

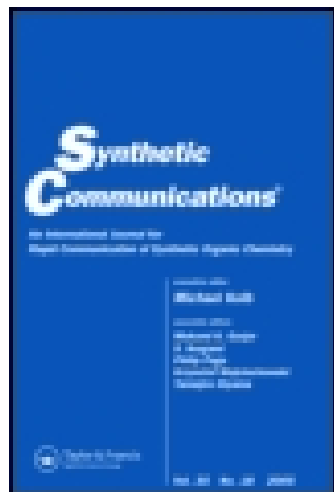
This article was downloaded by: [Washington University in St Louis]

On: 23 December 2014, At: 12:10

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office:

Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/lcyc20>

Efficient DMF-Catalyzed Coupling of Epoxides with CO₂ under Solvent-Free Conditions to Afford Cyclic Carbonates

Jia-Li Jiang^a & Ruimao Hua^a

^a Department of Chemistry, Tsinghua University, Innovative Catalysis Program, Key Laboratory of Organic Optoelectronics and Molecular Engineering of Ministry of Education, Beijing, China

Published online: 24 Nov 2006.

To cite this article: Jia-Li Jiang & Ruimao Hua (2006) Efficient DMF-Catalyzed Coupling of Epoxides with CO₂ under Solvent-Free Conditions to Afford Cyclic Carbonates, *Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry*, 36:21, 3141-3148, DOI: [10.1080/00397910600908744](https://doi.org/10.1080/00397910600908744)

To link to this article: <http://dx.doi.org/10.1080/00397910600908744>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

Efficient DMF-Catalyzed Coupling of Epoxides with CO₂ under Solvent-Free Conditions to Afford Cyclic Carbonates

Jia-Li Jiang and Ruimao Hua

Department of Chemistry, Tsinghua University, Innovative Catalysis Program, Key Laboratory of Organic Optoelectronics and Molecular Engineering of Ministry of Education, Beijing, China

Abstract: To develop a simple, low-molecule, and cost-effective organocatalyst for the coupling of epoxides with CO₂, we have screened this coupling reaction in different organic solvents and found that DMF is an efficient organic catalyst for the coupling of epoxides with CO₂ to give cyclic carbonates in high yield. In some cases, the catalytic activity of DMF can be significantly increased by the addition of catalytic amount of H₂O.

Keywords: Carbon dioxide, catalysis, cyclic carbonate, DMF, epoxide

1. INTRODUCTION

Carbon dioxide fixation into organic substrates is a very important and a challenge research area in CO₂ chemistry.^[1] Because cyclic carbonates are valuable intermediates in synthetic organic chemistry,^[2] recently a variety of efficient catalyst systems such as alkali metal compounds,^[3] ionic liquids,^[4] and transition metal complexes^[5] have been developed.

In recent years, organocatalytic reactions using metal-free organic molecules as catalysts have been extensively investigated.^[6] The catalytic reaction can be carried out under air, and the catalysts are usually inexpensive

Received in R.O.C. March 9, 2006

Address correspondence to Ruimao Hua, Department of Chemistry, Tsinghua University, Innovative Catalysis Program, Key Laboratory of Organic Optoelectronics and Molecular Engineering of Ministry of Education, Beijing 100084, China. E-mail: ruimao@mail.tsinghua.edu.cn

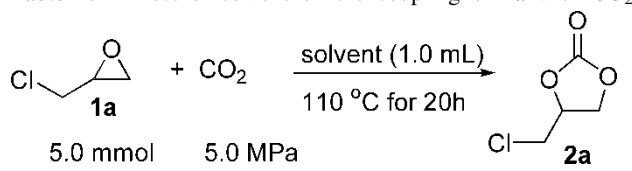
and stable. In this work, with the purposes of screening and developing simple, low molecule organocatalysts for the reaction of epoxides with CO₂ to afford cyclic carbonates, we have studied the coupling of 1-chloro-2,3-epoxypropane **1a** with CO₂ in difference solvents. DMF was found to be an efficient organic catalyst for the coupling of epoxides with CO₂ to afford cyclic carbonates in good to excellent yields.

2. RESULTS AND DISCUSSION

The coupling reaction was carried out using 5.0 mmol of **1a** in 1.0 mL of solvent in an autoclave with stirring at 110 °C for 20 h, and CO₂ (5.0 MPa) was pressurized directly into the autoclave under an air atmosphere at ambient temperature. Table 1 lists the results of **1a** with CO₂, affording 4-chloromethyl-[1,3]dioxolan-2-one **2a** in different solvents. The coupling reactions were markedly influenced by the nature of the employed solvents. Under the identified reaction conditions, neither polymerization of **1a** nor copolymerization of **1a** with CO₂ occurred under the chosen solvents. The unreacted **1a** could be recovered.

