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Catalytic Enantioselective Synthesis of 4-Vinyl-2-trichloromethyloxazoline: An Access to Enantioenriched Vinylglycinol Surrogate

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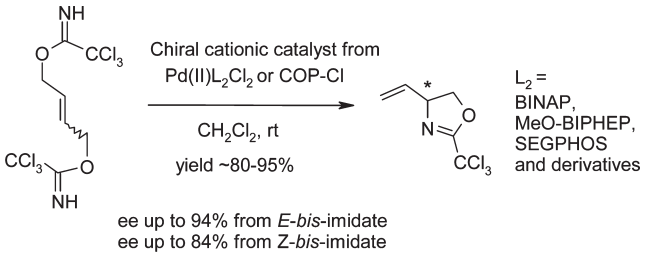
Received September 10, 2010



Cationic Pd(II) catalysts generated from chiral biphenyl diphosphine complexes or from COP-Cl promote enantioselective cyclization of *E*- and *Z*-configured allylic bis-trichloroacetimidates to highly enantioenriched 2-trichloromethyl-4-vinyloxazoline. This represents an exclusive example for olefin amination in high yield and enantioselectivity with trichloroacetimidate as the *N*-nucleophile by using a cationic palladium(II) complex as a catalyst providing an easy-to-deprotect enantioenriched vinylglycinol derivative.

Vinylglycinol **1** and its protected analogues (Figure 1) have been widely used as building blocks for the synthesis of unnatural amino acids,[1] pharmaceutically relevant compounds,[2] and natural products.[3] Protected vinylglycinol **1** has been obtained in enantiomerically pure form by separation of racemic mixture[4] or starting from enantiopure serine,[2a,5] methionine,[1b,c,2a,6] and buten-1,2-diol.[7] Chiral auxiliary-controlled diastereoselective addition of vinyl-organometallic reagents to oxime ethers[8] or sulfinylimines[9] has also been used to obtain vinylglycinol **1** derivatives in high enantiomeric purity. In addition, several synthetically useful enantioselective catalytic methods have been developed. Asymmetric Pd(0)-catalyzed allylic alkylation of phthalimide with butadiene monoxide provided *N*-Phth protected vinylglycinol **2**.[3a−c,10] Enantioselective Ir catalysis has been used for the amination of allylic carbonates leading to a range of *N*,*O*- or *N*-protected vinylglycinols **3**.[11] Asymmetric Ni(0)- and Pd(II)-catalyzed cyclization of allylic carbamates to *N*-protected vinyloxazolidinones **4** has been reported.[12,13] Rearrangement of *O*-allylic acetimidates catalyzed by planary chiral Pd(II) complexes has provided *N*-trichloroacetyl- and *N*-trifluoroacetylvinylglycinol derivatives **5** in high enantiomeric excess (Figure 1).[14]

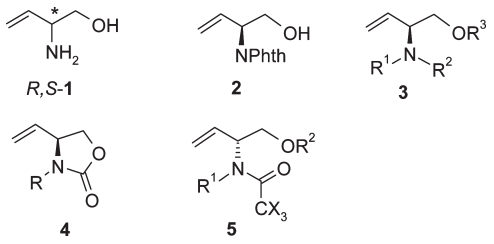


FIGURE 1. Vinylglycinol **1** and its derivatives **2**−**5** obtained by enantioselective catalysis.

2-Trichloromethyl-4-vinyloxazoline (**8**) (Scheme 1) is a useful vinylglycinol surrogate for the synthesis of complex products.[4,15] Unfortunately, it has been obtained only in racemic form by a Pd(II)-catalyzed cyclization of bis-trichloroacetimidate *Z*-**7**. The high synthetic utility of vinyloxazoline **8** prompted

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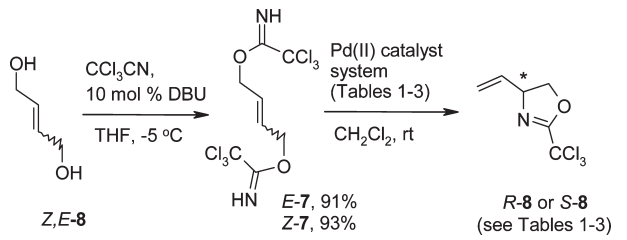
DOI: 10.1021/jo101781y Published on Web 10/25/2010

SCHEME 1. Synthesis of 4-Vinyloxazolines *R*-8 and *S*-8



us to achieve the enantioselective cyclization of imidate **7** to enantiomers *R*-**8** and *S*-**8** (Scheme 1).

