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Carbon Nanotube–Gold Nanohybrid Catalyzed N-Formylation of Amines by using Aqueous Formaldehyde

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The N-formylation of a variety of primary and secondary amines by using aqueous formaldehyde at room temperature in open air affords the corresponding formamides in excellent yield under the catalytic influence of a gold–carbon nanotube nanohybrid. The reaction is also marked by excellent chemoselectivity, low catalyst loading, and recyclability of the catalyst.

Formamides are valuable intermediates in organic synthesis and medicinal chemistry.[1,2] For example, the synthesis of the quinolone antibiotic norfloxacine was achieved via a substituted formanilide as the key intermediate.[2] The role of formamides as intermediates in the synthesis of other N-heterocycles[3] and as catalysts in the allylation and hydrosilylation of carbonyl compounds[4] has been well documented. Formamides have been extensively employed in Vilsmeier formylation[5,6] and as key amino protecting groups in peptide synthesis.[6,7] The formylation of various amines has been reported with reagents such as formic acid/amide,[1,8] acetic formic anhydride,[9] formate,[10] cyanide,[11] and chloral.[12] However, the wide applicability of these methods has been curtailed by one or more shortcomings such as undesirable side reactions, the toxicity of the reagents, the requirement for the pre-preparation of the formylating agents, elevated temperatures, and anhydrous conditions.

Recently, the direct N-formylation of amines by using MeOH[13] or formalin[14] as a formyl source in the presence of AuNPs (gold nanoparticles) was reported. Although these are elegant approaches, the requirement for a higher temperature (60–100 °C) along with an oxygen atmosphere in the former case and a higher catalyst loading combined with a lack of recyclability in the latter case prompted us to further investigate the N-formylation of various amines.

From the state of being a catalytically inert or ineffective transition metal, gold has emerged in recent years as an attractive catalyst for a variety of organic transformations, especially after downsizing into nanometer-sized particles.[15] Recently, we disclosed the superior catalytic activity of carbon nanotube (CNT)-supported nanogold in the oxidation of silanes,[16] alcohols,[17] and phenols[18] and the reductive amination of aldehydes.[19] CNTs were chosen as a support owing to their low cost, high surface area, tunable topography, inertness, and their extraordinary stability and ability to stabilize transient higher oxidation states of the supported metal.[20]

The AuCNT nanohybrids were prepared by introducing a two-layer assembly around a CNT and then adding preformed AuNPs.[16] The polyanionic inner layer is derived from a micelle consisting of a photopolymerizable polyacetylenic hydrophobic tail and a polar carboxylate head group (DANTA amphiphile). The polycationic quaternary ammonium (PDADMAC) outer layer stabilizes the AuNPs on the surface (Figure 1).

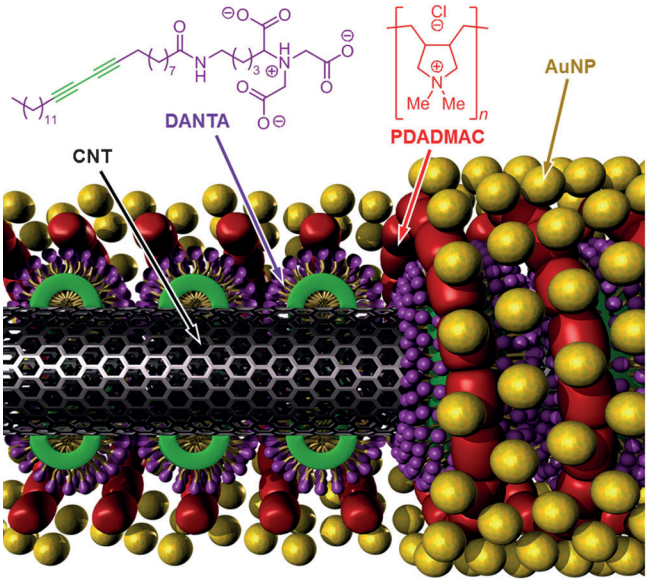

Figure 1. Overview of the AuCNT structure. DANTA = diacetylene nitrilotriacetate amphiphile, PDADMAC = poly(diallyldimethylammonium chloride), AuNP = gold nanoparticle, CNT = multiwalled carbon nanotube.

