Pergamon

Tetrahedron Vol. 50, No. 44, pp. 12579-12592, 1994

0040-4020/94 $7.00+0.00

0040-4020(94)00812-4

STEREOSELECTIVE ALLYLATION OF DICHLOROCYCLOBUTANONES AND SEQUENTIAL RING EXPANSIONS: CONSTRUCTION OF *CIS*-FUSED CYCLOHEPTANONES

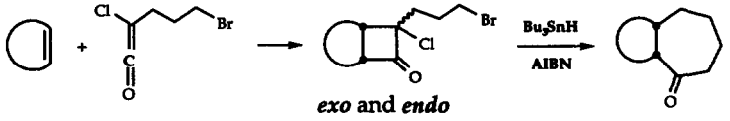
Wei Zhang, Ye Hua, Steven J. Geib, Garrett Hoge and Paul Dowd*

Department of Chemistry
University of Pittsburgh
Pittsburgh, PA 15260

Abstract: *Stereoselective allylation of fused dichlorocyclobuatanones, using allyl tributyltin, introduces an exo-oriented side chain on the ring. Sequential hydrohalogenation and free radical ring expansion of cyclobutanones gives, three-carbon, ring-expanded, cis-fused cycloheptanones.*

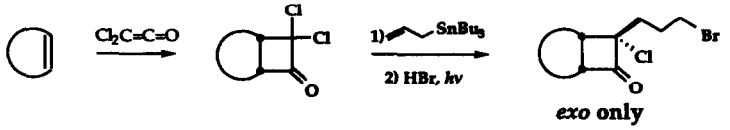
Introduction

Annulation of alkenes to form seven-membered rings in stereospecific fashion would be a valuable adjunct to synthetic chemistry. We recently reported a new method to make seven-and eight-membered ketones through ring expansion of cyclobutanones (eq 1).[1-2] The ring



exo and *endo* (1)

expansion occurs stereospecifically and in good yield. However, there are two drawbacks to the preparation of the fused-cyclobutanones:[3] (i) Chloroalkylketenes react best with conjugated dienes but in low yields with simple alkenes. (ii) The ketene addition yields a mixture of *exo* and *endo* products and only the *exo* adducts undergo ring expansion.[1b] Both problems have now been resolved by the design of a new reaction sequence that introduces the *exo*-haloalkyl side chain stereoselectively (eq 2).[4] This improvement makes the ring expansion of cyclobutanones more

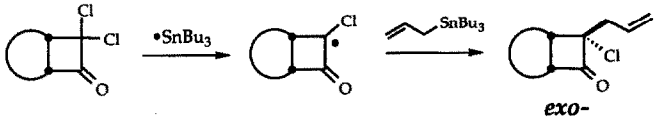


exo only (2)

attractive in synthetic terms.

Results and Discussion

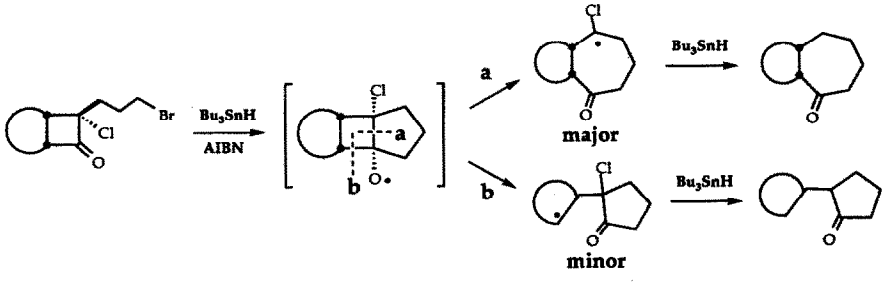
In situ generated dichloroketene reacts in excellent yield with simple alkenes, as well as with dienes, to give a series of dichlorocyclobutanones.[5] Allylation of dichlorocyclobutanones using allyl tributyltin is the key step required to introduce the *exo*-oriented side chain. Allylation of alkylbromides or alkyliodides using allyl tributyltin has been well developed by Keck.[6] Extension of this reaction to alkylchlorides has not been tried because alkylchlorides are generally not good radical chain precursors. In our studies of the intramolecular cyclization of dichlorocyclobutanones,[7] we found that α,α-dichloro-substituted cyclobutanones are good radical precursors since the unpaired electron is stabilized by both the α-acyl and chlorine substituents. In the present case, we observe high yield intermolecular additions of the chlorocyclobutyl radical to allyl tributyltin. Moreover, the addition reaction proceeds to yield *only* the desired *exo*-allyl adduct as a consequence of steric constraints (eq 3). The *exo*-allylation products are readily



