Green Chemistry

Accepted Manuscript

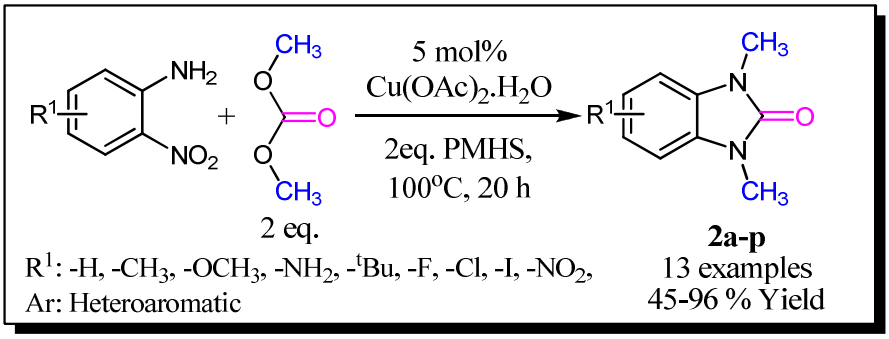
ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/greenchem

Copper Catalyzed Efficient Synthesis of 2-Benzimidazolone Scaffold from 2-Nitroaniline and Dimethyl Carbonate via Hydrosilylation Reaction

Deepak B. Nale and Bhalchandra M. Bhanage*

Department of Chemistry, Institute of Chemical Technology,
Matunga, Mumbai- 400 019, India



Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Copper Catalyzed Efficient Synthesis of 2-Benzimidazolone Scaffold from 2-Nitroaniline and Dimethyl Carbonate *via* Hydrosilylation Reaction

Deepak B. Nale and Bhalchandra M. Bhanage*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

This work reports copper catalyzed novel protocol for the tandem synthesis of 2-benzimidazolones derivatives from dimethyl carbonate (DMC) and various 2-nitroanilines by using polymethylhydrosiloxane (PMHS) as an inexpensive, stable and environmentally benign reducing agent. This methodology is applicable for the preparation of a broad range of biologically active 2-benzimidazolone derivatives with a good scope in good to excellent yields.

Introduction

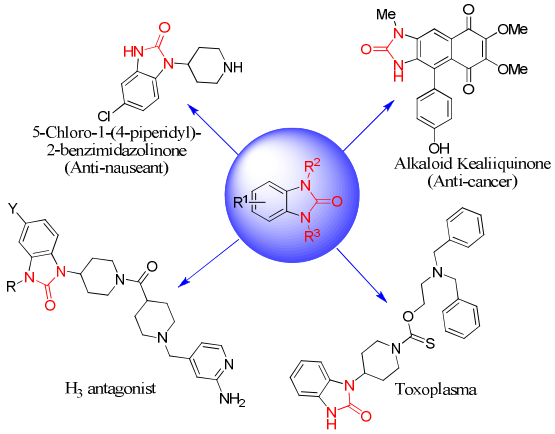
Benzimidazolones are important building blocks in the pharmaceuticals, agrochemicals, inhibitors, pigments, herbicides and fine chemicals.[1] The compounds containing benzimidazolone moiety have gained increasing attention in the area of medicinal chemistry, as they exhibits biological activity such as anticancer (Kealiiquin), H_3-receptor antagonist, antinauseant, antifungal, antithyroid, and antimicrobial (Toxoplasma) activity (Scheme 1).[2] Conventionally, 2-benzimidazolones were synthesized from the carbonylation of different *o*-phenylenediamine moieties with phosgene[3] which is highly toxic and corrosive gas, and hence it is highly desirable to develop a new greener, phosgene free protocol. There are few reports in the literature to synthesize 2-benzimidazolones from *o*-phenylenediamines and carbon dioxide (CO_2). Lu *et al*. reported the selenium catalyzed synthesis of 2-benzoxazolones or 2-benzimidazolones by one-pot reductive carbonylation of 2-nitrophenols or 2-nitroanilines in the presence of a base under high pressure of carbon monoxide (CO).[4] Furthermore, Mizuno's group synthesized 2-benzimidazolones from *o*-phenylenediamines and CO_2 in *N*-methylpyrrolidone solvent.[5] Recently, Liu and his co-workers also reported the synthesis of 2-benzimidazolone from *o*-phenylenediamine with CO_2 by using 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) based ionic liquids under solvent free conditions.[6]

Department of Chemistry, Institute of Chemical Technology, Matunga, Mumbai- 400 019, India

** Corresponding author. Tel.: + 91- 22 3361 1111/2601; Fax: (+91)-22-33611020.*

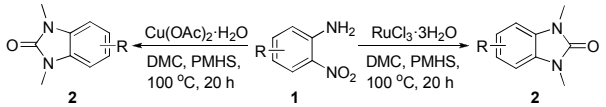
E-mail address: bm.bhanage@gmail.com, bm.bhanage@ictmumbai.edu.in (B. M. Bhanage).

† Electronic Supplementary Information (ESI) available: Characterization data of selected products. See DOI: 10.1039/b000000x/



Scheme 1. The 2-Benzimidazolone derivatives; a key intermediates for the synthesis of 5-Chloro-1-(4-piperidyl)-2-benzimidazolone, Kealiiquin, H_3 antagonist and Toxoplasma, respectively.

