

## Simple copper/TEMPO catalyzed aerobic dehydrogenation of benzylic amines and anilines†

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CuBr<sub>2</sub> with 2,2,6,6-tetramethylpiperidyl-1-oxy (TEMPO) has been successfully employed for the aerobic oxidation of primary and secondary benzyl amines in aqueous acetonitrile. Such catalytic systems have previously been used extensively in alcohol oxidation reactions. The same catalyst system was also used for oxidative cross-couplings of benzylamines with anilines. The electronic and steric properties of the aniline partner were found to be of crucial importance in determining reactivity or lack thereof. A mechanism for these reactions is proposed based on the data obtained to date. In the absence of benzyl amines, electron-rich anilines were found to undergo dehydrogenative coupling and yields of the resulting azo products could be increased by replacing CuBr<sub>2</sub> with CuBr. No ligand (*e.g.* pyridine) is required for either reaction to proceed and presumably water and acetonitrile solvate the copper-containing intermediates.

## Introduction

Imines are important intermediates which can be used as electrophilic reagents in many transformations such as alkylations, condensations and cycloadditions including aza-Diels-Alder reactions.<sup>1</sup> Imines also serve as versatile starting materials for the synthesis and racemisation of chiral amines, which are important intermediates in the preparation of biologically active compounds.<sup>2</sup> The traditional protocol for the synthesis of imines involves the condensation of an amine with a carbonyl compound such as aldehyde or ketone but alternative routes are desirable. For example, the syntheses of some imines through the reaction of alcohols and amines have been reported during the past decade.<sup>3</sup> Recently, direct oxidations of amines to imines have attracted much attention. Nicolaou *et al.* developed stoichiometric oxidations of secondary amines to imines using 2-iodoxybenzoic acid and excellent yields were obtained.<sup>4</sup> Largeron *et al.* reported an environmentally friendly biomimetic electrocatalytic method for the oxidation of primary aliphatic amines to imines.<sup>5</sup> A few transition metal catalyzed oxidations of amines with PhIO,<sup>6</sup> K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>,<sup>7</sup> MnO<sub>2</sub><sup>8</sup> and <sup>t</sup>BuOOH<sup>9</sup> have also been reported. Significant progress has been made in the development of mild and green methods for the synthesis of imines

including metal-catalyzed dehydrogenation of amines,<sup>10</sup> aerobic oxidation of amines using cobalt,<sup>11</sup> copper,<sup>12</sup> gold,<sup>13</sup> palladium,<sup>14</sup> ruthenium<sup>15</sup> and vanadium<sup>16</sup> complexes. Very recently, Zhao *et al.* reported the selective aerobic photocatalytic oxidation of amines to imines on TiO<sub>2</sub>.<sup>17</sup> However, many of these catalytic systems have limited substrate scope and are only active for secondary amines.

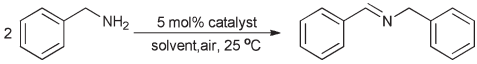
As an efficient hydrogen extraction reagent, 2,2,6,6-tetramethylpiperidyl-1-oxy (TEMPO) has been broadly used in catalytic oxidation reactions of alcohols.<sup>18</sup> However, TEMPO has been used to a much lesser extent in oxidation reactions of amines. Semmelhack and Schmid reported TEMPO assisted electrooxidation of amines to nitriles and carbonyl compounds in 1983,<sup>19</sup> and as far as we are aware this is the only example to date. Herein, we report a simple CuBr<sub>2</sub>-TEMPO catalytic system for aerobic oxidations of primary and secondary benzyl amines. Also, we report CuBr-TEMPO catalyzed dehydrogenative coupling of electron-rich anilines, which yield azo compounds.

