

Supported by



Accepted Article

Title: Utilization of renewable formic acid from lignocellulosic biomass for the selective hydrogenation and/or N-methylation

Authors: Yang Li, Chao-Zheng Zhou, Yu-Rou Zhao, Fang-Fang Tan, and Yan-Jun Guo

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: *ChemCatChem* 10.1002/cctc.202101099

Link to VoR: <https://doi.org/10.1002/cctc.202101099>

Utilization of renewable formic acid from lignocellulosic biomass for the selective hydrogenation and/or N-methylation

Chao-Zheng Zhou, Yu-Rou Zhao, Fang-Fang Tan, Yan-Jun Guo & Yang Li*

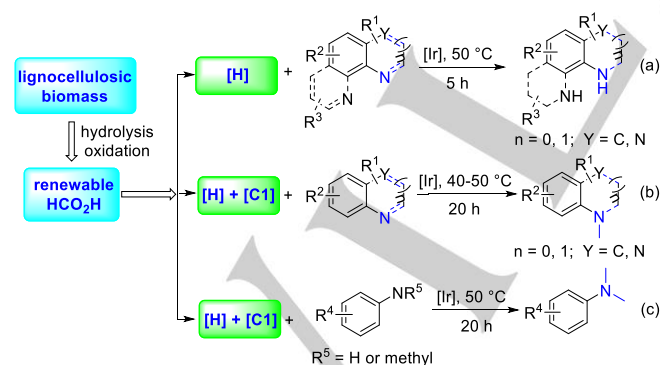
C.-Z. Zhou, Y.-R. Zhao, F.-F. Tan, Y.-J. Guo, and Prof. Y. Li
Center for Organic Chemistry of Frontier Institute of Science and Technology and State Key Laboratory of Multiphase Flow in Power Engineering
Xi'an Jiaotong University
Shaanxi, 710054 (China)
E-mail: liyq79@mail.xjtu.edu.cn

Supporting information for this article is given via a link at the end of the document.

Abstract: Lignocellulosic biomass is one of the most abundant renewable sources in nature. Herein, we have developed the utilization of renewable formic acid from lignocellulosic biomass as a hydrogen source and a carbon source for the selective hydrogenation and further N-methylation of various quinolines and the derivatives, various indoles under mild conditions in high efficiencies. N-methylation of various anilines is also developed. Mechanistic studies indicate that the hydrogenation occurs via a transfer hydrogenation pathway.

Introduction

Due to the dwindling supply of fossil resources, it is highly desirable to explore renewable resources for the sustainable development. Formic acid (HCO₂H),^[1] is widely used in various chemical processes, such as hydrogen source for the hydrogenation,^[2] and as C1 source for the N-methylation.^[3] Lignocellulosic biomass is one of the most abundant renewable sources in nature. Utilization of renewable HCO₂H from lignocellulosic biomass,^[4] would contribute to the sustainable hydrogenation and N-methylation.



Scheme 1 Utilization of the hydrogen source and carbon source from lignocellulosic biomass.

In this regard, we developed hydrolysis-oxidation of the lignocellulosic biomass into HCO₂H in up to quantitative yield, even in near 10-gram scale, by a NaVO₃-DMSO-H₂SO₄ catalytic system using air/oxygen as an oxidant.^[5] Renewable HCO₂H not only can produce green hydrogen (H₂),^[5] but also can be used for the hydrogenation directly, such as reduction of nitroarenes to arylamines.^[6] Moreover, renewable HCO₂H disproportionation

into CH₂O triggered by vanadium complexes, contained in the lignocellulosic biomass hydrolysis-oxidation aqueous solution (HOAS), with iridium catalysis was discovered in the N-methylation of the quinoline. The gram-scale reaction was also demonstrated.^[7]

Herein, we report efficient utilization of renewable HCO₂H from lignocellulosic biomass, wheat straw, for hydrogenation and further N-methylation of various quinolones and the derivatives, various indoles under mild conditions (Scheme 1a and 1b). Meanwhile, N-methylation of various anilines is also developed under mild conditions (Scheme 1c).

