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Room temperature synthesis of benzimidazole derivatives using reusable cobalt hydroxide (II) and cobalt oxide (II) as efficient solid catalysts

Murugulla Adharvana Chari, Donthabhakthuni Shobha, Takehiko Sasaki *

Department of Complexity Science and Engineering, School of Frontier Sciences, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561, Japan

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ABSTRACT

Here we demonstrate the synthesis of benzimidazoles through the coupling of 1,2-phenylenediamine with aldehydes by using $Co(OH)_2$ and similarly CoO(II) as efficient solid catalysts in ethanol at room temperature. The $Co(OH)_2$ solid catalyst gave better yields (82–98%) in short reaction times (4–7 h) than CoO(II) catalyst (80–94%, 6–9 h). These commercially available cheap catalysts are more active than many reported expensive heterogeneous catalysts.

Introduction

Among the various nitrogen containing heterocycles, benzimidazole derivatives exhibit antiviral, antiulcer, antihypertension, and anticancer properties.[1] The benzimidazoles are biologically potent[2] and this moiety is an important pharmacophore[3a,b] in drug discovery and also good intermediate[3c,d] for synthesis of many important organic compounds. Generally, the synthesis of 2-substituted benzimidazoles involves the treatment of 1,2-phenylenediamines either with carboxylic acids[4] or their derivatives (nitriles, imidates, or orthoesters),[5] under strongly acidic conditions and some times combined with very high temperatures (i.e., PPA, 180 °C) or the use of microwave irradiation.[6] These derivatives also often generated from the condensation of phenylenediamines with aldehydes[7] under oxidative conditions[8,9] using various oxidative and catalytic reagents, such as nitrobenzene (high-boiling point oxidant/solvent),[10] 1,4-benzoquinone,[11] $PhI(OAc)_2$,[12] Zn-proline,[13] heteropoly acids,[14] thionyl chloride-treatment,[15] 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ),[16] electron-deficient olefins,[9b] benzofuroxan,[17] MnO_2,[18] $Pb(OAc)_4$,[9a] oxone,[19] $NaHSO_3$,[20] H_2O_2/HCl,[21] iodine and hypervalent iodine (iodobenzene diacetate (IBD),[22] $Na_2S_2O_5$,[23] air,[24] sulfamic acid,[25] $FeCl_3{\cdot}6H_2O$,[26] $In(OTf)_3$,[27] $Yb(OTf)_3$,[28] $Sc(OTf)_3$,[29] $Cu(OTf)_2$,[30] $KHSO_4$,[31] IL,[32] (bromo dimethyl) sulfoniumbromide,[33] p-TSA,[34] $ZrOCl_2{\cdot}8H_2O$,[35] $ZrCl_4$,[36] $HfCl_4$,[36] borontrifluoride etherate,[37] copper complex,[38] polyaniline salt,[39] Heuland natural zeolite,[40] NaYzeolite,[41] polymer-supported hypervalent iodine,[42] TsOH/graphite and *N,N*-dimethylaniline/graphite,[43] cobalt(III) salen complex on activated carbon,[44] cobalt(II) chloride hexahydrate,[45] $VO(acac)_2$-$CeCl_3$ combo catalyst,[46] gold/CeO_2,[47] AlKIT-5,[48] and copper iodide catalysts[49] have been employed as the reagents or catalysts for the synthesis of benzimidazoles. Although the reaction was efficiently promoted by the above conditions they are often homogeneous catalysts and some of these methods suffer from one or more disadvantages, such as usage of stoichiometric or more quantity of reagent, high cost of the catalysts, prolonged reaction times, occurrence of several side reactions, severe reaction conditions, difficulty in separation of the products from the reaction mixture and strong oxidizing nature of the reagents. Therefore, the discovery of mild and practicable, stable, cheap, recyclable, and ecofriendly heterogeneous catalysts for the synthesis of 2-substituted benzimidazoles continues to attract the attention of researchers.

