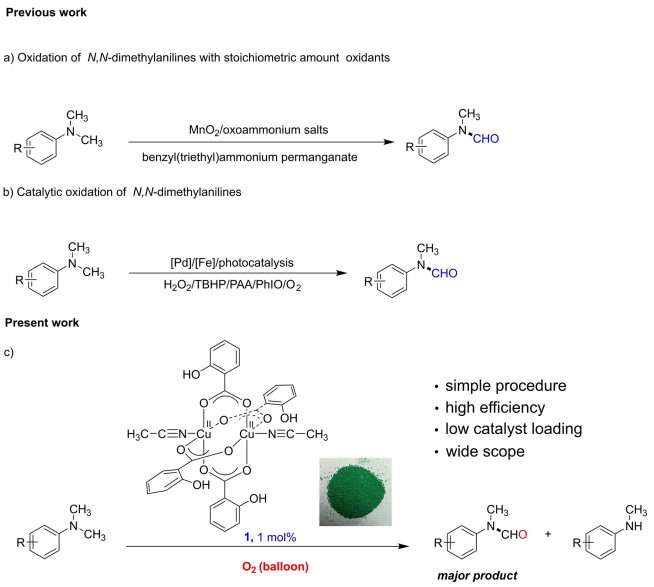
# Highly Efficient Binuclear Copper-catalyzed Oxidation of *N,N*-Dimethylanilines with $O_2$

Yuxia Liu,*[a] Yonggang Yan,[b] Dong Xue,[b] Zhongfu Wang,[a] Jianliang Xiao,[b, c] and Chao Wang*[b]

A binuclear copper-salicylate complex, $[Cu(Sal)_2(NCMe)]_2$ (Sal = salicylate), was found to be an active catalyst for the oxidation of *N,N*-dimethylanilines by $O_2$, affording the corresponding *N*-methyl-*N*-phenylformamides as major products. The reactions were carried out with a $O_2$ balloon and the S/C (substrate/catalyst ratio) of the model reaction could be up to $1\times10^5$, providing a practical and highly efficient catalytic protocol for accessing *N*-methyl-*N*-phenylformamides.

*N*-methyl-*N*-phenylformamides are widely used as precursors, intermediates, and reagents in the chemical and pharmaceutical industries.[1] A number of synthetic methods have been reported in the literature for the *N*-formylation of amines and various formylating reagents are available for this reaction, such as formic acid or formate,[2] *N,N*-dimethylformamide,[3] acetic formic anhydride,[4] ammonium formate,[5] and some special reagents.[6] Moreover, stoichiometric amounts of metal oxidants, such as manganese dioxide ($MnO_2$),[7] benzyl(triethyl)ammonium permanganate[8] and oxoammonium salts[9] were early used for selective oxidation of *N,N*-dimethylanilines to obtain *N*-methyl-*N*-phenylformamides (Scheme 1a). The catalytic oxidation of *N,N*-dimethylanilines to *N*-methyl-*N*-phenylformamides with greener oxidant is more desirable.[10] For example, the Pd-catalyzed[11] and the Fe-catalyzed oxidation of *N,N*-dimethylanilines with $H_2O_2$[12] or $O_2$[13] as oxidants have been reported (Scheme 1b). Wang and co-workers reported the photoinduced oxidation of *N,N*-dimethylanilines with molecular oxygen, providing the corresponding formamides in good yields[14] (Scheme 1b). Recently, Yamaguchi and co-workers successfully developed a highly regioselective and efficient aerobic methyl-




**Scheme 1.** Aerobic oxidation of *N,N*-dimethylanilines

selective α-oxygenation of tertiary amines by employing a Cu/nitroxyl radical catalytic system.[15] Despite the progress, inexpensive and readily available catalysts with broad substrate scope, low catalyst loading and green oxidants are still highly desirable.

Copper is found in the active site of many metalloenzymes that catalyze selective aerobic oxidation reactions, with many of them featuring binuclear structures.[16] Great efforts have been made to prepare binuclear copper complexes, aiming to mimic the oxidation ability of enzymes.[17] Recently, we have discovered that a binuclear paddle-wheel copper salicylate complex, $[Cu(Sal)_2NCMe)]_2$ (Sal = salicylate) **1**, readily prepared from simple CuCl and salicylic acid as fine green crystals, can serve as effective catalyst for the aerobic cross dehydrogenative coupling of *N*-aryltetrahydroisoquinolines,[18] the aerobic oxidation of amines to amides with the aid of a vitamin B1 analogue,[19] as well as the selective oxidation of alkenes to carbonyls with $O_2$.[20] Herein, we report that **1** could catalyze the aerobic oxidation of *N,N*-dimethylanilines to *N*-methyl-*N*-phenylformamides as the major products by $O_2$ with TBAC (tetrabutylammonium chloride) and $NaBF_4$ as additives, without the aid of a vitamin B1 analogue (Scheme 1c).

