JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
COMMUNICATION
pubs.acs.org/JACS

Tetravalent Metal Complexes as a New Family of Catalysts for Copolymerization of Epoxides with Carbon Dioxide

Koji Nakano, Kazuki Kobayashi, and Kyoko Nozaki*

Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

S *Supporting Information*

ABSTRACT: New tetravalent metal complexes with a trianionic [ONNO]-tetradentate ligand and an ancillary chloride ligand were synthesized as catalysts for the copolymerization of epoxides with carbon dioxide (CO_2). All of the titanium, zirconium, germanium, and tin complexes were found to copolymerize epoxides with CO_2. In particular, the copolymerization of propylene oxide with CO_2 gave the almost-completely alternating copolymers by using titanium or germanium complexes. These results are the first example of the copolymerization using tetravalent metal complexes as a main component of catalysts.

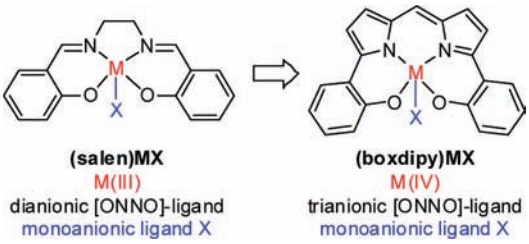
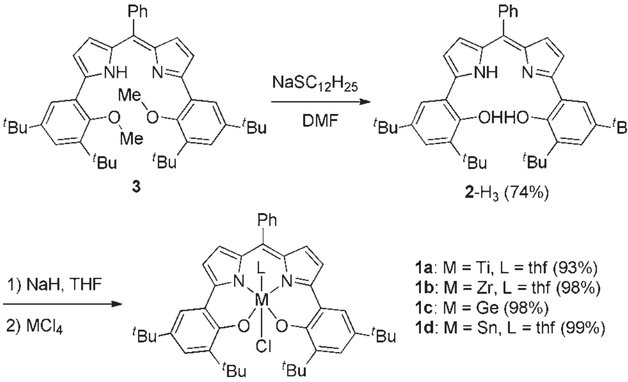


Figure 1. Design strategy for the tetravalent metal complexes.

Scheme 1. Synthesis of (BOXDIPY)MCl Complexes (M = Ti, Zr, Ge, and Sn)



The alternating copolymerization of epoxides with carbon dioxide (CO_2) is one of the most promising processes for CO_2 utilization.[1] Since the first report by Inoue and co-workers with Et_2Zn/H_2O as a catalyst in the late 1960s,[2] a variety of combinations of metal centers and ligands have been investigated to improve the catalyst performance. The previously reported active catalysts are based on either divalent (Zn[3]) or trivalent (Al,[4] Sc,[5] Cr,[6] Mn,[7] Fe,[8] Co,[9] Y,[5,10] Dy,[5,10] Lu[5,10]) metal complexes: the representatives are $Zn(OAr)_2$,[3a,c] (BDI)ZnX,[3b,d,e] and (salen)MX complexes [Ar = aryl; basic skeleton of BDI-H = 2-amino-4-iminopent-2-ene; basic skeleton of salen-H_2 = *N*,*N*′-disalicylidene-1,2-ethylenediamine; X = monoanionic ancillary ligand; M = Al(III),[4d] Co(III),[9a−h,j,l] and Cr(III)[6b−e]]. There has been no literature ever reported on the use of a tetravalent metal complex as an active catalyst component.[11] Here we report the first achievement in the copolymerization by using tetravalent metal complexes.

Our design strategy for the use of tetravalent metal complexes is drawn in Figure 1. The (salen)MX complexes, which have been known as a catalyst with the highest performance, are composed of a trivalent metal ion (M), a dianionic [ONNO]-tetradentate salen ligand, and a monoanionic ancillary ligand (X). We conceived of an idea that the combination of a tetravalent metal ion, a *trianionic* [ONNO]-tetradentate ligand, and a monoanionic ancillary ligand would accurately mimic (salen)MX complexes. Based on this strategy, we designed the tetravalent metal complexes with a 1,9-bis(2-oxidophenyl)dipyrrinate (BOXDIPY) ligand (Figure 1). BOXDIPY ligands are promising trianionic analogues of salen ligands because of their rigid structure and [ONNO]-tetradentate coordination mode. Recently, boron(III),[12] aluminum(III),[12b] manganese(III, V),[13] and silicon(IV)[14] complexes with a BOXDIPY ligand were reported. Although the coordination geometry of metal-BOXDIPY complexes depends on the nature of the central metal ions and ancillary ligands, the BOXDIPY ligand was found to occupy four equatorial sites in the octahedral manganese(III) complex,[13] similar to the typical salen ligands.