Nowadays, short-chain dialkyl carbonates such as dimethyl carbonate (DMC), has renowned as an essential chemical building block for the development of sustainable chemical processes,[7] e.g. for the production of polycarbonate and other chemicals,[8] an additive to fuel oil owing to a high octane number[9] and an electrolyte in lithium batteries due to its high dielectric constant.[10] Nowadays, DMC is produced by clean processes[11] and widely used as an efficient eco-sustainable substitute for phosgene, methyl halide, methyl sulphate which are toxic and highly corrosive agents.[3] DMC is also well-known as green monomer possessing properties like high biodegradability, non-hazardous nature, which make them interesting green solvents.[12]



Scheme 2. Synthesis of 1,3-dimethyl-1*H*-benzo[*d*]imidazol-2(3*H*)-one derivatives from various 2-nitroanilines.

Among the specific synthetic and environmental advantages of DMC, most important properties is environmentally acceptable compound that does not cause any emissions in the environment.

Polymethylhydrosiloxane (PMHS) is an abundant,

inexpensive, commercially available, stable to air and non-toxic reagent in the organic chemistry.[13] It was used as an environmentally benign reducing reagent for various functional groups such as reduction of ketones,[14] carboxylic acids, esters,[15] imines,[16] dehalogenation,[17] carboxamides,[18] lactones[19] and nitro[20] compounds.

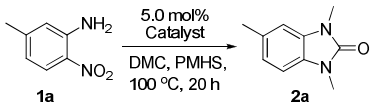
Recently Baba *et al.* reported the synthesis of 2-benzimidazolone by carbonylation of *o*-phenylenediamine using lead acetate as a catalyst.[21] They used the lead as a catalyst, which is toxic and also required more than one step for the synthesis of desired product **2**. The other synthetic methods have also been reported like direct carbonylation with *o*-phenylenediamine by using selenium, palladium or base.[4] Also a very few reports were performed on *in situ* nitro group reduction.[20e,f,g] Most of the catalytic protocols required organic solvents, high catalyst loading and Lewis base co-catalyst as well as severe reaction conditions. They required harsh reaction conditions such as high temperature, poisonous catalyst, and longer reaction time, limited substrate scopes and tedious work up procedures which hinders the commercial viability of these processes.[6] Hence, the development of facile and efficient catalytic system for the synthesis of 2-benzimidazolone from 2-nitroanilines using environmentally benign conditions is still a challenging task.

In continuation of our ongoing research,[22] herein we have developed a simple, efficient and environmentally benign copper catalyzed protocol for the synthesis of biologically important heterocyclic motif **2** from **1** and DMC by using PMHS as a greener reductant under solvent free conditions (Scheme 2). Furthermore, this protocol is highly efficient with respect to various electron-rich and electron-deficient groups on the 2-nitroanilines providing good to excellent yield of the desired corresponding products. To the best of our knowledge, this is the first report on the synthesis of 2-benzimidazolones derivatives from 2-nitroanilines using copper as a catalyst to display its catalytic activity under mild conditions.

Results and discussion

The model substrate for the initial screening was 5-methyl-2-nitroaniline (**1a)** when treated with DMC, leads to 1,3,5-trimethyl-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**2a)** in excellent yield. A series of experiments were performed to examine the influences of various reaction parameters such as catalyst, carbonate sources, catalyst loading, DMC/PMHS ratio, temperature and time (Table 1, 2 and 3). Initially, the reaction was performed in absence of catalyst maintaining other reaction parameters unvarying, the desired product was not detected (Table 1, entry 1), and it shows that Ru or Cu catalysts were only responsible for the transformation of 2-nitroanilines into 2-benzimidazolones. The investigation of the effect of different catalysts (5.0 mol%) such as $RuCl_3{\cdot}3H_2O$, $Cu(OAc)_2{\cdot}H_2O$, CuI, CuO, $Cu(acac)_2$ and CuCl were performed (Table 1, entries 2–11). The preliminary reaction of **1a** with DMC and PMHS catalyzed by [$RuCl_3{\cdot}3H_2O$] was performed at 100 °C for 20 h resulting **2a** as a sole product in 99% yield with 100% conversion (Table 1, entry 2) along with formation of methanol and carbon dioxide as by-products. However, the catalysts CuI and CuCl did not give any conversion, whereas CuO, $Cu(acac)_2$ provided the desired product with moderate to good yield of **2a** (Table 1, entries 8–11).

