Enantiocontrolled Synthesis of 3-Pyrrolines from α-Amino Allenes

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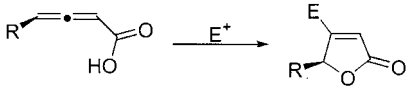
Keywords: Allenes / Cyclization / Nitrogen heterocycles

Cyclization of α-amino allenes in the presence of *N*-bromosuccinimide afforded pyrrolines in good yields. The products were obtained with high enantiomeric excesses when optically active allenes were used as substrates. The synthesis of a 2,5-dehydroprolinol derivative is also presented.

Introduction

Electrophile-induced cyclization of allenes bearing a nucleophile in the α-position is a useful route for making partially oxidized five-membered heterocycles [Equation (1)].

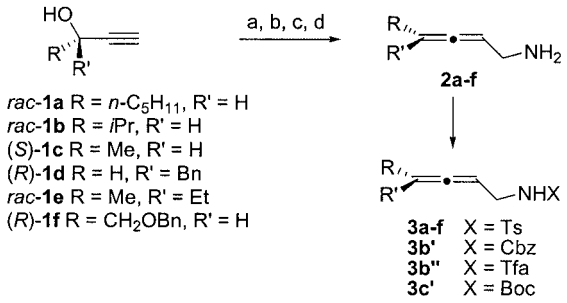


(1)

α-Allenyl alcohols,[1,2] acids,[3−5] and one amide[6] have been shown to cyclize to dihydrofurans, butenolides, and pyrrolin-2-one, respectively. A wide variety of electrophiles have been used to initiate the reactions including PhSeCl,[2,7] halogens[4,8] and other halonium ion sources, such as *N*-bromosuccinimide[2] and $CuCl_2$ or $CuBr_2$.[5,6] In some cases the axial chirality of the allene was successfully transferred to central chirality in the product.[2,5] 3-Pyrrolines are important compounds due to their biological activity,[9] and are also useful intermediates in the synthesis of amino acid analogues and antibiotics.

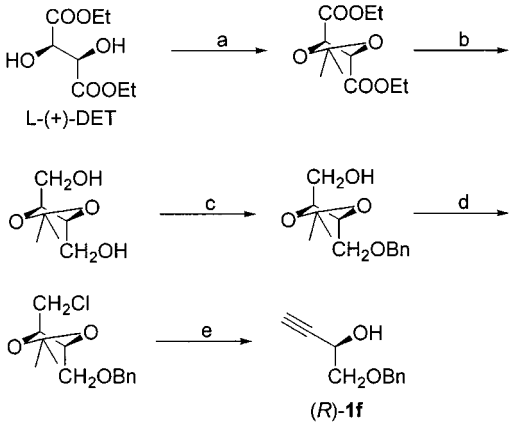
Results and Discussion

α-Allenylamines **2a**−**f** were prepared from the corresponding protected propargylic alcohols through copper(I)-mediated S_N2' reactions,[10] as shown in Scheme 1. Protection of the primary amine by standard methods afforded allenes **3a**−**f**.



Scheme 1. Synthesis of protected α-amino allenes; reagents: (a) MsCl, Et_3N; (b) $CuCH_2N{=}Ph_2$; (c) $(COOH)_2$; (d) NaOH

All of the propargylic alcohols used are commercially available, with the exceptions of alcohol (*R*)-**1d**, which was prepared by enzymatic kinetic resolution of the racemic mixture, and alcohol (*R*)-**1f**. The latter compound was synthesized from diethyl L-tartrate as depicted in Scheme 2.



