CHEMISTRY
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Accepted Article

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To be cited as: *Chem. Asian J.* 10.1002/asia.201601537

Link to VoR: http://dx.doi.org/10.1002/asia.201601537

A Journal of
ACES
Asian Chemical Editorial Society

A sister journal of **Angewandte Chemie** and **Chemistry – A European Journal**

WILEY-VCH

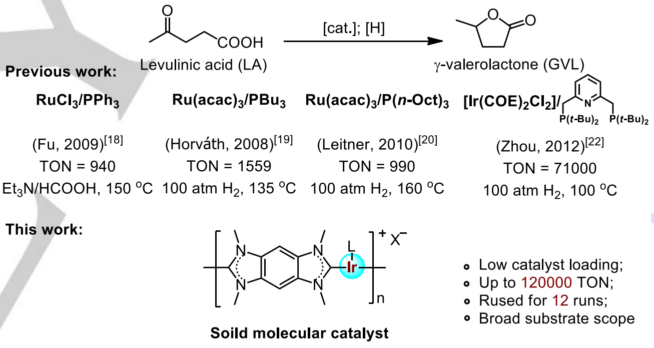
Highly Efficient Hydrogenation of Biomass Oxoacids to Lactones by Using NHC-Iridium Coordination Polymers as Solid Molecular Catalysts

Yaoqi Liu,[a] Zheming Sun,[a] Changyu Huang[a] and Tao Tu*[a, b]

Abstract: A series of NHC-iridium coordination polymers have been demonstrated as robust, efficient and recyclable solid molecular catalysts toward hydrogenation of biomass LA to GVL. Along with quantitative yield attained at 0.01 mol% catalyst loading under 50 atm H_2 atmosphere, the solid molecular catalyst was readily recovered and reused for 12 runs without obvious loss of the selectivity and activity. Remarkably, up to 1.2×10^5 TON, an unprecedented value could be achieved in this important transformation. In addition, a number of LA's homologues, analogues and derivatives were well tolerated to deliver various intriguing and functional lactones in good to excellent yields, which further confirmed the feasibility of the solid molecular catalysts.

Introduction

Along with the continuous consumption of fossil resources, demands for alternatives from lignocellulosic biomass to biofuels and other valuable chemicals are dramatically increasing in recent years.[1] Therefore, tremendous efforts have been devoted to search diverse biomass-derived platform molecules and develop suitable methodologies in this field.[2–6] In this context, γ-valerolactone (GVL) is regarded as one of the most attractive candidates to produce various value-added chemicals, biofuels, environmental benign solvents as well as functional additives for foods and fuels.[7–10] Currently, selective transformations of suitable and inexpensive biomass for the sustainable production of GVL are under intensive investigation.[11] Among them, the hydrogenation of biomass levulinic acid (LA) and its derivatives followed by cyclization constitute one of the most attractive and effective approaches to access GVL. Until now, a plenty of heterogeneous[12–18] and homogenous[19–25] catalysts have been developed and investigated. In general, heterogeneous catalysts offer several prominent advantages including easy separation and possible reusability of the catalysts.[13,14] However, due to their low activities, high reaction temperatures and H_2 pressures are required to achieve satisfactory outcomes. In contrast, most reported homogenous catalysts derived from noble metal (mainly Ru and Ir) precursors and sensitive phosphine ligands usually exhibit high catalytic activity and selectivity (Scheme 1). To the best of our knowledge, up to 7.1×10^4 TON could be obtained with the homogenous phosphine iridium pincer complex develope by Zhou and coworkers.[22] However, this air sensitive system requires the strict absence of water, especially, the catalyst is hard to be recovered. Despite all these advances, from a practical perspective, it is quite important and necessary to process large volume LA continuously, therefore, the development of robust and recyclable catalysts based on the highly active homogenous complexes may be considered as a suitable option for this crucial and sustainable transformation under mild reaction conditions.



Scheme 1. Hydrogenation of levulinic acid (LA) to γ-valerolactone (GVL).

As "mimics" of phosphine ligands, N-heterocyclic carbenes (NHCs) represent one of robust and environment-benign ligands,[26,27] which exhibit good activity in a wide range of transition metal catalyzed reactions.[28,29] However, to the best of our knowledge, there is no report on NHC-based transition metal complexes catalyzed hydrogenation of LA to GVL. In addition, by using "self-supporting" strategy,[30–34] a number of NHC-based coordination polymers could be readily accessed from conformationally rigid bis-imidazolium salts and corresponding metal precursors,[35] which may allow us to investigate their applicability and reusability as solid catalysts. Recently, we reported a series of robust NHC-Ir coordination polymers, which function as highly efficient solid molecular catalysts in the selective oxidative dehydrogenation of glycerol to potassium lactate under relatively mild reaction conditions even at ppm catalyst loadings.[36] Therefore, we subsequently sought to explore their catalytic efficiency in the hydrogenation reactions. Following our recent works on the synthesis organometallic assemblies and exploring their potentials in catalysis, sensors,

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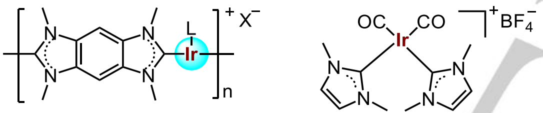
10.1002/asia.201601537

and material sciences,[37–41] herein, we demonstrated the NHC-Ir coordination polymers could function as solid molecular catalysts and exhibit extremely high activity and selectivity in the hydrogenation of LA to GVL by using H_2 as hydrogen source under mild reaction conditions. Remarkably, the solid molecular catalysts could be reused 12 times without obvious loss of activity and selectivity, and up to 1.2×10^5 turnover numbers (TONs) could be achieved.

