Aqueous-Phase One-Pot Synthesis of 2-Aminothiazole- or 2-Aminoselenazole-5-carboxylates from β-Keto Esters, Thiourea or Selenourea, and *N*-Bromosuccinimide under Supramolecular Catalysis

Mendu Narender, Majjigapu Somi Reddy, Vydyula Pavan Kumar, Boga Srinivas, Regati Sridhar, Yadavalli Venkata Durga Nageswar, Kakulapati Rama Rao*

Organic Chemistry Division-I, Indian Institute of Chemical Technology, Hyderabad 500 007, India
E-mail: drkrrao@yahoo.com

Received 15 June 2007; revised 29 August 2007

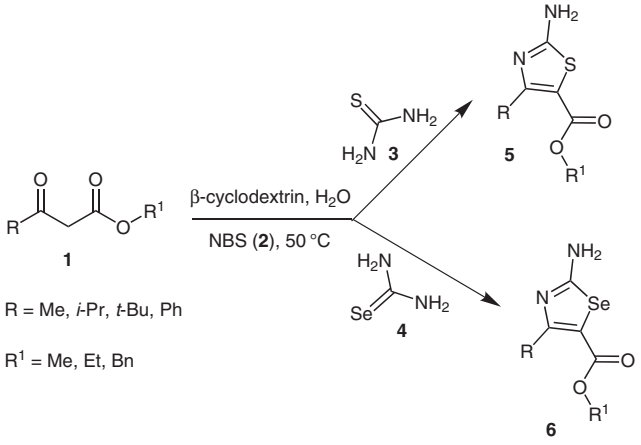
Abstract: 2-Amino-4-alkyl- and 2-amino-4-arylthiazole-5-carboxylates and their selenazole analogues were synthesized by α-halogenation of β-keto esters with *N*-bromosuccinimide, followed by cyclization with thiourea or selenourea, respectively, in the presence of β-cyclodextrin in water at 50 °C.

Key words: thiazoles, selenazoles, β-keto esters, *N*-bromosuccinimide, cyclodextrins

Thiazoles play a prominent role in nature and have broad applications in agricultural and medicinal chemistry. For example, the thiazole in vitamin B_1 serves as an electron sink, and its coenzyme form is important for the decarboxylation of α-keto acids[1] and is present in various natural products[2] and herbicides.[3] A large number of thiazole derivatives have emerged as active pharmaceutical ingredients in several drugs because of their potential antitumor,[4] anti-hypertensive,[5] anti-inflammatory,[6] anti-hyperlipidemic,[7] and other biological properties.[8] Selenazole derivatives also play an important role in antitumor and antibacterial activities[9] and inhibit lipopolysaccharide-induced nitric oxide production in BV-2 cells.[10] Several groups have developed various methods for the synthesis of these thiazole and selenazole derivatives. Hantzsch synthesis is the most widely used methodology.[11] Based on this concept, some newer methods, such as cycloaddition of TosMIC (tosylmethyl isocyanide) to thione derivatives,[12] the Ugi reaction,[13] oxidation of thiazoline and thiazolidine ring systems,[14] and others,[15] have been developed.

In the last decade, further methods have been developed for introducing various aryl and olefinic moieties onto the thiazole ring system, such as palladium-mediated coupling processes[16] and the nucleophilic reaction of lithiothiazole to afford substituted thiazoles.[17] Georgia and Tsolomitis have also reported the synthesis of 5-acetamido-2-amino-4-phenylthiazoles by bromination of γ-keto esters.[18] Many of the syntheses of thiazole and selenazole derivatives have been reported because of the compounds' interesting reactivities and potential biological activities. All of these reactions were carried out in hazardous organic solvents and involved tedious workup because of the reagents used. In view of these shortcomings, there is a need to develop a mild and eco-friendly synthetic methodology for these high-value compounds by replacing organic solvents, most of which are flammable, toxic, or carcinogenic, with water and by using a recyclable catalyst as part of a green chemistry approach.[19]

Water is cheap, nontoxic, and the most readily available reaction medium, making it an environmentally and economically attractive solvent.[20] However, the fundamental problem in performing reactions in water is that many organic substrates are hydrophobic and insoluble. In our efforts to develop biomimetic approaches through supramolecular catalysis[21] and also to overcome some of the drawbacks of the existing methodologies for synthesizing thiazole and selenazole derivatives, we have attempted for the first time the aqueous-phase synthesis of thiazole and selenazole derivatives from β-keto esters, *N*-bromosuccinimide (NBS), and the appropriate thiourea or selenourea in the presence of β-cyclodextrin (Scheme 1).