Scheme 2. Reagents: (a) 2,2-dimethoxypropane, *p*TSA, 97%; (b) $LiAlH_4$, 62%; (c) BnCl, NaH; (d) CCl_4, Ph_3P; (e) LDA, 59% overall for c, d, e

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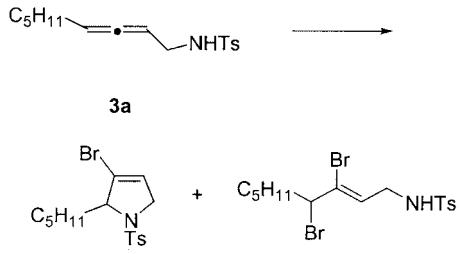
  DOI: 10.1002/ejoc.200400211

After protection of the vicinal diol moiety,[11] hydride reduction[12] afforded the dihydroxy-1,3-dioxolane, which was monobenzylated.[13] Substitution of the remaining unprotected hydroxy group,[14] followed by base-induced elimination,[15] afforded the desired propargylic alcohol (*R*)-**1f**.

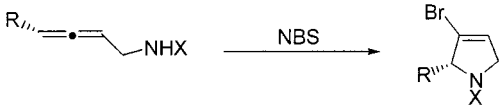
Treatment of allenyl amide **3a** with 4.5 equiv. of $CuBr_2$ in acetonitrile at −30 °C afforded a mixture of the desired pyrroline **4a** and the dibrominated by-product **5** in a 62:38 ratio [Equation (2)]. A better result was obtained with 1.5 equiv. of Br_2 in the presence of 1.5 equiv. of K_2CO_3 (**4a/5**, 91:9) or with 1.1 equiv. of NBS (**4a/5**, 98:2). Performing the latter reaction at 0 °C did not result in any loss of selectivity, and so these reaction conditions (1.1 equiv. of NBS in a 0.1 M solution of acetonitrile at 0 °C) were chosen to perform the transformations.



(2)

After the optimal reaction conditions had been established, several common protecting groups were tested. The *p*-toluenesulfonyl (Ts) derivative **3b** turned out to be the preferred substrate (Table 1, Entry 1), while the benzyloxycarbonyl-protected (Cbz) amine gave the pyrroline in lower yield (Entry 2). *N*-(Allenyl)trifluoroacetamide **3b′′** did not react under the reaction conditions, while the unprotected primary amine **2b** gave the product only in very low yield (Entries 3 and 4).

Table 1. Substrate optimization



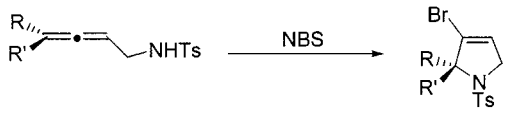
Entry[a]	Substrate	Product	Yield[b] (*ee*)
1	*rac*-**3b** R = *i*Pr, X = Ts	**4b**	81%
2	*rac*-**3b′** R = *i*Pr, X = Cbz	**4b′**	66%
3	*rac*-**3b′′** R = *i*Pr, X = Tfa	−	−
4	*rac*-**2b** R = *i*Pr, X = H	−	traces
5	(*R*)-**3c′** R = Me, X = Boc[c]	(*R*)-**4c′**	49% (96%)
6	(*R*)-**3c** R = Me, X = Ts[c]	(*R*)-**4c**	82% (93%)

[a] Reactions were carried out in acetonitrile (0.1 M) at 0 °C with 1.1 equiv. of NBS. [b] Isolated yields after column chromatography. [c] Enantiopurity of the precursor alcohol **1c** was 98%.

To test the efficiency of chirality transfer, pyrroline (*R*)-**4c′** was prepared from the optically active allene (*R*)-**3c′**. Analysis of the product showed that the selectivity of the overall chirality transfer is 98% [(*S*)-**1c** of 98% *ee* gave (*R*)-**4c′** of 96% *ee*]. The reaction of the tosyl-protected analogue **3c** gave the corresponding heterocycle **4c** in better yield (82%) and with only a slightly lower selectivity of chirality transfer (95% chirality transfer; **3c** of 98% *ee* gave **4c** of 93% *ee*).

