http://dx.doi.org/10.5012/bkcs.2012.33.11.3853

L-Tartaric Acid as a New Chiral Auxiliary for Asymmetric Synthesis of Piperazinones, Morpholinones, Dihydroquinoxalinones and Dihydrobenzoxazinones

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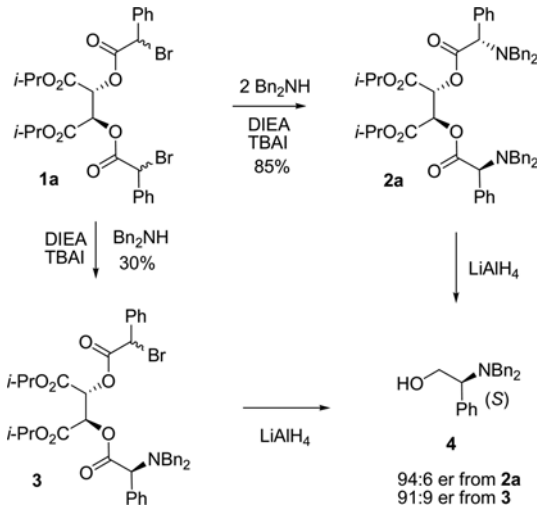
Received July 19, 2012, Accepted August 10, 2012

Key Words : Dynamic resolution, Nucleophilic substitution, Tartaric acid, Chiral auxiliary, Asymmetric synthesis

Dynamic resolution of α-haloacyl compounds in nucleophilic substitution has been recently developed as an asymmetric synthetic method for α-substituted carboxylic acids.[1] While many chiral auxiliaries have successfully been used in the dynamic resolution, it is still highly desirable to develop a new chiral auxiliary for practical purposes. Tartaric acid derivatives are one of the most promising candidates for chiral auxiliary, as it is relatively inexpensive and readily available in both enantiomeric forms. However, so far it has not been used as a chiral auxiliary for the dynamic resolution of α-haloacyl compounds. In continuation of our ongoing efforts to develop efficient synthetic methods for dynamic resolution of α-haloacyl compounds,[2] we herein report the first example of L-tartaric acid-mediated asymmetric nucleophilic substitution for the preparation of 6-membered heterocycles containing 1,4-heteroatoms such as piperazin-2-ones, morpholin-2-ones, dihydroquinoxalinones and dihydrobenzoxazinones.

Initial studies on L-tartaric acid-mediated dynamic resolution were performed with α-bromo ester **1a** and dibenzylamine (Bn_2NH) as shown in Scheme 1. A mixture of diastereomers of α-bromo ester **1a** was readily prepared from diisopropyl L-tartrate in 79% yield by reacting it with α-bromo phenylacetic acid using DCC and DMAP. L-Tartaric acid-derived α-bromo ester **1a** has two substitution sites and the two nucleophilic substitutions with dibenzylamine may show different stereoselectivity because the second substitution takes place under the influence of the first substitution. When the diastereomeric mixture of diisopropyl ester **1a** was treated with tetrabutylammonium iodide (TBAI, 1.0 equiv), diisopropylethylamine (DIEA, 1.0 equiv) and dibenzylamine (2.5 equiv) in CH_2Cl_2 at room temperature for 12 h, the disubstituted amino acid derivative **2a** was produced in 85% yield. Also, mono-substituted amino acid derivative **3** was obtained in 30% yield when we carried out the substitution of diisopropyl ester (α*RS*)-**1a** with 1.0 equiv of dibenzylamine for 5 h. In order to determine the stereoselectivity of the substitutions, the chiral auxiliary was removed from the amino substituted products by reductive cleavage. Treatment of **2a** with $LiAlH_4$ furnished enantioenriched *N,N*-dibenzyl 2-aminoalcohol (*S*)-**4** with 94:6 enantiomeric ratio (er), while the reduction of **3** provided the amino alcohol (*S*)-**4** with 91:9 er. The results imply that α-bromo ester **1a** is dynamically resolved in the nucleophilic substitution and the second substitution with dibenzylamine is more stereoselective than the first substitution (91:9 er).

