub>O, 298 K):  $\delta = 215.4 (C^2), 37.0 (C^3), 29.0 (C^1)$ . (Figures S14, S17, S31, S33, and S34)

#### 2,5-Bis(hydroxymethyl)tetrahydrofuran (2,5-BHMTHF)

![](_page_11_Figure_4.jpeg)

<u>Major Diastereomer</u>: <sup>1</sup>H-NMR (500 MHz, D<sub>2</sub>O, 298 K):  $\delta = 4.15 - 10^{-1}$ 4.00 (m, 2H, H<sup>2</sup>), 3.64 – 3.59 (m, 2H,  $CH_2OH$ ), 3.53 – 3.46 (m, 2H,  $CH_2OH$ ), 2.08 – 1.84 (m, 2H, H<sup>3</sup>), 1.73 – 1.60 (m, 2H, H<sup>3</sup>). <sup>13</sup>C{<sup>1</sup>H}-**NMR (125 MHz, D<sub>2</sub>O, 298 K):**  $\delta = 80.0$  (C<sup>2</sup>), 63.9 (CH<sub>2</sub>OH), 26.6 (C<sup>3</sup>). Minor Diastereomer: <sup>1</sup>H-NMR (500 MHz, D<sub>2</sub>O, 298 K):  $\delta = 3.96 - 3.85$  (m, 2H, H<sup>2</sup>), 3.66 - 3.62 (m, 4H, CH<sub>2</sub>OH), 2.07 - 2.01 (m, 2H, H<sup>3</sup>), 1.90 - 1.78 (m, 2H, H<sup>3</sup>). (Figures S22 -25, S27, and S28)

#### Poly-5-(hydroxymethyl)tetrahydrofuran-2-carbaldehyde (PHMTHF)

![](_page_11_Figure_7.jpeg)

<sup>1</sup>H-NMR (500 MHz, D<sub>2</sub>O, 298 K):  $\delta = 4.83$  (d,  ${}^{3}J_{\text{H-H}} = 5.7$  Hz, 1H, CHOH<sup>2a</sup>), 4.69 (wide s, 1H, CHOH<sup>2b</sup>), 4.29 (m, 1H, H<sup>5b</sup>), 4.25 (m, 1H, H<sup>5a</sup>), 4.312 (m, 3H, CH<sub>2</sub>O<sup>5b</sup>/H<sup>2a</sup>/H<sup>2b</sup>), 3.82 (m, 1H, CH<sub>2</sub>O<sup>5a</sup>), 3.59 (m, 1H, CH<sub>2</sub>O<sup>5a</sup>), 3.32 (dt,  ${}^{2}J_{\text{H-H}} = 11.5$  Hz,  ${}^{3}J_{\text{H-H}} = 1.0$  Hz, 1H, CH<sub>2</sub>O<sup>5b</sup>), 2.10-1.54 (m, 8H, H<sup>3a</sup>/H<sup>3b</sup>/H<sup>4a</sup>/H<sup>4b</sup>).  ${}^{13}C{^{1}H}$ -NMR (125 MHz, D<sub>2</sub>O,

**298 K):**  $\delta = 92.1$  (CHOH<sup>2b</sup>), 91.4 (CHOH<sup>2a</sup>), 77.0 (C<sup>2a</sup>), 76.8 (C<sup>2b</sup>), 75.4 (C<sup>5b</sup>), 74.2 (C<sup>5a</sup>), 70.4 (CH<sub>2</sub>O<sup>5a</sup>), 65.4 (CH<sub>2</sub>O<sup>5b</sup>), 26.3 (C<sup>4a</sup>), 25.3 (C<sup>4b</sup>), 24.8 (C<sup>3b</sup>), 22.1 (C<sup>3a</sup>). (Figures S25 and S26)