Previously it has been reported that only neutral Pd(II) catalysts[14,16] are compatible with allylic trichloroacetimidates. In turn, cationic Pd(II) complexes promote elimination of trichloroacetamide by generation of an allyl cation[17] that prohibits the use of commercially available chiral polydentate ligands. Nevertheless, we speculated that bis-trichloroacetimidate **7** could serve as a substrate for cationic Pd(II)-catalyzed reactions because the tendency to form allylic cation might be reduced due to the field effect of the second imidate functional group. Indeed, brief screening of Pd(II) catalysts derived from commercially available ligands revealed that in situ generated cationic diphosphine Pd(II) complexes afford the desired product **8** in high chemical yield from both bis-imidate isomers *E*-**7** and *Z*-**7** in a short time under mild reaction conditions (Tables 1 and 2; see Figure 2 for diphosphine ligands).

Isomeric bis-imidates *E*-**7** and *Z*-**7** required different catalytic systems to achieve high enantioselectivity of vinyloxazoline **8** formation as shown in Tables 1 and 2. We were pleased to find that bis-trichloroacetimidate *E*-**7** was transformed to vinyloxazoline *R*-**8** in high enantiomeric excess by using a (*R*)-BINAPPdCl$_2$/AgBF$_4$ catalytic system (Table 1, entry 1). An efficient catalytic system could also be prepared in situ from PdCl$_2$(MeCN)$_2$ by mixing it with (*R*)- or (*S*)-BINAP followed by addition of AgBF$_4$ (Table 1, entries 2 and 3). Other axially chiral diphosphines such as (*R*)-T-BINAP, (*S*)-Xyl-BINAP, (*S*)-MeO-BIPHEP, and (*S*)-DTB-MeO-BIPHEP were also found to be efficient for the enantioselective cyclization of imidate *E*-**7** (Table 1, entries 4−7) while (*S*)-SEGPHOS induced moderate enantioselectivity (Table 1, entries 8). Control experiments with imidate *E*-**7** were performed to confirm that (*R*)-BINAPPdCl$_2$ complex in its coordinatively saturated form has no catalytic activity and that AgBF$_4$ alone cannot promote the reaction (Table 1, entries 9 and 10).

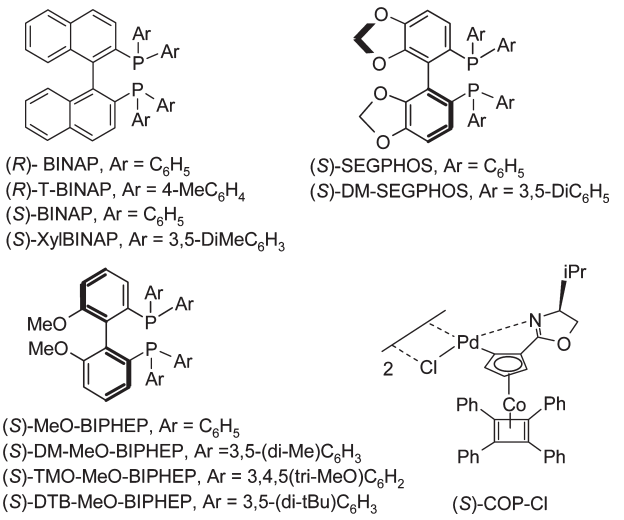


FIGURE 2. Diphosphine ligands and COP-Cl complex used to generate the Pd(II) catalyst system for the synthesis of vinyloxazolines *R*-**8** and *R*-**8**.

