$H_3COC_6H_4CH(CH_3)OSO_2C_6H_5$, 114200-07-6; *p*-$H_3COC_6H_4CH(CH_3)OSO_2C_6H_4$-*p*-Cl, 114200-08-7; *p*-$H_3COC_6H_4CH(CH_3)OSO_2C_6H_4$-*p*-$NO_2$, 114200-09-8; *p*-$H_3CC_6H_4CH(CH_3)OSO_iC_6H_4$-*p*-$CH_3$, 82925-34-6; *p*-$H_3CC_6H_4CH(CH_3)OSO_2C_6H_5$, 114200-10-1; *p*-$H_3CC_6H_4CH(CH_3)OSO_2C_6H_4$-*p*-Cl, 114200-11-2; *p*-$H_3CC_6H_4CH(CH_3)OSO_2C_6H_4$-*p*-$NO_2$, 114200-12-3; $C_6H_5CH(CH_3)OSO_2C_6H_4$-*p*-$CH_3$, 6749-54-8; $C_6H_5CH(CH_3)OSO_2C_6H_5$, 113694-01-2; $C_6H_5CH(CH_3)OSO_2C_6H_4$-*p*-Cl, 114200-13-4; $C_6H_5CH(CH_3)OSO_2C_6H_4$-*p*-$NO_2$, 114200-14-5; *p*-$ClC_6H_4CH(CH_3)OSO_2C_6H_4$-*p*-$CH_3$, 114200-15-6; *p*-$ClC_6H_4CH(CH_3)OSO_2C_6H_5$, 114200-16-7; *p*-$ClC_6H_4CH(CH_3)OSO_2C_6H_4$-*p*-Cl, 114200-17-8; *p*-$ClC_6H_4CH(CH_3)OSO_2C_6H_4$-*p*-$NO_2$, 114200-18-9; *p*-Methoxyacetophenone, 100-06-1; *p*-methylacetophenone, 122-00-9; *p*-chloroacetophenone, 99-91-2; acetophenone, 98-86-2; 1-(*p*-methoxyphenyl)ethyl benzanilide, 114200-19-0; 1-(*p*-methoxyphenyl)ethyl methyl ether, 77525-91-8.

A Novel Carbon–Carbon Bond Formation Reaction at the C_4 Position of an Azetidin-2-one by Means of Radical Cyclization[1]

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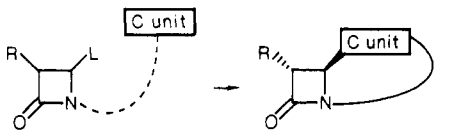
A novel synthesis of carbacepham and carbacephem ring systems through 1,6-bond coupling by a radical cyclization reaction is described.

Recently much attention has been focused on the exploration of a synthetic strategy for nonclassical β-lactam antibiotics, such as thienamycin[2] and PS-5,[3] originating from their attractive physiological activities.[4] Among the number of synthetic routes[5] the carbon–carbon bond formation reaction at the C_4 position of an azetidinone has become of increasing interest[6] (Scheme I). We have already reported a new carbon–carbon bond formation reaction at the C_4 position of an azetidinone by employing an enolate anion[7] and carbene species[6] as nucleophiles, and the application of this reaction led to a short synthesis of PS-5 antibiotics.[8] As an extension of our work on the synthesis of nonclassical β-lactam antibiotics, we have explored the radical cyclization reaction[9] of 4-(phenylthio)azetidin-2-one.

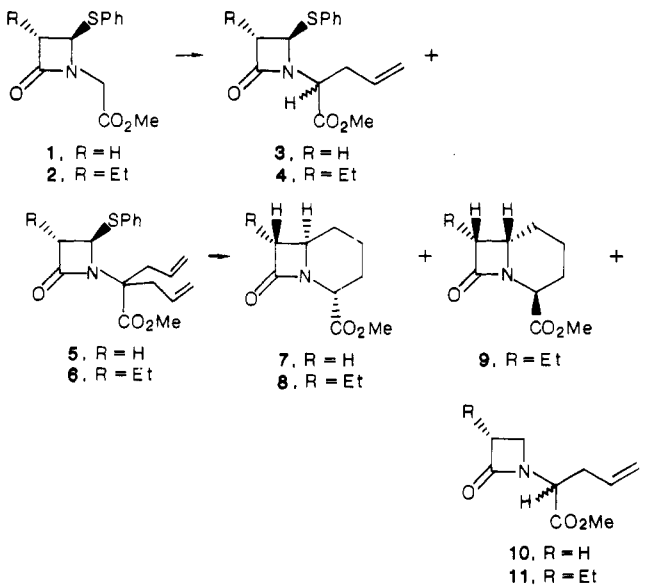
Results and Discussion

Alkylation of *N*-[(methoxycarbonyl)methyl]-4-(phenylthio)azetidin-2-one (1) with allyl bromide in the presence of lithium hexamethyldisilazide in dry tetrahydrofuran at −78 °C gave the allyl derivative **3** as an inseparable mixture of diastereomers in a ratio of 2:3, in 77% yield, together with the diallyl compound **5**. Radical cyclization of the mixture **3** was carried out by treatment with tri-*n*-butyltin hydride in the presence of a catalytic amount of α,α′-azobis(isobutyronitrile) (AIBN) for 18 h, yielding the carbacepham derivative **7** in 43% yield (66% yield based on consumed starting material), together with a small amount of the desulfurized compound **10**. Formation of a carbapenam ring system, which might be an another possible cyclization product, could not be observed under these conditions. This observation was rationalized by assuming that a larger energy would be required for the formation of the 1-azabicyclo[3.2.0]heptan-7-one ring system having a large strain energy than the 1-azabicyclo[4.2.0]octan-7-one ring system. Therefore, the formation of a carbacepham would be the predominant reaction, although a similar reaction[10] with the pyrrolidinone de-