<sup>1</sup>H-NMR (500 MHz, THF-*d*<sub>8</sub>, 298 K):  $\delta = 5.60$  (d, <sup>3</sup>*J*<sub>H-H</sub> = 5.3 Hz, 1H, OH<sup>a</sup>), 5.30 (d, <sup>3</sup>*J*<sub>H-H</sub> = 7.9 Hz, 1H, OH<sup>b</sup>), 4.73 (dd,  ${}^{3}J_{H-H}$  = 5.3/1.5 Hz, 1H, CHOH<sup>2a</sup>), 4.42 (d,  ${}^{3}J_{H-H}$  = 7.9 Hz, 1H, CHOH<sup>2b</sup>), 4.09 (m, 2H, CH<sub>2</sub>O<sup>5b</sup>/H<sup>5b</sup>), 4.02 (d,  ${}^{3}J_{H-H} = 6.5$  Hz, 1H, H<sup>5a</sup>), 3.96 (d,  ${}^{3}J_{H-H} = 6.6$ Hz, 1H, H<sup>2b</sup>), 3.88 (d,  ${}^{3}J_{H-H} = 7.0$  Hz, 1H, H<sup>2a</sup>), 3.72 (d,  ${}^{3}J_{H-H} = 11.0$  Hz, 1H, CH<sub>2</sub>O<sup>5a</sup>), 3.45  $(d, {}^{3}J_{H-H} = 11.0 \text{ Hz}, 1\text{H}, \text{CH}_{2}\text{O}^{5a}), 3.11 (d, {}^{3}J_{H-H} = 11.0 \text{ Hz}, 1\text{H}, \text{CH}_{2}\text{O}^{5b}), 2.18 (m, 1\text{H}, \text{H}^{3a}),$ 1.93 (m, 2H, H<sup>3b</sup>), 1.84 (m, 4H, H<sup>4a</sup>/H<sup>4b</sup>), 1.61 (m, 1H, H<sup>3a</sup>). <sup>13</sup>C{<sup>1</sup>H}-NMR (125 MHz, THF $d_8$ , 298 K):  $\delta = 94.0$  (CHOH<sup>2a</sup>), 92.8 (CHOH<sup>2b</sup>), 77.5 (C<sup>2a</sup>), 77.2 (C<sup>2b</sup>), 75.1 (C<sup>5b</sup>), 73.8 (C<sup>5a</sup>), 70.2 (CH<sub>2</sub>O<sup>5a</sup>), 65.0 (CH<sub>2</sub>O<sup>5b</sup>), 27.1 (C<sup>4a</sup>), 26.1 (C<sup>4b</sup>), 25.6 (C<sup>3b</sup>), 22.6 (C<sup>3a</sup>). (Figures S27 and S28)

#### 3.2 NMR spectra and experiments for the corresponding HMF valorization products

![](_page_12_Figure_1.jpeg)

**Figure S12**. <sup>1</sup>H-NMR spectrum of HMF (500 MHz, D<sub>2</sub>O, 298 K). IS denotes the signal of the Internal Standard (Tetramethylammonium bromide = TMAB).

![](_page_12_Figure_3.jpeg)

**Figure S13**. <sup>1</sup>H-NMR spectrum of reaction mixture (500 MHz, D<sub>2</sub>O, 298 K). IS denotes the signal of the Internal Standard (TMAB). <u>Reaction conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of water, 5 mg of Ru@IMesPrSO<sub>3</sub>, at 30 °C, 5 bar of H<sub>2</sub>, 800 rpm, during 2.5 h.

![](_page_13_Figure_0.jpeg)

**Figure S14**. Selected regions of <sup>1</sup>H-NMR spectrum of reaction mixture (500 MHz, D<sub>2</sub>O, 298 K). IS denotes the signal of the Internal Standard (TMAB). <u>Reaction conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of water, 5 mg of Ru@IMesPrSO<sub>3</sub>, at 140 °C, 5 bar of H<sub>2</sub>, 800 rpm, during 4 h.

![](_page_14_Figure_0.jpeg)

**Figure S15**. <sup>1</sup>H-<sup>1</sup>H COSY spectrum (D<sub>2</sub>O, 298 K). <u>Reaction conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of water, 5 mg of Ru@IMesPrSO<sub>3</sub>, at 140 °C, 5 bar of H<sub>2</sub>, 800 rpm, during 4 h.