Recently the use of heterogeneous catalysts[38–51] including zeolites[40,41,50] and nanoporous materials[51] has received considerable importance in organic synthesis because of ease of handling, enhanced reaction rates, greater selectivity, and simple workup. Since we have published the preparation of nanocrystals of cobalt oxides and hydroxides,[52] we have sought the application as catalysts for organic reactions. Along this process, we have found that $Co(OH)_2$ or CoO(II) which are as-purchased solid catalysts exhibit catalytic activity for benzimidazole derivative synthesis. These solid catalysts are commercially available, nonhazardous, clean, cost effective than other heterogeneous catalysts. In continuation of our interest on catalytic applications of various heterogeneous catalysts, herein we report for the first time a simple, convenient,

* Corresponding author. Fax: +81 4 7136 3910.
E-mail address: takehiko@k.u-tokyo.ac.jp (T. Sasaki).

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and efficient method for the synthesis of benzimidazole and its derivatives by condensation of 1,2-phenylenediamines with aldehydes under open oxygen atmospheric conditions at room temperature in ethanol using $Co(OH)_2$ or CoO(II) as reusable solid catalysts. However, to the best of our knowledge, there has been no report available on the synthesis of benzimidazoles using these solid catalysts in the open literature so far.

Results and discussion

Initially, we have attempted the condensation of 1,2-phenylenediamine **1** (1.0 mmol) with benzaldehyde **2** (R=Ph) (1.2 mmol) at room temperature in ethanol condition for 6 h at open oxygen atmosphere, in the absence of catalyst and we observed 27.6% of product **3** and 0.1% of product **4** at 6 h and on long reaction time (12 h) resulted in the formation of a mixture like 2-phenyl benzimidazole **3** (29.1%) and 1-benzyl-2-phenyl-1*H*-benzimidazole **4** (2%) as side-products. The detailed mechanistic study on oxygen-catalyzed coupling of 1,2-phenylenediamine and benzaldehyde was carried out by Smith and Ho.[53] We have performed control experiments in the absence of air under N_2 atmosphere using Co_3O_4(II,III), CoO, and $Co(OH)_2$ catalysts, but the reaction was not proceeding much, these gave very low yields of **3** (7%, 9%, and 17%) at 6 h under optimized conditions. This indicates that the presence of oxygen is important for the reaction.

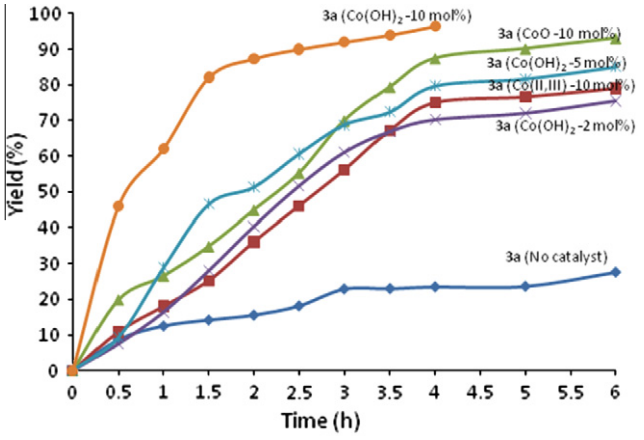


Figure 1. Time course of the various catalysts in the synthesis of benzimidazole **3a** using G.C.

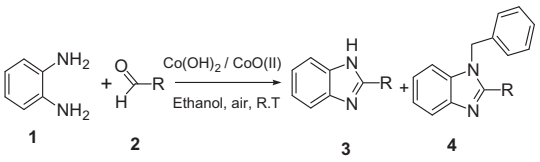
Table 1
Effect of the amount and catalytic activity of the various catalysts in the synthesis of benzimidazole **3a**

Entry	Catalyst	Amount of the catalyst (mol %)	Time (h)	Yield[a] (%)
1	No catalyst	—	6	27.6, 0.1[b]
			12	29.1, 2.0[b]
2	$Co(OH)_2$	2	4	75.5
3	$Co(OH)_2$	5	4	85.0
4	$Co(OH)_2$	10	4	96.4
5	CoO(II)	2	6	71.8
6	CoO(II)	5	6	81.3
7	CoO(II)	10	6	93.0
8	Co_3O_4(II,III)	10	6	78.9

Reaction and conditions: Substrates: 1,2-phenylenediamine (108 mg, 1.0 mmol), benzaldehyde (127 mg, 1.2 mmol), amount of catalyst = 10 mol %, amount of tetradecane:20 mg as internal standard, reaction was conducted at room temperature in ethanol as solvent.