Scheme I



Scheme II



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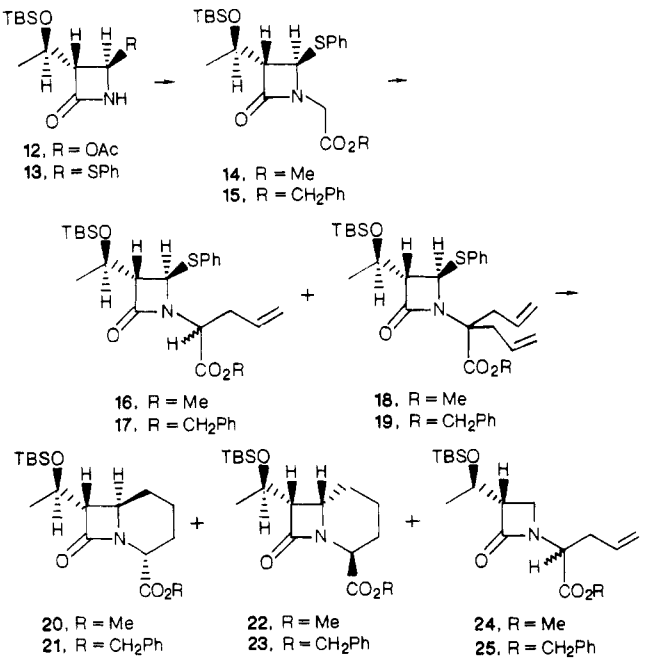
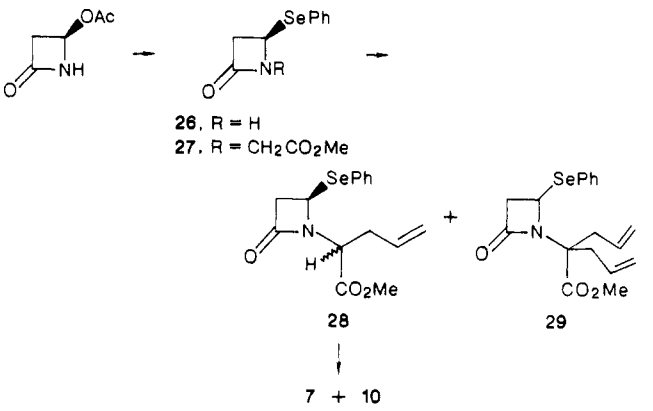
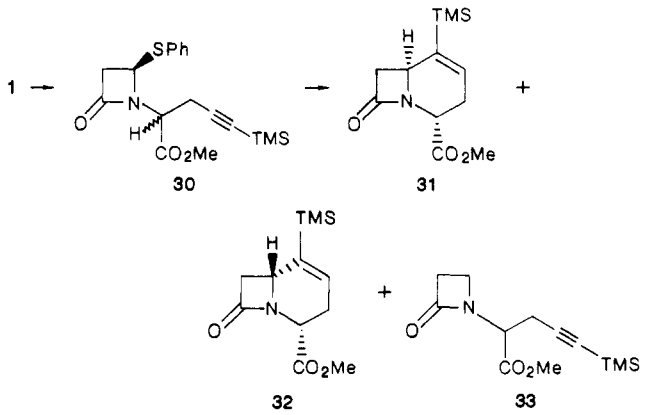
Scheme III



Scheme IV



Scheme V



rivative instead of azetidinone afforded the 1-azabicyclo-[3.3.0]octane ring system predominantly. When the radical cyclization was attempted for the corresponding 4-(methylthio)azetidin-2-one derivative, none of the desired product was formed and only starting material was recovered. The stereochemistry of the cyclized product **7** was determined from the NMR spectra[11] to be $6R^* + 2R^*$ and this was further supported by failure of **7** to react with strong base (DBU), since **7** was known[9,11] to be the thermodynamically more stable diastereomer. Interestingly, the recovered starting material in this reaction was only one stereoisomer, whose structure was tentatively assigned to have S^* configuration at the position α to the carbomethoxy group, based on the consideration of the stereochemistry of the product having R^* configuration at the C_2 position. When the radical cyclization reaction was applied to 3-ethyl-4-(phenylthio)-2-azetidinone derivative **4** (the diastereomer ratio = 9:11), derived from **2**, the 6,7-*cis*- (**9**) and 6,7-*trans*-carbacephams **8** were isolated in 18.3% and 31.1% yields, respectively (Scheme II).

Optically active carbacepham was also prepared as follows. (3*R*,4*R*)-4-Acetoxy-3-[(*R*)-[(1′-*tert*-butyldimethylsilyl)oxy]ethyl]-2-azetidinone (**12**)[12] was first converted into its 4-(phenylthio)azetidinone derivative **13** by treatment with sodium thiophenoxide in methanol. N-Alkylation of **13** with bromoacetate esters gave the corresponding esters **14** and **15** in 89.3% and 89.6% yields, respectively. These esters were further transformed into the allyl derivatives **16** and **17** in a ratio of ca. 2:3, in 73.8% and 72.4% yields, respectively, accompanied by the diallyl compounds **18** and **19**. Again, the radical cyclization reaction of the ester **16** by treatment with tri-*n*-butyltin hydride in refluxing benzene in the presence of AIBN provided the desired carbacephams **20** and **22** in 31% and 19.4% yields, respectively, together with the desulfurized compound **24**. The stereochemistry of the carbacephams **20** and **22** was easily determined on the basis of their NMR spectra, which showed characteristic coupling constants for 6-H and 7-H. A similar result was obtained from the radical cyclization of the ester **17**, leading to the carbacephams **21** and **23** and the desulfurized compound (**25**) in 32.4%, 20.1% and 9.2% yields, respectively (Scheme III).

In all the above reactions, the recovered starting materials were mainly one stereoisomer, suggesting that cyclization of one stereoisomer was much faster than the other. Although the mechanism is not clear, the yields of the products did not always parallel the diastereomer ratio of the starting materials. It cannot be excluded that the cyclization is nonselective and is accompanied by epimerization of one isomer at the C_2 position.

Since we had observed that a phenylthio group was a good progenitor for generation of the radical in this reaction, a phenylselenenyl group[13] was also examined to produce the radical center in order to increase the cyclization yield.

Thus, 4-acetoxy-2-azetidinone was converted to the 4-(phenylseleno)-2-azetidinone (**26**) on treatment with diphenyl diselenide and sodium borohydride[14] in 89.2% yield. N-Alkylation of **26**, followed by allylation of the resulting ester **27**, afforded the allyl compound **28** in 73% yield. Radical cyclization of **28** under conditions similar to those for the conversion of **3** to **7** brought about the formation of the desired carbacepham **7** in 59% yield. The conversion yield was clearly increased as expected (Scheme IV).

Finally, the acetylenic derivative **30**, derived from **1** by treatment with (trimethylsilyl)propargyl bromide in the

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presence of lithium hexamethyldisilazide in tetrahydrofuran, was subjected to radical cyclization in order to prepare a carbacephem ring system. Heating of **30** with tri-*n*-butyltin hydride and AIBN in refluxing benzene gave the carbacephems **31** and **32** as an inseparable mixture in 10.3% yield in a ratio of ca. 5:1. The desulfurized compound **33** was isolated as a major product in 54% yield from this reaction. Although radical addition to triple bonds has been recognized[15] to be an efficient process, the poor yield of cyclized products in this β-lactam chemistry was rationalized by the linearity of acetylenic function, and thus its remoteness from the radical center (Scheme V).

Thus, a novel construction of carbacepham and carbacephem ring systems was achieved by radical cyclization reaction through 1,6-bond coupling.

Experimental Section

Infrared spectra were run on a Hitachi 260-10 spectrophotometer. Nuclear magnetic resonance (NMR) spectra were measured on JEOL PMX-60, JNM-FX-100, or JNM-GX-400 spectrometers. Chemical shifts are reported as δ values relative to internal tetramethylsilane (Me_4Si). Mass spectra were taken on a JEOL JMS-D 300 spectrometer. All melting points were determined with a Yanaco microapparatus and are uncorrected.