![](_page_14_Figure_2.jpeg)

**Figure S16**. Selected regions of the overlay of  ${}^{1}\text{H}{}^{-13}\text{C}$  HSQC (red) and  ${}^{1}\text{H}{}^{-13}\text{C}$  HMBC (blue) spectra (D<sub>2</sub>O, 298 K) for a) aliphatic fragments and b) and quaternary carbons. <u>Reaction conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of water, 5 mg of Ru@IMesPrSO<sub>3</sub>, at 140 °C, 5 bar of H<sub>2</sub>, 800 rpm, during 4 h.

![](_page_15_Figure_0.jpeg)

**Figure S17**. Selected regions of <sup>1</sup>H-NMR spectrum of reaction mixture (500 MHz, D<sub>2</sub>O, 298 K). IS denotes the signal of the Internal Standard (TMAB) and the asterisks denote the signals for non-identified minor products. <u>Reaction conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of water, 5 mg of Ir@IMesPrSO<sub>3</sub>, at 160 °C, 5 bar of H<sub>2</sub>, 800 rpm, during 2.5 h.

![](_page_16_Figure_0.jpeg)

**Figure S18**. Selected regions of the <sup>1</sup>H-<sup>1</sup>H TOCSY spectrum (D<sub>2</sub>O, 298 K). <u>Reaction</u> <u>conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of water, 5 mg of Ir@IMesPrSO<sub>3</sub>, at 160  $^{\circ}$ C, 5 bar of H<sub>2</sub>, 800 rpm, during 2.5 h.

![](_page_16_Figure_2.jpeg)

**Figure S19**. Selected regions of the overlay of <sup>1</sup>H-<sup>13</sup>C HSQC (red) and <sup>1</sup>H-<sup>13</sup>C HMBC (blue) spectra (D<sub>2</sub>O, 298 K). <u>Reaction conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of water, 5 mg of Ir@IMesPrSO<sub>3</sub>, at 160 °C, 5 bar of H<sub>2</sub>, 800 rpm, during 2.5 h.

![](_page_17_Figure_0.jpeg)

**Figure S20**. Selected regions of the a)  ${}^{1}\text{H}{}^{-1}\text{H}$  COSY spectrum and b), c)  ${}^{1}\text{H}{}^{-13}\text{C}$  HMBC spectrum (D<sub>2</sub>O, 298 K) for different regions. <u>Reaction conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of water, 5 mg of Ir@IMesPrSO<sub>3</sub>, at 160 °C, 5 bar of H<sub>2</sub>, 800 rpm, during 15 h.

![](_page_17_Figure_2.jpeg)

**Figure S21**. Selected region of <sup>13</sup>C{<sup>1</sup>H}-NMR spectrum (125 MHz, D<sub>2</sub>O, 298 K). <u>Reaction</u> <u>conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of water, 5 mg of Ir@IMesPrSO<sub>3</sub>, at 160 °C, 5 bar of H<sub>2</sub>, 800 rpm, during 15 h.

![](_page_18_Figure_0.jpeg)

**Figure S22.** <sup>1</sup>H-NMR spectrum of reaction mixture (500 MHz, D<sub>2</sub>O, 298 K). IS denotes the signal of the Internal Standard (TMAB), b denotes signals of the minor isomer of 2,5-BHMTHF, the asterisks denote the signals for byproducts and the square denotes solvent impurities signals (Acetone: 2.13 ppm). <u>Reaction conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of water, 5 mg of Pd@IMesPrSO<sub>3</sub>, at 25 °C, 5 bar of H<sub>2</sub>, 800 rpm, during 15 h. Notes: (i) Signals for the minor isomer denoted with superindex b.

![](_page_19_Figure_0.jpeg)

**Figure S23**. Selected region of the <sup>1</sup>H, <sup>1</sup>H-COSY spectrum (D<sub>2</sub>O, 298 K) for tetrahydrofuran signals region. b symbol denotes signals of the minor isomer of 2,5-BHMTHF. <u>Reaction conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of water, 5 mg of Pd@IMesPrSO<sub>3</sub>, at 25 °C, 5 bar of H<sub>2</sub>, 800 rpm, during 15 h.