To begin the study, 4-bromo-*N,N*-dimethylaniline **2a** was selected as a model substrate for condition optimization. Following the screening of a wide range of conditions (SI,

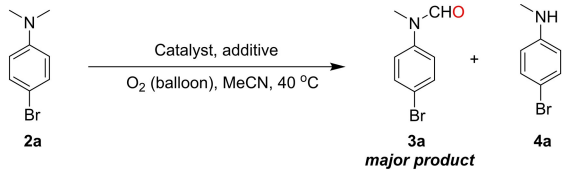
[a] Dr. Y. Liu, Prof. Z. Wang
Shaanxi Natural Carbohydrate Resource Engineering Research Center
College of Food Science and Technology
Northwest University
Xi'an, 710069 (P. R.China)
E-mail: yuxialiu@nwu.edu.cn
[b] Y. Yan, Prof. D. Xue, Prof. J. Xiao, Prof. C. Wang
Key Laboratory of Applied Surface and Colloid Chemistry
Ministry of Education and School of Chemistry and Chemical Engineering
Shaanxi Normal University
Xi'an, 710062 (P. R. China)
E-mail: c.wang@snnu.edu.cn
[c] Prof. J. Xiao
Department of Chemistry
University of Liverpool
Liverpool L69 7ZD (UK)

Supporting information for this article is available on the WWW under https://doi.org/10.1002/cctc.201901962

Table S1), we were delighted to find that using **1** as catalyst, the corresponding formamides product *N*-(4-bromophenyl)-*N*-methylformamide (**3a**) was formed with 56% isolated yield, along with 38% isolated yield of the demethylated product 4-bromo-*N*-methylaniline (**4a**), after 0.75 h, in MeCN at 40 °C. Notably, the catalyst and dioxygen are both essential for the reaction. In the absence of any of these components, none of the products were detected and the starting material remained unreacted (Table 1, entries 1 and 2). The screening results demonstrated that addition of TBAC (tetrabutylammonium chloride, 2 mol%) was found to improve the activity of **1** (Table 1, entry 4). The role of TBAC might be to stabilise the active catalytic intermediate via chloride anion coordination.[18] Interestingly, when a catalytic amount (30 mol%) of $NaBF_4$ was added, the yields of **3a** and **4a** were all increased remarkably (Table 1, entry 5). The reason for the acceleration effect of $NaBF_4$ is unclear at present; As ionic intermediates are produced during the reaction, a possible role of $NaBF_4$ in the reaction is to increase the ionic strength of the reaction media to stabilize the ionic species during the reaction. Investigation of the solvent effect revealed that MeCN is the best solvent for the reaction; Other solvents, such as MeOH, DMF, DMSO, toluene, 1,4-dioxane and DCM are not good for the reaction (SI, Table S1, entries 18–24). Although DCE was effective for the reaction, it was inferior to MeCN (SI, Table S1, entry 14). The reaction temperature also plays an important role, lowering or increasing temperature does not benefit the reaction (Table 1, entries 6–8). The reaction also took place under air, but the yield of **3a** was reduced to 27%, along with 15% yield of **4a** (Table 1, entry 14). Pleasingly, catalyst **1** is highly effective for the oxidation reaction (Table 1, entries 9–13). With only 0.0001 mol% of catalyst, a combined isolated yield of 77% was still obtained for **3a** and **4a** in 96 h at 20.0 gram scale (Table 1, entry 13, *vide infra*). Common copper salts such as $CuCl_2$, $Cu_2O$, CuI, and $Cu(MeCN)_4PF_6$ could not catalyze the reaction under our reaction conditions (Table 1, entries 15–18).