(3)

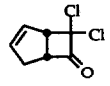
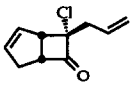
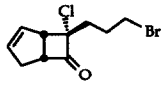
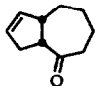
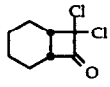
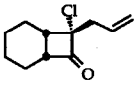
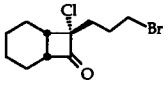
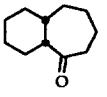
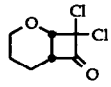
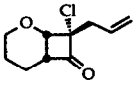
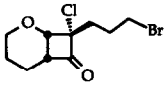
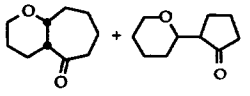
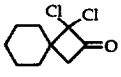
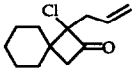
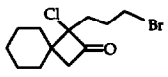
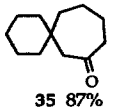
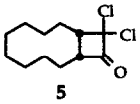
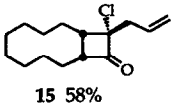
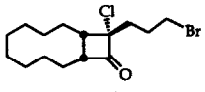
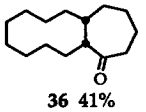
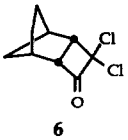
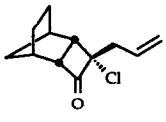
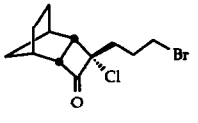
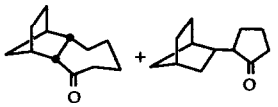
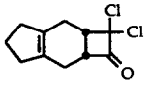
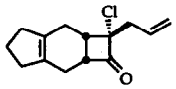
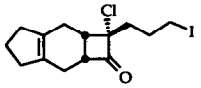
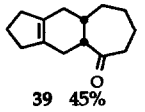
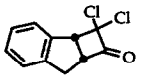
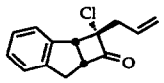
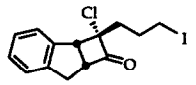
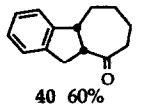
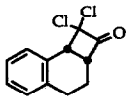
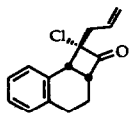
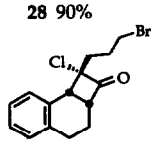
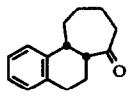
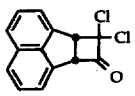
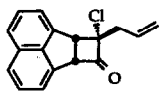
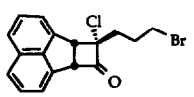
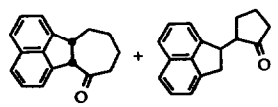
transformed to the appropriate bromide or iodide by free radical-promoted hydrobromination or by the treatment with 9-BBN and I_2.[8] Tributyltin hydride-promoted free radical ring expansion then yields *cis*-fused cycloheptanone products (Scheme 1, path a). Direct reduction products and

Scheme 1



ring attachment products are also observed. The latter are generated from alternative β-scission of alkoxy radicals (Scheme 1, path b).[9] In most cases, ring expansion is the major pathway for the β-scission of the intermediate alkoxy radicals. The amount of direct reduction product can be controlled by syringe pump addition of the tributyltin hydride.

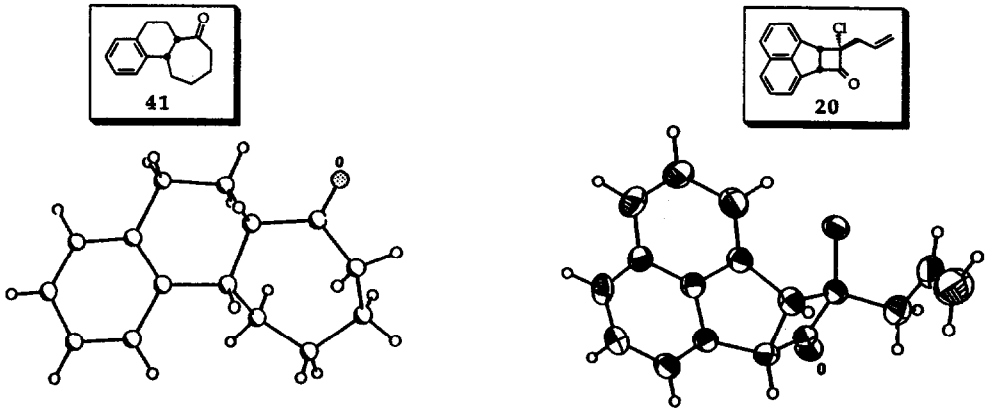
Table 1. Allylation and Ring Expansion of Dichlorocyclobutanones