## Results and discussion

The oxidative self-coupling of benzylamine was chosen as a model reaction to optimize the reaction conditions (Table 1). Copper salt and TEMPO are crucial for the oxidation of benzylamine (Table 1, entries 1 and 2). Different copper salts were tested for catalytic oxidation activity. Copper(II) bromide gave the best activity with 86% conversion of benzylamine to *N*-benzylidene-benzylamine in 8 h (Table 1, entry 3). Copper(II) chloride and copper(II) acetate led to only 58% and 62% conversions, respectively, under the same reaction conditions (Table 1, entries 4 and 5). These differences are possibly associated with a ligand

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† Electronic supplementary information (ESI) available: general experimental information, NMR data for imines and azo compounds, catalyst loading and kinetic study for oxidation of dibenzylamine. See DOI: 10.1039/c2ob06670j

**Table 1** Copper-catalyzed oxidative self-coupling of benzylamine<sup>a</sup>


Entry	Catalyst	Solvent mixture (v/v)	Conv. (%) <sup>b</sup>
1	CuBr <sub>2</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (2/1)	trace
2	TEMPO	CH <sub>3</sub> CN/H <sub>2</sub> O (2/1)	n.r.
3	CuBr <sub>2</sub> + TEMPO	CH <sub>3</sub> CN/H <sub>2</sub> O (2/1)	86(100 <sup>c</sup> )
4	CuCl <sub>2</sub> + TEMPO	CH <sub>3</sub> CN/H <sub>2</sub> O (2/1)	58
5	Cu(CH <sub>3</sub> COO) <sub>2</sub> ·H <sub>2</sub> O + TEMPO	CH <sub>3</sub> CN/H <sub>2</sub> O (2/1)	62
6	FeCl <sub>3</sub> + TEMPO	CH <sub>3</sub> CN/H <sub>2</sub> O (2/1)	n.r.
7	CuBr <sub>2</sub> + TEMPO	CH <sub>3</sub> CN	n.r.
8	CuBr + TEMPO	CH <sub>3</sub> CN/H <sub>2</sub> O (1/2)	53
9	CuBr <sub>2</sub> + TEMPO	Toluene/H <sub>2</sub> O (2/1)	8

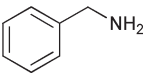
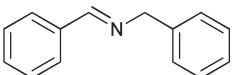
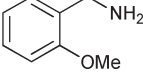
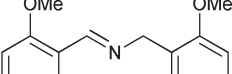
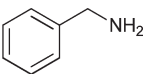
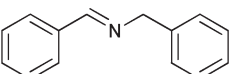
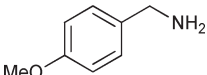
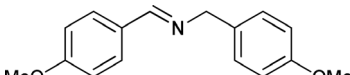
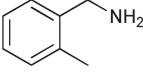
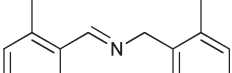
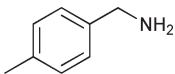
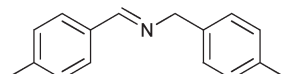
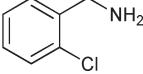
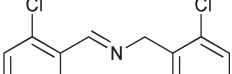
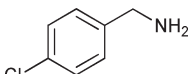
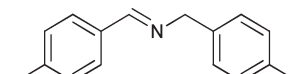
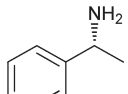
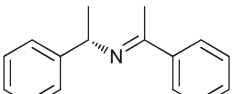
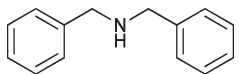
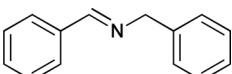
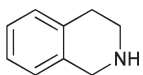
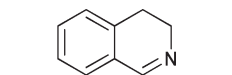
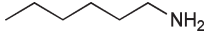
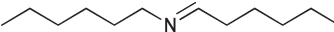
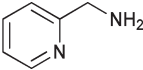
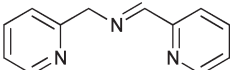
<sup>a</sup> Reaction conditions: benzylamine (2 mmol), catalyst (0.05 mmol), solvent (9 ml), air (1 atm), 8 h. <sup>b</sup> Selectivity in imine >98%, determined by GC using dodecane as an internal standard. n.r. = no reaction. <sup>c</sup> 12 h reaction time.

