View Article Online View Journal

# ChemComm

### Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: T. Zhao, G. Zhai, J. Liang, P. Li, X. Hu and Y. Wu, *Chem. Commun.*, 2017, DOI: 10.1039/C7CC03860G.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/chemcomm

Published on 22 June 2017. Downloaded by Newcastle University on 23/06/2017 04:48:48.



Journal Name

## Catalyst-free *N*-formylation of amines using BH<sub>3</sub>NH<sub>3</sub> and CO<sub>2</sub> at mild conditions

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

Tian-Xiang Zhao, Gao-Wen Zhai, Jian Liang, Ping Li, Xing-Bang Hu,\*and You-Ting Wu\*

DOI: 10.1039/x0xx00000x

www.rsc.org/

Catalyst-free *N*-formylation of amines using  $CO_2$  as the  $C_1$  source and BH<sub>3</sub>NH<sub>3</sub> as the reductant is developed for the first time. The corresponding formylated products of both primary and secondary amines are obtained in good to excellent yields (up to 96% of isolated yield) under mild conditions.

Carbon dioxide, a notorious greenhouse gas, has been a worldwide focus due to its serious effect in the atmosphere. The capture and utilization of CO<sub>2</sub> become one of the greatest scientific and technological challenges of the 21<sup>st</sup> century.<sup>1</sup> The CO<sub>2</sub> capture and storage (CCS) approach, which is based on the idea of capturing CO<sub>2</sub> into adsorbents such as solids<sup>1a</sup> and solutions, <sup>1b,c</sup> or with membranes,<sup>1d</sup> is obvious. In comparison with CCS, the approach of CO<sub>2</sub> capture and utilization (CCU) is more attractive if economical processes are available for the conversion of CO<sub>2</sub> into useful products.<sup>1e,h</sup>

A promising methodology in this area is the reductive functionalization of CO<sub>2</sub> with amines and reductants to produce formamides.<sup>2</sup> Formamides are a kind of versatile chemicals or important building blocks that are generally produced via the Nformylation of amines with carboxylic acid or CO in the presence of a catalyst.<sup>2j</sup> A green and attractive development is to use CO<sub>2</sub> instead of toxic CO. As we all know,  $CO_2$  is characteristic of it inherent stability and inertness, so that the conversion of CO<sub>2</sub> is full of challenge.<sup>1e-h</sup> Hence, chemists have been committed to developing many efficient methods for the conversion of CO<sub>2</sub> into formamides.<sup>2</sup> However, the reported routes generally require expensive or complex catalysts (i.e., compounds containing Ru,<sup>2d,j</sup> Rh,<sup>2i</sup> Ir,<sup>2h,j</sup> Pd,<sup>2v</sup> Au,<sup>2v</sup> Cu,<sup>2c,e,m</sup> Co,<sup>2a</sup> Fe,<sup>2t,x</sup>, Zn,<sup>2u</sup> NHC,<sup>2l</sup> NHP-H,<sup>2r</sup> NHO,<sup>2b</sup> GVL,<sup>2f</sup> TBD,<sup>2w</sup> GB,<sup>2y</sup> ILs,<sup>2g,k,n,o</sup> or alkali carbonate<sup>2p,q</sup>). It is still difficult to recycle these catalysts.<sup>2</sup> In addition, most of these processes suffer from high temperature and pressure ( $H_2$  as reductant),<sup>2a,c,d,j</sup> or low atomic economy (hydrosilanes as reductants)<sup>2b,f-i,k-s,w-y</sup> (Scheme 1). Therefore, the exploration of catalyst-free and atom-economic methods at mild conditions is of

E-mail: huxb@nju.edu.cn (X.-B. Hu); ytwu@nju.edu.cn (Y.-T. Wu)

great significance.