[a] Yields of the product calculated by G.C. using Tetradecane as internal standard.

[b] Yield of the side product **4** (1-benzyl-2-phenyl-1*H*-benzimidazole).



Scheme 1. Room temperature synthesis of benzimidazoles using $Co(OH)_2$ and similarly CoO(II) solid catalysts. Side-product **4** is only formed in the absence of cobalt catalysts.

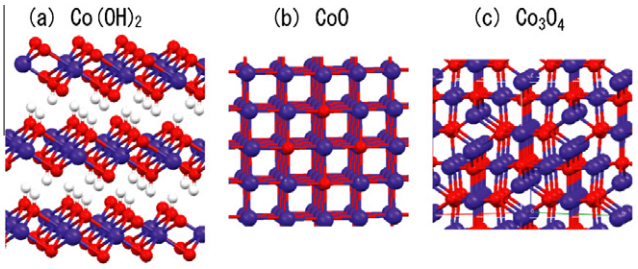


Figure 2. The crystal structures of $Co(OH)_2$ (ICSD-88940) (a), CoO(II) (ICSD-9865) (b) and Co_3O_4(II,III) (ICSD-69367) (c).

We have carried out the reaction using different amounts of the various catalysts (Fig. 1 and Table 1). It was observed that the amount of catalyst plays a significant role in controlling the activity of the catalyst. Among the various amounts of catalyst studied, 10 mol % of the $Co(OH)_2$ and similarly 10 mol % of CoO(II) solid catalysts were found to be the best at room temperature in ethanol condition and only 2-phenyl benzimidazole **3** was isolated in high yield within short time (Scheme 1).

In the case of $Co(OH)_2$ catalyst, the yields of the final product increases from 75% to 96% and whereas in the case of CoO(II)

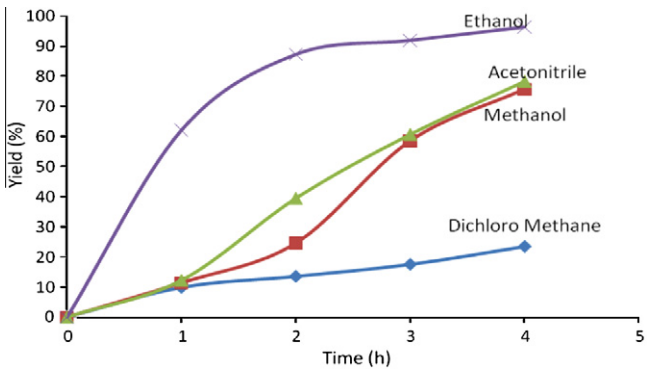
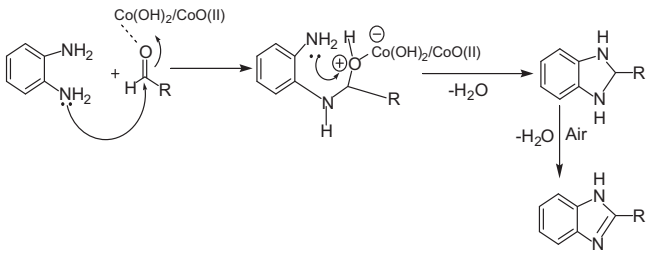
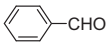
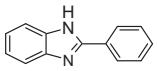
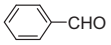
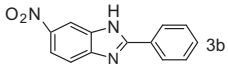
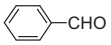
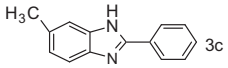
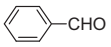
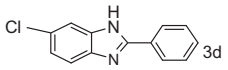
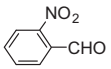
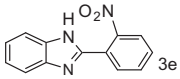
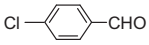
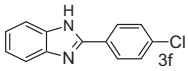
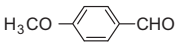
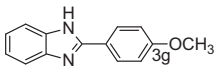
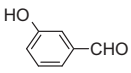
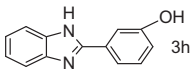
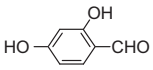
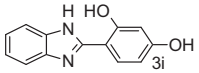
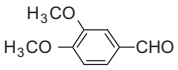
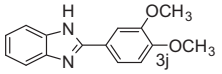
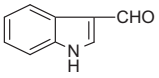
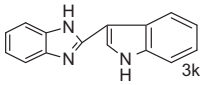
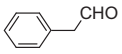
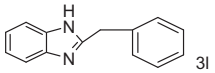
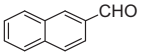
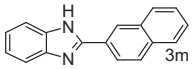
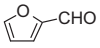
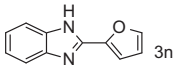
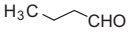
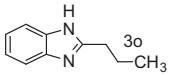
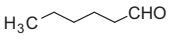
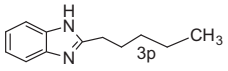
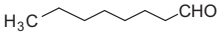
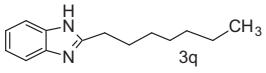
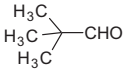
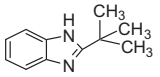
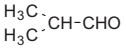
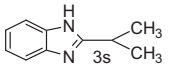


