Preparation of Chiral *N*-Vinyl Oxazolidinones by a Simple General Procedure

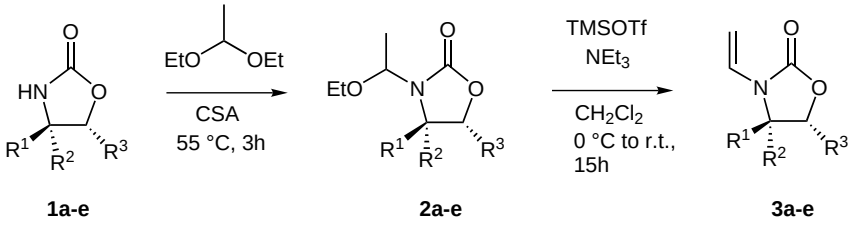
Catherine Gaulon, Robert Dhal,* Gilles Dujardin

Laboratoire de Synthèse Organique, UCO2M, UMR 6011 CNRS, Université du Maine, 72085, Le Mans,Cedex 9, France
Fax +33(2)43833902; E-mail: rdhal@univ-lemans.fr

Received 22 May 2003; revised 3 July 2003

Abstract: A high yielding, general, and practical procedure for the *N*-vinylation of 2-oxazolidinones via TMSOTf-promoted dehydroalkoxylation of *N*,*O*-acetals is described.

Key words: oxazolidinone, *N*-vinylation, TMSOTf, *N*,*O*-acetal



1a-e **2a-e** **3a-e**

Scheme 1

N-Vinyl-2-oxazolidinones derived from enantiopure β-aminoalcohols have attracted much interest in asymmetric Pd-promoted carboacylations and alkylations,[1] [2+2]-photocycloadditions[2] and cyclopropanations.[3a,b] In connection with our ongoing studies concerning the dienophilicity and dipolarophilicity of such chiral *N*-vinylcarbamates, we were interested in developing a general and reliable preparation of these compounds. Direct N-vinylation of 2-oxazolidinones has already been described by using an excess of low-boiling vinyl ether catalyzed by mercuric salts, with low yields (35–55%).[4] Hegedus and co-workers reported a one-pot method starting from the corresponding β-aminoalcohol based on the formation of an aminocarbene complex and its subsequent base-mediated treatment with diphenyl carbonate.[1a] This original procedure proved to give high yields but is somewhat complicated. More recently, an efficient route to aryl *N*-vinyl-2-oxazolidinones was proposed by Akiba and co-workers[3] and was based on the acid-catalyzed transacetalization of acetaldehyde dimethylacetal with 2-oxazolidinones, producing an *N*,*O*-acetal which in turn underwent thermal elimination of methanol.[5] Although practical, this method required appropriate elimination conditions for each compound and proceeded with moderate to good yields. For this dehydroalkoxylation step, we searched for a general method, which could be applied to a range of *N*,*O*-acetals under non-thermal conditions. Bach and Brummerhop demonstrated the efficiency of TMSOTf in combination with Hünig base to promote the dehydromethoxylation of 2-methoxy-*N*-carbomethoxypyrrolidines into the corresponding dihydropyrrols.[6] On this basis, we recently described[7] an efficient access to *N*-vinyl-2-oxazolidinone from the corresponding *N*,*O*-acetal by using such Gassman-type conditions (TMSOTf/Et_3N).[8] We now report the high-yielding preparation of representative chiral *N*-vinyl-2-oxazolidinones by such a two-step, mercury-free, general procedure.

As in the achiral series, the *N*,*O*-acetals **2a**–**e** were quantitatively prepared from the corresponding 2-oxazolidinones **1a**–**e** by treatment with acetaldehyde diethyl acetal using camphorsulfonic acid[9] as the catalyst (Scheme 1). Minor improvements were made to Akiba's procedure concerning the catalyst ratio (reduced to 5%) and the reaction time (reduced to 3 h).

