

## Efficient Cycloaddition Reaction of Carbon Dioxide with Epoxide by Rhodamine Based Catalyst Under 1 atm Pressure

Qing Gong, Huadong Luo, Di Cao, Haibo Zhang,\* Wenjing Wang, and Xiaohai Zhou\*

College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, 430072, P. R. China

\*E-mail: haibo Zhang1980@gmail.com (H. Zhang); zhx7954@hotmail.com (X. Zhou)

Received February 18, 2012, Accepted March 15, 2012

Rhodamine B (RhB) and rhodamine 6G (Rh6G) were employed as catalysts for the synthesis of cyclic carbonate from carbon dioxide and epoxide. It turned out that the catalytic activity of Rh6G was nearly 29 times higher than that of RhB at 1 atm pressure, 90 °C. Furthermore, the catalytic efficiency of RhB and Rh6G was greatly enhanced with triethylamine as co-catalyst. Under the optimized conditions, the best isolated yield (93%) of cyclic carbonate was achieved without organic solvent and metal component.

**Key Words :** Carbon dioxide, Epoxide, Cycloaddition, Rhodamine

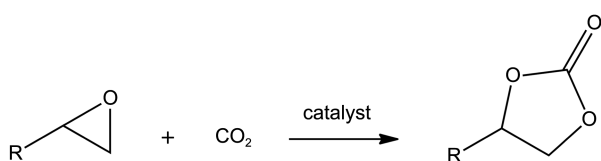
### Introduction

The development of efficient catalytic systems to transform atmospheric carbon dioxide (CO<sub>2</sub>) into value added chemicals and fuels is an amazing topic in recent years, due to the global environmental concerns including the greenhouse effect and global warming, which is caused by the rapid accumulation of CO<sub>2</sub> in atmosphere since the 1<sup>st</sup> industrial revolution.<sup>1-5</sup> Meanwhile, as a cheap, non-toxic, non-flammable, abundant C1 feedstock gas, the physical absorption and chemical transformation of carbon dioxide has drawn much interests in industrial chemistry. Among the many means that carbon dioxide can be consumed, the chemical coupling reaction of carbon dioxide and epoxide proves to be the most promising one (Scheme 1).<sup>6,7</sup> It is a process of nearly 100% 'atom efficiency', and the product cyclic carbonates are excellent aprotic polar solvents, which have found general applications in lithium ion batteries as electrolytes, monomers for producing poly-carbonates and as chemical precursors or intermediates for preparing medicines or agricultural chemicals.<sup>8-10</sup>

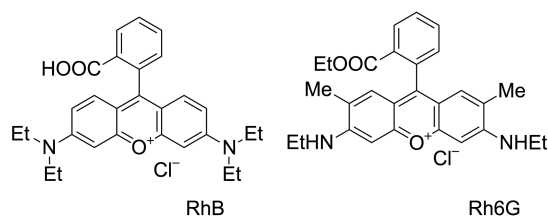
During the past decades, various homogeneous and heterogeneous catalysts have been synthesized for this cycloaddition reaction, including metal complexes,<sup>11-13</sup> organic bases or onium salts,<sup>14-16</sup> metal oxides,<sup>17</sup> ionic liquids,<sup>18-21</sup> etc. Though great strides have been achieved, most of these catalysts suffer from low efficiency, low stability, water or moisture sensitivity, the need for co-solvent or the requirement for high pressure. Due to the inert nature of CO<sub>2</sub>, searching novel catalysts that can promote the chemical

insertion of carbon dioxide into epoxide at 1 atm and near ambient temperature still remains a challenge, and only limited literatures have been reported.<sup>22-27</sup> Nowadays, as the universal awareness of environmental protection, eliminating metal component involvement for catalyst design and abating volatile organic solvent usage in the process of chemical carbon dioxide fixation is more pressing and promising for our future.