Herein, we report for the first time the highly selective direct N-formylation of amines with aqueous HCHO as the formyl source under the catalytic influence of a AuCNT nanohybrid.

Our recent results in the aerobic oxidation of alcohols by AuCNTs[17] inspired us to attempt the N-formylation of *N*-methylaniline (**1a**) through the in situ generation of formaldehyde from methanol (Table 1). However, no reaction was observed even after 24 h of stirring **1a** in MeOH/H_2O (1:1) in the pres-

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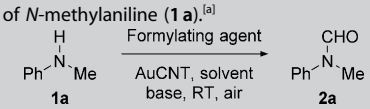
Table 1. Optimization of the reaction conditions for the AuCNT-catalyzed N-formylation of *N*-methylaniline (**1a**).[a]

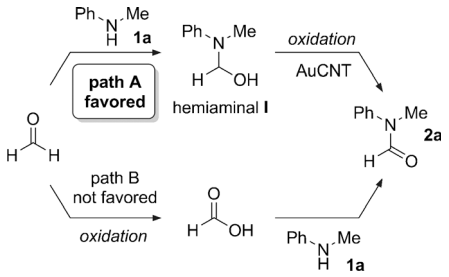


Entry	Formylating agent	Base (equiv.)	Solvent	Yield [b] [%]
1[c]	MeOH	NaOH (3)	H_2O	NR[d]
2[e]	HCHO	NaOH (3)	toluene/H_2O	87
3	HCHO	NaOH (3)	toluene/H_2O	94
4	HCHO	LiOH (3)	toluene/H_2O	76
5	HCHO	NaOH (3)	CH_2Cl_2/H_2O	87
6	HCHO	NaOH (2)	toluene/H_2O	83
7	HCHO	NaOH (1)	toluene/H_2O	80
8	HCHO	none	toluene/H_2O	NR[d]
9[f]	HCHO	NaOH (3)	toluene/H_2O	NR[d]
10[g]	HCHO	NaOH (3)	toluene/H_2O	NR[d]
11[h]	HCHO	NaOH (3)	toluene/H_2O	NR[d]
12	HCO_2H	NaOH (3)	toluene/H_2O	NR[d]

[a] Conditions (unless otherwise stated): Methylaniline (**1a**, 0.1 mmol), formylating agent (2 equiv.), AuCNT (aqueous suspension, 0.34 mol%), base (1–3 equiv.), toluene/H_2O or CH_2Cl_2/H_2O (1:1, 1 mL), RT, open flask (air), 24 h. [b] Yield of purified isolated product. [c] AuCNT (0.17 mol%). [d] NR = no reaction. [e] AuCNT (0.17 mol%), 30 h. [f] No catalyst. [g] Only CNT was used. [h] CNT with the bilayer assembly, but without AuNP, was used.

ence of AuCNT (0.17 mol%) and NaOH (3 equiv.) at room temperature (Table 1, entry 1). This suggested that direct N-formylation of amines through the in situ oxidation of MeOH was not feasible under our experimental conditions. Subsequently, N-formylation of **1a** was performed by using 38% aqueous HCHO as the formyl source under aerobic conditions under the catalytic influence of AuCNTs (0.17 mol%), which afforded expected product **2a** in 87% yield after 30 h (Table 1, entry 2). The turnover number (TON) and turnover frequency (TOF) calculated for this reaction were 512 and 17 h^{-1}, respectively (see the Experimental Section for details). Increasing the catalyst loading to 0.34 mol% further improved the yield to 94% and shortened the reaction time to 24 h (Table 1, entry 3). Changing the base from NaOH to LiOH (Table 1, entry 4), the solvent from toluene/H_2O to CH_2Cl_2/H_2O (Table 1, entry 5), or reducing the quantity of base (Table 1, entries 6 and 7) did not have any positive effect. The reaction did not take place in the absence of either the base (Table 1, entry 8) or the catalyst (Table 1, entry 9) or if CNT/CNT with a bilayer assembly was used in the absence of the AuNPs (Table 1, entries 10 and 11). There was also no reaction if formaldehyde was replaced by formic acid under otherwise identical conditions (Table 1, entry 12). This observation shed light onto the plausible mechanism of formylation in that oxidation of formaldehyde to formic acid followed by amidation was ruled out (Scheme 1, path B). Instead, formation of hemiaminal **I** followed by its oxidation (catalyzed by AuCNT) to formamide **2a** appeared to be the favored pathway (Scheme 1, path A).[14]

