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Shengdong Wang, Haiyun Huang, Christian Bruneau, Cedric Fischmeister. Formic acid as a hydrogen source for the iridium-catalyzed reductive amination of levulinic acid and 2-formylbenzoic acid. *Catalysis Science & Technology*, 2019, 9 (15), pp.4077-4082. 10.1039/c9cy01019j . hal-02303385

HAL Id: hal-02303385

<https://univ-rennes.hal.science/hal-02303385v1>

Submitted on 21 Mar 2022

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ARTICLE

Formic acid as hydrogen source for the iridium-catalyzed reductive amination of levulinic acid and 2-formylbenzoic acid

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

The aqueous phase catalytic reductive amination of levulinic acid (LA) into pyrrolidones and 2-formylbenzoic acid into *N*-arylisoindolines is reported. The catalytic reaction involves an iridium catalyst bearing an electron-rich dipyriddyamine ligand and uses formic acid as hydrogen source. The chemoselective iridium catalyst displayed high efficiency for the synthesis of a variety of *N*-substituted 5-methyl-2-pyrrolidones, *N*-substituted 6-methyl-2-piperidinone and *N*-arylisoindolines.

Introduction

Green and sustainable catalytic processes for the transformation of biomass-derived platform compounds has been recognized as a key technology for tackling the problems resulting from the massive use of fossil resources.¹ Levulinic acid (LA) that is produced from carbohydrates or biomass wastes is one of the most valuable platform chemicals with multiple applications.^{1g, 2} For instance, levulinic acid is the precursor of γ -valerolactone, a compound that can be used as liquid fuel or food additive³ and reaction media in numerous transformations.⁴ LA is also a precursor of succinic acid via oxidation reactions.⁵ Pyrrolidone derivatives are important structural units in organic chemistry which find applications in various domains such as surfactants, intermediates for inks, fibers and drugs.⁶ Recently, *N*-substituted 5-methyl-2-pyrrolidones were identified as biosourced substitutes for the extensively used NMP (*N*-methylpyrrolidone) solvent in the ruthenium catalyzed C-H bond functionalization reaction.⁷ Despite the availability of synthetic methods including intramolecular hydroamination,⁸ hydroamination-cyclization,⁹ *N*-Alkylation¹⁰ and intramolecular hydroamidation,¹¹ there is an ongoing interest for the development of greener synthesis of *N*-heterocyclic compounds in particular those employing renewable resources and environmentally friendly and safe conditions. Since the early report by Frank in 1947,¹² the synthesis of *N*-substituted 5-methyl-2-pyrrolidones by reductive amination of levulinic acid has been investigated with various heterogeneous¹³ and homogeneous¹⁴ catalysts using diverse hydrogen sources. In 2017, we initiated a project

based on dipyriddyamine-containing organometallic catalysts. A first generation of ruthenium and iridium complexes enabling the reduction of levulinic acid into γ -valerolactone in the presence of triethylamine was reported. It is noteworthy that two examples of reductive amination of levulinic acid by formic acid and a two-fold excess of benzylamine or *o*-aniline were described, highlighting some selectivity issues.^{15a} The same year, we reported the synthesis of second generation catalysts with enhanced performances^{15b} that were used for the base-free synthesis of a broad scope of *N*-heterocycles by reductive amination of stoichiometric amounts of levulinic acid and various amines including very bulky derivatives using molecular hydrogen as hydrogen source.⁷ In particular, an iridium-dipyriddyamine catalyst operated at 110 °C under low hydrogen pressure (5 bar). More recently, we disclosed a third generation of catalyst incorporating an electron-enriched dipyriddyamine ligand as very efficient for the dehydrogenation of formic acid^{15c} and the reversible hydrogenation/dehydrogenation of quinoline derivatives.^{15d} These results prompted us to investigate the synthesis of *N*-heterocycles by reductive amination of levulinic acid with amines using formic acid, a hydrogen source less studied than dihydrogen. In 2011, Fu^{14a} prepared several pyrrolidone derivatives by reductive amination of levulinic acid catalyzed by [RuCl₂(*p*-cymene)]₂ and *t*-Bu₃PHBF₄ using formic acid. This catalyst showed good performances with alkylamines but much lower activity with arylamines. At the same period, several amines were successfully transformed into pyrrolidones at 130 °C in water with an Au-based heterogeneous catalyst using FA as reductant.^{13a} In 2013, Xiao reported an iridium catalyst operating at pH 3.5 using a mixture of formic acid and sodium formate^{14b} while García^{13c} described Ru-NPs catalyst operating at 120 °C, the latter suffering from selectivity issues. Coordination polymers were also employed for the synthesis one compound (5-methyl-2-pyrrolidone) from levulinic acid and ammonium formate at 120 °C, *N*-heterocycles being synthesized by a one-pot synthesis