Results and Discussion

Synthesis and Characterization of NHC-Ir Coordination Polymers: According to our previous protocols, a series of robust NHC-Ir(I) coordination polymers **1a**–**d** (Scheme 2) were readily fabricated in excellent yields from conformationally rigid bis-benzimidazolium salts and iridium precursors via self-assembly process in the presence of lithium bis(trimethylsilyl)amid (LiHMDS) as a base.[36] IR analysis, solid NMR, energy dispersive X-ray (EDX) and X-ray photoelectron spectroscopy (XPS) analysis all indicated the obtained solids were consistent with its elemental composition and state as expected. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and powder X-ray diffraction (PXRD) confirmed their amorphous nature as our previous studies (See the Supporting Information, Figures S1–S23).



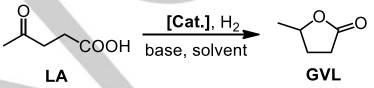
1a: L = $(CO)_2$, X = BF_4;
1b: L = $(CO)_2$, X = I;
1c: L = COD, X = BF_4;
1d: L = COD, X = I.

2

Scheme 2. NHC-Ir coordination polymers **1** and molecular complex **2**.

Investigation of Catalytic Activity of NHC-Ir Complex and Coordination Polymers in the Hydrogenation of LA to GVL: With these fully characterized solid coordination polymers in hands, the initial investigation of their catalytic activity in the reduction of LA was carried out with different hydrogen sources. In general, there are two different hydrogen sources applied in the hydrogenation of LA. One is hydrogen gas and the other is formic acid. When formic acid was used along with Et_3N, 84% yield of GVL could be achieved with 1 mol% solid **1a** at 100 °C with relatively long reaction time (72 h, See the Supporting Information, Table S1). Whilst, when the reaction was carried out under the 50 atm H_2 atmosphere, the reaction processed very efficiently (Table 1). In the presences of 0.05 mol% solid **1a**, LA can selectively and completely convert to GVL in *i*-PrOH with KOH as base at 100 °C within 4 h (Table 1, entry 1), indicating the NHC-Ir coordination polymer catalytic efficiency. However, when MeOH was applied, only a 34% yield of GVL was obtained, possibly due to its low boiling point (Table 1, entry 2). When other alcohols were involved, similar but slightly inferior outcomes were observed (Table 1, entry 3). Aprotic solvents including DMF, THF, Toluene and DCE are not favorable in this transformation, only trace mount of GVL could be detected, which highlights the strong solvent effects in the system (Table S1, entries 5–12). Subsequently, other inorganic bases including LiOH, NaOH, K_3PO_4 and *t*-BuOK were also tested. No better outcomes were found. Furthermore, organic bases including DBU, Et_3N and pyridine all resulted in unsatisfactory yields (Table 1, entries 4, 5 and Table S1, entries 13–19). Decreasing the reaction time, temperature or the pressure of H_2, all leds to inferior results (Table 1, entries 6, 7 and Table S1, entries 20–21).

Table 1. Optimization of reaction conditions.[a]



Entry	[Cat.]	Solvent	Base	Time (h)	T (°C)	Yield (%)
1	**1a**	*i*-PrOH	KOH	4	100	>99
2	**1a**	MeOH	KOH	4	100	34
3	**1a**	EtOH	KOH	4	100	90
4	**1a**	*i*-PrOH	NaOH	4	100	88
5	**1a**	*i*-PrOH	*t*-BuOK	4	100	8
6	**1a**	*i*-PrOH	KOH	1	100	65
7	**1a**	*i*-PrOH	KOH	4	80	42
8	**1c**	*i*-PrOH	KOH	4	100	48
9[b]	**1a**	*i*-PrOH	KOH	4	100	97
10[b]	**1b**	*i*-PrOH	KOH	4	100	81
11[b]	**1d**	*i*-PrOH	KOH	4	100	90
12[b]	**2**	*i*-PrOH	KOH	4	100	31
13[c]	**1a**	*i*-PrOH	KOH	24	100	>99
14[d]	**1a**	*i*-PrOH	KOH	72	100	85
15[e]	**1a**	*i*-PrOH	KOH	72	120	60

[a] Reactions were carried out with LA (10 mmol), catalyst (0.05 mol%), base (1.0 equiv.), H_2 (50 atm) in the selected solvent (5 mL), the yield was determined by ^1H NMR with mesitylene as an internal standard. [b] With 0.025 mol% catalyst. [c] With 0.01 mol% catalyst. [d] With 0.001 mol% catalyst. [e] With 0.0005 mol% catalyst.

With the optimized reaction conditions in hand, the catalytic activity of other solid catalysts **1b**–**d** was then evaluated (Table 1, entries 8-11). Pleasantly, at 0.05 mol% catalyst loading, solids **1b** and **1d** also revealed high activity, whereas, solid **1c** was less efficient (Table 1, entry 8 and Table S1, entries 24–26). In the case of solid **1a**, even at 0.025 mol% catalyst loading, 97% yield of GVL was still obtained within 4 h (entry 9), whilst, low outcomes were found with **1b** and **1d** (entries 10 and 11). However, when a homogeneous analogou of **1a**, NHC-Ir complex **2**, was applied instead under identical reaction conditions, only 31% yield was observed (Table 1, entry 12), which may arouse by the possible inactive dinuclear iridium species formation during the reaction[42] and further highlight the advantage of solid catalysts.

