# *Electronic supplementary information (ESI) for* Efficient Hydrogenation of Levulinic Acid Catalysed by Spherical NHC-Ir Assemblies with Atmospheric Pressure of Hydrogen

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### 1. General

All commercial reagents were used directly without further purification, unless otherwise stated. Hydrogen gas (99.99%) was purchased from Dumaoai. Deuterated solvents were purchased from Cambridge Isotope Laboratories. <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectra were recorded on Jeol ECA-400 and Bruker 400 DRX spectrometers. The chemical shifts ( $\delta$ ) for <sup>1</sup>H NMR are given in parts per million (ppm) referenced to the residual proton signal of the deuterated solvent (CHCl<sub>3</sub> at  $\delta$  7.26 ppm, DMSO at  $\delta$  2.50 ppm); coupling constants are expressed in hertz (Hz). <sup>13</sup>C NMR spectra were referenced to the carbon signal of CDCl<sub>3</sub> (77.0 ppm) or DMSO (39.4 ppm). The following abbreviations are used to describe NMR signals: s = singlet, d = doublet, t =triplet, m = mulitplet, dd = doublet of doublets, q = quartet. ESI-MS spectra were recorded on a Bruker microTOF II instrument. IR spectra were recorded on AVATAR FT-IR 360 instrument. Powder XRD studies were performed on a Bruker AXS D8. SEM experiments were carried out on a Nova NanoSem 450 microscope operated at 20 kV. TEM experiments were carried out on a JEOL JEM-2010 transmission electron microscope. Dynamic Light Scattering (DLS) experiments were carried out on a ALV/CGS-3, Germany. Solid-state <sup>13</sup>C NMR experiments were carried out on a 400WB AVANCE III. The X-ray photoemission spectroscopy (XPS) was performed in a PHI 5000C ESCA system. Nitrogen and hydrogen soption experiments were performed on a Quantachrome AUTOSORB-IQ. The H<sub>2</sub>-TPD was performed in a TP-500.

### 2. Syntheses of catalysts

### 2.1 Syntheses of tetraimidazolium salts



**Scheme S1** General synthetic procedure of tetraimidazolium salts and complex **5**. Note: tetraimidazolium halides were synthesized according to the literature reports.<sup>S1,S2</sup>

A Schlenk tube was charged with tetraimidazolium halides (1 mmol), triethyloxonium tetrafluoroborate (1.9 g, 8 mmol), dry CH<sub>3</sub>I (20 mL), dry MeOH (10 mL) and sealed with a Teflon-lined cap. The resulting reaction mixture was stirred for 12 hours and then poured into excess diethyl ether (50 mL). After precipitation completed, the solids were collected via filtration and dried under reduced pressure to afford the desired salts.

Salt **L2**: white solid, 88% yield. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ , 298 K)  $\delta$  = 9.67 (s, 4H), 8.25 (s, 4H), 7.95 (s, 4H), 7.76 (d, J = 8.8 Hz, 8H), 7.61 (d, J = 8.8 Hz, 8H), 3.94 (s, 12H). <sup>19</sup>F NMR (376 MHz, DMSO- $d_6$ , 298 K):  $\delta$  = -148.32. <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ , 298 K):  $\delta$  = 147.21, 136.28, 133.46, 132.13, 125.01, 122.23, 121.33, 64.45, 36.65. HRMS [M-2(BF<sub>4</sub>)]<sup>2+</sup> m/z, calcd. for C<sub>41</sub>H<sub>40</sub>N<sub>8</sub>(BF<sub>4</sub>)<sub>2</sub>: 409.1717; found: 409.1718.

NHC-Ir complex **5** was synthesized according to previously reported procedures.<sup>53,54</sup> <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  7.58 (dd, J = 5.1, 1.8 Hz, 6H), 7.37 (d, J = 2.0 Hz, 2H), 7.30 – 7.23 (m, 6H), 4.54 (s, 2H), 3.45-3.51 (m, 2H), 2.97 (s, 6H), 2.23-2.33 (m, 2H), 2.09-2.15 (m, 2H), 1.96-2.04 (m, 2H), 1.54 – 1.62 (m, 2H).