Scheme 1

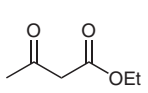
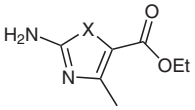
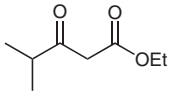
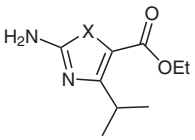
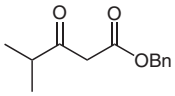
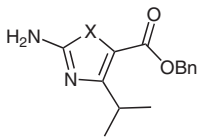
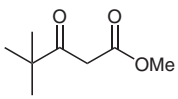
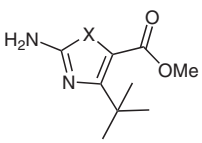
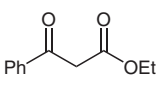
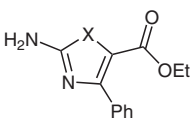
Cyclodextrins, which are cyclic oligosaccharides with hydrophobic cavities, exert microenvironmental effects leading to selective reactions. They catalyze reactions involving supramolecular catalysis through noncovalent bonding as seen in enzymes.[22] These biomimetic reactions can be effectively carried out in water without generating any toxic waste products. Thus, mimicking biochemical conditions with the reactions carried out in water will be

SYNTHESIS 2007, No. 22, pp 3469–3472
Advanced online publication: 29.10.2007
DOI: 10.1055/s-2007-990849; Art ID: Z14707SS

superior to chemical selectivity. These attractive features of cyclodextrins prompted us to carry out the synthesis of thiazole and selenazole derivatives from β-keto esters in water in the presence of β-cyclodextrin as this is one of the most useful synthetic transformations.

In general, the reactions were carried out by the in situ formation of the β-cyclodextrin complex of the β-keto ester **1** in water at 50 °C, followed by the addition of NBS (**2**) and either thiourea (**3**) or selenourea (**4**); stirring at the same temperature gave the corresponding thiazole **5** and selenazole **6** derivatives in excellent yields (Table 1). The treatment of β-keto esters with NBS may afford α-bromo-β-keto esters as intermediates, which then undergo cyclization with thiourea or selenourea to give the corresponding thiazole and selenazole derivatives. The reactions were smooth and succinimide was obtained as a byproduct, which could be recycled to give NBS[23] as described below. However, it was observed previously that bromination of carbonyl compounds using NBS requires a radical initiator, such as 2,2′-azobis(isobutyronitrile) or dibenzoyl peroxide.[24]

Table 1 Synthesis of Substituted Thiazole and Selenazole Ring Systems in the Presence of β-Cyclodextrin

Entry	Substrate	Product[a]	X	Time (h)	Yield[b] (%)
1			S	1.3	90
2			Se	1.5	92
3			S	1.4	88
4			Se	2.0	90
5			S	1.5	92
6			Se	2.0	93
7			S	1.3	87
8			Se	1.5	89
9			S	1.2	92
10			Se	1.3	94

[a] All products were characterized by ^{1}H NMR and infrared spectroscopy, mass spectrometry, and elemental analysis.
[b] Isolated yields after column chromatography.

In this synthesis, the role of cyclodextrin appears to be to allow the β-keto ester to dissolve and to activate it through hydrogen bonding, thereby promoting the reaction. In the absence of β-cyclodextrin, the reaction did take place after long reaction times (12 h), but the yields were poor (15%) and a mixture of products were formed. β-Cyclodextrin can be easily recovered and reused. These reactions do take place with α-cyclodextrin; however, β-cyclodextrin was chosen as the catalyst since it is inexpensive and easily accessible.

