The Diastereoselective Barbier-Type Addition to Chiral *N*-Tosylimines

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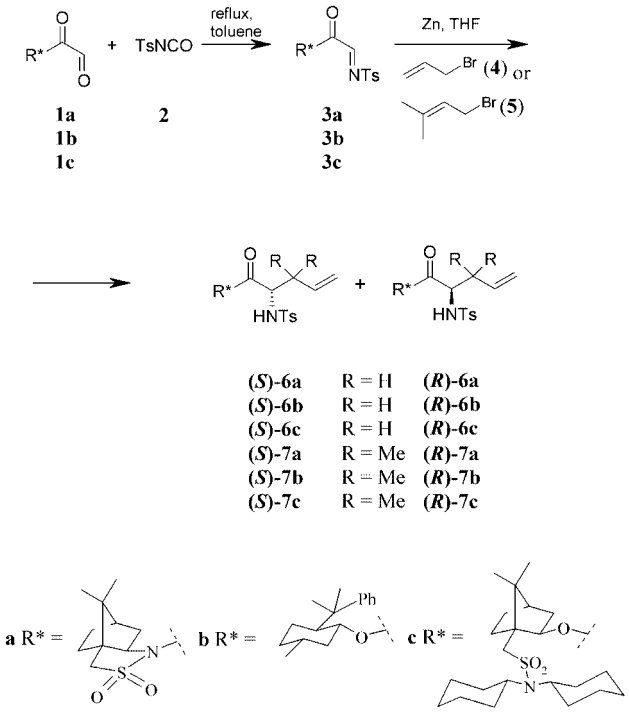
Abstract: The Barbier approach was used for diastereoselective formation of allylamino acid derivatives. The stereochemical models for nucleophilic addition to *N*-tosylimines bearing various chiral auxiliaries such as (2*R*)-bornano-10,2-sultam, (*R*)-8-phenylmenthol, and 10-*N*,*N*-dicyclohexylsulfamoyl-(*R*)-isoborneol are proposed.

Key words: chiral auxiliaries, imines, nucleophilic additions, organometallic reagents, stereoselectivity



Scheme 1

The demand for stereochemically pure, nonproteogenic amino acids in pharmaceutical industry triggers intensive research effort in this area. The methodology that uses specifically glyoxyloyl-derived imines for nucleophilic addition provides a straightforward route to target amino acids. Many 1,2-nucleophilic asymmetric additions of organometallic compounds to chiral imines were exploited involving Grignard reagents, organozinc compounds, etc. in enantioselective and diastereoselective ways.[1] Recently, the Barbier reagents were applied for the reactions of O-alkylated oximes with the assistance of chiral auxiliaries.[2,3] Imines having the stereogenic center (responsible for the asymmetric induction) connected to the nitrogen atom[4,5]were also used in the Barbier-type addition.

In our previous reports on the stereoselectivity of *N*-glyoxyloyl-(2*R*)-bornano-10,2-sultam in nucleophilic addition[6] and hetero-Diels–Alder reaction,[7,8] we described a stereochemical substantiation of asymmetric induction and the benefits of using (2*R*)-bornano-10,2-sultam as a chiral auxiliary. 10-*N*,*N*-Dicyclohexylsulfamoyl-(*R*)-isobornyl glyoxylate was found less beneficial, in terms of diastereoselectivity, for the nucleophilic addition of allyltrimethylsilane to the carbonyl group.[9] We have recently reported the diastereoselective hetero-Diels–Alder reaction of *N*-tosylimine derivatives of *N*-glyoxyloyl-(2*R*)-bornano-10,2-sultam that showed very high diastereofacial differentiation.[10] Then we focused our attention on nucleophilic addition reactions of allyltrimeth-

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ylsilane to imines bearing chiral auxilliaries.[11,12] In the present work, we decided to conduct the comparative studies concerning three different chiral auxiliaries as carriers of chirality in the asymmetric Barbier reaction. The procedure requires mild, nonbasic conditions for the nucleophilic attack and affords high stereoselectivities. The asymmetric induction in this reaction results from coordination of the electron lone-pair at nitrogen with zinc; this can be modulated by chelation with another heteroatom (C=O, SO_2) to form a rigid transition state.