Ammonia borane (BH<sub>3</sub>NH<sub>3</sub>) is known as the excellent hydrogen storage material because of its high hydrogen capacity.<sup>3</sup> The pyrolytic dehydrogenation of BH<sub>3</sub>NH<sub>3</sub> usually require noble metal catalyst and high temperature.<sup>3</sup> Recently, we developed a method for the room temperature dehydrogenation of BH<sub>3</sub>NH<sub>3</sub>.<sup>4</sup> However, catalyst is still vital for this process. Hence, it is not surprise that big challenge may exist in the production of useful chemicals using CO<sub>2</sub> as the C<sub>1</sub> source and BH<sub>3</sub>NH<sub>3</sub> as the reductant.<sup>5</sup> As an ongoing effort in the capture and utilization of CO<sub>2</sub>.<sup>6</sup> herein, we report the successful development of catalyst-free *N*-formylation of amines using CO<sub>2</sub> as the C<sub>1</sub> source and BH<sub>3</sub>NH<sub>3</sub> as the reductant at mild conditions. The direct synthesis of formamides from CO<sub>2</sub> and amines under mild conditions (50°C) enables excellent conversion of amines and good selectivity of formamides.

Precedents



Cat = Ru; Rh; Ir; Pd; Au; Cu; Co; Zn; Fe; Cs<sub>2</sub>CO<sub>3</sub>; K<sub>2</sub>CO<sub>3</sub>; NHC; NHP-H; NHOs; [Et<sub>4</sub>NBr]-Py-OFs; [BMIm]Cl; TBAF; GVL; GB; TBD

This work



**Scheme 1.** The difference between literatures and this work in the *N*-formylation of amines.

In a first experiment, the formylation of *N*-methylaniline **1** with  $CO_2$  as the C1 source and  $BH_3NH_3$  as the reductant was performed in various solvents (Table 1). Inferior conversions of **1** are obtained in benzene, toluene, and CHCl<sub>3</sub> (entries 1-3), which are due to the poor solubility of  $BH_3NH_3$  in these solvents. Weakly polar solvents such as 1,4-dioxane, THF, and acetone are also not suitable for this reaction because of unsatisfactory conversion and selectivity (entries 4-6). Although CH<sub>3</sub>CN and DMSO lead to considerable conversion of **1** (entries 7 and 8), they are also abandoned due to the inferior selectivity of the product **1a**. Almost complete

School of Chemistry and Chemical Engineering, Separation Engineering Research Center, Nanjing University, Nanjing 210093 (P. R. China).

Electronic Supplementary Information (ESI) available: Experiment methods, characterization of products and original NMR spectra, See DOI: 10.1039/x0xx00000x

#### COMMUNICATION

Published on 22 June 2017. Downloaded by Newcastle University on 23/06/2017 04:48:48.

DOI: 10.1039/C7CC03860G Journal Name

conversion of **1** with a 94% yield of **1a** is achieved in DMF at 80°C for 24 h (entry 9). It can probably be rationalized with the good solubility of  $CO_2$  and  $BH_3NH_3$  in DMF, and the appropriate basicity and nucleophilicity of amines.<sup>25</sup> The reaction is also tested under solvent-free conditions, resulting in poor conversion of **1** and low yield of the desired product (entry 10). It can be seen that the solvent has a prominent effect on the *N*-formylation reaction, namely, intensive polar solvent can activate the N-H bond in *N*-methylaniline through solvation and polarization.<sup>2f,s</sup>

Table 1. Optimization of reaction conditions.

• •		+
1	1a	1b

Entry	Solvent	<i>T</i> (°C)	<i>t</i> (h)	Con. of	Yield of	Yield of
				<b>1</b> (%) <sup>a</sup>	<b>1a</b> (%) <sup>a</sup>	<b>1b</b> (%) <sup>a</sup>
1	toluene	80	24	21	13	7
2	benzene	80	24	22	13	9
3	CHCl₃	80	24	11	8	3
4	1,4-dioxane	80	24	75	60	15
5	THF	80	24	95	79	16
6	acetone	80	24	> 99	75	25
7	CH₃CN	80	24	> 99	78	22
8	DMSO	80	24	91	76	15
9	DMF	80	24	> 99	94	6
10 <sup>b</sup>	—	80	24	18	17	1
11 <sup>c</sup>	DMF	80	24	> 99	82	18
12	DMF	80	8	88	82	6
13	DMF	30	24	64	58	6
14	DMF	50	24	> 99	96	4
15	DMF	120	24	> 99	93	7
16 <sup>d</sup>	DMF	80	24	88	51	37
17 <sup>e</sup>	DMF	80	24	32	30	2
18 <sup>f</sup>	DMF	80	24	0	0	0
19 <sup>g</sup>	DMF	80	24	0	0	0
20 <sup>h</sup>	DMF	80	24	81	78	3
21	H <sub>2</sub> O	80	24	0	0	0