Thus, we have demonstrated, for the first time, the novel and efficient biomimetic conversion of β-keto esters into thiazole and selenazole derivatives using easily accessible NBS and the appropriate thiourea or selenourea with β-cyclodextrin as a promoter and water as the reaction medium. This novel methodology may find a wide range of applications.

Melting points were measured in an Electrothermal apparatus and are uncorrected. Infrared spectra were recorded on a Nicolet FT-IR spectrophotometer. ^{1}H NMR spectra were recorded in $CDCl_3$ at 200 MHz or 300 MHz on a Varian-200 or Bruker-300 spectrometer using TMS as an internal standard. Mass spectra were recorded on a V. G. autospectrometer using ESI and EI techniques. Column chromatography was performed with 60–120 mesh silica gel.

All reactions were carried out without any special precautions in an atmosphere of air. Ethyl acetoacetate (99%) was purchased from Spectrochem. Ethyl 4-methyl-3-oxopentanoate (95%), methyl 4,4-dimethyl-3-oxopentanoate (99%), ethyl 3-oxo-3-phenylpropanoate (90%) and selenourea (99.9%) were purchased from Aldrich. Thiourea (99%) and NBS (98%) were purchased from S.D. Fine-Chem Ltd. and β-cyclodextrin (99%) was purchased from Fluka. Benzyl 4-methyl-3-oxopentanoate was synthesized from ethyl 4-methyl-3-oxopentanoate via transesterification.[25]

4-Substituted 2-Aminothiazole- 5 and 2-Aminoselenazole-5-carboxylates 6; General Procedure

β-Cyclodextrin (1 mmol) was dissolved in H_2O (20 mL) by warming the mixture to 50 °C until a clear solution was formed. Then, β-keto ester **1** (1 mmol) dissolved in acetone (1 mL) was added dropwise, followed by NBS (**2**; 1.2 mmol) and the appropriate thiourea (**3**) or selenourea (**4**) (1.2 mmol). The mixture was stirred at 50 °C until the reaction was complete (as monitored by TLC, see Table 1 for reaction times). The mixture was then extracted with EtOAc and the extract was filtered. The organic layer was dried (anhyd Na_2SO_4) and the solvent was removed under reduced pressure. The resulting product was further purified by column chromatography (EtOAc–hexane, 2:8). The aqueous layer was cooled to 5 °C and β-cyclodextrin was recovered from it by filtration. To the filtrate that contained succinimide and HBr, $NaBrO_3$ and concd H_2SO_4 were added,[23] and the mixture was stirred for 30 min. Then, the mixture was extracted with EtOAc and the solvent was removed under vacuum to regenerate NBS in an isolated yield of 75–80%.

Ethyl 2-Amino-4-methylthiazole-5-carboxylate (Table 1, Entry 1)

White solid.

Mp 174–176 °C.

IR (KBr): 3372, 3300, 1675, 1650, 1516, 1279, 1095 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.35 (t, *J* = 7.9 Hz, 3 H), 2.05 (br s, 2 H), 2.49 (s, 3 H), 4.25 (q, *J* = 7.9 Hz, 2 H).

ESI-MS: *m*/*z* = 187 (100) $[M + 1]^+$.

Anal. Calcd for $C_7H_{10}N_2O_2S$: C, 45.15; H, 5.41; N, 15.04; S, 17.22. Found: C, 45.27; H, 5.28; N, 14.89; S, 17.09.

Ethyl 2-Amino-4-methylselenazole-5-carboxylate (Table 1, Entry 2)
White solid.

Mp 163–165 °C.

IR (KBr): 3375, 3064, 2929, 2757, 1665, 1124, 1086 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 1.35 (t, *J* = 7.03 Hz, 3 H), 2.05 (s, 3 H), 4.22 (q, *J* = 7.03 Hz, 2 H), 7.73 (br s, 2 H).