It is generally recognized that many homogeneous or heterogeneous catalysts catalyze this coupling reaction through an acid-base or electrophile-nucleophile bifunctional mechanism.<sup>14</sup> On the whole, this chemical transformation of carbon dioxide concerns mainly three steps: epoxide opening, incorporation of carbon dioxide, and finally ring closure. As scientists' continuing efforts towards developing novel catalysts working at extremely mild condition (1 atm pressure, nearly ambient temperature, metal-free and solventless), many functional groups have been incorporated into the catalyst design. One of the most successful methods is to search for appropriate factor that can stabilize the oxyanion species, not only just through simple opposite electrostatic attraction. It was proved that the synthesized catalyst with hydrogen bond donor would exhibit high catalytic activity for this transformation of carbon dioxide.<sup>28,29</sup> Han *et al.* designed a series of betaine-based salts containing quaternary ammonium ion and carboxylic acid group, and demonstrated that the carboxylic acid group in the catalyst had synergetic effect with halide anion to promote cycloaddition of CO<sub>2</sub> under mild conditions.<sup>30</sup> Similar results of the synergistic effect of acidic site and halide anion were also reported by Zhang and Park.<sup>31,32</sup> However, the carboxylic acid moiety might protonate the alkoxide anion intermediate, increase the reaction activation energy of CO<sub>2</sub> insertion step or the ring closure, and finally reduces the yield of cyclic carbonate. To address this issue, the aim of this paper is to explore the catalytic compatibility of acidic carboxylic moiety and starting epoxide substrate, and make some primary trial in high effective catalyst design towards



**Scheme 1.** Synthesis of cyclic carbonate from carbon dioxide and epoxide.



**Figure 1.** The structure of rhodamine B (RhB) and rhodamine 6G (Rh6G).

atmospheric pressure carbon dioxide chemical fixation.

## Results and Discussion

We adopted rhodamine B (RhB) and rhodamine 6G (Rh6G) as the model catalysts for cycloaddition of CO<sub>2</sub> with epoxide to carry out the primary investigations. As shown in Figure 1, RhB is the ideal analog that possesses both carboxylic acid and amino group. Whereas, being the structure isomer to RhB, Rh6G has one ester group and two surplus amine moieties directly connecting to the aromatic ring.

Although the catalysts for this cycloaddition reaction were well studied, less research focused on the transformation of styrene oxide (**1a**) due to steric hindrance of the substrate. Thus, we chose the coupling reaction of carbon dioxide with styrene oxide (**1a**) as a model reaction and the results were listed in Table 1. Obviously, the catalytic activity of Rh6G was nearly 29 times higher than that of RhB at 1 atm pressure, 90 °C (Table 1, entry 1 and 3). Accordingly, the yield of styrene carbonate (**1b**) was nearly halved after adding acetic acid (AcOH) to Rh6G (Table 1, entry 4), and the RhB catalytic ability was almost quenched in the present of AcOH (Table 1, entry 2). It was worth noting that acetic

**Table 1.** Synthesis of styrene carbonate from styrene oxide with different catalysts under 1 atm CO<sub>2</sub> pressure<sup>a</sup>

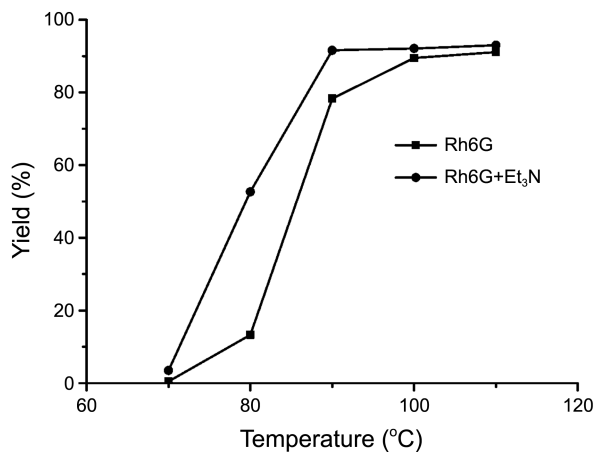
Entry	Catalyst	Co-Catalyst	Ca/Co-Ca Ratio in mol	Catalyst Loading (mol %)	Yield <sup>b</sup> (%)	Selectivity <sup>c</sup> (%)
1	RhB			1	2.7	99
2	RhB	AcOH	1:1	1	trace	
3	Rh6G			1	78	99
4	Rh6G	AcOH	1:1	1	34	98
5	RhB	Et <sub>3</sub> N	1:1	1	74	98
6	Rh6G	Et <sub>3</sub> N	1:1	1	92	99
7	Rh6G	DBU	1:1	1	94	98
8	Rh6G	DMAP	1:1	1	93	97
9	Rh6G	Bu <sub>3</sub> N	1:1	1	88	97
10	Rh6G			0.1	0.34	99
11	Rh6G			0.5	39	99
12	Rh6G	Et <sub>3</sub> N	1:1	0.1	5.5	99
13	Rh6G	Et <sub>3</sub> N	1:1	0.5	55	99
14		AcOH		1	trace	
15		Et <sub>3</sub> N		1	0.93	99
16	KCl			1	trace	