In order to further evaluate the catalytic efficiency of solid **1a**, a series of experiments at low catalyst loading with extended reaction time was carried out. Pleasingly, even at the catalyst loading of 0.01 mol%, reaction can proceed smoothly, producing GVL in quantitative yield with 1×10^4 TON within 24 h under the optimized reaction conditions (Table 1, entry 13). Further decreasing catalyst loading to 0.001 mol%, still 85% yield was obtained within 72 h (8.5×10^{4} TON, Table 1, entry 14). Remarkably, up to 1.2×10^{5} TON could be attained simply decreasing the catalyst loading to 0.0005 mol% and elevating reaction temperature to 120 °C (Table 1, entry 15), which is the highest TON achieved so far for this crucial transformation.

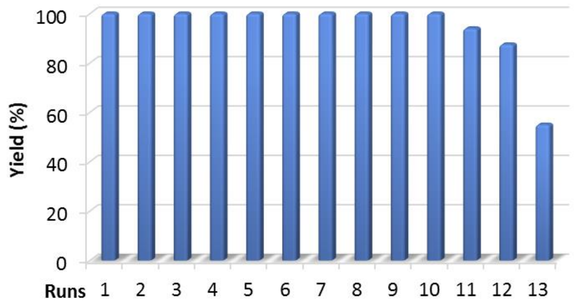


Figure 1. Recycling and reuse of the solid NHC-Ir catalyst **1a** in the hydrogenation of LA to GVL (the reactions were carried out in 20 mmol scale with 0.1 mol% solid **1a** under the optimized reaction conditions for 4 h and the average yields of two parallel recycling sequences were provided).

The Recyclability of NHC-Ir Solid Catalyst: In light of the insolubility of solid **1a** in all selected organic solvents, the catalyst is readily recovered quantitatively by simple centrifugation and decantation after the reaction completion. To our delight, the product obtained by aforementioned process is pure enough for NMR analysis. Especially, the recovered solids **1a** after washing with *i*-PrOH can be directly reused as the catalyst in the second run without additional activation steps, just simply charging LA, base and solvent, without obvious decreasing in the selectivity and yield of GVL. Due to its high catalytic efficiency, the solid catalyst **1a** could be reused up to 13 times, even in the 12th runs, 88% yield of GVL could be still obtained (Figure 1).

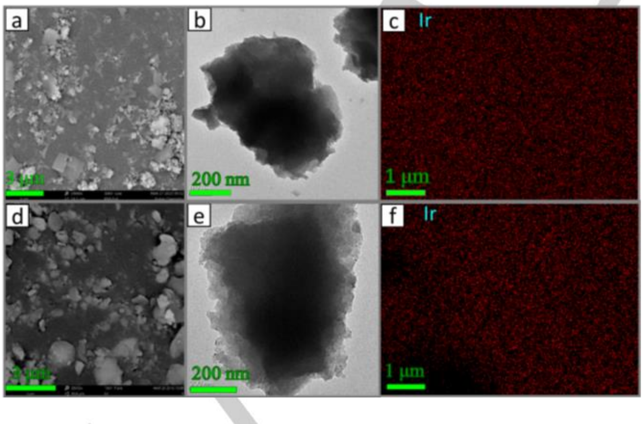
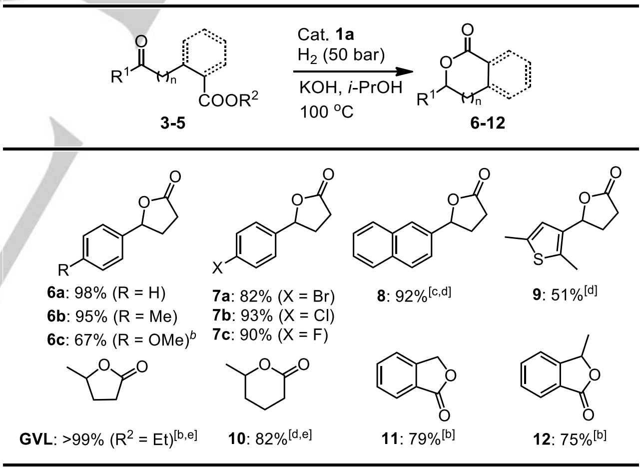


Figure 2. a–c): SEM, TEM, EDS images of the freshly prepared NHC-Ir coordination polymer **1a**; d–f): corresponding images of the recovered solid **1a** after the 13th run.

In order to get the catalytic nature of solid **1a** during the reaction and recycling, the filtration after each run was analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) for possible iridium leaching. In attention, the orignal Ir content in the polymer **1a** is 31.2%, detected by ICP-AES, which is accordance with the theoretical value (30.9%) of $(C_{12}H_{12}BF_4IrN_4O_2\bullet DMF)_n$. Delightedly, only trace amount of iridium could be detected in the filtrates, which may also explain the decreasing of yields after the 10th run. Pleasingly, no metal nanoparticle or cluster was formed, indicating the solid polymer act as the true catalyst in this transformation. Moreover, investigated by SEM, TEM and EDS mapping, the morphology and distribution of recovered solid **1a** after the 13th run were relatively similar with the newly prepared one (Figure 2, a–c *vs.* d–f), which may highlight the catalyst **1a** preserves the structural features and functions as a robust solid molecular catalyst. However, the IR spectra of the recovered solids **1a** are somewhat different from that of the freshly prepared one. The absorption bands of CO ligand in the solid **1a** around 1984 and 2047 cm^{-1} do not exist anymore (See the Supporting Information Figure S65), which may suggest that CO ligands are relatively labile to the iridium center of solid **1a**, and gradually dissociate from the metal during reaction and leave more vacant sites for substrates activation.