In order to prepare the chiral *N*-vinyloxazolidinones **3a**–**e**, we successfully applied the eliminative conditions that proved efficient to generate chiral vinyl ethers from mixed *O*,*O*-acetals to the *N*,*O*-acetals **2a**–**e**.[10] Treatment of the *N*,*O*-acetal in solution in dichloromethane with triethylamine (1.5 equiv) and then trimethylsilyl trifluoromethanesulfonate (1.3 equiv) led in each case to a highly regiocontrolled elimination reaction, no *N*-silyl oxazolidinone that could result from the other elimination pathway was detected in the crude product. Another point of interest was the optimal rate of dehydroalkoxylation observed in these reactions. Because of the completion of such reactions, the purified *N*-vinyl oxazolidinones **3** were obtained in high yields and free from the starting *N*,*O*-acetal **2**. Such contamination can be a serious drawback,[11] since compounds **2** and **3** proved to be difficult to separate from each other in most cases.

SYNTHESIS 2003, No. 14, pp 2269–2272
Advanced online publication: 24.09.2003
DOI: 10.1055/s-2003-41443; Art ID: T04703SS.pdf

The level of enantiopurity of *N*-vinyloxazolidinones **3** was accurately determined by chiral GC, the ee values were found to be higher than 99% in all cases (Table 1).

Table 1 Synthesis of *N*-Vinyloxazolidinones **3a–e**

3	R^1	R^2	R^3	Overall Yield (%)	ee (%)	Lit. Yield (%)
3a	Et	H	H	73	99.5	46[4]
3b	H	*i*-Bu	H	78	>99.5	–
3c	Ph	H	H	80	>99.5	55[4]
						56[3b,2b]
						77[1a,b]
3d	Bn	H	H	90	n.d.	66[2b]
3e	H	Me	Ph	90	99.3	–

To conclude, we describe here a general procedure for the preparation of various enantiopure *N*-vinyl oxazolidinones. This two-steps method requires only one purification at the final step and can be performed from millimol to multigram scale. Yields obtained by this easy-made procedure compares well with those reported in the literature.

All solvents were dried using standard procedures. Commercial acetaldehyde diethyl acetal can be employed without prior distillation. Chromatography was performed with 40–60 μm Merk Si 60 silica gel under medium pressure (1 bar). All melting points are uncorrected. Infrared spectra were performed on a FT Genesis (Mattson) spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-400 and Bruker DPX 200 spectrometers in $CDCl_3$ using TMS as a reference. LCMS (EI or CI) were performed on a Fisons MD800 LCD mass spectrometer. HRMS were performed at the University of Rennes-1 with a Varian Matt 311 spectrometer. Optical rotations were measured on a Perkin-Elmer 343 polarimeter. Enantiomeric excesses were determined by chiral GC performed on a HP 6890 gas chromatograph with fid detector using a 25 m (length), 0.25 mm (ID), 0.25 μm (df) R+βDEXCST capillary column and He (2 bar, flow rate 3.4 mL/min) as the carrier gas (split 1/50).

N,O-Acetals 2; General Procedure

A mixture of oxazolidinone **1** (10 mmol), acetaldehyde diethyl acetal (100 mmol) and (*d,l*)-camphorsulfonic acid (0.5 mmol) was heated for 3 h at 55 °C. After cooling and dilution with Et_2O (40 mL), $NaHCO_3$ solution (10 mL) was added and the organic phase was washed with brine (10 mL) and dried over $MgSO_4$. Removal of solvent yielded a crude diastereoisomeric mixture of *N,O*-acetal **2** used without further purification.

(4*R*)-3-(1-Ethoxyethyl)-4-ethyl-oxazolidin-2-one (2a)

From **1a** (1.65 g, 14.4 mmol), **2a** (2.69 g, quantitative yield) was obtained as a pale yellow oil; R_f 0.30 (cyclohexane–EtOAc, 7:3).