Results and Discussion

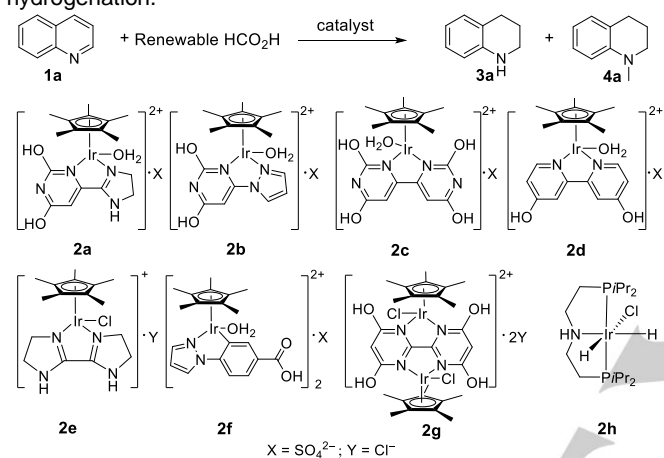
Hydrogenation of quinolines and indoles

Initially, quinoline (**1a**) was selected as a model substrate for the hydrogenation^[2c,2f,2k-n,2s-w] by applying renewable HCO₂H (6 equiv, contained in the wheat straw HOAS) at 80 °C without extra solvent (Table 1). In the wheat straw HOAS, minor components of [V] (4 mol%), DMSO (7 mol%), DMSO₂ (8 mol%), 1,4-dioxane (13 mol%), HOAc (7 mol%), MeOH (2 mol%) and Na₂SO₄ (12 mol%) were also contained besides HCO₂H as a major component.^[5] The iridium catalyst containing the ligands of Cp* and 6-(4,5-dihydro-1H-imidazol-2-yl)pyrimidine-2,4-diol (**2a**)^[8] was tested based on its excellent activity during H₂ production from the wheat straw HOAS (Table 1, entry 1).^[5] Tetrahydroquinoline **3a** was obtained in 40% yield accompanying with N-methyl-tetrahydroquinoline **4a** in 14% yield (Table 1, entry 1). Various iridium catalysts containing Cp* with N,N-ligands including 6-(1H-pyrazol-1-yl)pyrimidine-2,4-diol (**2b**),^[8] 2,2',6,6'-tetrahydroxy-4,4'-bipyrimidine,4,4'-dihydroxy-2,2'-bipyridine (**2c**),^[9] 2,2'-biimidazolin (**2e**)^[10] and C,N-ligand of 4-(1H-pyrazol-1-yl)benzoic acid (**2f**),^[11] dinuclear Cp*Ir bearing 4,4',6,6'-tetrahydroxy-2,2'-bipyrimidine (**2g**)^[12] as well as IrH₂Cl(PNP)^{i-Pr} [PNP = HN[CH₂CH₂(PR₂)₂]₂, R = *i*-Pr] (**2h**)^[13] were tested further (Table 1, entries 2-8). Except of no conversion by using **2h** as a catalyst (Table 1, entry 8), other iridium catalysts induced the conversions with the different yields of **3a** and **4a** (Table 1, entry 2-7). Notably, catalyst **2d**^[9] resulted higher yields of **3a** in 62% (Table 1, entry 4). No activities were observed for other catalysis systems of [IrCl(coe)₂]₂, [Cp*IrCl₂]₂, [RuCl₂(benzene)]₂ with dppe,^[14] RuCl₃ with *m*-TPPTS,^[15] and Fe(BF₄)₂ with (Ph₂PCH₂CH₂)₃P^[16] (Table 1, entries 9-13). Decreasing the amount of renewable HCO₂H to 2.5

FULL PAPER

equiv induced **3a** in 79% yield (Table 1, entries 16). Further decreasing the reaction temperature to 50 °C, the yield of **3a** was increased to 93% with trace amount of **4a** (Table 1, entry 18). Moreover, the reaction time can be shortened in 5 h with **3a** in 92% yield (Table 1, entry 19). The lower temperature with higher reaction efficiency may attribute to decrease the decomposition of HCO₂H to H₂ and CO₂ to increase the possibility of transfer hydrogenation pathway. And more equiv of renewable HCO₂H with lower reaction efficiency should attribute to the further N-methylation.^[7] To demonstrate the potential application of the hydrogenation of quinoline, the gram-scale reaction was conducted by using quinoline **1a** as a substrate. With 0.25 mol% **2d**, 0.8 g of **3a** was obtained in 81% yield by using 1.0 g wheat straw for production of renewable HCO₂H (Table 1, entry 20).

Table 1. Optimization of the reaction conditions for the hydrogenation.