Table 2. Hydrogenation of various levulinic acid homologues, analogues and derivatives.[a]



6a: 98% (R = H)
6b: 95% (R = Me)
6c: 67% (R = OMe)^{b}

7a: 82% (X = Br)
7b: 93% (X = Cl)
7c: 90% (X = F)

8: 92%[c,d]

9: 51%[d]

GVL: >99% (R^2 = Et)[b,e]

10: 82%[d,e]

11: 79%[b]

12: 75%[b]

[a] Reactions were carried out with oxoacids (5 mmol), catalyst (0.1 mol%), KOH (2.0 equiv.), H_2 (50 bar) in *i*-PrOH (5 mL) at 100 °C for 4 h, isolated yield. [b] LA derivatives (1 mmol), catalyst (1 mol%). [c] *i*-PrOH (20 mL). [d] 24 h. [e] Yield was calculated by ^{1}H NMR spectroscopy with mesitylene as an internal standard.

Substrate Scope: In light of high efficiency of solid molecular catalyst **1a** in the reduction of LA to GVL, we sought to further investigate it feasibility to catalyze the reduction of various substituted LAs, LA derivatives or even analogues to access a number of functional lactones (Table 2).[43,44] When the ketone terminal of LA was substituted by aromatic rings, all substrates with different electronic and steric properties are well tolerated (**6–9**); up to 95% isolated

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yield could be obtained in the presence of 0.1 mol% solid **1a**. Whilst substrate containing -OMe substitute, only a moderate yield could be produced even with increased catalyst loading to 1 mol% (**6c**), whereas, its methyl analogue resulted in 95% yield of **6b** at 0.1 mol% catalyst loading. Notably, halides are well compatible and delivery the corresponding halides containing lactones (**7**) in good yields, which may also provid an opportunity for their further transformation.[45–48] In the heterocyclic case, when substrate containing thiophene with strong coordination ability was involved, 51% yield of bi-heterocycle **9** was still obtained by simply extending reaction time to 24 h. Delightedly, the protocol could be also applied in the reduction of LA ester, up to >99% yield was obtained under the optimized reaction conditions. Furthermore, in the presence of 0.1 mol% solid **1a**, the LA homologues, oxoacid with longer space between two carbonyl groups, also produce the corresponding lactones in good yields (**10**). In consideration of the importance of phthalates in pharmaceuticals and nature products,[49–51] we also test its catalytic activity of solid **1a** in the reduction of benzoannelated LA analogues. With 1 mol% catalyst loading, good isolated yields for corresponding benzoannelated products **11** and **12** could be obtained, which further indicated the catalytic efficiency of the solid molecular catalyst **1a**.

Conclusions

In summary, a series of NHC-iridium coordination polymers have been demonstrated as robust, efficient and recyclable solid molecular catalysts in the selective hydrogenation of biomass LA to GVL by using H_2 as hydrogen source. Along with quantitative yield could be attained at catalyst loading as low as 0.01 mol% under relatively mild reaction conditions, the solid catalyst was readily recovered and reused for 12 runs without obvious loss of the selectivity and activity. In addition, the solid molecular catalyst shows better catalytic activity than its homogenous counterpart under the identical reaction condtions, clearly indicating the advantage of the solid molecular catalysts. Remarkably, the highest 1.2×10^5 TON in this crucil transformation could be achieved in this study. Furthermore, the protocol is fully compitible with other LA homologues, analogues and derivatives and produces a variety of intriguing and functional lactones in good to excellent yields, highlighting the solid molecular catalyst efficiency.

Experimental Section

General: All commercial reagents were used as purchased without further purification, unless otherwise noted. Hydrogen gas (99.99%) was purchased from Dumaoai. $CDCl_3$ was purchased from Cambridge Isotope Laboratories. ^1H, ^{13}C and ^{19}F NMR spectra were recorded on Jeol ECA-400 and Bruker 400 DRX spectrometers. The chemical shifts (δ) for ^1H NMR are given in parts per million (ppm) referenced to the residual proton signal of the deuterated solvent ($CHCl_3$ at δ 7.26 ppm, DMSO at δ 2.50 ppm); coupling constants are expressed in hertz (Hz). ^{13}C NMR spectra were referenced to the carbon signal of $CDCl_3$ (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. 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.

General protocol to synthesize solid NHC-Ir coordination polymer: A Schlenk tube was charged with 1,3,5,7-tetramethyl-benzodiimidazolium, diiodide or ditetrafluoroborate[36] (0.5 mmol) and the iridium precursor (0.5 mmol). The mixture was dissolved in DMF (1 mL) under N_2 at room temperature, LiHMDS (1 mmol) solution in THF was then added in dropwise. The resulting mixture was stirred under N_2 at 80 °C for 12 h. The dark brown solids were isolated after filtration and washed with deionized water for three times. The polymer solids were then dried over under vacuum to deliver the desired NHC-Ir coordination polymer.

NHC-Ir coordination polymer (**1a**): dark-brown solid, 93% yield. IR (KBr pellet) *v* 418.22, 424.01, 599.84, 1084.05, 1257.84, 1383.96, 465.51, 1629.09, 1984.76, 2045.68, 2273.14, 3443.20 cm^{-1}; Elemental analysis (%) *Calcd. for* $(C_{12}H_{12}BF_4IrN_4O_2\bullet DMF)_n$: C, 32.81; H, 3.40; N, 11.25; *found:* C, 31.35; H, 3.60; N, 11.94; Solid state ^{13}C-NMR(150 MHz): δ = 231.95, 171.53, 132.86, 92.53, 34.19.