At first, we heated **1a** under CO₂ at 110 °C for 20 h without using any solvents; the coupling reaction did not proceed at all with the recovery of

Table 1. Effect of solvent on the coupling of **1a** with CO₂



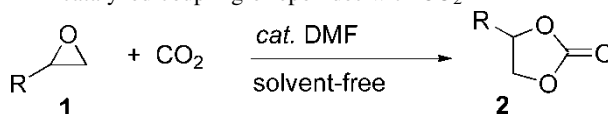
Entry	Solvent	Yield of 2a (%) ^a
1	—	0
2	CHCl ₂ CHCl ₂	0
3	CH ₃ CN	0
4	THF	~1
5	CH ₃ NO ₂	~1
6	Toluene	3
7	1,4-Dioxane	73
8	CH ₃ OH	90
9	C ₂ H ₅ OH	90
10	Benzyl alcohol	12
11	CH ₃ COCH ₃	8
12	CH ₃ COOC ₂ H ₅	45
13	DMF	>99

^aGC yield based on **1a**.

1a (entry 1). In CHCl₂CHCl₂ or CH₃CN, **2a** was not detectable by gas chromatography (GC) analysis (entries 2 and 3). The same reaction produced a trace amount of **2a** when tetrahydrofuran (THF), CH₃NO₂, and toluene were used as solvents (entries 4–6). Compared to THF, however, in 1,4-dioxane, **2a** was formed in moderate yield (73% GC, entry 7). Protic alcohol solvents, such as methanol and ethanol, were good solvents for the formation of **2a**; **2a** was obtained in 90% and 82% GC yield in methanol and ethanol, respectively (entries 8 and 9). Although methanol and ethanol were suitable solvents for the formation of **2a**, the use of the higher-molecular-weight alcohols, such as benzyl alcohol, resulted in the decrease of **2a** (12% GC yield, entry 10). In other solvents, such as acetone and ethyl acetate, **2a** was formed in 8% and 45% GC yield, respectively (entries 11 and 12). Among the chosen solvents, DMF was the most efficient solvent for the formation of **2a**; in this case, **2a** was obtained in quantitative yield (entry 13). DMF-scCO₂ had been reported to be a good solvent system for the coupling of 1,2-epoxyethylbenzene with CO₂ to give styrene carbonate.^[7] Therefore, we examined the same reaction in the presence of different amounts of DMF and found that the present coupling reaction could proceed using a catalytic amount of DMF. As shown in entries 1 and 2 of Table 2, in the presence of 20% or 10% DMF, the coupling of **1a** with CO₂ at 110°C for 15 h afforded **2a** in 95% and 84% GC yield, respectively. Interestingly, although the addition of methanol (10%) could not improve the coupling reaction (Table 2, entry 3), H₂O was a good additive to accelerate the DMF-catalyzed coupling of **1a** with CO₂. Thus, in the presence of DMF (10 mol%) and H₂O (10 mol%), 87% yield of **2a** could be obtained at 110°C in 4 h (Table 2, entry 4). However, when using H₂O as additive, a trace amount of diol, which arose from the hydration of **1a**, was detectable by GC.

The results of DMF-catalyzed coupling reactions of other epoxides with CO₂ under different conditions are shown in Table 2. Compared with **1a**, 1,2-epoxypropane **1b**, 1,2-epoxybutane **1c**, 1,2-epoxyhexane **1d**, and 1,2-epoxyethylbenzene **1e** were relatively sluggish: at 110°C for 15 h, the corresponding cyclic carbonates **2b–e** were formed in 5%, 37%, 10%, and 8% yields, respectively. However, if the reactions were performed at higher temperatures (130–160°C), and/or with the addition of a catalytic amount of H₂O, **2b–e** could be obtained in good yields (Table 2, entries 5–20). In the absence of DMF, H₂O could not catalyze the formation of cyclic carbonates at all. For example, in the presence of 20% of H₂O, heating **1e** under an initial CO₂ pressure of 5.0 MPa for 130°C and 160°C for 15 h resulted in the formation of 1-phenyl-1,2-ethanediol, arising from the hydrolysis of **1e** in 6% and 8% yield, respectively. In both cases, no the corresponding cyclic carbonate was detected by GC and GC-MS.