The *N*-tosylimines were obtained from the corresponding derivatives of glyoxylic acid using the method introduced recently by Holmes et al.[13] The reaction of compounds **1a**,[14,15] **1b**,[16–19] and **1c**[9] with *p*-toluenesulfonyl isocyanate (**2**), in refluxing toluene, afforded the expected imines **3a**,[10] **3b**,[20] and **3c**,[12] respectively (Scheme 1). Table 1 presents the results of the Barbier addition of allylzinc bromide (**4**) and 2,2-dimethylallylzinc bromide (**5**) to the imines **3a**–**c**. The more sterically-demanding zinc derivative **5** gave the better diastereoselectivities and, in the case of (*R*)-8-phenylmenthyl ester **3b**, allylamine (*S*)-**7b** was obtained with excellent asymmetric induction. Imines **3a** and **3b**, derived from (2*R*)-bornano-10,2-sultam and 10-*N*,*N*-dicyclohexylsulfamoyl-(*R*)-isoborneol, respectively, gave relatively low asymmetric inductions. All results presented in Table 1 confirm the superiority of γ-substituted allyl nucleophiles.

Table 1 Results of the Barbier-Type Addition to Chiral Imines

Entry	*N*-Tosylimine	Allylic Reagent	Yield (%)	Adducts	Diastereoisomeric Ratio of Adducts C-2′ (*S*:*R*)
1	**3a**	**4**	46	**6a**	60: 40
2	**3a**	**5**	63	**7a**	70: 30
3	**3b**	**4**	57	**6b**	71: 29
4	**3b**	**5**	50	**7b**	100: 0
5	**3c**	**4**	50	**6c**	42: 58
6	**3c**	**5**	55	**7c**	88: 12

In order to rationalize the stereochemical course of allylic addition to the imine derived from *N*-glyoxyloyl-(2*R*)-bornano-10,2-sultam (**1a**), we propose two chelates of type **A** and **B** (Figure 1) that lead to opposite diastereoisomers and explain the low diastereoselectivities in entries 1 and 2. The explanation involves an analogy to the proposed rationale for the hetero-Diels–Alder reaction that is based on two concepts: (a) the sterically controlled approach of the thermodynamically more stable SO_2/CO antiperiplanar, CO/CHNTs *s*-*cis* planar conformer **A**, as proposed by Oppolzer et al.[21]and by Curran et al.[22] for *N*-acryloyl- and *N*-crotonoyl-(2*R*)-bornano-10,2-sultam; and (b) the high reactivity of the less stable SO_2/CO synperiplanar, CO/CHNTs *s*-*cis* planar conformer **B**, reinforced by the cooperative stereoelectronic effect, as recently formulated by Chapuis et al.[7,8]for *N*-glyoxyloyl-(2*R*)-bornano-10,2-sultam (**1a**).

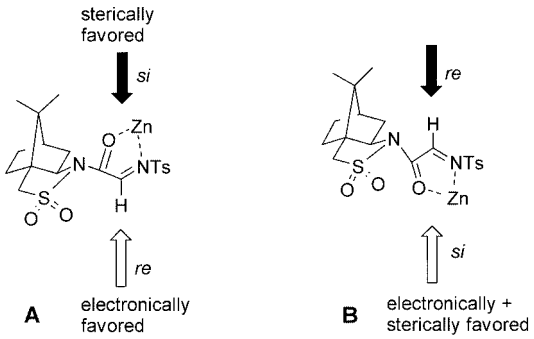

Figure 1 Conformations of chelates **A** and **B** derived from **1a**.