NHC-Ir coordination polymer (**1b**): dark-brown solid, 97% yield. IR (KBr pellet) *v* 668.94, 830.13, 1108.12, 1347.58, 1458.87, 1559.86, 1617.67, 1654.08, 1684.89, 1932.80, 2023.33, 2239.64, 3421.95 cm^{-1}; Elemental analysis (%) *Calcd. for* $(C_{12}H_{12}BF_4IrN_4O_2\bullet 1.5\ DMF\bullet 4\ H2O)_n$: C, 28.82; H, 4.25; N, 9.99; *found:* C, 29.39; H, 4.42; N, 9.67.

NHC-Ir coordination polymer (**1c**): dark-brown solid, 99% yield. IR (KBr pellet) *v* 455.20, 763.95, 1023.98, 1273.33, 1383.97, 1523.04, 1571.54, 1629.33, 2932.07, 3432.38 cm^{-1}; Elemental analysis (%) *Calcd. for* $(C_{20}H_{26}BF_4IrN_4)n$: C, 39.94; H, 4.36; N, 9.31; *found:* C, 39.68; H, 4.65; N, 9.55.

NHC-Ir coordination polymer (**1d**): dark-brown solid, 95% yield. IR (KBr pellet) *v* 763.93, 1000.21, 1023.75, 1083.79, 1356.68, 1383.97, 1425.38, 1437.69, 1449.00, 1458.54, 1466.11, 1523.03, 1571.52, 1629.31, 1636.52, 1653.94, 2830.75, 2879.73, 2932.08, 2956.61, 2983.15, 3432.45, 3629.71 cm^{-1}; Elemental analysis (%) *Calcd. for* $(C_{23}H_{33}IIrN_5O\bullet DMF)_n$: C, 38.65; H, 4.65; N, 9.80; *found:* C, 38.21; H, 4.50; N, 9.59.

Catalytic procedure of hydrogenation of LA to GVL with NHC-Ir coordination polymer：A stainless autoclave equipped with a magnetic stirring bar was charged with LA (10 mmol), NHC-Ir coordination polymer (0.05 mol%), KOH (85% purity) (660 mg, 10 mmol) and isopropanol (5 mL). The autoclave was tightened and flushed with hydrogen three times and was finally charged with hydrogen to 50 atm. The reaction mixture was stirred under hydrogen pressure at 100 °C for 4 h. The autoclave was then cooled to room temperature and the pressure was released. After pH regulation and additional 1 h stirring at room temperature, mesitylene (120 mg, 1 mmol) was added to the reaction mixture as an internal standard for ^1H NMR analysis to determine the yield.

Operation procedure for the solid catalyst 1a recovery: A stainless autoclave equipped with a magnetic stirring bar was charged with LA (2.3 g, 20 mmol), solid catalyst **1a** (11 mg, 0.1 mol%), KOH (85% purity) (1.3

g, 20 mmol) and isopropanol (5 mL). After the hydrogenation by the aforementioned general operation procedure and the pressure was released, the solid catalysts were readily recovered after centrifugation and decantation. The recovered catalysts **1a** was washed with isopropanol (5 mL × 3), the recovered solid catalysts were reused directly in the next run without additional activation steps, just simply recharging LA, KOH and *i*-PrOH in the autoclave.

General synthetic procedure of substrates 3：Succinic anhydride (3 g, 30 mmol) was treated with aryl derivatives (60 mmol) in the presence of anhydrous aluminium chloride (8 g, 60 mmol). The reaction mixture was stirred for 6 h. The desired product was purified by dissolving in 5 % sodium hydroxide solution and filtered. Dilute hydrochloric acid was added to mother liquor to precipitate the product. The solid was obtained after filtration. After washing with cold water, drying and recrystallization, the desired compounds **3** could be delivered.

3-Benzoylpropanoic acid (**3a**): white solid, 77% yield. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ = 8.00 (d, *J* = 8.0 Hz, 2H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 2H), 3.34 (t, *J* = 6.0 Hz, 2H), 2.83 (t, *J* = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$, 298 K) δ = 197.83, 179.01, 136.26, 133.25, 128.56, 127.96, 33.06, 27.99.

3-(4-Methylbenzoyl)propanoic acid (**3b**): white solid, 64% yield. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ = 7.89 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 3.30 (t, *J* = 6.0 Hz, 2H), 2.81 (t, *J* = 6.0 Hz, 2H), 2.42 (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$, 298 K) δ = 197.56, 178.72, 144.06, 133.82, 129.21, 128.01, 32.96, 28.02, 21.52.

3-(4-Methoxybenzoyl)propanoic acid (**3c**): white solid, 35% yield. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ = 7.96 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 3.87 (s, 1H), 3.27 (t, *J* = 6.0 Hz, 2H), 2.80 (t, *J* = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-D$_6$, 298 K) δ = 197.27, 174.35, 163.52, 130.55, 129.81, 114.28, 55.92, 33.09, 28.33.

3-(4-Bromobenzoyl)propanoic acid (**3d**): white solid, 26% yield. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ = 7.85 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 3.28 (t, *J* = 4.8 Hz, 2H), 2.82 (t, *J* = 4.8 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$, 298 K) δ = 196.82, 178.21, 135.08, 131.97, 129.55, 128.54, 33.09, 27.86.

