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A poly(ethylene glycol)-supported quaternary ammonium salt for highly efficient and environmentally friendly chemical fixation of CO_2 with epoxides under supercritical conditions

Ya Du,[a] Jin-Quan Wang,[a] Jian-Yu Chen,[b] Fei Cai,[b]
Jie-Sheng Tian,[a] De-Lin Kong[a] and Liang-Nian He[a,*]

[a]*Institute of Elemento-organic Chemistry, State Key Laboratory of Elemento-organic Chemistry, Nankai University, Tianjin 300071, PR China*

[b]*National Pesticide Engineering and Research Center (Tianjin), Nankai University, Tianjin 300071, PR China*

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Abstract—A PEG-supported quaternary ammonium salt is proved to be an efficient and recyclable homogeneous catalyst for solvent-free synthesis of cyclic carbonates from carbon dioxide and epoxides under supercritical conditions. Supporting Bu_4NBr on soluble polymer PEG6000 enhances the catalytic activity. The workup procedure is straightforward, and the catalyst can be reused over five times with no appreciable loss of catalytic activity and selectivity.

1. Introduction

Chemical fixation of CO_2 into useful organic compounds has attracted intense attention in view of resource utilization and pollution prevention.[1] One of the most promising methodologies in this area is the direct synthesis of carbonates via coupling of CO_2 with epoxides since one carbon atom and two oxygen atoms can be incorporated in one step without forming any co-products with high atom efficiency. Moreover, cyclic carbonates have been widely used as polar aprotic solvents, intermediates for organic and polymeric synthesis, and ingredients for pharmaceutical/fine chemicals in biomedical applications.[2] Many organic and inorganic compounds,[3,4] such as metal oxides, quaternary ammonium salts, transition metal complexes, and ionic liquid, have been developed to catalyze the cycloaddition of carbon dioxide with epoxides for the synthesis of cyclic carbonates. The current processes employing homogeneous catalysts, such as tetraethylammonium bromide and potassium iodide dissolved in a phase containing cyclic carbonate, are undesirable in the industry. To separate the catalyst from the product by a purification process, such as distillation after the reaction, is a complicated process and may result in the decomposition of the catalyst or formation of by-products. Therefore, developing new processes[5] to reserve the benefits of a homogeneous catalyst while co-opting the primary benefits of a heterogeneous catalyst is highly desirable and of particular significance. Accordingly, the real process would be that the catalyst is homogeneously dissolved during the reaction and precipitates quantitatively in the separation stage. In this context, attachment of the active catalyst to soluble polymer has received considerable attention in recent years.[5a,6]

Polyethylene glycol (PEG) and its derivatives are known to be inexpensive, thermally stable, recoverable, almost negligible vapor pressure, toxicologically innocuous and environmentally benign media[7] for chemical reactions, and biphasic catalysis in supercritical CO_2. The properties of PEG offer the possibility for immobilizing and recycling of a homogeneous catalyst.[7c,d,f]

In the framework of our continuous effort on developing new methods to recycle a homogeneous catalyst, we used one polyethylene glycol (PEG, Mw = 6000) derivative, which was covalently bound to a quaternary

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Keywords: Supported catalyst; Cyclic carbonate; Supercritical CO_2; Polyethylene glycol; Homogeneous catalyst recycling.

* Corresponding author. Tel.: +86 22 23504216; fax: +86 22 23503627; e-mail: heln@nankai.edu.cn

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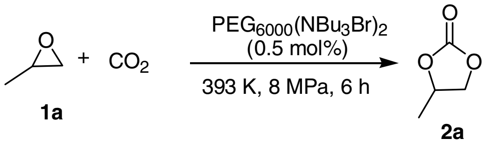


Scheme 1. Synthesis of propylene carbonate from propylene oxide and CO_2 promoted by $PEG_{6000}(NBu_3Br)_2$.

ammonium salt,[8] as a homogeneous catalyst for CO_2 fixation with propylene oxide (**1a**) without any organic additive under supercritical conditions to afford propylene carbonate (PC, **2a**) in quantitative yield and excellent selectivity (Scheme 1). Furthermore, the PEG_{6000}-supported catalyst was readily recovered by simple filtration and reused over 5 times without appreciable loss of activity.