<sup>a</sup>Reaction condition: **1a** (16 mmol), 90 °C, 24 h. <sup>b</sup>Isolated yield. <sup>c</sup>Selectivity was determined by GC.

acid itself did not catalyze the reaction effectively (Table 1, entry 14). These results revealed that acidic carboxylic acid moiety in catalyst might hamper the efficient transformation of CO<sub>2</sub> under 1 atm conditions.











Then, in order to verify our hypothesis, additional amine was employed as co-catalyst. As the acid anhydride of carbonic acid, carbon dioxide is Lewis acid species with somewhat electron deficiency, which can react with basic amidine amine to yield the “activated carbon dioxide” intermediate. In order to avoid this impact, we focused on employing Et<sub>3</sub>N as additive. As expected, the catalytic activities of RhB and Rh6G were greatly improved after adding Et<sub>3</sub>N, the isolated yield of **1b** was 74% and 92%, respectively (Table 1, entry 5 and 6). Meanwhile, Et<sub>3</sub>N or potassium chloride (KCl) proved not to be the suitable catalyst for this cycloaddition reaction either (Table 1, 15 and 16), which indicated the existence of synergistic effect between rhodamine based catalyst and Et<sub>3</sub>N. Interesting, when other amines such as 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), 4-Dimethylaminopyridine (DMAP), and Tri-*n*-butylamine (Bu<sub>3</sub>N) were employed as co-catalyst, the yield of **1b** kept almost constant (Table 1, entry 7, 8 and 9), which confirmed the acid-base corporation mechanism of this cycloaddition under our selected conditions. When the Rh6G loading was reduced to 0.5 mol%, the yield of cyclic carbonate **1b** was only 39% (Table 1, entry 11). The chemical transformation of epoxide **1a** could hardly take place with further reduction of Rh6G loading to 0.1 mol % (Table 1, entry 10). After the employment of Et<sub>3</sub>N as co-catalyst, the yield of **1b** was 5.5% and 55%, respectively (Table 1, entry 12 and 13).

Figure 2 demonstrated the dependence of styrene carbonate **1b** yield on temperature at 1 atm CO<sub>2</sub> pressure in the range of 70–110 °C, using Rh6G as catalyst with or without Et<sub>3</sub>N. It was shown that temperature had a notable effect on the catalyst activity. The yield of **1b** increased with increasing temperature, and exceeded over 90% at 100 °C, then reached a plateau with further increase of temperature. It was clear that the catalytic activity of Rh6G was greatly enhanced with the addition of Et<sub>3</sub>N, and Rh6G solely lost



**Figure 2.** Styrene carbonate yield versus temperature using Rh6G with and without Et<sub>3</sub>N. Reaction conditions: **1a** (16 mmol), Rh6G (1 mol %), Et<sub>3</sub>N (1 mol %) if used, 1 atm, 24 h.

**Table 2.** Synthesis of other cyclic carbonates using Rh6G as catalyst under 1 atm CO<sub>2</sub> pressure<sup>a</sup>

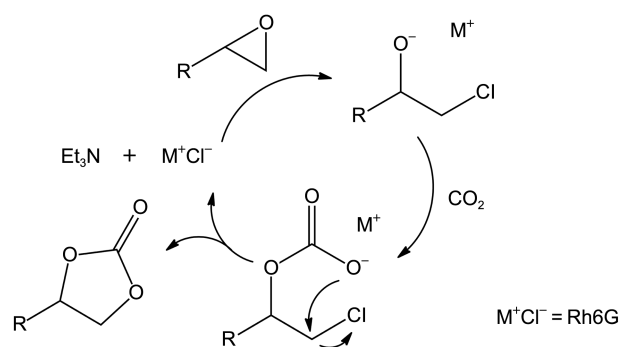
Entry	Epoxide	Product	Additive	Yield <sup>b</sup> (%)	Selectivity <sup>c</sup> (%)
1				78	99
2			Et <sub>3</sub> N	92	99
3				97	98
4			Et <sub>3</sub> N	93	95
5				44	99
6			Et <sub>3</sub> N	79	99
7				8.0	99
8			Et <sub>3</sub> N	71	98
9				trace	
10 <sup>d</sup>			Et <sub>3</sub> N	75	99