To investigate the scope and limitation of the reaction further, several other racemic and optically active allenes were cyclized to pyrrolines with the use of NBS as the oxidant (Table 2). In most cases cyclization proceeded smoothly to afford the pyrrolines in good yields and without loss of the chiral information. Unfortunately, the reaction of allene **3f** was less efficient, the dehydro-prolinol derivative (*R*)-**4f** being isolated in a moderate yield (51%).

Table 2. Cyclization of tosylamino allenes



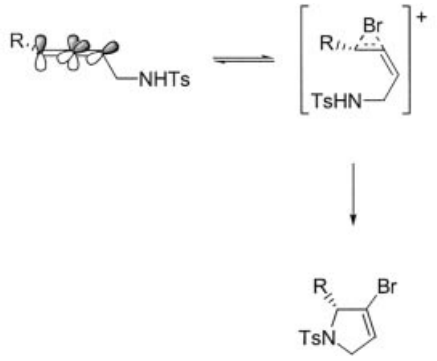
Entry[a]	Substrate	Product	Yield[b] (*ee*)
1	*rac*-**3a** R = *n*-C_5H_{11}, R′ = H	**4a**	85%
2	*rac*-**3b** R = *i*Pr, R′ = H	**4b**	81%
3	(*R*)-**3c** R = Me, R′ = H	(*R*)-**4c**	82% (93%)
4	(*S*)-**3d** R = H, R′ = Bn	(*S*)-**4d**	44% (72%)[c]
5	*rac*-**3e** R = Me, R′ = Et	**4e**	89%
6[d]	(*R*)-**3f** R = CH_2OBn, R′ = H	(*R*)-**4f**	51% (> 99%)

[a] Unless otherwise noted, reactions were carried out in acetonitrile (0.1 M) at 0 °C with 1.1 equiv. of NBS. [b] Isolated yields after column chromatography. [c] The optical purity of the precursor alcohol **1d** was 72% *ee*. [d] 2 equiv. of NBS were used at 20 °C.

The reaction most probably proceeds through a cyclic bromonium ion formed as Br^+ approaches the double bond closer to the R group from the direction *trans* to the aminomethyl substituent (from above in Scheme 3). It is the rigidity of this intermediate that is responsible for the enantioselectivity and efficiency of the reaction. Coordination of Br^+ *cis* to the aminomethyl group (from below in Scheme 3) is not only sterically disfavored but would place the nitrogen too far from the electrophilic carbon atoms. Coordination of Br^+ to the other double bond could produce an aziridine, but its formation was not observed under the mild reaction conditions.

Conclusion

A mild and enantio-controlled bromocyclization reaction of α-amino allenes has been developed. This novel transformation affords 3-bromo-pyrrolines in good yields and with excellent optical purity when optically active allenes



Scheme 3

are used. The products, being vinyl bromides, should be viable coupling partners in various palladium-catalyzed coupling reactions.

Experimental Section

General Methods: Acetonitrile was distilled from CaH_2, diethyl ether and THF were distilled from sodium benzophenone ketyl, diethyl L-tartrate was vacuum-distilled, and pyridine was distilled from $LiAlH_4$ and kept over KOH pellets. All other reagents and solvents were used without further purification. ^1H NMR (400 or 300 MHz) and ^{13}C NMR (100 or 75 MHz) spectra were recorded with a Varian Mercury spectrometer with use of the residual peaks of [D]chloroform (δ = 7.26 ppm for ^1H and 77 ppm for ^{13}C) or [D_6]DMSO (δ = 2.50 ppm for ^1H and 39.51 ppm for ^{13}C) as internal standards. For the determination of optical purity we used a Varian 3800 analytical GC fitted with a CP-Chirasil-Dex CB column for compound **1d** and **4c′** and a Waters 2690 analytical HPLC with OD-H column for compounds **4c**, **4d** and **4f**. Matrex silica 60-Å (35−70 mm) was used for column chromatography, and analytical TLC was performed on Merck precoated silica 60-F_{254} plates. Melting points are uncorrected.