Figure 3. Solvent effect for synthesis of benzimidazole **3a** using 10 mol % $Co(OH)_2$ catalyst by G.C.



Scheme 2. A plausible mechanism for the synthesis of benzimidazoles.

Table 2
$Co(OH)_2$ and CoO catalyzed synthesis of benzimidazole derivatives

Entry	Aldehyde	Product (3)[a]	CoO(II)		$Co(OH)_2$	
			Time (h)	Yield (%)[b]	Time (h)	Yield (%)[b]
a		 3a	6	93[c]	4	96[c]
b		 3b	8	84	6	87
c		 3c	8	83	6	86
d		 3d	6	94	4	98
e		 3e	8	86	6	88
f		 3f	6	94	4	98
g		 3g	8	89	6	92
h		 3h	8	88	6	89
i		 3i	8	86	6	88
j		 3j	8	88	6	89
k		 3k	9	80	7	85
l		 3l	8	86	6	90
m		 3m	8	82	6	90
n		 3n	8	86	6	92
o		 3o	9	80	7	82
p		 3p	9	82	7	85
q		 3q	9	86	7	85
r		 3r	6	86	5	94
s		 3s	6	85	5	90

[a] All products were characterized by IR, NMR, and mass spectroscopy.
[b] Yield refers to pure products after purification by column chromatography.
[c] Yields of the product calculated by G.C.

catalyst, the product yield increases from 71% to 93% with increasing the catalyst weight from 2 to 10 mol %. We also investigated the 10 mol % Co_3O_4(II,III) activity on this synthesis, but the yield 79% was lower than that by $Co(OH)_2$ and CoO(II) solid catalysts. The order of activity was found as $Co(OH)_2 > CoO(II) > Co_3O_4$. It was found that the present reaction readily proceeds, whereas no simple oxidation of aldehyde was observed.

The crystal structures of $Co(OH)_2$, CoO(II), and Co_3O_4(II,III) are given below (Fig. 2) based on Inorganic Crystal Structures Database (ICSD, FIZ Karlsruhe) .

$Co(OH)_2$ geometry is a layered structure. In the present study $Co(OH)_2$ showed better activity than CoO(II) and Co_3O_4(II,III). This may be due to the layer structure of $Co(OH)_2$ and/or that all cobalt atoms are attached with hydroxyl groups influencing the reaction rates.

The effect of the solvents affecting the catalytic activity of the $Co(OH)_2$ was also investigated under the optimized reaction conditions (Fig. 3). Among various solvents like dichloro methane, methanol, acetonitrile, and ethanol used for this transformation, ethanol showed the highest yield (96%) in 4 h and was found to be the best solvent. Acetonitrile (78%) and methanol (75%) exhibited almost the same activity and dichloro methane showed poor activity (23%). A compromise between polarity and a little hydrophobicity might result in the best performance for ethanol.

As per a plausible mechanism, the reaction proceeds via the activation of aldehyde by $Co(OH)_2$ or CoO(II) followed by imine formation and this resulting imine further reacts with another $-NH_2$ group of 1,2-phenylenediamine resulting in the formation of dihydroimidazole which subsequently undergoes aromatization under the oxidative conditions to give the benzimidazole as shown in Scheme 2.

