# Stereochemical Study of a Lewis Acid-Promoted Reaction of 2-Silyloxypyrrole with Aliphatic and Aromatic Aldehydes

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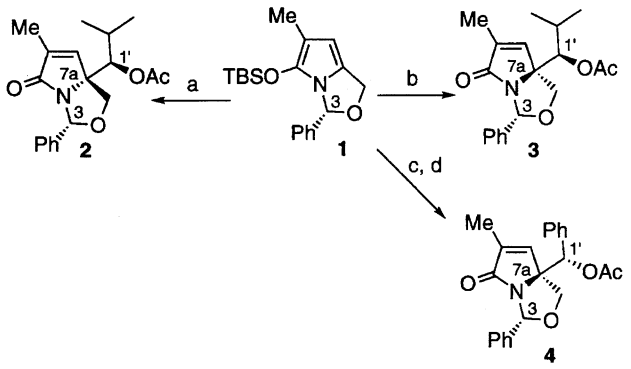
In the presence of $BF_3$·$OEt_2$, the reaction of 1-*t*-butoxycarbonyl-2-*t*-butyldimethylsiloxypyrrole with aliphatic and aromatic aldehydes in ether occurred stereoselectively to give the corresponding *erythro* and *threo* isomers, respectively, while a similar reaction in the presence of $SnCl_4$ showed completely opposite selectivity. The transition states leading to the major isomers are discussed.

Mukaiyama-type aldol reactions are commonly employed in organic synthesis, since a variety of methods have been developed to achieve high stereo- and regioselectivities.[1] The stereochemistries of newly created stereogenic centers are well-known to depend upon the reaction conditions, including the choice of Lewis acids and solvents, and the transition states leading to the major products are often discussed in terms of chelation and dipolar effects. However, these effects failed to rationalize some examples. We have reported a remarkable alteration of the diastereoselectivity in the $SnCl_4$- and $BF_3$·$OEt_2$-assisted reactions of chiral siloxypyrrole **1** with isobutyraldehyde and benzaldehyde[2] (Scheme 1). In the presence of $SnCl_4$, the reaction of **1** with isobutyraldehyde occurred from the same face of the 3-phenyl group to give **2** (7a, 1′-*threo*). On the other hand, the reaction of **1** with isobutyraldehyde and benzaldehyde in the presence of $BF_3$·$OEt_2$ occurred from the opposite face to the 3-phenyl group to give **3** (7a, 1′-*erythro*) and **4** (7a, 1′-*threo*), respectively, as a main product.[3] Concerning the face selectivity of aldehydes, the observed selectivity was different in reactions with isobutyraldehyde and benzaldehyde. Because a few data were so far reported concerning the stereoselectivity in Lewis acid-mediated reactions of 2-siloxy-substituted pyrroles with aromatic aldehydes,[4] we decided to investigate the reactions of 1-*t*-butoxycarbonyl-2-(*t*-butyldimethylsilyloxy)-pyrrole (TBSOP; **5**) in order to understand the stereochemical alteration.




Scheme 1. *Reagents, conditions, and yields:* (a) isobutyraldehyde, $SnCl_4$, ether, −78 °C; pyridine, $Ac_2O$; 63%; (b) isobutyraldehyde, $BF_3$·$OEt_2$, ether, −78 °C; pyridine, $Ac_2O$; 64%. (c) benzaldehyde, $BF_3$·$OEt_2$, ether, −78 °C; pyridine, $Ac_2O$; 47%. (d) benzaldehyde, $SnCl_4$, ether, −78 °C; pyridine, $Ac_2O$; 20%.

## Results and Discussion

***Erythro/Threo* Selectivity in the Lewis Acid-Promoted Reactions.** First, the reaction of TBSOP (**5**) with various aldehydes was carried out in the presence of $BF_3$·$OEt_2$ at −78 °C (Eq. 1); the results are summarized in Table 1. In $BF_3$·$OEt_2$-promoted reactions with aliphatic aldehydes, the major products had smaller coupling constants between $H^5$ and $H^{1'}$ to the minor products, and the major products were assigned to be *erythro* based on reports by Rassu et al. (Table 1; Entries 8, 9, and 10).[5—7] This selectivity was in good accord with the reported data.[5—7] In a similar reaction of TBSOP (**5**) with benzaldehyde, however, the coupling constant of the major isomer of **6c** ($J_{H^5-H^{1'}}$ = 6.1 Hz) was larger than that of the minor isomer ($J_{H^5-H^{1'}}$ = 2.4 Hz). If the structure determination in the aliphatic cases is applied ($J_{threo} > J_{erythro}$), the major isomer would be *threo*. Recently, a reliable method for the determination of *erythro/threo* stereochemistry was successfully applied for the stereochemical determination of naturally occurring acyclic polyols based on $^{2,3}J_{C-H,H-H}$ couplings.[8] In our case, however, the stereochemistry could not be assigned by this method.[8] Because we could not obtain any suitable crystal for an X-ray analysis in spite of our effort, we decided to carry out derivatizations of the products. Since the epimerization between *erythro* and *threo*-**6c** easily took place under basic conditions,[6] the double bond of each isomer was first hydrogenated to give **8c** (Eq. 1). Fortunately enough, fine crystals were obtained

Table 1. The $BF_3 \cdot OEt_2$-Promoted Reaction of TBSOP (**5**) with Various Aldehydes

| Entry | $R^1CHO$ $R^1$ | $BF_3 \cdot OEt_2$ (equiv) | Solvent | Yield[a] % | Ratio[b] *erythro* (**6**/**7**) | Ratio[b] *threo* (**6**/**7**) |
|---|---|---|---|---|---|---|
| 1 | *p*-$O_2NC_6H_4$ | 1 | Ether/$CH_2Cl_2$ | 35 | 14 (1/—) | 86 (1/—) |
| 2 | *p*-$NCC_6H_4$ | 1 | Ether/$CH_2Cl_2$ | 96 | 33 (1/—) | 67 (1/—) |
| 3 | *p*-$NCC_6H_4$ | 7.5 | Ether/$CH_2Cl_2$ | 95 | 40 (1/—) | 60 (1/—) |
| 4 | Ph | 1 | Ether | 75 | 19 (1/—) | 81 (1/—) |
| 5 | *p*-$MeOC_6H_4$ | 1 | Ether | 88 | 78 (1/12) | 22 (1/2) |
| 6 | *p*-$MeOC_6H_4$ | 7.3 | Ether | 80 | 74 (1/7) | 26 (4/1) |
| 7 | $Me_2C{=}CH$ | 1 | Ether | 80 | 30 (1/2) | 70 (1/2) |
| 8 | Et | 1 | Ether | 83 | 81 (1/—) | 19 (1/—) |
| 9 | *i*-Pr | 1 | Ether | 78 | 86 (1/—) | 14 (1/—) |
| 10 | *t*-Bu | 1 | Ether | 83 | 100 (1/—) | — |

a) Combined yield. b) Determined by $^1H$ NMR.

by the recrystallization of minor **8c** derived from the minor isomer of **6c**. An X-ray analysis of this crystal was performed, and the stereochemistry was unambiguously determined to be *erythro* (Fig. 1). Therefore, the major isomer of **6c** obtained in the reaction of TBSOP (**5**) with benzaldehyde was *threo*, contrary to the cases of aliphatic aldehydes. This *threo* selectivity was in accord with the results reported for the reactions of 1-[(*R*)-2-methoxy-1-phenylethyl]-2-(*t*-butyldimethylsilyloxy)pyrrole[4a] and 1-(*t*-butoxycarbonyl)-2-(*t*-butyldimethylsilyloxy)-3-methylpyrrole[4b] with benzaldehyde. Similar results were realized in the reaction of aromatic aldehydes with an electron-withdrawing group, such as *p*-nitrobenzaldehyde and *p*-cyanobenzaldehyde (Entries 1—3). The product determination was done by comparing of the $^1H$ NMR spectra. On the other hand, *erythro* products (*erythro*-**6d** and *erythro*-**7d**) were preferentially obtained in the case of *p*-anisaldehyde, and the silylated product **7d** was favorably formed (Scheme 2).