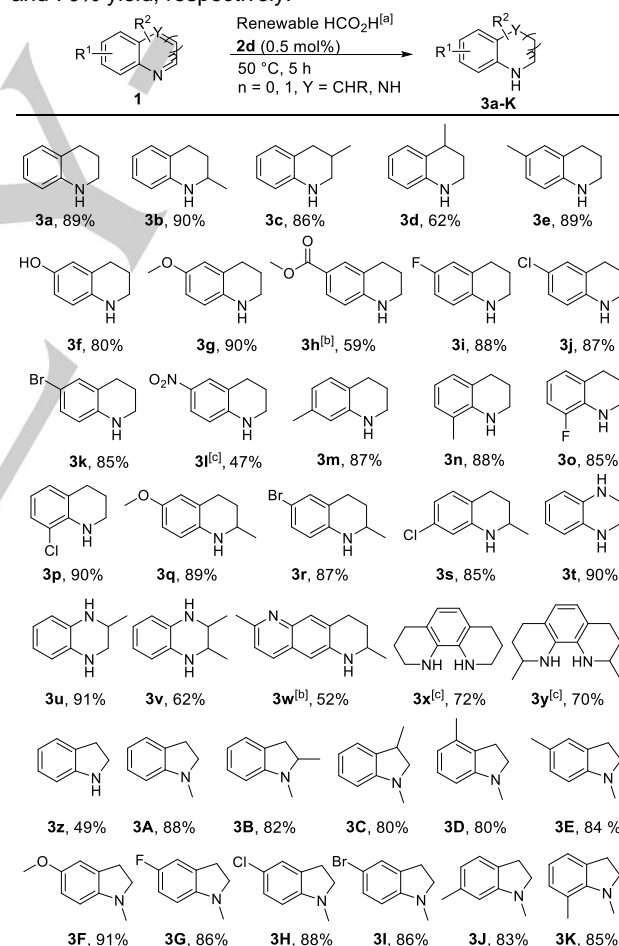


Entry ^[a]	Catalyst (mol%)	Renewable HCO ₂ H (equiv)	T (°C)	Time (h)	3a ^[b]	4a ^[b]
1	2a (0.5)	6	80	10	40	14
2	2b (0.5)	6	80	10	54	22
3	2c (0.5)	6	80	10	45	16
4	2d (0.5)	6	80	10	62	25
5	2e (0.5)	6	80	10	40	12
6	2f (0.5)	6	80	10	52	17
7	2g (0.25)	6	80	10	51	19
8	2h (0.5)	6	80	10	—	—
9	[IrCl(coe) ₂] ₂ (0.25)	6	80	10	—	—
10	[Cp*IrCl ₂] ₂ (0.25)	6	80	10	—	—
11	[RuCl ₂ (benzene)] ₂ (0.25)/dppe (0.5)	6	80	10	—	—
12	RuCl ₃ (0.5)/m-TPPTs (0.25)	6	80	10	—	—
13	Fe(BF ₄) ₂ (0.5)/(Ph ₂ PCH ₂ CH ₂) ₃ P (0.5)	6	80	10	—	—
14	2d (0.5)	6	60	10	63	20
15	2d (0.5)	3	60	10	74	9
16	2d (0.5)	2.5	60	10	79	6
17	2d (0.5)	2	60	10	68	<5
18	2d (0.5)	2.5	50	10	93	<5
19	2d (0.5)	2.5	50	5	92 (89) ^[c]	<5
20 ^[d]	2d (0.25)	2.5	50	13	81 ^[c]	<5

[a] Reaction conditions: quinoline **1a** (0.5 mmol, 64.5 mg), renewable HCO₂H contained in the wheat straw HOAS, catalyst. [b] Yields were determined by ¹H NMR using Cl₂CHCHCl₂ as an internal standard. [c] Isolated yield. [d] Quinoline **1a** (7.74 mmol, 1.0 g), renewable HCO₂H produced by 1.0 g wheat straw.

Under the optimized reaction conditions, the substrate scope was investigated (Scheme 2). Generally, both electron-donating groups and electron-withdrawing groups were well tolerated.

Similar to the quinoline, 2-methylquinoline, 3-methylquinoline, 6-methylquinoline displayed good reaction efficiencies (**3b**, **3c**, **3e**). 4-Methylquinoline induced lower reaction efficiency with **3d** in 62% yield. Changing the substituents, from methyl to hydroxyl, methoxy, on 6-position of the quinoline resulted in good to excellent yields (**3f**, **3g**). 6-Fluoro, 6-chloro, 6-bromo groups induced high efficiencies (**3i**–**3k**) and 6-ester group induced **3h** in 59%. 6-Nitroquinoline afforded **3l** in 47% yield, which may be caused by the low solubility of 6-nitroquinoline in the reaction system. 7-Methyl, 8-methyl, 8-fluoro and 8-chloro groups induced excellent efficiencies (**3m**–**3p**). Moreover, quinolines bearing two substituents, 6-methoxy with 2-methyl groups, 6-bromo with 2-methyl groups, and 7-chloro with 2-methyl groups also induced high efficiencies (**3q**–**3s**). The method was also applied to the hydrogenation of the quinoxaline and 2-methylquinoxaline to give excellent yields (**3t**, **3u**). 2,3-dimethylquinoxaline gave **3v** in 62% yield. 2,7-dimethylpyrido[2,3-g]quinoline was tested for the hydrogenation, but only one N-heterocyclic ring was hydrogenated to afford **3w** in 52% yield. Interestingly, two N-heterocyclic rings of 1,10-phenanthroline and 2,9-dimethyl-1,10-phenanthroline were hydrogenated to afford **3x** and **3y** in 72% and 70% yield, respectively.



Scheme 2. The substrate scope of hydrogenation quinolines, indoles and the derivatives.

