The First Asymmetric Cyclopropanation Reactions Involving a Stable Carbene

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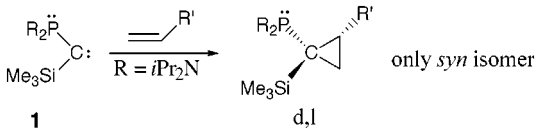
Introduction

The search for efficient methods for preparation of enantiomerically pure cyclopropanes continues to be of primary importance. Indeed, chiral cyclopropanes play an important role in bioorganic chemistry[1] and are useful building blocks in organic synthesis since they may be converted to a variety of cyclic and acyclic compounds.[2] The most efficient methods for the asymmetric synthesis of cyclopropanes are the Simmons−Smith reaction[3] and metal-catalyzed decomposition of diazo compounds in the presence of alkenes.[4] Although these methods can provide substituted cyclopropanes with a high level of enantioselectivity, they are generally not highly diastereoselective; thus, a mixture of cis and trans isomers are obtained.[3,4,5] After having demonstrated that stable singlet nucleophilic (phosphino)(silyl)carbenes **1**[6] give cyclopropanation reactions with monosubstituted olefins with a total syn diastereoselectivity (with respect to the phosphino group) (Scheme 1),[7] we report here preliminary results concerning the asymmetric version of this reaction.

Results and Discussion

The reaction of the carbene **1** with (−)-menthyl acrylate **2a**, at −78 °C, cleanly yields the corresponding cyclopropanes as a mixture of two diastereomers **3a** and **3′a** (de = 23%) as indicated by ^{31}P NMR spectroscopy (δ = +79.2 and +78.4) prior to any purification. After addition of elemental sulfur the corresponding diastereomers **4a** and **4′a** were separated (76% total yield) by column chromatography on silica gel (Scheme 2). Both compounds were fully characterized including an X-ray diffraction analysis[8] for the major diastereomer **4a**, which revealed the *S*-absolute configuration of the two newly formed chiral centers.

Scheme 1



1 d,l

A better diastereomeric excess (de = 52%) was observed with 4(*S*)-*N*-acryloyl-4-isopropyl-2-oxazolidinone **2b**. After thiolation, both diastereomers **4b** and **4′b** were separated in moderate yields (40% total yield) and structurally characterized. The X-ray diffraction analyses[8] confirm the syn diastereoselectivity of the cyclopropanation reaction, and the *S*- and *R*-absolute configurations at the two newly formed chiral centers of the major and minor isomers **4b** and **4′b**, respectively.

The use of Oppolzer's camphor sultam[9] as a chiral auxiliary gave the best results with regard to asymmetric induction (de = 87%). However, in this case we observed some polymerization of the olefin **2c**, and the major isomer **4c** was isolated in only 15% yield. An X-ray diffraction study[8] again revealed the *S*-absolute configuration of the newly formed chiral centers. The dramatic improvement of the asymmetric induction can be attributed to the structure of the substrate **2c**. Similar olefins have been studied in the solid state and have been shown to exhibit a *syn*-planarity between the CC-double bond and the carbonyl group which is anti to the SO_2-group.[9a] Thus, the carbene attacks the olefin with the phosphorus group on the same side as the carbonyl group (syn diastereoselectivity)[7] and at the *si*-face, which is by far the less hindered (*S,S*-absolute configuration) (Figure 1).

Cleavage of the chiral auxiliary and the trimethylsilyl group was achieved in the case of the menthyl derivatives. Saponification of a methanol solution of each of the diastereomers **4a** and **4′a** (NaOH, reflux, 3 days) gave, cleanly, the corresponding enantiomers **5(S,S)** and **5(R,R)** (δ^{31}P: +76.4), respectively; (−)-menthol was recovered in almost quantitative yield (90%). Both enantiomers **5(S,S)** (α_D = −12) and **5(R,R)** (α_D = +10) were isolated as oily compounds (Scheme 3).

To improve the asymmetric induction, cyclopropanation reactions using stable chiral carbenes are under active investigation.