### 2.2 Syntheses of solid NHC-Ir catalysts



**Scheme S2** General synthetic procedure of solid NHC-Ir assemblies **3a-c** ([Ir] is [Ir(acac)(CO)<sub>2</sub>] or [Ir(COD)CI]<sub>2</sub>).

A Schlenk tube was charged with tetraimidazolium salts (0.5 mmol) and the iridium precursor ([Ir(acac)(CO)<sub>2</sub>] or [Ir(COD)CI]<sub>2</sub>) (1 mmol), the mixture were dissolved in DMF (5 mL) under N<sub>2</sub> at room temperature, LiHMDS (2 mmol) solution in THF was added in dropwise. The resulting mixture was stirred at 80 °C for 12 h. The solids were isolated after filtration and washed with DMF, 1,4-dioxane, MeOH, deionized water for three times respective. The Soxhlet extraction was used after the filtration of the 3D catalysts in order to remove the metal precursors and solvent. The solids were then dried over under vacuum.

NHC-Ir assembly **3a:** yellow solid, 85% yield; IR (KBr pellet) *v* 617.24, 682.62, 823.55, 1246.19, 1363.81, 1476.16, 1507.57, 1559.45, 1617.61, 1636.60, 1653.83, 3421.67 cm<sup>-1</sup>; Elemental analysis (%) *Calcd. for* (C<sub>57</sub>H<sub>60</sub>I<sub>2</sub>Ir<sub>2</sub>N<sub>8</sub>)<sub>n</sub>: C, 45.78; H, 4.04; N, 7.49; *found:* C, 45.57; H, 4.41; N, 7.52.

NHC-Ir assembly **3b**: orange solid, 84% yield; IR (KBr pellet) v 1363.72, 1477.25, 1507.74, 1544.43, 1559.43, 1636.66, 1647.43, 1653.87, 1684.71, 2023.41, 3447.30 cm<sup>-1</sup>; Elemental analysis (%) *Calcd. for* (C<sub>45</sub>H<sub>36</sub>I<sub>2</sub>Ir<sub>2</sub>N<sub>8</sub>O<sub>2</sub>·2H<sub>2</sub>O)<sub>n</sub>: C, 37.67; H, 2.94; N, 8.17; *found:* C, 37.58; H, 2.53; N, 8.14.

NHC-Ir assembly **3c:** brown solid, 80% yield; IR (KBr pellet) *v* 521.29, 533.30, 680.42, 1034.08, 1083.63, 1246.58, 1363.77, 1406.53, 1474.86, 1506.86, 1559.33, 1624.03, 3404.43 cm<sup>-1</sup>; Elemental analysis (%) *Calcd. for* (C<sub>57</sub>H<sub>60</sub>B<sub>2</sub>F<sub>8</sub>Ir<sub>2</sub>N<sub>8</sub>·3C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>)<sub>n</sub>: C, 49.29; H, 5.16; N, 6.66; *found*: C, 49.31; H, 4.88; N, 6.23.