Table 1. Effect of various Catalyst, Bases and Solvents on the synthesis of **2a** from **1a** and DMC.[a]



1a **2a**

Sr. No.	Catalyst	Solvent	Base	Conversion (%)[b]	Yield (%)[b]
1	–	DMF	DBU	–	ND
2[c]	$RuCl_3{\cdot}3H_2O$	DMF	DBU	100	99
3	$Cu(OAc)_2{\cdot}H_2O$	DMF	DBU	100	91
4	$Cu(OAc)_2{\cdot}H_2O$	DMF	DABCO	100	97
5	$Cu(OAc)_2{\cdot}H_2O$	THF	DABCO	–	ND
6	$Cu(OAc)_2{\cdot}H_2O$	–	DBU	100	95
7[c]	$Cu(OAc)_2{\cdot}H_2O$	–	–	100	96
8	CuI	–	–	–	ND
9	CuO	–	–	90	70
10	$Cu(acac)_2$	–	–	50	45
11	CuCl	–	–	–	ND

[a] Reaction conditions: **1a** (1 mmol), catalyst (5.0 mol%), DMC (**3**, 5 mmol), PMHS (4 mmol), base (10 mol%), 20 h at 100 °C.

[b] Yield based on GC-GC/MS analysis. The yield is quantified by using the external standard method using 1,3,5-trimethyl-1*H*-benzo[*d*]imidazol-2(3*H*)-one.

[c] Isolated yield.

ND – not detected.

acac = acetylacetonate.

DMF = *N*,*N*-dimethylformamide

DBU = 1,8-diazabicyclo-[5.4.0]undec-7-ene

DABCO = 1,4-diazabicyclo[2.2.2]octane.

Among the various copper catalysts, copper acetate offered the excellent yield of the **2a** (Table 1, entry 3). Initial studies were carried out in solvent like DMF, THF, bases like DBU, DABCO for the synthesis of **2a** (Table 1, entries 3–6). Later, the experiments were carried out in absence of both the solvent and bases, interestingly, formation of **2a** was observed with excellent conversion and yield (Table 1, entry 7). Thus, the best conditions described in the Scheme 2 was used for the model copper-catalyzed reaction.

We then turned our attention to test the generality of the various carbonate sources such as dimethyl carbonate (DMC), diethyl carbonate (DEC), diphenyl carbonate (DPC), Di-*tert*-butyl di-carbonate, Phenyl carbamate and *N*,*N*'-disuccinimidyl carbonate (Table 2, entries 1–6), respectively. Among, all the screened carbonate sources, only DMC was provided an excellent yield of the desired product. Whereas employing other carbonates, results no desired product formation (Table 5, entries 2–6, see supporting information).

Subsequently, to enhance the yield of desired product **2a**, the reaction was performed by using various catalyst loadings along with DMC and PMHS. Further, we studied the catalyst loading (Table 3, entry 1–4) and it was found that 5.0 mol% catalyst furnished the excellent conversion and yield (Table 3, entry 3).

Table 2 Effect of different commercial sources of $Cu(OAc)_2 \cdot H_2O$ on the synthesis of 1,3,5-trimethyl-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**2a**).[a]

Entry	$Cu(OAc)_2 \cdot H_2O$ (Grade)[b]	Yield (%)[c]
1	>95% (S. D. fine)	95
2	>99.99+% (Aldrich)	96
3	>98% (Merck)	95

[a] Reaction conditions: **1a** (1 mmol), $Cu(OAc)_2 \cdot H_2O$ (5.0 mol%), DMC (2.5 eq), PMHS (2.0 eq), 20 h at 100 °C.

[b] Purity grades of the chemicals.

[c] Isolated Yield.

Next, the effect on reaction time was studied and it was observed that increasing the time from 5 h to 22 h, increase in yield of the desired product was obtained. Therefore, 20 h is optimum reaction time (Table 3, entries 5–7). We have also performed the reactions at different temperatures to observe the effect of temperature ranging from 60–150 °C (Table 3, entries 8–10) on the yield of product. The studies revealed that 100 °C was the optimum temperature required to achieve the highest yield of **2a**. Besides this, we have also studied the effect of mole ratio of DMC/PMHS and it was found that 5 mmol of DMC and 4 mmol of PMHS *i.e.* 5:4 mole ratio furnished the highest yield of the desired product (Table 3, entries 11–17). Hence, the best optimized reaction conditions for the desired product **2a** are: 5-methyl-2-nitroaniline (1.0 mmol), DMC (5.0 mmol), PMHS (4.0 mmol) and 5 mol% $Cu(OAc)_2 \cdot H_2O$ catalyst at the 100 °C for 20 h under solvent free condition.

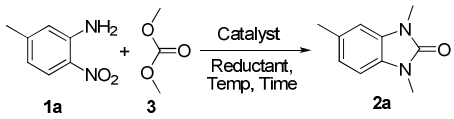
Finally, we ensured that whether the reaction was catalyzed by tracing (ppm-level) impurities in $Cu(OAc)_2 \cdot H_2O$, we were carried out the same experiments with different sources of $Cu(OAc)_2 \cdot H_2O$ (from >95% to 99.99+% purity) (Table 2, entries 1–3). The higher purity of $Cu(OAc)_2 \cdot H_2O$ as well as others have also an excellent impact on the yield of **2a** (Table 2, entry 2), and it was used for the subsequent substrate study.

On the basis of ICP-MS (Inductively coupled plasma-mass spectrometry) analysis,[23] the catalyst contained below detectable impurities.