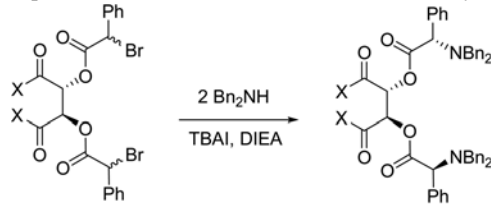


Scheme 1. L-Tartrate-mediated dynamic resolution in nucleophilic substitution.

A series of reactions were performed with diisopropyl ester **1a** and dibenzylamine to assess the effect of solvent and temperature on yield and stereoselectivity as shown in Table 1, entries 1-7. Most of the solvents explored gave similar stereoselectivities such as 93:7 er in CH_3CN, 93:7 er in ethyl acetate, 91:9 er in $CHCl_3$, 90:10 er in THF and 92:8 er in DMF (entries 1-5). Variation of temperature did not significantly affect the stereoselectivity and yield of the substitution (entries 6 and 7). Next, we examined the nucleophilic substitutions of two different tartaric acid derivatives **1b** and **1c**. Treatment of methyl ester **1b** with dibenzylamine for 12 h at room temperature gave **2b** in 82% yield with a ratio of 91:9 (entry 8). Also, the reactions of dimethyl amide **1c** provided **2c** with comparable stereoselectivities in both CH_2Cl_2 and CH_3CN (entries 9-10).

When the diastereomeric mixture of **1a** was allowed to reach thermodynamic equilibrium in the presence of TBAI and DIEA before the addition of benzylamine, the reaction gave the product **2a** with a stereoselectivity of 93:7 (entry 11). The same selectivity as the reaction in entry 1 indicates that thermodynamic stabilities of diastereomers of **1a** are not

Table 1. Optimization of reaction condition with dibenzylamine

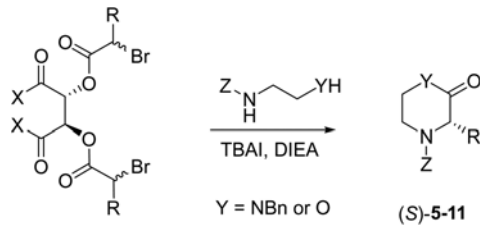


(αRS)-**1a-c** (αS)-**2a-c**

Entry[a]	X	Solvent	Temp	Yield[b] (%)	er[c]
1	*i*-PrO (**1a**)	CH_3CN	rt	63 (**2a**)	93:7
2	*i*-PrO(**1a**)	Ethyl acetate	rt	52 (**2a**)	93:7
3	*i*-PrO (**1a**)	$CHCl_3$	rt	76 (**2a**)	91:9
4	*i*-PrO (**1a**)	THF	rt	54 (**2a**)	90:10
5	*i*-PrO (**1a**)	DMF	rt	37 (**2a**)	92:8
6	*i*-PrO (**1a**)	CH_2Cl_2	0 °C	53 (**2a**)	94:6
7	*i*-PrO (**1a**)	CH_2Cl_2	40 °C	66 (**2a**)	93:7
8	MeO (**1b**)	CH_2Cl_2	rt	82 (**2b**)	91:9
9	Me_2N (**1c**)	CH_2Cl_2	rt	39 (**2c**)	93:7
10	Me_2N (**1c**)	CH_3CN	rt	45 (**2c**)	95:5
11[d]	*i*-PrO (**1a**)	CH_3CN	rt	67 (**2a**)	93:7

[a]All reactions are carried out for 12 h. [b]Isolated yield of **2a-c**. [c]Determined by er of **4** after reduction of **2a-c**. [d]Epimerization for 10 h before the addition of nucleophile.