In the presence of 20% DMF, 1,2-epoxy-3-phenoxypropane **1f**, which bears a phenylether group, showed high reactivity toward CO₂. In this

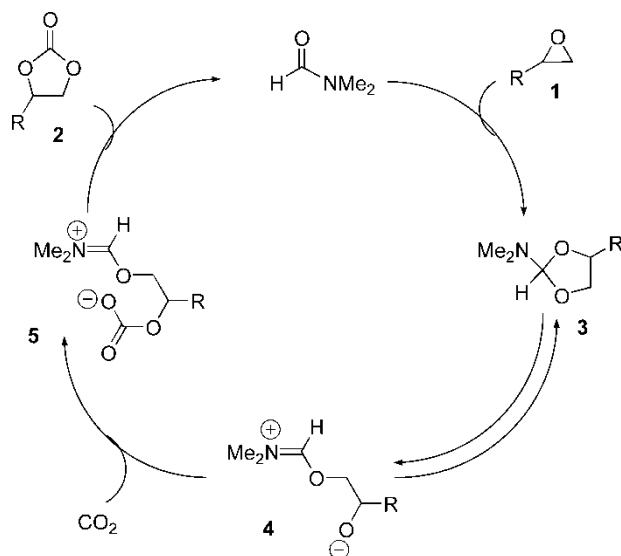
Table 2. DMF-catalyzed coupling of epoxides with CO₂^a

Entry	R	Catalyst (mol%)	Temp (°C)	Time (h)	Yield (%) ^b
1	CH ₂ Cl (1a)	DMF (20)	110	15	2a 95(91)
2		DMF (10)	110	15	84
3		DMF (10) + CH ₃ OH(10)	110	4	47
4		DMF (10) + H ₂ O (10)	110	4	87
5	CH ₃ (1b)	DMF (20)	110	15	2b ~5
6		DMF (20)	130	15	44
7		DMF (20)	160	15	71(63)
8	CH ₃ CH ₂ (1c)	DMF (20)	130	15	2c 37
9		DMF (20)	160	15	69(52)
10		DMF (10) + H ₂ O (10)	130	15	67
11	<i>n</i> -C ₄ H ₉ (1d)	DMF (20)	110	15	2d 10
12		DMF (10) + H ₂ O (10)	110	15	22
13		DMF (20)	130	15	21
14		DMF (10) + H ₂ O (10)	130	15	45
15		DMF (20)	160	15	52
16		DMF (20)	160	30	87(80)
17	Ph (1e)	DMF (20)	110	15	2e 8
18		DMF (10) + H ₂ O (10)	110	15	20
19		DMF (20)	130	15	62
20		DMF (10) + H ₂ O (10)	130	15	82(76)
21	PhOCH ₂ (1f) (MeO) ₃ Si(CH ₂) ₃ OCH ₂ (1g)	DMF (20)	110	15	2f > 99(89)
22		DMF (20)	110	15	2g 3
23		DMF (10) + H ₂ O (10)	130	15	82
24		DMF (20)	160	15	93(86)

^a5.0 mmol of **1** in a 25-mL autoclave under an initial pressure of 5.0 MPa.^bGC yield based on **1**. Number in parenthesis is the isolated yield.

case, at 110°C for 15 h, the corresponding cyclic carbonate **2f** was formed quantitatively (Table 2, entry 21). Although the reaction of 3-glycidoxypropyltrimethoxysilane **1g** with CO₂ catalyzed by DMF at 110°C for 15 h produced only a trace amount of **2g** (Table 2, entry 22), at 130°C and by addition of H₂O, or at 160°C, the reaction was greatly accelerated (Table 2, entries 23 and 24).

Scheme 1 shows a possible mechanism for the DMF-catalyzed coupling of epoxides with CO₂. It involves the formation of N,N-dimethylformamide

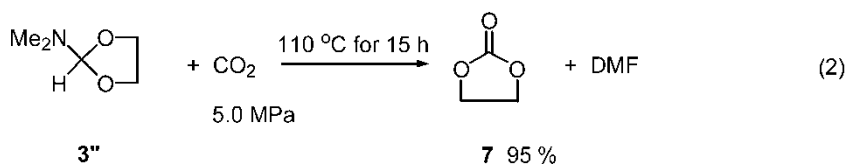
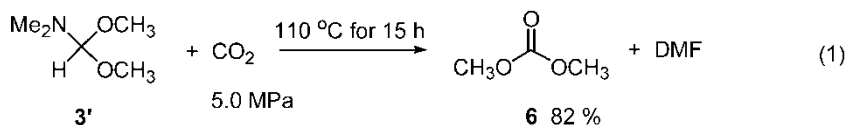


Scheme 1.

ethylene acetal derivative **3** from the reaction of DMF with epoxide. Compound **3** is converted into imine salt **4**, bearing a nucleophilic oxygen ion, which subsequently reacts with CO₂ to give intermediate **5**. Then C–O bond formation affords cyclic carbonate **2** and regenerates DMF.