Methyl 2-[2-Oxo-4-(phenylthio)-1-azetidinyl]-4-pentenoate (3). To a stirred solution of hexamethyldisilazane (1.02 mL, 4.6 mmol) in dry tetrahydrofuran (30 mL) was added *n*-butyllithium (1.57 M in hexane) (2.8 mL, 4.4 mmol) at −10 °C, and the mixture was further stirred at −78 °C for 20 min. To the above solution was added a solution of the azetidinone **1** (1 g, 4 mmol) in tetrahydrofuran (10 mL) at −78 °C, and the resulting mixture was stirred for 30 min. Allyl bromide (0.34 mL, 4 mmol) was then added and the mixture was gradually warmed to −10 °C and was further stirred for 1 h. After addition of aqueous saturated ammonium chloride (10 mL) to the solution, most of the solvent was evaporated and the residue was extracted with ether. The ethereal layer was washed with brine, dried over sodium sulfate, and evaporated to leave the residue, which was subjected to column chromatography on silica gel. Elution with hexane–acetone (47:3 v/v) afforded the allyl compound **3** (0.9 g, 77.3%) as an inseparable diastereomeric mixture as a yellowish oil: IR ($CHCl_3$) 1775, 1750 cm^{-1}; ^1H NMR (100 MHz) ($CDCl_3$) δ 2.66 (t, J = 7.5 Hz, 0.8 H, $CH_2C{=}C$), 2.77 (t, J = 7.5 Hz, 1.2 H, $CH_2C{=}C$), 2.80 (dd, J = 2.2 and 15.5 Hz, 0.6 H, $C_{3\beta}H$), 2.85 (dd, J = 2.2 and 15.5 Hz, 0.4 H, $C_{3\beta}H$), 3.33 (dd, J = 5.0 and 15.5 Hz, 0.6 H, $C_{3\alpha}H$), 3.40 (dd, J = 5.0 and 15.5 Hz, 0.4 H, $C_{3\alpha}H$), 3.67 (s, 1.2 H, CO_2Me), 3.71 (s, 1.8 H, CO_2Me), 4.08 (t, J = 7.5 Hz, 0.6 H, $NCHCO_2$), 4.27 (t, J = 7.5 Hz, 0.4 H, $NCHCO_2$), 4.93 (dd, J = 2.2 and 5.0 Hz, 1 H, C_4H), 5.20 (m, 2 H, $C{=}CH_2$), 5.50–6.10 (m, 1 H, $CH{=}C$), 7.30 (m, 5 H, Ar H); exact mass calcd for $C_{15}H_{17}NO_3S$ (M^+) m/z 291.0927, found m/z 291.0909.

Further elution with hexane–acetone (23:2 v/v) gave the starting material **1** (65 mg, 6.5%) and elution with hexane–acetone (19:1 v/v) afforded the diallyl compound **5** (103 mg, 7.8%) as a yellowish oil: IR ($CHCl_3$) 1760, 1740 cm^{-1}; ^1H NMR (60 MHz) ($CDCl_3$) δ 2.87 (m, 4 H, 2 × $CH_2C{=}C$), 2.96 (m, 1 H, $C_{3\beta}H$), 3.37 (dd, J = 5.0 and 15.0 Hz, 1 H, $C_{3\alpha}H$), 3.75 (s, 3 H, CO_2Me), 4.16 (dd, J = 2.2 and 5.0 Hz, 1 H, C_4H), 5.00–5.30 (m, 4 H, 2 × $C{=}CH_2$), 5.55–6.10 (m, 2 H, 2 × $CH{=}C$), 7.30 (m, 5 H, Ar H); exact mass calcd for $C_{12}H_{16}NO_3$ (M^+ − SPh) m/z 222.1128, found m/z 222.1127.

Methyl 2-[(3*S,4*R**)-3-Ethyl-2-oxo-4-(phenylthio)-1-azetidinyl]-4-pentenoate (4).** The azetidinone **2** (1.12 g, 4 mmol) was allylated with allyl bromide (0.34 mL, 4 mmol) in the presence of lithium hexamethyldisilazide [prepared from *n*-butyllithium (1.57 M in hexane) (2.8 mL, 4.4 mmol) and hexamethyldisilazane (1.02 mL, 4.6 mmol)] in tetrahydrofuran by the same procedure as described for the preparation of **3** to give the allyl compound **4** (1.04 g, 81.6%) as a colorless oil [IR ($CHCl_3$) 1750, 1735 cm^{-1}; ^1H NMR (100 MHz) ($CDCl_3$) 0.97 (t, J = 7.2 Hz, 1.35 H, Me), 1.00 (t, J = 7.2 Hz, 1.65 H, Me), 1.73 (m, 2 H, CH_2), 2.68 (t, J = 7.5 Hz, 0.9 H, $CH_2C{=}C$), 2.76 (t, J = 7.5 Hz, 1.1 H, $CH_2C{=}C$), 3.07 (m, 1 H, C_3H), 3.70 (s, 1.35 H, CO_2Me), 3.74 (s, 1.65 H, CO_2Me), 4.11 (t, J = 7.5 Hz, 0.55 H, $CHCO_2$), 4.32 (t, J = 7.5 Hz, 0.45 H, $CHCO_2$), 4.65 (d, J = 2.2 Hz, 0.55 H, C_4H), 4.95 (d, J = 2.2 Hz, 0.45 H, C_4H), 5.17 (m, 2 H, $C{=}CH_2$), 5.81 (m, 1 H, $CH{=}C$), 7.36 (m, 5 H, Ar H); exact mass calcd for $C_{17}H_{21}NO_3S$ (M^+) m/z 319.1241, found m/z 319.1226] and the diallyl compound **6** (0.12 g, 8.3%) as a yellowish oil [IR ($CHCl_3$) 1750, 1735 cm^{-1}; ^1H NMR (60 MHz) ($CDCl_3$) δ 0.93 (t, J = 7.2 Hz, 3 H, Me), 1.68 (m, 2 H, CH_2), 2.85 (d, J = 7.5 Hz, 4 H, 2 × $CH_2C{=}C$), 3.72 (s, 3 H, CO_2Me), 4.85 (d, J = 2.2 Hz, 1 H, C_4H), 5.18 (m, 4 H, 2 × $C{=}CH_2$), 5.77 (m, 2 H, 2 × $CH{=}C$), 7.36 (m, 5 H, ArH); exact mass calcd for $C_{20}H_{25}NO_3S$ (M^+) m/z 359.1555, found m/z 359.1557].

Methyl 8-Oxo-1-azabicyclo[4.2.0]octane-2-carboxylate (7). To a stirred refluxing solution of **3** (400 mg, 1.37 mmol) in dry benzene (15 mL) was added dropwise a solution of tri-*n*-butyltin hydride (1.47 mL, 5.5 mmol) and α,α'-azobis(isobutyronitrile) (AIBN) (45 mg, 0.27 mmol) in dry benzene (30 mL) over the period of 16 h under an atmosphere of nitrogen. After refluxing for a further 2 h, the solvent was evaporated to give the residue, which was subjected to column chromatography on silica gel. Elution with hexane–acetone (23:2 v/v) afforded the carbacepham **7** (108 mg, 43%) as a colorless oil: IR ($CHCl_3$) 1760, 1740 cm^{-1}; ^1H NMR (100 MHz) ($CDCl_3$) δ 1.15–2.10 (m, 6 H, 3 × CH_2), 2.62 (m, 1 H, C_6H), 3.73 (s, 3 H, CO_2Me), 4.50 (br d, J = 6.5 Hz, 1 H, C_4H); exact mass calcd for $C_9H_{13}NO_3$ (M^+) m/z 183.0894, found m/z 183.0884. Elution with hexane–acetone (47:3 v/v) gave the starting material **3** (140 mg) and further elution with hexane–acetone (93:7 v/v) gave the desulfurized compound **10** (32 mg, 12.7%) as a colorless oil: IR ($CHCl_3$) 1740, 1725 cm^{-1}; ^1H NMR (60 MHz) ($CDCl_3$) δ 2.58 (t, J = 6.5 Hz, 2 H, $CH_2C{=}C$), 2.87 (m, 2 H, C_3H), 3.37 (m, 2 H, C_4H), 3.70 (s, 3 H, CO_2Me), 4.47 (dd, J = 6.5 and 9.0 Hz, 1 H, $NCHCO_2$), 5.10 (m, 2 H, $C{=}CH_2$), 5.40–5.95 (m, 1 H, $CH{=}C$); exact mass calcd for $C_9H_{13}NO_3$ (M^+) m/z 183.0896, found m/z 183.0899.