dissociation step in the reaction mechanism, as the bromide anion would be weakly coordinated to the copper centre compared with chloride and acetate anions. This means that for the CuBr<sub>2</sub> system it is easier for the substrate to enter the coordination sphere of the copper and become activated. Good conversion was also achieved when copper(i) bromide was used. No conversion was obtained when CuBr<sub>2</sub> was replaced with FeCl<sub>3</sub>. Acetonitrile has been broadly used as a solvent in Cu(II)-catalyzed oxidation reactions.<sup>20</sup> 86% conversion was obtained in 8 h with a 2 : 1 (v/v) acetonitrile/water solvent mixture (Table 1, entry 3). No conversion was achieved in neat CH<sub>3</sub>CN due to the formation of a green precipitate (Table 1, entry 7) that is presumably a coordination polymer of copper. Conversion was decreased when the amount of CH<sub>3</sub>CN was decreased in acetonitrile/water solvent mixtures, probably because of a decrease in the solubility of the organic substrate (Table 1, entry 8). Only 8% conversion was obtained when a biphasic solvent mixture was used (Table 1, entry 9). This may be explained by unsatisfactory mixing of the reactants, catalysts and co-catalysts. With the optimized reaction conditions above in hand, we investigated CuBr<sub>2</sub>-TEMPO catalyzed oxidations for a range of primary and secondary benzylic amines (Table 2). The electronic properties of substituents had no significant effect on the conversions and selectivities. This differs from a previously reported CuCl-catalyzed reaction where reaction selectivity was affected by substituents.<sup>12d</sup> All the benzylic amines studied whether containing electron-withdrawing or -donating groups were smoothly oxidized to the corresponding imines (Table 2, entries 1–8). This also contrasts with a recently reported V<sub>2</sub>O<sub>5</sub>-H<sub>2</sub>O<sub>2</sub> catalytic system,<sup>21</sup> where significantly different reaction conditions were needed for the two classes of substrate, with benzyl amines bearing electron donating groups being significantly less reactive than those containing electron withdrawing groups. Also, when using this Cu(II)/TEMPO catalytic system, the *p*-methoxy benzylamine substrates achieved slightly faster reaction rates compared with *p*-chloro benzylamine (Table 2, entries 4 and 8). 80% GC-MS conversion was achieved in 8 h for the oxidation of *p*-

methoxy benzylamine, whereas 72% conversion was obtained for the oxidation of *p*-chloro benzylamine in 8 h. This is possibly due to a faster transamination for the phenylmethanimine intermediate when a more basic (electron-donating) amine is used (Fig. 1). Unfortunately, the CuBr<sub>2</sub>-TEMPO catalyst system was inactive for the oxidation of (*R*)-1-phenylethanamine (Table 2, entry 9). This could be explained by the steric demands of the β-methyl group of the amine, which would hinder the formation of the crucial species **III** in the proposed catalytic cycle (Fig. 1). For such a substrate, it would be challenging for C<sub>α</sub>-H abstraction by the coordinated TEMPO to occur. However, some secondary amines could be converted to their corresponding imines in good to excellent yields. However, the reaction conditions were more demanding than for the self-condensation of benzylic amines. In order to achieve high conversions, higher catalyst loadings and reaction temperatures were essential (Table 2, entries 10 and 11). If the catalyst loading was decreased to 5 mol % for the oxidation of dibenzylamine, the conversion dramatically dropped to 50% (see Electronic Supplementary Information†). From this graph of catalyst loading and conversion (Figure S1†), the reaction appears to be first order in CuBr<sub>2</sub>-TEMPO, but more studies are needed to confirm this and to determine the relative reaction orders for both catalyst and co-catalyst. Also, it should be noted that dibenzylamine could not be transformed to the imine at room temperature. Kinetic studies showed a first-order dependence for the reaction rate on the dibenzylamine concentration at 45 °C (see Electronic Supplementary Information†). Under optimised conditions, *N*-benzylidene-benzylamine could be isolated in 94% yield from dibenzylamine (Table 2, entry 10), whereas only 66% yield is obtained under neat reaction conditions using CuCl.<sup>12d</sup> However, the CuBr<sub>2</sub>-TEMPO catalytic system reported herein was not effective for the self-coupling of non-activated aliphatic amines, only a small amount of the resulting imine was detected (Table 2, entry 12). No reactions were observed for some functional amines studied such as 2-picolyamine (Table 2, entry 13). This could be explained by strong coordination of N-donors to the copper centre and a difficulty in dissociating these to yield a vacant site at the metal centre for subsequent TEMPO coordination (Fig. 1, II → III).