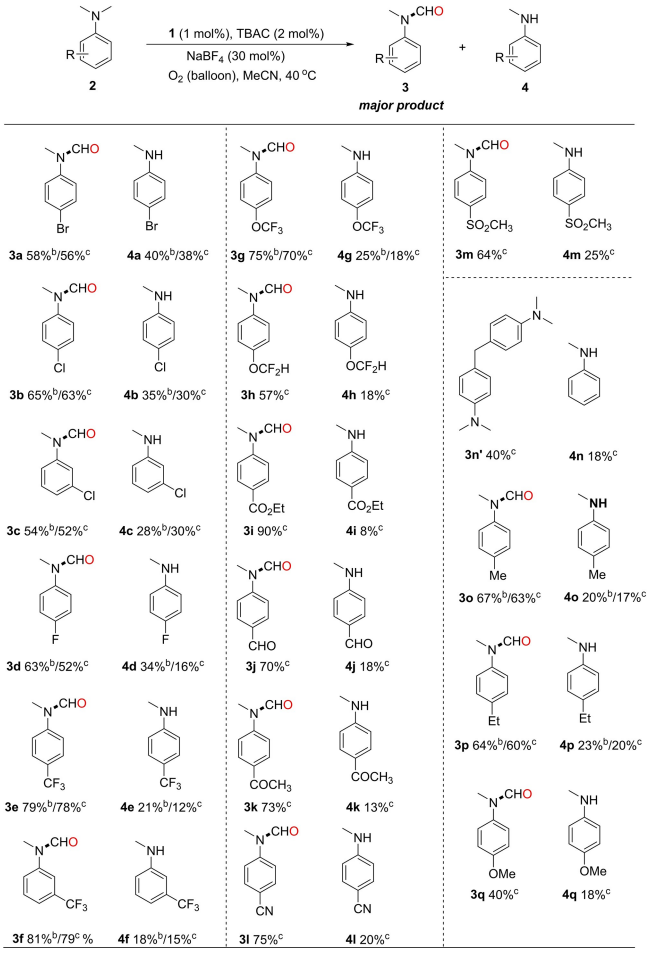
Having established the optimized reaction conditions, we tested a variety of substituted *N,N*-dimethylanilines (**2**) to probe the versatility of our catalytic system (Scheme 2). Firstly, the effect of the electron-deficient substituents on the reaction was examined. To our delight, *N,N*-dimethylanilines carrying halogen substituents, such as F, Cl, and Br were successfully oxidized, and converted to the corresponding *N*-methyl-*N*-phenylformamides **3a–d** and *N*-methyl phenylamines **4a–d** in

**Table 1.** Catalytic oxidation of 4-bromo-*N,N*-dimethylaniline **2a** (See SI for experimental details).




| Entry | Catalyst [mol%] | Additive [mol%] | Yield [%][a,b] | |
|---|---|---|---|---|
| 1 | – | – | 0 | 0 |
| 2 | – | – | 0 | 0 |
| 3 | **1** (1) | – | 29 | 16 |
| 4 | **1** (1) | TBAC (2) | 38 | 26 |
| **5** | **1 (1)** | **TBAC (2) + $NaBF_4$ (30)** | **58** | **40** |
| 6[d] | **1** (1) | TBAC (2) + $NaBF_4$ (30) | trace | trace |
| 7[e] | **1** (1) | TBAC (2) + $NaBF_4$ (30) | 30 | 20 |
| 8[f] | **1** (1) | TBAC (2) + $NaBF_4$ (30) | 50 | 40 |
| 9[g] | **1** (0.1) | TBAC (0.2) + $NaBF_4$ (30) | 51 | 36 |
| 10[h] | **1** (0.03) | TBAC (0.06) + $NaBF_4$ (30) | 48 | 35 |
| 11[i] | **1** (0.001) | TBAC (0.002) + $NaBF_4$ (30) | 45 | 37 |
| 12[j] | **1** (0.0003) | TBAC (0.0006) + $NaBF_4$ (30) | 45 | 38 |
| 13[k] | **1** (0.0001) | TBAC (0.0002) + $NaBF_4$ (30) | 45 | 32 |
| 14[l] | **1** (1) | TBAC (2) + $NaBF_4$ (30) | 27 | 15 |
| 15 | $CuCl_2$ (1) | TBAC (2) + $NaBF_4$ (30) | 0 | 0 |
| 16 | $Cu_2O$ (1) | TBAC (2) + $NaBF_4$ (30) | 0 | 0 |
| 17 | CuI (1) | TBAC (2) + $NaBF_4$ (30) | 0 | 0 |
| 18 | $Cu(MeCN)_4PF_6$ (1) | TBAC (2) + $NaBF_4$ (30) | 0 | 0 |

[a] Reaction conditions: **2a** (0.5 mmol), additives, solvent (1.0 mL), $O_2$ balloon, 40 °C, 0.75 h. [b] Determined by $^1H$ NMR with 1,3,5-trimethoxybenzene as internal standard. [c] The reaction was carried out under argon. [d] The reaction was carried out at 0 °C. [e] The reaction was carried out at 25 °C. [f] The reaction was carried out at 70 °C. [g] The reaction time was 12 h, isolated yield. [h] The reaction time was 16 h, isolated yield. [i] The reaction time was 42 h, isolated yield. [j] The reaction time was 72 h, isolated yield. [k] The reaction time was 96 h, isolated yield. [l] The reaction was carried out under air.