MS (EI, 70 eV): *m*/*z* = 233 (100) [M^+].

Anal. Calcd for $C_7H_{10}N_2O_2Se$: C, 36.06; H, 4.32; N, 12.02. Found: C, 35.90; H, 4.20; N, 12.15.

Ethyl 2-Amino-4-isopropylthiazole-5-carboxylate (Table 1, Entry 3)
White solid.

Mp 179–181 °C.

IR (KBr): 3386, 3304, 1659, 1511, 1305, 1081 cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz): δ = 1.15 (d, *J* = 6.49 Hz, 6 H), 1.35 (t, *J* = 6.49 Hz, 3 H), 3.85 (sept, *J* = 6.49 Hz, 1 H), 4.25 (q, *J* = 6.49 Hz, 2 H), 5.60 (br s, 2 H).

ESI-MS: *m*/*z* = 215 (100) $[M + 1]^+$.

Anal. Calcd for $C_9H_{14}N_2O_2S$: C, 50.45; H, 6.59; N, 13.07; S, 14.96. Found: C, 50.32; H, 6.48; N, 13.19; S, 15.12.

Ethyl 2-Amino-4-isopropylselenazole-5-carboxylate (Table 1, Entry 4)
White solid.

Mp 192–194 °C.

IR (KBr): 3395, 3298, 3105, 2962, 1632, 1502 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 1.15 (d, *J* = 7.89 Hz, 6 H), 1.30 (t, *J* = 7.06 Hz, 3 H), 3.85 (sept, *J* = 7.89 Hz, 1 H), 4.15 (q, *J* = 7.06 Hz, 2 H), 7.30 (br s, 2 H).

ESI-MS: *m*/*z* = 263 (100) $[M + 2]^+$.

Anal. Calcd for $C_9H_{14}N_2O_2Se$: C, 41.39; H, 5.40; N, 10.73. Found: C, 41.23; H, 5.25; N, 10.92.

Benzyl 2-Amino-4-isopropylthiazole-5-carboxylate (Table 1, Entry 5)
White solid.

Mp 166–168 °C.

IR (KBr): 3380, 3316, 3161, 2957, 1692, 1646, 1517, 1470, 1306, 1264, 1194, 1086 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 1.17 (d, *J* = 7.53 Hz, 6 H), 3.85 (sept, *J* = 7.53 Hz, 1 H), 5.21 (s, 2 H), 5.51 (br s, 2 H), 7.25–7.40 (m, 5 H).

ESI-MS: *m*/*z* = 277 (100) $[M + 1]^+$.

Anal. Calcd for $C_{14}H_{16}N_2O_2S$: C, 60.85; H, 5.84; N, 10.14; S, 11.60. Found: C, 60.72; H, 5.98; N, 10.29; S, 11.49.

Benzyl 2-Amino-4-isopropylselenazole-5-carboxylate (Table 1, Entry 6)
White solid.

Mp 176–178 °C.

IR (KBr): 3385, 3285, 3134, 2961, 2926, 2860, 1664, 1633, 1500 cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz): δ = 1.17 (d, *J* = 7.64 Hz, 6 H), 3.90 (sept, *J* = 7.64 Hz, 1 H), 5.20 (s, 2 H), 5.65 (br s, 2 H), 7.25–7.40 (m, 5 H).

ESI-MS: *m*/*z* = 325 (100) $[M + 2]^+$.

Anal. Calcd for $C_{14}H_{16}N_2O_2Se$: C, 52.02; H, 4.99; N, 8.67. Found: C, 52.24; H, 5.12; N, 8.79.

Methyl 2-Amino-4-*tert*-butylthiazole-5-carboxylate (Table 1, Entry 7)
White solid.

Mp 161–163 °C.

IR (KBr): 3442, 3285, 1691, 1504, 1256, 1085 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 1.40 (s, 9 H), 3.75 (s, 3 H), 5.50 (br s, 2 H).

ESI-MS: *m*/*z* = 215 (100) $[M + 1]^+$.