Table 2. Asymmetric syntheses of piperazinones and morpholinones



(αRS)-**1a-d** (S)-**5-11**

Entry[a]	X	R	Nucleophile	Yield[b] (%)	er[c,d]
1	*i*-PrO (**1a**)	Ph	$BnNH(CH_2)_2NHBn$	98 (**5**)	83:17
2	Me_2N (**1c**)	Ph	$BnNH(CH_2)_2NHBn$	43 (**5**)	91:9
3	*i*-PrO (**1d**)	CH_3	$BnNH(CH_2)_2NHBn$	65 (**6**)	78:22
4	*i*-PrO (**1a**)	Ph	$BnNH(CH_2)_2OH$	44 (**7**)	85:15
5	*i*-PrO (**1d**)	CH_3	$BnNH(CH_2)_2OH$	75 (**8**)	80:20
6	Me_2N (**1c**)	Ph	$BnNH(CH_2)_2OH$	69 (**7**)	92:8
7	Me_2N (**1c**)	Ph	*m*-Me-$PhCH_2NH(CH_2)_2OH$	88 (**9**)	86:14
8	Me_2N (**1c**)	Ph	*p*-MeO-$PhCH_2NH(CH_2)_2OH$	60 (**10**)	91:9
9	Me_2N (**1c**)	Ph	*p*-MeO-$PhNH(CH_2)_2OH$	76 (**11**)	93:7

[a]All reactions are carried out for 12 h in CH_3CN at rt. [b]Isolated yields. [c]Ers are determined by CSP-HPLC. [d]The absolute configuration of **5-11** was assigned by comparison of CSP-HPLC retention time with the reported value in ref. 2a and 3b.

quite different under the reaction condition and the primary pathway of the asymmetric induction may be a dynamic kinetic resolution.[1a,2d]

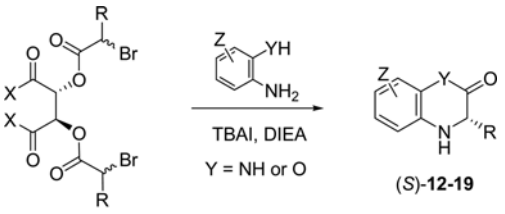
Encouraged by the high enantioselectivities in the reactions with dibenzylamine, we set out to examine the substitutions with *N,N*-dibenzyl ethylenediamine nucleophile for asymmetric syntheses of piperazin-2-ones as shown in Table 2, entries 1-3.[2a] The first step of the reaction is the stereoselective nucleophilic attack of an amino group of ethylenediamine at the α-bromo carbon center and the subsequent ring closure removes the chiral auxiliary to produce piperazin-2-ones.[3] The optimized protocol for the reactions with dibenzylamine was employed to the reaction with *N,N*-dibenzyl ethylenediamine nucleophile. The reaction of **1a** with $BnHNCH_2CH_2NHBn$ in CH_3CN gave (*S*)-1,4-dibenzyl piperazin-2-one (**5**) with an er of 83:17. When *N,N,N′,N′*-tetramethyl L-tartaric acid diamide was used as a chiral auxiliary, the substitution and spontaneous ring closure gave piperazin-2-one with a significantly increased selectivity of 91:9 er (entry 2). However, the reaction of α-bromo propionate **1d** afforded 3-methyl piperazin-2-one **6** with a lower stereoselectivity of 78:22 er (entry 3).

