CHEMISTRY AN ASIAN JOURNAL

www.chemasianj.org

Accepted Article

Title: Rhodium-terpyridine Catalyzed Transfer Hydrogenation of Aromatic Nitro Compounds in Water

Authors: Yuxuan Liu, Wang Miao, Weijun Tang, Dong Xue, Jianliang Xiao, Chao Wang, and Changzhi Li

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: Chem. Asian J. 10.1002/asia.202100321

Link to VoR: https://doi.org/10.1002/asia.202100321



ACES Asian Chemical Editorial Society A sister journal of Angewandte Chemie and Chemistry – A European Journal



COMMUNICATION

WILEY-VCH

Rhodium-terpyridine Catalyzed Transfer Hydrogenation of Aromatic Nitro Compounds in Water

Yuxuan Liu,^{[a][b]} Wang Miao,^[a] Weijun Tang,^[a] Dong Xue,^[a] Jianliang Xiao,^[c] Chao Wang,^{*[a]} Changzhi Li^{*[b]}

[a]	Y. Liu, W. Miao, Prof. W. Tang, Prof. D. Xue, Prof. J. Xiao, Prof. C. Wang	
	Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Educati	ion, School of Chemistry and Chemical Engineering
	Shaanxi Normal University	
	Xi'an, 710119, China	
	E-mail: c.wang@snnu.edu.cn	
[b]	Y. Liu, Prof. C. Li	
	CAS Key Laboratory of Science and Technology on Applied Catalysis	
	Dalian Institute of Chemical Physics, Chinese Academy of Sciences	
	Dalian, 116023, China	
	E-mail: licz@dicp.ac.cn	
[c]	Prof. J. Xiao	
	Department of Chemistry	
	University of Liverpool	
	Liverpool, L69 7ZD, United Kingdom	
	Supporting information for this article is available on the WWW.	

Abstract: Rhodium terpyridine complexes catalyzed transfer hydrogenation of nitroarenes to anilines with *i*-PrOH as hydrogen source and water as solvent has been developed. The catalytic system can work at a substrate/catalyst (S/C) ratio of 2000, with a turnover frequency (TOF) up to 3360 h⁻¹, which represents one of the most active catalytic transfer hydrogenation systems for nitroarene reduction. The catalytic system is operationally simple and the protocol could be scaled up to 20 gram scale. The water-soluble catalyst bearing a carboxyl group could be recycled 15 times without significant loss of activity.

Aromatic amines are an important class of compounds, which are used as intermediates in the synthesis of numerous fine chemicals.^[1] There are a wide variety of methods available to obtain amine compounds, including hydrogen-borrowing^[2], reductive amination^[3], *N*-arylation^[1, 4], reduction of imines^[3b, 5] or nitriles^[6], and the reduction of nitro compounds^[7], etc. Amongst them, the reduction of nitro compounds is perhaps the most widely utilized method in industrial processes. Traditional noncatalytic reduction processes (that consume Fe/HCl^[8] or Sn/HCl^[9]) generate large amounts of undesirable waste, which is not environmentally acceptable nowadays. The catalytic hydrogenation of nitro aromatics to anilines is a favorable process, and a number of transition metal catalysts (based on Pt^[10], Pd^[11], Au^[12], Ni^[13], Co^[14] etc.) have been employed for the transformation. However, this protocol is not easy to operate and usually requires harsh reaction conditions (such as high hydrogen pressure and high temperature). Apart from the use of hydrogen gas, several other reducing agents such as silanes^[15], boranes^[16], and sodium borohydride^[17] have also been used in combination with a number of different metal catalysts. In addition, CO/H₂O^[18] is also reported as hydrogen source for nitroarene reduction. Alternatively, transfer hydrogenation of nitro compounds has appeared as a very attractive method, due to the simple experimental setups and easy operation procedure. Progress has been made with *i*-PrOH^[19], ethanol^[20], formic acid^[21], and hydrazine^[22] as hydrogen sources. Notably, Kappe and coworkers reported an example with a turnover frequency (TOF) up

to 12000 h⁻¹ at a substrate/catalyst (S/C) ratio of 400 using hydrazine as reducing agent for transfer hydrogenation of nitrobenzene in a continuous flow system.^[22a] Despite the progress, the development of simple, green, efficient and practical catalytic transfer hydrogenation systems for nitroarene reduction is still highly desirable.