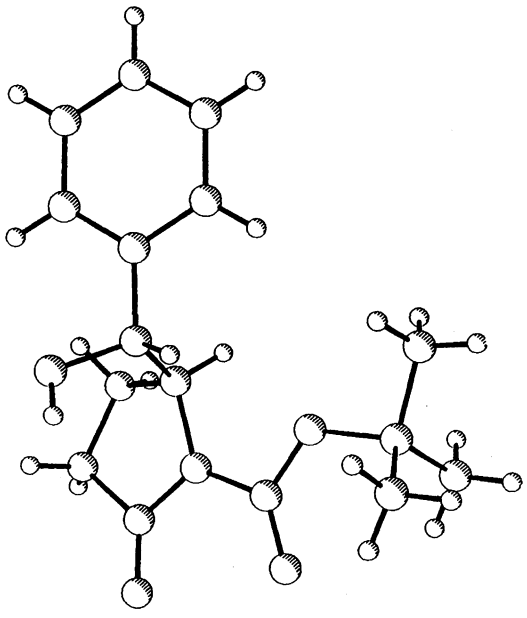
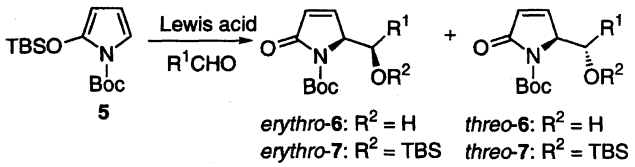
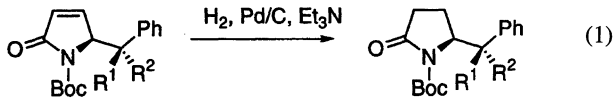


Fig. 1. Molecular structure of *erythro*-**8c**.




Scheme 2. $R^1$ = **a**: 4-$O_2NC_6H_4$; **b**: 4-$NCC_6H_4$; **c**: Ph; **d**: 4-$MeOC_6H_4$; **e**: $CH{=}CMe_2$; **f**: Et; **g**: *i*-Pr; **h**: *t*-Bu.




(1)

Next, the reaction of TBSOP (**5**) with various aldehydes was carried out in the presence of $SnCl_4$ at −78 °C (Eq. 1); the results are summarized in Table 2. *Threo* selectivity was realized in reactions with aliphatic aldehydes, while *erythro* products were preferentially formed in reactions with aromatic aldehydes. The formation of *t*-butyldimethylsilyl ethers **7** was preferred in all cases (Table 2). The formation of **7** indicates that the Lewis acid must keep promoting activity during the reaction, because the strongest Lewis base in this reaction system is the aldehyde used. Thus, the reaction of **5** with benzaldehyde using a catalytic amount (0.1 equiv) of $SnCl_4$ was performed to give **7c** in good yield, and similar selectivity was observed (Table 2, Entry 4).

Other promotors, including lanthanoide triflates[9] and triphenylcarbenium perchlorate,[10] were also examined in reactions with isobutyraldehyde and benzaldehyde (Table 3). However, the selectivity in the reactions with benzaldehyde was similar, at best, to those obtained as mentioned above, although the reaction of 1-(*t*-butoxycarbonyl)-2-(*t*-butyldimethylsilyloxy)-3-methylpyrrole with benzaldehyde was recently reported to give an *erythro* or *threo* isomer exclusively in the presence of tetrabutylammonium fluoride (TBAF) or $TiCl_4$, respectively.[4b]

**Transition State Consideration.** The changes in the stereochemical selectivity would be explained as follows. The transition states leading to *threo* and *erythro* products in Lewis acid-mediated reactions of 2-siloxypyrroles have been discussed in terms of steric, orbital, charge, and chelation in-

Table 2. The $SnCl_4$-Promoted Reaction of TBSOP (**5**) with Various Aldehydes

| Entry | $R^1CHO$ $R^1$ | $SnCl_4$ (equiv) | Solvent | Yield[a] % | Ratio[b] *erythro* (**6**/**7**) | Ratio[b] *threo* (**6**/**7**) |
|---|---|---|---|---|---|---|
| 1 | *p*-$NCC_6H_4$ | 1 | Ether/$CH_2Cl_2$ | 88 | 60 (1/2) | 40 (1/1) |
| 2 | Ph | 1 | Ether | 98 | 84 (1/27) | 16 (8/9) |
| 3 | Ph | 1.5 | Ether | 83 | 90 (—/1) | 10 (—/1) |
| 4 | Ph | 0.1 | Ether | 84 | 88 (—/1) | 12 (3/9) |
| 5 | *p*-$MeOC_6H_4$ | 1 | Ether | 87 | 90 (—/1) | 10 (—/1) |
| 6 | *p*-$MeOC_6H_4$ | 4 | Ether | 86 | 86 (—/1) | 14 (—/1) |
| 7 | $Me_2C$=CH | 1 | Ether | 75 | 28 (—/1) | 72 (—/1) |
| 8 | Et | 1 | Ether | 91 | 11 (1/2) | 89 (3/1) |
| 9 | *i*-Pr | 1 | Ether | 68 | 11 (—/1) | 89 (—/1) |
| 10 | *t*-Bu | 1 | Ether | —[c] | — | — |

a) Combined yield. b) Determined by $^1$H NMR. c) No reaction was observed.

Table 3. The Lewis Acid-Promoted Reaction of TBSOP (**5**) with Various Aldehydes

| Entry | $R^1CHO$ $R^1$ | Lewis Acid (equiv) | Solvent | Yield[a] % | Ratio[b] *erythro* (**6**/**7**) | Ratio[b] *threo* (**6**/**7**) |
|---|---|---|---|---|---|---|
| 1 | Ph | $Ph_3CClO_4$ (0.1) | $CH_2Cl_2$ | 79 | 21 (1/4) | 79 (—/1) |
| 2 | Ph | $TiCl_4$ (2) | Ether | 56 | 26 (2/5) | 74 (36/1) |
| 3 | Ph | $TiCl_4$ (2) | THF | 83 | 38 (2/1) | 62 (1/61) |
| 4 | Ph | $TiCl_4$ (1) | $CH_2Cl_2$ | 70 | 60 (—/1) | 40 (2/3) |
| 5 | Ph | TBAF (1) | THF | 59 | 85 (10/7) | 15 (1/—) |
| 6 | Ph | $Yb(OTf)_3$ (0.3) | MeCN | 19 | 71 (—/1) | 29 (—/1) |
| 7 | Ph | $Sc(OTf)_3$ (0.05)[c] | MeCN | 70 | 64 (—/1) | 36 (—/1) |
| 8 | Ph | $Sn(OTf)_2$ (0.2) | EtCN | 66 | 54 (1/2) | 46 (—/1) |
| 9 | *i*-Pr | $TiCl_4$ (2) | Ether | 70 | — | 100 (6/1) |
| 10 | *i*-Pr | TBAF (1) | THF | 48 | — | 100 (1/—) |

a) Combined yield. b) Determined by $^1$H NMR. c) The reaction temperature was 0 °C.

teractions. In the case of $BF_3$·$OEt_2$, the chelation would be neglected. The preferential *threo* selectivity observed in the siloxyheterocycles with aldehydes was rationalized by the *exo* Diels–Alder-like arrangement between the heterocycles and aldehydes (Fig. 2, **T1**) in the previous paper.[5] In the case of TBSOP, however, a severe steric interaction with the t-Boc moiety would be expected in **T1**. Thus, other transition states, such as an *endo* Diels–Alder-like transition state (Fig. 2, **T2**) and a synclinal transition state (Fig. 2, **T3**), would become competitive. In the cases of aromatic aldehydes, a π–π interaction between the aromatic and pyrrole moieties would prefer the synclinal stacking model **T3** to the *endo* Diels–Alder-like transition state **T2**. On the other hand, the least-hindered transition state **T2** would be preferred in the cases of aliphatic aldehydes, leading to *erythro* products, due to the lack of such an interaction. In the case of the bidentate Lewis acid $SnCl_4$, chelation effects should be considered (Fig. 2, **T5** and **T6**). The less-hindered transition state **T5** would be favored in reactions with aliphatic aldehydes, while the other transition states **T6** would be preferred in reactions with aromatic aldehydes due to a similar reason.

If the chelation mechanism is the reason for the reverse selectivity in the $SnCl_4$- and $BF_3$·$OEt_2$-promoted reactions of TBSOP, 2-trimethylsilyloxyfuran (**9**; TMSOF) would give similar selectivity. This has been proved to be the case. In order to compare the results directly, we carried out a reaction of TMSOF (**9**) with benzaldehyde and isobutyraldehyde under similar conditions, although the *threo* isomers were reported to be preferred commonly.[11] The $BF_3$·$OEt_2$-promoted reactions of **9** with isobutyraldehyde and benzaldehyde preferentially gave the *threo* isomer (*threo*-**10** : *erythro*-**10** = 80 : 20 and 84 : 16, respectively) in good yields (83 and 81%, respectively) (Scheme 3).[12] The $SnCl_4$-promoted reactions of **9** with isobutyraldehyde and benzaldehyde also showed a similar *threo* preference (*threo*-**11** : *erythro*-**11** = 83 : 17 and 60 : 40, respectively).