To assess the substrate scope of this tandem reaction, we examined the developed protocol for the transformation of a variety of 2-nitroanilines (**1a**–**p**) under optimized reaction parameters. The various 2-nitroanilines moieties bearing electron donating and withdrawing substituent's on the phenyl ring were well tolerated under the present reaction condition and provided the corresponding desired products (**2a**–**p**) in good to excellent yield (Table 4, entries 1–16).

The electronic character of the 2-nitroaniline species influenced the outcome of the reaction having electron donating group furnished the desired product in good yields(Table 4, entries 1 and 3). The 2-nitroaniline was smoothly converted into the corresponding **2b** as desired product in good yields of 90% (Table 4, entry 2). Next, we studied the effect of halogen substituents on the 2-nitroaniline, the use of 4-fluoro-2-nitroaniline gave good yield of **2d** (90%) whereas the reaction of 4-chloro-2-nitroaniline provided **2e** in 82% yield (Table 4, entries 4–5). Employing 4-iodo-2-nitroaniline, 71% desired product formation was observed along with dehalogenation of **2f** in 10% (Table 4, entry 6). The 4-amino-2-nitroaniline was furnished in good yield of **2g** (85%), however, tri-methylated product was also obtained in 7% yield (Table 4, entry 7). To our delight, an electron withdrawing group on the phenyl ring of 2-nitroaniline afforded the good to moderate yield (Table 4, entry 8). Notably, the nitroaniline derivative bearing a tertiary alkyl group also gave the corresponding desired product in 81% yield (Table 4, entry 9). Moreover, we have also applied this catalytic protocol to check the effectiveness of catalyst for six membered *N*-heterocyclic 2-nitroaniline. But, it was observed that the 4-methyl-2-nitropyridin-3-amine (**1j**) gave 1,3,7-trimethyl-1*H*-imidazo[4,5-*b*]pyridin-2(3*H*)-one (**2j**) in lower yield (45%), which was due to the steric effect of the methyl group under the present reaction condition (Table 4, entry 10). Furthermore, we have also extended our catalytic protocol to *N*-substituted 2-nitroanilines, employing *N*-methyl-2-nitroaniline and *N*-phenyl-2-nitroaniline and interestingly the corresponding products were obtained in good to moderate yield (Table 4, entries 11–12). The reaction with 1,2-dinitrobenzene led to the isolation of 1,3-

Table 3 Effect of reaction parameters on the synthesis of 1,3,5-trimethyl-1*H*-benzo[*d*]imidazol-2(3*H*)-one.[a]



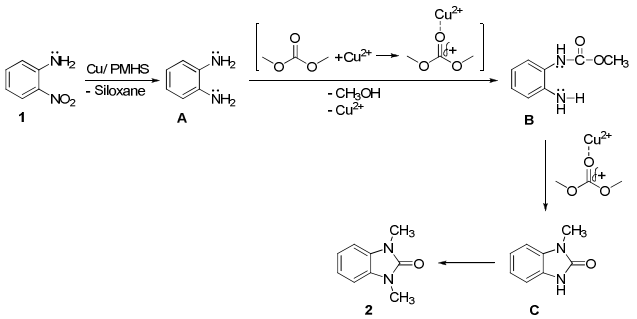
1a 3 2a

Entry	Catalyst (mol%)	**3**/PMHS (mmol)	Temp (°C)	Time (h)	Conv. (%)[b]	Yield (%)[b]
Catalyst loading						
1	0	5/4	100	20	-	ND
2	2.5	5/4	100	20	90	85
3	5	5/4	100	20	100	96[c]
4	10	5/4	100	20	100	97
Effect of Time						
5	5	5/4	100	22	100	95
6	5	5/4	100	16	100	89
7	5	5/4	100	12	80	72
Effect of Temperature						
8	5	5/4	120	20	100	95
9	5	5/4	80	20	95	70
10	5	5/4	60	20	60	55
Effect of DMC : PMHS ratio						
11	5	5/4	100	20	100	96
12	5	5/2	100	20	90	74
13	5	4/0	100	20	-	ND
14	5	3/3	100	20	80	70
15	5	2/2	100	20	60	48
16	5	1/2	100	20	50	35
17	5	0/4	100	20	-	ND

[a] Reaction conditions: **1c** (1.0 mmol), $Cu(OAc)_2 \cdot H_2O$ (mol%), DMC (**3**) (mmol), PMHS (mmol), time (h) and temperature (°C).
[b] Yield based on GC-GC/MS analysis. The yield is quantified by using the external standard method using 1,3,5-trimethyl-1*H*-benzo[*d*]imidazol-2(3*H*)-one.
ND – not detected.
[c] Isolated Yield.

dimethyl-1*H*-benzo[*d*]imidazol-2(3*H*)-one in 91% yield (Table 4, entry 13). Furthermore, 4-bromo-2-nitroaniline (**1n**) substrate was also converted into the corresponding desired product in 87% yield (Table 4, entry 14). 2-nitroaniline substrate bearing a –CN substituent (**1o**) gave of the target product in 81% yield (**2o**) in addition to 10% yield of the derivative resulting from the complete reduction of –CN moiety. When performing the reaction with the nitroaniline derivative (**1p**) containing –C=O functional group, the corresponding desired product (**2p**) was selectively obtained in 79% yield, with the –C=O substituent unaffected (Table 4, entries 15–16). This aspects strongly emphasized that the affirmative effect played by DMC/PMHS on the scope of the reaction and supports its employment as alternative reagents in the development of a synthesis of biologically important molecules.