Oppolzer has earlier proposed,[23] that the most favorable conformation was reached when the alkoxy C–H bond was *syn*-periplanar to the C=O moiety of the ester (as supported by recent X-ray analysis).[24] As a consequence, all these groups possess an identical sterically-induced C_α-*si* topicity, where the (*E*)-C=N bond is *s*-*cis* to that of the C=O bond. The PM3 calculations confirmed the thermodynamic stability and higher reactivity of the *s*-*cis* over *s*-*trans* conformer for *N*-benzyl protonated analogues.[25]

Since the zinc reagent presumably forms the 5-membered chelate with oxygen and nitrogen (Figure 2), the following rationale is proposed. The (*R*)-8-phenylmenthyl chiral auxiliary (cf. **1b**) provides excellent diastereoselectivities that hypothetically result from the π-π stacking between the aryl moiety and the reacting site.[26] The *pro*-*R* side is effectively shielded by the aryl moiety. Moreover, the chelation by zinc additionally stabilizes the transition state shown below.

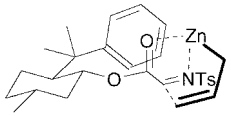

Figure 2 Structure of 5-membered Zn-chelate derived from **1b**.

The configuration 2′*S* of the major diastereoisomer **6a** and 2′*R* of the major diastereoisomer **6c** were earlier determined by X-ray analysis.[12] The absolute configuration of the adduct **6b** was obtained by converting the two major diastereoisomers **6a** and **6b**, and the minor diastereoisomer **6c** to alcohol **8**, and comparing the optical rotations of the respective products (Scheme 2). A similar approach was used for the series of adducts **7**. The configuration 2′*S* of **7a** was determined by X-ray analysis (Figure 3). The absolute configurations of adducts **7b** and **7c** were obtained by converting all derivatives **7a**, **7b** and **7c** to alcohol **9** and comparing the optical rotations of the respective products (Scheme 2).

6a	R = H	**8**
6b	R = H	**8**
6c	R = H	**8**
7a	R = Me	**9**
7b	R = Me	**9**
7c	R = Me	**9**

Scheme 2

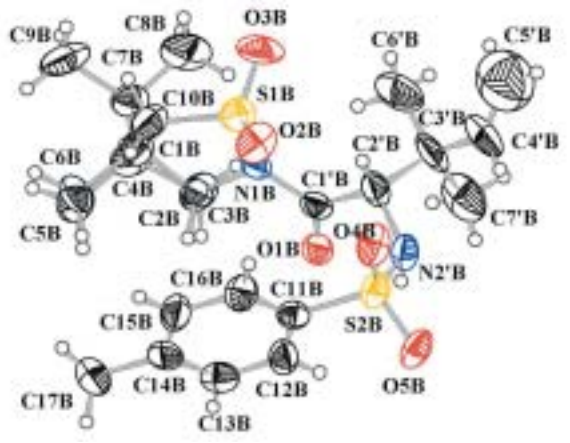

Figure 3 Crystal Structure of Compound **7a**.

The reagent-grade solvents, CH_2Cl_2, hexanes, EtOAc, THF, were distilled prior use. All the reported NMR spectra were recorded on a Varian Gemini spectrometer at 200 MHz (^{1}H NMR) and at 50 MHz (^{13}C NMR). The chemical shifts are reported in δ relative to the TMS signal at δ = 0.00 (^{1}H NMR) or δ = 0.00 (^{13}C NMR). The IR spectra were obtained on a Perkin-Elmer 1640 FTIR spectrophotometer. The major bands are reported in cm^{-1}. Mass spectra were obtained on an AMD-604 Intectra instrument using the EI or LSIMS technique. Chromatography was performed on silica gel (Kieselgel 60, 200–400 mesh). Optical rotations were recorded using a Jasco DIP-360 polarimeter with a thermally jacketed 10 cm cell. All air- or moisture-sensitive reactions were carried out using flame-dried glassware under argon.

N-Toluenesulfonylimines 3a–c; General Procedure

To a solution of the corresponding glyoxylate (1.5 mmol) in toluene (10 mL) was added tosyl isocyanate (0.23 mL, 1.5 mmol) under argon and the reaction mixture was refluxed for 24 h. The obtained imines were used in situ for allylations.