We turn our attention to the transition states in the reaction of the bicyclic siloxypyrrole **1**. In the $BF_3$-assisted reactions of **1** with aliphatic aldehydes, we thought that the *erythro* selectivity would be due to an *endo* Diels–Alder-like transition state similar to **T2**, because the steric influence of the oxazolidine ring would severely disfavor an *exo* model similar to **T1**.[3] Because both Lewis acids ($BF_3$·$OEt_2$ and $SnCl_4$) gave similar *threo* selectivity in the case of aromatic aldehydes, the transition state would be a stacking synclinal transition state like **T3**. In this case, π–π stacking between the pyrrole moiety and the aromatic ring would be expected.

## Experimental

**General Details.** The melting points are uncorrected. Unless otherwise specified, NMR spectra were obtained with a JEOL GSX-270 or JMN-400 spectrometer at ambient temperature using $CDCl_3$ as a solvent and tetramethylsilane as an internal standard for $^1$H and $^{13}$C. Mass spectra and high-resolution mass spectra were measured

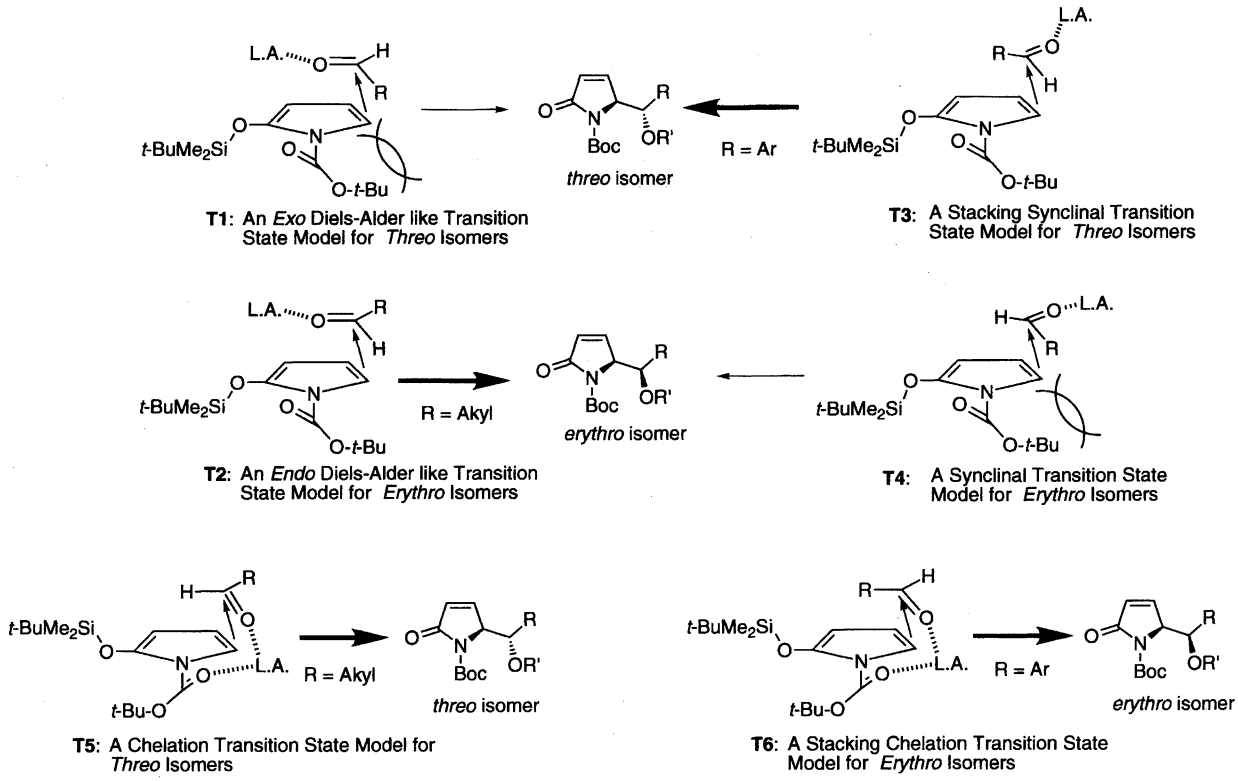
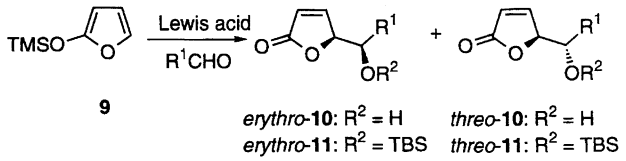



Fig. 2. Possible transition states.




Scheme 3. $R^1$ = **c**: Ph; **g**: *i*-Pr.

with a Hitachi M80B-LCAPI spectrometer under the CI (chemical ionization, 70 eV, isobutane as CI gas) ionizing conditions. Column chromatography and TLC analysis were carried out using Wakogel C-200 and Kieselgel 60 $F_{254}$ (Merck), respectively. Ether and THF were freshly distilled from sodium benzophenone ketyl. Dichloromethane, benzene, toluene, and triethylamine were distilled from $CaH_2$ under an inert atmosphere. Other commercially available materials were used without further purification. TBSOP (**5**) was prepared according to a literature procedure.

**General Procedure for the Lewis Acid-Promoted Reaction of TBSOP (5) with Aldehydes.** To a stirred solution (5 ml) of TBSOP (5; 0.5 mmol) and an aldehyde (0.5 mmol) was added a Lewis acid by a syringe at −78 °C under an inert atmosphere. After 1 h, a saturated aq-$NaHCO_3$ solution (15 ml) was added at the same temperature and the mixture was allowed to warm up to room temperature. The mixture was extracted with EtOAc (3×25 ml). The organic phase was washed with brine, dried over $Na_2SO_4$, and concentrated. The residue was chromatographed on silica gel (hexane/EtOAc). In most cases, isomers could not be completely separated, and the major isomers could be isolated by recrystallyzation from $CH_2Cl_2$/ether/hexane in some cases. In such cases, the melting points are given.

***N*-(*t*-Butoxycarbonyl)-5-[hydroxy(*p*-nitrophenyl)methyl]-1, 5-dihydro-2*H*-pyrrol-2-one.** (5*S**,1′*R**)-isomer (*erythro*-**6a**): $^1$H NMR $\delta$ = 1.62 (9H, s, BOC), 4.06 (1H, d, $J$ = ca. 1 Hz, OH), 4.92 (1H, m, $H^5$), 5.58 (1H, m, $H^{1'}$), 6.14 (1H, dd, $J$ = 6.1 and 1.8 Hz, $H^3$), 6.87 (1H, dd, $J$ = 6.1 and 1.8 Hz, $H^4$), 7.57 (2H, m, Ar), and 8.25 (2H, m, Ar).

(5*S**,1′*S**)-isomer (*threo*-**6a**): White powder, mp 154—156 °C; $^1$H NMR $\delta$ = 1.62 (9H, s, BOC), 3.86 (1H, d, $J$ = 3.7 Hz, OH), 4.98 (1H, m, $H^5$), 5.48 (1H, dd, $J$ = 5.8 and 3.7 Hz, $H^{1'}$), 5.94 (1H, dd, $J$ = 6.1 and 1.8 Hz, $H^3$), 7.13 (1H, dd, $J$ = 6.1 and 2.1 Hz, $H^4$), 7.37 (2H, m, Ar), and 8.16 (2H, m, Ar); $^{13}$C NMR $\delta$ = 28.1 (*t*-Bu), 66.5 (C5), 73.4 (C1′), 84.3 (*t*-Bu), 123.3 (Ar), 127.5 (Ar), 128.2 (C3), 145.6 (*ipso*), 147.0 (C4), 147.8 (C–$NO_2$), 151.1 ($OCO_2$), and 168.0 (C2); IR (KBr) 3412vs, 1756vs, 1520vs, 1374vs, 1348vs, and 1312vs cm$^{-1}$. Found: C, 57.45; H, 5.47; N, 8.33%. Calcd for $C_{16}H_{18}N_2O_6$: C, 57.48; H, 5.43; N, 8.38%.