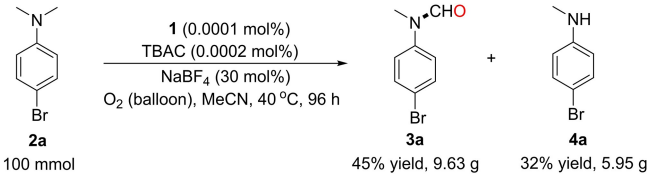

**Scheme 2.** Scope of **1**-catalyzed aerobic oxidation of *N,N*-dimethylanilines. See SI for experimental details. [a] Reaction conditions: **2** (0.5 mmol), 1 mol% **1**, 2 mol% TBAC, 30 mol% $NaBF_4$, MeCN (1.0 mL), $O_2$ balloon, 40 °C. [b] Determined by $^1H$ NMR with 1,3,5-trimethoxybenzene as an internal standard. [c] Isolated yield.

moderate yields. The very electron-deficient *N,N*-dimethylanilines, such as $CF_3$, $OCF_3$, $OCF_2H$, and CN, also reacted smoothly to provide the corresponding major products in moderate to good yields (**3e** 78%, **3g** 70%, **3h** 57%, and **3l** 75%). It is noteworthy that various sensitive functional groups on the phenyl ring, such as $CO_2Et$, CHO, $COCH_3$ and $SO_2CH_3$ were tolerated, affording the desired major products in excellent yields (**3i** 90%, **3j** 70%, **3k** 73%, and **3m** 64%). Substrates with *meta*-substituted phenyl rings were also viable (**3c** 52%, **3f** 79%).

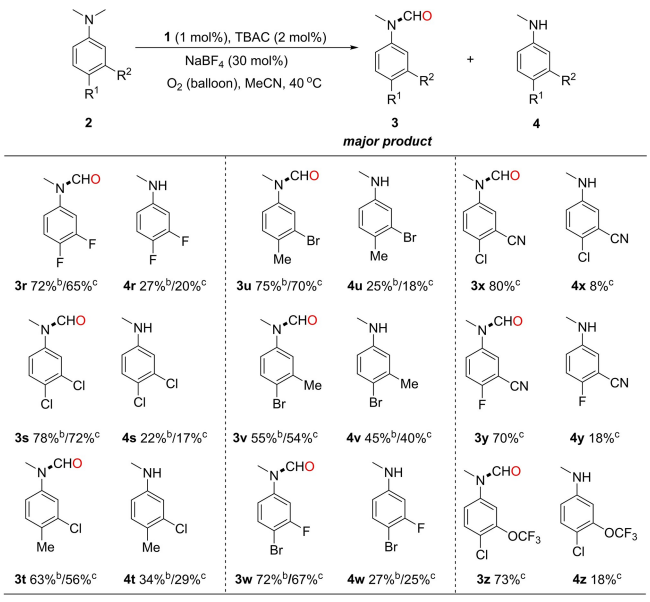
Interestingly, when *N,N*-dimethylaniline **2n** was used as the substrate, different products were obtained, with 40% yield of compound **3n′** and 18% yield of the demethylated product **4n** formed. The formation of **3n′** could be from the reaction of *N,N*-dimethylaniline with in-situ generated formaldehyde (See SI, section 5.4) from the demethylation reaction (*vide infra*);[11,21] formaldehyde could react with the electron rich aromatic ring of **2n** via an electrophilic substitution mechanism to give **3n′**. Further, *N,N*-dimethylanilines derivatives bearing electron-donating substituents at the *para*-position of the phenyl ring, such as Me, Et and MeO groups, were examined. In general, these substrates showed lower activities than electron-deficient ones (e.g. **3e**-**3g** *vs* **3o** and **3p**). In particular, low yields were obtained for the MeO group substituted substrate (**3q** 40%, **4q** 18%), even with prolonged reaction time and higher catalyst loading.

We further examined the generality of this catalytic method with disubstituted substrates. The results showed that substrates with substituents on the *para*- and *meta*- positions of the phenyl ring all reacted well with **1**, TBAC and $NaBF_4$ under $O_2$ giving good product yields(Scheme 3). Notably, substrates bearing both electron-deficient substituents on the phenyl ring, for example, F, Cl, CN, and $OCF_3$, successfully underwent the reaction to furnish the corresponding major products in satisfactory yields (**3r** 65%, **3s** 72%, **3w** 67%, **3x** 80%, **3y** 70%, **3z** 73%). To showcase the synthetic applicability of our procedure, a gram-scale aerobic oxidation reaction of **2a** on a 100 mmol scale was carried out (Scheme 4). **3a** was obtained in 9.63 g (45% yield), along with 5.95 g (32% yield) of the demethylated product 4-bromo-*N*-methylaniline **4a** with 0.0001 mol% of **1**.