Barbier Addition to *N*-Toluenesulfonylimines 3; General Procedure

To a stirred solution of the imine **3** (1 mmol) in toluene in an ice bath, were added the Barbier reagent **4** or **5** [prepared in situ by reacting metallic zinc (126 mg, 2 mmol) and corresponding allyl bromide (1.5 mmol) at 0 °C in THF]. The reaction mixture was stirred for 12 h at 0 °C. The reaction was quenched by dropwise addition of 10% HCl. The aqueous phase was extracted with Et_2O and the combined organic extracts were washed with $NaHCO_3$, dried ($MgSO_4$) and rotary-evaporated under reduced pressure. The products were purified by flash chromatography using 30% Et_2O–hexane as an eluent for the adducts of the imines derived from *N*-glyoxyloyl-(2*R*)-bornano-10,2-sultam (**1a**) as well as 10-*N*,*N*-dicyclohexylsulfamoyl-(*R*)-isobornyl glyoxylate (**1c**), and using 10% EtOAc–hexane as an eluent for the adduct of the imine derived from (*R*)-8-phenylmenthyl glyoxylate (**1b**). The separate diastereoisomers were thus obtained.

N-[(2′*R*)-*N*′-*p*-Toluenesulfonylallylglycinoyl]-(2*R*)-bornano-10,2-sultam [(*R*)-6a]

Mp 154–157 °C (hexane–EtOAc); $[\alpha]_D^{20}$ –28.2 (*c* = 1, $CHCl_3$). All IR, ^{1}H NMR, ^{13}C NMR, EI-MS, and analytical data were identical with those obtained by us earlier.[12]

N-[(2′*S*)-*N*′-*p*-Toluenesulfonylallylglycinoyl]-(2*R*)-bornano-10,2-sultam [(*S*)-6a]

Mp 120–123 °C (hexane–EtOAc); $[\alpha]_D^{20}$ –34.6 (*c* = 1, $CHCl_3$). All IR, ^{1}H NMR, ^{13}C NMR, EI-MS, and analytical data were identical with those obtained by us earlier.[12]

N-[(2′*S*)-*N*′-*p*-Toluenesulfonylallylglycine] 8-(*R*)-Phenylmenthyl Ester [(*S*)-6b]

Oil; $[\alpha]_D^{20}$ +20.6 (*c* = 1, $CHCl_3$). All IR, ^{1}H NMR, ^{13}C NMR, EI-MS, and analytical data were identical with those obtained by us earlier.[12]

N-[(2′*R*)-*N*′-*p*-Toluenesulfonylallylglycine]-10-*N*,*N*-dicyclohexylsulfamoyl (2*R*)-Isobornyl Ester [(*R*)-6c]

Mp 171–172 °C; $[\alpha]_D^{20}$ –29.2 (*c* = 1, $CHCl_3$). All IR, ^{1}H NMR, ^{13}C NMR, EI-MS, and analytical data were identical with those obtained by us earlier.[12]

N-[(2′*S*)-*N*′-*p*-Toluenesulfonylallylglycine]-10-*N*,*N*-dicyclohexylsulfamoyl (2*R*)-Isobornyl Ester [(*S*)-6c]

Mp 167–168 °C; $[\alpha]_D^{20}$ –14.0 (*c* = 1, $CHCl_3$). All IR, ^{1}H NMR, ^{13}C NMR, EI MS, and analytical data were identical with those obtained by us earlier.[12]

N-[(2′*R*)-*N*′-*p*-Toluenesulfonyl-3′,3′-dimethylallylglycinoyl]-(2*R*)-bornano-10,2-sultam [(*R*)-7a]

Oil; $[\alpha]_D^{20}$ –29.0 (*c* = 1, $CHCl_3$).