Encouraged by these results, we examined several substituted aldehydes including aromatic, heteroaromatic and aliphatic groups, which underwent smooth conversion to afford a wide range of benzimidazoles (Table 2). Aromatic aldehydes containing both electron-donating and -withdrawing groups worked well in this reaction. Unfortunately metal oxides are not explored much in the synthesis of various benzimidazoles. As per our survey MnO_2[18] is used as a catalyst for oxidation in the synthesis of benzimidazoles from *p*- and *m*-nitrobenzylidene-*o*-phenylenediamines and gave 15% and 25% yield of *p*-and *m*-nitrophenylbenzimidazoles. It was found that transition metal oxide is more effective for oxidation than the corresponding zero-valent metal powders. Open air and cobalt oxides both may be sources for the oxidation process. Here, it seems that cobalt catalysts are acting as bifunctional like Lewis acid as well as oxidative reagent. Expensive Co(III) salen complexes[44] are used in the synthesis of benzimidazoles, but they have not achieved the products using aliphatic aldehydes. In the present study we obtained the products using aliphatic aldehydes as shown in Table 2 (entries o, p, and q). Although a homogeneous $CoCl_2.6H_2O$ catalyst has been used for this synthesis of benzimidazoles,[45] $CoCl_2$ in the presence of O_2 and water gets oxidized to give a black residue of a mixture of cobalt oxide and hydroxide which cannot be reused again. It is contrasted that the present commercially available solid catalysts, such as CoO, $Co(OH)_2$ are recyclable catalysts for benzimidazole synthesis as mentioned below. The present catalysts are simple, less expensive, and more convenient than many catalysts presented in the above introduction. These catalysts were also found to be very active in the synthesis of benzimidazoles using bulky naphthaldehyde (**3m**), an acid sensitive furfuraldehyde (**3n**), and sterically hindered aldehydes, such as pivaldehyde (**3r**) and isobutyraldehyde (**3s**). Indole-3-carboxaldehyde (**3k**) also worked well. Various substituted aldehydes have been used with similar success to provide the corresponding benzimidazoles in high yields (82–98%). Interestingly the products **3d** and **f** were obtained at a high yield of 98% and during the reaction time within 1 h, the entire reactant (**1**) was consumed as found by TLC observation.

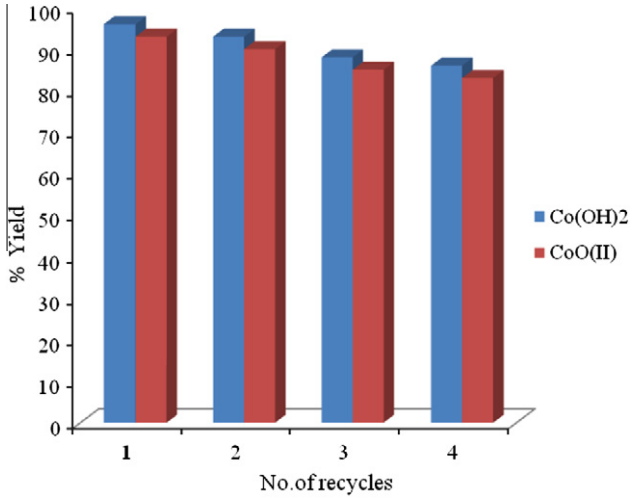


Figure 4. Recycle performances in the synthesis of benzimidazole **3a** using $Co(OH)_2$ and CoO(II) solid catalysts.

Finally, recycling experiments were conducted to find out the stability and reusability of the catalysts after the reaction. The catalyst was easily separated by centrifuge and reused after drying at 100 °C for 4 h. The efficiency of the recovered catalyst was verified with Entry **a**, Table 2. Using $Co(OH)_2$ as a fresh catalyst, the yield of product **3a** was 96%, while the recovered catalyst in the three subsequent cycles gave the yield of 93%, 88%, and 86%, respectively. Similarly using CoO(II) fresh catalyst, the yield of product **3a** was 93%, while the recovered catalyst gave the yield of 90%, 85%, and 83%, respectively (Fig. 4).