Conditions: *N*-methylaniline (1 mmol), solvent (5 mL), BH<sub>3</sub>NH<sub>3</sub> (3 mmol), CO<sub>2</sub> (1 MPa). [a] The yields were determined by GC/MS using dodecane as the internal standard. [b] solvent-free, *N*-methylaniline (5 mmol), BH<sub>3</sub>NH<sub>3</sub> (15 mmol). [c] BH<sub>3</sub>NH<sub>3</sub> (5 mmol). [d] morpholineborane (3 mmol). [e] dimethylaminoborane (3 mmol). [f] without BH<sub>3</sub>NH<sub>3</sub>. [g] without CO<sub>2</sub>. [h] CO<sub>2</sub> (0.5MPa).

Some previous works<sup>20,p,u,7</sup> suggested that formamide was the main intermediate for reductive methylation. It implies that increasing the amount of reductant supports to the reductive methylation. The amount of  $BH_3NH_3$  is thus raised to 5 mmol justifying the improvement in the selectivity of methylated product (entry 11). However, the yield of *N'N*-dimethylaniline (**1b**) is still quite low. To elucidate the mechanism, *N*-methylformanilide **1a** was further tested to react with the reductant, resulting in a

negligible yield of 3% of *N*,*N*-dimethylaniline (Eq. 1). It indicates that the reductive methylation through the formation of formamide is quite difficult in the absence of catalyst, which enables the high selectivity to the *N*-formylation products.

As for the effect of temperature on the reaction, it is found that reducing the temperature to 30°C results in an apparent decrease in the product yield (entry 13), whereas the reaction at 120 °C leads to a slightly lower yield compared with the case at 80°C (entries 9 and 15). The most appropriate temperature is around  $50^{\circ}$ C in which a yield of 96% for 1a can be obtained (entry 14). Previous literature had reported that the high temperature may favors the methylated product **1b**.<sup>2p</sup> It is not the case in the present study since the yield of 1b only shows a negligible increase at elevated temperatures (entries 9, 14 and 15). This may be due to the lack of catalyst to activate the methylation. Various borane-amine complexes are also employed to find out more suitable reductants. The use of morpholineborane as the reductant leads to a yield of 51% of 1a (entry 16), and the presence of dimethylaminoborane results in a yield of only 30 % of 1a (entry 17). Therefore, BH<sub>3</sub>NH<sub>3</sub> is regarded as the effective reductant and used in the following investigations. Some previous researches reported the transformylating of amine with DMF to formamide in the presence of Ni(II) metal complex or CeO<sub>2</sub>.<sup>8</sup> To eliminate the possibility of *N*-formylation using DMF as reactant, reactions in the absence of BH<sub>3</sub>NH<sub>3</sub> or CO<sub>2</sub> were performed and no products were obtained (entries 18 and 19). The effect of CO<sub>2</sub> pressure on the yield is also examined. The yield of **1a** decreases to 78% at 0.5 MPa (entry 20). In contrast, at higher pressures such as 1 MPa, more CO<sub>2</sub> can be dissolved in the system, resulting in higher yields of 1a (entries 9 and 14). BH<sub>3</sub>NH<sub>3</sub> dissolves in water guite well. If the N-formylation can be performed in water, the reaction will be more environmentally friendly. However, because the acid environment induced by the reaction between  $CO_2$  and  $H_2O$  can rapidly promote the hydrolysis of  $BH_3NH_3$ ,<sup>9</sup> no Nformylation of amines happens in water (Entry 21).



The substrate scope of this reaction was investigated (Scheme 2). A series of secondary amines are tested firstly. Both steric and electronic effect can control the reactivity of these substrates. The substrate 1 gives 1a with an isolated yield of 91%. The methyl substitutions position on the benzene ring of N-methylanilines has obvious influence on the activity (2a-4a). The substrate 4 that has a para-methyl group possesses a higher reactivity than 2 and 3. Due to the steric hindrance, the ortho-methyl substitution of Nmethylaniline leads to a low product yield of 2a (yield: 76%), and similar substrates that have branched chains in the vicinity of amine group also suffer from low yields (64 and 45% for 13a and 21a, respectively). Both electron-donating and electron-withdrawing groups are tolerated, affording the desired products in good to excellent yields (up to 95%, 5a-8a). However, N-methyl-4nitroaniline is inert with a yield of 16% (9a), due to a strong electron-withdrawing effect that weakens greatly the nucleophilicity of the amine. When ethyl, isopropyl, and phenyl Published on 22 June 2017. Downloaded by Newcastle University on 23/06/2017 04:48:48.