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

employing ketones, levulinic acid and ammonium formate.^{13d} Most recently, Burtoloso¹⁴ⁱ reported the reductive amination of LA using a homogeneous iron catalyst in water. In this study, several pyrrolidone derivatives were obtained in good yields but a very high reaction temperature was necessary, typically 180 °C hence lessening the green character of the process. It must also be mentioned that metal-free transformations were reported by Xiao^{14c} and Andrioletti^{14d} but these processes required either undesirable organic solvents and bases or harsh conditions of temperature and pressure. Apart from the impressive results obtained by Han with a Pt/P-TiO₂ heterogeneous catalyst operating at ambient conditions of pressure and temperature^{13m} and by Sun using AuPd nanoparticles at 1 bar of hydrogen pressure and 85 °C,¹³ⁿ the latter suffering from some scope limitations, it is still necessary to improve the sustainability of catalytic methods for the synthesis of pyrrolidone derivatives. This can be tackled by the implementation of modern synthetic tools such as flow synthesis¹⁶ or by the design and implementation of more efficient catalysts and catalytic process. Herein, we describe the efficient base-free reductive amination of levulinic acid and 2-formylbenzoic acid under mild conditions in water using tailor-made catalysts with enhanced performances.

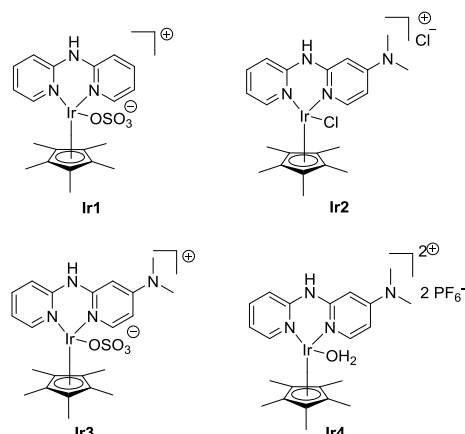


Figure 1. Iridium complexes used in this study.

We have recently reported that dipyriddyamine (dpa)-based **Ir1** complex (Figure 1) was a very effective catalyst for hydrogenation of levulinic acid using formic acid as hydrogen source^[15b] and we could further extend the scope of this catalyst to the reductive amination of levulinic acid under hydrogen pressure.^[7] The introduction of the electron-donating dimethylamino-group to the dpa ligand (Figure 1, **Ir2-Ir4**) resulted in the disclosure of **Ir3** as a very efficient catalyst for the dehydrogenation of aqueous or neat formic acid.^[15c] These results prompted us to investigate the potential of these catalysts in the aqueous phase reductive amination of levulinic acid using formic acid as source of hydrogen.

Results and discussion

We initiated our investigations with the reductive amination of levulinic acid with aniline as a model reaction. Several

experimental parameters were screened and optimized. As depicted in Table 1, we first explored the reductive amination of levulinic acid with our previously reported Iridium complexes (Table 1, entries 1-4). This catalyst screening revealed the superiority of the electron rich catalyst **Ir3**, which enabled full and selective conversion of LA into the corresponding pyrrolidone as detected by ¹H NMR of the crude reaction mixture. Further studies of the reaction parameters identified 60 °C and 0.05 mol% as the optimal temperature and catalyst loading, respectively. Interestingly, when the reaction was conducted at a lower temperature, the amino-acid intermediate **1a'** was detected giving some clues about the catalytic mechanism (Table 1, entries 7-8). It is also worth mentioning that low reaction temperature prevented the formation of γ -valerolactone as a side-product resulting from direct reduction of levulinic acid.