# 3. Catalytic hydrogenation of LA and derivatives

# **3.1 Optimization of reaction conditions**

		Соон н	<b>Cat.</b> , H (OH, <i>i</i> -Pr	2 <b>&gt;</b> -				
LA GVL								
Entry	[Cat.]	Base (equiv.)	Solvent	Р <sub>н2</sub> (atm)	Time (h)	Yield (%)		
1 <sup><i>b</i></sup>	За	KOH (1.1)	<i>i</i> -PrOH	30	4	95		
<b>2</b> <sup>b</sup>	3b	KOH (1.1)	<i>i</i> -PrOH	30	4	83		
3 <sup><i>b</i></sup>	3c	KOH (1.1)	<i>i</i> -PrOH	30	4	78		
<b>4</b> <sup>b</sup>	За	KOH (1.1)	<i>i</i> -PrOH	1	24	78		
5	За	KOH (1.1)	<i>i</i> -PrOH	1	24	>99		
6	За	KOH (2)	<i>i</i> -PrOH	1	24	89		
7	За	KOH (1.0)	<i>i</i> -PrOH	1	24	54		
8	За	KOH (0.5)	<i>i</i> -PrOH	1	24	25		
9	За	КОН (0)	<i>i</i> -PrOH	1	24	7		
10	За	KOH (1.1)	t-BuOH	1	24	8		
11	За	KOH (1.1)	MeOH	1	24	17		
12	3a	KOH (1.1)	H <sub>2</sub> O	1	24	40		
13	За	KOH (1.1)	Neat	1	24	32		
14 <sup>c</sup>	За	KOH (1.1)	$H_2O$	1	48	80		
15	3a	NaOH (1.1)	<i>i</i> -PrOH	1	24	84		
16	3a	K <sub>2</sub> CO <sub>3</sub> (1.1)	<i>i</i> -PrOH	1	24	41		
17	3a	Na <sub>2</sub> CO <sub>3</sub> (1.1)	<i>i</i> -PrOH	1	24	38		
18 <sup>d</sup>	3a	KOH (1.1)	<i>i</i> -PrOH	50	72	81		
19 <i>°</i>	3a	KOH (1.1)	<i>i</i> -PrOH	1	72	60		
20	3a	KOH (1.1)	<i>i</i> -PrOH	1	0.5	37		
<b>21</b> <sup><i>f</i></sup>	3a	KOH (0.1)	<i>i</i> -PrOH	1	24	92		

Table S1 Optimization of reaction conditions <sup>a</sup>

<sup>a</sup> Reactions were carried out with LA (15 mmol), catalyst (0.02 mol%), KOH (1.1 equiv.),

H<sub>2</sub> (1 atm) in *i*-PrOH (5 mL) at 100 °C for 24 h, the yield was determined by <sup>1</sup>H NMR with mesitylene as an internal standard. <sup>*b*</sup> With 0.01 mol% catalyst. <sup>*c*</sup> With 0.12 mol% catalyst.<sup>*d*</sup> With 0.0004 mol% catalyst. <sup>*e*</sup> With 0.00125 mol% catalyst. <sup>*f*</sup> 1 equiv. potassium levulinate as reagent.