2. Results and discussion

The carboxylation of propylene oxide **1a** with CO_2 into propylene carbonate **2a** in the presence of 0.5 mmol % of $PEG_{6000}(NBu_3Br)_2$ was conducted in a batch wise operation[8] under various conditions as shown in Table 1. In the presence of 858 mg of PEG6000 alone, the reaction did not occur at all (Table 1, entry 2). Whereas, ammonium salt (Bu_4NBr) exhibited a moderate catalytic activity (entry 1) under supercritical conditions (393 K, 8 MPa, 6 h). The $PEG_{6000}(NBu_3Br)_2$ displayed higher catalytic activity than the unsupported quaternary ammonium (Bu_4NBr) and the support (PEG6000) itself, even more effective than the simple physical mixture of Bu_4NBr and PEG6000 under the same conditions (Table 1, compare entry 5 with entries 1–3). Accordingly, the ammonium salt can be considered as the active species for the reaction and supporting Bu_4NBr on soluble polymer (PEG6000) improves the catalytic activity. The enhancement of catalyst performance by supporting Bu_4NBr on soluble PEG is presumably attributed to the benefits from changes in the physical properties[9] of the reaction mixture, such as lower melting points, lower viscosity, high diffusion rates, and increased solubility for propylene oxide and CO_2 through 'CO_2-expansion of a liquid' effect.[7a,9b] Indeed, as judged by visual inspection through a window-equipped high-pressure reactor, we found that PEG and its derivatives are expandable with CO_2 as reported in the literature.[7a] Obviously, simple addition of PEG6000 can accelerate the reaction (Table 1, entry 1 vs 3), probably due to the enhancement of the solubility of ammonium salt because of PEG's high affinity to cation.

Table 1. Synthesis of propylene carbonate from propylene oxide and CO_2 catalyzed by $PEG_{6000}(NBu_3Br)_2$[a]

Entry	Temp (K)	Pressure (MPa)	Time (h)	Propylene carbonate	
				Yield[b] (%)	Selectivity (%)
1[c]	393	8	6	70	99
2[d]	393	8	6	0	—
3[e]	393	8	6	82	98
4	373	8	6	31	100
5	393	8	6	98	99
6	453	8	6	88	88
7	423	8	3	94	99
8	423	8	6	99	99
9[f]	423	8	6	98	99
10	393	4	6	99	99
11	393	1	6	87	99
12	393	14	6	99	99
13[g]	393	8	6	98	99
14[h]	393	8	6	98	>99
15[i]	393	8	6	99	99
16[j]	393	8	6	98	99

[a] Reactions were carried out in a 25 ml autoclave under supercritical carbon dioxide conditions by using 28.6 mmol of **1a** and 0.5 mmol % of $PEG_{6000}(NBu_3Br)_2$ based on **1a** used.

[b] Determined by GC using biphenyl as an internal standard.

[c] In the presence of 0.5 mmol % of Bu_4NBr.

[d] 858 mg of PEG-6000 alone.

[e] In the presence of a physical mixture of 92 mg (1 mmol %) Bu_4NBr and PEG-6000 (858 mg).

[f] In the presence of 0.25 mmol % of $PEG_{6000}(NBu_3Br)_2$.

[g] The second run of the catalyst recovered after run in entry 5 (fresh catalyst).

[h] The third run of the catalyst.

[i] The fourth run of the catalyst.

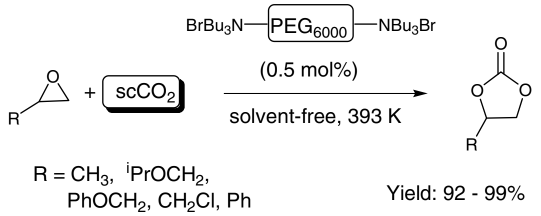
[j] The fifth run of the catalyst.

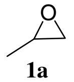
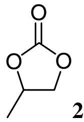
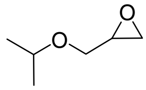
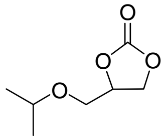
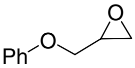
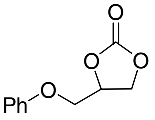
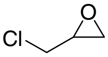
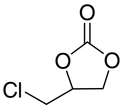
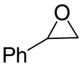
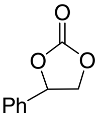
Table 1 (entries 4–6 and 8) shows the temperature dependence of the yield and selectivity of PC. The PC yield increases sharply with the temperature increasing from 373 to 393 K and maintains at this level at 423 K, whereas further increase in the temperature causes a decrease in PC selectivity, due to the formation of by-products such as acetone, 1,2-propylene diol. The reaction rate is higher at 423 K than that at lower temperature (393 K) without loss of selectivity (entries 5, 7, and 8). From the viewpoint of energy consumption and safety, 393 K is the optimal temperature. In addition, it is worth noting that the PEG-supported catalyst exhibits high activity even at low catalyst loading (Table 1, entry 9).