Also, we examined the substitutions with *N*-substituted 2-aminoethanol nucleophiles for asymmetric syntheses of 3-substituted morpholin-2-ones as shown in entries 4-9. When diisopropyl ester **1a** was treated with *N*-benzyl 2-aminoethanol, TBAI and DIEA for 12 h, the substitution and following spontaneous cyclization gave *N*-benzyl 3-phenylmorpholin-2-one **7** in 44% yield with 85:15 er (entry 4). The reaction of α-bromo propionate **1d** afforded 3-methylmorpholin-2-one **8** with a lower stereoselectivity of 80:20 er (entry 5). We were pleased to observe a significantly increased selectivity with dimethyl amide **1c** (entry 6). In an effort to improve the stereoselectivity, we tested three different 2-aminoethanol nucleophiles. The reactions with two *N*-benzyl 2-aminoethanol derivatives produced morpholin-2-ones **9** and **10** with similar yields and slightly lower enantioselectivities (entries 7-8). As with *N*-*p*-methoxyphenyl 2-aminoethanol nucleophile, the reaction provided 3-phenyl-morpholin-2-one **11** with a higher stereoselectivity (93:7 er) compared to the reaction with *N*-benzyl 2-aminoethanol (entry 9).

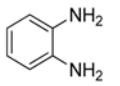
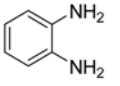
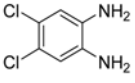
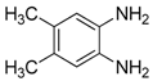
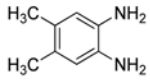
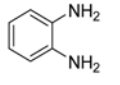
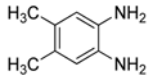
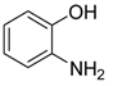
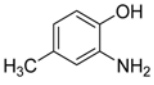
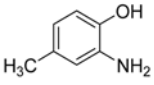
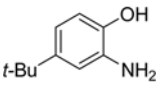
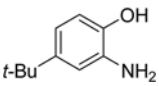
With the identification of L-tartaric acid drivatives as effective and convenient chiral auxiliary for the reactions of α-bromo esters **1a-d**, we next examined the dynamic resolution in substitutions with various 1,2-diaminobenzene nucleophiles for asymmetric syntheses of dihydroquinoxalinones as shown in Table 3, entries 1-7. When α-bromo phenylacetates **1a** and **1c** were treated with 1,2-phenylenediamine, TBAI and DIEA in CH_3CN for 12 h at room temperature, the substitution and following spontaneous cyclization gave 3-phenyl dihydroquinoxalinone **12** with 99:1 er and 97:3 er, respectively (entries 1 and 2). Treatment of **1a** with 4,5-dichloro-*o*-phenylenediamine gave dihydroquinoxalinone **13** in 75% yield with 99:1 er (entry 3), whereas the reactions with 4,5-dimethyl-*o*-phenylenediamine took place to afford dihydroquinoxalinones **14** with lower stereoselectivities of 92:8 and 91:9 ers (entries 4 and 5). The reactions of α-bromo propionate **1d** afforded 3-methyl substituted dihydroquinoxalinones **15** and **16** with lower stereoselectivities of 77:23 and 74:26 ers compared to the reaction of α-bromo phenylacetates **1a** and **1c** (entries 6 and 7).

In addition, we demonstrated that this methodology is also efficient for the asymmetric preparation of 3-phenyl dihydro-

Table 3. Asymmetric syntheses of dihydroquinoxalinones and dihydrobenzoxazinones



(αRS)-**1a-d** (*S*)-**12-19**

Entry[a]	X	R	Nucleophile	Yield (%)[b]	er (*S*:*R*)[c,d]
1	*i*-PrO (**1a**)	Ph		79 (**12**)	99:1
2	Me_2N (**1c**)	Ph		62 (**12**)	97:3
3	*i*-PrO (**1a**)	Ph		75 (**13**)	99:1
4	*i*-PrO (**1a**)	Ph		96 (**14**)	92:8
5	Me_2N (**1c**)	Ph		54 (**14**)	91:9
6	*i*-PrO (**1d**)	CH_3		64 (**15**)	82:18
7	*i*-PrO (**1d**)	CH_3		80 (**16**)	80:20
8	*i*-PrO (**1a**)	Ph		87 (**17**)	82:18
9	*i*-PrO (**1a**)	Ph		55 (**18**)	86:14
10	Me_2N (**1c**)	Ph		65 (**18**)	80:20
11	*i*-PrO (**1a**)	Ph		61 (**19**)	80:20
12	Me_2N (**1c**)	Ph		54 (**19**)	81:19