Very recently, Patil and Adimurthy reported CuCl-catalyzed aerobic oxidation of amines to imines under *neat* conditions with 0.5 mol% catalyst loading.<sup>12d</sup> The simple CuCl catalyst system could oxidize benzylic amines to imines efficiently and moderately oxidize aliphatic and functional amines to the corresponding imines. However, a higher reaction temperature was required compared with the system reported here. Also, for the oxidation of electron-donating benzyl amines, the selectivities for the imine products were not notable. As shown in Table 2, entry 4, only 78% selectivity was obtained due to the formation of *p*-methoxy benzaldehyde as a by-product. No benzaldehyde by-products were observed in our reactions. However, our catalytic system uses TEMPO as a co-catalyst. This is a disadvantage, as TEMPO is the most expensive component in our catalytic system. It would be desirable if TEMPO could be efficiently recycled and reused. Chung and Toy reported a recyclable PEG-modified Cu/TEMPO catalyst for selective aerobic alcohol oxidation.<sup>22</sup> The development of a recyclable Cu/TEMPO catalyst system or another reusable non-precious metal-based catalyst

**Table 2** CuBr<sub>2</sub>-TEMPO catalyzed primary and secondary benzylic amines<sup>a</sup>

Entry	Substrate	Product	Yield (%) <sup>b</sup>
1			87 (88 <sup>d</sup> )
2			94
3			93
4			94 (80 <sup>c</sup> ) (72 <sup>d</sup> )
5			93
6			88
7			82
8			76 (72 <sup>c</sup> )
9			0
10			94 <sup>e,f</sup> (66 <sup>d</sup> )
11			92 <sup>e,f</sup>
12			5 <sup>c</sup> (50 <sup>d</sup> , NMR yield)
13			0 (32 <sup>d</sup> )

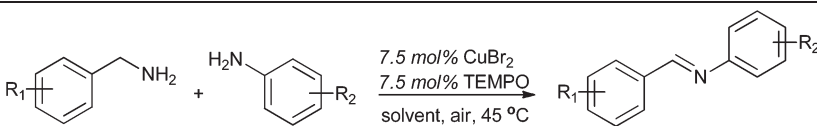
<sup>a</sup> Reaction conditions, unless otherwise stated: benzylamine (4 mmol), catalyst (0.10 mmol), solvent (9 ml), air (1 atm), 25 °C, 12 h. <sup>b</sup> Isolated yield. <sup>c</sup> GC conversion, 8 h. <sup>d</sup> Under conditions reported in ref. 12d; entry 4, 78% selectivity (92% combined yield of imine and aldehyde). <sup>e</sup> 7.5 mol% catalyst loading. <sup>f</sup> 45 °C reaction temperature.

system for aerobic oxidation reactions of amines is under way in our group.

Through the studies reported above, we propose a reaction mechanism for the condensation of benzyl amines using Cu(II)/TEMPO catalysts (Fig. 1). The mechanism is very similar to that reported by Sheldon *et al.* for CuBr<sub>2</sub>(bipyridine)-TEMPO catalyzed aerobic alcohol oxidation.<sup>20b</sup> Initially, a Cu<sup>II</sup> species **I** coordinates with the amine and the intermediate complex **II** is formed. **II** coordinates with TEMPO to form species **III**, which is crucial for the catalytic cycle. C–H abstraction from the amine

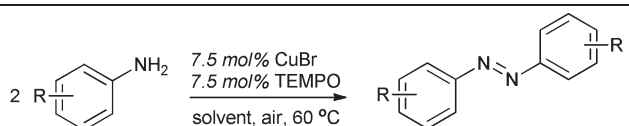
by the coordinated TEMPO molecule is the next step and the radical intermediate **IV** is formed which is stabilized by hydrogen bonding to the second β-hydrogen atom and the oxygen atom of TEMPO-H. Then TEMPO-H and intermediate imine, RCH=NH, dissociate from the radical species **IV** by single proton transfer. This results in the formation of a Cu(I) complex **V**. The product is obtained by transamination of RCH<sub>2</sub>NH<sub>2</sub> and the imine intermediate RCH=NH. The Cu(II) complex **I** and TEMPO are regenerated by the oxidation of Cu(I) complex **V** and TEMPOH with oxygen and thus the catalytic cycle is