Methyl (6*R,7*R**)-7-Ethyl-8-oxo-1-azabicyclo[4.2.0]octane-2-carboxylate (8) and Methyl (6*S**,7*R**)-7-Ethyl-8-oxo-1-azabicyclo[4.2.0]octane-2-carboxylate (9).** The radical cyclization of **4** (0.4 g, 1.25 mmol) with tri-*n*-butyltin hydride (1.34 mL, 5 mmol) and AIBN (41 mg, 0.25 mmol) in dry benzene (15 mL) was carried out by the same procedure as described for the preparation of **7** to give the *cis*-carbacepham **9** (48 mg, 18.3%) as a colorless oil: IR ($CHCl_3$) 1740 (sh), 1725 cm^{-1}; ^1H NMR (400 MHz) ($CDCl_3$) δ 1.01 (t, J = 6.5 Hz, 3 H, Me), 1.25–2.05 (m, 8 H, 4 × CH_2), 3.20 (ddd, J = 4.9, 7.1 and 9.4 Hz, 1 H, C_7H), 3.74 (s, 3 H, CO_2Me), 3.76 (m, 1 H, C_6H), 4.56 (d, J = 7.5 Hz, 1 H, C_4H); exact mass calcd for $C_{11}H_{17}NO_3$ (M^+) m/z 211.1207, found m/z 211.1191. Further elution with the same solvent furnished the *trans*-carbacepham **8** (82 mg, 31.1%) as a colorless oil: IR ($CHCl_3$) 1735 (sh), 1720 cm^{-1}; ^1H NMR (100 MHz) ($CDCl_3$) δ 1.02 (t, J = 6.5 Hz, 3 H, Me), 1.25–2.05 (m, 8 H, 4 × CH_2), 2.78 (ddd, J = 1.7, 6.1 and 8.3 Hz, 1 H, C_7H), 3.38 (ddd, J = 1.7, 4.5, and 11 Hz, C_6H), 3.74 (s, 3 H, CO_2Me), 4.58 (d, J = 7.5 Hz, 1 H, C_4H); exact mass calcd for $C_{11}H_{17}NO_3$ (M^+) m/z 211.1209, found m/z 211.1214. Elution with hexane–acetone (19:1 v/v) provided the starting material **4** (75 mg) as the third eluant, and elution with hexane–acetone (47:3 v/v) gave the desulfurized compound **11** (26 mg, 10%) as a colorless oil: IR ($CHCl_3$) 1735 (sh), 1725 cm^{-1}; ^1H NMR (100 MHz) ($CDCl_3$) δ 1.00 (t, J = 6.3 Hz, 3 H, Me), 1.73 (m, 2 H, CH_2), 2.57 (t, J = 7.8 Hz, 1 H, $CH_2C{=}C$), 3.04 (m, 1 H, C_3H), 3.19 (m, 1 H, $C_{4\alpha}H$), 3.51 (dd, J = 5.3 and 18.0 Hz, 1 H, $C_{4\beta}H$), 3.74 (s, 3 H, CO_2Me), 4.52 (dd, J = 5.7 and 9.0 Hz, 1 H, $NCHCO_2$), 5.17 (m, 2 H, $C{=}CH_2$), 5.84 (m, 1 H, $CH{=}C$); exact mass calcd for $C_{11}H_{17}NO_3$ (M^+) m/z 211.1207, found m/z 211.1204.

(3*S*,4*R*)-3-[(*R*)-1′-[(*tert*-Butyldimethylsilyl)oxy]ethyl]-1-[(methoxycarbonyl)methyl]-4-(phenylthio)-2-azetidinone (14). A mixture of the azetidinone **13** (1.01 g, 3 mmol), potassium carbonate (0.83 g, 6 mmol), and methyl bromoacetate (0.3 mL, 3.3 mmol) in dry *N*,*N*-dimethylformamide (15 mL) was stirred at ambient temperature for 24 h. The mixture was partitioned between benzene and water, and the organic layer was washed with brine and dried over sodium sulfate. Evaporation of the solvent gave the residue, which was subjected to column chromatography on silica gel. Elution with hexane–acetone (93:7 v/v)

(15) (a) Choi, J.-K.; Hart, D. J.; Tsai, Y.-M. *Tetrahedron Lett.* **1982**, *23*, 4765. (b) Stork, G.; Mook, R., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 3720. (c) Stork, G.; Mook, R., Jr.; Biller, S. A.; Rychnovsky, S. D. *Ibid.* **1983**, *105*, 3741.

afforded the ether **14** (1.1 g, 89.3%) as a colorless oil: IR ($CHCl_3$) 1755 (sh), 1740 cm^{-1}; ^1H NMR (100 MHz) ($CDCl_3$) δ 0.05 (s, 3 H, Me), 0.07 (s, 3 H, Me), 0.88 (s, 9 H, *t*-Bu), 1.23 (d, J = 6.3 Hz, 3 H, Me), 3.00 (dd, J = 2.2 and 4.6 Hz, 1 H, C_3H), 3.67 (s, 3 H, CO_2Me), 3.75 (d, J = 17.8 Hz, 1 H, $CHCO_2$), 4.20 (d, J = 17.8 Hz, 1 H, $CHCO_2$), 4.24 (dt, J = 4.6 and 6.3 Hz, 1 H, $C_{1'}H$), 5.25 (d, J = 2.2 Hz, 1 H, C_4H), 7.35 (m, 5 H, Ar H); exact mass calcd for $C_{16}H_{22}NO_4SiS$ (M^+ – *t*-Bu) m/z 352.1039, found m/z 352.1047; $[\alpha]^{25}_D$ –18.36° (*c* 2.2, $CHCl_3$).