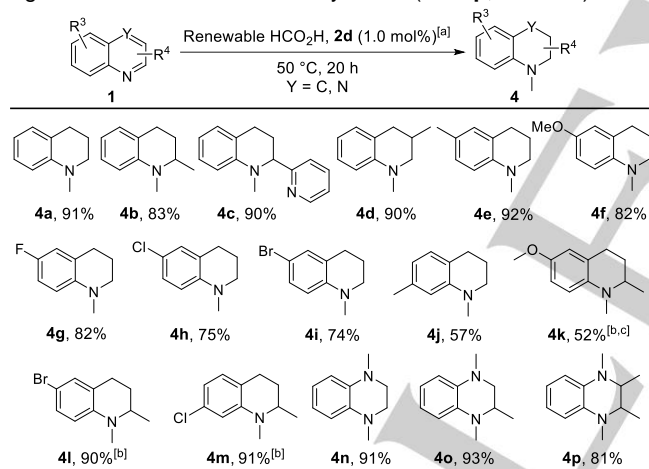
[a] Reaction conditions: substrate **1** (0.5 mmol), 2.5 equiv of renewable HCO₂H contained in the wheat straw HOAS, **2d** (0.5 mol%), isolated yields are reported. [b] 5.0 equiv of renewable HCO₂H, 60 °C, 10 h. [c] 5.0 equiv of renewable HCO₂H, 60 °C, 15 h.

FULL PAPER

Next, hydrogenation of various indoles was tested (Scheme 2, **3z–3k**). Under the optimal reaction conditions, the indole afforded **3z** in 49% yield. N-methyl indole afforded **3A** in 88% yield. N-methyl-indoles bearing methyl groups on the 2-, 3-, 4-, 5-, 6- and 7-positions, as well as 5-methoxy, 5-fluoro, 5-chloro, 5-bromo groups resulted in high efficiencies (**3B–3K**).

N-Methylation of quinolines, indoles, anilines and the derivatives

We discovered that renewable HCO₂H disproportionation into CH₂O triggered by vanadium complexes with iridium catalysis in the N-methylation of quinoline **1a** under mild conditions. Under optimized conditions, 30 equiv of renewable HCO₂H contained in wheat straw HOAS with 1 mol% of **2d**, **4a** was obtained in 91% yield in 20 h.^[7] Gram-scale N-methylation of **1a** afforded **4a** in 91% yield.^[7] The substrate scope was investigated (Scheme 3). Various substituents on different positions of quinoline were studied. Methyl, methoxy, fluoro, bromo, chloro were well tolerated with the products of **4b**, **4d–4i** in 74–92% yields. The pyridyl was kept untouched with **4c** in 90% yield. Relatively lower yields of **4h** and **4i** are caused by poor solubility of the starting materials. 7-Methyl resulted in **4j** in 57% yield with some unconverted starting material. Moreover, the substrates containing two substituents of methyl with bromo or chloro displayed excellent efficiencies (**4l** in 90%, **4m** in 91%). **4k** was obtained in 52% yield with the hydrogenation product **3q** in 24% yield. Notably, various methyl substituted quinoxalines showed high activities for double N-methylations (**4n–4p**, 81–93%).

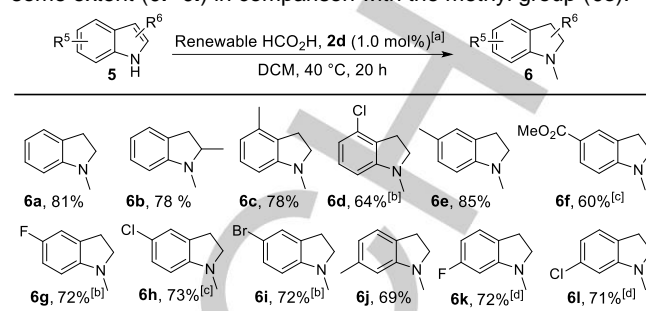


Scheme 3. The substrate scope of N-methylation of quinolines and quinoxalines.

[a] Reaction conditions: substrate **1** (0.25 mmol), 30 equiv of renewable HCO₂H contained in the wheat straw HOAS, **2d** (1.0 mol%), isolated yields are reported. [b] 60 °C. [c] **3q** was obtained in 24% yield.

Next, the N-methylation of the indole (**5a**) was conducted by this catalytic system to give some unidentified compounds (Scheme 4). When extra dichloromethane (DCM) was added as a solvent and the reaction temperature was decreased to 40 °C, 1-methylindoline (**6a**) was obtained in 81% yield. The influence of various substituents on different positions of indoles was detected. Methyl groups on 2-, 4-, 5- and 6-positions of the indoles resulted in 69–85% yields (**6b**, **6c**, **6e**, **6j**). Fluoro, chloro and bromo groups on 4-, 5- and 6-positions of the indoles induced 64–73% yields (**6d**, **6g–6i**, **6k–6l**). The ester group was also well tolerated

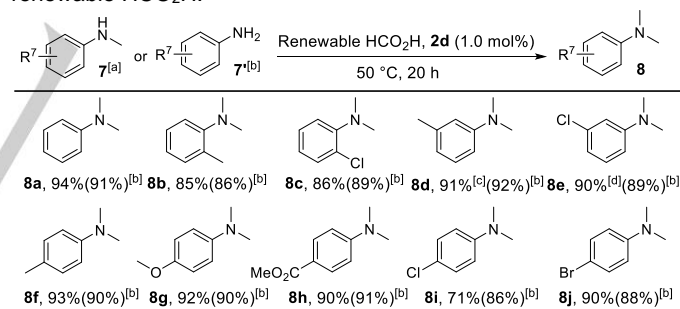
(**6f**). The electronic density of the substituents on the 5-position may directly affect the reactivity. Herein the electronic withdrawing groups displayed decreased reaction efficiencies to some extent (**6f–6i**) in comparison with the methyl group (**6e**).