Anal. Calcd for $C_9H_{14}N_2O_2S$: C, 50.45; H, 6.59; N, 13.07; S, 14.96. Found: C, 50.27; H, 6.38; N, 13.19; S, 15.17.

Methyl 2-Amino-4-*tert*-butylselenazole-5-carboxylate (Table 1, Entry 8)
White solid.

Mp 146–148 °C.

IR (KBr): 3403, 3308, 3156, 2956, 1687, 1642, 1468 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 1.40 (s, 9 H), 3.70 (s, 3 H), 7.30 (br s, 2 H)

ESI-MS: *m*/*z* = 263 (100) $[M + 2]^+$.

Anal. Calcd for $C_9H_{14}N_2O_2Se$: C, 41.39; H, 5.40; N, 10.73. Found: C, 41.54; H, 5.62; N, 10.59.

Ethyl 2-Amino-4-phenylthiazole-5-carboxylate (Table 1, Entry 9)
White solid.

Mp 170–172 °C.

IR (KBr): 3394, 3280, 1657, 1516, 1301, 1168, 1089 cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz): δ = 1.25 (t, *J* = 7.32 Hz, 3 H), 4.18 (q, *J* = 7.32 Hz, 2 H), 5.59 (br s, 2 H), 7.30–7.40 (m, 3 H), 7.60–7.70 (m, 2 H).

ESI-MS: *m*/*z* = 249 (100) $[M + 1]^+$.

Anal. Calcd for $C_{12}H_{12}N_2O_2S$: C, 58.05; H, 4.87; N, 11.28; S, 12.91. Found: C, 58.17; H, 5.08; N, 11.42; S, 12.77.

Ethyl 2-Amino-4-phenylselenazole-5-carboxylate (Table 1, Entry 10)
White solid.

Mp 178–180 °C.

IR (KBr): 3404, 3274, 1648, 1513, 1292, 1071 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ = 1.15 (t, *J* = 7.41 Hz, 3 H), 2.95 (br s, 2 H), 4.05 (q, *J* = 7.41 Hz, 2 H), 7.20–7.30 (m, 2 H), 7.50–7.60 (m, 3 H).

ESI-MS: *m*/*z* = 297 (100) $[M + 2]^+$.

Anal. Calcd for $C_{12}H_{12}N_2O_2Se$: C, 48.82; H, 4.10; N, 9.49. Found: C, 48.97; H, 4.25; N, 9.32.

Acknowledgment

We thank CSIR, New Delhi, India, for fellowships awarded to M.N., M.S.R., V.P.K., B.S., and R.S.