(3*S*,4*R*)-1-[[(Benzyloxy)carbonyl]methyl]-3-[(*R*)-1′-[(*tert*-butyldimethylsilyl)oxy]ethyl]-4-(phenylthio)-2-azetidinone (15). The azetidinone **13** (1.01 g, 3 mmol) was alkylated with potassium carbonate (0.83 g, 6 mmol) and benzyl bromoacetate (0.49 mL, 3.3 mmol) by the same procedure as described for the preparation of **14** to provide the ester **15** (1.3 g, 89.6%) as a colorless oil: IR ($CHCl_3$) 1755, 1740 cm^{-1}; ^1H NMR (100 MHz) ($CDCl_3$) δ 0.03 (s, 3 H, Me), 0.06 (s, 3 H, Me), 0.87 (s, 9 H, *t*-Bu), 1.22 (d, J = 6.1 Hz, 3 H, 1′-Me), 2.99 (dd, J = 2.0 and 4.9 Hz, 1 H, C_3H), 3.77 (d, J = 17.8 Hz, 1 H, $NCHCO_2$), 4.16 (dq, J = 4.9 and 6.1 Hz, 1 H, $C_{1'}H$), 4.21 (d, J = 17.8 Hz, 1 H, $NCHCO_2$), 5.08 (s, 2 H, CO_2CH_2Ph), 5.24 (d, J = 2.0 Hz, 1 H, C_4H), 7.32 (m, 10 H, 2 × Ar H); exact mass calcd for $C_{22}H_{26}NO_4SiS$ (M^+ – *t*-Bu) m/z 428.1350, found m/z 428.1339. $[\alpha]^{25}_D$ –28.61° (*c* 1.384, $CHCl_3$).

Methyl (3*S*,4*R*)-3-[[(*R*)-1′-[(*tert*-Butyldimethylsilyl)oxy]ethyl]-2-oxo-4-(phenylthio)-5-azetidinyl]-4-pentenoate (16). The allylation of the azetidinone **14** (0.82 g, 2 mmol) with allyl bromide (0.17 mL, 2 mmol) in the presence of lithium hexamethyldisilazide [prepared from *n*-butyllithium (1.57 M in hexane) (1.41 mL, 2.2 mmol) and hexamethyldisilazane (0.51 mL, 2.3 mmol)] was carried out by the same procedure as described for the preparation of **3** to give **16** (0.663 g, 73.8%) as a yellowish oil [IR ($CHCl_3$) 1750, 1730 cm^{-1}; ^1H NMR (100 MHz) ($CDCl_3$) δ 0.02 (s, 1.2 H, Me), 0.05 (s, 1.2 H, Me), 0.04 (s, 1.8 H, Me), 0.07 (s, 1.8 H, Me), 0.85 (s, 3.6 H, *t*-Bu), 0.88 (s, 5.4 H, *t*-Bu), 1.16 (d, J = 6.1 Hz, 1.2 H, 1′-Me), 1.20 (d, J = 6.1 Hz, 1.8 H, 1′-Me), 2.66 (t, J = 7.3 Hz, 0.8 H, CH_2C=C), 2.76 (t, J = 7.3 Hz, 1.2 H, CH_2C=C), 3.02 (dd, J = 2.2 and 4.8 Hz, 0.6 H, C_3H), 3.04 (dd, J = 2.2 and 4.8 Hz, 0.4 H, C_3H), 3.66 (s, 1.2 H, CO_2Me), 3.72 (s, 1.8 H, CO_2Me), 4.13 (t, J = 7.3 Hz, 0.6 H, $NCHCO_2$), 4.19 (d, J = 2.2 Hz, 0.6 H, C_4H), 4.30 (t, J = 7.3 Hz, 0.4 H, $NCHCO_2$), 5.17 (m, 2 H, C=CH_2), 5.31 (d, J = 2.2 Hz, 0.4 H, C_4H), 5.71 (m, 1 H, CH=C), 7.32 (m, 5 H, Ar H); exact mass calcd for $C_{19}H_{26}NO_4SiS$ (M^+ – *t*-Bu) m/z 392.1350, found m/z 392.1347] accompanied by the diallyl compound **18** (90 mg, 9.2%) as a yellowish oil [IR ($CHCl_3$) 1750 (sh), 1735 cm^{-1}; ^1H NMR (60 MHz) ($CDCl_3$) δ 0.06 (s, 6 H, 2 × Me), 0.90 (s, 9 H, *t*-Bu), 1.18 (d, J = 6.3 Hz, 3 H, 1′-Me), 2.85 (t, J = 7.0 Hz, 4 H, 2 × CH_2C=C), 3.07 (dd, J = 2.0 and 4.8 Hz, 1 H, C_3H), 3.67 (s, 3 H, CO_2Me), 4.18 (m, 1 H, $C_{1'}H$), 5.05–5.25 (m, 2 H, C=CH_2), 5.20 (d, J = 2.0 Hz, 1 H, C_4H), 5.50–6.00 (m, 1 H, CH=C), 7.40 (m, 5 H, Ar H); exact mass calcd for $C_{22}H_{30}NO_4SiS$ (M^+ – *t*-Bu) m/z 432.1663, found m/z 432.1653].

Benzyl (3*S*,4*R*)-3-[[(*R*)-1′-[(*tert*-Butyldimethylsilyl)oxy]ethyl]-2-oxo-4-(phenylthio)-1-azetidinyl]-4-pentenoate (17). The benzyl ester **15** (0.97 g, 2 mmol) was allylated with allyl bromide (0.17 mL, 2 mmol) in the presence of lithium hexamethyldisilazide (2.2 mmol) as above to give the allyl compound **17** (0.76 g, 72.4%) as a colorless oil [IR ($CHCl_3$) 1750, 1735 cm^{-1}; ^1H NMR (100 MHz) ($CDCl_3$) δ 0.02 (s, 3 H, Me), 0.05 (s, 3 H, Me), 0.85 (s, 3 H, Me), 0.87 (s, 6 H, 2 × Me), 1.13 (d, J = 6.1 Hz, 1 H, 1′-Me), 1.20 (d, J = 6.1 Hz, 2 H, 1′-Me), 2.69 (t, J = 7.4 Hz, 0.67 H, CH_2C=C), 2.74 (t, J = 7.4 Hz, 1.33 H, CH_2C=C), 3.00 (dd, J = 2.2 and 5.7 Hz, 1 H, C_3H), 4.13 (t, J = 7.4 Hz, 0.67 H, $NCHCO_2$), 4.20 (m, 1 H, $C_{1'}H$), 4.29 (t, J = 7.4 Hz, 0.33 H, $NCHCO_2$), 5.00 (d, J = 2.2 Hz, 0.67 H, C_4H), 5.12 (m, 2 H, C=CH_2), 5.16 (s, 2 H, CO_2CH_2), 5.31 (d, J = 2.2 Hz, 0.33 H, C_4H), 5.60–5.90 (m, 1 H, CH=C), 7.35 (m, 10 H, 2 × Ar H); exact mass calcd for $C_{25}H_{30}NO_4SiS$ (M^+ – *t*-Bu) m/z 468.1663, found m/z 468.1662] and the diallyl derivative **19** (97 mg, 8.6%) as a yellowish oil [IR ($CHCl_3$) 1745, 1730 cm^{-1}; ^1H NMR (100 MHz) ($CDCl_3$) δ 0.02 (s, 3 H, Me), 0.05 (s, 3 H, Me), 0.88 (s, 9 H, *t*-Bu), 1.16 (d, J = 6.1 Hz, 3 H, 1′-Me), 2.79 (t, J = 6.8 Hz, 4 H, 2 × CH_2C=C), 3.01 (dd, J = 2.2 and 4.8 Hz, 1 H, C_3H), 4.14 (dq, J = 4.8 and 6.1 Hz, 1 H, $C_{1'}H$), 5.11 (m, 3 H, C=CH_2 and C_4H), 5.69 (m, 1 H, CH=C); exact mass calcd for $C_{28}H_{34}NO_4SiS$ (M^+ – *t*-Bu) m/z 508.1976, found m/z 508.1970].