The reactions of *N,N*-dimethylformamide dimethyl acetal **3'** and *N,N*-dimethylformamide ethylene acetal **3''** with CO₂ at 110 °C under solvent-free conditions were examined. Both reactions proceeded smoothly to give dimethyl carbonate **6** (eq 1) and ethylene carbonate **7** (eq 2), together with the formation of DMF. These results strongly support the proposed mechanism.

Although it is not clear that a catalytic amount of H₂O could accelerate the present DMF-catalyzed coupling of epoxides with CO₂, increasing the solubility of CO₂ might be responsible for such an effect.



3. CONCLUSION

In summary, results reported in this article have demonstrated that DMF can effectively catalyze the coupling reaction of epoxides with CO₂ to give good to high yields of cyclic carbonates. Thus, this work has developed a solvent-free, metal-free, and halide-free stable organocatalyzed activation of CO₂ catalytic system.

4. EXPERIMENTAL

A typical experiment for the DMF-catalyzed coupling of 1-chloro-2,3-epoxypropane **1a** with CO₂ to give 4-chloromethyl-[1,3]dioxolan-2-one **2a** (Table 2, entry 1) follows. 1-Chloro-2,3-epoxypropane **1a** (5.0 mmol) and DMF (1.0 mmol) were charged in a 25-mL-autoclave, and then CO₂ was introduced at an initial pressure of 5.0 MPa at room temperature. The mixture was heated at 110°C with stirring for 15 h. After the autoclave was cooled to room temperature, CO₂ was released slowly. To the reaction mixture, mesitylene (1.0 mmol, as an internal standard for GC analysis) and CH₂Cl₂ (5.0 mL, as diluent) were added with stirring, and then the resulting mixture was analyzed by GC and GC-MS. Compound **2a** was isolated in 91% yield by Kugelrohr distillation. The analysis of the reaction mixture revealed that **2a** was formed in 95% GC yield.

All the products (**2a–e**,^[3f] **2f**,^[5a] and **2g** (patent DE 4423811) were known compounds and identified by ¹H, ¹³C NMR, and GC-MS.

ACKNOWLEDGMENTS

This project (20473043) was supported by National Natural Science Foundation of China.

REFERENCES

- (a) Inoue, S. *Organic and Bio-organic Chemistry of Carbon Dioxide*; John Wiley & Sons: New York, 1982; (b) Darensbourg, D. J.; Holtcamp, M. W. Catalysis for the reactions of epoxides and carbon dioxide. *Coord. Chem. Rev.* **1996**, *153*, 155; (c) Leitner, W. The coordination chemistry of carbon dioxide and its relevance for catalysis: A critical survey. *Coord. Chem. Rev.* **1996**, *153*, 257; (d) Gibson, D. H. The organometallic chemistry of carbon dioxide. *Chem. Rev.* **1996**, *96*, 2063.
- (a) Trost, B. M.; Angle, S. F. Palladium-mediated vicinal cleavage of allyl epoxides with retention of stereochemistry: A *cis* hydroxylation equivalent. *J. Am. Chem. Soc.* **1985**, *107*, 6123; (b) Fujinami, T.; Suzuki, T.; Kamiya, M.; Fukukawa, S.; Sakai, S. Palladium catalyzed reaction of butadiene monoxide with carbon dioxide. *Chem. Lett.* **1985**, 199; (c) Pfaendler, H. R.; Mueller, F. X.