![](_page_19_Figure_2.jpeg)

**Figure S24**. Selected regions of the overlay of  ${}^{1}\text{H}{}^{-13}\text{C}$  HSQC (red) and  ${}^{1}\text{H}{}^{-13}\text{C}$  HMBC (blue) spectra (D<sub>2</sub>O, 298 K) for a) 2,5-BHMF region and b) 2,5-BHMTHF. <u>Reaction conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of water, 5 mg of Pd@IMesPrSO<sub>3</sub>, at 25 °C, 5 bar of H<sub>2</sub>, 800 rpm, during 15 h.

![](_page_20_Figure_0.jpeg)

**Figure S25**. <sup>1</sup>H-NMR spectrum of reaction mixture (500 MHz, D<sub>2</sub>O, 298 K). <u>Reaction</u> <u>conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of D<sub>2</sub>O, 5 mg of Pd@IMesPrSO<sub>3</sub>, at 25 °C, 5 bar of H<sub>2</sub>, 800 rpm, during 15 h.

![](_page_20_Figure_2.jpeg)

**Figure S26**. Selected region of the <sup>1</sup>H-<sup>13</sup>C HSQC spectrum (D<sub>2</sub>O, 298 K). <u>Reaction</u> <u>conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of D<sub>2</sub>O, 5 mg of Pd@IMesPrSO<sub>3</sub>, at 25 °C, 2 bar of H<sub>2</sub>, 800 rpm, during 15 h.

![](_page_21_Figure_0.jpeg)

**Figure S27**. Selected region of the <sup>1</sup>H-NMR spectrum (500 MHz, THF-*d*<sub>8</sub>, 298 K). <u>Reaction</u> <u>conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of THF-*d*<sub>8</sub>, 5 mg of Pd@IMesPrSO<sub>3</sub>, at 25 °C, 5 bar of H<sub>2</sub>, 800 rpm, during 15 h.

![](_page_21_Figure_2.jpeg)

**Figure S28**. Selected regions of the  ${}^{13}C{}^{1}H$ -NMR spectrum (125 MHz, THF- $d_8$ , 298 K). <u>Reaction conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL THF- $d_8$ , 5 mg of Pd@IMesPrSO<sub>3</sub>, at 25 °C, 5 bar of H<sub>2</sub>, 800 rpm, during 15 h.

![](_page_22_Figure_0.jpeg)

**Figure S29**. <sup>1</sup>H-NMR spectrum of reaction mixture (500 MHz, D<sub>2</sub>O, 298 K). IS denotes the signal of the Internal Standard (TMAB). <u>Reaction conditions:</u> 63.1 mg (0.5 mmol) of 2,5-BHMF, 5 mL of water, 5 mg of RuIr<sub>2</sub>@IMesPrSO<sub>3</sub>, 5 mg of AgBF<sub>4</sub>, at 140 °C, 5 bar of Ar, 800 rpm, during 0.5 h.

![](_page_22_Figure_2.jpeg)

**Figure S30.** Selected region of the <sup>1</sup>H-<sup>1</sup>H COSY spectrum (D<sub>2</sub>O, 298 K). <u>Reaction</u> <u>conditions:</u> 63.1 mg (0.5 mmol) of 2,5-BHMF, 5 mL of water, 5 mg of RuIr<sub>2</sub>@IMesPrSO<sub>3</sub>, 5 mg of AgBF<sub>4</sub>, at 140 °C, 5 bar of Ar, 800 rpm, during 0.5 h.

![](_page_23_Figure_0.jpeg)

**Figure S31**. Selected region of the <sup>1</sup>H-NMR spectrum of reaction mixture (500 MHz, D<sub>2</sub>O, 298 K). IS denotes the signal of the Internal Standard (TMAB), the asterisks denote the signals for non-identified minor products and the square denotes solvent impurities signals (Isopropanol: 1.07 and 3.92 ppm). <u>Reaction conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of water, 5 mg of RuIr<sub>2</sub>@IMesPrSO<sub>3</sub>, at 140 °C, 5 bar of H<sub>2</sub>, 800 rpm, during 8 h.