IR (film): 1755 (C=O), 1415, 1379, 1225, 1104, 1051 (C–O), 941, 847, 770 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.91 (t, 3 H, J = 7.4 Hz, C*H*$_3$CH$_2$), 1.18 (t, 3 H, *J* = 7.0 Hz, C*H*$_3$CH$_2$O), 1.43 (d, 3 H, *J* = 6.2 Hz, C*H*$_3$CH), 1.60 and 2.05 (2 m, 2 H, CH$_3$C*H*$_2$), 3.58 (m, 2 H, CH$_3$C*H*$_2$O), 3.86 (m, 1 H, H-4), 4.01 (dd, 1 H, $J_{5A\text{-}4}$ = 5.7 Hz, J_{AB} = 8.5 Hz, H-5$_A$), 4.34 (t, 1 H, *J* = 8.5 Hz, H-5$_B$), 5.29 (q, 1 H, *J* = 6.2 Hz, C*H*CH$_3$).

(4*S*)-3-(1-Ethoxyethyl)-4-isobutyl-oxazolidin-2-one (2b)

From **1b** (1.5 g, 10.5 mmol), **2b** (2.26 g, quantitative yield) was obtained as an orange oil; R_f 0.35 (cyclohexane–EtOAc, 7:3).

IR (film): 1757 (C=O), 1415, 1377, 1254, 1223, 1100, 1052 (C–O), 941, 847, 764 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.96 [m, 6 H, (C*H*$_3$)$_2$CH], 1.18 (t, 3 H, *J* = 7.0 Hz, C*H*$_3$CH$_2$O), 1.43 (d, 3 H, *J* = 6.2 Hz, C*H*$_3$CH), 1.35–1.80 (m, 3 H, C*H*C*H*$_2$), 3.40–3.75 (m, 2 H, CH$_3$C*H*$_2$O), 3.97 (m, 2 H, H-4, H-5$_A$), 4.37 (m, 1 H, H-5$_B$), 5.28 (q, 1 H, *J* = 6.2 Hz, C*H*CH$_3$).

(4*R*)-3-(1-Ethoxyethyl)-4-phenyl-oxazolidin-2-one (2c)

From **1c** (1.2 g, 7.35 mmol), **2c** (1.73 g, quantitative yield) was obtained as a pale yellow oil; R_f 0.30 and 0.43 (cyclohexane–EtOAc, 7:3).

IR (film): 1755 (C=O), 1458, 1403, 1378, 1214, 1106, 1058 (C–O), 942, 841, 765, 702 (C–H$_{arom}$) cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ (major isomer) = 0.88 (d, 3 H, *J* = 6.3 Hz, C*H*$_3$CH), 1.25 (t, 3 H, *J* = 7.0 Hz, C*H*$_3$CH$_2$O), 3.55 (m, 2 H, CH$_3$C*H*$_2$O), 4.16 (dd, 1 H, $J_{5A\text{-}4}$ = 5.4 Hz, J_{AB} = 8.6 Hz, H-5$_A$), 4.65 (t, 1 H, J = 8.6 Hz, H-5$_B$), 4.89 (dd, 1 H, $J_{4\text{-}5A}$ = 5.4 Hz, $J_{4\text{-}5B}$ = 8.6 Hz, H-4), 5.35 (q, 1 H, *J* = 6.3 Hz, C*H*CH$_3$), 7.28–7.48 (m, 5 H, Ph).

^{1}H NMR (200 MHz, $CDCl_3$): δ (minor isomer) = 0.79 (t, 3 H, *J* = 7.0 Hz, C*H*$_3$CH$_2$O), 1.43 (d, 3 H, *J* = 6.1 Hz, C*H*$_3$CH), 3.38 (m, 2 H, CH$_3$C*H*$_2$O), 4.23 (dd, 1 H, $J_{5A\text{-}4}$ = 6.5 Hz, J_{AB} = 8.8 Hz, H-5$_A$), 4.62 (t, 1 H, *J* = 8.8 Hz, H-5$_B$), 4.90 (dd, 1 H, $J_{4\text{-}5A}$ = 6.5 Hz, $J_{4\text{-}5B}$ = 8.8 Hz, H-4), 5.23 (q, 1 H, *J* = 6.1 Hz, C*H*CH$_3$), 7.28–7.48 (m, 5 H, Ph).

(4*R*)-4-benzyl-3-(1-Ethoxyethyl)-oxazolidin-2-one (2d)

From **1d** (1.1 g, 6.2 mmol), **2d** (1.54 g, quantitative yield) was obtained as a colorless oil; R_f 0.38 (cyclohexane–EtOAc, 7:3).