Table 1. Ir-catalyzed reductive amination of Levulinic acid.^a


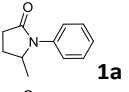
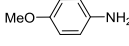
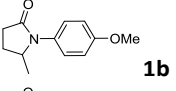
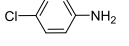
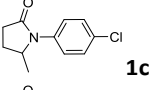
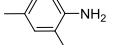
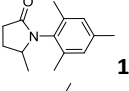
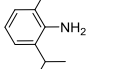
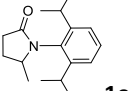
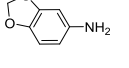
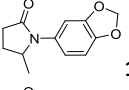
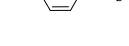
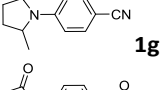
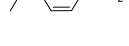
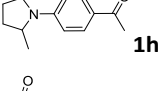

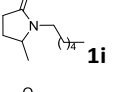

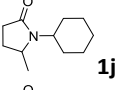
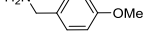
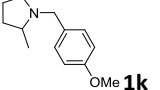
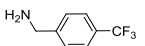
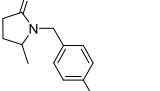

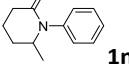
Entry	[Ir](mol%)	T(°C)	1a Yield/% ^b	1a' Yield/% ^b
1	Ir1	80	52	0
2	Ir2	80	31	0
3	Ir3	80	100	0
4	Ir4	80	71	0
5	Ir3	70	100	0
6	Ir3	60	100	0
7	Ir3	50	69	31
8	Ir3	40	25	75
9	Ir3 (0.04)	60	89	0
10	Ir3 (0.01)	60	18	0

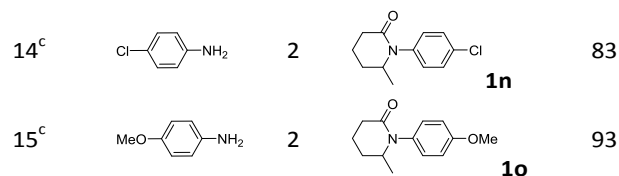
^a Reaction conditions: [Ir] (0.05 mol%), H₂O (2 mL), 17 h. ^b The yield of **A** and **B** was determined by ¹H NMR analysis

With the standard conditions in hands, we performed the reductive amination of levulinic acid with a number of commercially available amines. A broad scope of aniline derivatives with various steric and electronic demands was first evaluated. All these amines furnished the corresponding pyrrolidones in good to excellent yields (Table 2, entries 2, 3, 7, 8). It is noteworthy that the catalyst tolerated very bulky aniline derivatives allowing the synthesis of **1d** and **1e** in good yields. This is to the best of our knowledge, the first synthesis of these compounds using FA as hydrogen source. For comparison, they were previously obtained in similar yields under 5 bar of hydrogen pressure at 110 °C with 0.1 mol% of **Ir1**.⁷ Another important feature is depicted in Table 2, entries 7 and 8, where the chemoselective synthesis of **1g** and **1h** was achieved in good yields without any hydrogenation of the nitrile or ketone functionalities. The reductive amination of LA with two aliphatic amines including a linear (Table 2, entry 9) and a cyclic amine (Table 2, entry 10) was also successful, yielding the desired products in good yields (76-83%). Likewise, two benzyl amine derivatives led to the corresponding

pyrrolidones in good yields (Table 2, **1k**, **1l**). The reductive amination protocol was extended to the synthesis of 6-membered lactams (piperidone derivatives) which are also valuable compounds in organic chemistry. Three derivatives were thus prepared from 5-oxo-hexanoic acid. However, it was necessary to increase the reaction temperature to 100 °C to reach high yields (Table 2, entries 13-15)

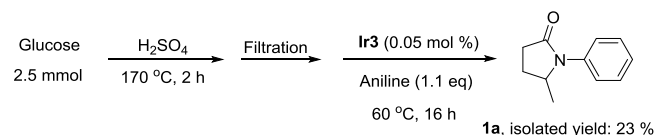
Table 2. Ir3-catalyzed reductive amination of keto acid: Substrate scope^a.