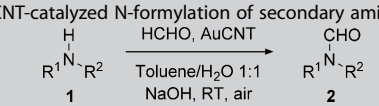
The scope of this formylation was investigated with various secondary and primary amines under the above-optimized conditions (Tables 2 and 3). Besides **1a**, an open-chain secondary amine (Table 2, entry 1), representative cyclic secondary amines such as piperidine (**1b**, a dialkylamine), and aryl alkylamines **1c** and **1d** were also subjected to N-formylation to afford corresponding formamides **2b**–**2d** in excellent yields (89–94%; Table 2, entries 2–4). Diarylamine **1e** did not undergo formylation even after 24 h, which was attributable to deactivation of the amino group by the two aryl groups (Table 2, entry 5).

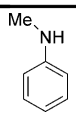
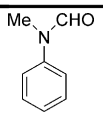
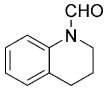
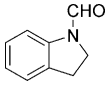
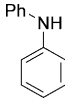
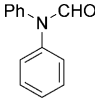


Scheme 1. Plausible mechanism for the N-formylation of amine **1a** with HCHO.

Having demonstrated the efficacy of our experimental conditions for the formylation of various secondary amines, the formylation of primary aromatic amines was investigated (Table 3). In general, amines with electron-withdrawing and electron-donating groups on the aromatic ring were amenable to the reaction over a period of 22–30 h at room temperature. However, the formylation of parent aniline **3a** and that of substrates **3b** and **3c** with electron-donating groups in the *para* position proceeded in marginally higher yields to deliver products **4a–c** (92–94%; Table 3, entries 1–3).

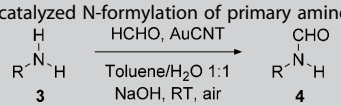
Table 2. AuCNT-catalyzed N-formylation of secondary amines **1**.[a]

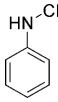
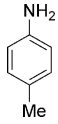
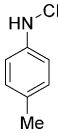
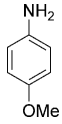
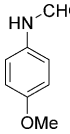
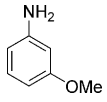
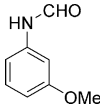
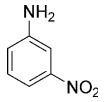
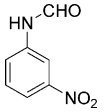
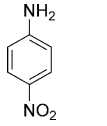
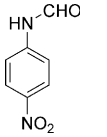
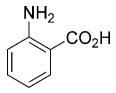
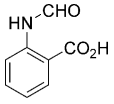
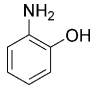
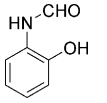
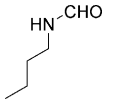


Entry	Substrate	1	Product	2	Yield[b] [%]
1		**1a**		**2a**	94
2		**1b**		**2b**	90
3		**1c**		**2c**	89
4		**1d**		**2d**	94
5		**1e**		**2e**	NR[c]

[a] Conditions: Amine **1** (0.1 mmol), formaldehyde (2 equiv.), AuCNT (aq. suspension, 0.34 mol%), NaOH (3 equiv.), toluene/H_2O (1:1, 1 mL), RT, open flask (air), 24 h. [b] Yield of purified isolated product. [c] NR = no reaction.