#### Journal Name

substituted amines are used as the substrates, the product yields are located in the range of 44 to 85% (**10a-14a**). The use of dibenzylamine results in the desired formamide **15a** with a perfect yield (96%). In particular, the reaction can be conveniently scaled up to grams with an isolated yield of 81% (Eq. 2).

The non-aromatic amines, such as *N*-methylcyclohexylamine, morpholine, piperidine, and dipropylamine, can also be converted to the corresponding formamides in high yields (**16a-19a**), whereas the hydroformylation of sterically hindered amines, such as diisopropylamine **20** and 2,2,6,6-tetramethylpiperidine **21**, is relatively sluggish. Several heterocyclic compounds have also been employed. When 1,2,3,4-tetrahydroquinoline **22** is used, the corresponding formamide **22a** is obtained in a yield of 88 %. In the case of Indoline **23**, the product **23a** is generated to have an excellent yield of 95%. However, indole or pyrrole (**24** and **25**) are completely ineffective for the formylation reaction, primarily due to a strong conjugative effect. To further expand the scope of the reaction, we also tested primary amines. All of the primary amines work well and the corresponding mono-formamides are produced with yields ranging from 74 to 90% (**26a-30a**).



**Scheme 2**. *N*-formylation of various amines using with  $BH_3NH_3$  and  $CO_2$ . Conditions: substrate (1 mmol),  $BH_3NH_3$  (3 mmol), DMF (5 mL). Isolated yield is given unless otherwise stated. [a] <sup>1</sup>H NMR yields (1,3,5-trimethyoxybenzene as an internal standard).

The obtained results indicate that  $BH_3NH_3$  is a highly effective reductant for the *N*-formylation of various amines using CO<sub>2</sub> as the C1 source without any catalyst. To look insight into the reaction mechanism, several control experiments are performed. It is confirmed that *N*-methylaniline does not react with DMF (Entries 18 and 19, Table 1), so that the pathway of transformylating amine with DMF to formamide can be excluded in the absence of catalyst.<sup>8</sup> The previous works presented that  $BH_3NH_3$  could be used as reductant for the conversion of CO<sub>2</sub> to CH<sub>3</sub>OH or HCOOH in the View Article Online DOI: 10.1039/C7CC03860G COMMUNICATION

presence of stoichiometric catalyst. <sup>5</sup> Besides, both CH<sub>3</sub>OH and HCOOH can serve as the C1 source for *N*-formylation or methylation promoted by catalysts. <sup>10</sup> A control experiment replacing CO<sub>2</sub> by CH<sub>3</sub>OH or HCOOH was performed and no any product was detected (Eq. 3).



Scheme 3. The possible reaction mechanism for the *N*-formylation of amines.

Since  $CO_2$  and the amine- $CO_2$  adduct coexist in equilibrium, the preferential reduction of  $\rm CO_2$  or the amine- $\rm CO_2$  adduct is a controversial subject till now.  $^{11}$  To distinguish these two possible reaction routes, the reduction of CO<sub>2</sub> and the CO<sub>2</sub>-amine adduct with BH<sub>3</sub>NH<sub>3</sub> is carried out separately under the standard conditions. When the morpholine-CO<sub>2</sub> adduct is used, the product 17a is generated in a very low yield (12%) and the methylated product 17b is undetectable (Eq. 4). However, for other substrates with weaker alkalinity, no detectable amine-CO<sub>2</sub> adduct can be formed (such as 1). Hence, the possibility of reaction via the amine-CO<sub>2</sub> adduct can be eliminated. To explore the reaction mechanism, some experiments have been further performed. It is interesting to find that two B peaks (-23.890 and -29.245 ppm) were detected in the <sup>11</sup>B-NMR when BH<sub>3</sub>NH<sub>3</sub> was dissolved in DMF (Figure S1(b)), suggesting there exists an equilibrium between I and II (Scheme 3). Adding CO<sub>2</sub> into the DMF solution of BH<sub>3</sub>NH<sub>3</sub> can produce a white solid.  ${}^{\bar{1}}\text{H}\text{-},\,{}^{\bar{1}3}\text{C},\,\text{and}\,\,{}^{11}\text{B}\text{-}\text{NMR}$  (including dept-90 and -135) analysis show that the white solid is a boron-formate DMF complex (III) (Figure S1 (c-f)). The insert of CO<sub>2</sub> into B-H bond to generate boronformate and B-OCH<sub>3</sub> can be found in previous researches.<sup>12</sup> The white solid III can further react with morpholine to produce 17a with a good yield of 86%. Considering that the N-formylation also works in other solvents (Entries 6-8, Table 1), we can image that 17 can replace DMF in III so that the reaction between 17 and boron-formate will be easier from the viewpoint of transition state theory. Based on these results, the plausible mechanism was presented in Scheme 3.