Entry	Substrate	n	Product	yield ^b (%)
1		1		97
2		1		92
3		1		85
4		1		88
5		1		75
6		1		91
7		1		83
8		1		77
9		1		82
10		1		76
11		1		83
12		1		80
13 ^c		2		91



^a Reaction conditions: keto acid (2 mmol), amine (2.2 mmol), HCOOH (4 mmol), Ir3 (0.05 mol%), water (2mL), 60 °C (oil bath), 17 h. ^b isolated yield. ^c 100 °C (oil bath).


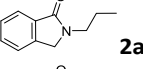

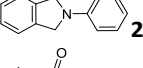
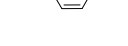
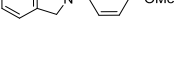
Having demonstrated the applicability of the catalysts to a number of amine using pure levulinic and formic acid, we turned our attention to a one-pot process starting from glucose. This one-pot process is an interesting approach considering that LA and FA can be obtained from the acidic treatment of glucose but their separation is difficult.¹⁷ The treatment of glucose with sulphuric acid at 170 °C led to a reaction mixture that was simply filtrated at room temperature in order to remove insoluble materials (humins). To the filtrate were directly added the iridium catalyst Ir3 and aniline (Scheme 1). After 16 h at 60 °C, the expected pyrrolidone **1a** was obtained in a modest but competitive 23 % yield since the one-pot process was performed without pH neutralization of the intermediate filtrate.^{14a}

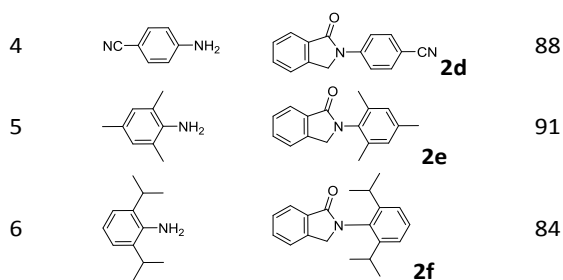


Scheme 1. One pot synthesis of **1a** from glucose

The generality of this catalytic reaction was further extended to the reaction of 2-formylbenzoic acid with amines aiming at preparing *N*-arylisoindolinone derivatives (Table 3). These compounds display interesting biological properties and therefore represent an attractive target in organic synthesis. Thus, when reacted with aliphatic (Table 3, entry 1) or aromatic amines (Table 3, entries 2-6), 2-formylbenzoic acid was converted into *N*-substituted isoindolinones in good to excellent yields. Here too, electron-donating (Table 3, entry 3), electron-withdrawing (Table 3, entry 4) and bulky amines (Table 3, entries 5, 6) were efficiently transformed into the desired compounds.

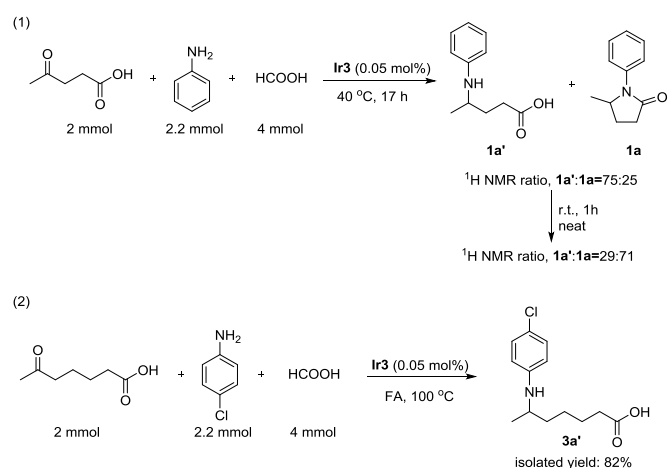
Table 3. Ir3-catalyzed reductive amination of 2-formylbenzoic acid: Substrate scope^a