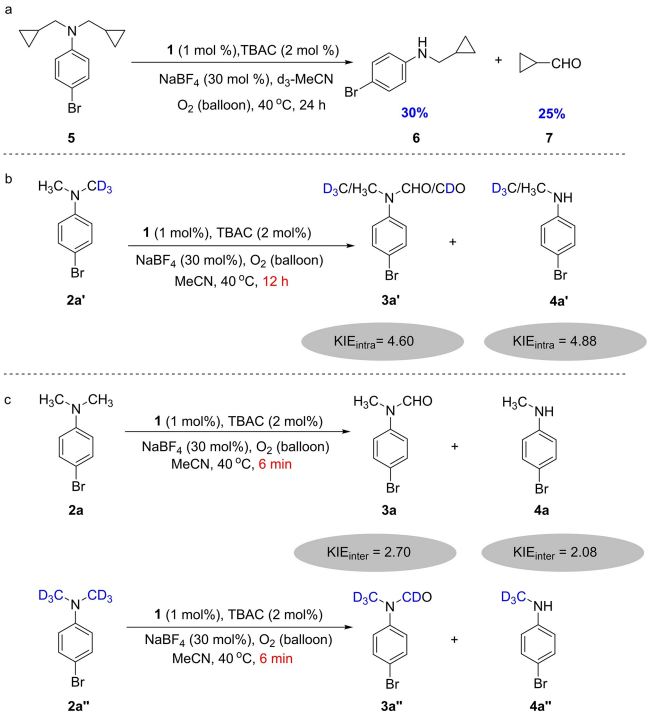
The mechanism of the reaction was next studied. There are several facts, which might have mechanistic implications. 1). The reaction was fully inhibited in the presence of a catalytic amount of radical scavengers, such as butylated hydroxytoluene (BHT), 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), and *p*-benzoquinone (BQ), which suggests that the reaction may proceed via radical intermediates (See SI, section 5.1). 2). The cyclopropyl ring structure is preserved in product **6** and **7** (Scheme 5a, also see SI, section 5.2), suggesting that carbon-based radicals may not be generated during the aerobic oxidation reaction. 3). KIE




**Scheme 4.** Gram-scale aerobic oxidation of **2a**. See SI for experimental details.



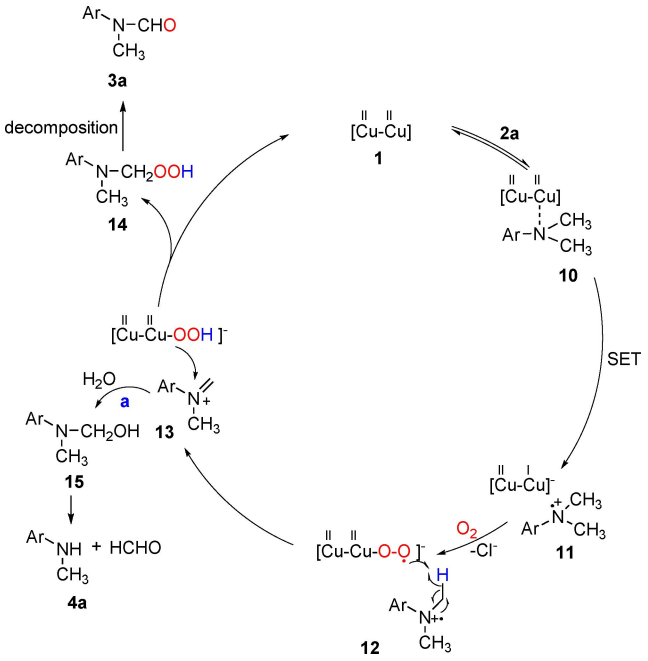

**Scheme 3.** Scope of **1**-catalyzed aerobic oxidation of disubstituted *N,N*-dimethylanilines. See SI for experimental details. [a] Reaction conditions: **2** (0.5 mmol), 1 mol% **1**, 2 mol% TBAC, 30 mol% $NaBF_4$, MeCN (1.0 mL), $O_2$ balloon, 40 °C. [b] Determined by $^1H$ NMR with 1,3,5-trimethoxybenzene as an internal standard. [c] Isolated yield.




**Scheme 5.** Reactions aimed to probe the mechanism. For details see section 5.2 and 5.3 of SI.

experiments showed that $KIE_{inter}$ (Scheme 5c) is smaller than $KIE_{intra}$ (Scheme 5b), which suggests that the reaction proceed via an ET (electron transfer) mechanism rather than a HAT (hydrogen atom transfer) mechanism, according to the studies by Karlin,[22] Baciocchi[23] and their coworkers. The absence of carbon based radicals also support a ET mechanism (*vide supra*). 4). Reacting the reaction mixture with dimedone produced the formaldehyde adduct of 1,3-cyclohexanedione **8**, suggesting that the demethylation side reaction produces formaldehyde (See SI, section 5.4).