(*R*)-1-Phenylbut-3-yn-2-ol [(*R*)-1d]: Ethynylmagnesium bromide (340 mL, 0.5 M in THF, 0.17 mol) was stirred at room temperature, and phenylacetaldehyde (20 mL, 0.17 mol) was added slowly. After the addition, the mixture was quenched with satd. NH_4Cl solution, the organic layer was separated and dried with Na_2SO_4, and the solvent was evaporated. Vacuum distillation gave the racemic **1d** (13.7 g, 55%) as a colorless oil. Vinyl acetate (12.1 mL, 131 mmol) and immobilized *Pseudomonas Species-C* lipase (Amano II, 223 mg, 6 mg/mmol) were added to **1d** (12.8 g, 87.5 mmol) in toluene (373 mL, 0.31 M), and the mixture was shaken. After 3 days and 43% conversion, the solvent and the excess vinyl acetate were evaporated, and the products were separated by column chromatography (pentane/ethyl acetate, 5:1) to afford the title compound with 72% *ee* and (*S*)-**1d** acetate with 95% *ee*. The characterization of the title compound has been published before.[16]

(*R*)-4-Benzyloxy-3-hydroxybut-1-yne [(*R*)-1f]: This compound was prepared over five steps by literature procedures (Scheme 2). Freshly distilled diethyl L-tartrate (42.67 g, 0.207 mol) was first protected by use of 2,2-dimethoxypropane (2 equiv.).[11] Distillation (85−94 °C, 0.20 mbar) afforded the 1,3-dioxolane in 97% yield (49.47 g, 0.201 mol). Reduction with $LiAlH_4$ [12] and subsequent mono-benzylation,[13] followed by substitution of the remaining unprotected alcohol[14] and elimination,[15] afforded (*R*)-**1f** in 36% overall yield. The characterization of the title compound has been published before.[15]

General Procedure for the Preparation of α-Allenyl Amines 2a−f. 5-Methylhexa-2,3-dienylamine (2b): A mixture of 4-methyl-1-pentyn-3-ol (7.73 g, 78.8 mmol) and triethylamine (10.1 mL, 78.8 mmol) in dichloromethane (79 mL, 1.0 M) was stirred at −20 °C, and mesyl chloride (6.10 mL, 78.8 mmol) was added slowly. After 1 h the reaction mixture was quenched with water, the organic layer was separated, washed twice with water, and dried with Na_2SO_4, and the solvent was evaporated to afford the mesylated propargylic alcohol in 99% crude yield (13.8 g). This was used without further purification. A solution of benzhydrylidene(methyl)amine (2.44 g, 12.5 mmol) in THF (12.5 mL, 1.0 M) was added over 10 min at −60 °C under argon to a solution of *t*BuLi (9.0 mL, 1.7 M in pentane, 15.3 mmol) in THF (75 mL, 0.2 M). After the mixture had been stirred for 5 min, a solution of CuCN (1.34 g, 15.0 mmol) and LiCl (1.27 g, 30.0 mmol) in THF was added over 2 min, and the mixture was stirred for another 5 min. The mesylated propargylic alcohol (2.2 g, 12.5 mmol) in THF (5 mL) was then added to the mixture over 5 min. The reaction mixture was stirred for 45 min at −50 °C and was then allowed to warm up to room temperature. It was quenched with water, the THF was evaporated, and the residue was extracted with diethyl ether. The combined organic layers were washed with a mixture of NaOH (2 M) and satd. NH_4Cl solution (1:3), and the solvent was evaporated. A solution of oxalic acid (0.99 g, 11.0 mmol) in a 1:6 mixture of 95% ethanol and diethyl ether (31.4 mL, 0.35 M) was added to the crude product, and the mixture was stirred for 30 minutes. After the hydrolysis of the imine and the crystallization of the oxalate salt were complete, the solid was filtered and washed with diethyl ether. NaOH solution (2 M) was added to the white powder, and the primary amine was extracted with dichloromethane. The organic layer was dried with Na_2SO_4, and the solvent was evaporated to afford the title compound in 42% yield (0.50 g) as a light yellow liquid: ^1H NMR ($CDCl_3$, 400 MHz): δ = 5.3 (m, 2 H), 3.25 (dd, 2 H), 2.35 (m, 1 H), 2.08 (br. s, 2 H), 1.03 (d, J = 6.9 Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 201.4, 101.4, 95.1, 41.1, 28.1, 22.79, 22.77 ppm.