Entry	Substrate	Product	Yield ^b (%)
1			93
2			96
3			90



^a Reaction conditions: 2-formylbenzoic (2 mmol), amine (2.2 mmol), HCOOH (4 mmol), **Ir3** (0.05 mol%), water (2 mL), 60 °C (oil bath), 17 h. ^b Isolated yield

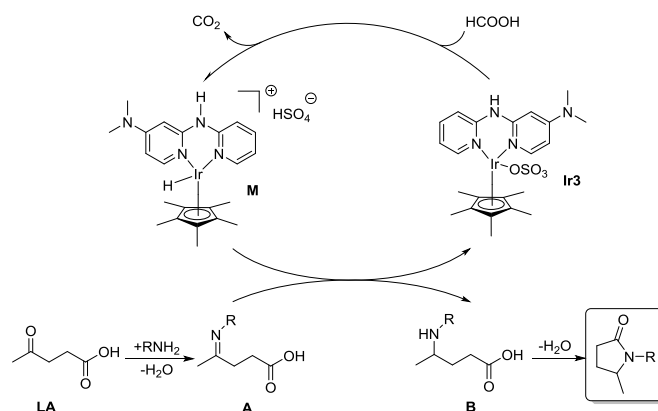
Following our investigations on the efficiency and scope of the reaction, we turned our attention to the reaction pathways. As generally accepted, the reaction mechanism first involves the formation of an imine and further reduction to the corresponding amine, which in turn reacts in an intramolecular fashion with the carboxylic acid. As observed in the initial optimization of the reaction conditions, an amine was detected as a side-product upon decreasing the reaction temperature to 40 °C. This reaction at 40 °C in the presence of 0.05 mol% of **Ir3** (Scheme 2, 1) was repeated and produced the expected mixture of **1a'**:**1a** in a 75:25 ratio. After solvent removal, this crude reaction mixture was left stirring for an additional hour resulting in an inverted 21/79 ratio of amine/pyrrolidone. This result demonstrates that the reaction mechanism follows the generally proposed mechanism. To confirm this transient amine intermediate, the reaction was performed with 6-oxo-heptanoic acid and 4-chloroaniline since, as observed in the initial screening, long chain derivatives are less reactive. As anticipated, the intermediate amine **3a'** was isolated in good yield without detection of the 7-membered cyclic product (Scheme 2).



Scheme 2. Reaction intermediates

On the basis of the above results and considering that an iridium hydride complex can be obtained upon reacting **Ir3** with formic acid,¹⁵ a plausible reaction pathway is proposed in Scheme 3. It must be mentioned that according to our previous studies,¹⁵ the reaction likely proceeds by transfer hydrogenation with FA but also by hydrogenation resulting

from the fast dehydrogenation of formic acid into carbon dioxide and dihydrogen. In both cases the key catalytic step is the reduction of the imine **A** by the metal-hydride species **M** leading to the amino-acid **B** which upon cyclisation delivers the desired product.



Scheme 3. Reaction pathway of reductive amination of LA.

Conclusions

In summary, we have achieved the reductive amination of levulinic acid into a number of pyrrolidone derivatives with direct extension to the synthesis of piperidones and *N*-arylisindolinones. Unlike most of the reported catalytic processes, our catalyst could efficiently involve very bulky amines. Most of all, this catalytic method makes use of the easily accessible and safe to handle formic acid as hydrogen source and a biosourced substrate hence ensuring a safe and sustainable process, the single co-product of the reaction being carbon dioxide. The green and sustainable features of this process are further strengthened by the mild reaction conditions and the use of an aqueous media. Nevertheless, efforts will be necessary to improve further the catalytic performances since we are using a rather expensive noble metal. The search for catalysts based on more accessible transition metals is currently underway in our group.

Experimental Section

Levulinic acid (98%), amines and 2,2'-dipyridylamine (98%) were purchased from Sigma-Aldrich. Water was HPLC grade and used as received. **Ir1**, **Ir2**, **Ir3**, **Ir4** were synthesized according to the previous synthetic procedures.¹⁵ NMR spectra were recorded on a Bruker Avance I 300 MHz or Avance III 400 MHz spectrometers.