IR (KBr): 3292, 2962, 2884, 1688, 1339, 1162 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.81 (dAB, *J* = 8.2 Hz, 2 H), 7.25 (dAB, *J* = 8.4 Hz, 2 H), 5.97 (m, 1 H), 5.15–4.98 (m, 3 H), 4.23 (br s, 1 H), 3.74 (br s, 1 H), 3.54–3.28 (m, 2 H), 2.41 (s, 3 H), 2.18–1.83 (m, 5 H), 1.44–1.13 (m, 4 H), 1.09 (s, 3 H), 1.00 (s, 3 H), 0.99–0.82 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 170.0, 142.4, 129.5, 127.7, 115.5, 60.4, 52.8, 52.2, 47.7, 44.5, 41.1, 38.4, 33.1, 26.3, 24.7, 23.2, 21.6, 20.6, 20.0.

^{13}C NMR DEPT (50 MHz, $CDCl_3$): δ = 142.4 (CH), 129.5 (CH), 127.7 (CH), 115.5 (CH_2), 60.4 (CH), 52.8 (CH_2), 52.2 (CH), 38.4, 33.1 (CH_2), 26.3 (CH_2), 24.7, 23.2, 21.6, 20.6, 20.0.

MS (EI): *m*/*z* (%) = 1011 ([2 M + Na]$^+$, 100), 517 ([M + Na]$^+$, 10), 425 (42), 252 (48), 155 (94), 91 (100), 69 (42), 41 (29).

HRMS (EI): *m*/*z* calcd for $C_{24}H_{34}O_5N_2NaS_2$ (M + Na): 517.1806; found: 517.1801.

N-[(2′*S*)-*N*′-*p*-Toluenesulfonyl-3′,3′-dimethylallylglycinoyl]-(2*R*)-bornano-10,2-sultam [(*S*)-7a]

Mp 131–134 °C (hexane–EtOAc); $[\alpha]_D^{20}$ –31.4 (*c* = 1, $CHCl_3$).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.82–7.72 (m, 2 H), 7.27–7.19 (m, 2 H), 5.87 (m, 1 H), 5.20–5.01 (m, 3 H), 4.41 (d, *J* = 10.2, 1 H), 3.75–3.58 (m, 1 H), 3.52–3.28 (m, 2 H), 2.40 (s, 3 H), 2.06–1.80 (m, 5 H), 1.43–0.80 (m, 14 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 171.1, 142.7, 129.9, 129.7, 128.2, 115.8, 62.0, 53.4, 48.4, 48.2, 45.3, 45.2, 42.6, 39.0, 27.0, 26.1, 23.2, 22.2, 21.4, 20.6.

X-ray Structural Analysis of (*S*)-7a

Formula: $C_{24}H_{34}N_2O_5S_2$, orthorhombic, space group $2_12_12_1$, scan range 3.24 <2θ <20.00, a = 10.650(2), b = 12.450(3), c = 39.010(8) Å, V = 5172.4(18) Å^3, Z = 8, d_{calcd} = 1.270 Mg·m^{-3}, u = 0.242 mm^{-1}, 4791 unique reflections, R = 0.0872, R_w = 0.1813.[27–30]

***N*-[(2′*S*)-*N*′-*p*-Toluenesulfonyl-3′,3′-dimethylallylglycine) 8-(*R*)-Phenylmenthyl Ester [(*S*)-7b]**

Mp 105–107 °C (hexanes–EtOAc); $[\alpha]_D^{20}$ –13.9 (*c* = 1, $CHCl_3$).

IR (KBr): 3283, 2965, 2928, 1719, 1340, 1163 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 8.2 Hz, 2 H), 7.36–7.10 (m, 5 H), 7.06–6.94 (m, 1 H), 5.51–5.32 (m, 2 H), 4.98–4.08 (m, 2 H), 4.42 (td, J_1 = 4.0 Hz, J_2 = 10.6 Hz, 1 H), 3.10 (d, J = 9.8 Hz, 1 H), 2.42 (s, 3 H), 2.04–1.84 (m, 2 H), 1.70–1.53 (m, 2 H), 1.50–1.28 (m, 1 H), 1.00 (s, 3 H), 0.91 (s, 3 H), 0.90–0.75 (m, 11 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 169.7, 151.8, 143.3, 142.8, 137.1, 129.5, 127.9, 127.3, 125.1, 125.0, 113.3, 62.4, 50.5, 40.8, 40.6, 39.1, 34.4, 31.2, 27.5, 26.4, 25.0, 24.2, 23.1, 21.6, 21.5.