The synthesis of metal(IV) complexes **1** with a BOXDIPY ligand **2** was described in Scheme 1. Methyl-protected ligand precursor **3** was synthesized by reference to the reported procedures.[12b,15] Demethylation was carried out by using sodium thiolate, giving the metal-free ligand precursor, 1,9-bis(3,5-di-*tert*-butyl-2-hydroxyphenyl)-5-phenyldipyrrin (**2**-H_3). Deprotonation of **2**-H_3 with NaH and the subsequent reaction with the corresponding metal chlorides afforded titanium, zirconium, germanium, and tin complexes in high yields (>93%). These

Received: April 12, 2011
Published: June 21, 2011

dx.doi.org/10.1021/ja203382q | J. Am. Chem. Soc. 2011, 133, 10720–10723

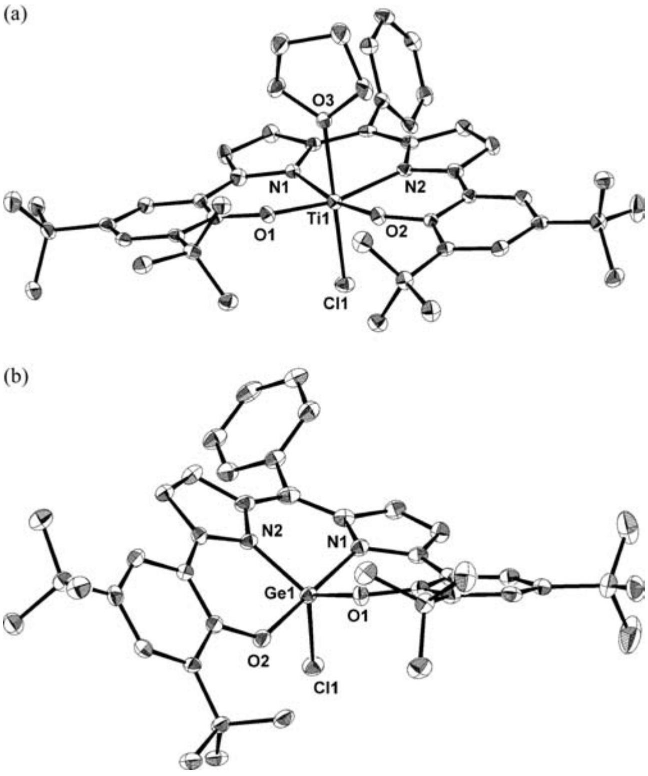


Figure 2. ORTEP drawings of (a) **1a** and (b) **1c** (50% thermal ellipsoids; solvent (CH_2Cl_2 for **1a**) and all hydrogen atoms are omitted for clarity).

are the first examples of group IV metal, germanium, and tin complexes with a BOXDIPY ligand. ^1H and ^{13}C NMR spectra showed that each complex forms a C_S-symmetry structure in solution, indicating the planar tetradentate coordination of the trianionic ligand. In addition, one tetrahydrofuran (THF) molecule was indicated to coordinate to the metal center in titanium (**1a**), zirconium (**1b**), and tin (**1d**) complexes by ^1H NMR spectra (vide infra), while no signal assigned to THF protons was detected for the germanium (**1c**) complex.