3-(4-Chlorobenzoyl)propanoic acid (**3e**): white solid, 38% yield. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ = 7.93 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 3.29 (t, *J* = 4.8 Hz, 2H), 2.82 (t, *J* = 4.8 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$, 298 K) δ = 196.63, 178.85, 139.73, 134.62, 129.40, 126.91, 33.04, 27.92.

3-(4-Fluorobenzoyl)propanoic acid (**3f**): white solid, 39% yield. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ = 8.01 (dd, *J* = 8.0, 4.0 Hz, 2H), 7.15 (t, *J* = 8.0 Hz, 2H), 3.29 (t, *J* = 4.8 Hz, 2H), 2.82 (t, *J* = 4.8 Hz, 2H); ^{19}F NMR (CDCl$_3$, 376 MHz, 298 K): δ = -104.74; ^{13}C NMR (100 MHz, CDCl$_3$, 298 K) δ = 196.28, 178.90, 167.07, 164.54, 132.76, 132.73, 130.68, 130.59, 115.79, 115.58, 32.97, 27.95.

3-(2-Naphthoyl)propanoic acid (**3g**): yellow solid, 14% yield. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ = 8.52 (s, 1H), 8.05 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.92 - 7.88 (m, 2H), 7.64 - 7.55 (m, 2H), 3.48 (t, *J* = 6.6 Hz, 2H), 2.89 (t, *J* = 6.6 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-D$_6$, 298 K) δ = 198.51, 174.01, 135.10, 133.76, 132.24, 129.81, 129.65, 128.66, 128.33, 127.69, 126.96, 123.49, 33.21, 28.04.

2,5-Dimethyl-γ-oxo-3-thiophenebutanoic acid (**3h**): white solid, 40% yield. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ = 7.03 (s, 1H), 3.12 (t, *J* = 4.0 Hz, 2H), 2.74 (t, *J* = 4.0 Hz, 2H), 2.66 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$, 298 K) δ = 193.67, 179.04, 147.79, 135.26, 134.74, 125.70, 35.89, 27.95, 15.98, 14.87.

General procedure of hydrogenation of various LA's homologues, analogues and derivatives: A stainless autoclave equipped with a magnetic stirring bar was charged with the substrate **3** (5 mmol), solid catalyst **1a** (2.7 mg, 0.1 mol%), KOH (85% purity) (660 mg, 10 mmol) and isopropanol (5 mL). The autoclave was tightened and flushed with hydrogen three times and was finally charged with hydrogen to 50 atm. The reaction mixture was stirred under hydrogen at 100 ^{o}C for 4 h. After the reaction completion, the autoclave was cooled to room temperature and the pressure was then released. After pH regulation and additional 1 h stirring at room temperature, the reaction mixture was purified by silica gel column chromatography to affording desired product.

γ-Phenyl-γ-butyrolactone (**6a**): colourless oil, 98% yield. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ = 7.42 - 7.33 (m, 5H without additional activation procedure, just simply charging LA, KOH and *i*-PrOH,), 5.52 (t, *J* = 5.2 Hz 1H), 2.68 - 2.64 (m, 3H), 2.24 - 2.17 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$, 298 K) δ = 176.88, 139.24, 128.62, 128.30, 125.17, 81.14, 30.80, 28.82.

γ-(4-Methylphenyl)-γ-butyrolactone (**6b**): white solid, 95% yield. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ = 7.20 (dd, J = 12.0, 8.0 Hz, 4H), 5.49 (dd, *J* = 8.0, 4.0 Hz, 1H), 2.68 - 2.62 (m, 3H), 2.37 (s, 1H), 2.21 - 2.18 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$, 298 K) δ = 177.03, 138.29, 136.33, 129.38, 125.37, 81.35, 30.92, 29.04, 21.12.

γ-(4-Methoxyphenyl)-γ-butyrolactone (**6c**): white solid, 67% yield. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ = 7.27 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 5.48 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.82 (s, 3H), 2.69 - 2.61 (m, 3H), 2.23 - 2.18 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$, 298 K) δ = 176.96, 159.66, 131.07, 126.93, 114.01, 81.30, 55.23, 30.77, 29.14.

γ-(4-Bromophenyl)-γ-butyrolactone (**7a**): white solid, 82% yield. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ = 7.53 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz 2H), 5.47 (dd, *J* = 8.0, 4.0 Hz, 1H), 2.69 - 2.63 (m, 3H), 2.19 - 2.12 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$, 298 K) δ = 176.49, 138.36, 131.82, 126.91, 122.28, 80.37, 30.81, 28.77.

γ-(4-Chlorophenyl)-γ-butyrolactone (**7b**): yellow solid, 93% yield. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ = 7.37 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz 2H), 5.48 (dd, *J* = 8.0, 4.0 Hz, 1H), 2.68 - 2.64 (m, 3H), 2.19 - 2.13 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$, 298 K) δ = 176.51, 137.80, 134.12, 128.93, 126.62, 80.36, 30.81, 28.78.

γ-(4-Fluorophenyl)-γ-butyrolactone (**7c**): colourless oil, 90% yield. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ = 7.32 (dd, *J* = 8.4, 5.2 Hz, 2H), 7.08 (t, *J* = 8.4 Hz, 2H), 5.49 (dd, *J* = 8.0, 4.0 Hz, 1H), 2.69 - 2.64 (m, 3H), 2.20 - 2.17 (m, 1H); ^{19}F NMR (CDCl$_3$, 376 MHz, 298 K): δ = -113.31; ^{13}C NMR (100 MHz, CDCl$_3$, 298 K) δ = 176.68, 163.75, 161.29, 135.01, 134.98, 127.19, 127.11, 115.68, 115.46, 80.60, 30.86, 28.90.