<sup>a</sup>Reaction condition: epoxide (16 mmol), Rh6G (1 mol %), Et<sub>3</sub>N (1 mol %) if used, 90 °C, 24 h. <sup>b</sup>Isolated yield. <sup>c</sup>Selectivity was determined by GC. <sup>d</sup>10 atm CO<sub>2</sub>.

most of its catalytic efficiency when temperature was set below 90 °C without Et<sub>3</sub>N. Whereas, taking the catalyst activity and energy consumption into account, 90 °C was selected as the optimal temperature for further investigation.

Then, Rh6G was chosen for the preparation of some other cyclic carbonates from corresponding monosubstituted terminal epoxides to investigate the substrates selectivity (Table 2). Satisfactory yield of **1b** was obtained when 1% Rh6G was employed as catalyst (Table 2, entry 1). Though epoxide **3a** and **2a** gave moderate to good results (Table 2, entry 5 and 3), the transformation of **4a** did not afford satisfactory yield (Table 2, entry 7), even at elevated temperature. Meanwhile, the cycloaddition of epoxide **5a** with carbon dioxide rarely worked under 1 atm, owing to low polarity of the substrate and poor solubility of the catalyst (Table 2, entry 9). The transformation of **1a**, **2a**, **3a** and **4a** went quite well (Table 2, entry 2, 4, 6 and 8), after adding one equivalent of Et<sub>3</sub>N to Rh6G. Interesting, the transformation of epoxide **5a** worked smoothly under 10 atm CO<sub>2</sub> with one equivalent of Et<sub>3</sub>N to Rh6G (Table 2, entry 10). Today, great efforts should be devoted to develop highly efficient catalyst, which can promote the incorporation of CO<sub>2</sub> into the unfunctional or steric epoxide under 1 atm pressure and near ambient temperature without metal component involvement and volatile solvent usage.

Plausible catalytic cycle is shown in Scheme 2. Initially, the epoxide ring is opened by means of the chloride, yielding an oxy-anion species (as a naked nucleophilic anion), which is stabilized by the Rh6G cation counterpart through electrostatic interaction. Then, this oxyanion intermediate reacts with carbon dioxide, to form the corresponding cyclic carbonate and regenerates the catalyst. The additional Et<sub>3</sub>N might interact with acidic proton in the catalyst to facilitate the formation the cyclic carbonate. To confirm this catalytic

**Scheme 2.** Possible catalytic cycle.

role of Et<sub>3</sub>N to Rh6G catalytic system, we simplify our catalytic system and employ aniline instead of Rh6G for clearness, to see if there is any interaction between aniline and epoxide. As shown in Figure S1 (see supporting information), a downshift of 0.041 ppm in <sup>1</sup>H NMR was observed to the hydrogen in the amino group of aniline, though subtle, which can be ascribed to the formation of hydrogen bonding. Then, we argue that the hydrogen of N-ethyl group in the Rh6G might also present this tendency to form hydrogen bond with the alkoxide anion intermediate, which could raise the activation energy for this transformation of epoxide. Adding basic Et<sub>3</sub>N (the basic order alkyl amine > aromatic amine) might eliminate this impact and improve the yield of cyclic carbonate.

## Conclusions

In conclusion, the cycloaddition of carbon dioxide with epoxide was achieved by rhodamine based catalyst without metal and organic solvent. Meanwhile, adding Et<sub>3</sub>N as co-catalyst would greatly enhance the catalytic activity, with the

best isolated yield (93%) of cyclic carbonate at 90 °C under 1 atm pressure. The acidic hydrogen in the catalyst might interact with alkoxide anion intermediate, adding basic Et<sub>3</sub>N would eliminate this impact and improve the yield of cyclic carbonate. These would inspire new exploration in the high effective catalyst design towards atmospheric pressure carbon dioxide chemical fixation.