Scheme 4. The substrate scope of N-methylation of indoles.

[a] Reaction conditions: substrate **5** (0.25 mmol), 30 equiv of renewable HCO₂H, **2d** (1.0 mol%), DCM (2.5 mL), isolated yields are reported. [b] Without DCM. [c] 50 °C, without DCM. [d] DCM (0.5 mL).

Furthermore, N-methylation of anilines were investigated (Scheme 5). By using the N-methyl aniline (**7a**) as the substrate, **8a** was obtained in excellent efficiency. Thus various N-methyl anilines were studied. Methyl as an example of electronic donating groups and chloro as an example of electronic donating groups on *ortho*- and *meta*-positions of anilines resulted in **8b–8e** in 85–91% yields. Methyl, methoxy, ester, bromo on *para*-position also resulted in excellent efficiencies (**8f–8h**, **8j**, 90–93%). Chloro induced a decreased efficiency with **8i** in 71% yield. Notably, methylation of the corresponding anilines (**7'**) also resulted in **8a–8j** in excellent yields (86–92%) with near double amount of renewable HCO₂H.



Scheme 5. The substrate scope of N-methylation of anilines.

[a] Reaction conditions: substrate **7** (0.25 mmol), 30 equiv of renewable HCO₂H contained in the wheat straw HOAS, **2d** (1.0 mol%), 50 °C, 20 h, isolated yields are reported. [b] Substrate **7'** (0.25 mmol), 56 equiv of renewable HCO₂H contained in the wheat straw HOAS, **2d** (1.0 mol%), 50 °C, 25 h, isolated yields are reported in parentheses. [c] 40 h. [d] 30 h. [e] 25 h.

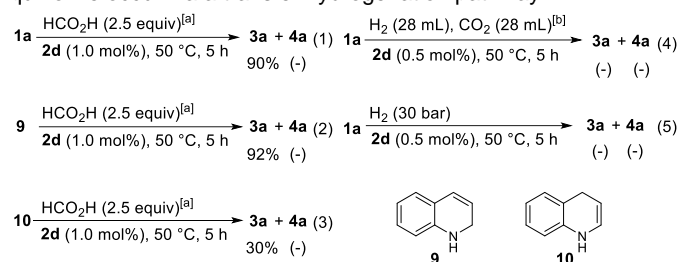
Mechanism studies

To give more insights into the reaction mechanism, a series of experiments were conducted. First, quinoline **1a**, the possible hydrogenation intermediate **9** or **10** was used as a starting material in the presence of 2.5 equiv of HCO₂H, respectively (Scheme 6, Eqs. 1, 2, 3). Hydrogenation product **3a** was obtained in 90%, 92% or 30% yield in 5 h (Scheme 6, Eqs 1, 2, 3). Regarding 30% yield of **3a** should be caused by the instability of compound **10** (Scheme 6, Eq. 3). Accompanying with HCO₂H,

FULL PAPER

other minor components including Na₂SO₄, HOAc, MeOH, 1,4-dioxane, DMSO, DMSO₂, CH₂O were also included in the wheat straw HOAS.^[5] These components were used as additives for hydrogenation of **1a** with HCO₂H, which did not cause distinct influence on the reaction yields (Table S2). These results suggest that HCO₂H contained in the wheat straw HOAS as the major active component for the hydrogenation via **9** and **10**.

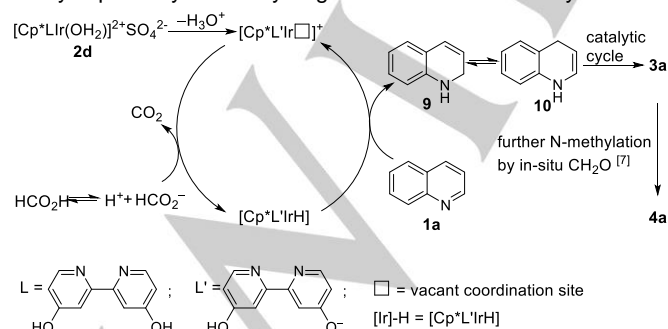
In addition, quinoline **1a** can not be hydrogenated under the atmosphere of H₂ and CO₂, which eques to the atmosphere of produced H₂ and CO₂ from 2.5 equiv of HCO₂H, or the higher H₂ pressure (30 bar H₂) under similar conditions (Scheme 6, Eqs. 4, 5). In comparison these results with the result of **3a** in 97% under optimized conditions, it indicates that the hydrogenation of quinoline occur via a transfer hydrogenation pathway.



Scheme 6. Control experiments.

[a] Reaction conditions: **1a**, **9**, **10** (0.5 mmol), **2d** (0.5 mol%), 50 °C, 20 h, aqueous solution. [b] H₂ (28 mL) and CO₂ (28 mL) was added into the reactor with less than 2 bar. The calculation of the volumes of H₂ and CO₂ is based on the amount of the produced H₂ and CO₂ from 2.5 equiv of HCO₂H. Yields were determined by ¹H NMR by using Cl₂CHCHCl₂ as an internal standard.