TABLE 1. Diphosphine−Pd(II) Complex Catalyzed Cyclization of Bis-imidate *E*-7 to Enantioenriched Vinyloxazoline 8

entry	catalyst system[a]	time	ee,[b] (*S* or *R*)[c]	yield, %
1	(*R*)-BINAPPdCl$_2$/ AgBF$_4$	1 h	94%,[d] (*R*)	93
2	(*R*)-BINAP/PdCl$_2$(CH$_3$CN)$_2$ /AgBF$_4$	1 h	90%, (*R*)	88[e]
3	(*S*)-BINAP/PdCl$_2$(CH$_3$CN)$_2$/ AgBF$_4$	1 h	93%, (*S*)	94[e]
4	(*R*)-T-BINAP/PdCl$_2$(CH$_3$CN)$_2$ /AgBF$_4$	1 h	89%, (*R*)	91[e]
5	(*S*)-Xyl-BINAP PdCl$_2$(CH$_3$CN)$_2$ /AgBF$_4$	2.5 h	87%, (*S*)	84
6	(*S*)-MeO-BIPHEP PdCl$_2$(CH$_3$CN)$_2$ /AgBF$_4$	2.5 h	93%, (*S*)	89
7	(*S*)-DTB-MeO-BIPHEP PdCl$_2$(CH$_3$CN)$_2$ /AgBF$_4$	2.5 h	94%, (*S*)	93
8	(*S*)-SEGPHOS PdCl$_2$(CH$_3$CN)$_2$ /AgBF$_4$	2.5 h	66%, (*S*)	87
9	(*R*)-BINAPPdCl$_2$	>1 d		n.r.
10	AgBF$_4$	>1 d		n.r.

[a]Substrate/ligand/PdCl$_2$(CH$_3$CN)$_2$/AgBF$_4$ ratio 100/3/2.5/8 or 100/4/3/10. [b]Determination of ee by GC on 6-TBDMS-2,3-Me-β-CD column unless otherwise indicated. [c]Configuration of the major enantiomer. [d]Determination of ee by reverse phase HPLC after hydrolysis and subsequent derivatization with chiral reagents.[18] [e]Average yield of two runs. Please see the Supporting Information for details

TABLE 2. Diphosphine−Pd(II) Complex Catalyzed Cyclization of Bis-imidate *Z*-7 to Enantioenriched Vinyloxazoline 8

entry	catalyst system[a]	time, h	ee,[b] (*S* or *R*)[c]	yield, %
1	(*R*)-BINAPPdCl$_2$/ AgBF$_4$	1	30%,[d] (*R*)	85
2	(*S*)-MeO-BIPHEP/PdCl$_2$(CH$_3$CN)$_2$ /AgBF$_4$	2	50%, (*S*)	76
3	(*S*)-SEGPHOS/PdCl$_2$(CH$_3$CN)$_2$ /AgBF$_4$	2 h	44%, (*S*)	86
4	(*S*)-Xyl-BINAP/PdCl$_2$(CH$_3$CN)$_2$ /AgBF$_4$	2 h	80%, (*S*)	79
5	(*S*)-DM-SEGPHOS/PdCl$_2$(CH$_3$CN)$_2$ /AgBF$_4$	2 h	84%, (*S*)	78
6	(*S*)-3,5-DM-MeO-BIPHEP/PdCl$_2$(CH$_3$CN)$_2$ /AgBF$_4$	2 h	83%, (*S*)	88
7	(*S*)-TMO-MeO-BIPHEP/PdCl$_2$(CH$_3$CN)$_2$ /AgBF$_4$	2 h	80%, (*S*)	83
8	(*S*)-DTB-MeO-BIPHEP/PdCl$_2$(CH$_3$CN)$_2$ /AgBF$_4$	2 h	6%, (*R*)	97

[a]Substrate/ligand/PdCl$_2$(CH$_3$CN)$_2$/AgBF$_4$ ratio 100/3/2.5/8 or 100/4/3/10. [b]Determination of ee by GC on 6-TBDMS-2,3-Me-β-CD column unless otherwise indicated. [c]Configuration of the major enantiomer. [d]Determination of ee by reverse phase HPLC after hydrolysis and subsequent derivatization with chiral reagents. Please see the Supporting Information for details.