### **3.2 Literature overview**

Catalyst	P <sub>H2</sub> (atm)	TON	TOF	Ref.	
			(h⁻¹)		
3D NHC-Ir coordination	50	2.4.405			
assamblies <b>3a</b>	50	2.1×10 <sup>3</sup>	-	I NIS WORK	
3D NHC–Ir coordination	1	48000	3630	This work	
assamblies <b>3a</b>					
Ni(OAc), 4H <sub>2</sub> O/Triphos	30	10000	-	S5	
		2100	2100	S.C.	
	-	2100	2100	50	
PNP-pincer iron complex	50	23000	1917	S7	
1D NHC-Ir coordination	50	1 2.105		60	
assamblies	50	1.2×10°	-	20	
Ru/TiO2-n	30	-	41.5	<b>S</b> 9	
POMPs	30	1.01×10 <sup>6</sup>	-	S10	
IrH <sub>3</sub> /PNP	100	71000	1479	S11	
Ir complex	10	78000	2167	S12	
Co(BF <sub>4</sub> ) <sub>2</sub> /PP3	1	62 <sup>b</sup>	-	S13	
	Catalyst 3D NHC–Ir coordination assamblies <b>3a</b> 3D NHC–Ir coordination assamblies <b>3a</b> Ni(OAc) <sub>2</sub> . 4H <sub>2</sub> O/Triphos [(dtbpe)PdCl <sub>2</sub> ] PNP-pincer iron complex [(dtbpe)PdCl <sub>2</sub> ] [(dtbpe)PdCl <sub>2</sub> ] [(	Catalyst $P_{H2}$ (atm)3D NHC-Ir coordination assamblies <b>3a</b> $50$ 3D NHC-Ir coordination1assamblies <b>3a</b> 1assamblies <b>3a</b> $30$ Ni(OAc)_2 · 4H_2O/Triphos $30$ [(dtbpe)PdCl_2]-PNP-pincer iron complex $50$ 1D NHC-Ir coordination $50$ 1D NHC-Ir coordination $50$ assamblies $30$ ID NHC-Ir coordination $10$ IrH_3/PNP $100$ Ir complex $10$ Ir complex $10$ Co(BF_4)_2/PP3 $1$	Catalyst $P_{H2}$ (atm)       TON         3D NHC-Ir coordination $30$ $2.1 \times 10^5$ assamblies <b>3a</b> $50$ $2.1 \times 10^5$ 3D NHC-Ir coordination       1 $48000$ assamblies <b>3a</b> 1 $48000$ assamblies <b>3a</b> 1 $48000$ assamblies <b>3a</b> 1 $48000$ assamblies <b>3a</b> 1 $48000$ I(OAc)_2 · 4H_2O/Triphos $30$ $10000$ [(dtbpe)PdCl_2]       - $2100$ PNP-pincer iron complex $50$ $23000$ 1D NHC-Ir coordination $50$ $23000$ 1D NHC-Ir coordination $50$ $1.2 \times 10^5$ assamblies $70$ $-1$ Ru/TiO2-n $30$ $-1.01 \times 10^6$ Ir H_3/PNP $100$ $71000$ Ir complex $10$ $78000$ Ir complex $10$ $78000$ Co(BF_4)_2/PP3 $1$ $62^b$	Catalyst $P_{H2}$ (atm)         TON         TOF (h <sup>-1</sup> )           3D NHC-Ir coordination assamblies <b>3a</b> 50 $2.1 \times 10^5$ -           3D NHC-Ir coordination         1         48000         3630           3D NHC-Ir coordination         1         48000         3630           assamblies <b>3a</b> 1         48000         -           3D NHC-Ir coordination         1         48000         -           assamblies <b>3a</b> -         -         -           Ni(OAc) <sub>2</sub> . 4H <sub>2</sub> O/Triphos         30         10000         -           [(dtbpe)PdCl <sub>2</sub> ]         -         2100         2100           PNP-pincer iron complex         50         23000         1917           1D NHC-Ir coordination assamblies         50         1.2×10 <sup>5</sup> -           Ru/TiO2-n         30         -         41.5           POMPs         30         1.01×10 <sup>6</sup> -           Ir H <sub>3</sub> /PNP         100         71000         1479           Ir complex         10         78000         2167           Co(BF <sub>4</sub> ) <sub>2</sub> /PP3         1         62 <sup>b</sup> -	

### Table S2 The TON and TOF values for the conversion of LA into GVL<sup>a</sup>

<sup>*a*</sup> quoted from the corresponding references. <sup>*b*</sup> Calculated by Yield/catalyst amount.

### 3.3 Catalytic procedure of hydrogenation of LA to GVL with NHC-Ir

### assemblies

A Schlenk tube equipped with a magnetic stirring bar and a hydrogen balloon was

charged with LA (15 mmol), solid NHC-Ir assemblies (0.02 mol%), KOH (16 mmol) and isopropanol (5 mL). The reaction mixture was stirred under hydrogen at 100 °C for 24 h. The Schlenk tube was then cooled to room temperature and the pressure was released. After pH regulation with HCl and additional 1 h stirring at room temperature, mesitylene (3 mmol) was added to the reaction mixture as an internal standard for <sup>1</sup>H NMR analysis to determine the yield.