On the basis of the above observations, a tentative reaction mechanism is proposed, for the synthesis of **2** from **1**, DMC and PMHS using copper acetate as a catalyst as shown in Scheme 3. First, the **1** was transformed into the *o*-phenylenediamine (**A**) through *in situ* reduction by reductant PMHS and copper as an unprecedented catalytic system pathway. This result suggests that the formation of copper hydride as the catalytically active species by reaction between PMHS and copper acetate.[24] Recently, Baba *et al.* reported the plausible reaction mechanism for the synthesis of 1,3-dimethyl-1*H*-benzo[*d*]Imidazol-2(3*H*)-one (**2**) from *o*-phenylenediamine.[21] Here, the same role of copper species is a Lewis acid to enhance the polarization of the carbonyl group of DMC, which interacts with the $–NH_2$ group of **A**. In the meanwhile, the carbonylation of **A** with DMC and copper in which there is generation of copper-DMC complex. The carbonylation of **A** is to deliver an active intermediate carbamate ester **B**. Next, the nucleophilic intramolecular cyclization of **B** in the presence of copper-DMC complex, providing the monomethylated compound **C**.[24] In the subsequent step, the methylation of **C** with DMC in the presence of copper catalyst provide **2** as a final product.

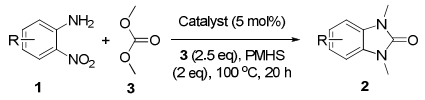


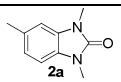
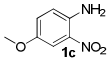
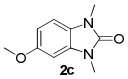
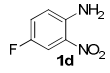
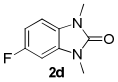
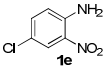
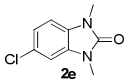
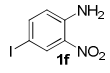
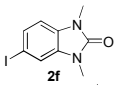
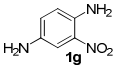
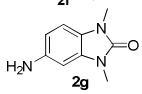
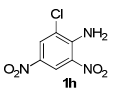
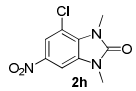
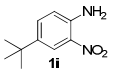
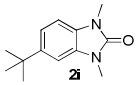
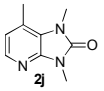
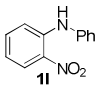
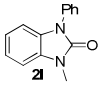
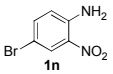
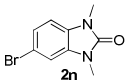
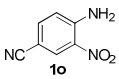
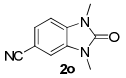
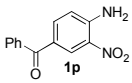
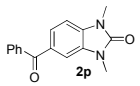
Scheme 3 A tentative reaction mechanism pathway

Conclusions

In summary, herein we have demonstrated an efficient, simple, economical and environmentally benign protocol for the synthesis of 2-benzimidazolones from various 2-nitroanilines using copper as a catalyst and PMHS as the reductant. The present protocol displays the features such as (i) a novel, simple and inexpensive catalytic reaction system (ii) first time one pot synthesis of 1,3-dimethyl-1*H*-benzo[*d*]Imidazol-2(3*H*)- one (2)

Table 4 Synthesis of various 1,3-dimethyl-1*H*-benzo[*d*]imidazol-2(3*H*)-one derivatives.[a]



Entry	Substrate	Product	Yield (%)[c]
1			96
2			90
3			95
4			90
5			82
6[b]			71
7[d]			85
8			75
9			81
10			45
11		**2b**	80
12			71
13		**2b**	91
14			87
15[e]			81
16			79

[a] Reaction conditions: Substrate (2 mmol), 5 mol% of $Cu(OAc)_2 \cdot H_2O$, 2.5 eq. of DMC, 2 eq. of PMHS, temperature (100 °C), time (20 h).

[b] Dehalogenation product was obtained in 10% yield.

[c] Isolated Yield.

[d] Tri-methylating product was obtained in 7% yield.

[e] Complete reduction of –CN was obtained in 10% yield.

i.e. 2-Benzimidazolones by using 2-nitroanilines was successfully achieved with a good scope (iii) use of non toxic and inexpensive copper catalyst without adding extra base, solvent and additives (iv) use of PMHS as a greener reductant (v) applicability to broaden the substrate scope. Thus, the developed catalytic protocol provides an unprecedented reactivity pattern, economically attractive and environmentally benign alternative route for the production of benzimidazolone, and widens the synthesis of related compounds in organic synthesis.