**Table 3** CuBr<sub>2</sub>-TEMPO catalyzed oxidative coupling of benzylamines with anilines<sup>a</sup>


Entry	R <sub>1</sub>	R <sub>2</sub>	Time (h)	Conv. (%) <sup>b</sup>
1	H	H	12	48 (18 <sup>c</sup> )
2	<i>p</i> -Me	H	12	58
3	<i>p</i> -OMe	H	12	64
4	<i>o</i> -Cl	H	18	44
5	H	<i>o</i> -CH <sub>3</sub>	12	66 ( <i>p</i> -CH <sub>3</sub> 14 <sup>c</sup> )
6	<i>o</i> -Cl	<i>o</i> -CH <sub>3</sub>	12	55
7	H	<i>p</i> -OMe	12	73 (74 <sup>c</sup> )
8	<i>p</i> -Me	<i>p</i> -OMe	12	78
9	<i>o</i> -OMe	<i>p</i> -Br	24	38 <sup>d</sup>
10	<i>o</i> -OMe	<i>p</i> -NO <sub>2</sub>	24	16 <sup>d</sup>
11	H	2,6-CH <sub>3</sub>	24	n.r.

<sup>a</sup> Reaction conditions, unless otherwise stated: benzylamine (4 mmol), aniline (4 mmol), CuBr<sub>2</sub> (0.3 mmol), TEMPO (0.3 mmol), solvent (6 ml CH<sub>3</sub>CN and 3 ml H<sub>2</sub>O), air (1 atm), 45 °C. <sup>b</sup> Conversion determined by GC using dodecane as an internal standard. n.r. = no reaction. <sup>c</sup> Yields of unsymmetrical imine under conditions reported in ref. 12d: entry 1, 23% selectivity (78% combined yield of symmetrical and unsymmetrical imines); entry 5, 17% selectivity (82% combined yield of symmetrical and unsymmetrical imines). <sup>d</sup> 75 °C reaction temperature.

**Table 4** CuBr-TEMPO catalyzed aerobic dehydrogenative coupling of anilines<sup>a</sup>


Entry	R	Time (h)	Yield <sup>b</sup>
1	H	24	86
2	<i>o</i> -CH <sub>3</sub>	24	89
3	3,5-dimethyl	18	92
4	<i>p</i> -OCH <sub>3</sub>	18	91 <sup>c</sup>
5	<i>p</i> -Br	48	8 <sup>d</sup>
6	<i>p</i> -NO <sub>2</sub>	48	n.r. <sup>e</sup>
7	<i>o</i> -C(CH <sub>3</sub> ) <sub>3</sub>	48	n.r. <sup>e</sup>
8	2,6-dimethyl	48	n.r. <sup>e</sup>

<sup>a</sup> Standard reaction conditions: anilines (4 mmol), aniline (4 mmol), CuBr (0.15 mmol), TEMPO (0.15 mmol), solvent (9 ml CH<sub>3</sub>CN), air (1 atm), 60 °C. <sup>b</sup> Isolated yield. n.r. = no reaction. <sup>c</sup> 60% yield when using CuBr<sub>2</sub>. <sup>d</sup> 75 °C reaction temperature. <sup>e</sup> 85 °C reaction temperature.

investigated. As shown in Table 4, some electron-donating anilines could be smoothly oxidized to form the self-coupling azo compounds (Table 4, entries 2–4). However, the homocoupling of anilines with electron-withdrawing substituents proceeded to a very limited extent (Table 4, entries 5 and 6). Furthermore, sterically demanding substituents in the 2-position or di-substituted 2,6-anilines led to lower or no yield of the oxidative coupling product (Table 4, entries 7 and 8). In the previous research by Zhang and Jiao,<sup>27c</sup> CuBr was used with 3 equiv. pyridine in toluene using air or O<sub>2</sub> (1 atm) as the oxidant. In contrast to their work, in this study high yields were observed for the dehydrogenative coupling of *p*-methoxy aniline (66% *cf.* 91%). Therefore, the mechanisms at play in the two systems are likely

different and a radical mechanism is likely to dominate in the method described here. However, further mechanistic studies are required to understand and further develop Cu-catalyzed dehydrogenative couplings of anilines.

## Conclusions

A simple catalyst system for CuBr<sub>2</sub>-TEMPO catalyzed aerobic oxidation of amines has been developed. Primary and secondary benzylic amines can be oxidized to the corresponding imines in excellent yields. A possible reaction mechanism has been proposed. The same catalytic system is also efficient for oxidative cross-coupling of benzylamines and anilines. Notably, CuBr-TEMPO is an efficient catalyst system for aerobic oxidative dehydrogenative couplings of electron-donating anilines to yield azo compounds in good yields.