### 3.4 Operation procedure for the recovery of solid 3a

A Schlenk tube equipped with a magnetic stirring bar and a hydrogen balloon was charged with LA (15 mmol), solid **3a** (0.06 mol%), KOH (16 mmol) and isopropanol (5 mL). After the hydrogenation by the aforementioned general operation procedure, the solids were readily recovered after centrifugation and decantation. The recovered solids **3a** were washed with isopropanol (5 mL × 3), the recovered solids were reused directly in the next run without additional activation steps, simply recharging LA, KOH and *i*-PrOH in the Schlenk tube.

### **3.5 Mechanistic studies**



A Schlenk tube equipped with a magnetic stirring bar and a hydrogen balloon was charged with LA (15 mmol), solid **3a** (0.02 mol%), KOH (16 mmol) and isopropanol (5 mL). The reaction mixture was stirred under nitrogen at 100 °C for 24 h. The Schlenk tube was then cooled to room temperature and the pressure was released. After pH regulation with HCl and additional 1 h stirring at room temperature, mesitylene (3 mmol) was added to the reaction mixture as an internal standard for <sup>1</sup>H NMR analysis to determine the yield.



A Schlenk tube equipped with a magnetic stirring bar and a hydrogen balloon was

charged with LA (15 mmol), solid **3a** (0.02 mol%), KOH (16 mmol) and different solvents (5 mL). The reaction mixture was stirred under nitrogen at 100 °C for 24 h. The Schlenk tube was then cooled to room temperature and the pressure was released. After pH regulation with HCl and additional 1 h stirring at room temperature, mesitylene (3 mmol) was added to the reaction mixture as an internal standard for <sup>1</sup>H NMR analysis to determine the yield.



A Schlenk tube equipped with a magnetic stirring bar and a hydrogen balloon was charged with  $\alpha$ -angelica lactone (15 mmol), solid **3a** (0.02 mol%), KOH (16 mmol) and isopropanol (5 mL). The reaction mixture was stirred under nitrogen at 100 °C for 24 h. The Schlenk tube was then cooled to room temperature and the pressure was released. After pH regulation with HCl and additional 1 h stirring at room temperature, mesitylene (3 mmol) was added to the reaction mixture as an internal standard for 1H NMR analysis to determine the yield.

$$\begin{array}{c} \overset{O}{\longrightarrow} \\ \overset{H_2, H_2O, KOH}{\longrightarrow} \\ \hline 3a, 48 \text{ h}, 100 \text{ °C} \end{array} \xrightarrow{O} \\ \end{array}$$

A Schlenk tube equipped with a magnetic stirring bar and a hydrogen balloon was charged with LA (15 mmol), solid **3a** (0.12 mol%), KOH (16 mmol) and H<sub>2</sub>O (5 mL). The reaction mixture was stirred under nitrogen at 100 °C for 48 h. The Schlenk tube was then cooled to room temperature and the pressure was released. After pH regulation with HCl and additional 1 h stirring at room temperature, mesitylene (3 mmol) was added to the reaction mixture as an internal standard for <sup>1</sup>H NMR analysis to determine the yield.

$$\frac{H_2, i-PrOH, KOH}{3a, 24 h, 100 °C} \rightarrow 0 \xrightarrow{0}$$

A Schlenk tube equipped with a magnetic stirring bar and a hydrogen balloon was charged with potassium levulinate (15 mmol), solid **3a** (0.02 mol%), KOH (1 mmol) and

*i*-PrOH (5 mL). The reaction mixture was stirred under nitrogen at 100 °C for 24 h. The Schlenk tube was then cooled to room temperature and the pressure was released. After pH regulation with HCl and additional 1 h stirring at room temperature, mesitylene (3 mmol) was added to the reaction mixture as an internal standard for <sup>1</sup>H NMR analysis to determine the yield.