Experimental Section

General. All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques. Dry, oxygen-free solvents were employed. ^{1}H, ^{13}C, and ^{31}P NMR

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(8) Results of the X-ray crystallographic studies for compounds **4a**, **4b**, **4′b**, and **4c**, are included in the Supporting Information.
(9) (a) Oppolzer, W.; Chapuis, C.; Bernardinelli, G. *Helv. Chim. Acta* **1984**, *67*, 1397. (b) Oppolzer, W. *Pure Appl. Chem.* **1988**, *60*, 39.

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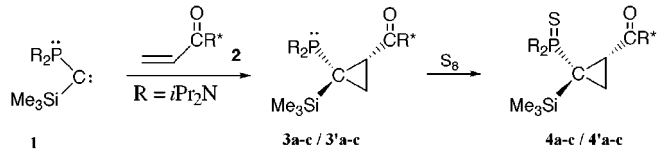
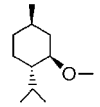
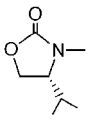
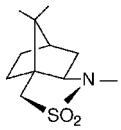
Scheme 2



R*	compounds	yield, %[a]	syn, %[b]	de, %[c]	Abs. config.[d]
	**4a / 4'a**	76	100	23	(S,S)
	**4b / 4'b**	40	100	52	(S,S)
	**4c / 4'c**	15	100	87	(S,S)

[a] Total isolated yield. [b] Syn slectivity determined by ^{31}P NMR spectroscopy and X-ray diffraction analysis (**4a**−**c** and **4′b**). [c] Ratio 4:4′ determined by ^{31}P NMR spectroscopy. [d] Absolute configuration of the ring carbons for the major isomers **4a**−**c**.

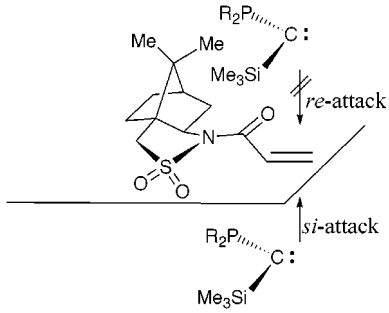
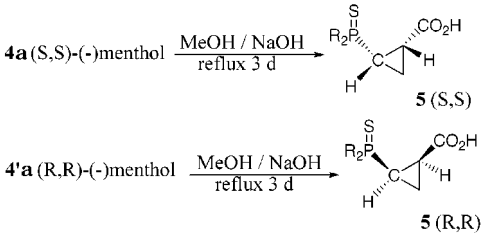


Figure 1. Preferential attack of phosphino(silyl)carbene **1**.

Scheme 3



spectra were recorded on Bruker AC80, AC200, WM250 or AMX400 spectrometers. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external standard. ^{31}P NMR downfield chemical shifts are expressed with a positive sign, in ppm, relative to external standards of 85% H_3PO_4. Infrared spectra were recorded on a Perkin-Elmer FT-IR Spectrometer 1600. Mass spectra were obtained on a Ribermag R10 10E instrument.

General Procedure for Cycloaddition Reactions with Carbene 1. To a pentane solution (3 mL) of carbene **1** (0.1 g, 0.3 mmol) was added at −78 °C 3 equiv of alkene. The resulting mixture was stirred at room temperature, and the progress of reaction was monitored by ^{31}P NMR spectroscopy. When the reaction was complete the solution mixture was evaporated under vacuum, and the phosphinocyclopropanes **3** were analyzed without any further purification. Treatment of a THF solution of phosphinocyclopropanes **3** with an excess of elemental sulfur gave the corresponding thioxo derivatives **4**, which were purified by column chromatography on silica gel. Chemical yields and diastereomeric excesses are shown in Scheme 2. Spectral and analytical data are listed below.