Methyl (2*R*,6*R*,7*S*)- and (2*S*,6*S*,7*S*)-7-[(*R*)-1′-[(*tert*-Butyldimethylsilyl)oxy]ethyl]-8-oxo-1-azabicyclo[4.2.0]octane-2-carboxylates (20 and 22). The radical cyclization of **16** (0.36 g, 0.8 mmol) with tri-*n*-butyltin hydride (0.86 mL, 3.2 mmol) and AIBN (26 mg, 0.16 mmol) was carried out by the same procedure as described for the preparation of **7** to give the (6*S*,7*S*)-carbacepham **22** (53 mg, 19.4%) as a colorless oil [IR ($CHCl_3$) 1740 (sh), 1730 cm^{-1}; ^1H NMR (400 MHz) ($CDCl_3$) δ 0.07 (s, 3 H, Me), 0.09 (s, 3 H, Me), 0.87 (s, 9 H, *t*-Bu), 1.32 (d, J = 6.1 Hz, 3 H, 1′-Me), 1.60–2.05 (m, 8 H, 4 × CH_2), 3.25 (dd, J = 5.0 and 8.0 Hz, 1 H, C_7H), 3.74 (s, 3 H, CO_2Me), 3.77 (m, 1 H, C_6H), 4.25 (dq, J = 6.1 and 8.0 Hz, 1 H, $C_{1'}H$), 4.55 (d, J = 6.6 Hz, 1 H, C_4H); exact mass calcd for $C_{13}H_{22}NO_4Si$ (M^+ – *t*-Bu) m/z 284.1316, found m/z 284.1311; $[\alpha]^{25}_D$ –66.47° (*c* 0.34, $CHCl_3$)] and the (6*R*,7*S*)-carbacepham **20** (83 mg, 31%) as a colorless oil [IR ($CHCl_3$) 1735 (sh), 1725 cm^{-1}; ^1H NMR (100 MHz) ($CDCl_3$) δ 0.07 (s, 6 H, 2 × Me), 0.88 (s, 9 H, *t*-Bu), 1.23 (d, J = 6.1 Hz, 2 H, 1′-Me), 1.58–2.07 (m, 8 H, 4 × CH_2), 2.78 (dd, J = 1.8 and 5.7 Hz, 1 H, C_7H), 3.61 (m, 1 H, C_6H), 3.73 (s, 3 H, CO_2Me), 4.16 (dq, J = 5.7 and 6.1 Hz, 1 H, $C_{1'}H$), 4.56 (d, J = 6.5 Hz, 1 H, C_4H); exact mass calcd for $C_{13}H_{22}NO_4Si$ (M^+ – *t*-Bu) m/z 284.1319, found m/z 284.1321; $[\alpha]^{25}_D$ +39.27° (*c* 0.55, $CHCl_3$)], together with the starting material **16** (74 mg) and the desulfurized compound **24** (24 mg, 8.8%) as a colorless oil [IR ($CHCl_3$) 1745 (sh), 1725 cm^{-1}; ^1H NMR (100 MHz) ($CDCl_3$) δ 0.06 (s, 3 H, Me), 0.07 (s, 3 H, Me), 0.88 (s, 9 H, *t*-Bu), 1.21 (d, J = 6.1 Hz, 3 H, 1′-Me), 2.57 (m, 2 H, CH_2C=C), 3.17 (dt, J = 2.4 and 4.8 Hz, 1 H, C_3H), 3.27 (dd, J = 2.4 and 11.5 Hz, 1 H, $C_{4\alpha}H$), 3.46 (dd, J = 4.8 and 11.5 Hz, 1 H, $C_{4\beta}H$), 3.73 (s, 3 H, CO_2Me), 4.16 (dq, J = 4.8 and 6.1 Hz, 1 H, $C_{1'}H$), 4.47 (dd, J = 6.0 and 9.0 Hz, 1 H, $NCHCO_2$), 5.19 (m, 2 H, C=CH_2), 5.60–5.90 (m, 1 H, CH=C); exact mass calcd for $C_{13}H_{22}NO_4Si$ (M^+ – *t*-Bu) m/z 284.1316, found m/z 284.1300].

Benzyl (2*R*,6*R*,7*S*)- and (2*S*,6*S*,7*S*)-7-[(*R*)-1′-[(*tert*-Butyldimethylsilyl)oxy]ethyl]-8-oxo-1-azabicyclo[4.2.0]octane-2-carboxylates (21 and 23). Treatment of the allyl compound **17** (0.42 g, 0.8 mmol) with tri-*n*-butyltin hydride (0.86 mL, 3.2 mmol) and AIBN (26 mg, 0.16 mmol) as above afforded the (6*S*,7*S*)-carbacepham **23** (67 mg, 20.1%) as a colorless oil [IR ($CHCl_3$) 1735 (sh), 1725 cm^{-1}; ^1H NMR (100 MHz) ($CDCl_3$) δ 0.07 (s, 3 H, Me), 0.08 (s, 3 H, Me), 0.87 (s, 9 H, *t*-Bu), 1.31 (d, J = 6.3 Hz, 3 H, 1′-Me), 1.70–2.05 (m, 8 H, 4 × CH_2), 3.24 (dd, J = 4.9 and 7.8 Hz, 1 H, C_7H), 3.77 (dt, J = 4.9 and 10 Hz, 1 H, C_6H), 4.24 (dq, J = 6.3 and 7.8 Hz, 1 H, $C_{1'}H$), 4.58 (d, J = 6.8 Hz, 1 H, C_4H), 5.14 (d, J = 12.2 Hz, 1 H, CO_2CHPh), 5.17 (d, J = 12.2 Hz, 1 H, CO_2CHPh), 7.34 (m, 5 H, Ar H); exact mass calcd for $C_{19}H_{26}NO_4Si$ (M^+ – *t*-Bu) m/z 360.1630, found m/z 360.1615; $[\alpha]^{25}_D$ –54.87° (*c* 0.82, $CHCl_3$)] and the (6*R*,7*S*)-carbacepham **21** (108 mg, 32.4%) as a colorless oil [IR ($CHCl_3$) 1730 (sh), 1720 cm^{-1}; ^1H NMR (400 MHz) ($CDCl_3$) δ 0.03 (s, 3 H, Me), 0.06 (s, 3 H, Me), 0.86 (s, 9 H, *t*-Bu), 1.24 (d, J = 6.1 Hz, 3 H, 1′-Me), 1.60–2.05 (m, 8 H, 4 × CH_2), 2.78 (dd, J = 1.7 and 6.7 Hz, 1 H, C_7H), 3.62 (dq, J = 1.7 and 3.0 Hz, 1 H, C_6H), 4.11 (dq, J = 6.1 and 6.7 Hz, 1 H, $C_{1'}H$), 4.60 (d, J = 6.8 Hz, 1 H, C_4H), 5.11 (d, J = 12.2 Hz, 1 H, CO_2CHPh), 5.20 (d, J = 12.2 Hz, 1 H, CO_2CHPh), 7.34 (m, 5 H, Ar H); exact mass calcd for $C_{19}H_{26}NO_4S$ (M^+ – *t*-Bu) m/z 360.1631, found m/z 360.1132; $[\alpha]^{25}_D$ +33.01° (*c* 1.26, $CHCl_3$)], together with the starting material **17** (78 mg) and the desulfurized compound **25** (31 mg, 9.2%) as a colorless oil [IR ($CHCl_3$) 1745 (sh), 1720 cm^{-1}; ^1H NMR (100 MHz) ($CDCl_3$) δ 0.04 (s, 3 H, Me), 0.06 (s, 3 H, Me), 0.88 (s, 9 H, *t*-Bu), 1.20 (d, J = 6.4 Hz, 3 H, 1′-Me), 2.57 (m, 2 H, CH_2C=C), 3.16 (dt, J = 2.4 and 5.2 Hz, 1 H, C_3H), 3.33 (m, 1 H, $C_{4\alpha}H$), 3.44 (dd, J = 5.2 and 10 Hz, 1 H, $C_{4\beta}H$), 4.10 (dt, J = 5.2 and 6.4 Hz, 1 H, $C_{1'}H$), 4.49 (dd, J = 5.9 and 8.3 Hz, 1 H, $NCHCO_2$), 5.05 and 5.21 (m, 2 H, C=CH_2), 5.15 (s, 2 H, CO_2CH_2), 5.50–5.78 (m, 1 H, CH=C), 7.34 (m, 5 H, Ar H); exact mass calcd for $C_{19}H_{26}NO_4Si$ (M^+ – *t*-Bu) m/z 360.1629, found m/z 360.1623].