General Procedure for the Preparation of *p*-Toluenesulfonamides 3a−f. *N*-(5-Methylhexa-2,3-dienyl)-*p*-toluenesulfonamide (3b): *p*-Toluenesulfonyl chloride (0.94 g, 5.0 mmol) was added at −20 °C to a solution of amine **2b** (0.5 g, 4.5 mmol) in pyridine (4.5 mL, 1.0 M), and the mixture was stirred overnight. After quenching with water and extraction with diethyl ether the combined organic layers were washed with NH_4Cl (satd.) and brine and dried with Na_2SO_4. Column chromatography (pentane/diethyl ether, 1:1) afforded the title compound as a yellow liquid in 68% yield (0.82 g): ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.75 (d, J = 8.2 Hz, 2 H), 7.31 (d, J = 8.2 Hz, 2 H), 5.24 (m, 1 H), 5.10 (m, 1 H), 4.36 (br. m, 1 H), 3.56 (ddd, J = 8.8, 6.1, 3.1 Hz, 2 H), 2.43 (s, 3 H), 2.26 (m, 1 H), 0.97 (dd, J = 7.0, 1.4 Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 201.9, 143.4, 137.0, 129.6 (2 C), 127.1 (2 C), 101.9, 88.8, 42.0, 27.7, 22.3, 22.2, 21.5 ppm.

General Procedure for the Preparation of 3-Bromo-2,5-dihydropyrroles 4a−4f. 3-Bromo-2-isopropyl-1-(*p*-tolylsulfonyl)-2,5-dihydropyrrole (4b): A solution of NBS (86.2 mg, 0.48 mmol) in acetonitrile (4.4 mL) was added at 0 °C to allene **3b** (115.7 mg, 0.44 mmol). The reaction was monitored by TLC [samples quenched with satd. $Na_2S_2O_3$(aq)]. After the reaction was complete, silica was added to the reaction mixture at 0 °C. The solvent was evaporated, and column chromatography (pentane/diethyl ether, 2:1) gave the title compound in 81% isolated yield (121 mg) as a yellow liquid: ^1H

NMR ($CDCl_3$, 400 MHz): δ = 7.68 (m, 2 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 5.73 (m,1 H), 4.39 (m, 1 H), 4.05 (ddd, *J* = 15.9, 2.7, 1.1 Hz, 1 H), 3.91 (ddd, *J* = 15.9, 4.8, 1.7 Hz, 1 H), 2.42 (s, 3 H), 2.24 (d sept, *J* = 2.4, 7.1 Hz, 1 H), 1.12 (d, *J* = 7.1 Hz, 3 H), 0.94 (d, *J* = 7.1 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 143.8, 134.3, 129.8 (2 C), 127.5 (2 C), 126.4, 118.4, 74.6, 56.1, 31.9, 21.5, 18.7, 16.5 ppm.

***N*-Benzyloxycarbonyl-3-bromo-2-isopropyl-2,5-dihydropyrrole (4b′):** This compound was prepared from allene **3b′** by the general procedure in 66% yield (86.8 mg); light yellow liquid. ^1H NMR ([D_6]DMSO, 100 °C, 400 MHz): δ = 7.35 (m, 5 H), 6.19 (m, 1 H), 5.11 (s, 2 H), 4.49 (m, 1 H), 4.23 (ddd, *J* = 15.7, 2.7, 1.8 Hz, 1 H), 3.92 (ddd, *J* = 15.7, 5.1, 1.8 Hz, 1 H), 2.24 (d sept, *J* = 2.4, 7.0 Hz, 1 H), 0.92 (dd, *J* = 7.0, 3.5 Hz, 6 H) ppm. ^{13}C NMR ([D_6]DMSO, 100 °C, 100 MHz): δ = 154.9, 137.5, 129.0, 128.6, 128.5, 128.2, 117.2, 71.9, 67.1, 55.0, 31.7, 18.7, 17.7 ppm.