## Experimental

General experimental information and product characterization data are available in Electronic Supplementary Information†.

### General procedure for the preparation of imines

The oxidation reactions were carried out under air in a 25 ml three-necked round-bottom flask equipped with a magnetic stirrer. Typically, 4.0 mmol amine was dissolved in 6 ml acetonitrile and 3 ml water. 0.10 mmol (22.3 mg) of CuBr<sub>2</sub> and 0.10 mmol (15.6 mg) TEMPO were then added leading to a blue solution. The reaction mixture was stirred vigorously at room temperature for 12 h. After reaction completion, the mixture was extracted with diethyl ether. Then the organic layer was washed with water and brine. The organic phase was dried with anhydrous magnesium sulfate and filtered through a short silica

column. For benzyl amine as the substrate, after concentrating the sample under vacuum, the product was obtained as a pale yellow liquid, 340 mg (87%)

### *N*-Benzylidene-benzylamine<sup>21</sup>

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C): δ = 8.41 (s, 1H), 7.84–7.81 (m, 2H), 7.64–7.43 (m, 3 H), 7.39–7.38 (m, 4 H), 7.35–7.27 (m, 1H), 4.86 ppm (s, 2 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ = 161.88, 139.19, 136.05, 130.65, 128.50, 128.29, 128.19, 65.59 ppm. MS (EI): *m/z* (%) 195 [M]<sup>+</sup> (25), 194 (26), 117 (14), 91 (100), 65 (16). Anal. Calc. for C<sub>14</sub>H<sub>13</sub>N: C, 86.12; H, 6.71; N, 7.17. Found: C, 85.84; H, 6.77; N, 6.97.

### General procedure for the preparation of benzylideneanilines

The oxidative coupling reactions were carried out under air in a 25 ml reaction tube using a Radleys Carousel Reactor™ equipped with a magnetic stirrer. Typically, 2.0 mmol benzylamine and aniline were dissolved in 6 ml acetonitrile and 3 ml water. 0.15 mmol (33.4 mg) of CuBr<sub>2</sub> and 0.15 mmol (23.4 mg) TEMPO were then added leading to a blue solution. The reaction mixture was stirred vigorously at 45 °C for 12 h. After completion, the reaction mixture was extracted with diethyl ether. Then the organic layer was washed with water and brine. The conversion was determined by GC-MS based on aniline. Due to lower conversions in these reactions, the products were not isolated and yields were not determined.

### General procedure for the preparation of diphenyldiazenes

The oxidative homo-coupling of anilines to diphenyldiazenes were carried out under air in a 25 ml reaction tube using a Radleys Carousel Reactor™ equipped with a magnetic stirrer. As a typical example, 4-methoxybenzylamine (492 mg, 4 mmol) was dissolved in 9 ml acetonitrile, CuBr (21 mg, 0.15 mmol) and TEMPO (23.4 mg, 0.15 mmol) were then added. The reaction mixture was stirred vigorously at 60 °C for 18 h. After completion, the reaction mixture was extracted with diethyl ether. Then the organic layer was washed with water and brine. The organic phase was dried with anhydrous magnesium sulfate and filtered through a short silica column. After concentrating the sample under vacuum without further purification, it gave 441 mg (91%) of a yellow solid.

### (*E*)-1,2-Bis(4-methoxyphenyl)diazene<sup>27c</sup>

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ = 7.88 (d, *J* = 9.0 Hz, 2H), 7.70 (d, *J* = 9.0 Hz, 4H), 3.89 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ = 161.56, 147.07, 124.34, 114.16, 55.57 ppm; IR (neat): ν = 3413, 1592, 1579, 1496, 1249, 841 cm<sup>-1</sup>. MS (EI): *m/z* (%) 242 [M]<sup>+</sup> (75), 243 (10), 135 (31), 107 (100), 92 (32), 77 (50), 64 (13). HRMS (TOF MS EI+) *m/z* calcd for C<sub>14</sub>H<sub>14</sub>N<sub>2</sub> 242.1059, found 242.1055. Anal. Calc. for C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>: C, 69.41; H, 5.82; N, 11.56. Found: C, 69.51; H, 5.55; N, 11.66