Herein, we report a new transfer hydrogenation system for the reduction of nitro compounds to the corresponding anilines with *i*-PrOH as hydrogen source catalyzed by simple Rh terpyridine complexes in water. The catalytic system can work at a substrate/catalyst (S/C) ratio of 2000, with a turnover frequency (TOF) up to 3360 h⁻¹, providing one of the most active transfer hydrogenation systems for nitro reduction.^[7c, 22a] The robustness of the protocol is demonstrated with a 20-gram scale reaction and the water-soluble catalyst can be recycled 15 times without significant loss of activity.

Terpyridine metal complexes are oxidatively and thermally robust^[23], and their use as catalysts for organic synthesis are relatively few.^[24] Crabtree and co-workers reported that Ru and Ir terpyridine complexes could catalyze borrowing hydrogen reactions between alcohols.^[25] Our recent work showed that Rh terpyridine complexes are an effective catalyst for dehydrogenation of alcohols^[26], dehydrogenative coupling reactions^[27], and aqueous redox-neutral depolymerization of lignin in water via a hydrogen transfer process.^[28] The hydrogentransfer ability of Rh terpyridine complexes for alcohols "in water"[29] renders them possible catalysts for transfer hydrogenation reaction, which would be more economical and environmental benefits with water as solvent. Indeed, they are found to be suitable catalysts for transfer hydrogenation of nitroarenes into anilines in water with *i*-PrOH as hydrogen source in this work. Initial results showed that in the presence of 0.25 mol% complex 1a and 0.1 equivalent of Na₂CO₃ in water at 100 °C for 10 minutes, nitroarene 2a was completely converted, providing three dominant products, viz. 3a (azoxybenzene, 37% yield), 4a (azobenzene, 10% yield), and 5a (aniline, 50% yield) (Table 1, entry 1). Catalyst with an electron-rich phenyl substituent provided the best activity amongst the catalysts tested (1a, Table

COMMUNICATION

1, entries 1-6). Eletron-rich catalyst would form a Rh-H intermediate with high hydricity, which will be benificial for reduction. The higher activities observed for catalysts with a hydrophobicity aryl group suggest that the reaction could proceed faster in an "on water"[30] manner. Switching the base from Na₂CO₃ to K₃PO₄, the selectivity towards product 5a was improved (Table 1, entry 7). Raising the reaction temperature to 120 °C further increased the selectivity of 5a (91% yield in 10 minutes, Table 1, entry 8). Impressively, a turnover frequency (TOF) of 3360 h⁻¹ was observed when the reaction was performed at 120 °C for 6 minutes (Table 1, entry 9). Full conversion of 2a, with almost exclusive formation of 5a (up to 96% yield determined by GC) was achieved with 1a as catalyst in the presence of K₃PO₄ (0.1 equiv) and i-PrOH (20 equiv) in water at 120 °C for 3 h (Table 1, entry 10 and SI). The reaction could be conduct at a S/C of 2000 with high yield of 5a (Table 1, entry 11).

Table 1. Rh catalyzed transfer hydrogenation of nitrobenzene in water^a



^a Reaction conditions: **2a** (1 mmol), catalyst (0.0025 mmol), Na₂CO₃ (0.1 mmol), *i*-PrOH (20 equiv), H₂O (1 mL), 100 °C, 10 mins, under Ar. ^b Yields were determined by GC-FID with biphenyl as internal standard. ^cK₃PO₄ (0.1 mmol). ^d TOF = 3360 h⁻¹. ^e**2a** (2.5 mmol), **1a** (0.00125 mmol, S/C = 2000), K₃PO₄ (0.25 mmol), *i*-PrOH (20 equiv), H₂O (2 mL), 120 °C, 96 h, under Ar.