3-Bromo-2-pentyl-1-(*p*-tolylsulfonyl)-2,5-dihydropyrrole (4a): This compound was prepared from allene **3a** (106.1 mg, 0.3616 mmol) by the general procedure in 85% yield (114.5 mg, 0.3075 mmol); colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.75 (dm, *J* = 8.4 Hz, 2 H), 7.31 (m, 2 H), 5.76 (app q, *J* = 2.0 Hz, 1 H), 4.46 (m, 1 H), 4.08 (app dt, *J* = 14.7, 2.6 Hz, 1 H), 4.02 (ddd, *J* = 14.7, 5.2, 2.0 Hz, 1 H), 2.43 (s, 3 H), 1.94 (m, 1 H), 1.76 (m, 1 H), 1.40−1.13 (m, 6 H), 0.88 (t, *J* = 6.9 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 143.7, 134.4, 129.8 (2 C), 127.4 (2 C), 125.2, 118.9, 69.2, 55.4, 32.3, 31.6, 22.6, 22.0, 21.5, 14.0 ppm.

(*R*)-3-Bromo-2-methyl-1-(*p*-tolylsulfonyl)-2,5-dihydropyrrole [(*R*)-4c]: This compound was prepared from allene (*R*)-**3c** (93.9 mg, 0.3957 mmol) by the general procedure in 82% yield (102.6 mg, 0.3244 mmol); colorless oil, crystallizable from pentane/ether, 95:5. Recrystallization from hexane gave enantiomerically pure white needles; m.p. 51−57 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.70 (dm, *J* = 8.3 Hz, 2 H), 7.32 (m, 2 H), 5.73 (app q, *J* = 2.0 Hz, 1 H), 4.36 (m, 1 H), 4.10 (ddd, *J* = 14.5, 5.5, 2.0 Hz, 1 H), 4.01 (app dt, *J* = 14.5, 2.5 Hz, 1 H), 2.43 (s, 3 H), 1.51 (d, *J* = 6.4 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 143.8, 134.2, 129.9 (2 C), 127.4 (2 C), 124.3, 120.5, 65.4, 54.6, 21.5, 21.2 ppm.

(*R*)-*tert*-Butyl 3-Bromo-2-methyl-2,5-dihydro-1-pyrrolecarboxylate [(*R*)-4c′]: This compound was prepared from allene (*R*)-**3c′** (97.1 mg, 0.5299 mmol) by the general procedure in 49% yield (55.2 mg, 0.2106 mmol); colorless liquid. ^1H NMR ([D_6]DMSO, 300 MHz): δ = 6.07 (dd, *J* = 3.9, 2.1 Hz, 1 H), 4.39 (m, 1 H), 4.08 (app dt, *J* = 15.3, 2.3 Hz, 1 H), 3.95 (ddd, *J* = 15.3, 5.4, 2.1 Hz, 1 H),1.45 (s, 9 H), 1.33 (d, *J* = 6.3 Hz, 3 H) ppm. ^{13}C NMR ([D_6]DMSO, 100 MHz): δ = 152.2, 128.8, 127.8 (2 C), 125.2 (2 C), 119.2, 78.6, 61.8, 52.1, 27.6, 18.0 ppm.