Based on the above mechanistic studies and the literature, a tentative mechanism of the reaction is proposed (Scheme 6). The amine substrate **2a** could coordinate to complex **1** to form **10**. Our previous studies with **1** and *N*-aryltetrahydroisoquinolines showed that amines could coordinate to **1**,[18] and coordination of amino compounds, e.g. pyridine, to similar Cu(II)-carboxylate dimers has been reported.[24] The next step is a SET (single electron transfer) process, with one electron from the nitrogen atom of **2a** being transferred to the **2a** coordinated $Cu^{II}$ center to form a Cu(II)-Cu(I) intermediate **11** and a radical cation of **2a**. This electron transfer process might be reversible, which was demonstrated by Doyle and Ratnikov[25] in the metal-catalyzed oxidation of *N,N*-dialkylanilines by TBHP. On reacting with $O_2$, compound **11** is converted into the Cu(II)-Cu(II) superoxo radical **12**, which abstracts a α-hydrogen atom from the amine radical cation to give **13**. The formation of Cu(II) superoxo radicals and subsequent hydrogen abstract reactions to form Cu(II) hydroperoxo species have been well documented in enzymatic and biomimetic catalysis.[26] The hydroperoxo anion [Cu(II)-Cu(II)-OOH]$^-$ in **13** could undergo nucleophilic attack at the iminium cation of **13** to produce **14** and regenerate the active catalyst. **14** could decompose to **3a** via thermal rearrangement.[13b,27] Alternatively, the iminium cation of **13** might be attacked by $H_2O$ to undergo hydrolysis reaction to give the demethylated product **4a** and formaldehyde via **15** (Scheme 6).[28]




**Scheme 6.** Proposed mechanism for aerobic oxidative of *N,N*-dimethylanilines.

In summary, this study shows that structurally well-defined binuclear copper-salicylate complex **1** reported by us before[18–20] is a powerful catalyst for the aerobic oxidation of *N,N*-dimethylanilines. The reactions were carried out under very low loading of the binuclear copper catalyst with an oxygen balloon being sufficient in most cases. The present protocol would be a particularly ideal and environmentally benign approach to obtain a library of *N*-methyl-*N*-phenylformamides in good yields with favorable functional group tolerance.

## Experimental Section

General procedure for oxidation of **2**. In a Schlenk tube equipped with a magnetic stir bar, **2** (0.5 mmol), **1** (0.005 mmol, 6.0 mg), TBAC (0.01 mmol, 5.6 mg), and $NaBF_4$ (0.15 mmol, 16.5 mg) were added. MeCN (1.0 mL) was then introduced by a syringe, and the reaction tube was degassed (3 times), charged with dioxygen gas and kept under an oxygen atmosphere by using an oxygen balloon. After stirring at 40 °C for the time indicated, the reaction mixture was diluted with water, and then extracted with ethyl acetate (3× 15 mL). The organic layers were combined, washed with brine, and dried over $Na_2SO_4$. Finally, the solvent was removed via rotary evaporation and the crude products were purified by column chromatography on silica gel using ethyl acetate/petroleum ether to afford the desired product.

## Acknowledgements

*This research was supported by the National Natural Science Foundation of China (21902126, 21773145), the China Postdoctoral Science Foundation (2019 M663947XB), the Program for Changjiang Scholars and Innovative Research Team in University (IRT14R33), and the 111 project (B14041).*

## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** copper · homogeneous catalysis · dioxygen · oxidation · amides

[1] a) A. Vilsmeier, A. Haack, *Ber. Dtsch. Chem. Ges. B* **1927**, *60*, 119; b) Z. Ke, Y. Zhang, X. Cui, F. Shi, *Green Chem.* **2016**, *18*, 808–816; c) M.-C. Fu, R. Shang, W.-M. Cheng, Y. Fu, *Angew. Chem.* **2015**, *127*, 7170–7174; *Angew. Chem. Int. Ed.* **2015**, *54*, 9042–9046; d) H. Lv, Q. Xing, C. Yue, Z. Lei, F. Li, *Chem. Commun.* **2016**, *52*, 6545–6548; e) B. Dong, L. Wang, S. Zhao, R. Ge, X. Song, Y. Wang, Y. Gao, *Chem. Commun.* **2016**, *52*, 7082–7085; f) Y.-D. Du, C.-W. Tse, Z.-J. Xu, Y. Liu, C.-M. Che, *Chem. Commun.* **2014**, *50*, 12669–12672.

[2] a) J. Deutsch, R. Eckelt, A. Kockritz, A. Martin, *Tetrahedron* **2009**, *65*, 10365–10369; b) G. Brahmachari, S. Laskar, *Tetrahedron Lett.* **2010**, *51*, 2319–2322; c) B. Das, M. Krishnaiah, P. Balasubramanyam, B. Veeranjaneyulu, D. N. Kumar, *Tetrahedron Lett.* **2008**, *49*, 2225–2227; d) M.

Rahman, D. Kundu, A. Hajra, A. Majee, *Tetrahedron Lett.* **2010**, *51*, 2896–2899; e) D. R. Hill, C. N. Hsiao, R. Kurukulasuriya, S. J. Wittenberger, *Org. Lett.* **2002**, *4*, 111–113; f) M. Hosseini-Sarvari, H. Sharghi, *J. Org. Chem.* **2006**, *71*, 6652–6654; g) L. D. De Luca, G. Giacomelli, A. Porcheddu, M. Salaris, *Synlett* **2004**, *14*, 2570–2572; h) B. Desai, T. N. Danks, G. Wagner, *Tetrahedron Lett.* **2005**, *46*, 955–957.