Experimental Section

All the organic chemicals, solvents and reagents were of analytical grade purchased from Sigma Aldrich, Merck and S. D. fine chemicals Ltd., India and commercial suppliers and were used without further purification/pre-treatment. PMHS (Poly-methyl hydrosiloxane) procured from Aldrich (cat#: 176206), average Mn: 1700–3200. The $Cu(OAc)_2 \cdot H_2O$ and the various substrates of 2-nitroanilines were procured from Sigma-Aldrich (purity >99.99+%). Reactions were monitored by using thin layer chromatography using Merck silica gel 60 F254 plates (TLC) and Perkin Elmer Clarus 400 gas chromatography equipped with flame ionization detector with a capillary column (Elite - 1, 30 m × 0.32 mm × 0.25 μm). The isolated products were confirmed by GC-MS, FT-IR, ^{1}H NMR, and ^{13}C NMR spectroscopic techniques. GC-MS (Shimadzu QP 2010) instrument (Rxt-17, 30 m × 25 mm, film thickness 0.25 μm df) (column flow 2 mL min^{-1}, 80–240 °C at 10 °C / min rise). An IR spectrum was recorded on Shimadzu IRAffinity-1, FT-IR 8400S using KBr pellets. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker Avance 400 MHz or 500 MHz NMR spectrometer with $CDCl_3$ as a solvent. The chemical shifts are reported in parts per million (δ) relative to tetramethylsilane (TMS) as an internal standard. *J* (coupling constant) values were reported in Hz. Splitting patterns of proton are described as s (singlet), d (doublet), dd (doublet of doublets), t (triplet) and m (multiplet).

General experimental procedure for synthesis of 1,3-dimethyl-1*H*-benzo[*d*] imidazole -2(3*H*)-one derivatives

All the reactions were carried out in a 100 mL stainless-steel reactor equipped with an over head stirrer and an automatic temperature control system. In a typical experimental procedure, catalyst-$Cu(OAc)_2 \cdot H_2O$ (5 mol%), 5-methyl-2-nitroaniline (**1a**, 1 mmol), DMC (2.5 eq) and PMHS (2.0 eq) were successively introduced into the autoclave. After being sealed, flushed with 10 atm. of nitrogen three times, the reactor was heated to the desired temperature at a stirring speed of 600 rpm. During the course of the reaction, there was *in situ* generation of the pressure of carbon dioxide and methanol at 100 °C. Since the use of DMC as a methylating as well as carbonylating agent requires the temperature at or above 100 °C (which is above the boiling point of DMC *i.e.* 90 °C), such reactions need to be conducted in a sealed high pressure reactor. The reaction mixture was analyzed at different time intervals to examine the progress of the reaction. After completion of the reaction, the autoclave was cooled to room temperature, and the pressure generated during the course reaction was carefully vented and then reactor was opened. Then, at room temperature the basic hydrolysis was done for 30 minutes to remove the unreacted PMHS present in the reaction mixture. The mixture was then extracted several times with dichloromethane (30 mL × 3). The combined organic layers were dried over Na_2SO_4 and evaporated in vacuo. The crude products were further purified by column chromatography on 100–200 mesh size silica gels (Elution with 20:1 to 10:1 Petroleum ether/Ethyl acetate) to furnish the corresponding pure product. The spectroscopic data are consistent with those reported in the earlier literature and in agreement with assigned structures.[25]

Acknowledgements

The author D. B. Nale is greatly thankful to the university grant commission, India for providing financial support under UGC-SAP-SRF program, Green Technology Centre of Institute of Chemical Technology (ICT), Mumbai, India. We also thank to Prof. Sasaki for ^{1}H and ^{13}C NMR spectrometric data analysis of some compounds, Research Hub for Advanced Nano characterization, the University of Tokyo, supported by the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

Notes and references

1 a) K. Hofmann, in "*The Chemistry of Imidazole and its Derivatives (Part I)*," Vol. Interscience Publishers, London, 1953, pp. 285–359; b) D. M. Smith, in "*The Chemistry of Heterocyclic Compounds, Benzimidazoles and Congeneric Tricyclic Compounds*" Vol. **40** (Eds.: P. N. Preston), Wiley, New York, 1981, pp. 311; c) G. V. Boyd, A. R. Katritzky, and C. W. Rees, in "*Comprehensive Heterocyclic Chemistry*," Vol. **8**, Pergamon Press, Oxford, 1984, pp. 178; d) P. F. Gordon, P. Gregory, *Organic Chemistry in Colour*; Springer, Berlin, 1987; e) H. Zollinger, Color Chemistry, 3rd ed.; VHCA: Zu¨ rich and Wiley-VCH, Weinheim, 2003.

2 a) C. Guidon, V. Loppinet and P. Greiveldinger, *Soc. pharm. et biol. Lorraine.* 1975, **3**, 50–61; b) N. Saidani, C. Y. Botte, M. Deligny, A.-L. Bonneau, J. Reader, R. Lasselin, G. Merer, A. Niepceron, F. Brossier, J. C. Cintrat, B. Rousseau, L.-M. Birkholtz, M.-F. C.-Delauw, J. F. Dubremetz, C. Mercier, H. Vial, R. Lopez and E. Marechal, *Antimicrob. Agents Chemother*. 2014, **58**, 2586–2597; c) J. van de Streek, J. Bruning, S. N. Ivashevskaya, M. Ermrich, E. F. Paulus, M. Bolte and M. U. Schmidt, *Acta Cryst*. 2009, **B65**, 200–211; d) Q. Zeng, S. B. Rosenblum, Z. Yang, Y. Jiang, K. D. McCormick, R. G. Aslanian, L. Duguma, J. A. Kozlowski, N.-Y. Shih, J. A. Hey, R. E. West Jr., W. A. Korfmacher, M. Berlin, C. W. Boyce, *Bioorg. Med. Chem. Lett*. 2013, **23**, 6001–6003.