A significant drawback associated with using CO_2 as a reagent and a reaction medium in organic synthesis is the potential dangers operating at high pressure. As shown in Table 1 (entries 5, 10, and 12), a remarkable feature of the reaction is that the carbon dioxide pressure shows no effect on the PC yield in the range of 4–14 MPa. Indeed, the catalyst efficiently operated at 4 MPa (Table 1, entry 10). Even at the pressure below 1 MPa, the decline in activity is small (Table 1, entry 11).

A series of catalytic cycles were examined to test the catalyst recycling. In each cycle, the catalyst, PEG_{6000}-$(NBu_3Br)_2$, was solidified by cooling after the reaction and recovered by a simple filtration, and then subjected to a second run of the reaction by charging with the same substrates. The 5 runs (Table 1, entries 5, and 13–16) are almost consistent in yield and selectivity. Moreover, a high purity (>99.0%) of the product was obtained in each cycle without any additional purification process. In addition, the recyclability of the catalyst makes the reaction economically and potentially viable for commercial applications. Hence, immobilization of an ammonium salt on a soluble polymer (e.g., PEG)

Table 2. Synthesis of various carbonates catalyzed by $PEG_{6000}(NBu_3Br)_2$[a]



Entry	Epoxide **1**	Carbonate **2**	Yield[b] (%)	Selectivity (%)
1	 **1a**	 **2a**	98	99
2	 **1b**	 **2b**	98	99
3	 **1c**	 **2c**	>99	>99
4	 **1d**	 **2d**	92	96
5	 **1e**	 **2e**	94	98

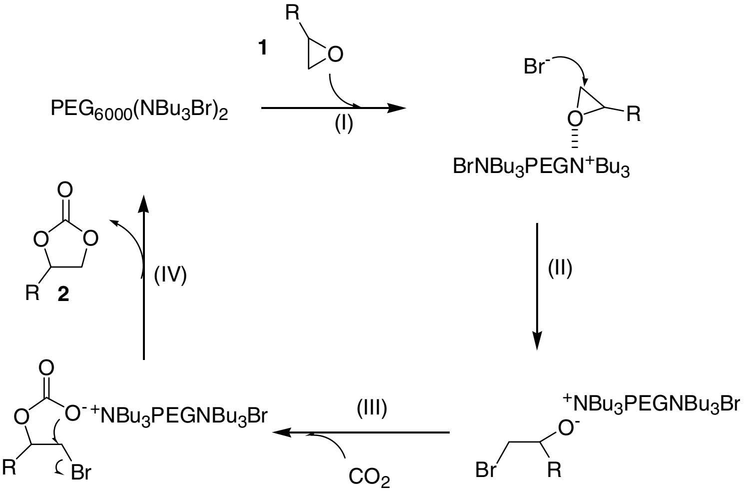
[a] Reaction conditions: epoxides (28.6 mmol), catalyst: $PEG_{6000}(NBu_3Br)_2$ (0.5 mmol %), 393 K, 8 MPa, 6 h.

[b] GC yield based on epoxides used.

provides an alternative pathway for realizing homogeneous catalyst recycling. As encouraged by the results from batch-wise recycling, cyclic carbonate synthesis will be carried out as a continuous-flow process, which could combine reaction and separation in only one integrated process for homogeneous catalysis.

In order to survey the applicability of various epoxides to this process, we examined the cycloaddition reactions of other terminal epoxides with CO_2 catalyzed by $PEG_{6000}(NBu_3Br)_2$. The results are summarized in Table 2. The PEG-supported catalyst, $PEG_{6000}(NBu_3Br)_2$, was found to be applicable to a variety of terminal epoxides, providing the corresponding cyclic carbonates **2** in 92–99% yields and with excellent selectivities. Propylene oxide (**1a**), isopropyl glycidyl ether (**1b**), and glycidyl phenyl ether (**1c**) are good substrates to give cyclic carbonates in nearly 100% yield. However, with epichlorohydrin (**1d**) and styrene oxide (**1e**), the carbonates were obtained in relatively low yields.