- A simple preparation of enol ether lipids. *Synthesis* **1992**, 350; (d) Minami, T.; Hanaoka, M. Synthesis of α,β -unsaturated aldehydes through palladium-catalyzed regioselective hydrogen migration. *Tetrahedron Lett.* **1994**, *35*, 9425; (e) Mizojiri, R.; Kobayashi, Y. Regioselectivity in the nickel-catalysed coupling of cyclic carbonates of but-3-ene-1,2-diols with organoborates. *J. Chem. Soc., Perkin Trans. 1.* **1995**, 2073; (f) Matsumoto, K.; Fuwa, S.; Kitajima, H. Enzyme-mediated enantioselective hydrolysis of cyclic carbonates. *Tetrahedron Lett.* **1995**, *36*, 6499; (g) Streicher, H.; Geyer, A.; Schmidt, R. R. C-disaccharides of ketoses. *Chem. Eur. J.* **1996**, *2*, 502; (h) Chang, H.-T.; Sharpless, K. B. A practical route to enantiopure 1,2-aminoalcohols. *Tetrahedron Lett.* **1996**, *37*, 3219; (i) Schultze, L. M.; Chapman, H. H.; Dubree, N. J. P.; Jones, R. J.; Kent, K. M.; Lee, T. T.; Louie, M. S.; Postich, M. J.; Prisbe, E. J.; Rohloff, J. C.; Yu, R. H. Practical synthesis of anti-HIV drug, PMPA. *Tetrahedron Lett.* **1998**, *39*, 1853; (j) Mannafov, T. G.; Berdnikov, E. A.; Samuilov, Y. D. Reactions of dichlorocarbene and arenesulfonyl chlorides with 3,4-epoxy-1-butene and vinylethylene carbonate. *Russ. J. Org. Chem.* **2001**, *37*, 339; (k) Bhanage, B. M.; Fujita, S.-I.; He, Y.; Ikushima, Y.; Shirai, M.; Torii, K.; Arai, M. Concurrent synthesis of dimethyl carbonate and ethylene glycol via transesterification of ethylene carbonate and methanol using smectite catalysts containing Mg and/or Ni. *Catal. Lett.* **2002**, *83*, 137; (l) Clements, J. H. Reactive applications of cyclic alkylene carbonates. *Ind. Eng. Chem. Res.* **2003**, *42*, 663; (m) Webster, D. C. Cyclic carbonate functional polymers and their applications. *Progr. Org. Coat.* **2003**, *47*, 77.
3. (a) Yamaguchi, K.; Ebitani, K.; Yoshida, T.; Yoshida, H.; Kaneda, K. Mg-Al mixed oxides as highly active acid-base catalysts for cycloaddition of carbon dioxide to epoxides. *J. Am. Chem. Soc.* **1999**, *121*, 4526; (b) Kim, H. S.; Kim, J. J.; Lee, B. G.; Jung, O. S.; Jang, H. G.; Kang, S. O. Isolation of a pyridinium alkoxy ion bridged dimeric zinc complex for the coupling reactions of CO₂ and epoxides. *Angew. Chem. Int. Ed.* **2000**, *39*, 4096; (c) Darensbourg, D. J.; Wildeson, J. R.; Yarbrough, J. C.; Reibenspies, J. H. *bis*-2,6-Difluorophenoxide dimeric complexes of zinc and cadmium and their phosphine adducts: Lessons learned relative to carbon dioxide/cyclohexene oxide alternating copolymerization processes catalyzed by zinc phenoxides. *J. Am. Chem. Soc.* **2000**, *122*, 12487; (d) Allen, S. D.; Moore, D. R.; Lobkovsky, E. B.; Coates, G. W. High-activity, single-site catalysts for the alternating copolymerization of CO₂ and propylene oxide. *J. Am. Chem. Soc.* **2002**, *124*, 14284; (e) Kim, H. S.; Kim, J. J.; Kwon, H. N.; Chung, M. J.; Lee, B. G.; Jang, H. G. Well-defined highly active heterogeneous catalyst system for the coupling reactions of carbon dioxide and epoxides. *J. Catal.* **2002**, *205*, 226; (f) Huang, J.-W.; Shi, M. Chemical fixation of carbon dioxide by NaI/PPh₃/PhOH. *J. Org. Chem.* **2003**, *68*, 6705; (g) Kim, H. S.; Kim, J. J.; Lee, S. D.; Lah, M. S.; Moon, D.; Jang, H. G. New mechanistic insight into the coupling reactions of CO₂ and epoxides in the presence of zinc complexes. *Chem. Eur. J.* **2003**, *9*, 678.
4. (a) Calo, V.; Nacci, A.; Monopoli, A.; Fanizzi, A.. Cyclic carbonate formation from carbon dioxide and oxiranes in tetrabutylammonium halides as solvents and catalysts. *Org. Lett.* **2002**, *4*, 2561; (b) Kawanami, H.; Sasaki, A.; Matsui, K.; Ikushima, Y. A rapid and effective synthesis of propylene carbonate using a supercritical CO₂-ionic liquid system. *Chem. Commun.* **2003**, 896; (c) Sun, J.; Fujita, S.; Arai, M. Development in the green synthesis of cyclic carbonate from carbon dioxide using ionic liquids. *J. Organomet. Chem.* **2005**, *690*, 3490.