![](_page_23_Figure_2.jpeg)

**Figure S32**. Selected region of the <sup>1</sup>H-<sup>1</sup>H COSY spectrum (D<sub>2</sub>O, 298 K) for aliphatic signals region. <u>Reaction conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of water, 5 mg of RuIr<sub>2</sub>@IMesPrSO<sub>3</sub>, at 140 °C, 5 bar of H<sub>2</sub>, 800 rpm, during 8 h.

![](_page_24_Figure_0.jpeg)

**Figure S33**. Selected regions of the overlay of <sup>1</sup>H-<sup>13</sup>C HSQC (red) and <sup>1</sup>H-<sup>13</sup>C-HMBC (blue) spectra (D<sub>2</sub>O, 298 K). <u>Reaction conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of water, 5 mg of RuIr<sub>2</sub>@IMesPrSO<sub>3</sub>, at 140 °C, 5 bar of H<sub>2</sub>, 800 rpm, during 8 h.

![](_page_24_Figure_2.jpeg)

**Figure S34**. Selected region of the <sup>1</sup>H-NMR spectrum of reaction mixture (500 MHz, D<sub>2</sub>O, 298 K). IS denotes the signal of the Internal Standard (TMAB). <u>Reaction conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mg of AgBF<sub>4</sub>, 5 mL of water, 5 mg of RuIr<sub>2</sub>@IMesPrSO<sub>3</sub>, at 140 °C, 5 bar of H<sub>2</sub>, 800 rpm, during 8 h.

#### 3.3 Formulas used in our catalytic studies

We must specify all the molecules corresponding to the different products identified throughout this study in the liquid phase of the reaction mixture have the same number of C atoms.

- HMF conversion (*X*):

$$X_{HMF}^{t}(\%) = \frac{n_{HMF}^{0} - n_{HMF}^{t}}{n_{HMF}^{0}} \cdot 100 \qquad (Equation S1)$$

Where  $n_{HMF}^0$  corresponds to the initial moles of HMF and  $n_{HMF}^t$  corresponds to the remaining moles of HMF at a specific time (t).

- Yield of each product (*Y*):

$$Y_i^t(\%) = \frac{n_i^t}{n_{\text{HMF}}^0} \cdot 100 \qquad (\text{Equation S2})$$

Where  $n_i^t$  corresponds to the number of moles of each product at a specific time (t).

- Total carbon balance (CB):

$$CB^{t}(\%) = \frac{\sum n_{\text{product}_{i}}^{t} \cdot 6 \text{ C atoms}}{n_{\text{HMF}}^{0} \cdot 6 \text{ C atoms}} \cdot 100$$
 (Equation S3)

Where  $\sum n_{product_i}^t$  corresponds to the summatory of moles of all the products.

- Turnover frequency (TOF):

$$TOF = \frac{n_{HMF}^0 - n_{HMF}^t}{n_M^0 \times t}$$
(Equation S4)

Where  $n_M^0$  corresponds to the total amount of moles of metal.

- Specific productivity:

Specific Productivity = 
$$\frac{n_{2,5-BHMF}^{t}}{\text{catalyst mass} \times t}$$
 (Equation S5)

# 4. Reaction conditions optimization and kinetic studies

### 4.1 5-HMF purity

Table S2. Purity<sup>a</sup> of commercial 5-HMF used in this study.

5-HMF batch	DMSO (%)	HMF(%)
1 <sup>st</sup> batch	0.8	99.2
2 <sup>nd</sup> batch	0.3	99.7

<sup>a</sup> Determined by <sup>1</sup>H NMR (considering only 5-HMF and DMSO in the quantification).

#### 4.2 Kinetic studies

![](_page_26_Figure_6.jpeg)

**Figure S35.** Sampling test monitoring product distribution in the hydrogenation of 5-HMF using Ru@IMesPrSO<sub>3</sub> NPs as a catalyst. <u>Reaction conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of water, 5 mg of catalyst, at 30 °C, 5 bar of H<sub>2</sub>, and 800 rpm. Notes: (i) Dashed lines are only visual guidelines.