# 3.6 Catalytic procedure of hydrogenation of LA derivatives with NHC-Ir assemblies



A Schlenk tube equipped with a magnetic stirring bar and a hydrogen balloon was charged with LA derivatives (5 mmol), solid **3a** (0.1 mol%), KOH (10 mmol) and isopropanol (5 mL). The reaction mixture was stirred under hydrogen pressure at 100 °C for 24 h. The Schlenk tube was then cooled to room temperature and the pressure was released. After pH regulation with HCl and additional 1 h stirring at room temperature, mesitylene (3 mmol) was added to the reaction mixture as an internal standard for <sup>1</sup>H NMR analysis to determine the yield.



**2b**,<sup>s8</sup> Yellow oil, 94% yield, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K)  $\delta$  7.41 – 7.27 (m, 5H), 5.55 – 5.43 (m, 1H), 2.73 – 2.58 (m, 3H), 2.17 (s, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$ 176.98 , 139.42 , 131.05, 122.89, 81.27 , 29.98 .



**2c**,<sup>s8</sup> Brown solid, 92% yield, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) δ 7.22 (m, 4H), 5.48 (t, J

= 6.3 Hz, 1H), 2.65 (m, 3H), 2.36 (s, 3H), 2.19 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 177.04, 138.26, 136.32, 129.36, 125.36, 81.35, 30.91, 29.05, 21.12.



**2d**,<sup>s8</sup> Yellow solid, 76% yield, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) δ 7.25 (d, *J* = 6.4 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 5.54 – 5.36 (m, 1H), 3.80 (s, 3H), 2.70 – 2.51 (m, 3H), 2.18 (dd, *J* = 10.7, 9.7 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 176.98, 159.71, 131.11, 126.95, 114.07, 81.35, 55.30, 30.84, 29.20.



**2e**,<sup>58</sup> Yellow oli, 94% yield, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) δ 7.39 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 5.58 – 5.44 (m, 1H), 2.77 – 2.61 (m, 3H), 2.17 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 176.65, 137.89, 134.15, 128.88, 126.74, 80.45, 30.87, 28.87.



**2f**,<sup>58</sup> White solid, 94% yield, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) δ 7.52 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 5.46 (dd, *J* = 8.1, 6.2 Hz, 1H), 2.73 – 2.60 (m, 3H), 2.23 – 2.08 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 176.60, 138.54, 132.02, 127.07, 80.53, 31.01, 28.95.



**2h**,<sup>58</sup> White solid, 81% yield, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) δ 7.85 (dd, *J* = 13.8, 8.7 Hz, 4H), 7.51 (q, *J* = 3.6 Hz, 2H), 7.41 (d, *J* = 6.1 Hz, 1H), 5.68 (t, *J* = 7.1 Hz, 1H), 2.78 –

2.63 (m, 3H), 2.42 – 2.23 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 176.94, 136.66, 133.07, 128.80, 128.01, 127.71, 126.58, 126.42, 124.24, 122.83, 81.27, 30.88, 28.88.



**2j**,<sup>58</sup> White solid, 70% yield, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ = 7.97 (d, *J* = 8.0 Hz, 1H), 7.73 (t, *J* = 8.0 Hz, 1H), 7.56 - 7.52 (m, 2H), 5.35 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K) δ = 170.99, 146.41, 133.90, 128.86, 125.46, 125.46, 122.04, 69.55.



**2k**,<sup>58</sup> Yellow oil, 71% yield, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) δ 7.96 (d, *J* = 7.7 Hz, 1H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.61 – 7.50 (m, 2H), 5.35 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 170.46, 151.19, 134.09, 129.05, 125.56, 121.63, 77.76, 20.38. 4. SEM, TEM & EDS images of solid NHC-Ir assemblies



4.1 SEM images of solid NHC-Ir assemblies

Fig. S1 SEM image of fresh prepared solid **3a** (scale bar: 0.2  $\mu$ m).