With the optimal reaction condition identified, we then explored the scope of aromatic nitro compounds to probe the versatility of the catalyst (Table 2). It should be noted that the isolated yield of **5a** (82%) is lower than GC yield (96%) because it is easy to volatilize. It is found that electron-donating substituents at *ortho-*, *meta-* or *para-*positions are all tolerated (**5a-5q**), but some of substrates worked better with the water-

soluble complex **1f** as catalyst (**5c-5j**, **5g**). Upon full conversion for these substrates, the corresponding aromatic amines were obtained in good isolated yields (78%-97% for **5a-5q**). However, substrates with electron-withdrawing substituents (such as carbonyl or CN) (Table 2, **5r**, **5s**) failed to give high yields of the desired products even reacting for longer time with higher catalyst loading. To our delight, nitrocyclohexane could be transfer hydrogenated to cyclohexylamine with high yield in the system (up to 94% yield based on normalization method) (Table 2, **5t**).

Table 2. The scope of nitro compounds^a



^a Reaction conditions: **2a-2s** (1 mmol), **1a** (0.0025 mmol), K₃PO₄ (0.1 mmol), *i*-PrOH (20 equiv), H₂O (1 mL), 120 °C, 3 h, under Ar, isolated yield. ^b**1a** (0.01 mmol). ^c**1f** (0.01 mmol), *i*-PrOH (3 mL), no water. ^d**1f** (0.02 mmol). ^e**1f** (0.01 mmol), *i***1a** (0.01 mmol), *i*-PrOH (3 mL), no water. ^g**1f** (0.01 mmol), Na₂CO₃ (1 equiv).

Experiments were then carried out to demonstrate the practical usefulness of the catalytic system. **1f** was chosen as the catalyst in these studies as it is water-soluble in the presence of a base, which makes it easy to be separated from the products and possible for catalyst recycle. Firstly, gram-scale reactions were carried out (Scheme 1). Starting with 20.30 g of **2a**, the desired product **5a** could be easily isolated from the reaction mixture through simple extraction, with a yield of 80% (12.28 g). Noting that **5p** is an important precursor of lidocaine (typical anesthetic), the reduction of **2p** was conducted. Pleasingly, despite its steric hindrance, 20.39 g of **2p** was converted to 16.00 g of **5p** with isolated yield up to 98% after extraction. ICP-OES analysis of the large scale reaction products showed that only a trace amount of rhodium was leached (5.15 ppm in **5a**, 6.65 ppm in **5p**).

10.1002/asia.202100321

WILEY-VCH

COMMUNICATION



Scheme 1 Gram scale reactions catalyzed by 1f in water. See the SI for details.

Catalyst recyclability is a key factor that determines the application potential of a catalytic process. The recyclability of **1f** was further investigated with **2a** as substrate (See the SI for details). As **1f** is water-soluble in the presence of a base, and the product **5a** has low solubility in water, **5a** was easily extracted with petroleum ether after the reaction. The catalyst **1f** remained in the aqueous phase, which was directly used for the reduction of freshly added **2a**. As shown in Figure 1, **1f** could be reused at least 15 times without significant decreases in catalytic activity and selectivity. To the best of our knowledge, this is the highest recycle times ever reported for homogeneous catalytic transfer hydrogenation of nitroarenes in water (Figure 1).



Figure 1. Reuse of the catalyst 1f in water. See the SI for detailed reaction conditions.