References

(1) Breslow, R. *J. Am. Chem. Soc.* **1958**, *80*, 3719.
(2) (a) You, S.-L.; Kelly, J. W. *Chem. Eur. J.* **2004**, *10*, 71. (b) Kelly, J.; Schraft, W. C.; Kutscher, A. H.; Tuoti, F. *Antibiot. Chemother.* **1959**, *9*, 87.
(3) Matsunaka, S.; Nakamura, H. *Zasso Kenkyu* **1972**, *13*, 29.
(4) (a) Kumar, Y.; Green, R.; Borysko, K. Z.; Wise, D. S.; Wotring, L. L.; Townsend, L. B. *J. Med. Chem.* **1993**, *36*, 3843. (b) Ei-Subbagh, H. I.; AI-Obaid, A. M. *Eur. J. Med. Chem.* **1996**, *31*, 1017.
(5) Tsuruni, Y.; Ueda, H.; Hayashi, K.; Takase, S.; Nishikawa, M.; Kiyoto, S.; Kuhara, M. *J. Antibiot.* **1995**, *48*, 1066.
(6) (a) Miwatashi, S.; Arikawa, Y.; Kotani, E.; Miyamoto, M.; Naruo, K.-I.; Kimura, H.; Tanaka, T.; Asahi, S.; Ohkawa, S. *J. Med. Chem.* **2005**, *48*, 5966. (b) Papadopoulou, C.; Geronikaki, A.; Hadjipavlou-Litina, D. *Farmaco* **2005**, *60*, 969; and references cited therein.
(7) Pereira, R.; Gaudon, C.; Iglesias, B.; Germain, P.; Gronemeyer, H.; De Lera, A. R. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 49.
(8) (a) Millan, D. S.; Prager, R. H.; Brand, C.; Hart, P. H. *Tetrahedron* **2000**, *56*, 811. (b) Wang, W.-L.; Yao, D.-Y.; Gu, M.; Fan, M.-Z.; Li, J.-Y.; Xing, Y.-C.; Nan, F.-J. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 5284.
(9) (a) Shafiee, A.; Mazloumi, A.; Cohen, V. I. *J. Heterocycl. Chem.* **1979**, *16*, 1563. (b) Shafiee, A.; Shafaati, A.; Khamench, B. H. *J. Heterocycl. Chem.* **1989**, *26*, 709. (c) Shafiee, A.; Khashayarmanesh, Z.; Kamal, F. *J. Sci., Islamic Repub. Iran* **1990**, *1*, 111. (d) Maeda, H.; Kambe, N.; Sonoda, N.; Fujiwara, S.; Shin-ike, T. *Tetrahedron* **1997**, *53*, 13667.
(10) (a) Koketsu, M.; Ishihara, H.; Wu, W.; Murakami, K.; Saiki, I. *Eur. J. Pharm. Sci.* **1999**, *9*, 157. (b) Wu, W.; Murakami, K.; Koketsu, M.; Yamada, Y.; Saiki, I. *Anticancer Res.* **1999**, *19*, 5375. (c) Cho, S. I.; Koketsu, M.; Ishihara, H.; Matsushita, M.; Nairn, A. C.; Fukazawa, H.; Uehara, Y. *Biochim. Biophys. Acta* **2000**, *1475*, 207. (d) Koketsu, M.; Choi, S. Y.; Ishihara, H.; Lim, B. O.; Kim, H.; Kim, S. Y. *Chem. Pharm. Bull.* **2002**, *50*, 1594. (e) Gutzkow, K. B.; Lahne, H. U.; Naderi, S.; Torgersen, K. M.; Skaalthegg, B.; Koketsu, M.; Uehara, Y.; Blomhoff, H. K. *Cell. Signalling* **2003**, *15*, 871.
(11) (a) Metzger, J. V. In *Comprehensive Heterocyclic Chemistry*, Vol. 6; Katritzky, A. R.; Rees, C. W., Eds.; Pergamon: New York, **1984**, 235–332. (b) Hantzsch, A.; Weber, J. H. *Ber. Dtsch. Chem. Ges.* **1887**, *20*, 3118. (c) Aguilar, E.; Meyers, A. I. *Tetrahedron Lett.* **1994**, *35*, 2473. (d) Varma, R. S. *Pure Appl. Chem.* **2001**, *73*, 193. (e) Ochiai, M.; Nishi, Y.; Hashimoto, S.; Tsuchimoto, Y.; Chen, D.-W. *J. Org. Chem.* **2003**, *68*, 7887; and references cited therein.
(12) Bergstrom, D. E.; Zhang, P.; Zhou, J. *J. Chem. Soc., Perkin Trans. 1* **1994**, 3029.
(13) Kazmaier, U.; Ackermann, S. *Org. Biomol. Chem.* **2005**, *3*, 3184.