Quinoline **1a** was selected as a model substrate for the standard mercury (Hg) poisoning experiments.^[17] First, mercury was added before the reaction, **3a** was obtained in a comparable yield of 88%. Second, mercury was added after 1 h of the reaction to afford **3a** in a comparable yield of 86%. Third, mercury was added after 1 h of the reaction, **3a** was obtained in the yield of 43%, 60%, 86% after 2 h, 3 h, 5 h, in comparison with the yield of 45%, 64%, 87% after 2 h, 3 h, 5 h without mercury, respectively. The standard mercury poisoning experiments were also carried out for the N-methylation of quinoline **1a**,^[7] indole **5a** and aniline **7a'**. **4a**, **6a**, **8a**, were obtained in the yield of 87%, 76%, 92%, in comparison with the yield of 91%, 81%, 91% under standard conditions, respectively. These results indicate homogeneous catalytic pathway for the hydrogenation and the N-methylation.



Scheme 7. The proposed mechanism.

Based on these results, we propose a plausible reaction pathway of the hydrogenation as shown in Scheme 7. The iridium catalyst precursor **2d** releases H₃O⁺ to afford the [Cp*L'lr]²⁺

complex (L' = the anion of 4,4'-dihydroxy-2,2'-bipyridine), which is followed by coordination with formate (HCO₂⁻) and decarboxylation to generate the [Ir]-H complex of [Cp*L'lrH]. The [Cp*L'lrH] complex was observed by ESI-MS as 517.1462 ([M+H]⁺) under optimized conditions.^[9] **1a** is hydrogenated to **3a** via **9** and **10** by the [Ir]-H complex.^[9] Next, **3a** is further N-methylated to afford **4a**.^[7]

Conclusion

We have developed the utilization of renewable HCO₂H produced from lignocellulosic biomass for the selective hydrogenation various quinolines and the derivatives, various indoles, and the further N-methylation of various quinolines and the derivatives, various indoles under mild conditions in high efficiencies. N-methylation of various anilines is also developed. It enriches the conversion and utilization of lignocellulosic biomass and would inspire utilization of renewable HCO₂H for various transformations.

Acknowledgements

This work was supported by National Key R&D Program of China (Nos: 2018YFB1501601) and the Instrument Analysis Center of the Xi'an Jiaotong University.

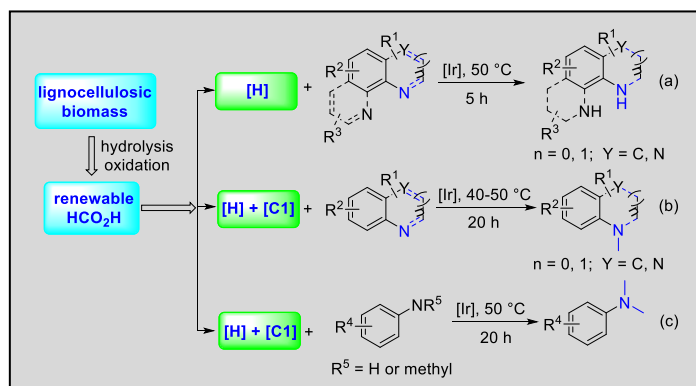
Keywords: renewable formic acid, lignocellulosic biomass, hydrogen source, hydrogenation, N-methylation

- [1] a) X. Yu, P. G. Pickup, *J. Power Sources* **2008**, *182*, 124-132; b) J. Hietala, A. Vuori, P. Johnsson, I. Pollari, W. Reutemann, H. Kieczka, Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim **2016**; c) <http://www.intermediates.basf.com/chemicals/formic-acid/applications>, accessed in August, 2020; d) S. Chatterjee, I. Dutta, Y. Lum, Z. Lai, K.-W. Huang, *Energy Environ. Sci.* **2021**, *14*, 1194-1246.
- [2] a) R. A. W. Johnstone, A. H. Wilby, *Chem. Rev.* **1985**, *85*, 129-170; b) A. Fujii, S. Hashiguchi, N. Uematsu, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1996**, *118*, 2521-2522; c) H. Li, H. Yin, F. Zhang, H. Li, Y. Huo, Y. Lu, *Environ. Sci. Technol.* **2009**, *43*, 188-194; d) O. Soltani, M. A. Ariger, H. Va'zquez-Villa, E. M. Carreira, *Org. Lett.* **2010**, *12*, 2893-2895; e) X. Liu, S. Li, Y. Liu, Y. Cao, *Chin. J. Catal.* **2015**, *36*, 1461-1475; f) D. Talwar, H. Y. Li, E. Durham, J. Xiao, *Chem. Eur. J.* **2015**, *21*, 5370-5379; g) H. Xu, P. Yang, P. Chuanpravit, H. Hirao, J. S. Zhou, *Angew. Chem. Int. Ed.* **2015**, *54*, 5112-5116; h) P. G. Echeverria, C. Féraud, P. Phansavath, V. Ratovelomanana-Vidal, *Catal. Commun.* **2015**, *62*, 95-99; i) C. Xu, L. Zhang, C. Dong, J. Xu, Y. Pan, Y. Li, H. Zhang, H. Li, Z. Yu, L. Xu, *Adv. Synth. Catal.* **2016**, *358*, 567-572; j) M. Butt, X. Feng, Y. Yamamoto, A. I. Almansour, N. Arumugam, R. S. Kumar, M. Bao, *Asian J. Org. Chem.* **2017**, *6*, 867-872; k) B. Vilhanová, J. A. van Bokhoven, M. Ranocchiaro, *Adv. Synth. Catal.* **2017**, *359*, 677-686; l) H. Yang, R. Nie, W. Xia, X. Yu, D. Jin, X. Lu, D. Zhou, Q. Xia, *Green Chem.* **2017**, *19*, 5714-5722; m) J.-F. Zhang, R. Zhong, Q. Zhou, X. Hong, S. Huang, H.-Z. Cui, X.-F. Hou, *ChemCatChem* **2017**, *9*, 2496-2505; n) G. Li, H. Yang, H.