In conclusion, we have developed a green, catalyst-free and effective procedure for the *N*-formylation using  $CO_2$  as the  $C_1$  source and BH<sub>3</sub>NH<sub>3</sub> as the reductant under mild conditions. *N*-formylation works quite well in the absence of catalyst whereas the

DOI: 10.1039/C7CC03860G

Journal Name

#### COMMUNICATION

*N*-methylation is highly catalyst dependent, which makes the reaction reported here affording the formamides in good to excellent yield. The reported reactions do not require an inert atmosphere and is applicable to a wide range of substrates. It provides an easy access to different formamides. Some catalytic systems using cheap catalysts (e.g.  $Cs_2CO_3$ ,  $K_2CO_3$ , Cu, Zn) have been reported.<sup>2m,p,q,u</sup> Most of these examples adopted silane as reductant, which has a low atomic economy. Besides, the separation of the N-formylation product and silane by-product is not easy because they have similar solubility. On the contrary, the BH<sub>3</sub>NH<sub>3</sub> by-product is water soluble and catalyst-free process further simplify the separation of product.

Thanks are given to Prof. Guy Bertrand for useful suggestion and discussion. This work was supported by National Natural Science Foundation of China (No.21376115, and 21676134) and the Fundamental Research Funds for the Central Universities (0205 14380106).