A possible mechanism for the $PEG_{6000}(NBu_3Br)_2$-catalyzed cycloaddition of CO_2 with epoxide is proposed as shown in Scheme 2. As mentioned above, the ammonium salt part is suggested to be the active species for the reaction. This proposal is analogous to that of the quaternary ammonium salt-catalyzed version of the same reaction.[3a,e] The proposed mechanism involves the activation of propylene oxide by the ammonium cation (step I), the ring opening of the epoxide via nucleophilic attack of bromine at the least-hindered carbon (step II), and the insertion of CO_2 into the N–O bond (step III). Subsequent cyclization via an intramolecular nucleophilic attack (step IV) leads to the propylene carbonate and the regeneration of the catalyst, $PEG_{6000}(NBu_3Br)_2$. The independence of the PC yield on the CO_2 pressure suggests that the insertion of CO_2 into the N–O bond is not the rate-determining step of the catalytic process. The reaction of (*R*)-styrene oxide (**R-1e**) with CO_2 in the presence of 0.5 mmol % of $PEG_{6000}(NBu_3Br)_2$ affords (*R*)-1-phenyl-1,2-ethanediol carbonate (**R-2e**)[10,12] in 99% ee with retention of stereochemistry,[13] supporting



Scheme 2. Proposed mechanism for $PEG_{6000}(NBu_3Br)_2$-catalyzed cycloaddition of CO_2 with epoxides.

this mechanism which does not involve any change of stereochemistry at the chiral carbon center, that is not attacked.

3. Conclusion

In conclusion, the PEG-supported quaternary ammonium salt, $PEG_{6000}(NBu_3Br)_2$, efficiently catalyzes the chemical fixation of carbon dioxide with epoxides under solvent-free conditions. Supporting Bu_4NBr on soluble polymer (PEG6000) enhances the catalytic activity. The workup procedure is simple and the catalyst can be recovered by filtration and reused over 5 times without loss of catalytic activity and selectivity. Remarkably, a high purity (>99.0%) of the product was obtained in each cycle without any additional purification process. This environmentally friendly protocol presented here offers simplicity of operation and enables recyclability of homogeneous catalyst. The effects of the counter anion, the chain length of PEG, and the bulk of alkyl group on the catalytic activity for cyclic carbonate synthesis and possible applicability of the PEG-supported catalysts to other reactions are currently under investigation in our laboratory.

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Supplementary data

Experimental details and the charts of ^1H NMR and ^{13}C NMR for cyclic carbonates (**2a**–**e**, **R-2e**) and $PEG_{6000}(NBu_3Br)_2$. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2005.12.077.