Entry	Dichloro-cyclobutanone	Allylation Product	*Exo*-Halide	Ring Expansion Product
1	 **1**	 **11** 78%	 **21** 83%	 **31** 74%
2	 **2**	 **12** 51%	 **22** 97%	 **32** 51%
3	 **3**	 **13** 55%	 **23** 54%	 **33** 74% (79:21) **34**
4	 **4**	 **14** 50%	 **24** 60%	 **35** 87%
5	 **5**	 **15** 58%	 **25** 50%	 **36** 41%
6	 **6**	 **16** 64%	 **26** 92%	 **37** 89% (70:30) **38**
7	 **7**	 **17** 42%	 **27** 50%	 **39** 45%
8	 **8**	 **18** 67%	 **28** 90%	 **40** 60%
9	 **9**	 **19** 44%	 **29** 81%	 **41** 49%
10	 **10**	 **20** 54%	 **30** 89%	 **42** 64% (40:60) **43**

The products and yields in Table 1 attest to the versatility of the new method. Fused and spiro bicycloketones (entries 1, 2 and 4)[1a,b,d] are readily prepared. A bicyclo[8.5.0] system represents a novel application (entry 5). Entry 3 demonstrates that an enol ether can be employed to provide access to the 2-oxa-bicyclo[5.4.0]undecan-7-one system **33**, together with a minor amount of the alternative ring-opened by-product.

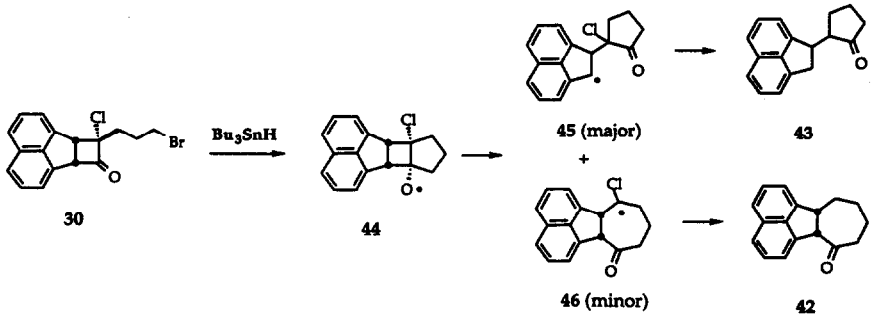
Unconjugated, bicyclic alkenes are likewise encompassed as indicated in entries 6 and 7. Indene and 1,2-dihydronaphthalene yield the interesting benzoperhydroazulenones **40** and **41** shown in entries 8 and 9. The structure of **41** was established by X-ray analysis (Figure 1).

Figure 1. X-Ray Structures of 41 and 20



Dichlorocyclobutanone **10** reacts with allyl tributyltin affords allylation product **20**. The structure of **20** was also established by X-ray analysis (Figure 1). In the reaction of the acenaphthalene derivative **30** with tributyltin hydride (Scheme 2), β-scission of the alkoxy radical

Scheme 2



44 to form the stabilized radical **45** and the subsequent ring attachment product **43** is the dominant pathway. Ring expansion product **42** derived from radical **46** is formed as the minor product.

In summary, we have developed a useful and straightforward reaction sequence for transforming alkenes to *cis*-fused cycloheptanones.