^{13}C NMR DEPT (50 MHz, $CDCl_3$): δ = 142.8 (CH), 129.5 (CH), 127.9 (CH), 127.3 (CH), 125.1 (CH), 125.0 (CH), 113.3 (CH_2), 62.4 (CH), 50.5 (CH), 40.8 (CH_2), 40.6, 34.4 (CH_2), 31.2, 27.5, 26.4 (CH_2), 25.0, 24.2, 23.1, 21.6, 21.5.

ESI: *m*/*z* (%) = 1045 ([2M + Na]$^+$, 100), 795 ([M + Na]$^+$, 3).

HRMS (EI): *m*/*z* calcd for $C_{33}H_{50}O_4N_2S_1Na$ (M + Na): 534.2615; found: 534.2615.

Anal. Calcd for $C_{33}H_{50}N_2NaO_4S$: C, 70.5; H, 8.0; N, 2.7; S, 6.3. Found: C, 70.2; H, 8.2; N, 2.8; S, 6.2.

***N*-[(2′*R*)-*N*′-*p*-Toluenesulfonyl-3′,3′-dimethylallylglycine]-10-*N*,*N*-dicyclohexylsulfamoyl (2*R*)-Isobornyl Ester [(*R*)-7c]**

Oil; $[\alpha]_D^{20}$ –14.8 (*c* = 1, $CHCl_3$).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.71 (dAB, *J* = 8.2 Hz, 2 H), 7.29 (dAB, *J* = 8.2 Hz, 2 H), 5.80 (m, 1 H), 5.08–4.93 (m, 3 H), 4.63 (q_{AB}, J_1 = 3.4 Hz, J_1 = 7.8 Hz, 1 H), 3.94 (d, *J* = 9.8 Hz, 1 H), 3.40–3.20 (m, 3 H), 2.70 (dAB, *J* = 13.4 Hz, 1 H), 2.39 (s, 3 H), 2.10–1.20 (m, 29 H), 1.16 (s, 3 H), 1.09 (s, 3 H), 0.97 (s, 3 H), 0.88 (s, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 169.7, 143.4, 143.0, 137.7, 129.8, 127.0, 114.2, 81.7, 64.2, 57.6, 53.9, 49.6, 489.0, 44.2, 40.8, 39.7, 33.3, 32.5, 30.8, 26.8, 26.5, 26.3, 25.3, 25.1, 23.6, 21.5, 20.5, 20.5.

MS (EI): *m*/*z* (%) = 699 ([M + Na]$^+$, 100), 677([M + H]$^+$, 30), 380 (15), 91 (47), 84 (100), 47 (19).

HRMS (EI): *m*/*z* calcd for $C_{36}H_{56}N_2NaO_6S_2$ (M + Na): 699.3509; found: 699.3472.

Anal. Calcd for $C_{36}H_{56}N_2NaO_6S_2$: C, 63.9; H, 8.3; N, 4.1; S, 9.5. Found: C, 63.5; H, 8.4; N, 4.1; S, 9.7.