FULL PAPER

- Zhang, Z. Qi, M. Chen, W. Hu, L. Tian, R. Nie, W. Huang, *ACS Catal.* **2018**, *8*, 8396-8405; o) Z. Yang, W. Cheng, Z. Li, *Catal. Commun.* **2018**, *117*, 38-42; p) A. Matsunami, Y. Kayaki, *Tetrahedron Lett.* **2018**, *59*, 504-513; q) W. Wu, T. Seki, K. L. Walker, R. M. Waymouth, *Organometallics* **2018**, *37*, 1428-1431; r) G. K. Zielinski, J. Majtczak, M. Gutowski, K. Grela, *J. Org. Chem.* **2018**, *83*, 2542-2553; s) A. K. Kar, R. Srivastava, *ACS Sustainable Chem. Eng.* **2019**, *7*, 13136-13147; t) M. Butt, Y. Zhao, X. Feng, Y. Lu, T. Jin, Y. Yamamoto, M. Bao, *ChemistrySelect* **2019**, *4*, 6572-6577; u) Y. Pan, Z. Luo, X. Xu, H. Zhao, J. Han, L. Xu, Q. Fan, J. Xiao, *Adv. Synth. Catal.* **2019**, *361*, 3800-3806; v) S. Zhou, F. Dai, C. Dang, M. Wang, D. Liu, F. Lu, H. Qi, *Green Chem.* **2019**, *21*, 4732-4747; w) P. Pandey, P. Daw, N. U. Din Reshi, K. R. Ehmann, M. Hölscher, W. Leitner, J. K. Bera, *Organometallics* **2020**, *39*, 3849-3863; x) B. He, P. Phansavath, V. Ratovelomanana-Vidal, *Org. Chem. Front.* **2020**, *7*, 975-979; y) A. H. Romero, *ChemistrySelect* **2020**, *5*, 13054-13075; z) J. Wang, G. Zhang, M. Liu, Q. Xia, X. Yu, W. Zhang, J. Shen, C. Yang, X. Jin, *Chem. Eng. Sci.* **2020**, 222; aa) R. Luo, Y. Xia, L. Ouyang, J. Liao, X. Yang, *SynOpen* **2021**, *05*, 36-42.
- [3] a) S. Savourey, G. Lefevre, J. C. Berthet, T. Cantat, *Chem. Commun.* **2014**, *50*, 14033-14036; b) I. Sorribes, K. Junge, M. Beller, *Chem. Eur. J.* **2014**, *20*, 7878-7883; c) J. Zheng, C. Darcel, J. B. Sortais, *Chem. Commun.* **2014**, *50*, 14229-14232; d) M. C. Fu, R. Shang, W. M. Cheng, Y. Fu, *Angew. Chem. Int. Ed.* **2015**, *54*, 9042-9046; e) Y. Li, I. Sorribes, C. Vicent, K. Junge, M. Beller, *Chem. Eur. J.* **2015**, *21*, 16759-16763; f) A. K. Singh, Y.-H. Hwang, D.-P. Kim, *NPG Asia Mater.* **2015**, *7*, 222; g) L. Zhu, L.-S. Wang, B. Li, W. Li, B. Fu, *Catal. Sci. Technol.* **2016**, *6*, 6172-6176; h) J. R. Cabrero-Antonino, R. Adam, K. Junge, M. Beller, *Catal. Sci. Technol.* **2016**, *6*, 7956-7966; i) C. Qiao, X. F. Liu, X. Liu, L. N. He, *Org. Lett.* **2017**, *19*, 1490-1493; j) E. Pedrajas, I. Sorribes, E. Guillamon, K. Junge, M. Beller, R. Llusar, *Chem. Eur. J.* **2017**, *23*, 13205-13212; k) J. R. Cabrero-Antonino, R. Adam, J. Wärnå, D. Y. Murzin, M. Beller, *Chem. Eng. J.* **2018**, *351*, 1129-1136; l) W. Liu, B. Sahoo, A. Spannenberg, K. Junge, M. Beller, *Angew. Chem. Int. Ed.* **2018**, *57*, 11673-11677; m) C. Qiao, X. Y. Yao, X. F. Liu, H. R. Li, L. N. He, *Asian J. Org. Chem.* **2018**, *7*, 1815-1818; n) Y. Wei, Q. Xuan, Y. Zhou, Q. Song, *Org. Chem. Front.* **2018**, *5*, 3510-3514; o) Y. Huang, W. Deng, B. L. Lin, *Chin. J. Chem.* **2020**, *31*, 111-114; p) F. Yan, S. Cai, W. Wen, W. Wen, B. Li, L. Wang, L. Zhu, *Chin. J. Org. Chem.* **2020**, *40*, 1874-1890.