4-(Phenylselenenyl)-2-azetidinone (26). To a stirred suspension of diphenyl diselenide (0.86 g, 2.75 mmol) in absolute ethanol (15 mL) was added sodium borohydride (0.21 g, 5.5 mmol) at 0 °C under an atmosphere of nitrogen, until the bright yellow solution turned clear. After addition of a solution of 4-acetoxy-2-azetidinone (0.65 g, 5 mmol) in absolute ethanol (10 mL) at 0 °C, the resulting mixture was further stirred at ambient temperature for 1 h. Removal of the solvent gave the residue, which was taken up with ether and the ethereal layer was washed with brine and dried over sodium sulfate. Evaporation of the solvent

gave the residue, which was subjected to column chromatography on silica gel. Elution with benzene–acetone (10:1 v/v) afforded the azetidinone **26** (1.016 g, 89.2%) as colorless needles: mp 59.5 °C (from hexane); IR ($CHCl_3$) 3400, 1765 cm^{-1}; ^1H NMR (100 MHz) ($CDCl_3$) δ 2.97 (ddd, J = 1.2, 2.2 and 15.5 Hz, 1 H, $C_{3\beta}H$), 3.43 (ddd, J = 1.2, 5.0 and 15.5 Hz, $C_{3\alpha}H$), 5.10 (dd, J = 2.2 and 5.0 Hz, 1 H, C_4H), 6.49 (br s, 1 H, NH), 7.45 (m, 5 H, Ar H); mass spectrum, m/z 227 (M^+ + 1). Anal. Calcd for C_9H_9NOSe: C, 47.80; H, 4.01; N, 6.19. Found: C, 48.04; H, 4.04; N, 6.18.

1-[(Methoxycarbonyl)methyl]-4-(phenylselenenyl)-2-azetidinone (27). The acetidinone **26** (0.9 g, 4 mmol) was treated with methyl bromoacetate (0.37 mL, 4 mmol) in dry tetrahydrofuran in the presence of lithium hexamethyldisilazide [prepared from n-butyllithium (1.57 M in hexane) (2.8 mL, 4.4 mmol) and hexamethyldisilazane (0.97 mL, 4.6 mmol)] to give the ester **27** (1.02 g, 85.5%) as a colorless oil: IR ($CHCl_3$) 1760, 1750 cm^{-1}; ^1H NMR (100 MHz) ($CDCl_3$) δ 2.95 (ddd, J = 0.8, 2.2 and 15.7 Hz, 1 H, $C_{3\beta}H$), 3.45 (dd, J = 4.8 and 15.7 Hz, 1 H, $C_{3\alpha}H$), 3.69 (s, 3 H, CO_2Me), 3.76 (d, J = 18.0 Hz, 1 H, $NCHCO_2$), 4.26 (d, J = 18.0 Hz, 1 H, $NCHCO_2$), 5.31 (dd, J = 2.2 and 4.8 Hz, 1 H, C_4H), 7.43 (m, 5 H, Ar H); mass spectrum, m/z 298 (M^+), 142 (M^+ – SePh).

Methyl 2-[2-Oxo-4-(phenylselenenyl)-1-azetidinyl]-4-pentenoate (28). The ester **27** (0.9 g, 3 mmol) was treated with allyl bromide (0.25 mL, 3 mmol) in tetrahydrofuran in the presence of lithium hexamethyldisilazide [prepared from n-butyllithium (1.57 M in hexane) (2.1 mL, 3.3 mmol) and hexamethyldisilazane (0.73 mL, 3.45 mmol)] as described before to give the allyl compound **28** (0.74 g, 73%) as a yellowish oil [IR ($CHCl_3$) 1750, 1740 cm^{-1}; ^1H NMR (100 MHz) ($CDCl_3$) δ 2.76 (m, 2 H, $CH_2C{=}C$), 3.01 (dd, J = 2.2 and 15.7 Hz, 0.42 H, $C_{3\beta}H$), 3.05 (dd, J = 2.2 and 15.7 Hz, 0.58 H, $C_{3\beta}H$), 3.43 (dd, J = 5.0 and 15.7 Hz, 0.42 H, $C_{3\alpha}H$), 3.47 (dd, J = 5.0 and 15.7 Hz, 0.58 H, $C_{3\alpha}H$), 3.71 (s, 1.75 H, CO_2Me), 3.74 (s, 1.25 H, CO_2Me), 4.08 (t, J = 6.8 Hz, 0.58 H, $CHCO_2$), 4.30 (t, J = 6.8 Hz, 0.42 H, $CHCO_2$), 5.10–5.30 (m, 2 H, $C{=}CH_2$), 5.05–5.30 (m, 1 H, C_4H), 5.77 (m, 1 H, $CH{=}C$), 7.30 (m, 5 H, Ar H); mass spectrum, m/z 338 (M^+), 279 (M^+ – CO_2Me), 182 (M^+ – SePh)], together with the diallyl derivative **29** (120 mg, 10.6%) as a yellowish oil [IR ($CHCl_3$) 1745, 1730 cm^{-1}; ^1H NMR (100 MHz) ($CDCl_3$) δ 2.77 (m, 4 H, 2 × $CH_2C{=}C$), 3.00 (dd, J = 2.2 and 15.5 Hz, 1 H, $C_{3\beta}H$), 3.43 (dd, J = 4.8 and 15.5 Hz, 1 H, $C_{3\alpha}H$), 3.71 (s, 3 H, CO_2Me), 5.16 (m, 4 H, 2 × $C{=}CH_2$), 5.32 (dd, J = 2.2 and 4.8 Hz, 1 H, C_4H), 5.73 (m, 2 H, 2 × $CH{=}C$), 7.29 (m, 5 H, Ar H); mass spectrum, m/z 378 (M^+), 319 (M^+ – CO_2Me), 222 (M^+ – SePh)].