#### Notes and references

- 1 (a) J. Y. Wang, L. Huang, R. Y. Yang, Z. Zhang, J. W. Wu, Y. S. Gao, Q. Wang, D. O'Hare and Z. Y. Zhong, Energy Environ. Sci., 2014, 7, 3478-3518; (b) S. Ma, G. Chen, M. Guo, Z. Li, T. Han and S. Zhu, Renew. Sust. Energ. Rev., 2014, 37, 687-697; (c) Z. Yang, L. He, J. Gao, A. Liu and B. Yu, Energy Environ. Sci., 2012, 5, 6602-6639; (d) M. Pera-Titus, Chem. Rev., 2014, 114, 1413-1492; (e) J. Klankermayer, S. Wesselbaum, K. Beydoun and W. Leitner, Angew. Chem. Int. Ed., 2016, 55, 7296-7343; (f) A. W. Kleij, M. North and A. Urakawa, ChemSusChem, 2017, 10, 1036-1038; (g) W. H. Wang, Y. Himeda, J. T. muckerman, G. F. Manbeck and E. Fujita, Chem. Rev., 115, 12936-12973; (h) Q. Liu, L. Wu, R. Jackstell and M. Beller, Nature Comm., 2015, 6, 5933, (i) A. Otto, T. Grube, S. Schiebahn and D. Stolten, Energy Environ. Sci., 2015, 8, 3283-3297, (j) Q. Song, Z. Zhou and L. He, Green. Chem., 2017, DOI: 10.1039/C7GC00199A.c
- 2 (a) P. Daw, S. Chakraborty, G. Leitus, Y. Diskin-Posner, Y. Ben-David and D. Milstein, ACS Catal., 2017, 7, 2500-2504; (b) V. B. Saptal and B. M. Bhanage, ChemSusChem, 2016, 9, 1980-1985; (c) O. Santoro, F. Lazreg, Y. Minenkov, L. Cavallob and C. S. J. Cazin, Dalton Trans., 2015, 44, 18138-18144; (d) N. M. Rezayee, C. A. Huff and M. S. Sanford, J. Am. Chem. Soc., 2015, 137, 1028-1031; (e) H. Liu, Q. Mei, Q. Xu, J. Song, H. Liu and B. X. Han, Green Chem., 2017, 19, 196-201; (f) J. Song, B. Zhou, H. Liu, C. Xie, Q. Meng, Z. Zhang and B. X. Han; Green Chem., 2016, 18, 3956-3961; (g) L. Hao, Y. Zhao, B. Yu, Z. Yang, H. Zhang, B. X. Han, X. Gao and Z. Liu, ACS Catal., 2015, 5, 4989-4993; (h) A. Juli, V. Polo, E. A. Jaseer, F. J. Ferandez-Alvarez and L. A. Oro, ChemCatChem, 2015, 7, 3895-3902; (i) T. V. Q. Nguyen, W. Yoo and S. Kobayashi, Angew. Chem. Int. Ed., 2015, 54, 9209-9212; (j) L. Zhang, Z. Han, X. Zhao, Z. Wang and K. Ding, Angew. Chem. Int. Ed., 2015, 54, 6186-6189; (k) M. Hulla, F. D. Bobbink, S. Das and P. J. Dyson, ChemCatChem, 2016, 8, 3338-3342; (I) S. Das, F. D. Bobbink, S. Bulut, M. Soudania and P. J. Dyson, Chem. Commun., 2016, 52, 2497-2500; (m) S. Zhang, Q. Mei, H. Liu, H. Liu, Z. Zhang and B. X. Han, RSC Adv., 2016, 6, 32370-32373; (n) B. Dong, L. Wang, S. Zhao, R. Ge, X. Song, Y. Wang and Y. Gao, Chem. Commun., 2016, 52, 7082-7085; (o) X. F. Liu, R. Ma, C. Qiao, H. Cao and L. N. He, Chem. Eur. J., 2016, 22, 16489-16493; (p) C. Fang, C. Lu, M. Liu, Y. Zhu, Y. Fu and B. L. Lin, ACS Catal., 2016, 6, 7876-7881; (q) D. B. Nale and B. M. Bhanage, Synlett 2016, 27, 1413-1417; (r) C. C. Chong and R. Kinjo, Angew. Chem. Int. Ed., 2015, 54, 12116-12120; (s) H. Lv, Q. Xing, C. Yue, Z. Lei and F. Li. Chem.

*Commun.*, 2016, **52**, 6545-6548; (t) Y. H. Li, X. J. Cui, K. W. Dong, K. Junge, M. Beller, *ACS Catal.*, 2017, **7**, 1077-1086; (u) Z. Z. Yang, B. Yu, H. Y. Zhang, Y. F. Zhao, G. P. Ji and Z. M. Liu, *RSC Adv.*, 2015, **5**, 19613-19619; (v) P. Ju, J. Chen, A. Chen, L. Chen and Y. Yu, *ACS Sustainable Chem. Eng.*, 2017, **5**, 2516-2528; (w) C. D. N. Gomes, O. Jacquet, C. Villiers, P. Thuery, M. Ephritikhine and T. Cantat, *Angew. Chem. Int. Ed.*, 2012, **51**, 187-190; (x) X. Frogneux, O. Jacquet and T. Cantat, *Catal. Sci. Technol.*, 2014, **4**, 1529-1533; (y) F. Liu, X. Li, Chang Q, H. Fu and L. He, *Angew. Chem. Int. Ed.*, 2017, **56**,7425-7429; z) H. Niu, L. Lu, R. Shi, C. Chiang, A. W. Lei, *Chem. Commun.*, 2017, **53**, 1148-1151.