- [4] a) M. Wang, J. Ma, H. Liu, N. Luo, Z. Zhao, F. Wang, *ACS Catal.* **2018**, *8*, 2129-2165; b) S. Li, W. Deng, S. Wang, P. Wang, D. An, Y. Li, Q. Zhang, Y. Wang, *ChemSusChem* **2018**, *11*, 1995-2028; c) D. A. Bulushev, J. R. H. Ross, *ChemSusChem* **2018**, *11*, 821-836; d) X. Chen, Y. Liu, J. Wu, *Mol. Catal.* **2020**, *483*, 110716-110731; e) Y. Hou, M. Niu, W. Wu, *Ind. Eng. Chem. Res.* **2020**, *59*, 16899-16910; f) F. Shen, R. L. Smith Jr, J. Li, H. Guo, X. Zhang, X. Qi, *Green Chem.* **2021**, *23*, 1536-1561; g) P. K. Sahoo, T. Zhang, S. Das, *Eur. J. Org. Chem.* **2021**, *2021*, 1331-1343.
- [5] P. Zhang, Y. J. Guo, J. Chen, Y. R. Zhao, J. Chang, H. Junge, M. Beller, Y. Li, *Nat. Catal.* **2018**, *1*, 332-338.
- [6] F. F. Tan, K. L. Tang, P. Zhang, Y. J. Guo, M. Qu, Y. Li, *ChemCatChem* **2019**, *11*, 4189-4195.
- [7] C. Z. Zhou, Y. R. Zhao, Y. J. Guo, P. Zhang, Y. Li, *Green Chem.* **2021**, *23*, 2918-2924.
- [8] W. H. Wang, M. Z. Ertem, S. Xu, N. Onishi, Y. Manaka, Y. Suna, H. Kambayashi, J. T. Muckerman, E. Fujita, Y. Himeda, *ACS Catal.* **2015**, *5*, 5496-5504.
- [9] W. H. Wang, S. Xu, Y. Manaka, Y. Suna, H. Kambayashi, J. T. Muckerman, E. Fujita, Y. Himeda, *ChemSusChem* **2014**, *7*, 1976-1983.
- [10] Z. Wang, S. M. Lu, J. Li, J. Wang, C. Li, *Chem. Eur. J.* **2015**, *21*, 12592-12595.
- [11] Y. Maenaka, T. Suenobu, S. Fukuzumi, *Energy Environ. Sci.* **2012**, *5*, 7360-7367.
- [12] J. F. Hull, Y. Himeda, W. H. Wang, B. Hashiguchi, R. Periana, D. J. Szalda, J. T. Muckerman, E. Fujita, *Nat. Chem.* **2012**, *4*, 383-388.
- [13] Z. E. Clarke, P. T. Maragh, T. P. Dasgupta, D. G. Gusev, A. J. Lough, K. Abdur-Rashid, *Organometallics* **2006**, *25*, 4113-4117.
- [14] A. Boddien, B. Loges, H. Junge, M. Beller, *ChemSusChem* **2008**, *1*, 751-758.
- [15] C. Fellay, P. J. Dyson, G. Laurenczy, *Angew. Chem. Int. Ed.* **2008**, *47*, 3966-3968.
- [16] A. Boddien, D. Mellmann, F. Gärtner, R. Jackstell, H. Junge, P. J. Dyson, G. Laurenczy, R. Ludwig, M. Beller, *Science* **2011**, *333*, 1733-1736.
- [17] J. A. Widegren, R. G. Finke, *J. Mol. Catal. A: Chem.* **2003**, *198*, 317-341.

Entry for the Table of Contents



Chao-Zheng Zhou, Yu-Rou Zhao, Fang-Fang Tan, Yan-Jun Guo, Yang Li *

Page No. – Page No.

Utilization of renewable formic acid from lignocellulosic biomass for the selective hydrogenation and/or N-methylation

Lignocellulosic biomass is one of the most abundant renewable sources in nature. Herein, we have developed the utilization of renewable formic acid from lignocellulosic biomass as a hydrogen source and a carbon source for the selective hydrogenation and further N-methylation of various quinolines and the derivatives, various indoles under mild conditions in high efficiencies. N-methylation of various anilines is also developed. Mechanistic studies indicate that the hydrogenation occurs via a transfer hydrogenation pathway.