(*S*)-2-Benzyl-3-bromo-1-(*p*-tolylsulfonyl)-2,5-dihydropyrrole [(*S*)-4d]: This compound was prepared from allene (*S*)-**3d** by the general procedure but with the use of 2 equiv. NBS at 20 °C in 44% yield (71 mg); white solid. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.71 (d, *J* = 9.6 Hz, 2 H), 7.37−7.19 (m, 7 H), 5.54 (app. br. q, *J* = 1.9, 1 H), 4.66 (m, 1 H), 3.82 (app. dt, *J* = 14.6, 2.3 Hz, 1 H), 3.77 (ddd, 14.6, 5.2, 1.9 Hz, 1 H), 3.31 (dd, *J* = 13.9, 4.8 Hz, 1 H), 3.12 (dd, *J* = 13.9, 2.3 Hz, 1 H), 2.43 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 144.1, 135.6, 134.6, 131.1 (2 C), 130.2 (2 C), 128.1 (2 C), 127.5(2 C), 127.0, 126.9, 117.9, 70.2, 55.5, 38.6, 21.8 ppm.

3-Bromo-2-ethyl-2-methyl-1-(*p*-tolylsulfonyl)-2,5-dihydropyrrole (4e): This compound was prepared from allene **3e** by the general procedure in 89% yield (74.8 mg); light yellow liquid. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.75 (d, *J* = 7.8 Hz, 2 H), 7.28 (d, *J* = 7.8 Hz, 2 H), 5.88 (t, *J* = 2.3 Hz, 1 H), 4.05 (dd, *J* = 13.4, 2.2 Hz, 1 H), 4.00 (dd, *J* = 13.4, 2.2 Hz, 1 H), 2.41 (s, 3 H), 2.24 (app. sext, *J* = 7.5 Hz, 1 H), 1.66 (app. sext, *J* = 7.1 Hz, 1 H), 1.51 (s, 3 H), 0.73 (t, *J* = 7.8 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 143.4, 137.9, 129.7 (2 C), 127.4 (2 C), 124.5, 123.7, 76.8, 54.9, 31.0, 25.5, 21.7, 8.3 ppm.

(*R*)-2-[(Benzyloxy)methyl]-3-bromo-1-(*p*-tolylsulfonyl)-2,5-dihydropyrrole [(*R*)-4f]: This compound was prepared from allene **3f** (100.6 mg, 0.2929 mmol) by the general procedure but with the use of 2 equiv. NBS at 20 °C in 51% yield (63.6 mg, 0.1506 mmol); colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.70 (m, 2 H), 7.36−7.25 (m, 7 H), 5.87 (dd, *J* = 4.0, 2.1 Hz, 1 H), 4.62 (d, *J* = 12.4 Hz, 1 H), 4.53 (d, *J* = 12.4 Hz, 1 H), 4.45 (m, 1 H), 4.10 (dd, *J* = 4.0, 2.1 Hz, 2 H), 3.86 (dd, 10.7, 2.2 Hz, 1 H), 3.83 (dd, *J* = 10.7, 2.7 Hz, 1 H), 2.42 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ143.8, 138.2, 134.6, 129.8 (2 C), 128.2 (2 C), 127.5, 127.4 (2 C), 127.3 (2 C), 126.6, 116.6, 73.5, 69.6, 69.5, 55.3, 21.5 ppm.

***N*-(3,4-Dibromooct-2-enyl)-*p*-toluenesulfonamide (5):** This compound was isolated as a by-product from the treatment of allene **3a** with $CuBr_2$. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.75 (m, 2 H), 7.33 (m, 2 H), 6.07 (t, *J* = 6.2 Hz, 1 H), 4.65 (br. t, *J* = 6.1 Hz, 1 H), 4.48 (t, *J* = 7.3 Hz, 1 H), 3.73 (t, *J* = 6.2 Hz, 2 H), 2.44 (s, 3 H), 1.93 (m, 2 H), 1.28 (m, 6 H), 0.88 (m, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 143.8, 136.6, 131.6, 129.9 (2 C), 127.6, 127.2 (2 C), 57.0, 43.8, 37.9, 30.9, 27.0, 22.3, 21.6, 13.9 ppm.

Acknowledgments

Financial support from the Swedish Research Council is gratefully acknowledged.

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Received March 30, 2004