General procedure for reductive amination of LA: Levulinic acid (2 mmol) or formylbenzoic acid (2 mmol), formic acid (4 mmol), amine (2.2 mmol), catalyst (0.01–0.05 mol %) and 2 mL of water were added to a heavy walled Schlenk tube equipped with a Teflon screw cap. The mixture was stirred at the appropriate temperature for the desired time. Volatile compounds were removed under vacuum. The crude mixtures were analysed by ¹H NMR. and purified by column

chromatography using petroleum ether and ethyl acetate with 1% triethylamine as eluent.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors acknowledge the China Scholarship Council for a grant to SW.

Notes and references

- 1 a) J. R. Rostrup-Nielsen, *Science* 2005, **308**, 1421-1422; b) G. W. Huber, S. Iborra, A. Corma, *Chem. Rev.* 2006, **106**, 4044-4098; c) A. Corma, S. Iborra, A. Velty, *Chem. Rev.* 2007, **107**, 2411-2502; d) P. Gallezot, *Catal. Today* 2007, **121**, 76-91; e) L. D. Schmidt and P. J. Dauenhauer, *Nature* 2007, **447**, 914-915; f) G. Yong, Y. Zhang, J. Y. Ying, *Angew. Chem., Int. Ed.* 2008, **47**, 9345-9348; g) J. J. Bozell, G. R. Petersen, *Green Chem.* 2010, **12**, 539-554; h) J. C. Serrano-Ruiz, J. A. Dumesic, *Energy Environ. Sci.* 2011, **4**, 83-99; i) P. Gallezot, *Chem. Soc. Rev.* 2012, **41**, 1538-1558; j) L. T. Mika, E. Cséfalvay, Á. Németh, *Chem. Rev.* 2018, **118**, 505-613; k) Z. Xue, Q. Liu, J. Wang, T. Mu, *Green Chem.* 2018, **20**, 4391-4408.
- 2 a) F. D. Pileidis, M.-M. Titirici, *ChemSusChem*, 2016, **9**, 562-582; b) L. Yan, Q. Yao, Y. Fu, *Green Chem.* 2017, **19**, 5527-5547; c) Z. Xue, Q. Liu, J. Wang, T. Mu, *Green Chem.* 2018, **20**, 4391-4408; d) U. Omoruyi, S. Page, J. Hallett, P. W. Miller, *ChemSusChem* 2016, **9**, 2037-2047; e) F. Liguori, C. Moreno-Marrodan, P. Barbaro, *ACS Catal.* 2015, **5**, 1882-1894; f) J. M. Tukacs, T. A. Holló, N. Rétfalvi, E. Cséfalvay, G. Dibó, D. Havasi, L. T. Mika, *ChemistrySelect*, 2017, **2**, 1375-1380
- 3 a) I. T. Horváth, H. Mehdi, V. Fabos, L. Boda, L. T. Mika, *Green Chem.* 2008, **10**, 238-242; b) M. Mehdi, V. Fabos, R. Tuba, A. Bodor, L. T. Mika, I. T. Horváth, *Top. Catal.* 2008, **48**, 49-54; c) L. Deng, J. Li, D. Lai, Y. Fu, Q. G., *Angew. Chem. Int. Ed.* 2009, **48**, 6529-6532; d) J. Q. Bond, D. M. Alonso, D. Wang, R. M. West, J. A. Dumesic, *Science* 2010, **327**, 1110-1114; e) J. Deng, Y. Wang, T. Pan, Q. Xu, Q.-X. Guo, Y. Fu, *ChemSusChem* 2013, **6**, 1113-1167.