[a]The reactions are carried out in CH_3CN for 12 h (in CH_2Cl_2 for 6 h for **17-19**) at rt. [b]Isolated yields. [c]Ers are determined by CSP-HPLC. [d]The absolute configurations of **12-19** were assigned by comparison of CSP-HPLC retention time with the reported value in ref. 3c.

benzoxazinones **17-19** with good stereoselectivities and yields as shown in entries 8-12. For example, when α-bromo phenylacetate **1a** was treated with 2-aminophenol in CH_2Cl_2 for 6 h, dihydrobenzoxazinone **17** was obtained in 87% yield with 82:18 er. Also, the reactions of **1a** and **1c** with two different 2-aminophenols produced dihydrobenzoxazinones **18** and **19** with similar yields and enantioselectivities ranging from 86:14 er to 80:20 er (entries 9-12). Curiously, when the reactions with 2-aminophenols were carried out in CH_3CN, dihydrobenzoxazinones were obtained with lower enantioselectivities and yields compared to the reactions in CH_2Cl_2.

In this paper, we have reported the dynamic resolution of α-bromo esters in nucleophilic substitution using L-tartaric acid derivatives as a new effective chiral auxiliary. In the substitutions with ethylenediamine and 2-aminoethanol nucleophiles, spontaneous cyclization can provide a convenient procedure for asymmetric syntheses of 3-substituted piperazin-2-ones and morpholin-2-ones. In addition, the substitutions with arylamine nucleophiles such as 1,2-diaminobenzene and 2-aminophenol can provide an efficient method for asymmetric syntheses of dihydroquinoxalinones and dihydrobenzoxazinones. The simple protocol with mild condition suggests further applications to asymmetric syntheses of various heterocyclic compounds.

Experimental

General Procedure for the Preparation of α-Bromo Acetyl Tartaric Acid Derivatives 1a-1d. L-Tartaric acid derived ester or amide (1.0 mmol, 1.0 equiv), racemic α-bromo acid (1.0 equiv), DCC (1.0 equiv) and DMAP (0.1 equiv) were dissolved in CH_2Cl_2 (10 mL) and stirred at room temperature for 10 h. The precipitate was filtered off and the organic phase was washed with water. The organic phase was dried over $MgSO_4$, filtered and concentrated to provide the crude product that was purified by column chromatography on silica gel.

***O,O′*-Di(α-bromo-α-phenylacetyl)-L-tartaric Acid Diisopropyl Ester (1a):** 79% Yield (mixture of diastereomers) as a colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, mixture of diastereomers) δ 7.57 (m, 4H), 7.35 (m, 6H), 5.79-5.71 (m, 2H), 5.44 (m, 2H), 4.99 (m, 1H), 4.83 (m, 1H), 1.22-0.90 (m, 12H).

***O,O′*-Di(α-bromo-α-phenylacetyl)-L-tartaric Acid Dimethyl Ester (1b):** 65% Yield (mixture of diastereomers) as a pale yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz, mixture of diastereomers) δ 7.54 (m, 4H), 7.34 (m, 6H), 5.81-5.71 (m, 2H), 5.47-5.42 (m, 2H), 3.64-3.39 (m, 6H).

***O,O′*-Di(α-bromo-α-phenylacetyl)-*N,N,N′,N′*-tetramethyl-L-tartaric Diamide (1c):** 67% Yield (mixture of diastereomers) as a pale yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz, mixture of diastereomers) δ 7.52-7.28 (m, 10H), 6.02-5.96 (m, 2H), 5.38-5.09 (m, 2H), 3.08-2.83 (m, 12H).

***O,O′*-Di(α-bromopropanoyl)-L-tartaric Acid Diisopropyl Ester (1d):** 56% Yield (mixture of diastereomers) as a yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz, mixture of diastereomers) δ 5.75 (m, 2H), 5.09 (m, 2H), 4.53-4.43 (m, 2H), 1.87 (m, 6H), 1.30-1.22 (m, 12H).