[3] a) R. B. Sonawane, N. K. Rasal, S. V. Jagtap, *Org. Lett.* **2017**, *19*, 2078–2081; b) M. Srinivas, A. D. Hudwekar, V. Venkateswarlu, G. L. Reddy, K. A. A. Kumar, R. A. Vishwakarma, S. D. Sawant, *Tetrahedron Lett.* **2015**, *56*, 4775–4779; c) J. Ma, F. Zhang, J. Zhang, H. Gong, *Eur. J. Org. Chem.* **2018**, *35*, 4940–4948; d) J. Chen, J. Jia, Z. Guo, J. Zhang, M. Xie, *Tetrahedron Lett.* **2019**, *60*, 1426–1429.

[4] P. Strazzolini, A. G. Giumanini, S. Cauci, *Tetrahedron* **1990**, *46*, 1081–1118.

[5] a) P. G. Reddy, G. D. K. Kumar, S. Baskaran, *Tetrahedron Lett.* **2000**, *41*, 9149–9151; b) X. Dong, Z. Wang, Y. Duan, Y. Yang, *Chem. Commun.* **2018**, *54*, 8913–8916.

[6] Some selected examples: a) M. Neveux, C. Bruneau, P. H. Dixneuf, *J. Chem. Soc., Perkin Trans.* 1 **1991**, 5, 1197–1199; b) A. R. Katritzky, H. X. Chang, B. Z. Yang, *Synthesis* **1995**, *1995*, 503–505; c) R. S. L. Chapman, R. Lawrence, J. M. J. Williams, S. D. Bull, *Org. Lett.* **2017**, *19*, 4908–4911; d) R. Luo, X. Lin, Y. Chen, W. Zhang, X. Zhou, H. Ji, *ChemSusChem* **2017**, *10*, 1224–1232; e) S. Zhang, Q. Mei, H. Liu, H. Liu, Z. Zhang, B. Han, *RSC Adv.* **2016**, *6*, 32370–32373; f) X.-F. Liu, C. Qiao, X.-Y. Li, L.-N. He, *Green Chem.* **2017**, *19*, 1726–1731; g) O. Jacquet, C. D. N. Gomes, M. Ephritikhine, T. Cantat, *J. Am. Chem. Soc.* **2012**, *134*, 2934–2937; h) C. Fang, C. Lu, M. Liu, Y. Zhu, Y. Fu, B.-L. Lin, *ACS Catal.* **2016**, *6*, 7876–7881; i) L. Hao, Y. Zhao, B. Yu, Z. Yang, H. Zhang, B. Han, X. Gao, Z. Liu, *ACS Catal.* **2015**, *5*, 4989–4993; j) C. C. Chong, R. Kinjo, *Angew. Chem.* **2015**, *127*, 12284–12288; *Angew. Chem. Int. Ed.* **2015**, *54*, 12116–12120; k) N. Ortega, C. Richter, F. Glorius, *Org. Lett.* **2013**, *15*, 1776–1779; l) X.-F. Li, X.-G. Zhang, F. Chen, X.-H. Zhang, *J. Org. Chem.* **2018**, *83*, 12815–12821; m) D.-Z. Lin, J.-M. Huang, *Org. Lett.* **2018**, *20*, 2112–2115; n) G. L. Beutner, I. S. Young, M. L. Davies, M. R. Hickey, H. Park, J. M. Stevens, Q. Ye, *Org. Lett.* **2018**, *20*, 4218–4222; o) Z.-W. Xu, W.-Y. Xu, X.-J. Pei, F. Tang, Y.-S. Feng, *Tetrahedron Lett.* **2019**, *60*, 1254–1258.

[7] H. B. Henbest, A. Thomas, *J. Chem. Soc.* **1957**, 3032–3039.

[8] H. J. Schmidt, H. J. Schaefer, *Angew. Chem.* **1981**, *93*, 124–125; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 109–109.

[9] D. H. Hunter, D. H. R. Barton, W. J. Motherwell, *Tetrahedron Lett.* **1984**, *25*, 603–606.

[10] a) D. Lakk-Bogáth, B. Kripli, B. I. Meena, G. Speier, J. Kaizer, *Polyhedron*, **2019**, *169*, 169–175; b) Z. Zhang, Y.-H. Liu, X. Zhang, X.-C. Wang, *Tetrahedron* **2019**, *75*, 2763–2770.

[11] T. Sakakibara, S. Karasumaru, I. Kawano, *J. Am. Chem. Soc.* **1985**, *107*, 6417–6419.

[12] a) E. Kotani, T. Takeya, H. Shimizu, H. Egawa, T. Tamamoto, S. Tobinaga, *Chem. Pharm. Bull.* **1997**, *45*, 2089–2092; b) Y.-D. Du, C.-W. Tse, Z.-J. Xu, Y. Liu, C.-M. Che, *Chem. Commun.* **2014**, *50*, 12669–12672.

