An Efficient Synthesis of 4(S)-Hydroxycyclopent-2-enone

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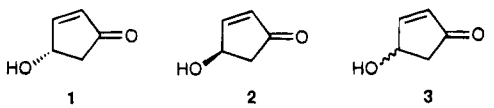
An efficient synthesis of 4(*S*)-hydroxycyclopent-2-enone of high optical purity, a key synthon used in natural product synthesis, is described. The method is suitable for large-scale synthesis.

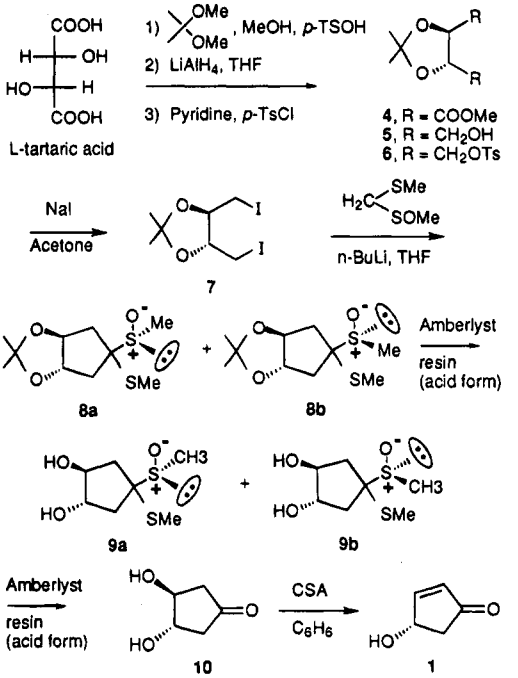
4(*S*)-Hydroxy- and 4(*R*)-hydroxycyclopent-2-enone synthons **1** and **2** have been the key starting materials for a variety of applications, most notably for the synthesis of one of the most popular routes[1] to prostaglandins, natural products such as pentenomycin[2] antibiotics and ophiobolins,[3] as well as marine natural products such as clavulones,[4] antimicrobial diterpene halimedatrial,[5] and antimicrobial and antileukemic didemnenones.[6] As a result, several good syntheses have appeared, which can be classified in two categories: enzymatic[7] and synthetic.[8] We were interested to develop a synthetic procedure for the large-scale preparation of the (*S*)-isomer **1** with high optical purity. The simplest one available, which also afforded good ee (~95%), was the BINAL-H reduction of cyclopentenedione;[8a] however, this approach would have been difficult to adapt to a large-scale synthesis and financially prohibitive. In another interesting procedure, L-tartaric acid was used as a source of chirality. Unfortunately, the optical purity of the target compound **1** was a rather low 85%.[8b] Recently, a novel enantioselective deprotonation of substituted cyclopentene oxide with phenylglycine based ligand was applied for the target compound **1**, with an enantioselectivity of 88%.[7e]



1 **2** **3**

As can be seen in Scheme 1, the essential focus of our synthesis is the dihydroxy ketone **10**. We surmised that this unknown intermediate would allow acidic as well as basic elimination of a hydroxy group to yield the target molecule **1**. In addition, it would be a useful intermediate in the synthesis of other natural products by the appropriate manipulation of the ketone function.

Scheme 1



First, we prepared in kilogram quantities the commercially available but rather expensive bistosyl acetonide **6** in three steps from L-tartaric acid[9a,b] in 83–85% overall yield. Condensation of lithio derivative of methyl methylsulfinyl sulfide with bisiodo compound **7** afforded a 1:1 diastereomeric mixture of **8a** and **8b** due to the formation of (*S*)- and (*R*)-stereoisomers at sulfoxide. Since this group is to be deblocked at the end of the synthesis, separation of these isomers is not necessary. We have succeeded in obtaining one of the stereoisomers by crystallization from ether. One of the most important and delicate steps in the synthesis was the removal of the acetonide and dithioketal protective groups in **8** under mild conditions. Our attempts to deblock the dithioacetal *S*-oxide using $NCS/AgNO_3$, $NBS/AgNO_3$, and $I_2/AgNO_3$ were unsuccessful and resulted in decomposition of the starting material. No reaction occurred under very mild conditions such as using $HgCl_2/CaCO_3$ or TMSCl/NaI, and only starting material was recovered.