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## Notes and references

- J. P. Adams, *J. Chem. Soc., Perkin Trans. 1*, 2000, 125–139.
- (a) R. Bloch, *Chem. Rev.*, 1998, **98**, 1407–1438; (b) S. Kobayashi and H. Ishitani, *Chem. Rev.*, 1999, **99**, 1069–1094; (c) O. Pàmies, A. H. Éll, J. S. M. Samec, N. Hermanns and J.-E. Bäckvall, *Tetrahedron Lett.*, 2002, **43**, 4699–4702; (d) N. Hermanns, S. Dahmen, C. Bolm and S. Bräse, *Angew. Chem., Int. Ed.*, 2002, **41**, 3692–3694; (e) B. Török and G. K. Surya Prakash, *Adv. Synth. Catal.*, 2003, **345**, 165–168.
- (a) L. Blackburn and R. J. K. Taylor, *Org. Lett.*, 2001, **3**, 1637–1639; (b) M. S. Kwon, S. Kim, S. Park, W. Bosco, R. K. Chidrala and J. Park, *J. Org. Chem.*, 2009, **74**, 2877–2879; (c) B. Gnanaprakasam, J. Zhang and D. Milstein, *Angew. Chem. Int. Ed.*, 2010, **49**, 1468–1471; (d) S. Kegnaes, J. Mielby, U. V. Mentzel, C. H. Christensen and A. Riisager, *Green Chem.*, 2010, **12**, 1437–1441; (e) M. A. Esteruelas, N. Honczek, M. Oliván, E. Oñate and M. Valencia, *Organometallics*, 2011, **30**, 2468–2471.
- (a) K. C. Nicolaou, C. J. N. Mathison and T. Montagnon, *Angew. Chem., Int. Ed.*, 2003, **42**, 4077–4082; (b) K. C. Nicolaou, C. J. N. Mathison and T. Montagnon, *J. Am. Chem. Soc.*, 2004, **126**, 5192–5201.
- M. LARGERON, A. CHIARONI and M.-B. FLEURY, *Chem.–Eur. J.*, 2008, **14**, 996–1003.
- (a) P. Müller and D. M. Gilibert, *Tetrahedron*, 1988, **44**, 7171–7175; (b) F. Porta, C. Crotti, S. Cenini and G. Palmisano, *J. Mol. Catal.*, 1989, **50**, 333–341.
- S. Yamazaki, *Chem. Lett.*, 1992, **21**, 823–826.
- A. H. Ell, J. S. M. Samec, C. Brasse and J.-E. Backvall, *Chem. Commun.*, 2002, 1144–1145.
- (a) S.-I. Murahashi, T. Naota and H. Taki, *J. Chem. Soc., Chem. Commun.*, 1985, 613–614; (b) H. Choi and M. P. Doyle, *Chem. Commun.*, 2007, 745–747.
- (a) X.-Q. Gu, W. Chen, D. Morales-Morales and C. M. Jensen, *J. Mol. Catal. A: Chem.*, 2002, **189**, 119–124; (b) R. Yamaguchi, C. Ikeda, Y. Takahashi and K.-i. Fujita, *J. Am. Chem. Soc.*, 2009, **131**, 8410–8412; (c) A. Prades, E. Peris and M. Albrecht, *Organometallics*, 2011, **30**, 1162–1167.
- A. Nishinaga, S. Yamazaki and T. Matsuura, *Tetrahedron Lett.*, 1988, **29**, 4115–4118.
- (a) M. Shimizu, H. Orita, T. Hayakawa, K. Suzuki and K. Takehira, *Heterocycles*, 1995, **41**, 773–779; (b) S. Minakata, Y. Ohshima, A. Takemiya, I. Ryu, M. Komatsu and Y. Ohshiro, *Chem. Lett.*, 1997, **26**, 311–312; (c) Y. Maeda, T. Nishimura and S. Uemura, *Bull. Chem. Soc. Jpn.*, 2003, **76**, 2399–2403; (d) R. D. Patil and S. Adimurthy, *Adv. Synth. Catal.*, 2011, **353**, 1695–1700.
- (a) B. Zhu and R. J. Angelici, *Chem. Commun.*, 2007, 2157–2159; (b) B. Zhu, M. Lazar, B. G. Trewyn and R. J. Angelici, *J. Catal.*, 2008, **260**, 1–6; (c) A. Grirrane, A. Corma and H. Garcia, *J. Catal.*, 2009, **264**, 138–144; (d) L. Aschwanden, B. Panella, P. Rossbach, B. Keller and A. Baiker, *ChemCatChem*, 2009, **1**, 111–115; (e) M.-H. So, Y. Liu, C.-M. Ho and C.-M. Che, *Chem.–Asian J.*, 2009, **4**, 1551–1561.
- J.-R. Wang, Y. Fu, B.-B. Zhang, X. Cui, L. Liu and Q.-X. Guo, *Tetrahedron Lett.*, 2006, **47**, 8293–8297.
- (a) A. J. Bailey and B. R. James, *Chem. Commun.*, 1996, 2343–2344; (b) K. Yamaguchi and N. Mizuno, *Angew. Chem., Int. Ed.*, 2003, **42**, 1480–1483; (c) J. S. M. Samec, A. H. Éll and J.-E. Bäckvall, *Chem.–Eur. J.*, 2005, **11**, 2327–2334; (d) S. I. Murahashi, Y. Okano, H. Sato, T. Nakae and N. Komiyama, *Synlett*, 2007, 1675–1678; (e) G. Jiang, J. Kodan, J.-S. Huang and C.-M. Che, *Org. Lett.*, 2009, **11**, 4568–4571.
- S. Kodama, J. Yoshida, A. Nomoto, Y. Ueta, S. Yano, M. Ueshima and A. Ogawa, *Tetrahedron Lett.*, 2010, **51**, 2450–2452.
- X. Lang, H. Ji, C. Chen, W. Ma and J. Zhao, *Angew. Chem., Int. Ed.*, 2011, **50**, 3934–3937.
- (a) W. Adam, C. R. Saha-Moller and P. A. Ganeshpure, *Chem. Rev.*, 2001, **101**, 3499–3548; (b) R. A. Sheldon and I. W. C. E. Arenas, *Adv. Synth. Catal.*, 2004, **346**, 1051–1071; (c) B.-Z. Zhan and A. Thompson, *Tetrahedron*, 2004, **60**, 2917–2935; (d) M. V. N. De Souza, *Mini-Rev. Org. Chem.*, 2006, **3**, 155–165; (e) T. Vogler and A. Studer, *Synthesis*,