***N*-(*t*-Butoxycarbonyl)-5-[*p*-cyanophenyl(hydroxy)methyl]-1, 5-dihydro-2*H*-pyrrol-2-one.** (5*S**,1′*R**)-isomer (*erythro*-**6b**): $^1$H NMR $\delta$ = 1.61 (9H, s, BOC), 3.62 (1H, d, $J$ = 5.1 Hz, OH), 4.91 (1H, m, $H^5$), 5.51 (1H, d, $J$ = 3.4 Hz, $H^{1'}$), 6.13 (1H, dd, $J$ = 4.4 and 1.7 Hz, $H^3$), 6.87 (1H, dd, $J$ = 4.4 and 2.0 Hz, $H^4$), 7.50 (2H, m, Ar), and 7.68 (2H, m, Ar); $^{13}$C NMR $\delta$ = 28.1 (*t*-Bu), 68.8 (C5), 70.9 (C1′), 84.0 (*t*-Bu), 111.6 (C bearing CN), 118.5 (CN), 126.4 (Ar), 128.4 (C3), 132.3 (Ar), 145.2 (C bearing CHOH), 146.1 (C4), 149.7 ($OCO_2$), and 169.7 (C2).

(5*S**,1′*S**)-isomer (*threo*-**6b**): White powder (*erythro*/*threo* = 1/1.7 mixture), mp 150—151 °C; $^1$H NMR $\delta$ = 1.62 (9H, s, *t*-Bu), 3.68 (1H, d, $J$ = 4.4 Hz, OH), 4.95 (1H, dt, $J$ = 2.4 and 2.0 Hz, $H^5$), 5.35 (1H, dd, $J$ = 4.4 and 2.4 Hz, $H^{1'}$), 5.95 (1H, dd, $J$ = 4.7 and 2.0 Hz, $H^3$), 7.04 (1H, dd, $J$ = 4.9 and 2.0 Hz, $H^4$), 7.33 (2H, m, Ar), and 7.61 (2H, m, Ar); $^{13}$C NMR $\delta$ = 28.1 (*t*-Bu), 66.4 (C5), 73.0 (C1′), 84.1 (*t*-Bu), 111.9 (C bearing CN), 118.5 (CN), 127.7 (Ar), 128.0 (C3), 131.8 (C4′), 143.8 (C bearing CHOH), 147.3 (C4), 150.7 ($OCO_2$), and 168.3 (C2); IR (KBr) 3448vs, 2228m, 1760vs, 1372vs, and 1160s cm$^{-1}$; MS (CI) *m*/*z* (rel intensity) 271 (5), 259 (5), 237 (8), 197 (100), 168 (9), and 132 (78). Found: C, 64.61;

H, 5.88; N, 8.78%. Calcd for $C_{17}H_{18}N_2O_4$: C, 64.96; H, 5.77; N, 8.91%.

***N*-(*t*-Butoxycarbonyl)-5-[*t*-butyldimethylsilyloxy(*p*-cyanophenylmethyl]-1,5-dihydro-2*H*-pyrrol-2-one.** ($5S^*,1'R^*$)-isomer (*erythro*-**7b**): White powder, mp 141—143 °C; $^1$H NMR $\delta$ = −0.14 (3H, s, SiMe), 0.02 (3H, s, SiMe), 0.84 (9H, s, Si–*t*-Bu), 1.62 (9H, s, O–*t*-Bu), 4.64 (1H, dm, $J$ = 1.8 Hz, $H^5$), 5.55 (1H, br s, $H^{1'}$), 6.12 (1H, br d, $J$ = 6.3 Hz, $H^3$), 6.75 (1H, dd, $J$ = 6.3 and 2.1 Hz, $H^4$), 7.54 (2H, m, Ar), and 7.69 (2H, m, Ar); $^{13}$C NMR $\delta$ = −5.4 (SiMe), −5.1 (SiMe), 18.0 (*t*-Bu), 25.6 (*t*-Bu), 28.2 (O–*t*-Bu), 68.6 (C5), 71.7 (C1′), 83.5 (O–*t*-Bu), 111.9 (C bearing CN), 118.5 (CN), 126.5 (Ar), 128.5 (C3), 132.4 (Ar), 145.4 (C4), 146.5 (C bearing CHOH), 150.1 ($OCO_2$), and 168.7 (C2); IR (NaCl) 2228m, 1780vs, 1746vs, 1714vs, 1320vs, and 1158vs cm$^{-1}$; MS (CI) *m/z* (rel intensity) 378 (12), 329 (5), 246 (25), 189 (16), and 132 (100). Found: C, 64.21; H, 7.53; N, 6.57%. Calcd for $C_{23}H_{32}N_2O_4Si$: C, 64.45; H, 7.53; N, 6.54%.

($5S^*,1'S^*$)-isomer (*threo*-**7b**): $^1$H NMR $\delta$ = −0.07 (3H, s, SiMe), 0.15 (3H, s, SiMe), 0.92 (9H, s, Si–*t*-Bu), 1.62 (9H, s, O–*t*-Bu), 4.83 (1H, dm, $J$ = 5.5 Hz, $H^5$), 5.58 (1H, d, $J$ = 5.5 Hz, $H^{1'}$), 5.87 (1H, dd, $J$ = 6.1 and ca. 1 Hz, $H^3$), 7.18 (2H, m, Ar), 7.23 (1H, dd, $J$ = 6.1 and 2.1 Hz, $H^4$), and 7.61 (2H, m, Ar).

***N*-(*t*-Butoxycarbonyl)-5-[hydroxy(phenyl)methyl]-1,5-dihydro-2*H*-pyrrol-2-one.** ($5S^*,1'R^*$)-isomer (*erythro*-**6c**): $^1$H NMR $\delta$ = 1.62 (9H, s, *t*-Bu), 3.11 (1H, d, $J$ = 5.2 Hz, OH), 4.87 (1H, m, $H^5$), 5.50 (1H, dd, $J$ = 5.2 and 2.4 Hz, $H^{1'}$), 6.12 (1H, dd, $J$ = 6.1 and 1.8 Hz, $H^3$), 6.92 (1H, dd, $J$ = 6.1 and 2.1 Hz, $H^4$), and 7.37 (5H, m, Ar); $^{13}$C NMR $\delta$ = 28.2 (*t*-Bu), 68.8 (C5), 71.7 (C1′), 83.8 (*t*-Bu), 125.5 (Ar), 128.0 (C3), 128.3 (*para* Ar), 139.3 (*ipso*), 146.5 (C4), 150.3 ($OCO_2$), and 169.4 (C2).

($5S^*,1'S^*$)-isomer (*threo*-**6c**): White powder, mp 161—162 °C (decomp); $^1$H NMR $\delta$ = 1.62 (9H, s, *t*-Bu), 3.63 (1H, d, $J$ = 3.0 Hz, OH), 4.94 (1H, dm, $J$ = 6.1 and 1.8 Hz, $H^5$), 5.22 (1H, dd, $J$ = 6.1 and 3.0 Hz, $H^{1'}$), 5.93 (1H, dd, $J$ = 6.1 and 1.5 Hz, $H^3$), 7.05 (1H, dd, $J$ = 6.1 and 2.1 Hz, $H^4$), 7.19 (2H, m, Ar), and 7.30 (3H, m, Ar); $^{13}$C NMR $\delta$ = 28.1 (*t*-Bu), 67.1 (C5), 75.1 (C1′), 83.9 (*t*-Bu), 126.6 (Ar), 127.5 (C3), 128.3 (Ar), 128.2 (*para* Ar), 128.5 (Ar), 138.7 (*ipso*), 147.8 (C4), 151.3 ($OCO_2$), and 168.5 (C2); IR (KBr) 3440vs, 1774vs, 1754vs, 1372vs, and 1294vs cm$^{-1}$. Found: C, 66.25; H, 6.62; N, 4.84%. Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84%.

***N*-(*t*-Butoxycarbonyl)-5-[*t*-butyldimethylsilyloxy(phenyl)methyl]-1,5-dihydro-2*H*-pyrrol-2-one.** ($5S^*,1'R^*$)-isomer (*erythro*-**7c**): White powder, mp 88—89 °C; $^1$H NMR $\delta$ = −0.14 (3H, s, SiMe), 0.01 (3H, s, SiMe), 0.84 (9H, s, Si–*t*-Bu), 1.63 (9H, s, O–*t*-Bu), 4.67 (1H, m, $H^5$), 5.50 (1H, d, $J$ = 2.0 Hz, $H^{1'}$), 6.09 (1H, dd, $J$ = 6.4 and 1.2 Hz, $H^3$), 6.86 (1H, dd, $J$ = 6.4 and 2.0 Hz, $H^4$), and 7.25—7.40 (5H, m, Ar); $^{13}$C NMR $\delta$ = −5.4 (SiMe), −5.0 (SiMe), 18.1 (Si–*t*-Bu), 25.7 (Si–*t*-Bu), 28.3 (O–*t*-Bu), 69.2 (C5), 72.1 (C1′), 83.1 (O–*t*-Bu), 125.8 (Ar), 127.8 (C3*), 127.9 (*para* Ar*), 128.4 (Ar), 141.0 (*ipso*), 146.6 (C4), 149.9 ($OCO_2$), and 169.4 (C2); IR (KBr) 1768vs, 1710s, 1364s, and 1172s cm$^{-1}$. Found: C, 65.20; H, 8.20; N, 3.45%. Calcd for $C_{22}H_{33}NO_4Si$: C, 65.47; H, 8.24; N, 3.47%.