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Deblocking of **8** using either I_2, I_2/KI, bis(trifluoroacetoxy)-iodobenzene[11a,b] or MeI in aqueous acetonitrile at room temperature gave the dihydroxy ketone **10** in moderate yields of 35–40%, along with small amounts of the dehydrated product **1**. We checked the enantiomeric purity of this dehydrated product and found it to be partially epimerized. Finally, we were able to obtain dihydroxy ketone **10** in good yield by treatment of **8** with Amberlyst ion-exchange resin (acidic form) in methanol: water (96:4) at room temperature. We found that stepwise cleavage of the acetonide functionality and the dithioacetal sulfoxide group was higher yielding than the one-pot procedure. Purification of the product was easy at both steps. Thus, the treatment of **8** with Amberlyst 15(wet) ion-exchange resin (acidic form) in methanol: water (96:4) at room temperature afforded a stereoisomeric mixture of sulfoxides **9a** and **9b** in 91% yield. A small quantity of this stereoisomeric mixture was easily separated either by column chromatography or preparative thin layer chromatography to give pure stereoisomers **9a** and **9b**. However, from ^{1}H and ^{13}C NMR data absolute configuration of the individual isomers was difficult to determine. The mixture of dithioacetal sulfoxides **9a** and **9b** was again treated with Amberlyst 15-(wet) ion-exchange resin (acidic form) in methanol:water (96:4) at room temperature to give dihydroxy ketone **10** in 63% yield along with 15% of the dehydrated product **1** for an effective yield of 78%. The enantiomeric purity of **1** was found to be >99%. The purified dihydroxy ketone **10** or the mixture of **10** and **1** can be used in the next step.

We then focused on the dehydration of **10** to yield **1** under mildly acidic conditions. Our initial experiment using camphorsulfonic acid (CSA) in acetonitrile at 45 °C gave pure 4(*S*)-hydroxycyclopentenone (**1**) of 99% ee in 75–80% yield. Dilute acid was necessary, hence limiting the scaleup of the reaction. Attempts to perform the dehydration under a more concentrated solution yielded a partially epimerized product. We decided to carry out the dehydration under conditions in which the water is eliminated. We hoped this would prevent epimerization and provide a more appropriate procedure for larger scale preparation. Refluxing **10** and a catalytic amount of CSA in benzene using a Dean–Stark apparatus to remove the water afforded **1** of 99% optical purity and in 77–80% yield. The latter procedure is the method of choice. It is worth mentioning that approximately 60–70% of the conversion is completed in 30 min. The reaction requires 8 h for completion.

Analytical Determination of Optical Purity of the Hydroxy Enone 1

From the outset, we were determined to obtain a very high optical purity for the target synthon **1**. An essential element of the strategy was the development of an easy method to analyze for the optical purity of the various batches of **1**. We decided to focus on an NMR methodology, as some information was already available in the literature.[8a,b] With that in mind, we prepared two derivatives of S-isomer **1** and racemic **3**, namely the acetyl **11a** and **12a** and the Mosher ester **11b** and **12b**.

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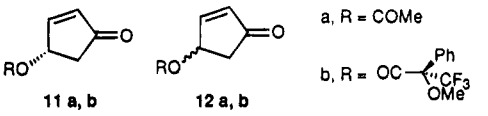

The ^{1}H NMR spectra of compounds **11a** and **12a** in the presence of tris[3-(trifluoromethylhydroxymethylene)-d-camphorato] europium, [Eu(TFC)$_3$], as a chiral shift reagent showed the following:[8b]

In CCl_4 with a ratio of Eu(TFC)$_3$/**11a** or **12a** = 0.3, separated methyl signals could be observed for the racemic compound **12a** as shown in Figure 1. As can be

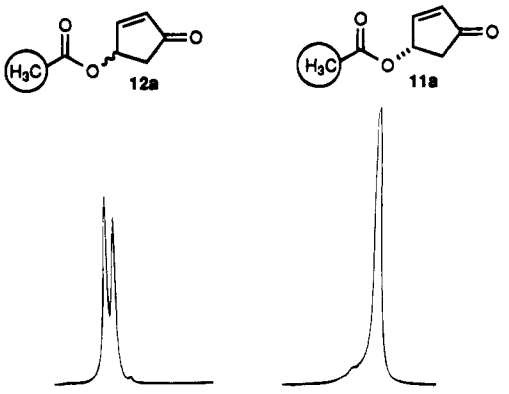

Figure 1. Methyl signals in the ^{1}H NMR spectra of **11a** and **12a** in the presence of Eu(TFC)$_3$.