IR (film): 1755 (C=O), 1454, 1417, 1378, 1237, 1095, 1056 (C–O), 942, 846, 745, 703 (C–H$_{arom}$) cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.22 (t, 3 H, *J* = 7.1 Hz, C*H*$_3$CH$_2$O), 1.55 (d, 3 H, *J* = 6.2 Hz, C*H*$_3$CH), 2.63 (dd, 1 H, *J* = 10.3 Hz, J_{AB} = 13.7 Hz, PhC*H*HCH), 3.48–3.80 (m, 3 H, CH$_3$C*H*$_2$O, PhCH*H*CH), 4.00–4.20 (m, 3 H, H-4, H-5$_{AB}$), 5.36 (q, 1 H, *J* = 6.1 Hz, C*H*CH$_3$), 7.14–7.40 (m, 5 H, Ph).

(4*S*-5*R*)-3-(1-Ethoxyethyl)-4-methyl-5-phenyl-oxazolidin-2-one (2e)

From **1e** (1 g, 5.6 mmol), **2e** (1.39 g, quantitative yield) was obtained as a colorless oil; R_f 0.36 (cyclohexane–EtOAc, 7:3).

IR (film): 1752 (C=O), 1453, 1412, 1379, 1227, 1102 (C–O), 843, 764, 706 (C–H)$_{arom}$ cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.89 (d, 3 H, *J* = 6.7 Hz, CH$_3$-4), 1.15 (t, 3 H, *J* = 7.1 Hz, C*H*$_3$CH$_2$O), 1.48 (d, 3 H, *J* = 6.2 Hz, C*H*$_3$CH), 3.60 (m, 2 H, CH$_3$C*H*$_2$O), 4.24 (dq, 1 H, $J_{4\text{-}5}$ = 8.0 Hz, $J_{4\text{-}CH3}$ = 6.7 Hz, H-4), 5.37 (q, 1 H, *J* = 6.2 Hz, C*H*CH$_3$), 5.55 (d, 1 H, *J* = 8.0 Hz, H-5), 7.25–7.47 (m, 5 H, Ph).

N-Vinyloxazolidinones 3; General Procedure

To a cooled solution (0 °C) of crude *N,O*-acetal **2** (10 mmol) in anhydrous CH_2Cl_2 (10 mL) was added under nitrogen distilled Et_3N (15 mmol), then dropwise, TMSOTf (13 mmol). After slowly warming to r.t. and stirring for 15 h, the mixture was treated with basic alumina to remove the excess of TMSOTf. After removal of the solvent, the residue was filtered on silica gel (Et_2O) to remove the ammonium triflate salts and was purified by chromatography.

(4*R*)-4-Ethyl-3-vinyl-oxazolidin-2-one (3a)
From **2a** (2.69 g, 14.4 mmol), chromatographic purification (silica gel; cyclohexane–EtOAc, 8:2 → 7:3) afforded **3a** (1.47 g, 73%) as a colorless oil; R_f 0.47 (cyclohexane–EtOAc, 1:1); $[\alpha]_D^{20}$ –70.2 (*c* 1.6, CH_2Cl_2); ee 99.5%; t_R (4*S*)-**3a** 14.5 min (0.2%), t_R (4*R*)-**3a** 14.9 min (99.7%) (bp 120–180 °C, 3 °C/min).

IR (film) : 1755 (C=O), 1635 (C=C), 1427, 1400, 1273, 1226, 1089, 1062 (C=O), 977, 854, 760 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.92 (t, 3 H, *J* = 7.4 Hz, CH_3), 1.77 (m, 2 H, CH_2), 4.05 (m, 1 H, H-4), 4.14 (dd, 1 H, $J_{5A\text{-}4}$ = 3.5 Hz, J_{AB} = 8.5 Hz, H-5_A), 4.40 (dd, 1 H, $J_{2'A\text{-}1'}$ = 16.2 Hz, J_{AB} = 1.2 Hz, H-$2'_A$), 4.42 (t, 1 H, *J* = 8.5 Hz, H-5_B), 4.46 (dd, 1 H, $J_{2'B\text{-}1'}$ = 9.3 Hz, J_{AB} = 1.2 Hz, H-$2'_B$), 6.77 (dd, 1 H, $J_{1'\text{-}2'A}$ = 16.2 Hz, $J_{1'\text{-}2'B}$ = 9.3 Hz, H-1′).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 7.2 (CH_3), 22.8 (CH_2),53.9 (C-4), 66.8 (C-5), 93.5 (C-2′), 128.4 (C-1′), 155.1 (C-2).

