**SUPPORTING INFORMATION**

**Highly Selective and Efficient Solvent-free Transformation of Bio-derived Levulinic acid to γ-Valerolactone by Ruthenium Arene Catalyst Precursors**

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**Table S1:** Hydrogenation of neat LA using formic acid without base.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Entry** | **Cat.c** | **Base** | **LA Conversion (%)a** | **GVL Selectivity (%)a** | **4-HVA Selectivity (%)a** |
| 1 | **1** | - | 9 | 100 | 0 |
| 2 | **2** | - | 12 | 100 | 0 |
| 3 | **3** | - | 21 | 100 | 0 |
| 4 | **4** | - | 1 | 100 | 0 |
| 5b | **-** | NEt3 | 10 | 100 | 0 |

Conditions: LA (20 mmol), formic acid (20 mmol), catalyst (0.02 mmol), 12 h, 150 °C.22 **[a]** Conversion and Selectivity determined by NMR. **[b]** No catalyst. **[c]** Cat. = catalyst precursor; Average error estimates: ±0.45 (**1**), ±0.53 (**2**), ±0.51 (**3**), ±0.49 (**4**), ±0.56.

**Table S2:** Aqueous hydrogenation of LA using formic acid.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Entry** | **Cat.k** | **LA Conversion (%)j** | **GVL Selectivity (%)j** | **4-HVA Selectivity (%)j** |
| 1g | **1** | 12 | 100 | 0 |
| 2g | **2** | 19 | 100 | 0 |
| 3e | **3** | 24 | 100 | 0 |
| 4g | **4** | 11 | 100 | 0 |
| 1h | **1** | 8 | 100 | 0 |
| 2h | **2** | 10 | 100 | 0 |
| 3h | **3** | 8 | 100 | 0 |
| 4h | **4** | 8 | 100 | 0 |
| 5i | **1** | 20 | 100 | 0 |
| 6i | **2** | 17 | 100 | 0 |
| 7i | **3** | 88 | 100 | 0 |
| 8i | **4** | 26 | 100 | 0 |

Conditions: LA (20 mmol), formic acid (20 mmol), catalyst (0.02 mmol), 2 mmol Et3N, 50 wt% H2O, 16 h. **[g]** 125 °C. **[h]** 175 °C. **[i]** Solvent-free, 125 °C. **[j]** Conversion and Selectivity determined by NMR. **[k]** Cat. = catalyst precursor; Average error estimates: ±0.77 (**1**), ±0.98 (**2**), ±0.93 (**3**), ±0.87 (**4**).



**Figure S1**: 1H NMR spectrum of a crude mixture obtained from the hydrogenation of LA in a J Young tube.



**Figure S2**: 1H NMR spectrum of mixture obtained from reaction of **1**, FA and base in a J Young tube showing the liberation of hydrogen gas.

MS\_Direct\_160908\_53 23 (0.114) Cm (23:26) 1: TOF MS ES+ 497.0570

[M]+

**Figure S3:** HR-MS (ESI+) of **1**.

**Figure S4:** HR-MS (ESI+) of **2**.

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**Figure S5:** HR-MS (ESI+) of **3**.

**Figure S6:** HR-MS (ESI+) of **4**.