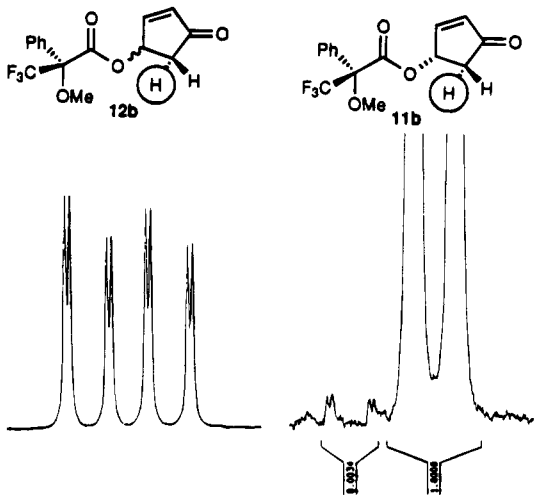

Figure 2. $H_{5\alpha}$ signals in the ^{1}H NMR spectra of **11b** and **12b**.

seen from the comparison of the ^{1}H NMR spectra of the racemic **12a** and optically active compound **11a**, it is difficult to ascertain the precise optical purity of our material. Even though we knew at that point that the optical purity of the material was very high, we decided to prepare Mosher esters **11b** and **12b**.

The diastereomeric esters **11b** and **12b** were prepared from the respective hydroxy enones by acylation with (*R*)-(−)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride in pyridine.[10] As is obvious from Figure 2, the ^{1}H NMR spectrum of the two diastereomeric mixtures exhibited considerably different chemical shifts for the C-5α and C-5β methylene protons of the cyclopentenone ring. The chemical shifts for C-5α and C-5β protons were assigned on the basis of an NOE experiment. The integration of the area under the peaks of C-5α proton shows an

apparent ratio of 99.6% to 0.4% for the two isomers. The ^{19}F NMR spectra of **11b** and **12b** are shown in Figure 3.

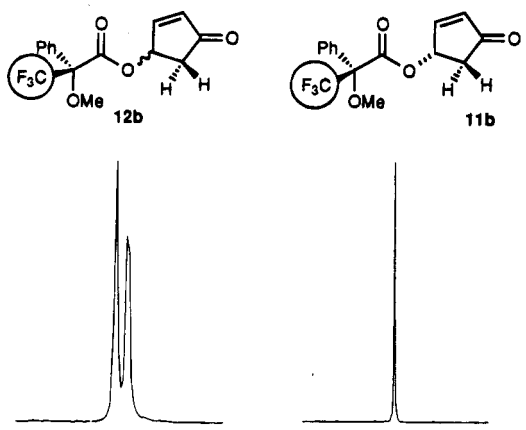

Figure 3. CF_3 signals in the ^{19}F NMR spectra of **11b** and **12b**.

The separation of CF_3 signals in this case is not as good as the ^1H NMR method. The ^1H NMR analysis of the Mosher ester was the method of choice to determine the optical purity of **1**. The limiting factor in our analysis is the optical purity of the commercial Mosher acid chloride, which is >99% ee.

This approach to the synthesis of **1** met our original goal, affords the best optical purity for **1** (> 99%), is easily amenable to large-scale synthesis. In addition, the dihydroxy ketone **10** is a new and potential versatile synthon for the synthesis of natural products containing a 5-membered ring.