![](_page_27_Figure_0.jpeg)

**Figure S36.** Temporal evolution of product distribution in the hydrogenation of 5-HMF using Ru@IMesPrSO<sub>3</sub> NPs as a catalyst at a) 70 °C (CB: 84%), b) 100 °C (CB: 75%), and c) 120 °C (CB: 74%). <u>Reaction conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of water, 5 mg of catalyst, 5 bar of H<sub>2</sub>, and 800 rpm. Notes: (i) Dashed lines are only visual guidelines.

![](_page_27_Figure_2.jpeg)

**Figure S37.** TOF estimation from initial reaction rate of 5-HMF using Ru@IMesPrSO<sub>3</sub> NPs as a catalyst. <u>Reaction conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of water, 5 mg of catalyst, at 30 °C, 5 bar of H<sub>2</sub>, and 800 rpm.

![](_page_28_Figure_0.jpeg)

**Figure S38.** a), b), c) Estimation of initial reaction rates based on 2,5-BHMF production using Ru@IMesPrSO<sub>3</sub> NPs as a catalyst, and d) initial reaction rates against initial 5-HMF concentration for the apparent kinetic constant and 5-HMF hydrogenation order estimation. <u>Reaction conditions</u>: a) 0.05 M, b) 0.06 M, c) 0.1 M of 5-HMF, 5 mL of water, 3 mol. % of catalyst, at 30 °C, 5 bar of H<sub>2</sub>, and 800 rpm.

![](_page_29_Figure_0.jpeg)

**Figure S39.** Temporal evolution of product distribution in the hydrogenation of 5-HMF using Pd@IMesPrSO<sub>3</sub> NPs as a catalyst at) 25 °C (CB: 90%), b) 70 °C (CB: 98%), c) 100 °C (CB: 97%, traces of HHD), and d) 120 °C (CB: 83%). <u>Reaction conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of water, 5 mg of catalyst, 5 bar of H<sub>2</sub>, 800 rpm. Notes: (i) Dashed lines are only visual guidelines.

![](_page_30_Figure_0.jpeg)

**Figure S40.** Temporal evolution of product distribution in the hydrogenation of 5-HMF using Ir@IMesPrSO<sub>3</sub> NPs as a catalyst at a) 80 °C (CB: 81%, traces of 4-HHCPEN and 2,5-HD), b) 120 °C (CB: 75%, traces of 2,5-HD), and c) 160 °C (CB: 69%, traces of 2,5-HD). <u>Reaction conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of water, 5 mg of catalyst, 5 bar of H<sub>2</sub>, and 800 rpm. Notes: (i) Dashed lines are only visual guidelines.

![](_page_30_Figure_2.jpeg)

Scheme S2. Piancatelli rearrangement mechanism for the oxidized cyclopentenone production starting with 2,5-BHMF.

The Piancatelli rearrangement (Scheme S2) was first proposed by G. Piancatelli et al.<sup>1</sup> to proceed through the protonation-dehydration sequence of the 2-furylcarbinol to yield furanoxonium intermediates, then the nucleophilic attack of a water molecule, resulting in a ring opening to generate the pentadienyl cation. The resulting cation provides the hydroxy-substituted-cyclopentenone through a  $4\pi$ -conrotatory cyclization (Scheme SX). This mechanism was later supported by De Lera and co-workers with theoretical calculations.<sup>2</sup>

![](_page_31_Figure_1.jpeg)

**Figure S41.** Temporal evolution of product distribution in the hydrogenation of 5-HMF using RuIr<sub>2</sub>@IMesPrSO<sub>3</sub> NPs as a catalyst at a) 100 °C (CB: 65%, traces of 2,5-HD), b) 120 °C (CB: 72%, traces of 2,5-HD), and c) 140 °C (CB: 65%). <u>Reaction conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of water, 5 mg of catalyst, 5 bar of H<sub>2</sub>, and 800 rpm. Notes: (i) Dashed lines are only visual guidelines.