### Experimental

CO<sub>2</sub> was supplied by Wuhan Ming Hui Gas Technology Co. Ltd. with a purity of 99.99%. Rhodamine 6G was from Sigma (St Louis, MO). Propylene oxide, epichlorohydrin, acetic acid, triethylamine, potassium chloride, rhodamine B, 4-Dimethylaminopyridine, and Tri-*n*-butylamine were analytical grade and produced by Sinopharm Chemical Reagent Shanghai Co., Ltd. Other epoxides and 1,8-Diazabicyclo-[5.4.0]undec-7-ene were purchased from Alfa Aesar. All chemicals were used as received.

**Representative Experimental Procedure for the Synthesis of Cyclic Carbonate (1b).** Styrene oxide (**1a**) (1.9 g, 16 mmol), Rh6G (0.078 g, 0.16 mmol) and Et<sub>3</sub>N (16 mg, 0.16 mmol) were placed in 10 mL schlenk flask, then CO<sub>2</sub> was charged through with 10 mL/min, and the mixture was allowed to stir at 90 °C under CO<sub>2</sub> atmosphere (1 atm) for the setting time. The yield of the product was obtained after purification by flash chromatography (hexane/EtOAc 2:1). The products of cyclic carbonates were analyzed at room temperature on a Mercury VX-300 <sup>1</sup>H NMR spectrometer using CDCl<sub>3</sub> as the solvent.

**4-Phenyl-1,3-dioxolan-2-one (1b):** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ<sub>H</sub> (ppm) 4.34 (t, *J* = 8.2, 1H), 4.80 (t, *J* = 8.4, 1H), 5.68 (t, *J* = 8.0, 1H), 7.35-7.45 (m, 5H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ<sub>C</sub> 154.756, 135.644, 129.530, 129.029, 125.751, 77.861, 71.032.

**4-Chloromethyl-1,3-dioxolan-2-one (2b):** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ<sub>H</sub> (ppm) 3.75 (dd, *J* = 3.6, 12.3, 1H), 3.84 (dd, *J* = 4.9, 12.3, 1H), 4.42 (dd, *J* = 5.8, 8.8, 1H), 4.61 (t, *J* = 8.4, 1H), 5.00-5.06 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ<sub>C</sub> 154.36, 74.30, 66.73, 44.01.

**4-Allyloxymethyl-1,3-dioxolan-2-one (3b):** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ<sub>H</sub> (ppm) 3.21-3.68 (m, 2H), 4.02-4.04 (m, 2H), 4.37 (dd, *J* = 6.0, 8.4, 1H), 4.48 (t, *J* = 8.4, 1H), 4.75-4.80 (m, 1H), 5.18-5.28 (m, 2H), 5.81-5.87 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ<sub>C</sub> 154.97, 133.56, 117.66, 75.05, 72.34, 68.69, 66.13.

**4-(Butoxymethyl)-1,3-dioxolan-2-one (4b):** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ<sub>H</sub> (ppm) 0.92 (t, *J* = 7.3, 3H), 1.30-1.44 (m, 2H), 1.67-1.46 (m, 2H), 3.56-3.43 (m, 2H), 3.75-3.56 (m, 2H), 4.39 (dd, *J* = 8.2, 6.2, 1H), 4.49 (t, *J* = 8.3, 1H), 4.79 (dd, *J* = 5.1, 3.1, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ<sub>C</sub> 154.926, 75.053, 71.603, 69.426, 66.105, 31.545, 19.032, 13.692.

**4-Butyl-1,3-dioxolan-2-one (5b):** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) δ<sub>H</sub> (ppm) 0.92 (t, *J* = 7.0, 3H), 1.61-1.20 (m, 6H), 4.16-3.97 (m, 1H), 4.53 (t, *J* = 8.1, 1H), 4.80-4.61 (m, 1H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ<sub>C</sub> 155.12, 75.14, 71.56, 69.40, 66.11, 31.30, 18.93, 13.64.

**Acknowledgments.** The authors thank Ph. D. Lu Chen for fruitful discussion of the manuscript. We gratefully acknowledge the financial support by the National Natural Science Foundation of China (No. 20972120).