- 2008, 1979–1993; (f) R. Ciriminna and M. Pagliaro, *Org. Process Res. Dev.*, 2010, **14**, 245–251; (g) K. U. Schonung, *Chim. Oggi-Chem. Today*, 2010, **28**, 18–23; (h) L. Tebben and A. Studer, *Angew. Chem., Int. Ed.*, 2011, **50**, 5034–5068.
- 19 M. F. Semmelhack and C. R. Schmid, *J. Am. Chem. Soc.*, 1983, **105**, 6732–6734.
- 20 (a) P. Gamez, C. Simons, R. Steensma, W. L. Driessen, G. Challa and J. Reedijk, *Eur. Polym. J.*, 2001, **37**, 1293–1296; (b) P. Gamez, I. Arends, R. Sheldon and J. Reedijk, *Adv. Synth. Catal.*, 2004, **346**, 805–811.
- 21 G. Chu and C. Li, *Org. Biomol. Chem.*, 2010, **8**, 4716–4719.
- 22 C. W. Y. Chung and P. H. Toy, *J. Comb. Chem.*, 2007, **9**, 115–120.
- 23 K. Tabuchi, M. Z. Ertem, H. Sugimoto, A. Kunishita, T. Tano, N. Fujieda, C. J. Cramer and S. Itoh, *Inorg. Chem.*, 2011, **50**, 1633–1647.
- 24 E. T. Kumpulainen and A. M. Koskinen, *Chem.–Eur. J.*, 2009, **15**, 10901–10911.
- 25 S. M. Landge, V. Atanassova, M. Thimmaiah and B. Török, *Tetrahedron Lett.*, 2007, **48**, 5161–5164.
- 26 C.-J. Li, *Acc. Chem. Res.*, 2009, **42**, 335–344.
- 27 (a) W. C. Lu and C. J. Xi, *Tetrahedron Lett.*, 2008, **49**, 4011–4015; (b) A. Gurrane, A. Corma and H. Garcia, *Science*, 2008, **322**, 1661–1664; (c) C. Zhang and N. Jiao, *Angew. Chem., Int. Ed.*, 2010, **49**, 6174–6177.