## 4.3 Literature comparison.

Table S3. Benchmarking of Ru@IMesPrSO<sub>3</sub> NPs in the 2,5-BHMF production under aqueous mild conditions.

Catalyst	[HMF] / mM	Temperature / °C	Pressure / bar	Time / h	Maximum Yield to 2,5- BHMF / %	<sup>a</sup> TOF / h <sup>-1</sup>	Specific productivity / mmol <sub>BHMF</sub> g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	Reference
Ru/C	40	55	6.9	1.0	43	493	34.4ª	Ref <sup>3</sup>
Ru/MSN	79	25	5.0	4.0	90	21	4.0	Ref <sup>4</sup>
Pt/MCM-41	1982	35	8.0	2.0	99	nd	19.6	Ref <sup>5</sup>
Ir-ReO <sub>x</sub> /SiO <sub>2</sub>	1000	30	8.0	6.0	99	nd	9.9	Ref <sup>6</sup>
Ni <sub>2</sub> P/HT	100	100	1.0	6.0	88	nd	0.4	Ref <sup>7</sup>
FeNi <sub>3</sub> -Lys	200	80 <sup>b</sup>	3.0	15.0	90	<1	2.4	Ref <sup>8</sup>
Pt@rGO/Sn <sub>0.8</sub>	15	25	5.0	5.0	97	nd	0.3	Ref <sup>9</sup>
				0.7	45			
Ru@IMesPrSO <sub>3</sub>	100	30	5.0	2.5	85	61	34.0°	This work
				16.0	89			

<sup>a</sup> Calculated at  $X_{\text{HMF}} < 35$  %. <sup>b</sup> Induction heating (temperature registered at the reactor wall with infrared camera). <sup>c</sup> Calculated at 2.5 h

Catalyst	[HMF] / mM	Temperature / °C	Pressure / bar	Time / h	Maximum Yield to 2,5- BHMTHF / %	Specific productivity / mmol <sub>BHMTHF</sub> g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>	Reference
Pd@MOF-303	100	60	10	6.0	95.8	8.0	Ref <sup>10</sup>
Pd/MIL-101(Al)-NH <sub>2</sub>	125	30	10	12.0	96	4.0	Ref <sup>11</sup>
Pd/mpg-C <sub>3</sub> N <sub>4</sub>	167	60	10	4.0	96	4.0	Ref <sup>12</sup>
RuPd/RGO	245	20	10	8.0	92.9	4.6	Ref <sup>13</sup>
Pd/CS-S	100	25	10	3	92.8	15.5	Ref <sup>14</sup>
Pd@IMesPrSO <sub>3</sub>	100	40	5.0	15	60	4.0	This work

 Table S4. Benchmarking of Pd@IMesPrSO3 NPs in the 2,5-BHMTHF production under aqueous mild conditions.

# 5. Post-catalysis characterization

#### 5.1 Compositional analyses of the different reaction mixtures after catalysis.

Table S5. Metal content loss after catalysis for the different water-soluble NPs (by ICP-OES).

NPs	Temperature, time	Metal content loss (%)
Ru@IMesPrSO3	30 °C, 15 h	0.33
Pd@IMesPrSO <sub>3</sub>	40 °C, 15 h	$0.00^{*}$
Ir@IMesPrSO <sub>3</sub>	140 °C, 5 h	0.05
RuIr <sub>2</sub> @IMesPrSO <sub>3</sub>	140 °C, 8 h	0.04 Ru; 0.09 Ir

<sup>\*</sup> Pd detection limit is 0.037 ppm. <u>Reaction conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of water, 5 mg of catalyst, 5 bar of  $H_2$ , 800 rpm.

Table S6. Organic content in	Ru@IMesPrSO <sub>3</sub> NPs before and	after catalysi	s (by TGA).
0	-	2	

NDa	Organic wt. (%)			
INFS	Before catalysis	After catalysis		
Ru@IMesPrSO3	33.6	74.3		

<u>Reaction conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of water, 5 mg of catalyst, 5 bar of  $H_2$ , 120 °C, 800 rpm, for 15 h.