- 3 (a) X. Zhang, L. Kam, R. Trerise and T. J. Williams, Acc. Chem. Res., 2017, 50, 86-95; (b) S. Kim, W. Han, T. Kim, T. Kim, S. W. Nam, M. Mitoraj, L. Piekos, A. Michalak, S. Hwang, and S. O. Kang, J. Am. Chem. Soc., 2010, 132, 9954-9955; (c) M. E. Bluhu, M. G. Bradley, R. Butterick, U. Kusari and L. G. Sneddon, J. Am. Chem. Soc., 2006, 128, 7748-7749; (d) Z. Lu, L. Schweighauser, H. Hausmann and H. A. Wegner, Angew. Chem. Int. Ed., 2015, 54, 15556-15559; (e) J. A. Buss, G. A. Edouard, C. Cheng, J. Shi and T. Agapie, J. Am. Chem. Soc., 2014, 136, 11272-11275.
- 4 X. Hu, M. Soleolhavoup, M. Melaimi, J. Chu and G. Bertrand, Angew. Chem. Int. Ed., 2015, **54**, 6008-6011.
- 5 (a) G. Zeng, S. Maeda, T. Taketsugu and S. Sakaki, *J. Am. Chem. Soc.*, 2016, **138**, 13481-13484; (b) G. Menard and D. W. Stephan, *J. Am. Chem. Soc.*, 2010, **132**, 1796-1797; (c) L. Roy, P. M. Zimmerman and A. Paul, *Chem. Eur. J.*, 2011, **17**, 435-439.
- 6 (a) T. X. Zhao, X. B. Hu, D. S. Wu, R. Li, G. Q. Yang and Y. T. Wu, *ChemSusChem*, 2017, **10**, 2046-2052; (b) K. Huang, X. M. Zhang, X. B. Hu and Y. T. Wu, *AIChE J.*, 2016, **62**, 4480-4490; (c) X. Zhang, K. Huang, S. Xia, Y. Chen, Y. Wu and X. Hu, *Chem. Eng. J.*, 2015, **274**, 30-38 (d) X. B. Hu, Y. X. Li, K. Huang, S. Ma, H. Yu and Y. T. Wu, *Green Chem.*, 2012, **14**, 1440-1446.
- 7 (a) S. Das, D. Addis, S. Zhou, K. Junge and M. Beller, J. Am. Chem. Soc., 2010, 132, 1770-1771; (b) O. Jacquet, X. Frogneux, C. D. N. Gomes and T. Cantat, Chem. Sci., 2013, 4, 2127-2131; (c) C. Qiao, X. Liu, X. Liu and L. He, Org. Lett., 2017, 19, 1490-1493; (d) A. Tlili, E. Blondiaux, X. Forgneux and T. Cantat, Green Chem., 2015, 17, 157-168.
- 8 (a) R. B. Sonawane, N. K. Rasal and S. V. Jagtap, Org. Lett. 2017, 19, 2078-2081; (b) Y. Wang, F. Wang, C. Zhang, J. Zhang, M. Li and J. Xu, Chem. Commun., 2014, 50, 2438-2441.
- 9 F. H. Stephens, R. T. Baker, M. H. Matus, D. J. Grant and D. A. Dixon, Angew. Chem. Int. Ed. 2007, 46, 746-749.
- 10 (a) A. Bruneau-Voisine, D. Wang, V. Dorcet, T. Roisnel, C. Darcel and J. Sortais, J. Catal., 2017, 347, 57-62; (b) N. Ortega, C. Richter and F Glorius, Org. Lett., 2013, 15, 1776-1779; (c) L. Zhu, L. Wang, B. Li, W. Li and B. Fu, Catal. Sci. Technol., 2016, 6, 6172-6176; (d) S. Chakraborty, U. Gellrich, Y. Diskin-Posner, G. Leitus, L. Avram and D. Milstein, Angew. Chem. Int. Ed., 2017, 56, 4229-4233.
- (a) W. Chen, J. Shen, T. Jurca, C. Peng, Y. Lin, Y. Wang, W. Shih, G. P. A. Yap and T. Ong, *Angew. Chem. Int. Ed.*, 2015, 54, 15207-15212; (b) Y. Li, I. Sorriber, T. Yan, K. Junge and M. Beller, *Angew. Chem. Int. Ed.*, 2013, 52, 12156-12160; (c) K. Beydoun, T. Stein, J. Klankermayer and W. Leitner, *Angew. Chem. Int. Ed.*, 2013, 52, 9554-9557; (d) Y. Li, X. Fang, K. Junge and M. Beller, *Angew. Chem. Int. Ed.*, 2013, 52, 9568-9571.
- 12 (a) I. Knopf and C. C. Cummins. Organometallics, 2015, 34, 1601-1603; (b) M. Lafage, A. Pujol, N. Saffon-Merceron and N. Mezailles. ACS Catal., 2016, 6, 3030-3035.



Formamides were produced by catalyst-free N-formylation of amines using CO<sub>2</sub> as the C<sub>1</sub> source and BH<sub>3</sub>NH<sub>3</sub> as the reductant at mild conditions with good to excellent yield.