($5S^*,1'S^*$)-isomer (*threo*-**7c**): $^1$H NMR $\delta$ = −0.05 (3H, s, SiMe), 0.14 (3H, s, SiMe), 0.94 (9H, s, Si–*t*-Bu), 1.63 (9H, s, O–*t*-Bu), 4.82 (1H, dm, $J$ = 5.5 Hz, $H^5$), 5.53 (1H, d, $J$ = 5.5 Hz, $H^{1'}$), 5.85 (1H, dd, $J$ = 6.1 and ca. 1 Hz, $H^3$), 7.05 (1H, dd, $J$ = 6.1 and 2.1 Hz, $H^4$), and 7.10—7.50 (5H, m, Ar).

***N*-(*t*-Butoxycarbonyl)-5-[hydroxy(*p*-methoxyphenyl)methyl]-1,5-dihydro-2*H*-pyrrol-2-one.** ($5S^*,1'R^*$)-isomer (*erythro*-**6d**): White powder (*erythro*/*threo* = 1/2 mixture), mp 129—143 °C; $^1$H NMR $\delta$ = 1.61 (9H, s, O–*t*-Bu), 2.91 (1H, d, $J$ = 6.2 Hz, OH), 3.82 (3H, s, OMe), 4.85 (1H, m, $H^5$), 5.42 (1H, m, $H^{1'}$), 6.12 (1H, dd, $J$ = 6.1 and 1.7 Hz, $H^3$), 6.91 (2H, m, Ar), 6.95 (1H, dd, $J$ = 6.1 and 2.1 Hz, $H^4$), and 7.26 (2H, m, Ar); $^{13}$C NMR $\delta$ = 28.2 (O–*t*-Bu), 55.3 (OMe), 68.7 (C5), 71.6 (C1′), 83.8 (O–*t*-Bu), 113.9 (Ar), 127.6 (Ar), 128.2 (C3), 131.2 (C bearing CHOH), 146.5 (C4), 153.0 ($OCO_2$), 159.3 (C bearing OMe), and 169.4 (C2).

($5S^*,1'S^*$)-isomer (*threo*-**6d**): White powder (*erythro*/*threo* = 1/2 mixture), mp 129—143 °C; $^1$H NMR $\delta$ = 1.62 (9H, s, O–*t*-Bu), 3.44 (1H, d, $J$ = 2.6 Hz, OH), 3.79 (3H, s, OMe), 4.93 (1H, dm, $J$ = 6.1 and 1.8 Hz, $H^5$), 5.19 (1H, dd, $J$ = 6.1 and 2.6 Hz, $H^{1'}$), 5.95 (1H, dd, $J$ = 6.1 and 1.5 Hz, $H^3$), 6.81 (2H, m, Ar), 7.01 (1H, dd, $J$ = 6.1 and 2.1 Hz, $H^4$), and 7.12 (2H, m, Ar); $^{13}$C NMR $\delta$ = 28.1 (O–*t*-Bu), 55.2 (OMe), 67.1 (C5), 74.8 (C1′), 83.9 (O–*t*-Bu), 113.7 (Ar), 126.7 (C3), 127.8 (Ar), 130.7 (C bearing CHOH), 147.9 (C4), 147.9 (C2), 151.3 ($OCO_2$), 159.6 (C-bearing OMe), and 168.7 (C2); IR (KBr) 3464vs, 1770vs, 1756vs 1374s, 1304s, 1294s, and 1158s cm$^{-1}$. Found: C, 63.60; H, 6.59; N, 4.51%. Calcd for $C_{17}H_{21}NO_5$: C, 63.94; H, 6.63; N, 4.39%.

***N*-(*t*-Butoxycarbonyl)-5-[*t*-butyldimethylsilyloxy(*p*-methoxyphenyl)methyl]-1,5-dihydro-2*H*-pyrrol-2-one.** ($5S^*,1'R^*$)-isomer (*erythro*-**7d**): White powder, mp 93—94 °C; $^1$H NMR $\delta$ = −0.14 (3H, s, SiMe), 0.00 (3H, s, SiMe), 0.83 (9H, s, Si–*t*-Bu), 1.62 (9H, s, BOC), 3.83 (3H, s, OMe), 4.62 (1H, m, $H^5$), 5.45 (1H, d, $J$ = ca. 1 Hz, $H^{1'}$), 6.10 (1H, dd, $J$ = 6.1 and 1.5 Hz, $H^3$), 6.89 (1H, dd, $J$ = 6.1 and 2.1 Hz, $H^4$), 6.91 (2H, m, Ar), and 7.30 (2H, m, Ar); $^{13}$C NMR $\delta$ = −5.4 (SiMe), −5.0 (SiMe), 18.1 (Si–*t*-Bu), 25.7 (Si–*t*-Bu) 28.3 (O–*t*-Bu), 55.3 (OMe), 69.4 (C5), 71.7 (C1′), 83.0 (O–*t*-Bu), 113.8 (Ar), 126.9 (Ar), 127.8 (C3), 132.9 (C bearing CHOTBS), 146.7 (C4), 149.9 ($OCO_2$), 159.1 (C bearing OMe), and 169.5 (C2); IR (NaCl) 1780vs, 1744vs, 1708vs 1714vs, 1322vs, 1252vs, and 1162vs cm$^{-1}$; MS (CI) *m/z* (rel intensity) 378 (0.5), 362 (1), 320 (5), 276 (3), 251(100), and 202 (24). Found: C, 63.60; H, 8.04; N, 3.19%. Calcd for $C_{23}H_{35}NO_5Si$: C, 63.71; H, 8.14; N, 3.23%.

($5S^*,1'S^*$)-isomer (*threo*-**7d**): $^1$H NMR $\delta$ = −0.05 (3H, s, SiMe), 0.13 (3H, s, SiMe), 0.92 (9H, s, Si–*t*-Bu), 1.62 (9H, s, O–*t*-Bu), 3.74 (3H, s, OMe), 4.81 (1H, m, $H^5$), 5.48 (1H, d, $J$ = ca. 1 Hz, $H^{1'}$), 5.88 (1H, dd, $J$ = 6.1 and 1.5 Hz, $H^3$), 6.73 (2H, m, Ar), 6.87 (2H, m, Ar), and 7.36 (1H, dd, $J$ = 6.1 and 2.0 Hz, $H^4$).

***N*-(*t*-Butoxycarbonyl)-5-(1-hydroxy-3-methyl-2-butenyl)-1,5-dihydro-2*H*-pyrrol-2-one.** ($5S^*,1'R^*$)-isomer (*erythro*-**6e**): $^1$H NMR $\delta$ = 1.58 (9H, s, O–*t*-Bu), 1.76 (3H, br s, $H^{4'}$), 1.77 (3H, br s, $H^{4'}$), 2.75 (1H, br, OH), 4.65 (1H, q, $J$ = 1.8 Hz, $H^5$), 5.03 (1H, dd, $J$ = 9.5 and ca. 2 Hz, $H^{1'}$), 5.32 (1H, dm, $J$ = 9.5 Hz, $H^{2'}$), 6.16 (1H, dd, $J$ = 6.1 and ca. 2 Hz, $H^3$), and 7.16 (1H, dd, $J$ = 6.1 and 2.1 Hz, $H^4$); $^{13}$C NMR $\delta$ = 18.0 (C4′), 26.0 (C4′), 28.0 (O–*t*-Bu), 64.9 (C5), 71.9 (C1′), 82.0 (O–*t*-Bu), 119.0 (C2′), 127.7 (C3), 141.7 (C3′), 148.1 (C4), 149.1 ($OCO_2$), and 169.3 (C2).