Radical Cyclization of the Selenenyl Derivative 28. To a stirred refluxing solution of **28** (340 mg, 1 mmol) in dry benzene (15 mL) was added dropwise a solution of tri-n-butyltin hydride (1.08 mL, 4 mmol) and AIBN (33 mg, 0.2 mmol) in dry benzene (30 mL) over a period of 5 h under an atmosphere of nitrogen. After being refluxed for a further 30 min, the mixture was concentrated to leave the residue, which was subjected to column chromatography on silica gel. Elution with hexane–acetone (23:2 v/v) afforded the carbacepham **7** (109 mg, 59%) and the desulfurized compound **10** (27 mg, 14.7%) together with the starting material **28** (42 mg). The products **7** and **10** were identical with authentic samples obtained as above.

Methyl 5-(Trimethylsilyl)-2-[2-oxo-4-(phenylthio)-1-azetidinyl]-4-pentynoate (30). The ester **1** (1 g, 4 mmol) was alkylated with 3-bromo-1-(trimethylsilyl)-1-propyne (0.764 g, 4 mmol) in dry tetrahydrofuran in the presence of lithium hexamethyldisilazide [prepared from n-butyllithium (1.57 M in hexane) (2.8 mL, 4.4 mmol) and hexamethyldisilazane (0.764 mL, 4 mmol)] by the same procedure as described for the preparation of **3** to give the acetylenic compound **30** (0.96 g, 66.5%) as a yellowish oil [IR ($CHCl_3$) 2155, 1755, 1740 cm^{-1}; ^1H NMR (100 MHz) ($CDCl_3$) δ 0.15 (s, 9 H, $SiMe_3$), 2.78 (m, 3 H, $CH_2C{\equiv}C$ and $C_{3\beta}H$), 3.38 (ddd, J = 0.8, 4.9 and 15.0 Hz, 1 H, $C_{3\beta}H$), 3.75 (s, 1.8 H, CO_2Me), 3.76 (s, 1.2 H, CO_2Me), 4.31 (t, J = 6.6 Hz, 0.4 H, $NCHCO_2$), 4.40 (t, J = 6.6 Hz, 0.6 H, $NCHCO_2$), 5.09 (dd, J = 2.4 and 4.9 Hz, 0.4 H, C_4H), 5.29 (dd, J = 2.4 and 4.9 Hz, 0.6 H, C_4H), 7.36 (m, 5 H, Ar H); exact mass calcd for $C_{18}H_{23}NO_3SiS$ (M^+) m/z 361.1166, found m/z 361.1145.

Methyl 8-Oxo-5-(trimethylsilyl)-1-azabicyclo[4.2.0]-4-octene-2-carboxylates (31 and 32). The radical cyclization of **30** (0.36 g, 1 mmol) with tri-n-butyltin hydride (1.08 mL, 4 mmol) and AIBN (33 mg, 0.2 mmol) was carried out by the same procedure as for the preparation of **7** to give the carbacephems **31** and **32** (26 mg, 10.3%) as a colorless oil [IR ($CHCl_3$) 1745 (sh), 1730 cm^{-1}; ^1H NMR (400 MHz) ($CDCl_3$) δ 0.10 (s, 7.5 H, $SiMe_3$ for **31**), 0.14 (s, 1.5 H, $SiMe_3$ for **32**), 1.39 (ddd, J = 7.4, 9.1 and 16 Hz, 1 H, C_3H), 1.64 (ddd, J = 7.4, 9.1 and 16 Hz, 1 H, C_3H), 2.58 (dd, J = 2.7 and 14.7 Hz, $C_{7\beta}H$), 3.28 (dd, J = 5.4 and 14.7 Hz, 1 H, $C_{7\alpha}H$), 3.73 (m, 1 H, C_6H), 3.74 (s, 3 H, CO_2Me), 4.60 (dd, J = 5.0 and 8.0 Hz, 0.17 H, C_4H for **32**), 4.71 (dd, J = 1.2 and 9.1 Hz, 0.83 H, C_4H for **31**), 6.01 (m, 1 H, C_2H); exact mass calcd for $C_{12}H_{19}NO_3Si$ (M^+) m/z 253.1133, found m/z 253.1131], together with the starting material **30** (94 mg) and the desulfurized compound **33** (137 mg, 54%) as a colorless oil [IR ($CHCl_3$) 2155, 1745 (sh), 1730 cm^{-1}; ^1H NMR (100 MHz) ($CDCl_3$) δ 0.14 (s, 9 H, $SiMe_3$), 2.75 (d, J = 6.5 Hz, 2 H, $CH_2C{=}C$), 3.00 (m, 2 H, C_3H), 3.54 (m, 2 H, C_4H), 3.76 (s, 3 H, CO_2Me), 4.61 (t, J = 6.5 Hz, 1 H, $NCHCO_2$); exact mass calcd for $C_{12}H_{19}NO_3Si$ (M^+) m/z 253.1133, found m/z 253.1126].

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Registry No. **1**, 76060-84-9; **2**, 82551-55-1; **3** (isomer 1), 83865-46-7; **3** (isomer 2), 83865-47-8; **4** (isomer 1), 114156-38-6; **4** (isomer 2), 114247-21-1; **5**, 114156-37-5; **6**, 114156-39-7; **7**, 83865-48-9; **8**, 114247-22-2; **9**, 114156-41-1; **10**, 114156-40-0; **11** (isomer 1), 114156-42-2; **11** (isomer 2), 114156-61-5; **13**, 85281-73-8; **14**, 114156-43-3; **15**, 114156-44-4; **16** (isomer 1), 114156-45-5; **16** (isomer 2), 114248-19-0; **17** (isomer 1), 114156-47-7; **17** (isomer 2), 114247-23-3; **18**, 114156-46-6; **19**, 114156-48-8; **20**, 114247-24-4; **21**, 114247-25-5; **22**, 114156-49-9; **23**, 114156-51-3; **24** (isomer 1), 114156-50-2; **24** (isomer 2), 114247-26-6; **25** (isomer 1), 114156-52-4; **25** (isomer 2), 114247-27-7; **26**, 89691-18-9; **27**, 114156-53-5; **28** (isomer 1), 114183-76-5; **28** (isomer 2), 114156-54-6; **29**, 114156-55-7; **30** (isomer 1), 114156-56-8; **30** (isomer 2), 114156-57-9; **31**, 114156-58-0; **32**, 114156-59-1; **33**, 114156-60-4; methyl bromoacetate, 96-32-2; benzyl bromoacetate, 5437-45-6; 4-acetoxy-2-azetidinone, 28562-53-0; 3-bromo-1-(trimethylsilyl)-1-propyne, 38002-45-8.