Experimental Section

General. ^1H and ^{13}C NMR spectra were recorded on 360-MHz NMR spectrometer, and ^{19}F NMR spectra were recorded on a 400-MHz NMR spectrometer. Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl before use. The other solvents were distilled over calcium hydride prior to use. Amberlyst 15(wet) ion-exchange resin, strongly acidic, macroreticular resin was purchased from Aldrich Chemical Co. For general comments refer to our earlier paper.[11b]

Dimethyl 2,3-*O*-Isopropylidene-L-tartrate (4). This compound was prepared as reported[9b] on a 2 mol scale. The reaction needed 4 days for completion. The product was obtained in nearly quantitative yield as a yellow-colored thick oil: bp 100−110 °C/0.7 mm (lit.[9b] bp 82−90 °C/0.02 mm); ^1H NMR ($CDCl_3$) δ 4.79 (s, 2 H), 3.80 (s, 6 H), 1.47 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 169.99, 113.79, 76.92, 52.72, 26.22.

2,3-*O*-Isopropylidene-L-threitol (5). The reduction of **4** with lithium aluminum hydride was carried out essentially as reported[9b] on a 0.5 mol scale. The product was purified by distillation to afford the pure product **5**: 72 g, yield 88%; bp 110−120 °C/0.5−0.7 mm (lit.[9a] bp 91−93 °C/0.01−0.02 mm); ^1H NMR ($CDCl_3$) δ 3.94 (m, 2 H), 3.71 (m, 4 H), 2.85 (broad s, 2 H); ^{13}C NMR ($CDCl_3$) δ 109.28, 78.19, 62.08, 26.98. The crude product can also be used as such in the next step.

1,4-Ditosyl-2,3-*O*-isopropylidene-L-threitol (6). The ditosylate **6** was prepared as reported[9a] on a 1 mol scale in 90−95% yield. We found that recrystallization of the product from hexane/ether is preferable to that from ethanol: mp 87 °C, (lit.[9a] mp 91.7−92.7 °C); ^1H NMR ($CDCl_3$) δ 7.76 (d, J = 8.2 Hz, 2 H), 7.34 (d, J = 8.1 Hz, 2 H), 4.06 (d, J = 1.1 Hz, 4 H), 3.95 (m, 2 H), 2.43 (s, 6 H), 1.27 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 145.39, 132.12, 130.12, 128.12, 110.95, 75.12, 68.52, 26.84, 22.81.

1,4-Dideoxy-1,4-diiodo-2,3-*O*-isopropylidene-L-threitol (7). To a solution of **6** (173.25 g, 0.375 mol) in dry acetone (2.25 lit.) was added sodium iodide (225 g, 1.5 mol) and the reaction mixture refluxed overnight. The reaction mixture was cooled and filtered and the filtrate evaporated under reduced pressure. The residue was extracted with ethyl acetate (3 × 500 mL). The combined extracts were washed with water, 5% sodium thiosulfate, and brine and then dried and evaporated at reduced pressure. The product was purified by filtration through silica gel (5% ethyl acetate: 95% hexane) to give the pure bisiodo compound **7**: 228.5 g, 94.5% yield; ^1H NMR ($CDCl_3$) δ 3.82 (m, 2 H), 3.36 (s, 4 H), 1.44 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 109.79, 79.70, 27.42, 6.19.

(3*S*,4*S*)-3,4-*O*-Isopropylidene-L-threitolcyclopentanone Dimethyldithioketal *S*-Oxide (8a and 8b). To a −78 °C cooled solution of methyl methylsulfinyl sulfide (79 g, 0.556 mol) in dry THF (2.7 lit.) was added 1.6 M n-BuLi (322 mL, 0.515 mol) dropwise over a period of 2 h. The reaction mixture was stirred at −78 °C for 2 h and then allowed to warm slowly to room temperature. The solution was stirred at room temperature for 2.5 h and became yellow. The reaction mixture was then cooled to −78 °C, and a solution of diiodo compound **7** (85 g, 0.222 mol) in dry THF (800 mL) was added dropwise over a period of 2 h. It was stirred at −78 °C for 2 h and then allowed to warm slowly to room temperature and stirred at room temperature for 3 days. Saturated aqueous ammonium chloride (400 mL) and triethylamine (4 mL) were added to the reaction mixture, the THF layer was separated, and the aqueous layer was extracted with methylene chloride (2 × 200 mL). The combined organic extracts were evaporated at reduced pressure, and the residue obtained was loaded on a silica gel column pretreated with 1% triethylamine in hexane and eluted with 20% acetone in ethyl acetate containing 1% triethylamine to give the pure product **8**, 36.3 g, 76% yield.