HRMS (EI): *m*/*z* calcd for $C_7H_{11}NO_2$: 141.07898; found: 141.0804.

(4*S*)-4-Isobutyl-3-vinyl-oxazolidin-2-one (3b)
From **3b** (1 g, 4.65 mmol), chromatographic purification (silica gel; cyclohexane–EtOAc, 9:1 → 8:2) afforded **3b** (614 mg, 78%) as a pale yellow oil; R_f 0.31 (cyclohexane–EtOAc, 4:1); $[\alpha]_D^{20}$ +103.8 (*c* 1.5, $CHCl_3$); ee > 99.5%; (4*R*)-**3b** 39.0 min (0.0%), t_R (4*S*)-**3c** 41.5 min (100%) (130 °C).

IR (film): 1764 (C=O), 1635 (C=C), 1427, 1400, 1250, 1224, 1076 (C–O), 977, 845, 760 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.97 and 0.98 [2 d, 6 H, *J* = 6.4 Hz, $(CH_3)_2CH$], 1.44 and 1.84 (2 m, 2 H, $CHCH_2CH$), 1.66 [m, 1 H, $(CH_3)_2CH$], 4.06 (m, 1 H, H-4), 4.12 (dd, 1 H, $J_{5A\text{-}4}$ = 3.0 Hz, J_{AB} = 8.5 Hz, H-5_A), 4.35 (dd, 1 H, $J_{2'A\text{-}1'}$ = 16.3 Hz, J_{AB} = 1.0 Hz, H-$2'_A$), 4.42 (dt, 1 H, *J* = 8.5, 1.0 Hz, H-5_B), 4.66 (dd, 1 H, $J_{2'B\text{-}1'}$ = 9.4 Hz, J_{AB} = 1.0 Hz, H-$2'_B$), 6.74 (dd, 1 H, $J_{1'\text{-}2'A}$ = 16.3 Hz, $J_{1'\text{-}2'B}$ = 9.4 Hz, H-1′).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.4 and 23.3 (2 × CH_3); 24.6 (CH); 39.1 (CH_2); 52.0 (C-4); 68.0 (C-5); 93.5 (C-2′); 128.4 (C-1′); 154.9 (C-2).

HRMS (EI): *m*/*z* calcd for $C_9H_{15}NO_2$: 169.11028; found: 169.1105.

Anal. Calcd for $C_9H_{15}NO_2$: C, 63.88; H, 8.93; N, 8.28. Found C, 63.51; H, 9.06; N, 8.35.

(4*R*)-4-Phenyl-3-vinyl-oxazolidin-2-one (3c)[3b]
From **2c** (1 g, 4.25 mmol), chromatographic purification (silica gel; cyclohexane–EtOAc, 85:15 → 8:2) afforded **3c** (647 mg, 80%) as a white solid; R_f 0.29 (cyclohexane–EtOAc, 4:1); mp 42–43 °C, (Lit.[3b] Mp 40.5–41.5 °C); $[\alpha]_D^{20}$ –116.5 (*c* 1.35, CH_2Cl_2) {Lit.[3b] $[\alpha]_D^{20}$ –117 (*c* 1.03, CH_2Cl_2)}; ee > 99.5%; t_R (4*S*)-**3c** 22.5 min (0.0%), t_R (4*R*)-**3c**, 23.2 min (100%) (130–180 °C, 3 °C/min).