In addition we have also carried out scale up experiments with 1.08 g of 1,2-phenylenediamine and 1.06 g of benzaldehyde using 10 mol % of $Co(OH)_2$ catalyst at room temperature in ethanol. The $Co(OH)_2$ catalyst gave 96% of product **3a**, that is almost similar to the yield obtained in Table 2 Entry **a**, indicates that the catalyst could be easily used on a large scale. In the present work, the catalytic activity of the $Co(OH)_2$ or CoO(II) has been studied for the synthesis of various benzimidazole derivatives at room temperature. It has been found that these commercially available catalysts are very cheap, recyclable, and showed superior activity at room temperature than Co(III) salen,[44] AlKIT-5,[48] and cheaper than many other expensive heterogeneous catalysts.[38–49]

Conclusion

In summary, benzimidazole and its derivatives were synthesized by the coupling of 1,2-phenylenediamine with aldehydes using commercially available $Co(OH)_2$ or CoO(II) as an efficient recyclable catalyst under open oxygen atmosphere at room temperature using ethanol as solvent. Benzimidazoles could successfully be synthesized using these catalysts with acid sensitive, sterically hindered, and substituted aromatic and aliphatic aldehydes. The reactions were performed in ethanol and the catalyst could be reused for several cycles without much decrease in activity. The salient features of the present method include mild conditions, short reaction times, high yields, recyclable catalyst, large scale synthesis, and simple procedure. These catalysts could replace the existing homogeneous and expensive heterogeneous catalysts which are currently being used in the synthesis of various industrially important and biologically active benzimidazoles.

Experimental section

All chemicals and solvents were obtained from Aldrich and Wako and used without further purification. Column chromatographic separations were carried out on silica gel 60–120 mesh size. The ^1H NMR spectra of samples were recorded on a JEOL 400-MHz NMR spectrometer using TMS as an internal standard in DMSO-d_6. Mass spectra were recorded on a MALDI-MS (Shimadzu Axima Resonance) with 2,5-DHB as matrix. GC studies were carried out using Shimadzu GC-17A and GC-Mass (QP-5050).

General procedure

To a mixture of 1,2-phenylenediamine (1.0 mmol) and aldehyde (1.2 mmol) in ethanol (3 mL) under open oxygen atmosphere, 10 mol % of the catalysts were added. The resulting mixture was stirred at room temperature for appropriate time (Table 2). After completion of the reaction, as monitored by TLC, the reaction mixture was diluted with ethanol (20 mL) and the catalyst was separated by filtration. The organic layer was concentrated under reduced pressure and the crude product was purified by silicagel column chromatography using ethyl acetate-*n*-hexane (1:9) as eluent to afford pure benzimidazole product. The spectral data are in full agreement with the data reported in literature.[48,54,55] Some of the compounds' spectral data are given below.

3a: 2-Phenyl-1*H*-benzimidazole (Table 2): Solid, mp 295–297 °C, IR (KBr): ν_{max} 3047, 2966, 1462, 1411, 1276, 970, 744, 703 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 12.91 (br s, 1H, NH), 8.20–8.18 (m, 2H), 7.61–7.56 (m, 2H), 7.53–7.43 (m, 3H), 7.21–7.18 (m, 2H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 150.80, 137.92, 137.90, 131.80, 129.40, 127.80, 125.73, 123.10, 122.80, 121.30, 121.13, 116.80, 111.21. MALDI-MS: *m/z* 195 $(M+H)^+$.

3k: 2-(3-Indolyl)-*1H*-benzimidazole (Table 2): Solid, mp 196–198 °C; IR (KBr): ν_{max} 3147, 2976, 1635 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz): δ 11.20 (br s, 1H, NH), 10.65 (br s, 1H, NH), 8.31 (s, 1H), 7.79-7.74 (m, 1H), 7.56–7.29 (m, 3H), 7.26–6.85 (m, 4H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 149.64, 137.22, 137.20, 136.39, 128.01, 125.90, 123.37, 123.31, 122.10, 121.27, 120.14, 113.10, 113.07, 111.79, 106.50; MALDI-MS: *m/z* 234 $(M+H)^+$.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.08.047.

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