The solid-state structure of each complex was revealed by single-crystal X-ray structural analysis. As shown in Figure 2a, titanium complex **1a** forms an octahedral geometry where four equatorial coordination sites are occupied by the BOXDIPY ligand **2**. One of the two apical coordination sites is occupied by a monoanionic chloride ligand, and the other site is ligated by a neutral THF molecule as indicated by NMR spectroscopy. The equatorial plane, which is defined by O1, N1, N2, O2, was nearly planar with an average atomic displacement of 0.0233(13) Å. The titanium center deviated by 0.1502(14) Å toward the apical chloride ligand. Zirconium and tin complexes **1b** and **1d** also form a similar structure (see Supporting Information). In contrast, germanium complex **1c** forms a distorted trigonal-bipyramidal geometry (Figure 2b). The atoms N1 and O2 are located in the two apical coordination sites with a N1−Ge1−O2 angle of 176.98(14)°. The equatorial plane is shared by N2, O1, and Cl1 with N2−Ge1−O1, O1−Ge1−Cl1, and N2−Ge1−Cl1 angles of 128.21(14)°, 116.56(10)°, and 115.22(11)°, respectively. The germanium center lies almost in the equatorial plane. Such a C_1-symmetry structure of complex **1c** in the solid state is contradictory to a C_S-symmetry structure expected by NMR spectroscopy, indicating the rapid interconversion between isomers in a solution state,[14] or the formation of a C_S-symmetrical octahedral geometry via THF-d_8 coordination.

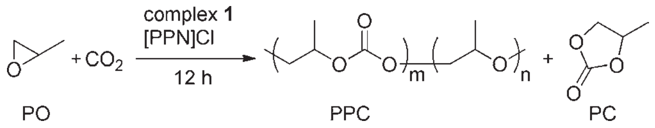
The copolymerization of propylene oxide (PO) with CO_2 ($[PO]/\mathbf{1} = 2000$; $CO_2 = 2.0$ MPa) was carried out at 60 °C for 12 h by using the complex **1a** as a catalyst. When the complex was used without any additive, the copolymerization did not proceed to give only propylene carbonate (PC). In contrast, the addition of ammonium salts $[Ph_3P{=}N{=}PPh_3]Cl$ ([PPN]Cl) resulted in the successful production of poly(propylene carbonate) (PPC) with a TOF of 29 and moderate PPC selectivity (PPC/PC = 71/29) (Table 1, entry 1). The obtained PPC had a highly alternating structure (carbonate linkage: 98%) based on its ^1H NMR spectrum. Higher polymerization temperatures of 80 and 100 °C gave a higher conversion of PO, while the selectivity for PPC significantly decreased to yield a larger amount of PC (entries 2 and 3). The PPC selectivity was also susceptible to the molar ratio of **1a**/[PPN]Cl (entries 4 and 5): a significant decrease in PPC selectivity was observed with a larger excess amount of [PPN]Cl (entry 5). CO_2 pressure did not show a significant effect on the polymerization behavior (entries 6 and 7). The nucleophilic anion of the ammonium salt was reported to affect the catalytic activity and the PPC/PC selectivity when using metal−salen complexes.[6e,9b,9c,9f] In the present system, the copolymerization with $[PPN]N_3$ or $[PPN][OCOC_6F_5]$ resulted in lower PPC/PC selectivity (entries 8 and 9).

The germanium complex was also found to copolymerize PO with CO_2 under the typical conditions ($[PO]/[\mathbf{1}] = 2000$; $CO_2 = 2.0$ MPa, 60 °C, 12 h) to give PPC with high carbonate-linkage content (entry 11), while the zirconium and tin complexes produced only PC (entry 10) and the copolymer with high ether-linkage content (entry 20), respectively. The copolymerization with germanium complex **1c** under higher temperature (entries 12, 13) or with an excess amount of [PPN]Cl (entry 15) led to a decrease in PPC selectivity, similar to that with titanium complex **1a**. It is noteworthy that the use of a lower amount of [PPN]Cl (0.75 equiv to **1c**) resulted in a higher PPC selectivity of >90% (entry 14). Furthermore, the higher catalytic activity and carbonate-linkage content were achieved under high CO_2 pressure (entry 17). Accordingly, the copolymerization with germanium complex **1c** was found to give almost-completely alternating copolymer selectively. The use of other ammonium salts resulted in a slightly lower PPC selectivity (entries 18 and 19).