(14) (a) Martin, L. M.; Hu, B.-H. *Tetrahedron Lett.* **1999**, *40*, 7951. (b) You, S.-L.; Kelly, J. W. *J. Org. Chem.* **2003**, *68*, 9506.
(15) (a) Mustafa, S. M.; Nair, V. A.; Chittoor, J. P.; Krishnapillai, S. *Mini-Rev. Org. Chem.* **2004**, *1*, 375. (b) Walek, W.; Pallas, M.; Augustin, M. *Tetrahedron* **1976**, *32*, 623. (c) Golankiewicz, B.; Januszczyk, P.; Gdaniec, M.; Kosturkiewicz, Z. *Tetrahedron* **1985**, *41*, 5989. (d) Lin, Y.-I.; Seifert, C. M.; Kang, S. M.; Dusza, J. P.; Lang, S. A. Jr. *J. Heterocycl. Chem.* **1979**, *16*, 1377. (e) Short, K. M.; Ziegler, C. B. Jr. *Tetrahedron Lett.* **1993**, *34*, 71. (f) Wardakhan, W. W.; Elkholy, Y. M. *Phosphorus, Sulfur Silicon Relat. Elem.* **2002**, *177*, 2661. (g) Hermitage, S. A.; Cardwell, K. S.; Chapman, T.; Cooke, J. W. B.; Newton, R. *Org. Process Res. Dev.* **2001**, *5*, 37.
(16) (a) Sapountzis, I.; Dube, H.; Lewis, R.; Gommermann, N.; Knochel, P. *J. Org. Chem.* **2005**, *70*, 2445. (b) Lipshutz, B. H.; Frieman, B.; Birkedal, H. *Org. Lett.* **2004**, *6*, 2305. (c) Nicolaou, K. C.; King, N. P.; Finlay, M. R. V.; Roschangar, F.; Vourloumis, D.; Vallberg, H.; Sarabia, F.; Ninkovic, S.; Hepworth, D. *Bioorg. Med. Chem.* **1999**, *7*, 665. (d) Feuerstein, M.; Doucet, H.; Santelli, M. *J. Organomet. Chem.* **2003**, *687*, 327. (e) Molander, G. A.; Biolatto, V. *J. Org. Chem.* **2003**, *68*, 4302. (f) Hodgetts, K. J.; Kershaw, M. T. *Org. Lett.* **2003**, *5*, 2911.
(17) Dondoni, A. *Synthesis* **1998**, 1681.
(18) Georgia, T.; Tsolomitis, A. *Synth. Commun.* **2006**, *36*, 501.
(19) (a) OECD (Organization for Economical Cooperation and Development) Workshop on Sustainable Chemistry, Venice, Italy, 1998. (b) Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press: Oxford, **1998**. (c) Anastas, P. T.; Williamson, T. C.; Hjeresen, D.; Breen, J. *Environ. Sci. Technol.* **1999**, *33*, 116A.
(20) (a) Jaeger, D. A.; Frey, M. R. *J. Org. Chem.* **1982**, *47*, 311. (b) Jaeger, D. A.; Jamrozik, J.; Golich, T. G.; Clennan, M. W.; Mohebalian, J. *J. Am. Chem. Soc.* **1989**, *111*, 3001. (c) Jaeger, D. A.; Sayed, Y. M.; Dutta, A. K. *Tetrahedron Lett.* **1990**, *31*, 449.
(21) (a) Surendra, K.; Krishnaveni, N. S.; Mahesh, A.; Rao, K. R. *J. Org. Chem.* **2006**, *71*, 2532. (b) Krishnaveni, N. S.; Surendra, K.; Rao, K. R. *Chem. Commun.* **2005**, 669. (c) Surendra, K.; Krishnaveni, N. S.; Reddy, M. A.; Nageswar, Y. V. D.; Rao, K. R. *J. Org. Chem.* **2003**, *68*, 2058. (d) Krishnaveni, N. S.; Surendra, K.; Reddy, M. A.; Nageswar, Y. V. D.; Rao, K. R. *J. Org. Chem.* **2003**, *68*, 2018.
(22) Szejtli, J.; Osa, T. *Comprehensive Supramolecular Chemistry*, Vol. 3; Pergamon: New York, **1996**.
(23) Fujisaki, S.; Hamura, S.; Eguchi, H.; Nishida, A. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2426.
(24) Schmid, H.; Karrer, P. *Helv. Chim. Acta* **1946**, *29*, 573.
(25) Yadav, J. S.; Reddy, B. V. S.; Krishna, A. D.; Suresh Reddy, Ch.; Narsaiah, A. V. *J. Mol. Catal. A: Chem.* **2007**, *261*, 93.