IR (film) : 1759 (C=O), 1637 (C=C), 1425, 1396, 1324, 1226, 1080 (C–O), 973, 852, 758, 700 (C–H_{arom}) cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 4.10 (dd, 1 H, $J_{2'A\text{-}1'}$ = 16.1 Hz, J_{AB} = 1.2 Hz, H-$2'_A$), 4.13 (dd, 1 H, $J_{5A\text{-}4}$ = 5.3 Hz, J_{AB} = 9.0 Hz, H-5_A), 4.32 (dd, 1 H, $J_{2'B\text{-}1'}$ = 9.2 Hz, J_{AB} = 1.2 Hz, H-$2'_B$), 4.73 (t, 1 H, *J* = 9.0 Hz, H-5_B), 5.04 (dd, 1 H, $J_{4\text{-}5A}$ = 5.3 Hz, $J_{4\text{-}5B}$ = 9.0 Hz, H-4), 6.83 (dd, 1 H, $J_{1'\text{-}2'A}$ = 16.1 Hz, $J_{1'\text{-}2'B}$ = 9.2 Hz, H-1′); 7.20–7.50 (m, 5 H, Ph).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 57.8 (C-4), 70.4 (C-5), 95.6 (C-2′), 125.6 (*o*-Ph), 128.4, 128.5 (C-1′, *p*-Ph), 129.1 (*m*-Ph), 137.8 (*n*-Ph), 155.5 (C-2).

(4*R*)-4-Benzyl-3-vinyl-oxazolidin-2-one (3d)[2b]
From **2d** (1.27 g, 5.1 mmol), chromatographic purification (silica gel; cyclohexane–EtOAc, 7:3) afforded **3d** (0.934 g, 90%) as a colorless oil, R_f 0.37 (cyclohexane–EtOAc, 7:3); $[\alpha]_D^{25}$ –97.8 (*c* 1.1, CH_2Cl_2) {Lit.[2b] (4*S*)-**3d**: $[\alpha]_D^{25}$ +96.5 (*c* 1.1, CH_2Cl_2)};

IR (film) : 1763 (C=O), 1640 (C=C), 1430, 1402, 1239, 1087 (C–O), 993, 855, 758, 711 (C–H_{arom}) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.79 (dd, 1 H, $J_{A\text{-}4}$ = 8.6 Hz, J_{AB} = 13.9 Hz, Ph-CH_A), 3.25 (dd, 1 H, $J_{B\text{-}4}$ = 3.0 Hz, J_{AB} = 13.9 Hz, Ph-CH_B), 4.20 (dd, 1 H, $J_{5A\text{-}4}$ = 3.0 Hz, J_{AB} = 8.6 Hz, H-5_A), 4.25 (t, 1 H, *J* = 8.6 Hz, H-5_B), 4.30 (tt, 1 H, *J* = 3.0, 8.6 Hz, H-4), 4.57 (dd, 1 H, $J_{2'A\text{-}1'}$ = 16.0 Hz, J_{AB} = 1.3 Hz, H-$2'_A$), 4.58 (dd, 1 H, $J_{2'B\text{-}1'}$ = 9.3 Hz, J_{AB} = 1.3 Hz, H-$2'_B$), 6.84 (dd, 1 H, $J_{1'\text{-}2'A}$ = 16.0 Hz, $J_{1'\text{-}2'B}$ = 9.3 Hz, H-1′), 7.20–7.35 (m, 5 H, Ph).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.7 (Ph-CH_2), 54.2 (C-4), 66.4 (C-5), 95.2 (C-2′), 127.2 (*o*-Ph), 128.7 (C-1′), 128.8 (*p*-Ph), 129.2 (*m*-Ph), 135.1 (*n*-Ph), 155.0 (C-2).

(4*S*-5*R*)-4-Methyl-5-phenyl-3-vinyl-oxazolidin-2-one (3e)
From **2e** (1.61 g, 6.46 mmol), chromatographic purification (silica gel; cyclohexane–EtOAc, 8:2 → 7:3) afforded **3e** (1.18 g, 90%) as a white solid; R_f 0.29 (cyclohexane–EtOAc, 8:2); mp 62.5–64 °C; $[\alpha]_D^{25}$ –26 (*c* 1.1, CH_2Cl_2); ee 99.2%; t_R (4*S*,5*R*)-**3e** 25.6 min (99.6%); t_R (4*R*,5*S*)-**3e** 26.0 min (0.4%) (130–180 °C, 3 °C/min).