***N*-[(2′*S*)-*N*′-*p*-Toluenesulfonyl-3′,3′-dimethylallylglycine]-10-*N*,*N*-dicyclohexylsulfamoyl (2*R*)-Isobornyl Ester [(*S*)-7c]**

Oil; $[\alpha]_D^{20}$ –36.1 (*c* = 1, $CHCl_3$).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.72 (dAB, *J* = 7.9 Hz, 2 H), 7.26 (dAB, *J* = 7.9 Hz, 2 H), 5.85 (m, 1 H), 5.47 (d, *J* = 9.8 Hz, 1 H), 5.16–5.00 (m, 2 H), 4.59 ((q_{AB}, J_1 = 3.2 Hz, J_1 = 7.6 Hz, 1 H), 3.51 (d, *J* = 9.8 Hz, 1 H), 3.35–3.19 (m, 2 H), 3.15 (dAB, *J* = 13.6 Hz, 2 H), 2.64 (dAB, *J* = 13.4 Hz, 2 H), 2.40 (s, 3 H), 2.05–1.26 (m, 26 H), 1.17 (s, 6 H), 1.10–0.88 (m, 3 H), 0.84 (s, 6 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 169.4, 143.5, 142.1, 137.1, 129.6, 127.6, 114.7, 81.1, 64.1, 57.5, 54.1, 49.4, 49.3, 44.2, 40.0, 39.7, 33.5, 32.2, 30.8, 27.0, 26.5, 26.5, 25.2, 24.8, 24.2, 21.6, 20.6, 20.3.

^{13}C NMR DEPT (50 MHz, $CDCl_3$): δ = 142.1 (CH), 129.6 (CH), 127.6 (CH), 114.7 (CH_2), 81.1 (CH), 64.1 (CH), 57.5 (CH), 54.1 (CH_2), 44.2, 39.7 (CH_2), 33.5 (CH_2), 32.2 (CH_2), 30.8 (CH_2), 27.0 (CH_2), 26.5 (CH_2), 26.5 (CH_2), 25.2 (CH_2), 24.8, 24.2, 21.6, 20.6, 20.3.

Reduction of 6a–c and 7a–c; General Procedure

To a stirred solution of **6a**, **6b**, **6c**, **7a**, **7b**, or **7c** (1 mmol) in THF was added $LiAlH_4$ (76 mg, 2 mmol). After 12 h, the reaction was quenched with H_2O and aq 1 M NaOH, and extracted with CH_2Cl_2. The organic layer was dried ($MgSO_4$), and rotary-evaporated. The product was purified by flash chromatography using 30% EtOAc–toluene as an eluent. General yield of the products **8** and **9**: ca. 80%.

(2′*S*)-*N*-*p*-Toluenesulfonylallylglycinol (8)

Mp 40–43 °C (hexanes–EtOAc); $[\alpha]_D^{20}$ +17.0 (*c* = 1, $CHCl_3$). All IR, ^{1}H NMR, ^{13}C NMR, EI-MS, and analytical data were identical with those obtained by us earlier.[12]

(2′*S*)-*N*-*p*-Toluenesulfonyl-3′,3′-dimethylallylglycinol (9)

Mp 115–118 °C (hexanes–EtOAc); $[\alpha]_D^{20}$ +3.2 (*c* = 1, $CHCl_3$).

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.77 (dAB, *J* = 8.4 Hz, 2 H), 7.31 (dAB, *J* = 8.4 Hz, 2 H), 5.66 (m, 1 H), 5.05–4.95 (m, 2 H), 4.78 (d, *J* = 8.4 Hz, 1 H), 3.57 (d, *J* = 8.4 Hz, 1 H), 3.08–2.98 (m, 1 H), 2.43 (s, 3 H), 0.97 (s, 3 H), 0.90 (s, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 144.0, 137.3, 129.7, 127.3, 114.1, 66.1, 62.5, 24.5, 23.9, 22.0, 21.6.

HRMS (EI): *m*/*z* calcd for $C_{14}H_{21}NNaO_3S$ (M + Na): 306.1134; found: 306.1152.

Anal. Calcd for $C_{14}H_{21}NNaO_3S$: C, 59.4; H, 7.4; N, 5.0; S, 11.3. Found: C, 59.3; H, 7.5; N, 4.8; S, 11.3.

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(30) The crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-194392. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK [fax (+44)1223336033; e-mail: deposit@ccdc.cam.ac.uk].