General Procedure for the Asymmetric Nucleophilic Substitution to Give 2a-c. To a solution of α-bromo esters derived from L-tartaric acid **1a-c** (1.0 mmol) in CH_3CN (*ca.* 0.1 M) at room temperature were added DIEA (1.0 equiv), TBAI (1.0 equiv) and dibenzylamine (2.5 equiv). After the

resulting reaction mixture was stirred at room temperature for 12 h, the solvent was evaporated and the crude material was purified by column chromatography to give a *N,N*-dibenzyl α-amino esters **2a-c**. The stereoselectivities of **2a-c** were determined after the conversion to 2-dibenzylamino-2-phenylethanol (**4**) by chiral stationary phase HPLC.

***O,O′*-Di(α-dibenzylamino-α-phenylacetyl)-L-tartaric Acid Diisopropyl Ester (2a):** 63% Yield; ^{1}H NMR ($CDCl_3$, 400 MHz, major diastereomer) δ 7.35-7.13 (m, 30H), 5.91 (s, 2H), 4.94 (m, 2H), 4.75 (s, 2H), 3.74 (q, 8H), 1.08 (d, J = 6.0 Hz, 1H), 1.02 (d, J = 6.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, major diastereomer) δ 171.2, 165.3, 139.4, 136.0, 129.1, 129.0, 128.3, 128.2, 128.0, 127.1, 71.6, 70.7, 65.8, 53.8, 21.7, 21.6. Subsequent reductive cleavage of **2a** using $LiAlH_4$ furnished 2-dibenzylamino-2-phenylethanol **4**. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44-7.25 (m, 15H), 4.14 (dd, J = 10.6, 10.6 Hz, 1H), 3.96-3.90 (m, 3H), 3.62 (m, 1H), 3.15 (d, J = 13.4 Hz, 1H), 3.01 (br, 1H). The enantiomeric ratio of **4** was determined to be 94:6 in favor of the *S* enantiomer by CSP-HPLC using racemic material as a standard. (Chiralcel OD column; 10% 2-propanol in hexane; 0.5 mL/min): 12.0 min (*R*), 18.1 min (*S*). When a reaction was carried out with 1.0 equiv of dibenzylamine for 6 h, mono dibenzylamino substituted L-tartaric acid diisopropyl ester (**3**) was obtained in 30% yield. ^{1}H NMR ($CDCl_3$, 400 MHz, mixture of diastereomers) δ 7.56-7.22 (m, 20H), 5.83-5.70 (m, 2H), 5.31-5.25 (m, 1H), 5.18-4.88 (m, 2H), 4.76-4.70 (m, 1H), 3.86-3.71 (m, 2H), 1.34-0.68 (m, 12H).

***O,O′*-Di(α-dibenzylamino-α-phenylacetyl)-L-tartaric Acid Dimethyl Ester (2b):** 82% Yield; ^{1}H NMR ($CDCl_3$, 400 MHz, major diastereomer) δ 7.33-7.16 (m, 30H), 5.97 (s, 2H), 4.73 (s, 2H), 3.73 (s, 8H), 3.60 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, major diastereomer) δ 171.3, 166.1, 139.3, 136.1, 129.0, 128.9, 128.4, 128.3, 128.0, 127.1, 71.1, 65.8, 53.9, 53.0. Subsequent reductive cleavage of **2b** using $LiAlH_4$ furnished 2-dibenzylamino-2-phenylethanol **4**. The enantiomeric ratio of **4** was determined to be 91:9 in favor of the *S* enantiomer.