Based on previous studies on nitro reduction^[19b-e, 21b, 31], the intermediates observed in our reaction and our previous studies Rh terpyridine complex catalyzed hydrogen transfer reactions^[28], possible reaction pathways for the reduction of nitroarenes are proposed in Scheme 2. Under basic conditions, the chloride in the Rh catalyst might first be replaced by a hydroxide to form complex I, which might be the real catalyst. Complex I could then deprotonate i-PrOH to form an intermediate II, followed by β-hydride elimination to produce acetone and an active species of Rh hydride. The Rh hydride could then reduce the nitrobenzene via two possible reaction pathways. The first (red dashed box) involves direct transfer hydrogenation of 2a to 5a via the intermediary of nitrosoarene III and hydroxylamine IV. The second (blue dashed box) is a condensation route involving the coupling of nitrosoarene III with hydroxylamine IV to afford azoxy compound 3a, which is finally reduced to 5a via 4a and intermediate V.



Scheme 2. Plausible reaction pathway for the transfer hydrogenation of 2a.

In order to determine which route the catalytic system follows, the time course of product formation for the transfer hydrogenation of **2a** was monitored. As shown in Figure 2, most of **2a** is selectively transformed into **3a**, **4a** and **5a** within 6 minutes under the standard conditions. The amount of **3a** and **4a** decreased after about 4 minutes, which suggests that **3a** and **4a** might serve as intermediates in this reaction. Several more control experiments were carried out. First, the reduction of **3a** to **5a** was probed under the standard conditions (Scheme 3, equation 1). Indeed, **3a** (77% conversion) could be transformed into **4a** (41%)

COMMUNICATION

and **5a** (35%) in 1 h under the standard conditions. Moreover, **4a** could be converted to **5a** in 1 h under the standard conditions (51% conversion, 49% yield, Scheme 3, equation 2). These



Figure 2. Time course of product formation for transfer hydrogenation of 2a.



Figure 3. Time course of product formation for transfer hydrogenation of IV.

4

6

Time (mins)

8

2

10

results further support the intermediary of **3a** and **4a** and a possible condensation pathway.

The possibility of a direct pathway^[19b-e, 21b, 31] was also examined, although intermediate IV was not observed during the reaction. Interestingly, the hydroxylamine IV, the intermediate for the direct route, could also be converted into 5a (83% yield) with a small amount of 3a (8% yield) and 4a (8% yield) in 1 h under the standard conditions, with an even faster rate than that of 3a and 4a (Scheme 3, equation 3). The time course for transfer hydrogenation of IV was then monitored. As shown in Figure 3, intermediate IV was indeed reduced to 5a in a faster rate. 3a and 4a were also detected during the reduction of IV. The formation of 3a might be due to a reversible dehydrogenation and hydrogenation process between intermediates IV and III, followed by the condensation of III and IV to form 3a.[19d, 31a] Taken the above results together, the reaction might proceed via both the direct and the condensation pathways, with the direct pathway being the dominant one.

In conclusion, we have developed a catalytic system for transfer hydrogenation of aromatic nitro compounds with simple Rh terpyridine complexes in water. This robust catalytic system can work at a S/C ratio of 2000, at 20 gram scale, with a TOF up to 3360 h⁻¹. The water-soluble catalyst is easy to be separated from the product by simple phase separation and reused 15 times without significant loss of catalytic activity. Mechanistic studies suggest that the transfer hydrogenation may proceed via both the direct route and the condensation route, with the direct pathway being the dominant one. Being easy to operate and scale up, the reaction provides a green and practical method for the reduction of nitroarenes to obtain aromatic amines.

Acknowledgements

This research was supported by the National Key R&D Program of China (2019YFC1905300, 2019YFC1905302), the 2017 Royal Society International Collaboration Award (IC170044, UK), the National Natural Science Foundation of China (21773145, 21473109, 21690083, 21878288), Projects for the Academic Leaders and Academic Backbones, Shaanxi Normal University (16QNGG008).

Conflict of Interest

Some of this research has been included in a Chinese patent (patent application number: CN201911234123.0).