Table 3. AuCNT-catalyzed N-formylation of primary amines **3**.[a]

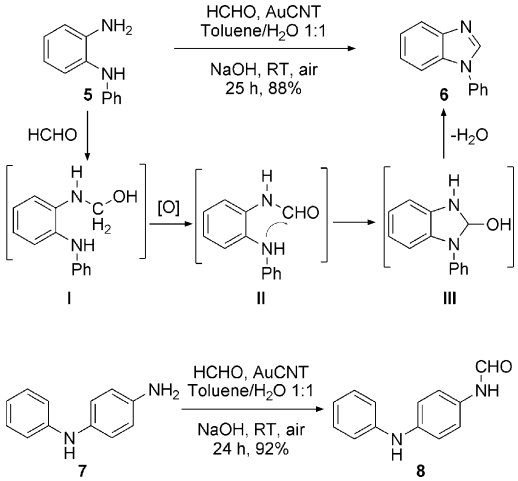


Entry	Substrate	3	Product	4	Time [h]	Yield[b] [%]
1		**3a**		**4a**	26	92
2		**3b**		**4b**	24	92
3		**3c**		**4c**	22	94
4		**3d**		**4d**	27	83
5		**3e**		**4e**	30	80
6		**3f**		**4f**	24	NR[c]
7		**3g**		**4g**	28	89
8		**3h**		**4h**	25	86
9		**3i**		**4i**	24	NR[c]

[a] Conditions: Amine **1** (0.1 mmol), formaldehyde (2 equiv.), AuCNT (aq suspension, 0.34 mol%), NaOH (3 equiv.), toluene/H_2O (1:1, 1 mL), RT, open flask (air), 24 h. [b] Yield of purified isolated product. [c] NR = no reaction.

Anilines substituted in the *meta* position reacted well, regardless of the electronic nature of the substituent; for example, **3d** and **3e** provided products **4d** and **4e** in 83 and 80% yield, respectively (Table 3, entries 4 and 5), whereas no reaction was observed in the case of *p*-nitroaniline (**3f**) even after 24 h, presumably owing to strong deactivation of the amino group (Table 3, entry 6). Anilines possessing various substituents in the *ortho* position, for example, anthranilic acid (**3g**) and *o*-aminophenol (**3h**), also underwent facile formylation under our experimental conditions to furnish products **4g** and **4h** in 89 and 86% yield, respectively (Table 3, entries 7 and 8). There was no competitive O-formylation in the latter case, and this indicates a high degree of chemoselectivity (Table 3, entry 8). However, primary alkyl amines were unreactive under our experimental conditions (Table 3, entry 9).

The inertness of diarylamine **1e** prompted us to further investigate the chemoselectivity in the N-formylation of primary and secondary amines. Thus N-formylation of diamine **5** led to the formation of benzimidazole **6** in 88% yield (Scheme 2).



Scheme 2. Chemoselectivity in the N-formylation of amines.

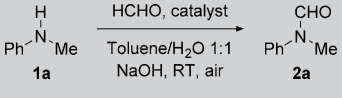
This is ascribable to a cascade reaction involving chemoselective N-formylation of the primary amino group to form intermediate **II** by hydroxymethylation of **5** and the AuCNT-catalyzed oxidation of **I**, followed by intramolecular cyclization of **II** to **III** and dehydration to give benzimidazole **6**. Upon performing this reaction in the absence of AuCNT, there was no conversion at all; this confirmed that benzimidazole formation proceeded through AuCNT-catalyzed N-formylation and not through an uncatalyzed imine/iminium intermediate. Yet another chemoselective formylation was performed by using *p*-aminodiphenylamine (**7**) as the substrate (Scheme 2). As expected, the primary amino group underwent selective formylation to provide formamide **8** in excellent yield (92%).

To compare the catalytic efficiency of AuCNT with that of colloidal AuNPs and a gold salt, the formylation of **1a** to **2a** was performed with identical loading (0.34 mol%) of different catalysts (Table 4). Only trace amounts of **2a** were observed in the presence of colloidal AuNPs (Table 4, entry 2), and there was no product formation at all in the presence of gold salt $HAuCl_4$ even after a reaction time of 3 days (Table 4, entry 3), which thus confirmed the superior catalytic activity of AuCNT (Table 4, entry 1).