(3*S*,4*S*)-3,4-Dihydroxy-L-threitolcyclopentanone Dimethyldithio Ketal *S*-Oxide (9a and 9b). To a solution of **8** (23.5 g, 94 mmol) in methanol (240 mL) and water (10 mL) was added strongly acidic Amberlyst 15(wet) ion-exchange resin (8 g), and the mixture was stirred at room temperature for 15 min. The resin was removed by filtration and washed with methanol (3 × 30 mL), and the filtrate was neutralized with potassium bicarbonate. The solution was then filtered through Florisil and eluted with 10% methanol in methylene chloride (500 mL). The evaporation of the filtrate at reduced pressure gave an oil (20.5 g) that was purified by column chromatography on silica gel (10% methanol:90% methylene chloride) to give 17.9 g (91%) of the pure product **9** as a colorless oil which solidified upon cooling. A 60 mg of the sample of this mixture was separated by preparative TLC to give the pure stereoisomers **9a** and **9b**. The less polar product was obtained: 28 mg; ^1H NMR (CD_3OD) δ 4.09 (m, 1 H), 3.96 (m, 1 H), 2.68 (dd, J = 15.0, 7.2 Hz, 1 H), 2.61 (s, 3 H), 2.47 (dd, J = 14.3, 6.0 Hz, 1H), 2.17 (s, 3H), 2.09 (dd, J = 13.4, 6.3 Hz, 1 H), 1.72 (dd, J = 15.0, 4.4 Hz, 1 H); ^{13}C NMR (CD_3OD) δ 78.6, 78.0,68.7, 40.7, 37.5, 33.0, 13.3. The more polar product was obtained: 28 mg; ^1H NMR (CD_3OD): δ 4.05 (dd, J = 14.6, 7.4 Hz, 1 H), 3.86 (dd, J = 14.6, 7.4 Hz, 1 H), 2.59 (s, 3 H), 2.51 (dd, J = 14.6, 7.8 Hz, 1 H), 2.24 (dd, J = 13.9, 8.9 Hz, 1H), 2.16 (s, 3H), 2.07 (dd, J = 14.6, 6.5 Hz, 1 H), 1.98 (dd, J = 13.9, 6.5 Hz, 1 H); ^{13}C NMR (CD_3OD): δ 78.3, 77.3, 66.5, 40.9, 36.3, 33.1, 12.8.

(3*S* 4*S*)-3,4-Dihydroxycyclopentanone (10). To a solution of **9** (14.6 g, 69.5 mmol) in methanol (144 mL) and water (6 mL) was added strongly acidic Amberlyst 15(wet) ion-exchange resin (29 g), and the mixture was stirred at room temperature for 1.5 h. The resin was removed by filtration and washed with methanol (3 × 20 mL), and the filtrate was neutralized with potassium bicarbonate. The solution was then filtered to remove any excess solid potassium bicarbonate and then passed through florisil and eluted with 10% methanol in methylene chloride (500 mL). The evaporation of the filtrate at reduced pressure gave an oil that was dissolved in benzene (50 mL), evaporated (to remove any traces of water), and then purified by column chromatography on silica gel (10% methanol: 90% methylene chloride) to give **10** (5.1 g, 63%) as a colorless oil: IR (neat) 1740.4 cm^{-1} (C=O), 3375.4 cm^{-1} (OH); ^1H NMR (d_6-acetone) δ 4.44 (m, 2H), 4.34 (broad s, 2H), 2.55 (dd, J = 17.6, 4.6 Hz, 2H), 2.09 (d, J = 18.1 Hz, 2 H); ^{13}C NMR (d_6-

acetone) δ 216.5, 74.8, 44.9; HREIMS *m/z* calcd for $C_5H_8O_3$ (M^+) 116.0473, found 116.0469. In addition, 0.982 g (15%) of **1** is isolated.