The copolymerization of cyclohexene oxide (CHO) with CO_2 was also investigated by using the tetravalent metal complexes **1**. The results are summarized in Table 2. The titanium and germanium complexes gave almost-completely alternating poly(cyclohexene carbonate) (PCHC) selectively without a concomitant amount of cyclohexene carbonate (CHC) (entries 1 and 3). Zirconium complex **1b**, which was not applicable to PO/CO_2 copolymerization, was found to produce PCHC, while the activity was quite low and ether-linkage content was high (entry 2). The copolymerization with tin complex **1d** gave the copolymer with high ether-linkage content (entry 4), similar to the case in PO/CO_2 copolymerization.

In summary, we have developed a variety of tetravalent metal complexes with a trianionic tetradentate BOXDIPY ligand as a new family of epoxide/CO_2 copolymerization catalysts. Especially, the titanium and germanium complexes were found to give the alternating copolymers. Although the catalytic activity is still lower than those of the previously reported catalysts such as metal−salen complexes, the results described here are the first example of the copolymerization using tetravalent metal

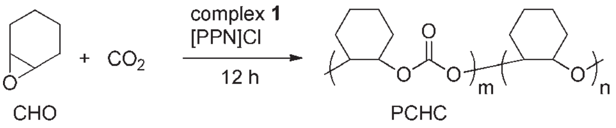
Table 1. Copolymerization of Propylene Oxide with CO_2 by Using Tetravalent Complexes 1[a]



entry	1	[PPN]Cl (equiv to 1)	CO_2 [MPa]	temp [°C]	yield of PPC + PC (%)[b]	PPC/PC[b]	TOF for PPC[c]	carbonate linkage [%][b]	M_n [g·mol^{-1}][d]	M_w/M_n[d]
1	**1a**	1.0	2.0	60	25	71/29	29	98	8100	1.19
2		1.0	2.0	80	55	33/67	30	96	9200	1.35
3		1.0	2.0	100	98	2/98	3	77	–	–
4		0.5	2.0	60	21	82/18	29	96	14 000	1.28
5		1.5	2.0	60	83	1/99	1	67	–	–
6		1.0	1.0	60	27	73/27	33	98	14 000	1.36
7		1.0	4.0	60	24	67/33	27	98	9100	1.13
8		1.0[e]	1.0	60	25	51/49	22	97	6300	1.14
9		1.0[f]	1.0	60	33	37/63	20	99	7100	1.15
10	**1b**	1.0	2.0	60	21	0/100	0	–	–	–
11	**1c**	1.0	2.0	60	15	71/29	10	95	7200	1.14
12		1.0	2.0	80	26	40/60	17	94	6500	1.16
13		1.0	2.0	100	82	0/100	–	–	–	–
14		0.75	2.0	60	13	93/7	19	91	6600	1.15
15		2.0	2.0	60	69	0/100	–	–	–	–
16		0.75	1.0	60	6	80/20	8	88	5300	1.21
17		0.75	4.0	60	17	93/7	26	97	18 000	1.22
18		0.75[e]	4.0	60	14	89/11	21	98	9400	1.54
19		0.75[f]	4.0	60	19	83/17	26	98	13 000	1.32
20	**1d**	1.0	2.0	60	22	32/68	12	87	4300	1.22

[a] PO (1.0 mL, 14.3 mmol), complex **1** (7.1–7.2 × 10^{-3} mmol) in a 50-mL autoclave for 12 h. [b] Determined on the basis of ^{1}H NMR spectroscopy of the crude product by using phenanthrene as an internal standard. [c] (mol of repeating unit)·(mol of **1**)$^{-1}$·h^{-1}. [d] Determined by size-exclusion chromatography analysis using a polystyrene standard. [e] $[PPN]N_3$ was used instead of [PPN]Cl. [f] $[PPN][OCOC_6F_5]$ was used instead of [PPN]Cl.