Besides the requirement for only a very low catalyst loading (0.34 mol%), the recyclability of AuCNT is remarkable (Table 5). The catalyst was easily recovered by simple centrifugation and was reused for N-formylation without any significant loss of activity up to four cycles with only a marginal drop in the yield from 94 to 92% (Table 5, entries 1–5).

The key role of the AuCNT nanohybrid as the active catalytic species and the heterogeneous nature of the catalyst were

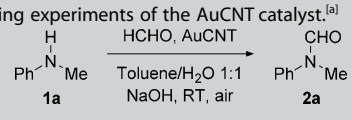
Table 4. Comparison of various Au sources in the N-formylation of *N*-methylaniline (**1a**).[a]



Entry	Catalyst	Loading [mol%]	Time [h]	Yield[b] [%]
1	AuCNT	0.34	24	94
2	AuNP colloid	0.34	72	trace
3	$HAuCl_4$	0.34	72	NR[c]

[a] Conditions: Amine **1a** (0.1 mmol), formaldehyde (2 equiv.), catalyst (0.34 mol%), NaOH (3 equiv.), toluene/H_2O (1:1, 1 mL), RT, open flask (air). [b] Yield of purified isolated product. [c] NR = no reaction.

Table 5. Recycling experiments of the AuCNT catalyst.[a]



Entry	AuCNT	Time [h]	Yield[b] [%]
1	fresh	24	94
2	recycle 1	24	93
3	recycle 2	24	93
4	recycle 3	24	92
5	recycle 4	24	92

[a] Conditions: Amine **1a** (0.1 mmol), formaldehyde (2 equiv.), AuCNT (aq suspension, 0.34 mol%), NaOH (3 equiv.), toluene/H_2O (1:1, 1 mL), RT, open flask (air), 24 h. [b] Yield of purified isolated product.

confirmed by performing the N-formylation of **1a** by using AuCNT (0.34 mol%) and removing the catalyst after 12 h by centrifugation. At that stage, approximately 44% conversion was observed and there was no further progress upon stirring the catalyst-free reaction mixture overnight at room temperature.

In conclusion, we developed a simple protocol for the N-formylation of primary and secondary amines with aqueous HCHO as the formyl source by using a AuCNT nanohybrid catalyst. The reported conditions are effective in open air, without an O_2 atmosphere, and require no heating. Excellent chemoselectivity was observed in that a primary amino group could be formylated in the presence of phenolic OH and diarylamino groups. The AuCNT nanohybrid compares favorably to other supported gold nanoparticle based catalytic systems in terms of catalyst loading, selectivity, recyclability, and mild reaction conditions.

Experimental Section

General procedure for the N-formylation of amines

A solution of amine **1**, **3**, **5**, or **7** (0.1 mmol) in a mixture of toluene/water (1:1, 1 mL) was prepared and 38% aqueous HCHO (25 μL, 2 equiv.), NaOH (12 mg, 0.3 mmol, 3 equiv.), and aqueous AuCNT (100 μL from 3.4 mM suspension in H_2O, 0.34 mol%) were added. The mixture was stirred until complete consumption of the starting material (24–30 h, as monitored by TLC). The aqueous layer was then extracted with EtOAc (3×10 mL). The combined organic layer was dried (anhydrous Na_2SO_4) and concentrated under vacuum. The crude residue was directly subjected to column chromatography to give pure product **2**, **4**, **6**, or **8**.

Recycling experiment

A solution of *N*-methylaniline (**1a**; 10.7 mg, 0.1 mmol) in a mixture of toluene/water (1:1, 1 mL) was prepared and aqueous HCHO (25 μL, 2 equiv.), NaOH (12 mg, 0.3 mmol, 3 equiv.), and aqueous AuCNT (100 μL, from 3.4 mM suspension in H_2O, 0.34 mol%) were added. The mixture was stirred until the complete consumption of the starting material (24 h, as monitored by TLC) at room temperature. The catalyst was then recovered by simple centrifugation and reused without further purification.