4a (major diastereomer): mp 143−145 °C; $[\alpha_D]^{20} = -18.6$; ^{31}P{^{1}H} NMR (C_6D_6): δ 95.8; ^{1}H NMR ($CDCl_3$): δ 0.25 (s, 9 H, $SiCH_3$), 0.79 (d, $^3J_{HH} = 6.8$ Hz, 3 H, CH_3), 0.89 (d, $^3J_{HH} = 6.4$ Hz, 3 H, CCHCH_3), 0.90 (d, $^3J_{HH} = 6.4$ Hz, 3 H, CCHCH_3), 1.21 (ddd, $^3J_{HH} = 4.0$ Hz, $^2J_{HH} = 8.4$ Hz, $^3J_{PH} = 12.4$ Hz, 1 H, CH_{ring}), 1.35 (d, $^3J_{HH} = 6.8$ Hz, 6 H, NCHCH_3), 1.36 (d, $^3J_{HH} = 6.8$ Hz, 6 H, NCHCH_3), 1.43 (d, $^3J_{HH} = 6.8$ Hz, 6 H, NCHCH_3), 1.47 (d, $^3J_{HH} = 6.8$ Hz, 6 H, NCHCH_3), 1.65 (m, 4 H, CH_2), 1.87 (ddd, $^2J_{HH} = {}^3J_{HH} = 8.4$ Hz, $^3J_{PH} = 16.4$ Hz, 1 H, CH_{ring}), 2.04 (m, $^3J_{PH} = 22.0$ Hz, 1 H, CH_{ring}), 2.25 (m, CCHCH$_3$ and CH_2CHO), 4.05 (sept d, $^3J_{HH} = 6.8$ Hz, $^3J_{PH} = 14.8$ Hz, 2 H, NCHCH$_3$), 4.19 (sept d, $^3J_{HH} = 6.8$ Hz, $^3J_{PH} = 12.0$ Hz, 2 H, NCHCH$_3$), 4.74 (td, $^3J_{HH} = 10.4$ and 4.0 Hz, 1 H, OCH); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 1.9 (s, $SiCH_3$), 16.8 (s, CHCHCH$_3$), 18.1 (s, CHCHCH$_3$), 21.4 (s, CH$_{2ring}$), 22.6 (s, CH$_2$CHCH$_3$), 23.8 (s, CHCH$_2$$CH_2$), 24.2 (d, $^3J_{PC} = 3.3$ Hz, NCHCH$_3$), 24.8 (s, NCHCH$_3$), 25.7 (d, $^3J_{PC} = 5.7$ Hz, NCHCH$_3$), 26.4 (s, CH$_2$$CHCH_3$), 31.9 (s, CH$CHCH_3$), 32.3 (s, CH$_{ring}$), 34.9 (s, CH$CH_2CH_2$), 40.3 (s, CHCHO), 47.5 (s, CH$_2$CHO), 47.7 (d, $^2J_{PC} = 4.7$ Hz, CH$_3$$C$HN), 48.1 (d, $^2J_{PC} = 6.4$ Hz, CH$_3$$C$HN), 75.0 (s, OCH), 170.1 (d, $^3J_{PC} = 8.0$ Hz, C═O). Anal. Calcd for $C_{29}H_{59}N_2O_2PSSi$: C, 62.32; H, 10.64; N, 5.01. Found: C, 62.38; H, 10.71; N, 4.98.