- 4 a) L. Qi, I. T. Horvath, *ACS Catal.* 2012, **2**, 2247-2249; b) X. Tian, F. Yang, D. Rasina, M. Bauer, S. Warratz, F. Ferlin, L. Vaccaro, L. Ackermann, *Chem. Commun.* 2016, **52**, 9777-9780; c) S. Santoro, F. Ferlin, L. Luciani, L. Ackermann, L. Vaccaro, *Green Chem.* 2017, **19**, 1601-1612; d) G. Strappaveccia, L. Luciani, E. Bartollini, A. Marrochi, F. Pizzo, L. Vaccaro, *Green Chem.* 2015, **17**, 1071-1076; e) F. Ferlin, L. Luciani, S. Santoro, A. Marrocchi, D. Lanari, A. Bechtoldt, L. Ackermann, L. Vaccaro, *Green Chem.* 2018, **20**, 2888-2893; f) P. Pongrácz, L. Kollár, L. T. Mika, *Green Chem.*, 2016, **18**, 842-847; g) D. Marosvölgyi-Haskó, B. Lengyel, J. M. Tukacs, L. Kollár, L. T. Mika, *ChemPlusChem*, 2016, **81**, 1224-1229.
- 5 a) A. P. Dunlop, S. Smith, US Patent 2676186, 1955; b) N. Sonoda, S. Tsutsumi, *Bull. Chem. Soc. Jpn.* 1963, **36**, 1311-1313; c) R. Kawasumi, S. Narita, K. Miyamoto, K.-i. Tominaga, R. Takita, M. Uchiyama, *Scientific Reports*, 2017, **7**, 17967; D. Carnevali, M. G. Rigamonti, T. Tabanelli, G. S. Patience, F. Cavani, *Applied Catal A: Gen*, 2018, **563**, 98-104.
- 6 a) Y. Isoda; M. Azuma, JP08053390, 1994; b) L. E. Manzer, US6743819B1, 2004; c) L. E. Manzer, US20060247443A1, 2006; d) A. Mehdinia; A. Ghassempour; H. Rafati; R. Heydari, *Analytica Chimica Acta*, 2007, **587**, 82-88; e) S. Shorvon, *The Lancet*, 2001, **358**, 1885-1892.
- 7 S. Wang, H. Huang, C. Bruneau, C. Fischmeister, *ChemSusChem* 2017, **10**, 4150-4154.
- 8 X.-Y. Liu, C.-H. Li, and C.-M. Che, *Org. Lett.* 2006, **8**, 2707-2710.
- 9 J. Davies, T. D. Svejstrup, D. Reina, N.S. Sheikh, D. Leonori, *J. Am. Chem. Soc.* 2016, **138**, 8092-8095.
- 10 M.-C. Fu, R. Shang, W.-M. Cheng, Y. Fu, *Angew. Chem. Int. Ed.* 2015, **54**, 9042-9046.
- 11 D. C. Miller, G.J. Choi, H. S. Orbe, R. R. Knowles, *J. Am. Chem. Soc.* 2015, **137**, 13492-13495.
- 12 R. L. Frank, W. R. Smith, B. Zeidman, *Org. Synth.* 1947, **27**, 28.
- 13 a) 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; b) A. S. Touchy, S. M. A. H. Siddiki, K. Kon, K.-i. Shimizu, *ACS Catal.* 2014, **4**, 3045-3050; c) C. Ortiz-Cervantes, M. Flores-Alamo, J. J. García, *Tetrahedron Lett.* 2016, **57**, 766-771; d) Z. Sun, J. Chen, T. Tu, *Green Chem.* 2017, **19**, 789-794; e) A. S. Amarasekara, Y. M. Lawrence, *Tetrahedron Lett.* 2018, **59**, 1832-1835; f) G. Gao, P. Sun, Y. Li, F. Wang, Z. Zhao, Y. Qin, F. Li, *ACS Catal.* 2017, **7**, 4927-4935; g) J. Zhang, B. Xie, L. Wang, X. Yi, C. Wang, G. Wang, Z. Dai, A. Zheng, F.