References and notes

1. (a) Anastas, P. T. *Green Chem.* **2003**, *5*, G29; (b) Anastas, P. T.; Lankey, R. L. *Green Chem.* **2000**, *2*, 289.
2. (a) Biggadike, K.; Angell, R. M.; Burgess, C. M.; Farrel, R. M.; Hancock, A. P.; Harker, A. J.; Irving, W. R.; Ioannou, C.; Procopiou, P. A.; Shaw, R. E.; Solanke, Y. E.; Singh, O. M. P.; Snowden, M. A.; Stubbs, R. J.; Walton, S.; Weston, H. E. *J. Med. Chem.* **2000**, *43*, 19; (b) Shaikh, A.-A. G.; Sivaram, S. *Chem. Rev.* **1996**, *96*, 951.
3. (a) Darensbourg, D. J.; Holtcamp, M. W. *Coord. Chem. Rev.* **1996**, *153*, 155; (b) Paddock, R. L.; Nguyen, S.-B. T. *J. Am. Chem. Soc.* **2001**, *123*, 11498; (c) Jiang, J. L.; Gao, F. X.; Hua, R. M.; Qiu, X. Q. *J. Org. Chem.* **2005**, *70*, 381; (d) Kawanami, H.; Sasaki, A.; Matsui, K.; Ikushima, Y. *Chem. Commun.* **2003**, 896; (e) Kihara, N.; Hara, N.; Endo, T. *J. Org. Chem.* **1993**, *58*, 6198; (f) Sun, J.; Fujita, S.-I.; Arai, M. *J. Organomet. Chem.* **2005**, *690*, 3490; (g) Du, Y.; Kong, D.-L.; Wang, H.-Y.; Cai, F.; Tian, J.-S.; Wang, J.-Q.; He, L.-N. *J. Mol. Catal. A: Chem.* **2005**, *241*, 233; (h) Huang, J. W.; Shi, M. *J. Org. Chem.* **2003**, *68*, 6705; (i) Du, Y.; Cai, F.; Kong, D.-L.; He, L.-N. *Green Chem.* **2005**, *7*, 518; (j) Sit, W. N.; Ng, S. M.; Kwong, K. Y.; Lau, C. P. *J. Org. Chem.* **2005**, *70*, 8583; (k) Yasuda, H.; He, L.-N.; Sakakura, T.; Hu, C.-W. *J. Catal.* **2005**, *233*, 119.
4. (a) Yamaguchi, K.; Ebitani, K.; Yoshida, T.; Yoshida, H.; Kaneda, K. *J. Am. Chem. Soc.* **1999**, *121*, 4526; (b) Nishikubo, T.; Kameyama, A.; Yamashita, J.; Tomoi, M.; Fukuda, W. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 939; (c) Tu, M.; Davis, R. J. *J. Catal.* **2001**, *199*, 85; (d) Yasuda, H.; He, L.-N.; Sakakura, T. *J. Catal.* **2002**, *209*, 547; (e) Yasuda, H.; He, L.-N.; Sakakura, T. *Stud. Surf. Sci. Catal.* **2003**, *145*, 259; (f) Lu, X.-B.; Zhang, Y.-J.; Jin, K.; Luo, L.-M.; Wang, H. *J. Catal.* **2004**, *227*, 537; (g) Aresta, M.; Dibenedetto, A.; Gianfrate, L.; Pastore, C. *J. Mol. Catal. A: Chem.* **2003**, *204–205*, 245; (h) Aresta, M.; Dibenedetto, A.; Gianfrate, L.; Pastore, C. *Appl. Catal. A* **2003**, *255*, 5; (i) Aresta, M.; Dibenedetto, A. *J. Mol. Catal.* **2002**, *182–183*, 399; (j) Sun, J.; Fujita, S.-I.; Zhao, F. Y.; Arai, M. *Green Chem.* **2004**, *6*, 613; (k) Shi, F.; Zhang, Q.; He, Y.; Deng, Y. *J. Am. Chem. Soc.* **2005**, *127*, 4182; (l) Srivastara, R.; Srinivas, D.; Ratnasamy, P. *J. Catal.* **2005**, *233*, 1, and references cited therein; (m) Ramin, M.; Grunwaldt, J.-D.; Baiker, A. *J. Catal.* **2005**, *234*, 256.
5. (a) Bergbreiter, D. E. *Chem. Rev.* **2002**, *102*, 3345; (b) Cole-Hamilton, D. J. *Science* **2003**, *299*, 1702; (c) Clapham, B.; Reger, T. S.; Janda, K. D. *Tetrahedron* **2001**, *57*, 4637; (d) Fan, Q.-H.; Li, Y.-M.; Chan, A. S. C. *Chem. Rev.* **2002**, *102*, 3385; (e) Kragl, U.; Dwars, T. *Trends Biotechnol.* **2001**, *19*, 442; (f) Mastrorilli, P.; Nobile, C. F. *Coord. Chem. Rev.* **2004**, *248*, 377; (g) Osburn, P. L.; Bergbreiter, D. E. *Prog. Polym. Sci.* **2001**, *26*, 2015; (h) Beckmann, E. J. *J. Supercrit. Fluids* **2004**, *28*, 121.
6. (a) Dickerson, T. J.; Reed, N. N.; Janda, K. D. *Chem. Rev.* **2002**, *102*, 3325; (b) Benaglia, M.; Puglisi, A.; Cozzi, F. *Chem. Rev.* **2003**, *103*, 3401; (c) Dioumaev, V. K.; Bullock, R. M. *Nature* **2000**, *424*, 530; (d) Bradley, D. *Science* **2003**, *300*, 2022; (e) Anyanwu, U. K.; Venkataraman, D. *Green Chem.* **2005**, *7*, 424; (f) Kinoshita, S.; Shibahara, F.; Nozaki, K. *Green Chem.* **2005**, *7*, 256.
7. (a) Heldebrant, D. J.; Jessop, P. G. *J. Am. Chem. Soc.* **2003**, *125*, 5600; (b) Annunziata, R.; Benaglia, M.; Cinquini, M.; Cozzi, F.; Tocco, G. *Org. Lett.* **2000**, *2*, 1737; (c) Reetz, M. T.; Wiesenhöfer, W. *Chem. Commun.* **2004**, 2750; (d) Chen, J.; Spear, S. K.; Huddleston, J. G.; Rogers, R. D. *Green Chem.* **2005**, *7*, 64, and references cited therein; (e) Chandrasekhar, S.; Narsihmulu, Ch.; Sultana, S. S.; Reddy, N. R. *Chem. Commun.* **2003**, 1716; (f) Solinas, M.; Jiang, J.; Stelzer, O.; Leitner, W. *Angew. Chem., Int. Ed.* **2005**, *44*, 2291; (g) Hou, Z.; Theyssen, N.; Brinkmann, A.; Leitner, W. *Angew. Chem., Int. Ed.* **2005**, *44*, 1346; (h) Černovská, K.; Kemter, M.; Gallmeier, H.-C.; Rzepecki, P.; Schrader, T.; König, B. *Org. Biomol. Chem.* **2004**, *2*, 1603; (i) Attanasi, O. A.; Crescentini, L. D.; Favi, G.; Filippone, P.; Lillini, S.; Mantellini, F.; Santeusanio, S. *Org. Lett.* **2005**, *7*, 2469.
8. The $PEG_{6000}(NBu_3Br)_2$ was synthesized according to the reported procedures: (a) Bhattacharya, S.; Goyal, P. S.; Aswal, V. K.; De, S. *J. Phys. Chem. B* **1998**, *102*, 6152; (b) Grinberg, S.; Shaubi, E. *Tetrahedron* **1991**, 2895; (c) Wu, G.; Wu, Y.; Keana, J. F. W. *J. Org. Chem.* **1987**, *52*, 2571, and Ref. 7b. The experimental procedures and NMR data are given in the Supplementary data.
9. (a) Guadagno, T.; Kazarian, S. G. *J. Phys. Chem. B* **2004**, *108*, 13995; (b) Jessop, P.; Wyne, D. C.; DeHaai, S.; Nakawatase, D. *Chem. Commun.* **2000**, 693, and refer-