TABLE 3. COP-Cl-Catalyzed Synthesis of Enantioenriched Vinyloxazoline 8

entry	imidate	catalyst system[a]	time	ee,[b] (*S* or *R*)[c]	yield, %
1	*E*-**7**	(*S*)-COP-Cl	6 d	6%, (*R*)	88[e]
2	*E*-**7**	(*S*)-COP-Cl/$AgBF_4$	1 h	94%, (*R*)	89[e]
3	*Z*-**7**	(*S*)-COP-Cl/ /$AgBF_4$	1 h	14%,[d] (*R*)	97

[a]Substrate/COP-Cl//$AgBF_4$ ratio 100/1/2. [b]Determination of ee by GC on 6-TBDMS-2,3-Me-β-CD column unless otherwise indicated. [c]Configuration of the major enantiomer. [d]Determination of ee by reverse phase HPLC after hydrolysis and subsequent derivatization with chiral reagents.[18] [e]Average yield of two runs. Please see the Supporting Information for details.

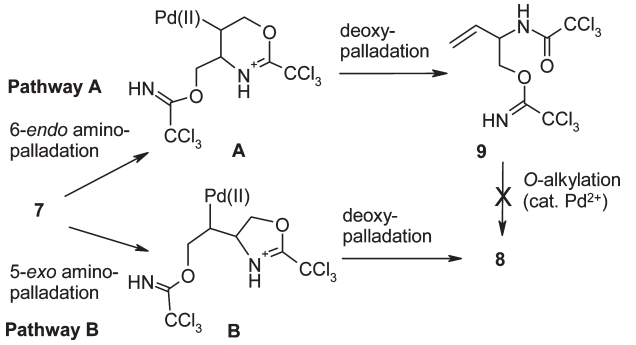
Isomeric bis-imidate *Z*-**7** was a more challenging substrate. Diphosphines (*R*)-BINAP, (*S*)-MeO-BIPHEP, and (*S*)-SEGPHOS as Pd(II) ligands induced low to moderate enantioselectivity (Table 2, entries 1−3). Gratifyingly, ligands bearing *m*-Me- or *m*-MeO-substituted phenyl groups such as (*S*)-Xyl-BINAP, (*S*)-DM-SEGPHOS, (*S*)-3,5-DM-MeO-BIPHEP, and (*S*)-TMO-MeO-BIPHEP allowed synthetically useful enantiomeric excess of enantioenriched vinyloxazoline **8** to be achieved (Table 2, entries 4−7). Increasing the bulk of substituents at the phenyl groups of the ligand, e.g., using (*S*)-DTB-MeO-BIPHEP, resulted in loss of enantioselectivity (Table 2, entry 8).

Overman's catalyst (COP-Cl, Figure 2) used for the enantioselective rearrangement of allylic imidates[13] was also explored for the cyclization of bis-trichloroacetimidates *E*-**7** and *Z*-**7**. Surprisingly, when COP-Cl catalyst was used in its neutral form, bis-imidate *E*-**7** gave nearly racemic vinyloxazoline **8**, and the rearrangement product was not observed (Table 3, entry 1).

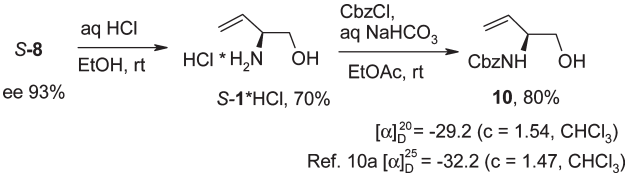
The cationic catalyst derived from COP-Cl exhibited markedly increased activity, leading to vinyloxazoline **8** formation in very high yield from both isomeric bis-imidates *E*-**7** and *Z*-**7** (Table 3, entries 2 and 3). However, high enantioselectivity was observed only when bis-imidate *E*-**7** was used as a substrate (Table 3, entry 2). Unfortunately, the enantioselectivity was low in the case of isomeric bis-imidate *Z*-**7** (Table 3, entry 3). It should be noted that it was difficult to purify the product **8** from the colored minor impurities by chromatography when using COP-Cl as a catalyst precursor in contrast to the Pd(II) catalysts derived from diphosphine ligands.