4′a (minor diastereomer): mp 150−151 °C; $[\alpha_D]^{20} = -30.7$; ^{31}P{^{1}H} NMR (C_6D_6): δ 93.6; ^{1}H NMR ($CDCl_3$): δ 0.24 (s, 9 H, $SiCH_3$), 0.78 (d, $^3J_{HH} = 6.8$ Hz, 3 H, CH_3), 0.88 (d, $^3J_{HH} = 6.8$ Hz, 3 H, CCHCH_3), 0.91 (d, $^3J_{HH} = 6.8$ Hz, 3 H, CCHCH_3), 1.24 (ddd, $^3J_{HH} = 4.4$ Hz, $^2J_{HH} = 8.0$ Hz, $^3J_{PH} = 10.4$ Hz, 1 H, CH_{ring}), 1.35 (d, $^3J_{HH} = 6.8$ Hz, 12 H, NCHCH_3), 1.44 (d, $^3J_{HH} = 6.8$ Hz, 6 H, NCHCH_3), 1.49 (d, $^3J_{HH} = 6.8$ Hz, 6 H, NCHCH_3), 1.66 (m, 4 H, CH_2), 1.91 (m, $^3J_{PH} = 18.4$ and 21.2 Hz, 2 H, CH_{ring}), 2.11 (sept broad, $^3J_{HH} = 6.8$ Hz, 1 H, CCHCH$_3$), 2.38 (d broad, $^3J_{HH} = 10.8$ Hz, 2 H, CH_2CHO), 4.01 (sept d, $^3J_{HH} = 6.8$ Hz, $^3J_{PH} = 14.4$ Hz, 2 H, NCHCH$_3$), 4.13 (sept d, $^3J_{HH} = 6.8$ Hz, $^3J_{PH} = 12.0$ Hz, 2 H, NCHCH$_3$), 4.61 (td, $^3J_{HH} = 10.8$ and 4.4 Hz, 1 H, OCH); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 1.8 (s, $SiCH_3$), 16.9 (s, CHCHCH$_3$), 17.4 (s, CHCHCH$_3$), 19.2 (d, $^1J_{PC} = 104.6$ Hz, PC), 21.5 (s, CH$_{2ring}$), 22.6 (s, CH$_2$CHCH$_3$), 23.8 (s, CHCH$_2$$CH_2$), 24.1 (s, NCH$CH_3$), 24.6 (s, NCH$CH_3$), 25.9 (d, $^3J_{PC} = 6.0$ Hz, NCHCH$_3$), 26.0 (d, $^3J_{PC} = 4.5$ Hz, NCHCH$_3$), 26.4 (s, CH$_2$$CHCH_3$), 31.8 (s, CH$CHCH_3$), 33.3 (s, CH$_{ring}$), 34.9 (s, CH$CH_2CH_2$), 40.4 (s, CHCHO), 47.3 (s, CH$_2$CHO), 47.8 (d, $^2J_{PC} = 5.0$ Hz, CH$_3$$C$HN), 76.0 (s, OCH), 170.7 (d, $^3J_{PC} = 8.0$ Hz, C═O). Anal. Calcd for $C_{29}H_{59}N_2O_2PSSi$: C, 62.32; H, 10.64; N, 5.01. Found: C, 62.44; H, 10.68; N, 5.08.

4b (major diastereomer): mp 170−171 °C; $[\alpha_D]^{20} = -79$; ^{31}P-{^{1}H} NMR (C_6D_6): δ 93.2; ^{1}H NMR ($CDCl_3$): δ 0.31 (s, 9 H,

$SiCH_3$), 0.96 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, CCHCH_3), 0.97 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, CCHCH_3), 1.38 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, NCHCH_3), 1.39 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, NCHCH_3), 1.47 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, NCHCH_3), 1.50 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, NCHCH_3), 1.58 (ddd, $^3J_{HH}$ = 5.2 Hz, $^2J_{HH}$ = 8.4 Hz, $^3J_{PH}$ = 13.6 Hz, 1 H, CH_{ring}), 2.12 (ddd, $^3J_{HH}$ = 8.0 Hz, $^2J_{HH}$ = 8.4 Hz, $^3J_{PH}$ = 16.8 Hz, 1 H, CH_{ring}), 2.27 (ddd, $^2J_{HH}$ = 5.2 Hz, $^3J_{HH}$ = 8.0 Hz, $^3J_{PH}$ = 22.8 Hz, 1 H, CH_{ring}), 2.52 (sept d, $^3J_{HH}$ = 6.8 Hz, $^3J_{HH}$ = 3.6 Hz, 1 H, CCHCH$_3$), 4,02 (sept d, $^3J_{HH}$ = 6.8 Hz, $^3J_{PH}$ = 15.6 Hz, 2 H, NCHCH$_3$), 4.20 (dd, $^2J_{HH}$ = 0.8 Hz, $^3J_{HH}$ = 8.0 Hz, 1 H, OCH_2), 4,27 (sept d, $^3J_{HH}$ = 6.8 Hz, $^3J_{PH}$ = 12.4 Hz, 2 H, NCHCH$_3$), 4.34 (t, $^3J_{HH}$ = $^2J_{HH}$ = 8.0 Hz, 1 H, OCH_2), 4.38 (ddd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 3.6 Hz, 1 H, OCH$_2$CH); ^{13}C{^{1}H} NMR ($CDCl_3$): _ 1.4 (s, $SiCH_3$), 15.1 (s, CCHCH$_3$), 18.3 (s, CCHCH$_3$), 20.0 (d, $^1J_{PC}$ = 95.0 Hz, PC), 21.7 (s, CH_{2ring}), 23.5 (s, NCHCH$_3$), 24.1 (s, NCHCH$_3$), 25.2 (d, $^3J_{PC}$ = 6.0 Hz, NCHCH$_3$), 25.4 (d, $^3J_{PC}$ = 5.0 Hz, NCHCH$_3$), 29.0 (s, CCHCH$_3$), 32.4 (d, $^2J_{PC}$ = 6.0 Hz, CH_{ring}), 47.4 (d, $^2J_{PC}$ = 5.0 Hz, CHN), 47.5 (d, $^2J_{PC}$ = 7.0 Hz, CH$_3$$C$HN), 60.9 (s, OCH$_2$$C$HN), 63.9 (s, OCH$_2$), 154.6 (s, O(N)C═O), 169.6 (s, C(N)C═O). Anal. Calcd for $C_{25}H_{50}N_3O_3PSSi$: C, 56.46; H, 9.48; N, 7.90. Found: C, 56.52; H, 9.53; N, 7.88.