TON and TOF experiments

A solution of *N*-methylaniline (**1a**; 10.7 mg, 0.1 mmol) in a mixture of toluene/water (1 ml, 1:1) was prepared and aqueous HCHO (25 μL, 2 equiv.), NaOH (12 mg, 0.3 mmol, 3 equiv.), and aqueous AuCNT (50 μL, from 3.4 mM suspension in H_2O, 0.17 mol%) were added. The mixture was stirred for 30 h at room temperature, and then the catalyst was removed by centrifugation. The mixture was concentrated under vacuum. The crude residue was directly subjected to silica gel column chromatography to afford pure **2a** (87% yield). The TON and TOF were calculated by using Equations (1) and (2):

$$\begin{aligned}\text{TON for amine} &= \text{product (mmol)} \,/\, \text{catalyst (mmol)} \\ &= 0.087 \,/\, 0.00017 \\ &= 512\end{aligned} \quad (1)$$

$$\begin{aligned}\text{TOF for amine} &= \text{TON} \,/\, \text{time} \\ &= 512 \,/\, 30 \\ &= 17\ \text{h}^{-1}\end{aligned} \quad (2)$$

The product was isolated in 94% yield by increasing the catalyst loading to 0.34 mol%, which also reduced the reaction time to 24 h.

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[1] M. Hosseni-Sarvari, H. Sharghi, *J. Org. Chem.* **2006**, *71*, 6652–6654.
[2] A. Jackson, O. Meth-Cohn, *J. Chem. Soc. Chem. Commun.* **1995**, 1319.
[3] a) B.-C. Chen, M. S. Bednarz, R. Zhao, J. E. Sundeen, P. Chen, Z. Shen, A. P. Skoumbourdis, J. C. Barrish, *Tetrahedron Lett.* **2000**, *41*, 5453–5456;

b) K. Kobayashi, S. Nagato, M. Kawakita, O. Morikawa, H. Konishi, *Chem. Lett.* **1995**, 575 – 576; c) A. Kakehi, S. Ito, S. Hayashi, T. Fujii, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 3573 – 3580.

[4] Allylation: a) S. Kobayashi, K. Nishio, *J. Org. Chem.* **1994**, *59*, 6620 – 6628; b) K. Iseki, S. Mizuno, Y. Kuroki, Y. Kobayashi, *Tetrahedron* **1999**, *55*, 977 – 988. Hydrosilylation: c) S. Kobayashi, M. Yasuda, I. Hachiya, *Chem. Lett.* **1996**, 407 – 408.

[5] I. M. Downie, M. J. Earle, H. Heaney, K. F. Shuhaibar, *Tetrahedron* **1993**, *49*, 4015 – 4035.

[6] J. Martinez, J. Laur, *Synthesis* **1982**, 979 – 981.

[7] A. Flörsheimer, M. R. Kula, *Monatsh. Chem.* **1988**, *119*, 1323 – 1331.

[8] Selected articles: Formic acid: a) J. Akbari, M. Hekmati, M. Sheykhan, A. Heydari, *ARKIVOC* **2009**, *xi*, 123; b) B. Das, M. Krishnaiah, P. Balasubramanyam, B. Veeranjaneyulu, D. Nandakumar, *Tetrahedron Lett.* **2008**, *49*, 2225 – 2227; c) A. Chandra Shekhar, A. Ravi Kumar, G. Sathaiah, V. Luke Paul, M. Sridhar, P. ShanthanRao, *Tetrahedron Lett.* **2009**, *50*, 7099 – 7101; d) S. Majumdar, J. De, J. Hossain, A. Basak, *Tetrahedron Lett.* **2000**, *41*, 9149 – 9151; e) F. M. F. Chen, N. L. Benoiton, *Synthesis* **1979**, 709 – 710; f) B. A. Aleiwi, K. Mitachi, M. Kurosu, *Tetrahedron Lett.* **2013**, *54*, 2077 – 2081. Formamide: g) M. Suchý, A. A. H. Elmehriki, R. H. E. Hudson, *Org. Lett.* **2011**, *13*, 3952 – 3955.