***O,O′*-Di(α-dibenzylamino-α-phenylacetyl)-*N,N,N′,N′*-tetramethyl-L-tartaric Diamide (2c):** 45% Yield; ^{1}H NMR ($CDCl_3$, 400 MHz, major diastereomer) δ 7.39-6.99 (m, 30H), 5.86 (s, 2H), 4.57 (s, 2H), 3.64 (q, 8H), 3.22 (s, 6H), 3.04 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz, major diastereomer) δ 171.2, 166.5, 139.4, 135.8, 129.0, 128.7, 128.5, 128.4, 128.3, 128.2, 127.7, 127.1, 70.0, 64.9, 54.0, 37.8, 36.3. Subsequent reductive cleavage of **2c** using $LiAlH_4$ furnished 2-dibenzylamino-2-phenylethanol **4**. The enantiomeric ratio of **4** was determined to be 95:5 in favor of the *S* enantiomer.

General Procedure for the Asymmetric Preparation of Heterocycles 5-19. To a solution of α-bromo carboxylic acid derivatives (1.0 mmol) in CH_3CN (*ca*. 0.1 M) at room temperature were added DIEA (1.0 equiv), TBAI (1.0 equiv) and a nucleophile (2.5 equiv). After the resulting reaction mixture was stirred at room temperature for 6-12 h, the solvent was evaporated and the crude material was purified by column chromatography to give heterocycles **5-19**. The spectral data of **5-19** were identical to those of the authentic material reported previously.[2a,3] The ers were determined by chiral stationary phase HPLC using Chiralcel OD column (for **5**, **6**, **17**, **18** and **19**), Chiralpak AD-H column (for **7**, **9**, **10** and **11**) and Chiralcel OJ-H column (for **8**, **12**, **13**, **14**, **15** and **16**).[2a,3]

Acknowledgments. This work was supported by a grant from Konkuk University in 2011.

References and Notes

1. (a) Park, Y. S. *Tetrahedron: Asymmetry* **2009**, *20*, 2421. (b) Treweeke, N. R.; Hitchcock, P. B.; Pardoe, D. A. Caddick, S. *Chem. Commun.* **2005**, 1868. (c) Ben, R. N.; Durst, T. *J. Org. Chem.* **1999**, *64*, 7700. (d) Kubota, H.; Kubo, A.; Takahashi, M.; Shimizu, R.; Tadamasa, D.; Okamura, K.; Nunami, K. *J. Org. Chem.* **1995**, *60*, 6776. (e) Ward, R. S.; Pelter, A.; Goubet, D.; Pritchard, M. C. *Tetrahedron: Asymmetry* **1995**, *6*, 469.
2. (a) Jang, J. I.; Kang, S. Y.; Kang, K. H.; Park, Y. S. *Tetrahedron* **2011**, *67*, 6221. (b) Kim, H. J.; Kim, Y.; Choi, E. T.; Lee, M. H.; No, E. S.; Park, Y. S. *Tetrahedron* **2006**, *62*, 6303. (c) Chang, J.-Y.; Shin, E.-K.; Kim, H. J.; Kim, Y.; Park, Y. S. *Tetrahedron* **2005**, *61*, 2743. (d) Nam, J.; Lee, S.-K.; Park, Y. S. *Tetrahedron* **2003**, *59*, 2397. (e) Lee, S.-K.; Lee, S. Y.; Park, Y. S. *Synlett* **2001**, 1941.
3. (a) Devine, P. N.; Foster, B. S.; Grabowski, E. J. J.; Reider, P. J. *Heterocycles* **2002**, *58*, 119. (b) Lee, Y. M.; Kang, K. H.; Min, H.-M.; Lim, H. J.; Park, E.-H.; Park, Y. S. *Arkivoc* **2010**, *ii*, 1. (c) Lee, Y. M.; Park, Y. S. *Heterocycles* **2009**, *73*, 2233. (d) Kim, Y.; Lee, M. H.; Choi, E. T.; No, E. S.; Park, Y. S. *Heterocycles* **2007**, *71*, 5. (e) Kang, K. H.; Jang, J. I.; Baek, S. B.; Ahn, J. H.; Park, Y. S. *Bull. Korean Chem. Soc.* **2011**, *32*, 1741.