($5S^*,1'S^*$)-isomer (*threo*-**6e**): $^1$H NMR $\delta$ = 1.56 (9H, s, O–*t*-Bu), 1.63 (3H, br s, $H^{4'}$), 1.68 (3H, br s, $H^{4'}$), 2.75 (1H, br, OH), 4.81 (1H, dt, $J$ = 5.2 and 1.8 Hz, $H^5$), 4.88 (1H, dm, $J$ = 9.5 Hz, $H^{2'}$), 5.07 (1H, dd, $J$ = 9.5 and 5.2 Hz, $H^{1'}$), 6.16 (1H, dd, $J$ = 6.1 and 1.8 Hz, $H^3$),and 7.34 (1H, dd, $J$ = 6.1 and 2.1 Hz, $H^4$); $^{13}$C NMR $\delta$ = 18.1 (C4′), 25.8 (C4′), 27.9 (O–*t*-Bu), 66.1 (C5), 67.9 (C1′), 82.8 (O–*t*-Bu), 121.0 (C2′), 127.5 (C3), 139.2 (C3′), 148.4 (C4), 149.9 ($OCO_2$), and 169.2 (C2); IR (NaCl) 3460vs, 2980vs, 2932vs, 1708vs, 1478vs, 1316vs, 1254vs, and 1168vs cm$^{-1}$.

***N*-(*t*-Butoxycarbonyl)-5-[1-(*t*-butyldimethylsilyloxy)-3-methyl-2-butenyl]-1,5-dihydro-2*H*-pyrrol-2-one.** ($5S^*,1'R^*$)-isomer (*erythro*-**7e**): $^1$H NMR $\delta$ = −0.08 (3H, s, SiMe), −0.06 (3H, s, SiMe), 0.76 (9H, s, TBS), 1.55 (9H, s, BOC), 1.74 (3H, brs, $H^{4'}$),

1.76 (3H, brs, $H^{4'}$), 4.43 (1H, q, $J$ = ca. 1.8 Hz, $H^5$), 5.0—5.15 (2H, m, $H^{1'}$ and $H^{2'}$), 6.10 (1H, dd, $J$ = 6.1 and 1.8 Hz, $H^3$), and 7.09 (1H, dd, $J$ = 6.1 and 2.1 Hz, $H^4$); $^{13}$C NMR $\delta$ = −5.4 (SiMe), −4.8 (SiMe), 17.8 (C4′), 18.6 (C4′), 25.6 (Si–*t*-Bu), 25.8 (Si–*t*-Bu), 28.2 (*t*-Bu), 67.4 (C5), 68.0 (C1′), 82.7 (*t*-Bu), 125.4 (C2′), 127.8 (C3), 135.1 (C3′), 147.4 (C4),149.8 ($OCO_2$), and 169.5 (C2).

(5*S**,1′*S**)-isomer (*threo*-**7e**): $^1$H NMR $\delta$ = 0.14 (3H, s, SiMe), 0.09 (3H, s, SiMe), 0.88 (9H, s, Si–*t*-Bu), 1.54 (9H, s, O–*t*-Bu), 1.57 (3H, d, $J$ = 1.2 Hz, $H^{4'}$), 1.60 (3H, d, $J$ = 1.2 Hz, $H^{4'}$), 4.6—4.7 (2H, m, $H^5$ and $H^{2'}$), 5.12 (1H, dd, $J$ = 9.6 and 5.1 Hz, $H^{1'}$), 6.10 (1H, dd, $J$ = 6.1 and 1.8 Hz, $H^3$), and 7.31 (1H, dd, $J$ = 6.1 and 1.8 Hz, $H^4$); $^{13}$C NMR $\delta$ = −5.0 (SiMe), −4.5 (SiMe), 17.9 (C4′), 18.1 (Si–*t*-Bu), 25.5 (C4′), 25.7 (Si–*t*-Bu), 28.1 (O–*t*-Bu), 66.6 (C5), 68.6 (C1′), 82.8 (O–*t*-Bu), 121.7 (C2′), 127.5 (C3), 137.4 (C3′), 148.9 (C4), 149.6 ($OCO_2$), and 169.5 (C2); IR (KBr) 2928vs, 2856vs, 1786vs, 1748vs, 1708vs, 1464vs, 1322vs, 1164vs, 834vs, and 1160vs cm$^{-1}$.

***N*-(*t*-Butoxycarbonyl)-5-(1-hydroxypropyl)-1,5-dihydro-2*H*-pyrrol-2-one.** (5*S**,1′*R**)-isomer (*erythro*-**6f**): White powder, mp 125—127 °C; $^1$H NMR $\delta$ = 1.07 (3H, t, $J$ = 7.5 Hz, $H^{3'}$), 1.56 (9H, s, O–*t*-Bu), 1.5—1.6 (2H, m, $H^{2'}$), 3.88 (1H, br, OH), 4.30 (1H, m, $H^{1'}$), 4.70 (1H, m, $H^5$), 6.15 (1H, m, $H^3$), and 7.17 (1H, dd, $J$ = 6.1 and 1.8 Hz, $H^4$); $^{13}$C NMR $\delta$ = 10.7 (C3′), 26.4 (C2′), 28.2 (O–*t*-Bu), 67.7 (C5), 71.6 (C1′), 83.2 (O–*t*-Bu), 127.8 (C3), 147.4 (C4), 149.7 ($OCO_2$), and 169.9 (C2); IR (KBr) 3472vs, 1776vs, 1768vs, 1368vs, 1304vs, and 1160vs cm$^{-1}$. Found: C, 59.87; H, 7.90; N, 5.89%. Calcd for $C_{12}H_{19}NO_4$: C, 59.73; H, 7.94; N, 5.80%.

(5*S**,1′*S**)-isomer (*threo*-**6f**): $^1$H NMR $\delta$ = 0.97 (3H, t, $J$ = 7.3 Hz, $H^{3'}$), 1.12 (1H, m, $H^{2'}$), 1.41 (1H, m, $H^{2'}$), 1.56 (9H, s, O–*t*-Bu), 2.81 (1H, br d, $J$ = 4.3 Hz, OH), 4.12 (1H, m, $H^{1'}$), 4.76 (1H, dt, $J$ = 5.2 and 1.8 Hz, $H^5$), 6.15 (1H, dd, $J$ = 6.1 and 1.8 Hz, $H^3$), and 7.29 (1H, dd, $J$ = 6.1 and 2.1 Hz, $H^4$); $^{13}$C NMR $\delta$ = 10.2 (C3′), 24.4 (C2′), 28.0 (O–*t*-Bu), 66.8 (C5), 71.6 (C1′), 83.5 (O–*t*-Bu), 127.4 (C3), and 148.7 (C4).

***N*-(*t*-Butoxycarbonyl)-5-[1-(*t*-butyldimethylsilyloxy)propyl]-1,5-dihydro-2*H*-pyrrol-2-one.** (5*S**,1′*R**)-isomer (*erythro*-**7f**): $^1$H NMR $\delta$ = −0.04 (3H, s, SiMe), 0.00 (3H, s, SiMe), 0.80 (9H, s, Si–*t*-Bu), 1.03 (3H, t, $J$ = 7.5 Hz, $H^{3'}$), 1.56, 1.62 (2H, m, $H^{2'}$), 1.63 (9H, s, O–*t*-Bu), 4.27 (1H, td, $J$ = 6.9 and ca. 2 Hz, $H^{1'}$), 4.61 (1H, q, $J$ = ca. 2 Hz, $H^5$), 6.09 (1H, dd, $J$ = 6.3 and 1.5 Hz, $H^3$), 7.15 (1H, dd, $J$ = 6.3 and 2.1 Hz, $H^4$).

(5*S**,1′*S**)-isomer (*threo*-**7f**): White powder, mp 59—60 °C; $^1$H NMR $\delta$ = 0.13 (3H, s, SiMe), 0.18 (3H, s, SiMe), 0.85 (3H, t, $J$ = 7.3 Hz, $H^{3'}$), 0.94 (9H, s, Si–*t*-Bu), 1.01 (1H, m, $H^{2'}$), 1.25 (1H, m, $H^{2'}$), 1.63 (9H, s, O–*t*-Bu), 4.33 (1H, m, $H^{1'}$), 4.64 (1H, dt, $J$ = 5.2 and ca. 2 Hz, $H^5$), 6.15 (1H, dd, $J$ = 6.1 and 1.8 Hz, $H^3$), and 7.29 (1H, dd, $J$ = 6.1 and 2.1 Hz, $H^4$); $^{13}$C NMR $\delta$ = −4.8 (SiMe), −4.3 (SiMe), 10.7 (C3′), 17.9 (Si–*t*-Bu), 23.3 (C2′), 25.7 (Si–*t*-Bu), 28.2 (O–*t*-Bu), 66.4 (C5), 72.5 (C1′), 83.0 (O–*t*-Bu), 127.4 (C3), 149.2 (C4), 149.4 ($OCO_2$), and 169.8 (C2); IR (KBr) 1752vs 1710vs and 1320vs cm$^{-1}$. Found: C, 60.47; H, 9.29; N, 3.97%. Calcd for $C_{18}H_{33}NO_4Si$: C, 60.81; H, 9.36; N, 3.94%.