[9] a) T. W. Green, P. G. M. Wuts, *Protective Groups in Organic Synthesis, 3rd ed.*, Wiley-Interscience, New York, **1999**; b) J. C. Sheehan, D. D. H. Yang, *J. Am. Chem. Soc.* **1958**, *80*, 1154 – 1158; c) P. Strazzolini, A. G. Giumanini, S. Cauci, *Tetrahedron* **1990**, *46*, 1081 – 1118.

[10] Ammonium formate: a) P. G. Reddy, G. D. K. Kumar, S. Baskaran, *Tetrahedron Lett.* **2000**, *41*, 9149 – 9151; b) B. Desai, T. N. Danks, G. Wagner, *Tetrahedron Lett.* **2005**, *46*, 955 – 957. Alkyl formate: c) H. Schmidhammer, A. Brossi, *Can. J. Chem.* **1982**, *60*, 3055 – 3060.

[11] K. Bao, W. Zhang, X. Bu, Z. Song, L. Zhanga, M. Cheng, *Chem. Commun.* **2008**, 5429 – 5431.

[12] F. F. Blicke, C.-J. Lu, *J. Am. Chem. Soc.* **1952**, *74*, 3933 – 3934.

[13] a) S. Tanaka, T. Minato, E. Ito, M. Hara, Y. Kim, Y. Yamamoto, N. Asao, *Chem. Eur. J.* **2013**, *19*, 11832 – 11836; b) T. Ishida, M. Haruta, *ChemSusChem* **2009**, *2*, 538 – 541.

[14] P. Preedasuriyachai, H. Kitahara, W. Chavasiri, H. Sakurai, *Chem. Lett.* **2010**, *39*, 1174 – 1176.

[15] a) A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem.* **2006**, *118*, 8064 – 8105; *Angew. Chem. Int. Ed.* **2006**, *45*, 7896 – 7936; b) A. Corma, H. Garcia, *Chem. Soc. Rev.* **2008**, *37*, 2096 – 2126; c) Y. Mikami, A. Dhakshinamoorthy, M. Alvaro, H. Garcıa, *Catal. Sci. Technol.* **2013**, *3*, 58 – 69; d) C. Della Pina, E. Falletta, L. Prati, M. Rossi, *Chem. Soc. Rev.* **2008**, *37*, 2077 – 2095; e) Y. Zhang, X. Cui, F. Shi, Y. Deng, *Chem. Rev.* **2012**, *112*, 2467 – 2505; f) C. Della Pina, E. Falletta, M. Rossi, *Chem. Soc. Rev.* **2012**, *41*, 350 – 369; g) S. Carrettin, M. C. Blanco, A. Corma, A. S. K. Hashmi, *Adv. Synth. Catal.* **2006**, *348*, 1283 – 1288.

[16] J. John, E. Gravel, A. Hagège, H. Li, T. Gacoin, E. Doris, *Angew. Chem.* **2011**, *123*, 7675 – 7678; *Angew. Chem. Int. Ed.* **2011**, *50*, 7533 – 7536.

[17] R. Kumar, E. Gravel, A. Hagège, H. Li, D. V. Jawale, D. Verma, I. N. N. Namboothiri, E. Doris, *Nanoscale* **2013**, *5*, 6491 – 6497.

[18] D. V. Jawale, E. Gravel, V. Geertsen, H. Li, N. Shah, I. N. N. Namboothiri, E. Doris, *ChemCatChem* **2014**, *6*, 719 – 723.

[19] R. Kumar, E. Gravel, A. Hagège, H. Li, D. Verma, I. N. N. Namboothiri, E. Doris, *ChemCatChem* **2013**, *5*, 3571 – 3575.

[20] J. John, E. Gravel, I. N. N. Namboothiri, E. Doris, *Nanotechnol. Rev.* **2012**, *1*, 515 – 539.

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