**Supplementary Materials.** Supplementary Figure S1 is available at the bkcs website.

### References

- Cokoja, M.; Bruckmeier, C.; Rieger, B.; Herrmann, W. A.; Kühn, F. E. *Angew. Chem., Int. Ed.* **2011**, *50*, 8510.
- Jessop, P. G.; Joó, F.; Tai, C. C. *Coord. Chem. Rev.* **2004**, *248*, 2425.
- Sakakura, T.; Choi, J. C.; Yasuda, H. *Chem. Rev.* **2007**, *107*, 2365.
- Yu, K. M.; Curcic, I.; Gabriel, J.; Tsang, S. C. *ChemSusChem*. **2008**, *1*, 893.
- Riduan, S. N.; Zhang, Y. G. *Dalton Trans.* **2010**, *39*, 3347.
- Sakakura, T.; Kohno, K. *Chem. Commun.* **2009**, 1312.
- Yoshida, M.; Ihara, M.; *Chem. Eur. J.* **2004**, *10*, 2886.
- Bayardon, J.; Holz, J.; Schäffner, B.; Andrushko, V.; Verevkin, S.; Preetz, A., et al. *Angew. Chem., Int. Ed.* **2007**, *46*, 5971.
- Clements, J. H. *Ind. Eng. Chem. Res.* **2003**, *42*, 663.
- Shaikh, A. A. G.; Sivaram, S. *Chem. Rev.* **1996**, *96*, 951.
- Kruper, W. J.; Dellar, D. D. *J. Org. Chem.* **1995**, *60*, 725.
- Paddock, R. L.; Nguyen, S. T. *J. Am. Chem. Soc.* **2001**, *123*, 11498.
- Shen, Y. M.; Duan, W. L.; Shi, M. *J. Org. Chem.* **2003**, *68*, 1559.
- Caló, V.; Nacci, A.; Monopoli, A.; Fanizzi, A. *Org. Lett.* **2002**, *4*, 2561.
- Bok, T.; Noh, E. K.; Lee, B. Y. *Bull. Korean Chem. Soc.* **2006**, *27*, 1171.
- Ra, C. S.; Hwang, J. C.; Lee, H. B.; Shim, J. *Bull. Korean Chem. Soc.* **2007**, *28*, 1060.
- Yano, T.; Matsui, H.; Koike, T.; Ishiguro, H.; Fujihara, H.; Yoshihara, M., et al. *Chem. Commun.* **1997**, 1129.
- Sun, J. M.; Fujita, S.; Arai, M. *J. Organomet. Chem.* **2005**, *690*, 3490.
- Nguyen, L. V.; Lee, B.; Nguyen, D. Q.; Kang, M.; Lee, H.; Ryu, S., et al. *Bull. Korean Chem. Soc.* **2008**, *29*, 148.
- Wang, J. Q.; Yue, X. D.; Cai, F.; He, L. N. *Catal. Commun.* **2007**, *8*, 167.
- Zhang, S. J.; Chen, Y. H.; Li, F. W.; Lu, X. M.; Dai, W. B.; Mori, R. *Catal. Today* **2006**, *115*, 61.
- Barkakaty, B.; Morino, K.; Sudo, A.; Endo, T.; *Green Chem.* **2010**, *12*, 42.
- Ochiai, B.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 5673.
- Kihara, N.; Hara, N.; Endo, T. *J. Org. Chem.* **1993**, *58*, 6198.
- Motokura, K.; Itagaki, S.; Iwasawa, Y.; Miyaji, A.; Baba, T.; *Green Chem.* **2009**, *11*, 1876.
- Meléndez, J.; North, M.; Pasquale, R. *Eur. J. Inorg. Chem.* **2007**, 3323.
- Yin, S. F.; Shimada, S. *Chem. Commun.* **2009**, 1136.
- Kim, Y. J.; Varma, R. S. *J. Org. Chem.* **2005**, *70*, 7882.
- Sun, J.; Ren, J.; Zhang, S.; Cheng, W. *Tetrahedron Lett.* **2009**, *50*, 423.
- Zhou, Y. X.; Hu, S. Q.; Ma, X. M.; Liang, S. G.; Jiang, T.; Han, B. X. *J. Mol. Catal. A: Chem.* **2008**, *284*, 52.
- Sun, J.; Han, L.; Cheng, W.; Wang, J.; Zhang, X.; Zhang, S. *ChemSusChem*. **2011**, *4*, 502.
- Han, L.; Choi, H.-J.; Choi, S.-J.; Liu, B.; Park, D.-W. *Green Chem.* **2011**, *13*, 1023.