γ-(2-Naphthyl)-γ-butyrolactone (**8**): white solid, 92% yield. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ = 7.90 - 7.82 (m, 4H), 7.53 - 7.51 (m, 2H), 7.43 - 7.40 (m, 1H), 5.70 (t, *J* = 7.6 Hz, 1H), 2.73 - 2.69 (m, 3H), 2.34 - 2.27 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$, 298 K) δ = 176.90, 136.58, 133.02, 132.91, 128.68, 127,91, 127.61, 126.47, 126.32, 124.17, 122.76, 81.18, 30.71, 28.78.

5-(2,5-Dimethyl-3-thienyl)dihydro-2(3H)-furanone (**9**): white solid, 51% yield. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) δ = 6.59 (s, 1H), 5.48 (dd, *J* = 8.4, 6.4 Hz, 1H), 2.67 - 2.63 (m, 2H), 2.54 - 2.50 (m, 2H), 2.73 (s, 3H), 2.27 (s, 3H), 2.25 - 2.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ = 176.85, 136.70, 134.34, 134.29, 123.13, 76.46, 29.55, 29.20, 14.99, 12.73.

Phthalide (**11**): white solid, 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 7.94 (d, *J* = 8.0 Hz, 1H), 7.70 (t, *J* = 8.0 Hz, 1H), 7.58 - 7.50 (m, 2H), 5.33 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ = 170.99, 146.41, 133.90, 128.86, 125.46, 125.46, 122.04, 69.55.

3-Methylphthalide (**12**): colourless oil, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ = 7.89 (d, *J* = 8.0 Hz, 1H), 7.69 - 7.66 (m, 1H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.45 - 7.43 (m, 1H), 5.56 (dd, *J* = 13.6, 7.2 Hz, 1H), 1.63 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ = 170.43, 151.04, 133.97, 128.91, 125.42, 125.42, 121.47, 77.67, 20.20.

Acknowledgements

Financial support from the National Natural Science Foundation of China (No. 21572036 and 91127041), Ministry of Science and Technology of China (2016YFA0202902), the Shanghai International Cooperation Program (14230710600), the Doctoral Fund of Ministry of Education of China (20130071110032) and Department of Chemistry, Fudan University is gratefully acknowledged.

Keywords: hydrogenation • iridium • lactones • levulinic acid • N-heterocyclic carbene