Two possible mechanistic pathways were considered to explain vinyloxazoline **8** formation (Scheme 2). Pathway A involves metal-catalyzed Overman rearrangement of bis-imidate **7** proceeding by well-established 6-*endo* aminopalladation−deoxypalladation sequence via an intermediate **A**.[19] The rearrangement product **9** theoretically can undergo cyclization to vinyloxazoline **8** promoted by Lewis acidic Pd^{2+} catalyst. To establish if Pathway A is operational, amide **9** was prepared by thermal Overman rearrangement from Z-**7**[20] and was subjected to 20 mol % of the catalytic system—(*S*)-BINAP/$PdCl_2(CH_3CN)_2$/$AgBF_4$ (4/3/10). No reaction of compound **9** was observed under these conditions

SCHEME 2. Possible Pathways for Vinyloxazoline 7 Formation



SCHEME 3. Synthesis of Vinylglycinol Hydrochloride *S*-1·HCl and Its *N*-Cbz Derivative 10



in 3 h time. On the basis of this observation we propose that the product **8** formation may proceed by Pathway B that involves 5-*exo* aminopalladation to form an intermediate **B** followed by the deoxypalladation step in analogy to the mechanism proposed for similar reactions.[13a,21]

It was an interesting finding that both bis-imidates *E*-**7** and *Z*-**7** were transformed to the same vinyloxazoline **8** enantiomer if the catalyst of the same configuration was used. Although the isomerization of imidate *Z*-**7** to *E*-**7** was not observed in the course of the reaction, it cannot be ruled out if proceeding faster than the cyclization.

Finally, we demonstrated that vinyloxazoline **8** can be transformed to vinylglycinol hydrochloride *S*-**1**·HCl under milder conditions than reported previously[4] and it was further transformed to the known *N*-Cbz-protected (*S*)-vinylglycinol **10** (Scheme 3). The value and the sign of optical rotation of compound **10** was in agreement to that reported in the literature.[10a]

In summary we have demonstrated that cationic Pd(II) catalysts generated from axially chiral biphenyl diphospine complexes or from COP-Cl promote enantioselective cyclization of bis-trichloroacetimidates *E*-**7** and *Z*-**7** to highly enantioenriched 2-trichloromethyl-4-vinyloxazoline (**8**). A short and high-yielding synthetic route as well as commercially available catalyst precursors in both enantiomeric forms renders this a practical method for the synthesis of enantioenriched vinylglycinol surrogate **8** possessing high derivatization potential.

Experimental Section

***E*-7.** Molecular sieves 4 Å and DBU (76 mg; 75 μL; 0.5 mmol) were added to a solution of *E*-but-2-en-1,4-diol[22] (**6**) (0.95 g; 10.8 mmol) in THF (15 mL) at room temperature. The solution

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was cooled to −5 °C and to this trichloroacetonitrile (3.75 g; 2.61 mL, 26.0 mmol) was added. The mixture was stirred for 1 h until complete consumption of the starting material (TLC control, eluent hexane/EtOAc = 8/1). The reaction mixture was diluted with light petroleum ether (150 mL) and filtered trough the pad of Celite. The solvent was removed in vacuo and the residue applied to short silica gel column eluting with a mixture of hexane/EtOAc = 8/1 to give *E*-**7** (3.70 g, 91%) as a viscous oil that solidified in the freezer. Mp 40−41 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (2H, s), 6.07−6.09 (2H, m), and 4.85−4.86 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 127.4, 91.2, and 68.4; HRMS (EI) $[M - Cl_3(C{=}O)NH]^+$ calcd for $C_6H_8NOCl_3$ 213.9593, found 213.9535. Elemental Anal. Calcd (%) for $C_8H_8Cl_6N_2O_2$ (376.88): C 25.50, H 2.14, N 7.43. Found: C 25.89, H 2.00, N 7.29.

***R*-8: Representative Procedure.** The catalyst system was prepared by mixing $PdCl_2(CH_3CN)_2$ (65 mg; 0.25 mmol), (*R*)-BINAP (187 mg; 0.30 mmol), $AgBF_4$ (156 mg; 0.80 mmol), and molecular sieves 4 Å in CH_2Cl_2 (50 mL) under Ar atmosphere at room temperature. The suspension was stirred intensively for 20 min and to this was added (*E*)-bis-trihloracetimidate *E*-**7** (3.90 g; 10.3 mmol) in one portion. The suspension was stirred at room temperature for ca. 1 h, until complete consumption of the starting material (TLC control, eluent hexane/EtOAc = 8/1). The reaction mixture was diluted with light petroleum ether (150 mL) and filtered through the pad of Celite. The solvent was removed in vacuo and the residue applied to silica gel column eluting with a mixture of hexane/EtOAc = 8/1 to give *R*-**8** (2.02 g, 92%) as a colorless oil. $[\alpha]^{20}_D$ +102.8 (*c* 4.0, CH_2Cl_2). The spectroscopic characterization was identical with the literature data of the racemic compound.[4] Enantiomeric excess: (a) ee 94% (by derivatization with chiral shift reagent, see the Supporting Information) and (b) ee 90% (GC on a chiral stationary phase). For the determination of absolute configuration see the Supporting Information.