Fig. S2 SEM image of the recovered solid **3a** after  $10^{th}$  run (scale bar: 0.2  $\mu$ m).



Fig. S3 SEM image of fresh prepared solid 3b (scale bar: 0.2  $\mu m).$ 



Fig. S4 SEM image of fresh prepared solid 3c (scale bar: 20  $\mu\text{m}).$ 

# 4.2 TEM images of solid NHC-Ir assemblies



Fig. S5 TEM image of fresh prepared solid **3a** (scale bar: 0.2  $\mu$ m).



Fig. S6 TEM image of the recovered solid **3a** after  $10^{th}$  run (scale bar: 0.2  $\mu$ m).

# 4.3 EDS images of solid NHC-Ir assemblies



Fig. S7 EDS image of fresh prepared solid **3a** (scale bar:  $1 \mu m$ ).



Fig. S8 EDS image of the recovered solid **3a** after  $10^{th}$  run (scale bar: 1  $\mu$ m).



Fig. S9 EDS image of fresh prepared solid 3b (scale bar: 1  $\mu m$ ).



Fig. S10 EDS image of fresh prepared solid 3c (scale bar: 1  $\mu\text{m}).$ 



# 4.4 EDX of solid NHC-Ir assemblies

Fig. S11 EDX pattern of new prepared solid NHC-Ir assembly 3a measured with SEM.

# 5. Powder XRD spectra of solid NHC-Ir assemblies



Fig. S12 XRD spectrum of fresh prepared solid 3a.



Fig. S13 XRD spectrum of recovered solid 3a.



Fig. S14 XRD spectrum of fresh prepared solid 3b.



Fig. S15 XRD spectrum of fresh prepared solid 3c.

# 6. XPS spectra of solid NHC-Ir assemblies



Fig. S16 XPS of freshly prepared solid 3a.



Fig. S17 XPS of recovered solid 3a after the 10<sup>th</sup> run.



Fig. S18 XPS of freshly prepared 5.



Fig. S19 XPS of freshly prepared 4b.

### 7. Solid-state <sup>13</sup>C NMR of solid NHC-Ir assemblies



Fig. S20 Solid-state <sup>13</sup>C NMR of NHC-Ir complex 5



Fig. S21 Solid-state <sup>13</sup>C NMR of solid 3a



Fig. S22 Solid-state <sup>13</sup>C NMR of solid 4b





Fig. S23  $N_2$  adsorption/desorption isotherm of 1D solid 4b (black line) and 3D solid 3a

(red line).



Fig. S24 H<sub>2</sub> adsorption and desorption isotherm of solid 3a and 4b at 298 K

# 9. Dynamic light scattering of the solid NHC-Ir assembly 3a



Fig. S25 Dynamic Light Scattering of solid 3a.

### **10. Metal-leaching test with ICP-AES**

[Cat.]	Run	Conc. of Ir (mg/L)
3a	1	0.080
<b>3</b> a	2	0.075
<b>3</b> a	3	0.074
<b>3</b> a	4	0.082
<b>3</b> a	5	0.062
<b>3</b> a	6	0.072
<b>3</b> a	7	0.076
<b>3</b> a	8	0.073
<b>3</b> a	9	0.078
<b>3</b> a	10	0.035

**Table S3** Iridium leaching test with the filtrates of the reaction mixture after consecutive run<sup>*a*</sup>.

<sup>*a*</sup> ICP-AES analysis of the filtrates after each consecutive run. After the reaction was quenched, the catalyst was separated with centrifuging. The pH value of the resulting clear solution was adjusted with HCl to about 3-4 and diluted to 1 L. The corresponding amount of Ir in the original mixture is 1× the concentration measured with ICP-AES (mg).