5. (a) Kruper, W. J.; Dellar, D. V. Catalytic formation of cyclic carbonates from epoxides and CO₂ with chromium metalloporphyrinates. *J. Org. Chem.* **1995**, *60*, 725; (b) Sivakumar, T.; Seshadri, R.; Gopalakrishnan, J. Bridging the Ruddlesden–Popper and the aurivillius phases: Synthesis and structure of a novel series of layered perovskite oxides, (BiO)LnTiO₄ (Ln = La, Nd, Sm). *J. Am. Chem. Soc.* **2001**, *123*, 11496; (c) Li, F.; Xia, C.; Xu, L.; Sun, W.; Chen, G. A novel and effective Ni complex catalyst system for the coupling reactions of carbon dioxide and epoxides. *Chem. Commun.* **2003**, 2042; (d) Shen, Y.-M.; Duan, W.-L.; Shi, M. Chemical fixation of carbon dioxide catalyzed by binaphthyldiamino Zn, Cu, and Co Salen-type complexes. *J. Org. Chem.* **2003**, *68*, 1559; (e) Shen, Y.-M.; Duan, W.-L.; Shi, M. Phenol and organic bases co-catalyzed chemical fixation of carbon dioxide with terminal epoxides to form cyclic carbonates. *Adv. Synth. Catal.* **2003**, *345*, 337; (f) Yoshida, M.; Ihara, M. Novel methodologies for the synthesis of cyclic carbonates. *Chem. Eur. J.* **2004**, *10*, 2886; (g) Jiang, J.-L.; Gao, F.; Hua, R.; Qiu, X. Re(CO)₅Br-catalyzed coupling of epoxides with CO₂ affording cyclic carbonates under solvent-free conditions. *J. Org. Chem.* **2005**, *70*, 381; (h) Man, M. L.; Lam, K. C.; Sit, W. N.; Ng, S. M.; Zhou, Z.; Lin, Z.; Lau, C. P. Synthesis of heterobimetallic Ru-Mn complexes and the coupling reactions of epoxides with carbon dioxide catalyzed by these complexes. *Chem. Eur. J.* **2006**, *12*, 1004.
6. (a) Dalko, P. I.; Moisan, L. Enantioselective organocatalysis. *Angew. Chem. Int. Ed.* **2001**, *40*, 3726; (b) Paras, N. A.; MacMillan, D. W. C. New strategies in organic catalysis: The first enantioselective organocatalytic Friedel–Crafts alkylation. *J. Am. Chem. Soc.* **2001**, *123*, 4370, and references therein; (c) McDaid, P.; Chen, Y.; Deng, L. A highly enantioselective and general conjugate addition of thiols to cyclic enones with an organic catalyst. *Angew. Chem. Int. Ed.* **2002**, *41*, 338; (d) Papageorgiou, C. D.; Ley, S. V.; Gaunt, M. J. Organic-catalyst-mediated cyclopropanation reaction. *Angew. Chem. Int. Ed.* **2003**, *42*, 828; (e) Benaglia, M.; Puglisi, A.; Cozzi, F. Polymer-supported organic catalysts. *Chem. Rev.* **2003**, *103*, 3401; (f) Dalko, P. I.; Moisan, L. In the golden age of organocatalysis. *Angew. Chem. Int. Ed.* **2004**, *43*, 5138; (g) Westermann, B.; Neuhaus, C. Dihydroxyacetone in amino acid catalyzed Mannich-type reactions. *Angew. Chem. Int. Ed.* **2005**, *L44*, 4077; (h) Casas, J.; Engqvist, M.; Ibrahem, I.; Kaynak, B.; Cordova, A. Direct amino acid catalyzed asymmetric synthesis of polyketide sugars. *Angew. Chem. Int. Ed.* **2005**, *44*, 1343.
7. Kawanami, H.; Ikushima, Y. Chemical fixation of carbon dioxide to styrene carbonate under supercritical conditions with DMF in the absence of any additional catalysts. *Chem. Commun.* **2000**, 2089.