[1] J. Fargione, J. Hill, D. Tilman, S. Polasky, P. Hawthorne, *Science* **2008**, *319*, 1235–1238.
[2] G. W. Huber, A. Corma, *Angew. Chem. Int. Ed.* **2007**, *46*, 7184–7201.
[3] G. W. Huber, S. Iborra, A. Corma, *Chem. Rev.* **2006**, *106*, 4044–4098.
[4] A. Corma, S. Iborra, A. Velty, *Chem. Rev.* **2007**, *107*, 2411–2502.
[5] D. M. Alonso, J. Q. Bond, J. A. Dumesic, *Green Chem.* **2010**, *12*, 1493–1513.
[6] J. N. Chheda, G. W. Huber, J. A. Dumesic, *Angew. Chem. Int. Ed.* **2007**, *46*, 7164–7183.
[7] J. Q. Bond, D. M. Alonso, D. Wang, R. M. West, J. A. Dumesic, *Science* **2010**, *327*, 1110–1114.
[8] I. T. Horváth, H. Mehdi, V. Fábos, L. Boda, L. T. Mika, *Green Chem.* **2008**, *10*, 238–242.
[9] I. T. Horváth, *Green Chem.* **2008**, *10*, 1024–1028.
[10] W. Li, J.-H. Xie, M.-L. Yuan, Q.-L. Zhou, *Green Chem.* **2014**, *16*, 4081–4085.
[11] H. Heeres, R. Handana, D. Chunai, C. B. Rasrendra, B. Girisuta, H. J. Heeres, *Green Chem.* **2009**, *11*, 1247–1255.
[12] H. A. Schuette, R. W. Thomas, *J. Am. Chem. Soc.* **1930**, *52*, 3010–3012.
[13] X.-L. Du, L. He, S. Zhao, Y.-M. Liu, Y. Cao, H.-Y. He, K.-N. Fan, *Angew. Chem. Int. Ed.* **2011**, *50*, 7815–7819.
[14] J. Yuan, S.-S. Li, L. Yu, Y.-M. Liu, Y. Cao, H.-Y. He, K.-N. Fan, *Energy Environ. Sci.* **2013**, *6*, 3308–3313.
[15] A. M. Hengne, C. V. Rode, *Green Chem.* **2012**, *14*, 1064–1072.
[16] K. Shimizu, S. Kannoa, K. Kon, *Green Chem.* **2014**, *16*, 3899–3903.
[17] R. R. Gowda, E. Y.-X. Chen, *ChemSusChem* **2016**, *9*, 181–185.
[18] Qi. Xu, X. Li, T. Pan, C. Yu, J. Deng, Q. Guo, Y. Fu, *Green Chem.* **2016**, *18*, 1287–1294.
[19] H. Mehdi, V. Fábos, R. Tuba, A. Bodor, L. T. Mika, I. T. Horváth, *Top. Catal.* **2008**, *48*, 49–54.
[20] F. M. A. Geilen, B. Engendahl, A. Harwardt, W. Marquardt, J. Klankermayer, W. Leitner, *Angew. Chem. Int. Ed.* **2010**, *49*, 5510–5514.
[21] L. Deng, J. Li, D.-M. Lai, Y. Fu, Q.-X. Guo, *Angew. Chem. Int. Ed.* **2009**, *48*, 6529–6532.
[22] W. Li, J.-H. Xie, H. Lin, Q.-L. Zhou, *Green Chem.* **2012**, *14*, 2388–2390.
[23] J. M. Tukacs, M. Novák, G. Dibó, L. T. Mika, *Catal. Sci. Technol.* **2014**, *4*, 2908–2912.
[24] J. M. Tukacs, D. Király, A. Strádi, G. Novodarszki, Z. Eke, G. Dibó, T. Kégl, L. T. Mika, *Green Chem.* **2012**, *14*, 2057–2065.
[25] N. Dai, R. Shang, M. Fu, Y. Fu, *Chin. J. Chem.* **2015**, *33*, 405–408.
[26] M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nature* **2014**, *510*, 485–496.
[27] F. E. Hahn, *Angew. Chem. Int. Ed.* **2006**, *45*, 1348–1352.
[28] E. Levin, E. Ivry, C. E. Diesendruck, N. G. Lemcoff, *Chem. Rev.* **2015**, *115*, 4607–4692.
[29] K. Riener, S. Haslinger, A. Raba, M. P. Högerl, M. Cokoja, W. A. Herrmann, F. E. Kühn, *Chem. Rev.* **2014**, *114*, 5215–5272.
[30] L.-X. Dai, *Angew. Chem. Int. Ed.* **2004**, *43*, 5726–5729.
[31] K. Ding, Z. Wang, X. Wang, Y. Liang, X. Wang, *Chem. Eur. J.* **2006**, *12*, 5188–5197.
[32] Y. Liang, Q. Jing, X. Li, L. Shi, K. Ding, *J. Am. Chem. Soc.* **2005**, *127*, 7694–7695.
[33] X. Wang, K. Ding, *J. Am. Chem. Soc.* **2004**, *126*, 10524–10525.
[34] L. Yu, Z. Wang, J. Wu, S. Tu, K. Ding, *Angew. Chem. Int. Ed.* **2010**, *49*, 3627–3630.
[35] Z. Wang, G. Chen, K. Ding, *Chem. Rev.* **2009**, *109*, 322–359.
[36] Z. Sun, Y. Liu, J. Chen, C. Huang, T. Tu, *ACS Catal.* **2015**, *5*, 6573−6578.
[37] T. Tu, W. Fang, X. Bao, X. Li, K. H. Dötz, *Angew. Chem. Int. Ed.* **2011**, *50*, 6601−6605.
[38] T. Tu, H. Mao, C. Herbert, M. Xu, K. H. Dötz, *Chem. Commun.* **2010**, *46*, 7796−7798.
[39] T. Tu, W. Fang, J. Jiang, *Chem. Commun.* **2011**, *47*, 12358−12360.
[40] W. Fang, Z. Sun, T. Tu, *J. Phys. Chem. C* **2013**, *117*, 25185−25194.
[41] T. Tu, W. Fang, Z. Sun, *Adv. Mater.* **2013**, *25*, 5304−5313.
[42] L. S. Sharninghausen, J. Campos, M. G. Manas, R. H. Crabtree, *Nat. Commun.* **2014**, *5*, 5084–5084.
[43] C. Forzato, R. Gandolfi, F. Molinari, P. Nitti, G. Pitacco, E. Valentin, *Tetrahedron: Asymmetry* **2001**, *12*, 1039–1046.
[44] P. Veeraraghavan Ramachandran, S. Pitre, H. C. Brown, *J. Org. Chem.* **2002**, *67*, 5315–5319.
[45] A. Díaz-Rodríguez, W. Borzęcka, I. Lavandera, V. Gotor, *ACS Catal.* **2014**, *4*, 386–393.
[46] S. Høg, P. Wellendorph, B. Nielsen, K. Frydenvang, I. F. Dahl, H. Bräuner-Osborne, L. Brehm, B. Frølund, R. P. Clausen, *J. Med. Chem.* **2008**, *51*, 8088–8095.
[47] S.-K. Kwon, Y.-N. Park, *Arch Pharm Res* **2000**, *23*, 329–331.
[48] D. C. Gerbino, D. Augner, N. Slavov, H.-G. Schmalz, *Org. Lett.* **2012**, *14*, 2338–2341.
[49] S. Omura, T. Fukuyama, Y. Murakami, H. Okamoto, I. Ryu, *Chem. Commun.* **2009**, *44*, 6741–6743.
[50] M. Peña-López, H. Neumann, M. Beller, *ChemCatChem* **2015**, *7*, 865–871.
[51] X. Xie, S. S. Stahl, *J. Am. Chem. Soc.* **2015**, *137*, 3767−3770.

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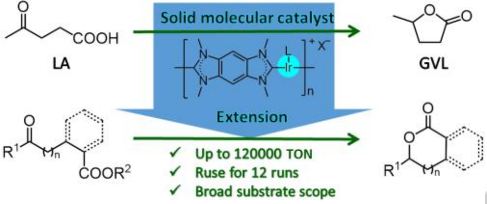
NHC-Iridium polymers function as robust, efficient and recyclable solid molecular catalyst in the hydrogenation of LA to GVL, which was readily recovered and reused for 12 runs. Besides up to 1.2×10^5 TON could be achieved, the protocol is readily to extend to other LA's homologues, analogues and derivatives producing a variety of intriguing functional lactones.



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