### 11. Hydrogen temperature programmed desorption of the solid

### catalyst 3a



Fig. S26 Hydrogen temperature programmed desorption of solid catalyst **3a**.

$$D(\%) = \frac{2 \times V_{ad} \times M \times SP}{m \times P \times V_m \times D_r} \times 100^{[S14]}$$

$$P = \frac{2 \times V_{ad} \times M \times SF}{m \times D \times V_m \times D_r} \times 100$$

In the equations,  $V_{ad}$  (mL) represents the volume of chemisorbed H<sub>2</sub> obtained from the TPD result, which was 75.1449 mL. M is 192.22 g mol<sup>-1</sup>, which is the molecular weight of Ir; SF means the stoichiometric factor (the Ir:H molar ratio in the chemisorption) usually supposed as 2 and m (g) means the catalyst mass used for TPD measurement, which is 101.2 mg. P is the mass fraction of Ir in the catalyst and V<sub>m</sub> is the molar volume of H<sub>2</sub> (22.4 L mol<sup>-1</sup>). D<sub>r</sub> is the reduction degree of iridum, which is usually taken as 100%. D is the dispersion of the catalyst which is taken as 100% because it is supposed as "sigle site". As a result, the mass fraction of Ir in the catalyst measured by TDP is 25.5%, which is consistent with the 26.6% measured by ICP.



12. <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR and IR spectra for important compounds

**Fig. S37** <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ , 298 K)spectrum of compound L1.



**Fig. S28** <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ , 298 K)spectrum of compound L2.



**Fig. S29** <sup>19</sup>F NMR (376 MHz, DMSO- *d*<sub>6</sub>, 298 K) spectrum of compound **L2**.



Fig. S30  $^{13}$ C NMR (101 MHz, DMSO- $d_6$ , 298 K) spectrum of compound L2.



**Fig. S31** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) spectrum after a typical catalytic reaction with 0.02% catalyst **3a**.



Fig. S32 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) spectrum of compound 2b.



Fig. S33 <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, 298K) spectrum of compound 2b.



Fig. S34 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) spectrum of compound 2c.







Fig. S36 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) spectrum of compound 2d.





Fig. S37 <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, 298K) spectrum of compound 2d.

Fig. S38 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) spectrum of compound 2e.



40 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1  $\delta(\text{ppm})$ 





Fig. S40 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) spectrum of compound 2f.



Fig. S41 <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, 298K) spectrum of compound 2f.



Fig. S42 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) spectrum of compound 2h.







Fig. S44 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) spectrum of compound 2j.



40 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1 δ(ppm)





Fig. S46 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) spectrum of compound 2k.



Fig. S47 <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, 298K) spectrum of compound 2k.



Fig. S48 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K) spectrum of the ligand of 4'<sup>S15</sup>







Fig. S50 IR spectrum of compound 3a after 6 times of reuse.



Fig. S51 IR spectrum of compound 3b.



Fig. S52 IR spectrum of compound 3c.



13. Recycling of 3a under 30 bar  $H_2$  pressure and 1 atm  $H_2$  pressure

Fig. S53 Recycling and reuse of the solid NHC-Ir catalyst 3a in the hydrogenation of LA to GVL under 30 bar H<sub>2</sub> pressure for 4h.



Fig. S54 Recycling and reuse of the solid NHC-Ir catalyst 3a in the hydrogenation of LA to GVL under 1 atm H<sub>2</sub> pressure for 24h.

### 14. The reaction profile of LA to GVL

A several reactions were preformed under the standard condition and stopped in different times. The Schlenk tubes were then cooled to room temperature and the pressure was released. After pH regulation and additional 1 h stirring at room temperature, mesitylene (3 mmol) was added to the reaction mixture as an internal standard for <sup>1</sup>H NMR analysis to determine the yield of GVL and the conversion of LA.



Fig. S55 The reaction profile for the hydrogenation of LA to GVL.



**Fig. S56** The <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ , 298K) spectrum of the hydrogenation of LA to GVL after 1 h reaction.

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