***N*-(*t*-Butoxycarbonyl)-5-(1-hydroxy-2-methylpropyl)-1,5-dihydro-2*H*-pyrrol-2-one.** (5*S**,1′*R**)-isomer (*erythro*-**6g**): White powder, mp 135—137 °C (decomp); $^1$H NMR $\delta$ = 1.06 (3H, d, $J$ = 7.0 Hz, *i*-Pr), 1.08 (3H, d, $J$ = 7.0 Hz, *i*-Pr), 1.57 (9H, s, O–*t*-Bu), 1.75 (1H, m, $H^{2'}$), 2.04 (1H, d, $J$ = 5.2 Hz, OH), 3.90 (1H, m, $H^{1'}$), 4.86 (1H, q, $J$ = ca. 2 Hz, $H^5$), 6.18 (1H, dd, $J$ = 6.1 and 1.7 Hz, $H^3$), and 7.15 (1H, dd, $J$ = 6.1 and 2.0 Hz, $H^4$); $^{13}$C NMR $\delta$ = 19.2, 20.0 ($CHMe_2$), 28.1 (O–*t*-Bu), 31.9 (C2′), 65.8 (C5), 75.3 (C1′), 83.3 (O–*t*-Bu), 128.3 (C3), 147.0 (C4), 149.5 ($OCO_2$), and 170.0 (C2); IR (KBr) 3472vs, 1774vs, 1686s, 1378vs, 1304vs, and 1162vs cm$^{-1}$. Found: C, 60.87; H, 8.21; N, 5.49%. Calcd for $C_{13}H_{21}NO_4$: C, 61.16; H, 8.29; N, 5.49%.

(5*S**,1′*S**)-isomer (*threo*-**6g**): $^1$H NMR $\delta$ = 0.86 (3H, d, $J$ = 6.4 Hz, *i*-Pr), 0.87 (3H, d, $J$ = 6.4 Hz, *i*-Pr), 1.47 (9H, s, O–*t*-Bu), 1.60 (1H, m, $H^{2'}$), 3.67 (2H, m, OH and $H^{1'}$), 4.69 (1H, dt, $J$ = 8.3 and ca. 2 Hz, $H^5$), 6.04 (1H, dd, $J$ = 6.1 and 1.8 Hz, $H^3$), and 7.21 (1H, dd, $J$ = 6.1 and 2.1 Hz, $H^4$).

***N*-(*t*-Butoxycarbonyl)-5-(1-hydroxy-2,2-dimethylpropyl)-1,5-dihydro-2*H*-pyrrol-2-one.** (5*S**,1′*R**)-isomer (*erythro*-**6h**): White powder, mp 153—154 °C; $^1$H NMR $\delta$ = 1.09 (9H, s, *t*-Bu), 1.56 (9H, s, O–*t*-Bu), 2.17 (1H, br, OH), 3.96 (1H, m, $H^{1'}$), 4.91 (1H, m, $H^5$), 6.12 (1H, dd, $J$ = 6.3 and 1.8 Hz, $H^3$), and 7.24 (1H, dd, $J$ = 6.3 and 1.9 Hz, $H^4$); $^{13}$C NMR $\delta$ = 27.0 (*t*-Bu), 28.2 (O–*t*-Bu), 35.0 (C2′), 65.1 (C5), 77.9 (C1′), 83.3 (O–*t*-Bu), 127.5 (C3), 148.5 (C4), 149.5 ($OCO_2$), 169.9 (C2); IR (KBr) 3468vs, 2976s—2932s, 1788vs, 1686s, 1410vs—1378vs cm$^{-1}$. Found: C, 62.22; H, 8.61; N, 5.16%. Calcd for $C_{14}H_{23}NO_4$: C, 62.43; H, 8.48; N, 5.20%.

***N*-(*t*-Butoxycarbonyl)-5-[hydroxy(phenyl)methyl]-2-pyrrolidinone.** (5*S**,1′*R**)-isomer (*erythro*-**8c**): Colorless crystals, mp 155—157 °C; $^1$H NMR $\delta$ = 1.61 (9H, s, BOC), 1.72 (1H, m, $H^4$), 1.76 (1H, m, $H^3$), 2.00 (1H, m, $H^4$), 2.32 (1H, ddd, $J$ = 17.7, 10.3, and 2.0 Hz, $H^3$), 2.79 (1H, br, OH), 4.36 (1H, dm, $J$ = 7.2 Hz, $H^5$), 5.31 (1H, m, $H^{1'}$), and 7.25—7.5 (5H, m, Ar); $^{13}$C NMR: $\delta$ = 17.1 (C4), 28.2 (O–*t*-Bu), 32.7 (C3), 63.8 (C5), 73.7 (C1′), 83.2 (O–*t*-Bu), 125.7 (*meta** Ar), 127.4 (*para* Ar), 128.4 (*ortho** Ar), 140.7 (*ipso*), 150.3 ($OCO_2$), and 176.1 (C2); IR (KBr) 3473vs, 1774vs, 1689m, 1367vs, 1294vs, 1259vs, and 1153vs cm$^{-1}$. Found: C, 65.98; H, 7.21; N, 4.68%. Calcd for $C_{16}H_{21}NO_4$: C, 65.96; H, 7.27; N, 4.81%.

(5*S**,1′*S**)-isomer (*threo*-**8c**): White crystals, mp 87—89 °C; $^1$H NMR $\delta$ = 1.55 (9H, s, O–*t*-Bu), 1.5—2.1 (4H, m, $H^3$, $H^4$), 3.18 (1H, br, OH), 4.46 (1H, q, $H^5$), 4.97 (1H, d, $J$ = 5.5 Hz, $H^{1'}$), and 7.32 (5H, m, Ar); $^{13}$C NMR $\delta$ = 19.0 (C4), 27.9 (*t*-Bu), 31.3 (C3), 62.0 (C5), 73.6 (C1′), 83.3 (*t*-Bu), 126.3 (*meta** Ar), 128.1 (*para* Ar), 128.5 (*ortho** Ar), 139.9 (*ipso*), 150.9 ($OCO_2$), and 174.6 (C2).

**X-Ray Analysis.** A colorless prismatic crystal of *erythro*-**8c** having approximate dimensions of 0.33×0.25×0.23 mm was mounted on a glass fiber. All of the measurements were made on a Rigaku AFC5R diffractometer with graphite-monochromated Mo $K\alpha$ radiation and a 12-kW rotating-anode generator. The cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using setting angles of 25 reflections in the range $23.50<2\theta<25.69°$, corresponded to a monoclinic cell with the following dimensions: $a$ = 29.112(8), $b$ = 7.200(1), $c$ = 18.568(6) Å, $\beta$ = 126.53(2)°, and $V$ = 3127(2) Å$^3$. For $Z$ = 8 and $FW$ = 291.35, the calculated density is 1.237 g cm$^{-3}$. Based on the systematic absences of $hkl$ ($h+k\neq 2n$) and $h0l$ ($l\neq 2n$) and the successful solution and refinement of the structure, the space group was determined to be $C2/c$ (#15). The data were collected at a temperature of 25±1 °C using the $\omega$ scan technique to a maximum $2\theta$ value of 55.0°. Omega scans of several intense reflections, made prior to data collection, had an average width at a half-weight of 0.23° with a taking-off angle of 6.0° min$^{-1}$ (in omega). The weak reflections [$I<10.0\sigma(I)$] were rescanned (maximum of 2 rescans) and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of the peak counting time to the background counting time was 2 : 1. The diameter of the incident beam collimator was 0.5 mm and the crystal-to-detector distance was 25.8 cm. Of the collected 3963 reflections, 3883 were unique ($R_{int}$ = 0.031). An empirical correction for the absorption was made based on

azimuthal ($\Psi$) scans of three reflections.[13] The structure was solved by the direct method using the MITHRIL program.[14] The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined isotropically. Calculations were carried out on a VAX station 3200 computer with TEXSAN programs,[15] which used the atomic-scattering factors taken from "International Tables for X-Ray Crystallography."[16] The final cycle of full-matrix least-squares refinement yields $R = 0.069$, $R_w = 0.095$ and goodness-of-fit = 1.22 for 1662 observed reflections [$I > 1.00\sigma(I)$] and 194 variable parameters. The final atomic parameters are deposited as Document No. 72024 at the Office of the Editor of Bull. Chem. Soc. Jpn.. The auther has also deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

**5-[Hydroxy(phenyl)methyl]-5*H*-furan-2-one.** ($5S^*,1'R^*$)-isomer (*erythro*-**10c**): $^1$H NMR $\delta$ = 3.00 (1H, br, OH), 5.05 (1H, d, $J$ = 4.3 Hz, $H^5$), 5.17 (1H, m, $H^{1''}$), 6.12 (1H, dd, $J$ = 5.8 and 1.8 Hz, $H^3$), 7.33 (1H, dd, $J$ = 5.8 and 1.5 Hz, $H^4$), and 7.39 (5H, m, Ar); $^{13}$C NMR $\delta$ = 72.7 (C5), 86.7 (C1′), 122.7 (C3), 126.3 (*para* Ar), 128.1 (Ar), 128.5 (Ar), 138.4 (*ipso*), 153.3 (C4), and 173.4 (C2).