4′b (minor diastereomer): mp 150−152 °C; $[\alpha_D]^{20}$ = −65; ^{31}P{^{1}H} NMR (C_6D_6): δ 91.5; ^{1}H NMR ($CDCl_3$): δ 0.32 (s, 9 H, $SiCH_3$), 0.94 (d, $^3J_{HH}$ = 6.4 Hz, 3 H, CCHCH_3), 0.96 (d, $^3J_{HH}$ = 6.4 Hz, 3 H, CCHCH_3), 1.38 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, NCHCH_3), 1.39 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, NCHCH_3), 1.46 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, NCHCH_3), 1.51 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, NCHCH_3), 1.54 (ddd, $^3J_{HH}$ = 4.8 Hz, $^2J_{HH}$ = 8.0 Hz, $^3J_{PH}$ = 12.4 Hz, 1 H, CH_{ring}), 2.05 (ddd, $^3J_{HH}$ = 4.8 Hz, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 22.8 Hz, 1 H, CH_{ring}), 2.53 (m, 2 H, CCHCH$_3$ and CH_{ring}), 4,10 (m, 2 H, NCHCH$_3$), 4,17 (sept d, $^3J_{HH}$ = 6.8 Hz, $^3J_{PH}$ = 12.0 Hz, 2 H, NCHCH$_3$), 4.21 (dd, $^3J_{HH}$ = 2.4 Hz, $^3J_{HH}$ = 8.8 Hz, 1 H, OCH_2), 4.32 (t, $^3J_{HH}$ = $^2J_{HH}$ = 8.4 Hz, 1 H, OCH_2), 4.45 (ddd, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 2.4 Hz, $^3J_{HH}$ = 3.6 Hz, 1 H, OCH$_2$CH); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 1.7 (s, $SiCH_3$), 14.4 (s, CCHCH$_3$), 18.1 (s, CCHCH$_3$), 18.8 (s, CH_{2ring}), 23.7 (s, NCHCH$_3$), 24.1 (d, $^1J_{PC}$ = 86.0 Hz, PC), 24.2 (s, NCHCH$_3$), 25.1 (d, $^3J_{PC}$ = 5.0 Hz, NCHCH$_3$), 25.3 (d, $^3J_{PC}$ = 6.0 Hz, NCHCH$_3$), 28.4 (s, CCHCH$_3$), 33.5 (d, $^2J_{PC}$ = 5.0 Hz, CH_{ring}), 47.6 (d, $^2J_{PC}$ = 5.0 Hz, CH$_3$$C$HN), 60.2 (s, OCH$_2$$C$HN), 63.5 (s, OCH$_2$), 154.3 (s, O(N)C═O), 169.5 (d, $^3J_{PC}$ = 10.0 Hz, C(N)C═O). Anal. Calcd for $C_{25}H_{50}N_3O_3PSSi$: C, 56.46; H, 9.48; N, 7.90. Found: C, 56.50; H, 9.51; N, 7.92.