### 5.2 BF-TEM images post-catalysis.

![](_page_34_Figure_9.jpeg)

**Figure S42.** BF-TEM micrographs corresponding to a) fresh and b) spent catalyst for Ru@IMesPrSO<sub>3</sub> NPs. <u>Reaction conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of water, 5 mg of catalyst, at 30 °C, 5 bar of H<sub>2</sub>, 800 rpm, for 30 h.

![](_page_35_Figure_0.jpeg)

**Figure S43.** BF-TEM micrographs corresponding to a) fresh and b) spent catalyst for Pd@IMesPrSO<sub>3</sub> NPs. <u>Reaction conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of water, 5 mg of catalyst, at 40 °C, 5 bar of H<sub>2</sub>, 800 rpm, for 15 h.

![](_page_35_Figure_2.jpeg)

**Figure S44.** BF-TEM micrographs corresponding to a) fresh and b) spent catalyst for Ir@IMesPrSO<sub>3</sub> NPs. <u>Reaction conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of water, 5 mg of catalyst, at 140 °C, 5 bar of H<sub>2</sub>, 800 rpm, for 4 h.

![](_page_35_Figure_4.jpeg)

**Figure S45.** BF-TEM micrographs corresponding to a) fresh and b) spent catalyst for RuIr<sub>2</sub>@IMesPrSO<sub>3</sub> NPs. <u>Reaction conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of water, 5 mg of catalyst, at 140 °C, 5 bar of H<sub>2</sub>, 800 rpm, for 8 h.

![](_page_36_Figure_0.jpeg)

**Figure S46.** a) Pd@IMesPrSO<sub>3</sub> NPs size distribution and BF-TEM micrographs for the catalytic reactions at b) 25 (15 h) c) 40 °C (15 h), and d) 100 °C (30 h). <u>Reaction conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of water, 5 mg of catalyst, 5 bar of H<sub>2</sub>, 800 rpm.

![](_page_36_Figure_2.jpeg)

**Figure S47.** BF-TEM micrographs corresponding to a) fresh and b) spent catalyst and their corresponding c) size distribution for Ru@IMesPrSO<sub>3</sub> NPs, and d) fresh and e) spent catalyst and their corresponding f) size distribution for Pd@IMesPrSO<sub>3</sub>. <u>Reaction conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of water, 5 mg of catalyst, 5 bar of H<sub>2</sub>, 800 rpm.

#### 5.3 DLS measurements post-catalysis.

![](_page_37_Figure_1.jpeg)

**Figure S48.** DLS measurements in water before and after catalysis for a) Ru@IMesPrSO<sub>3</sub> (30°C, 15 h), b) Pd@IMesPrSO<sub>3</sub> (40 °C, 15 h), c) Ir@IMesPrSO<sub>3</sub> (140 °C, 4 h), and d) RuIr<sub>2</sub>@IMesPrSO<sub>3</sub> (140 °C, 8 h) NPs. <u>Reaction conditions:</u> 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of water, 5 mg of catalyst, 5 bar of H<sub>2</sub>, 800 rpm.

#### 5.4 pH measurements

Entry	Mixture	рН
1	$5-HMF + H_2O$	6.64
2	$Ru@IMesPrSO_3 + 5-HMF + H_2O$	4.38
3	$RuIr_2@IMesPrSO_3 + AgBF_4 + 5-HMF + H_2O$	1.43
4	$RuIr_2@IMesPrSO_3 + AgBF_4 + 5-HMF + H_2O$	1.99ª

Table S7. pH measurements for different aqueous HMF and NPs mixtures.

<sup>a</sup> pH measurement after catalysis. <u>Reaction conditions</u>: 63.1 mg (0.5 mmol) of 5-HMF, 5 mL of water, 5 mg of catalyst, 5 mg AgBF<sub>4</sub>, at 140 °C, 5 bar of H<sub>2</sub>, 800 rpm, during 8 h.

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