IR (film): 1753 (C=O), 1638 (C=C), 1456, 1429, 1237, 1109 (C–O), 972, 859, 766, 703 (C–H arom.) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.86 (d, 3 H, *J* = 6.6 Hz, CH_3), 4.38 (q, 1 H, *J* = 6.6 Hz, H-4), 4.41 (dd, 1 H, $J_{2'A\text{-}1'}$ = 16.0 Hz, J_{AB} = 1.2 Hz, H-$2'_A$), 4.50 (dd, 1 H, $J_{2'B\text{-}1'}$ = 9.2 Hz, J_{AB} = 1.2 Hz, H-$2'_B$), 4.70 (d, 1 H, $J_{5\text{-}4}$ = 7.6 Hz, H-5), 6.83 (dd, 1 H, $J_{1'\text{-}2'A}$ = 16.0 Hz, $J_{1'\text{-}2'B}$ = 9.2 Hz, H-1′), 7.30–7.45 (m, 5 H, Ph).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.9 (CH_3), 53.8 (C-4), 79.1 (C-5), 94.1 (C-2′), 125.9 (*o*-Ph), 128.8(C-1′, *p*-Ph, *m*-Ph), 134.0 (*n*-Ph), 154.0 (C-2).

Anal. Calcd for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.45; N, 6.89. Found C, 70.24; H, 6.61; N, 6.67.

Acknowledgment

We thank Teddy Chapin for his helpful contribution.

References

(1) (a) Montgomery, J.; Wieber, G. M.; Hegedus, L. S. *J. Am. Chem. Soc.* **1990**, *112*, 6255. (b) Masters, J. J. M.; Hegedus, L. S.; Tamariz, J. *J. Org. Chem.* **1991**, *56*, 5666. (c) Laidig, G. J.; Hegedus, L. S. *Synlett* **1995**, 527.
(2) (a) Miller, M.; Hegedus, L. S. *J. Org. Chem.* **1993**, *58*, 6779. (b) Bach, T.; Schröder, J.; Brandl, T.; Hecht, J.; Harms, K. *Tetrahedron* **1998**, *54*, 4507.
(3) (a) Tamura, O.; Hashimoto, M.; Kobayashi, Y.; Katoh, T.; Nakatani, K.; Kamada, M.; Hayakawa, I.; Akiba, T.; Terashima, S. *Tetrahedron Lett.* **1992**, *33*, 3487. (b) Akiba, T.; Hashimoto, M.; Kobayashi, Y.; Katoh, T.; Nakatani, K.; Kamada, M.; Hayakawa, I.; Terashima, S. *Tetrahedron* **1994**, *50*, 3905. (c) Akiba, T.; Tamura, O.; Terashima, S. *Org. Synth.* **1998**, *75*, 45.
(4) Walles, W. E.; Tousignant, W. F.; Houtman, T. Jr. US Patent 2891058 19590616, **1959**.
(5) Shono, T.; Matsumura, Y.; Tsubata, K.; Sugihara, Y.; Yamane, S.; Kanazawa, T.; Aoki, T. *J. Am. Chem. Soc.* **1982**, *104*, 6697.
(6) (a) Bach, T.; Brummerhop, H. *J. Prakt. Chem.* **1999**, *341*, 312. (b) Bach, T.; Brummerhop, H. *J. Prakt. Chem.* **1999**, *341*, 410.
(7) Gaulon, C.; Gizecki, P.; Dhal, R.; Dujardin, G. *Synlett* **2002**, 952.

(8) Gassman, P. G.; Burns, S. J.; Pfister, K. B. *J. Org Chem.* **1993**, *58*, 1449.
(9) Camphorsulfonic acid can be conveniently replaced by *p*-toluenesulfonic acid.
(10) Dujardin, G.; Rossignol, S.; Brown, E. *Tetrahedron Lett.* **1995**, *36*, 1653.
(11) In our hands the *N*-vinyl oxazolidinones obtained via Hg(II)-catalyzed exchange contained typically (even after distillation or SiO_2 chromatography) 10–20% starting material.