($5S^*,1'S^*$)-isomer (*threo*-**10c**): Colorless oil; $^1$H NMR $\delta$ = 2.69 (1H, br, OH), 4.71 (1H, d, $J$ = 6.8 Hz, $H^5$), 5.16 (1H, dt, $J$ = 7.3 and 2.0 Hz, $H^{1''}$), 6.13 (1H, dd, $J$ = 5.9 and 2.0 Hz, $H^3$), 7.17 (1H, dd, $J$ = 5.9 and 2.0 Hz, $H^4$), and 7.39 (5H, m, Ar); $^{13}$C NMR $\delta$ = 74.6 (C5), 86.7 (C1′), 122.5 (C3), 126.0 (*para* Ar), 126.5 (Ar), 128.4 (Ar), 138.0 (*ipso*), 153.7 (C4), and 173.0 (C2); IR (KBr) 3432vs, 1758vs, 1198s, 1088s, and 756s cm$^{-1}$; MS (CI) *m/z* (rel intensity) 191 (28), 173 (39), and 107 (100).

**5-[*t*-Butyldimethylsilyloxy(phenyl)methyl]-5*H*-furan-2-one.** ($5S^*,1'R^*$)-isomer (*erythro*-**11c**): $^1$H NMR $\delta$ = 0.06 (9H, s, SiMe), 4.99 (1H, d, $J$ = 4.4 Hz, $H^5$), 5.06 (1H, q, $J$ = 2.0 Hz, $H^{1''}$), 6.15 (1H, dd, $J$ = 5.9 and 2.0 Hz, $H^3$), 7.32 (1H, dd, $J$ = 9.2 and 1.5 Hz, $H^4$), and 7.37 (5H, m, Ar); $^{13}$C NMR $\delta$ = −0.24 (SiMe), 73.9 (C5), 86.9 (C1′), 123.0 (C3), 126.0 (Ar), 128.4 (*para* Ar), 128.5 (Ar), 139.5 (*ipso*), 152.7 (C4), and 172.9 (C2).

($5S^*,1'S^*$)-isomer (*threo*-**11c**): Colorless oil; $^1$H NMR $\delta$ = 0.09 (9H, s, SiMe), 4.83 (1H, d, $J$ = 5.9 Hz, $H^5$), 5.11 (1H, dt, $J$ = 6.6 and 1.8 Hz, $H^{1''}$), 5.98 (1H, dd, $J$ = 5.9 and 2.0 Hz, $H^3$), 7.23 (1H, dd, $J$ = 5.9 and 1.5 Hz, $H^4$), and 7.29 (5H, m, Ar); $^{13}$C NMR $\delta$ = −0.11 (SiMe), 75.1 (C5), 86.3 (C1′), 122.8 (C3), 126.6 (Ar), 128.2 (Ar), 128.3 (*para* Ar), 138.5 (*ipso*), 153.4 (C4), and 172.6 (C2); IR (KBr) 1736vs, 1196s, 1068s, and 768s cm$^{-1}$; MS (CI) *m/z* (rel intensity) 263 (11), 219 (10), 180 (46), 179 (100), and 173 (36).

**5-(1-Hydroxy-2-methylpropyl)-5*H*-furan-2-one.** ($5S^*,1'R^*$)-isomer (*erythro*-**10g**): White powder, mp 85—86 °C; $^1$H NMR $\delta$ = 1.00 (3H, d, $J$ = 6.9 Hz, *i*-Pr), 1.02 (3H, d, $J$ = 6.9 Hz, *i*-Pr), 1.90 (1H, m, $H^{2'}$), 2.54 (1H, br, OH), 3.41 (1H, m, $H^{1'}$), 5.13 (1H, m, $H^5$), 6.12 (1H, dd, $J$ = 5.8 and 1.8 Hz, $H^3$), and 7.45 (1H, dd, $J$ = 5.8 and 1.5 Hz, $H^4$); $^{13}$C NMR $\delta$ = 17.8, 19.4 (CH*Me*$_2$), 31.6 (C2′), 76.5 (C5), 84.5 (C1′), 122.5 (C3), 154.3 (C4), and 173.1 (C2); IR (KBr) 3384vs, 1728vs, 1176s, 1032s, 918s, 840s, and 666vs cm$^{-1}$; MS (CI) *m/z* (rel intensity) 157 (100), 139 (19), and 125 (5). Found: C, 61.26; H, 7.67%. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.74%.

($5S^*,1'S^*$)-isomer (*threo*-**10g**): $^1$H NMR $\delta$ = 1.06 (3H, d, $J$ = 6.9 Hz, *i*-Pr), 1.07 (3H, d, $J$ = 6.9 Hz, *i*-Pr), 1.93 (1H, m, $H^{2'}$), 2.36 (1H, br, OH), 3.56 (1H, m, $H^{1'}$), 5.03 (1H, dm, $J$ = 5.9 Hz, $H^5$), 6.16 (1H, dd, $J$ = 5.8 and 1.8 Hz, $H^3$), and 7.61 (1H, dd, $J$ = 5.9 and 1.5 Hz, $H^4$).

**5-(1-*t*-Butyldimethylsilyloxy-2-methylpropyl)-5*H*-furan-2-one.** ($5S^*,1'R^*$)-isomer (*erythro*-**11g**): Colorless oil; $^1$H NMR $\delta$ = 0.09 (9H, s, SiMe), 0.90 (3H, d, $J$ = 6.7 Hz, *i*-Pr), 0.96 (3H, d, $J$ = 6.7 Hz, *i*-Pr), 1.70 (1H, m, $H^{2'}$), 3.57 (1H, q, $J$ = ca. 2 Hz, $H^{1'}$), 5.14 (1H, m, $H^5$), 6.11 (1H, dd, $J$ = 5.8 and 2.1 Hz, $H^3$), and 7.47 (1H, dd, $J$ = 5.9 and 1.5 Hz, $H^4$); $^{13}$C NMR $\delta$ = 0.4 (SiMe), 17.3, 19.8 (CH*Me*$_2$), 31.3 (C2′), 77.6 (C5), 85.5 (C1′), 122.7 (C3), 153.7 (C4), and 172.9 (C2); IR (KBr) 3088vs, 1768vs, 1254s, 1162s, 1086s, and 876vs cm$^{-1}$; MS (CI) *m/z* (rel intensity) 229 (11) and 145 (100).

($5S^*,1'S^*$)-isomer (*threo*-**11g**): $^1$H NMR $\delta$ = 0.11 (9H, s, SiMe), 0.84 (3H, d, $J$ = 6.7 Hz, *i*-Pr), 0.95 (3H, d, $J$ = 6.7 Hz, *i*-Pr), 1.83 (1H, m, $H^{2'}$), 3.60 (1H, t, $J$ = 4.8 Hz, $H^{1'}$), 5.03 (1H, dt, $J$ = 4.8 and 1.8 Hz, $H^5$), 6.11 (1H, dd, $J$ = 5.8 and 2.1 Hz, $H^3$), and 7.47 (1H, dd, $J$ = 5.8 and 1.5 Hz, $H^4$); $^{13}$C NMR $\delta$ = 0.3 (SiMe), 18.3, 19.2 (CH*Me*$_2$), 31.8 (C2′), — (C5), 84.3 (C1′), 122.5 (C3), 154.2 (C4), and 172.9 (C2).

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