4c (major diastereomer): mp 175−176 °C; $[\alpha_D]^{20}$ = −44.4; ^{31}P{^{1}H} NMR (C_6D_6): δ 95.7; ^{1}H NMR ($CDCl_3$): δ 0.24 (s, 9 H, $SiCH_3$), 1.20 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, NCHCH_3), 1.22 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, NCHCH_3), 1.24 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, NCHCH_3), 1.33 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, NCHCH_3), 1.50 (ddd, $^2J_{HH}$ = 5.0 Hz, $^3J_{HH}$ = 7.8 Hz, $^3J_{PH}$ = 21.6 Hz, 1 H, CH_{ring}), 1.76 (ddd, $^2J_{HH}$ = 5.0 Hz, $^3J_{HH}$ = 3.7 Hz, $^3J_{PH}$ = 23.4 Hz, 1 H, CH_{ring}), 2.49 (ddd, $^3J_{HH}$ = 3.7 Hz, $^3J_{HH}$ = 7.8 Hz, $^3J_{PH}$ = 12.2 Hz, 1 H, CH_{ring}), 3.64 (sept d, $^3J_{HH}$ = 6.8 Hz, $^3J_{PH}$ = 19.2 Hz, 2 H, NCHCH$_3$), 4.50 (m, 2 H, NCHCH$_3$), the protons of sultam were omitted for clarity; ^{13}C{^{1}H} NMR ($CDCl_3$): δ 1.8 (s, $SiCH_3$), 17.8 (d, $^1J_{PC}$ = 91.0 Hz, PC), 20.5 (s, CCH$_3$), 21.7 (s, CCH$_3$), 22.0 (s, CH$_{2ring}$), 23.8 (s, CHCH$_2$$CH_2$), 24.1 (s, NCH$CH_3$), 24.5 (s, NCH$CH_3$), 25.6 (d, $^3J_{PC}$ = 6.0 Hz, NCHCH$_3$), 25.7 (d, $^3J_{PC}$ = 4.6 Hz, NCHCH$_3$), 27.0 (s, CCH2CH$_2$C), 32.9 (d, $^2J_{PC}$ = 7.3 Hz, CH_{ring}), 33.8 (s, CCH2CH$_2$C), 37.4 [s, CH$_2$SO$_2$], 45.5 [s, CCH$_2$CHN], 47.8 (d, $^2J_{PC}$ = 4.8 Hz, CH$_3$$C$HN), 48.1 [s, (CH$_3$)$_2$$C$C(CH$_2$)$_2$], 48.2 (d, $^2J_{PC}$ = 6.7 Hz, CH$_3$$C$HN), 48.5 [s, (CH$_3$)$_2CC$(CH$_2$)$_2$], 54.0 (s, CCH$_2SO_2$), 66.7 (s, CHN), 169.0 (d, $^3J_{PC}$ = 8.0 Hz, C═O). Anal. Calcd for $C_{29}H_{56}N_3O_3PS_2Si$: C, 56.37; H, 9.13; N, 6.80. Found: C, 56.42; H, 9.15; N, 6.75.

5-(R,R)**:** $[\alpha_D]^{20}$ = 10; **5**-(S,S)**:** $[\alpha_D]^{20}$ = −12; ^{31}P{^{1}H} NMR ($CDCl_3$): δ 76.4; ^{1}H NMR ($CDCl_3$): δ 1.21 (d, $^3J_{HH}$ = 6.5 Hz, 6 H, NCHCH_3), 1.23 (d, $^3J_{HH}$ = 6.5 Hz, 6 H, NCHCH_3), 1.32 (d, $^3J_{HH}$ = 6.5 Hz, 12 H, NCHCH_3), 1.44 (m, 1 H, CH_{ring}), 1.62 (m, 1 H, CH_{ring}), 1.73 (m, 1 H, CH_{ring}), 2.25 (m, 1 H, CH_{ring}), 3.73 (sept d, $^3J_{HH}$ = 6.5 Hz, $^3J_{PH}$ = 11.9 Hz, 4 H, NCHCH$_3$), 9.3 (s broad, 1 H, OH); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 22.8 (d, J_{PC} = 22.5 Hz, CH_{ring}), 22.9, 23.1, 23.7, 24.0 (s, NCHCH$_3$), 29.5 (s, CH$_{2ring}$), 46.5 (d, J_{PC} = 5.9 Hz, CH$_3$$C$HN), 46.6 (d, J_{PC} = 5.0 Hz, CH$_3$$C$HN), 179.1 (d, $^3J_{PC}$ = 3.0 Hz, C═O); MS (EI) 348 (M^+).

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Supporting Information Available: X-ray crystallographic studies for compounds **4a**, **4b**, **4′b**, and **4c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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