ences cited therein; (c) Gourgouillon, D.; Avelino, H. M. N. T.; Fareleira, J. M. N. A.; da Ponte, M. N. *J. Supercrit. Fluids* **1998**, *13*, 177; (d) Kho, Y. W.; Conrad, D. C.; Shick, R. A.; Knutson, B. L. *Ind. Eng. Chem. Res.* **2003**, *42*, 6511; (e) Tomasko, D. L.; Li, H.; Liu, D.; Han, X.; Wingert, M. J.; Lee, L. J.; Koelling, K. W. *Ind. Eng. Chem. Res.* **2003**, *42*, 6431.

10. The enantiomeric excess of (*R*)-1-phenyl-1,2-ethanediol carbonate (**R-2e**) was determined by HPLC using Hewlett Packed Model HP 1100 series with a Chiralcel OD-H (eluent, hexane/isopropanol: 80:20) at rt. The retention times of **R-2e** and **S-2e** are 20.84 min and 23.09 min, respectively.
11. Cross, D. J.; Kenny, J. A.; Houson, I.; Campbell, L.; Walsgrovec, T.; Wills, M. *Tetrahedron: Asymmetry* **2001**, *12*, 1801.
12. The absolute configuration is *R*, as compared the optical rotation value with the literature datum.[11] The optical rotation values were recorded with Perkin–Elmer Instruments (model 341) $[\alpha]_D^{20}$ −51.8 (c 1.0, $CHCl_3$) {lit.[11] $[\alpha]_D^{22}$ +51.2 (c 1.0, $CHCl_3$) for (*S*)-1-phenyl-1,2-ethanediol carbonate}.
13. For the reaction of enantiomerically pure epoxides with CO_2 yielding enantiomerically pure cyclic carbonates with complete retention of the original stereochemistry. See: (a) Lu, X.-B.; Zhang, Y.-J.; Jun, K.; Luo, L.-M.; Wang, H. *J. Catal.* **2004**, *227*, 537; (b) Paddock, R. L.; Hiyama, Y.; McKay, J. M.; Nguyen, S. B. T. *Tetrahedron Lett.* **2004**, *45*, 2023; (c) Paddock, R. L.; Nguyen, S. B. T. *Chem. Commun.* **2004**, 1622; (d) Yano, T.; Matsui, H.; Koike, T.; Ishiguro, H.; Fujihara, H.; Yoshihara, M.; Maeshima, T. *Chem. Commun.* **1997**, 1129.