3 a) Y. Ono, *Appl. Catal. A: Gen*. 1997, **155**, 133–166; b) P. Tundo and M. Selva, *Chem. Tech*. 1995, **25**, 31–35; c) M. Israel and L. C. Jones, *J. Heterocyclic Chem*. 1969, **6**, 735–735; d) L. Cotarca, H. Ecket, *Phosgenations - A Handbook*, Wiley-VCH, 2003; e) A. K. Vaish, S. Consul, A. Agrawal, S. C. Chaudhary, M. Gutch, N. Jain and M. M. Singh, *J. Emerg Trauma Shock*. 2013, **6**, 271–275; f) B. H. Mathson, M. L. Taylor and M. S. Bogdanffy, *Fundam. Appl. Toxicol*., 1995, **28**, 255–263; g) J. D. Holbrey, W. M. Reichert, R. P. Swatloski, G. A. Broker, W. R. Pitner, K. R. Seddonb and R. D. Rogers, *Green Chem*., 2002, **4**, 407–413; h) M. Fabris, V. Lucchini, M. Noe, A. Perosa and M. Selva, *Chem. Eur. J*., 2009, **15**, 12273–12282.

4 a) X. Wang, G. Ling, Y. Xue, S. Lu, *Eur. J. Org. Chem*. 2005, **8**, 1675–1679; b) B. Gabriele, G. Salerno, R. Mancuso, M. Costa, *J. Org. Chem*. 2004, **69**, 4741–4750; c) L. B. Trownsend, R. V. Devivar, S. R. Turk, M. R. Nassiri, J. C. Drach, *J. Med. Chem*. 1995, **38**, 4098–4105.

5 T. Kimura, K. Kamata, and N. Mizuno, *Angew. Chem. Int. Ed*. 2012, **51**, 6700–6703.

6 B. Yu, H. Zhang, Y. Zhao, S. Chen, J. Xu, L. Hao, and Z. Liu, *ACS Catal*. 2013, **3**, 2076−2082.

7 a) Y. T. Kim, E. D. Park, *Appl. Catal. A: Gen*. 2009, **356**, 211–215; b) M. Aresta, A. Dibenedetto, A. Angelini, I. Papai, *in Top Catal*.

Springer Science and Business Media, New York, doi: 10.1007/s11244-014-0342-0, 2014; c) B. A. V. Santos, V. M. T. M. Silva, J. M. Loureiro and A. E. Rodrigues, *ChemBioEng. Rev.* 2014, **1**, 214–229; d) P. Tundo and M. Selva, *Acc. Chem. Res*., 2002, **35**, 706–716; e) B. Schaffner, F. Schaffner, S. P. Verevkin and A. Borne, *Chem. Rev*., 2010, **110**, 4554–4581.

8 a) S.-i. Fujita, B. M. Bhanage, Y. Ikushima and M. Arai, *Green Chem*. 2001, **3**, 87–91; b) F. Rivetti, U. Romano, D. Delledonne, *in Green Chemistry: Designing Chemistry for the Environment*, Vol. **626** (Eds.: P. Anastas, T. C. Williamson), ACS Symposium Series, American Chemical Society, Washington, DC, 1996, pp. 70–80.

9 M. A. Pacheco and C. L. Marshall, *Energy Fuels* 1997, **11**, 2–29.

10 T. Wei, M. Wang, W. Wei, Y. Sun and B. Zhong, *Green Chem*. 2003, **5**, 343–346.

11 Asahi Kasei Chemicals Corporation Patent, WO2007/34669A1, 2007.

12 a) O. Ilgen, A. N. Akin, *Appl. Catal. B*, 2012, **126**, 342–346; b) N. Boz, N. Degirmenbasi, D. M. Kalyon, *Appl. Catal. B*, 2009, **89**, 590–596; c) A.-A. G. Shaik, S. Sivaram, *Chem. Rev*. 1996, **96**, 951–976; d) F. Arico, P. Tundo, A. Maranzana, and G. Tonachini, *ChemSusChem*. 2012, **5**, 1–10; e) P. Tundo, F. Aric, A. E. Rosamilia, S. Grego, L. Rossi, *NATO Science for Peace and Security Series C: Environmental Security*, 2008, 213–232.

13 a) S. Chandrasekhar, G. Chandrasekhar, B. N. Babu, K. Vijeender, K. V. Reddy, *Tetrahedron Lett*. 2004, **45**, 5497–5499; b) K. K. Senapati, *Synlett*, 2005, **12**, 1960–1961; c) J.-F. Carpentier, V. Bette, *Curr. Org. Chem*. 2002, **6**, 913–936; d) N. J. Lawrence, M. D. Drew and S. M. Bushell, *J. Chem. Soc., Perkin Trans*. 1999, **1**, 3381–3391.