Table 2. Copolymerization of Cyclohexene Oxide with CO_2 by Using Tetravalent Complexes 1[a]



entry	1	yield (%)[b]	TOF for PCHC[c]	carbonate linkage [%][b]	M_n [g·mol^{-1}][d]	M_w/M_n[d]
1	**1a**	45	76	99	13 000	1.27
2	**1b**	5	8	54	1100	1.25
3	**1c**	36	60	99	14 000	1.12
4	**1d**	10	17	75	2500	1.73

[a] CHO (2.0 mL, 20 mmol), complex **1** (10 × 10^{-3} mmol), [PPN]Cl (1.0 equiv to **1**) in a 50-mL autoclave at 60 °C for 12 h. [b] Determined on the basis of ^{1}H NMR spectroscopy of the crude product by using phenanthrene as an internal standard. [c] (mol of repeating unit)·(mol of **1**)$^{-1}$·h^{-1}. [d] Determined by size-exclusion chromatography analysis using a polystyrene standard.

complexes as a main component of catalysts. Considering the toxicity of most of the active metals such as cobalt and chromium,[16] less toxic metals such as titanium and germanium here reported should provide attractive alternatives to metal-salen complexes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental procedures, characterization data for new compounds, crystallographic information files (CIF) for complexes **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

nozaki@chembio.t.u-tokyo.ac.jp

■ ACKNOWLEDGMENT

This work was supported by a Funding Program for World-Leading Innovative R&D on Science and Technology from the Japan Society for the Promotion of Science (JSPS) and by a Grant for Practical Application of University R&D Results under the Matching Fund Method from the New Energy and Industrial Technology Development Organization (NEDO).

REFERENCES

(1) (a) Coates, G. W.; Moore, D. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6618. (b) Sugimoto, H.; Inoue, S. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5561. (c) Darensbourg, D. J. *Chem. Rev.* **2007**, *107*, 2388. (d) Luinstra, G. A. *Polym. Rev.* **2008**, *48*, 192.

(2) Inoue, S.; Koinuma, H.; Tsuruta, T. *J. Polym. Sci., Part B: Polym. Lett.* **1969**, *7*, 287.

(3) (a) Darensbourg, D. J.; Holtcamp, M. W. *Macromolecules* **1995**, *28*, 7577. (b) Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **1998**, *120*, 11018. (c) Darensbourg, D. J.; Holtcamp, M. W.; Struck, G. E.; Zimmer, M. S.; Niezgoda, S. A.; Rainey, P.; Robertson, J. B.; Draper, J. D.; Reibenspies, J. H. *J. Am. Chem. Soc.* **1999**, *121*, 107. (d) Cheng, M.; Moore, D. R.; Reczek, J. J.; Chamberlain, B. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 8738. (e) Moore, D. R.; Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *Angew. Chem., Int. Ed.* **2002**, *41*, 2599.

(4) (a) Aida, T.; Ishikawa, M.; Inoue, S. *Macromolecules* **1986**, *19*, 8. (b) Sarbu, T.; Bekman, E. J. *Macromolecules* **1999**, *32*, 6904. (c) Sarbu, T.; Styranec, T.; Beckman, E. J. *Nature* **2000**, *405*, 165. (d) Sugimoto, H.; Ohtsuka, H.; Inoue, S. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 4172.

(5) Cui, D. M.; Nishiura, M.; Hou, Z. M. *Macromolecules* **2005**, *38*, 4089.

(6) (a) Mang, S.; Cooper, A. I.; Colclough, M. E.; Chauhan, N.; Holmes, A. B. *Macromolecules* **2000**, *33*, 303. (b) Darensbourg, D. J.; Yarbrough, J. C. *J. Am. Chem. Soc.* **2002**, *124*, 6335. (c) Eberhardt, R.; Allmendinger, M.; Rieger, B. *Macromol. Rapid Commun.* **2003**, *24*, 194. (d) Darensbourg, D. J.; Mackiewicz, R. M.; Rodgers, J. L.; Fang, C. C.; Billodeaux, D. R.; Reibenspies, J. H. *Inorg. Chem.* **2004**, *43*, 6024. (e) Darensbourg, D. J.; Mackiewicz, R. M. *J. Am. Chem. Soc.* **2005**, *127*, 14026. (f) Darensbourg, D. J.; Fitch, S. B. *Inorg. Chem.* **2007**, *46*, 5474. (g) Li, B.; Wu, G. P.; Ren, W. M.; Wang, Y. M.; Rao, D. Y.; Lu, X. B. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 6102. (h) Nakano, K.; Nakamura, M.; Nozaki, K. *Macromolecules* **2009**, *42*, 6972.