Experimental Section

Materials and Methods. All reactions were performed under a nitrogen atmosphere. Benzene and diethyl ether were distilled from blue or purple solutions of sodium benzophenone ketyl under nitrogen. Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were obtained on Bruker AC-300, or IBM AF-300 spectrometers (300 MHz for ^{1}H NMR, 75 MHz for ^{13}C NMR). Infrared (IR) spectra were obtained on an IBM IR/32 FTIR or a Mattson Cygnus 100 FTIR spectrometer. Gas chromatography and low resolution mass spectra (GC-MS) were obtained using a Hewlett-Packard gas chromatograph (5890 series II) equipped with a Hewlett-Packard mass spectrometer (5970 series) and a fused silica capillary column with 100% dimethyl polysiloxane (HP-1, Hewlett-Packard). High-Resolution mass spectra were obtained on Varian MAT CH-5DF spectrometer.

Preparation of Dichlorocyclobutanones

Dichlorocyclobutanones **1, 2, 3, 4, 5, 6, 8, 9,** and **10** are known substances[3a] and were prepared in 80-95% yields following literature procedures.[5a]

Data for **3,4-cyclopentyl-8,8-dichlorobicyclo[4.2.0]oct-3-en-7-one (7)**: ^{1}H NMR ($CDCl_3$) δ 4.07 (m, 1 H), 3.37 (m, 1 H), 2.60-2.40 (m, 2 H), 2.40-2.06 (m, 6 H), 1.79 (quintet, J=7.2 Hz, 2 H). ^{13}C NMR ($CDCl_3$) δ 198.4 (s), 133.4 (s), 132.7 (s), 88.9 (s), 53.7 (d, J=139 Hz), 45.2 (d, J=147 Hz), 36.0 (t, J=129 Hz), 35.6 (t, J=129 Hz), 23.9 (t, J=130 Hz), 22.6 (t, J=131 Hz), 21.3 (t, J=129 Hz). IR (neat) 1806 (s, C=O) cm^{-1}. MS *m/e* 234 (2), 232 (11), 230 (16, M^+), 202 (11), 167 (27), 153 (71), 131 (44), 125 (53), 91 (100), 77 (62). HRMS calcd for $C_{11}H_{12}O^{35}Cl_2$: 230.0265. Found: 230.0263.

Allylation of Dichlorocyclobutanones

General Procedure. (*1SR,5RS,7SR*)-7-(3'-Propenyl)-7-chlorobicyclo[3.2.0]hept-2-en-6-one (11). A solution of 1.76 g of dichlorocyclobutanone **1** (10 mmol), 6.2 mL of allyl tributyltin (20 mmol), and 164 mg of AIBN (1 mmol) in 15 mL of benzene was refluxed for 3-8 h until the reaction was complete as judged by GC analysis. After DBU workup,[10] flash chromatography (40:1 hexanes-

ether) of the crude product afforded 1.42 g (78%) of **11**. ^{1}H NMR ($CDCl_3$) δ 6.00-5.70 (m, 3 H), 5.32-5.17 (m, 2 H), 3.88 (t, *J*=7.8 Hz, 1 H), 3.67 (m, 1 H), 2.78 (m, 3 H), 2.51 (m, 1 H). ^{13}C NMR ($CDCl_3$) δ 206.8 (s), 134.5 (d, *J*=164 Hz), 130.9 (d, *J*=155 Hz), 129.4 (d, *J*=168 Hz), 119.9 (t, *J*=151 Hz), 81.2 (s), 57.4 (d, *J*=141 Hz), 50.9 (d, *J*=149 Hz), 41.8 (t, *J*=132 Hz), 35.1 (t, *J*=134 Hz). IR (neat) 1792 (s, C=O) cm^{-1}. MS *m/e* (rel. intensity) 182 (1, M$^+$), 147 (20, M$^+$-Cl), 119 (30), 91 (100), 77 (47), 66 (82).

(1*SR*,6*RS*,8*SR*)-8-(3'-Propenyl)-8-chlorobicyclo[4.2.0]octan-7-one (12). Following the general procedure above, treatment of **2** (150 mg, 0.78 mmol) with allyltributyltin (484 µL, 1.56 mmol) and AIBN (30 mg) in 2 mL of benzene afforded 78 mg (51%) of **12**. ^{1}H NMR ($CDCl_3$) δ 5.96-5.78 (m, 1 H), 5.27-5.13 (m, 2 H), 3.45 (m, 1 H), 2.76 (d, *J*=6.7 Hz, 2 H), 2.53 (m, 1 H), 2.16-1.88 (m, 2 H), 1.72-1.05 (m, 6 H). ^{13}C NMR ($CDCl_3$) δ 204.4, 131.7, 119.6, 81.0, 51.5, 43.5, 34.5, 25.2, 21.7, 21.6, 20.7. IR (neat) 1786 (s, C=O) cm^{-1}. MS *m/e* (rel. intensity) 198 (2, M$^+$), 163 (97, M$^+$-Cl), 154 (14), 135 (56), 113 (53), 93 (100). HRMS calcd for $C_{11}H_{15}O$ (M$^+$-Cl): 163.1123. Found: 163.1123.