***S*-8.** The synthetic procedure to obtain (*S*)-2-trichloromethyl-4-vinyloxazoline (*S*-**8**) was analogues to the synthesis of enantiomer *R*-**8**. To the catalyst system prepared by mixing $PdCl_2(CH_3CN)_2$ (31 mg; 0.12 mmol), (*S*)-BINAP (99 mg; 0.16 mmol), and $AgBF_4$ (79 mg; 0.41 mmol) in CH_2Cl_2 (8 mL) was added a solution of *E*-**7** (1.50 g; 4.0 mmol) in CH_2Cl_2 (7 mL) to give *S*-**8** (838 mg, 98%), $[\alpha]^{20}_D$ −108.1 (*c* 4.0, CH_2Cl_2), ee 92.6% (GC on a chiral stationary phase)

***S*-1·HCl.** 2-Trichloromethyl-4-vinyloxazoline (*S*-**8**) (200 mg, 0.93 mmol) was dissolved in EtOH (4 mL) and to the solution obtained was added 6 N aqueous HCl (4 mL). After the consumption of starting material was complete (TLC control, ca. 12 h), the reaction mixture was evaporated in vacuo. The residue was suspended in toluene and evaporated, this was repeated several times until crystalline material was obtained. The residue was treated with EtOAc and the precipitate was collected on a filter and dried in vacuo over P_2O_5 to give *S*-**1**·HCl (80.6 mg, 70%) as a crystalline, very hygroscopic compound. The spectroscopic characterization of compound *S*-**1**·HCl was identical with that described in the literature.[23] $[\alpha]_D$ +10.1 (MeOH, *c* 0.42) [lit.[9] for *S*-**10** $[\alpha]_D$ +10.0 (MeOH, *c* 0.53)]. Elemental Anal. Calcd (%) for $C_4H_{10}ClNO\cdot0.5H_2O$ (M = 132.6): C 36.23, H 8.36, N 10.56. Found: C 35.84, H 8.39, N 11.00.

***S*-10.** Vinylglycinol (*S*-**1**·HCl) (63 mg, 0.53 mmol) was dissolved in the biphasic mixture of saturated aqueous $NaHCO_3$ (7 mL) and EtOAc (13 mL). The mixture was cooled to 0 °C and to this was added CbzCl (182 μL, 1.2 mmol) in one portion. The stirring was continued at 0 °C for 2 h and then at room temperature for 6 h and the organic phase was separated. The aqueous phase was extracted with EtOAc (1 × 10 mL) and the combined organic phase was washed with water (2 × 10 mL) then with brine (2 × 10 mL) and dried over Na_2SO_4. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel, eluting with a mixture of light petroleum ether/EtOAc = 1/1 to give product *S*-**10** (91 mg, 80%). The spectroscopic characterization of compound *S*-**10** was identical with that described in the literature.[4] $[\alpha]_D$ −29.2 ($CHCl_3$, *c* 1.54) [lit.[10a] for *S*-**10** $[\alpha]_D$ −32.2 ($CHCl_3$, *c* 1.47)].

Acknowledgment. Funding from Latvian Council of Science is acknowledged. We thank Prof. E. Liepins for assistance in structure determination by NMR spectroscopy.

Supporting Information Available: Determination of the absolute configuration of *R*-**8** and *S*-**8** by derivatization with chiral shift reagents and ^{1}H NMR, ^{13}C NMR, and NOESY NMR spectra of derivatization products; copies of NMR spectra of *E*-**7**; and chromatograms for ee determination by GC on the chiral stationary phase. This material is available free of charge via the Internet at http://pubs.acs.org.

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