(7) Sugimoto, H.; Ohshima, H.; Inoue, S. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3549.

(8) Buchard, A.; Kember, M. R.; Sandeman, K. G.; Williams, C. K. *Chem. Commun.* **2011**, *47*, 212.

(9) (a) Qin, Z. Q.; Thomas, C. M.; Lee, S.; Coates, G. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 5484. (b) Lu, X. B.; Wang, Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 3574. (c) Cohen, C. T.; Chu, T.; Coates, G. W. *J. Am. Chem. Soc.* **2005**, *127*, 10869. (d) Paddock, R. L.; Nguyen, S. T. *Macromolecules* **2005**, *38*, 6251. (e) Nakano, K.; Kamada, T.; Nozaki, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 7274. (f) Lu, X. B.; Shi, L.; Wang, Y. M.; Zhang, R.; Zhang, Y. J.; Peng, X. J.; Zhang, Z. C.; Li, B. *J. Am. Chem. Soc.* **2006**, *128*, 1664. (g) Noh, E. K.; Na, S. J.; Sujith, S.; Kim, S. W.; Lee, B. Y. *J. Am. Chem. Soc.* **2007**, *129*, 8082. (h) Sujith, S.; Min, J. K.; Seong, J. E.; Na, S. J.; Lee, B. Y. *Angew. Chem., Int. Ed.* **2008**, *47*, 7306. (i) Sugimoto, H.; Kuroda, K. *Macromolecules* **2008**, *41*, 312. (j) Ren, W. M.; Liu, Z. W.; Wen, Y. Q.; Zhang, R.; Lu, X. B. *J. Am. Chem. Soc.* **2009**, *131*, 11509. (k) Okada, A.; Kikuchi, S.; Nakano, K.; Nishioka, K.; Nozaki, K.; Yamada, T. *Chem. Lett.* **2010**, *39*, 1066. (l) Nakano, K.; Hashimoto, S.; Nozaki, K. *Chem. Sci.* **2010**, *1*, 369.

(10) Cui, D. M.; Nishiura, M.; Tardif, O.; Hou, Z. M. *Organometallics* **2008**, *27*, 2428.

(11) Kobayashi et al. demonstrated that $Sc(O^{i}Pr)_3$ copolymerized epoxides with CO_2 and that the addition of $Ti(O^{i}Pr)_4$ improved its catalytic activity. However, $Ti(O^{i}Pr)_4$ itself was found to show no activity in the copolymerization. See: Kobayashi, S.; Akiyama, R.; Suzuki, K.; Fujimoto, K. (The University of Tokyo, Japan; Nippon Steel Corporation; Nippon Steel Engineering Co., Ltd.; Nippon Steel Chemical Co., Ltd.) Jpn. Kokai Tokkyo Koho JP 2009242794, 2009.

(12) (a) Kim, H.; Burghart, A.; Welch, M. B.; Reibenspies, J.; Burgess, K. *Chem. Commun.* **1999**, 1889. (b) Ikeda, C.; Ueda, S.; Nabeshima, T. *Chem. Commun.* **2009**, 2544.

(13) Rausaria, S.; Kamadulski, A.; Rath, N. P.; Bryant, L.; Chen, Z. M.; Salvemini, D.; Neumann, W. L. *J. Am. Chem. Soc.* **2011**, *133*, 4200.

(14) Sakamoto, N.; Ikeda, C.; Yamamura, M.; Nabeshima, T. *J. Am. Chem. Soc.* **2011**, *133*, 4726.

(15) Rieth, R. D.; Mankad, N. P.; Calimano, E.; Sadighi, J. P. *Org. Lett.* **2004**, *6*, 3981.

(16) Manahan, S. E. *Toxicological chemistry and biochemistry*, 3rd ed.; Lewis Pub.: Boca Raton, FL, 2003.