Keywords: Rhodium • terpyridine • transfer hydrogenation • nitroarenes • anilines

- [1] For selected reviews see: a) J. Bariwal, E. Van der Eycken, Chem. Soc. Rev. 2013, 42, 9283-9303; b) P. Ruiz-Castillo, S. L. Buchwald, Chem. Rev. 2016, 116, 12564-12649.
- [2] For selected reviews see: a) A. Mukherjee, D. Milstein, ACS Catal.
 2018, 8, 11435-11469; b) T. Irrgang, R. Kempe, Chem Rev. 2019, 119, 2524-2549.
 [3] For selected reviews see: a) S.-L. You, Chem. Asian J. 2007, 2,
 - For selected reviews see: a) S.-L. You, *Chem. Asian J.* **2007**, 2, 820-827; b) C. Wang, B. Villa-Marcos, J. Xiao, *Chem. Commun.* **2011**, *47*, 9773-9785.
- [4] For selected reviews see: a) P. A. Forero-Cortés, A. M. Haydl, Org. Process Res. Dev. 2019, 23, 1478-1483; b) J. Magano, J. R. Dunetz, Chem. Rev. 2011, 111, 2177-2250; c) S. Bhunia, G. G. Pawar, S. V.

COMMUNICATION

Kumar, Y. Jiang, D. Ma, *Angew. Chem., Int. Ed.* **2017**, *56*, 16136-16179; d) C. Sambiagio, S. P. Marsden, A. J. Blacker, P. C. McGowan, *Chem. Soc. Rev.* **2014**, *43*, 3525-3550.