[13] a) S. Murata, M. Miura, M. Nomura, *J. Org. Chem.* **1989**, *54*, 4702–4706; b) L. Ma, Y. Li, Z. Li, *Sci. China Chem.* **2015**, *58*, 1310–1315; c) D. Bhat, N. Sharma, *Aust. J. Chem.* **2017**, *70*, 233–236.

[14] a) S. Yang, P. Li, Z. Wang, L. Wang, *Org. Lett.* **2017**, *19*, 3386–3389; b) W. Ji, P. Li, S. Yang, L. Wang, *Chem. Commun.* **2017**, *53*, 8482–8485.

[15] S. Nakai, T. Yatabe, K. Suzuki, Y. Sasano, Y. Iwabuchi, J. Hasegawa, N. Mizuno, K. Yamaguchi, *Angew. Chem.* **2019**, *131*, 2–11; *Angew. Chem. Int. Ed.* **2019**, *58*, 2–11.

[16] G. Pettit, M. Kalnins, T. Liu, E. Thomas, K. Parent, *J. Org. Chem.* **1961**, *26*, 2563–2566.

[17] a) L. Que, W. B. Tolman, *Nature* **2008**, *455*, 333–334; b) P. Haack, C. Limberg, *Angew. Chem.* **2014**, *126*, 4368–4380; *Angew. Chem. Int. Ed.* **2014**, *53*, 4282–4293; c) *Copper Oxygen Chemistry*, (Eds.: K. D. Karlin, S. Itoh), Wiley, New York, **2011**; d) I. A. Koval, P. Gamez, C. Belle, K. Selmeczi, J. Reedijk, *Chem. Soc. Rev.* **2006**, *35*, 814–840.

[18] Y. Liu, C. Wang, D. Xue, M. Xiao, C. Li, J. Xiao, *Chem. Eur. J.* **2017**, *23*, 3051–3061.

[19] Y. Liu, C. Wang, D. Xue, M. Xiao, J. Liu, C. Li, J. Xiao, *Chem. Eur. J.* **2017**, *23*, 3062–3066.

[20] Y. Liu, D. Xue, C. Li, J. Xiao, C. Wang, *Catal. Sci. Technol.* **2017**, *7*, 5510–5514.

[21] a) S. Murata, M. Miura, M. Nomura, *J. Chem. Soc. Chem. Commun.* **1989**, *2*, 116–118; b) D. D. Agarwala, D. Bhat, *J. Porphyr. Phthalocya.* **2016**, *20*, 689–693; c) A. Wusiman, R. Hudabaierdi, *Tetrahedron Lett.* **2019**, *60*, 681–683.

[22] J. Shearer, C. X. Zhang, L. Q. Hatcher, K. D. Karlin, *J. Am. Chem. Soc.* **2003**, *125*, 12670–12671.

[23] E. Baciocchi, O. Lanzalunga, A. Lapi, L. Manduchi, *J. Am. Chem. Soc.* **1998**, *120*, 5783–578.

[24] M. Iqbal, S. Ali, N. Muhammad, M. Sohail, *Polyhedron* **2013**, *57*, 83–93.

[25] M. O. Ratnikov, M. P. Doyle, *J. Am. Chem. Soc.* **2013**, *135*, 1549–1557.

[26] a) L. Que, W. B. Tolman, *Nature* **2008**, *455*, 333–340; b) Y. Wang, J. L. DuBois, B. Hedman, K. O. Hodgson, T. D. P. Stack, *Science* **1998**, *279*, 537–540; c) P. Chaudhuri, M. Hess, T. Weyhermüller, K. Wieghardt, *Angew. Chem.* **1999**, *111*, 1165–1068; *Angew. Chem. Int. Ed.* **1999**, *38*, 1095–1098; d) J. I. Vlugt, F. Meyer, In *Organometallic Oxidation Catalysis* (Eds.: F. Meyer, C. Limberg), Springer, Berlin, **2007**, pp. 191–240; e) S. Itoh, *Acc. Chem. Res.* **2015**, *48*, 2066–2074.

[27] Q. Liao, C. Xi, *Chem. Res. Chin. Univ.* **2009**, *25*, 861–865.

[28] a) Z. Li, C. J. Li, *J. Am. Chem. Soc.* **2005**, *127*, 3672–3673; b) Z. Li, C. J. Li, *J. Am. Chem. Soc.* **2005**, *127*, 6968–6969; c) S. I. Murahashi, T. Naota, K. Yonemura, *J. Am. Chem. Soc.* **1988**, *110*, 8256–8258; d) S. I. Murahashi, T. Nakae, H. Terai, N. Komiya, *J. Am. Chem. Soc.* **2008**, *130*, 11005–11012.

Manuscript received: October 17, 2019
Revised manuscript received: February 2, 2020
Accepted manuscript online: February 3, 2020
Version of record online: March 10, 2020