-S. Xiao, *ChemCatChem* 2017, **9**, 2661-2667; h) J. D. Vidal, M. J. Climent, A. Corma, D. P. Concepcion, S. Iborra, *ChemSusChem* 2017, **10**, 119-128; i) J. J. Martínez, L. Silva, H. A. Rojas, G. P. Romanelli, L. A. Santos, T. C. Ramalho, M. H. Brijaldo, F. B. Passos, *Catal.Today* 2017, **296**, 118-126; j) S. M. A. H. Siddiki, A. S. Touchy, A. Bhosale, T. Toyao, Y. Mahara, J. Ohyama, A. Satsuma, K. Shimizu, *ChemCatChem* 2018, **10**, 789-795; k) I. Ogino, Y. Suzuki, S. R. Mukai, *Catal. Today* 2018, **314**, 62-69; l) P. Cao, T. Ma, H.-Y. Zhang, G. Yin, J. Zhao, Y. Zhang, *Catal. Commun.* 2018, **116**, 85-90; m) C. Xie, J. Song, H. Wu, Y. Hu, H. Liu, Z. Zhang, P. Zhang, B. Chen, B. Han, *J. Am. Chem. Soc.* 2019, **141**, 4002-4009; n) M. Muzzio, C. Yu, H. Lin, T. Yom, D. A. Boga, Z. Xi, N. Li, Z. Yin, J. Li, J. A. Dunn, S. Sun, *Green Chem.* 2019, 10.1039/C9GC00396G.
- 14 a) Y.-B. Huang, J.-J. Dai, X.-J. Deng, Y.-C. Qu, Q.-X. Guo, Y. Fu, *ChemSusChem* 2011, **4**, 1578-1581; b) Y. Wei, C. Wang, X. Jiang, D. Xue, J. Li, J. Xiao, *Chem. Commun.* 2013, **49**, 5408-5410; c) Y. Wei, C. Wang, X. Jiang, D. Xue, Z.-T. Liu, J. Xiao, *Green Chem.* 2014, **16**, 1093-1096; d) A. Ledoux, L. Sandjong Kuigwa, E. Framery, B. Andrioletti, *Green Chem.* 2015, **17**, 3251-3254; e) Y. Ogiwara, T. Uchiyama, N. Sakai, *Angew. Chem. Int. Ed.* 2016, **55**, 1864-1867; f) C. Wu, H. Zhang, B. Yu, Y. Chen, Z. Ke, S. Guo, Z. Liu, *ACS Catal.* 2017, **7**, 7772-7776; g) Z. Xu, P. Yan, H. Jiang, K. Liu, Z. C. Zhang, *Chin. J. Chem.* 2017, **35**, 581-585; h) C. Wu, X. Luo, H. Zhang, X. Liu, G. Ji, Z. Liu, Z. Liu, *Green Chem.* 2017, **19**, 3525-3529; i) G. Metzker, R. M. P. Dias, A. C. B. Burtoloso, *Chemistry Select* 2018, **3**, 368-372; j) D. Wei, C. Netkaew, C. Darcel, *Adv. Synth. Catal.* 2019, 10.102/adsc.201801656
- 15 a) S. Wang, V. Dorcet, T. Roisnel, C. Bruneau, C. Fischmeister, *Organometallics* 2017, **36**, 708-713; b) S. Wang, H. Huang, V. Dorcet, T. Roisnel, C. Bruneau, C. Fischmeister, *Organometallics* 2017, **36**, 3152-3162; c) S. Wang, H. Huang, T. Roisnel, C. Bruneau, C. Fischmeister, *ChemSusChem* 2019, **12**, 179-184; d) S. Wang, H. Huang, C. Bruneau, C. Fischmeister, *ChemSusChem*, 2019, DOI: 10.1002/cssc.201900626.
- 16 a) D. Rodríguez-Padrón, A. R. Puente-Santiago, A. M. Balu, A. A. Romero, M. J. Muñoz-Batista, R. Luque, *ACS Sustainable Chem. Eng.* 2018, **6**, 16637-16644; b) C. Altuğ, M. J. Muñoz-Batista, D. Rodríguez-Padrón, A. M. Balu, A. A. Romero, R. Luque, *Green Chem.* 2019, **21**, 300-306.
- 17 T. Brouwer, M. Blahusiak, K. Babic, B. Schuur, *Sep. Purif. Technol.* 2017, **185**, 186-195.