- [5] For selected reviews see: J. Barrios-Rivera, Y. Xu, M. Wills, V. K. Vyas, Org. Chem. Front. 2020, 7, 3312-3342.
- [6] For selected reviews see: a) D. B. Bagal, B. M. Bhanage, Adv. Synth. Catal. 2015, 357, 883-900; b) D. M. Sharma, B. Punji, Chem. - Asian J. 2020, 15, 690-708.
- [7] For selected reviews see: a) R. S. Downing, P. J. Kunkeler, H. van Bekkum, *Catal. Today* 1997, 37, 121-136; b) H. K. Kadam, S. G. Tilve, *RSC Adv.* 2015, *5*, 83391-83407; c) M. Orlandi, D. Brenna, R. Harms, S. Jost, M. Benaglia, *Org. Process Res. Dev.* 2018, *22*, 430-445; d) A. M. Tafesh, J. Weiguny, *Chem. Rev.* 1996, *96*, 2035-2052.
 [8] C. A. Merlic, S. Motamed, B. Quinn, *J. Org. Chem.* 1995, *60*, 3365-
- 3369.
- K. M. Doxsee, M. Feigel, K. D. Stewart, J. W. Canary, C. B. Knobler, D. J. Cram, J. Am. Chem. Soc. 1987, 109, 3098-3107.
- a) A. Corma, P. Serna, P. Concepción, J. J. Calvino, J. Am. Chem. Soc. 2008, 130, 8748-8753; b) L. Hu, X. Cao, L. Chen, J. Zheng, J. Lu, X. Sun, H. Gu, Chem. Commun. 2012, 48, 3445-3447.
- a) S. Sadjadi, M. Akbari, B. Léger, E. Monflier, M. M. Heravi, ACS Sustainable Chem. Eng. 2019, 7, 6720-6731; b) X. Chen, K. Shen, D. Ding, J. Chen, T. Fan, R. Wu, Y. Li, ACS Catal. 2018, 8, 10641-10648.
- a) D. He, H. Shi, Y. Wu, B.-Q. Xu, Green Chem. 2007, 9, 849-851;
 b) Y. Matsushima, R. Nishiyabu, N. Takanashi, M. Haruta, H. Kimura, Y. Kubo, J. Mater. Chem. 2012, 22, 24124-24131; c) X. Tan, Z. Zhang, Z. Xiao, Q. Xu, C. Liang, X. Wang, Catal. Lett. 2012, 142, 788-793.
- a) M. A. Harrad, B. Boualy, L. El Firdoussi, A. Mehdi, C. Santi, S. Giovagnoli, M. Nocchetti, M. Ait Ali, *Catal. Commun.* 2013, *32*, 92-100; b) W.-J. Liu, K. Tian, H. Jiang, *Green Chem.* 2015, *17*, 821-826.
- a) K. Shen, L. Chen, J. Long, W. Zhong, Y. Li, ACS Catal. 2015, 5, 5264-5271; b) X. Sun, A. I. Olivos-Suarez, D. Osadchii, M. J. V. Romero, F. Kapteijn, J. Gascon, J. Catal. 2018, 357, 20-28.
- [15] a) P. K. Verma, M. Bala, K. Thakur, U. Sharma, N. Kumar, B. Singh, *Catal. Lett.* **2014**, *144*, 1258-1267; b) Y. Gao, S. Yang, Y. Huo, X.-Q. Hu, *Adv. Synth. Catal*. **2020**, *362*, 3971-3986.
- a) H. Göksu, S. F. Ho, Ö. Metin, K. Korkmaz, A. Mendoza Garcia, M. S. Gültekin, S. Sun, ACS Catal. 2014, 4, 1777-1782; b) Q. Yang, Y.-Z. Chen, Z. U. Wang, Q. Xu, H.-L. Jiang, Chem. Commun. 2015, 51, 10419-10422.
- [17] a) F. Ferlin, M. Cappelletti, R. Vivani, M. Pica, O. Piermatti, L. Vaccaro, Green Chem. 2019, 21, 614-626; b) M. Gholinejad, E. Oftadeh, M. Shojafar, J. M. Sansano, B. H. Lipshutz, ChemSusChem 2019, 12, 4240-4248.
- [18] L. He, L.-C. Wang, H. Sun, J. Ni, Y. Cao, H.-Y. He, K.-N. Fan, Angew. Chem., Int. Ed. 2009, 48, 9538-9541.
- [19] a) C.-Y. Wang, C.-F. Fu, Y.-H. Liu, S.-M. Peng, S.-T. Liu, *Inorg. Chem.* 2007, 46, 5779-5786; b) R. V. Jagadeesh, G. Wienhöfer, F. A. Westerhaus, A.-E. Surkus, H. Junge, K. Junge, M. Beller, *Chem. Asian J.* 2011, 17, 14375-14379; c) X. Liu, S. Ye, H.-Q. Li, Y.-M. Liu, Y. Cao, K.-N. Fan, *Catal. Sci. Technol.* 2013, 3, 3200-3206; d) S. Chen, G. Lu, C. Cai, *New J. Chem.* 2015, 39, 5360-5365; e) B. Paul, K. Chakrabarti, S. Shee, M. Maji, A. Mishra, S. Kundu, *RSC Adv.* 2016, 6, 100532-100545; f) H. Asri, O. Dautel, A. Ouali, *ACS Appl. Nano Mater.* 2020, 3, 11811-11818; g) S. K. Mohapatra, S. U. Sonavane, R. V. Jayaram, P. Selvam, *Org. Lett.* 2002, 4, 4297-4300.
- [20] a) A. Gevorgyan, S. Mkrtchyan, T. Grigoryan, V. O. laroshenko, Org. Chem. Front. 2017, 4, 2437-2444; b) J. H. Kim, J. H. Park, Y. K. Chung, K. H. Park, Adv. Synth. Catal. 2012, 354, 2412-2418.
- [21] a) I. Sorribes, G. Wienhöfer, C. Vicent, K. Junge, R. Llusar, M. Beller, *Angew. Chem., Int. Ed.* 2012, *51*, 7794-7798; b) X. Cui, Y. Long, X. Zhou, G. Yu, J. Yang, M. Yuan, J. Ma, Z. Dong, *Green Chem.* 2018, 20, 1121-1130.
- [22] a) D. Cantillo, M. M. Moghaddam, C. O. Kappe, J. Org. Chem. 2013, 78, 4530-4542; b) C. Jiang, Z. Shang, X. Liang, ACS Catal. 2015, 5, 4814-4818.
- [23] a) C. Wei, Y. He, X. Shi, Z. Song, Coordin. Chem. Rev. 2019, 385, 1-19; b) A. Winter, U. S. Schubert, ChemCatChem 2020, 12, 2890-2941.
- [24] a) S. Enthaler, B. Hagemann, G. Erre, K. Junge, M. Beller, *Chem. Asian J.* 2006, 1, 598-604; b) A. Hazra, M. T. Lee, J. F. Chiu, G. Lalic, *Angew. Chem., Int. Ed.* 2018, 57, 5492-5496; c) K. Yamamoto, J. Li, J. A. O. Garber, J. D. Rolfes, G. B. Boursalian, J. C. Borghs, C. Genicot, J. Jacq, M. van Gastel, F. Neese, T. Ritter, *Nature* 2018, 554, 511-514; d) G. Zhang, H. Zeng, J. Wu, Z. Yin, S. Zheng, J. C. Fettinger, *Angew. Chem., Int. Ed.* 2016, 55, 14369-14372.
- [25] a) D. Gnanamgari, R. H. Crabtree, *Organometallics* 2009, 28, 922-924; b) D. Gnanamgari, C. H. Leung, N. D. Schley, S. T. Hilton, R. H. Crabtree, *Org. Biomol. Chem.* 2008, 6, 4442-4445.
- [26] X. Wang, C. Wang, Y. Liu, J. Xiao, Green Chem. 2016, 18, 4605-4610.
- [27] J. Cheng, M. Zhu, C. Wang, J. Li, X. Jiang, Y. Wei, W. Tang, D. Xue, J. Xiao, *Chem. Sci.* 2016, 7, 4428-4434.