(*S*)-4-Hydroxycyclopent-2-en-1-one (1). The mixture dihydroxycyclopentanone **10** (6.874 g, 59 mmol) and *dl*-10-camphorsulfonic acid (130 mg, 0.56 mmol) in benzene (700 mL) was refluxed for 4 h using a Dean–Stark apparatus. After 4 h the solution was concentrated to approximately 400 mL by removing the solvent from Dean Stark apparatus, and it was further refluxed for 3 more h (total reflux time 8 h). The solution was cooled and neutralized with $NaHCO_3$, filtered, and evaporated under reduced pressure. Purification of the residue by chromatography using methylene chloride:methanol (90:10) afforded **1** (4.47 g, 77%) as a colorless oil: $[\alpha]_D = -77°$ ($c = 1.0$, $CHCl_3$) and $[\alpha]_D = -90°$ ($c = 1.507$, MeOH); IR (neat) 1709.7 (C=O), 3400 (OH), 1600 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ 7.58 (dd, $J = 5.6$, 2.3 Hz, 1 H), 6.18 (dd, $J = 5.7$, 1.2 Hz, 1H), 5.01 (br s, 1H), 3.9 (m, 1H), 2.74 (dd, $J = 18.5$, 6.0 Hz, 1 H), 2.24 (dd, $J = 18.6$, 2.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 207.3, 163.90, 134.88, 70.24, 44.23.

(±)-4-Hydroxycyclopent-2-en-1-one (3). 4-Hydroxycyclopent-2-en-1-one **3** was prepared by a modified literature procedure.[12] 4-Cyclopentene-1,3-dione (0.5 g, 5.6 mmol) was added to a solution of $CeCl_3$ (9 mL, 0.4 M) at 0 °C. The reaction mixture was stirred at room temperature for 5 min, and then sodium borohydride (138 mg, 3.6 mmol) was added to the mixture over 10 min. The stirring was continued at room temperature for 5 h, and after the mixture was cooled to 0 °C, ether (30 mL) was added very slowly. The mixture was stirred at room temperature for 1 h and filtered. After the solvent was evaporated, the residue was purified by chromatography, using EtOAc/hexane (80/20) as the eluent, to afford racemic **3** (215 mg, 40%).

(*S*)-4-Acetoxycyclopent-2-en-1-one (11a) and (±)-4-Acetoxycyclopent-2-en-1-one (12a). Acetyl derivative **11a** was prepared from **1** using acetic anhydride in pyridine in 80% yield as a colorless oil: ^1H NMR ($CDCl_3$) δ 7.52 (dd, $J = 5.6$, 2.3 Hz, 1H), 6.30 (d, $J = 5.7$ Hz, 1 H), 5.8 (m, 1 H), 2.77 (dd, $J = 18.6$, 6.4 Hz, 1 H), 2.27 (dd, $J = 18.7$, 2.1 Hz, 1 H), 2.09 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 204.4, 171.10 158.65, 136.73, 71.63, 40.7, 20.57. Similarly, acetyl derivative **12a** was prepared from **3** in 80% yield.

Mosher Esters of (*S*)-4-Hydroxycyclopent-2-en-1-one (11b) and (*RR*+*RS*)-4-Hydroxycyclopent-2-en-1-one (12b). Mosher ester **11b** was prepared from **1** by acylation with (R)-(−)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride in pyridine[10] on a 0.04-mmol scale to give a colorless oil: ^1H NMR ($CDCl_3$) δ 7.63 (dd, $J = 5.7$, 2.3 Hz, 1 H), 7.47 (m, 5 H), 6.41 (d, $J = 5.7$ Hz, 1 H), 6.1 (m, 1 H), 3.56 (s, 3 H), 2.9 (dd, $J = 18.8$, 6.5 Hz, 1 H), 2.32 (dd, $J = 18.7$, 2.0 Hz, 1 H). Similarly, (*RR*+*RS*) Mosher ester derivative **12b** was prepared from **3**. The splitting pattern of $H_{5\alpha}$ in the ^1H NMR is shown in Figure 2.

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Supporting Information Available: ^1H NMR spectra of compounds **1**, **7**, **9a**,**b**, and **10** and ^{13}C NMR spectra of compounds **9a** and **9b** (7 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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