14 R. J. Rahaim Jr. and R. E. Maleczka Jr., *Org. Lett*. 2011, **13**, 584–587.

15 a) D. Addis, S. Das, K. Junge, and M. Beller, *Angew. Chem. Int. Ed*. 2011, **50**, 6004–6011; b) M. Falorni, A. Porcheddu, M. Taddei, *Tetrahedron Lett*. 1999, **40**, 4395-4396; c) R. H. Tale, K. M. Patil and S. E. Dapurkar, *Tetrahedron Lett*. 2003, **44**, 3427–3428; d) K. Junge, B. Wendt, H. Jiao and M. Beller, *ChemCatChem.* 2014, **6**, 2810–2814; e) S. Werkmeister, K. Junge and M. Beller, *Org. Process Res. Dev*., 2014, **18**, 289–302; f) M. Szostak, M. Spain, A. J. Eberhart and D. J. Procter, *J. Org. Chem*., 2014, **79**, 11988–12003; g) K. Revunova and G. I. Nikonov, *Chem. Eur. J*. 2014, **20**, 839 – 845.

16 V. Bette, A. Mortreux, C. W. Lehmann and J.-F. Carpentier, *Chem. Commun*. 2003, 332–333.

17 R. J. Rahaim Jr. and R. E. Maleczka Jr., *Tetrahedron Lett*. 2002, **43**, 8823–8826.

18 a) S. Hanada, E. Tsutsumi, Y. Motoyama, and H. Nagashima, *J. AM. CHEM. SOC*. 2009, **131**, 15032–15040; b) A. M. Smith and R. Whyman, *Chem. Rev*. 2014, **114**, 5477−5510.

19 X. Verdaguer, M. C. Hansen, S. C. Berk, and S. L. Buchwald, *J. Org. Chem*. 1997, **62**, 8522–8528.

20 a) J. Lipowitz, S. A. Bowman, *J. Org. Chem*. 1973, **38**, 162; b) J. Blum, G. Bitan, S. Marx, K. P. C. Vollhardt, *J. Mol. Catal*. 1991, **66**, 313; c) R. J. Rahaim Jr., R. E. Maleczka Jr., *Synthesis* 2006, **19**, 3316–3340; d) V. Kumar, M. Kumar, S. Sharma and N. Kumar, *RSC Adv*. 2014, **4**, 11826–11830; e) J. P. Patel, A.-H. Li, H. Dong, V. L. Korlipara, M. J. Mulvihill, *Tetrahedron Lett*. 2009, **50**, 5975–5977; f) S. Chandrasekhar, G. Chandrashekar, M. S. Reddy and P. Srihari, *Org. Biomol. Chem*. 2006, **4**, 1650–1652; g) L. Pehlivan, E. Metay, S. Laval, W. Dayoub, P. Demonchaux, G. Mignani, M. Lemaire, *Tetrahedron Lett*. 2010, **51**, 1939–1941; h) K. Junge, B. Wendt, N. Shaikh, M. Beller, *Chem. Commun*. 2010, **46**, 1769–1771; i) R. G. Noronha, C. C. Romao, and A. C. Fernandes, *J. Org. Chem*. 2009, **74**, 6960–6964; j) D. Damodara, R. Arundhathi, T. V. R. Babu, M. K. Legan, H. J. Kumpatyb and P. R. Likhar, *RSC Adv*. 2014, **4**, 22567-22574.

21 Y. Fu, T. Baba, and Y. Ono, *J. Catal*. 2001, **197**, 91–97.

22 a) B. M. Bhanage and M. Arai (Eds.), Transformation and Utilization of Carbon Dioxide, *Green Chemistry and Sustainable Technology*, Springer-Verlag, Berlin Heidelberg, doi: 10.1007/978-3-642-44988-8-1, 2014; b) D. B. Nale, S. Rana, K. M. Parida and B. M. Bhanage, *Catal. Sci. & Tech.* 2014, **4**, 1608–1614; c) D. B. Nale, S. Rana, K. M. Parida and B. M. Bhanage, *Appl. Catal. A: Gen.* 2014, **469**, 340–349; d) D. B. Nale, S. D. Saigaonkar, B. M. Bhanage, *J. CO_2 Util.*, 2014, **8**, 67–73.

23 a) S. L. Buchwald, C. Bolm, *Angew. Chem. Int. Ed*. 2009, **48**, 5586; b) Z. Gonda, G. L. Tolnai, Z. Novak, *Chem. Eur. J*. 2010, **16**, 11822-11826; c) T. Lauterbach, M. Livendahl, A. Rosellon, P. Espinet, A. M. Echavarren, *Org. Lett*.,2010, **12**, 3006-3009; d) A. Ouali, J.-P. Majoral, A.-M. Caminade, M. Taillefer, *ChemCatChem*. 2009, **1**, 504-509.

24 K. Motokura, D. Kashiwame, N. Takahashi, A. Miyaji, and T. Baba, *Chem. Eur. J*. 2013, **19**, 10030–10037.

25 a) R. L. Clark and A. A. Pessolano, *Contribution from the Merck sharp and Dohme research laboratories*, 1958, **80**, 1662–1664; b) T. Kimura, K. Kamata, N. Mizuno, *Angew. Chem., Int. Ed.* 2012, **51**, 6700−6703.