- [29] For selected reviews see: a) U. M. Lindström, Chem. Rev. 2002, 102, 2751-2772; b) C. I. Herrerías, X. Yao, Z. Li, C.-J. Li, Chem. Rev. 2007, 107, 2546-2562.
- [30] For selected reviews see: a) A. Chanda, V. V. Fokin, *Chem. Rev.* 2009, 109, 725-748; b) R. N. Butler, A. G. Coyne, *Chem. Rev.* 2010, 110, 6302-6337.
- a) H.-U. Blaser, *Science* 2006, 313, 312; b) S. Doherty, J. G. Knight, T. Backhouse, A. Bradford, F. Saunders, R. A. Bourne, T. W. Chamberlain, R. Stones, A. Clayton, K. Lovelock, *Catal. Sci. Technol.* 2018, 8, 1454-1467; c) F. A. Harraz, S. E. El-Hout, H. M. Killa, I. A. Ibrahim, J. Catal. 2012, 286, 184-192; d) S. Hohloch, L. Suntrup, B. Sarkar, *Organometallics* 2013, 32, 7376-7385; e) K. Layek, M. L. Kantam, M. Shirai, D. Nishio-Hamane, T. Sasaki, H. Maheswaran, *Green Chem.* 2012, 14, 3164-3174; f) X.-H. Li, Y.-Y. Cai, L.-H. Gong, W. Fu, K.-X. Wang, H.-L. Bao, X. Wei, J.-S. Chen, *Chem. - Asian J.* 2014, 20, 16732-16737; g) X.-B. Lou, L. He, Y. Qian, Y.-M. Liu, Y. Cao, K.-N. Fan, *Adv. Synth. Catal.* 2011, 353, 281-286; h) X. Zhan, S. Michaud-Chevallier, D. Hérault, F. Duprat, *Org. Process Res. Dev.* 2020, 24, 686-694.

5

COMMUNICATION

Entry for the Table of Contents



A green, efficient and recyclable catalytic system for transfer hydrogenation of nitro arenes to aromatic amines has been developed.