(1*SR*,6*RS*,8*SR*)-2-Oxa-8-(3'-propenyl)-8-chlorobicyclo[4.2.0]octan-7-one (13). Following the general procedure above, treatment of **3** (1.94 g, 10 mmol) with allyltributyltin (6.2 mL, 20 mmol) and AIBN (400 mg) in 10 mL of benzene afforded 1.1 g (55%) of **13**. ^{1}H NMR ($CDCl_3$) δ 5.84 (m, 1 H), 5.25-5.16 (m, 2 H), 4.23 (d, *J*=6.0 Hz, 1 H), 3.96 (m, 1 H), 3.42-3.36 (m, 2 H), 2.71 (d, *J*=6.8 Hz, 2 H), 2,16 (m, 1 H), 1.72-1.50 (m, 3 H). ^{13}C NMR ($CDCl_3$) δ 202.4 (s), 130.5 (d, *J*=135 Hz), 119.7(t, *J*=156 Hz), 79.14 (s), 68.9 (d, *J*=167 Hz), 64.5 (t, *J*=145 Hz), 51.3 (d, *J*=135 Hz), 40.8 (t, *J*=130 Hz), 21.1 (t, *J*=64.5 Hz), 18.3 (t, *J*=123 Hz). IR (neat) 1794 (s, C=O) cm^{-1}. *MS m/e* (rel. intensity) 200 (<1, M$^+$), 165 (20, M$^+$-Cl), 137 (10), 113 (2), 84 (50), 69 (7), 55 (100). HRMS calcd for $C_{10}H_{13}O_2$ (M$^+$-Cl): 165.0915. Found: 165.0904.

1-(3'-Propenyl)-1-chlorospiro[3.5]nonan-2-one (14). Following the general procedure above, treatment of **4** (206 mg, 1.0 mmol) with allyltributyltin (620 µL, 2.0 mmol) and AIBN (34 mg) in 1 mL of benzene afforded 108 mg (50%) of **14**. ^{1}H NMR ($CDCl_3$) δ 5.90 (m, 1 H), 5.18 (m, 2 H), 2.92 (d, *J*=4.0 Hz, 2 H), 2.69 (m, 2 H), 1.88-1.18 (m, 10 H). ^{13}C NMR ($CDCl_3$)δ 202.2 (s), 131.9 (d, J=156 Hz), 119.0 (t, *J*=156 Hz), 83.0 (s), 52.1 (t, *J*=137 Hz), 41.1 (s), 37.5 (t, *J*=128 Hz), 34.1 (t, *J*=131 Hz), 32.0 (t, *J*=125 Hz), 25.3 (t, *J*=131 Hz), 23.5 (t, *J*=129 Hz), 23.2 (t, *J*=125 Hz). IR (neat) 1792 (s, C=O) cm^{-1}. MS *m/e* (rel. intensity) 212 (<1, M$^+$), 172 (18), 170 (54, M$^+$-C_2H_2O), 135 (100, M$^+$-C_2H_2ClO), 107 (16), 93 (52). HRMS calcd for $C_{10}H_{15}{}^{35}Cl$ (M$^+$-C_2H_2O): 170.0862. Found: 170.0869.

12-(3'-Propenyl)-12-chlorobicyclo[8.2.0]tetradecan-11-one (15). A solution of 3.48 g of allyl tributyltin (10.5 mmol) and 140 mg of AIBN (0.9 mmol) in 2 mL of benzene was added to a refluxing solution of 1.74 g of **5** (7.0 mmol) in 7 mL of benzene over 0.5 h using a syringe pump. After the addition was complete, another 140 mg of AIBN was added and the reaction mixture was

refluxed for additional 2.5 h. After DBU workup, flash chromatography (hexanes 250 mL, 30:1 hexanes-ether 600 mL) of the crude product afforded 1.0 g (58%) of **15**. ^{1}H NMR ($CDCl_3$) δ 5.90-5.75 (m, 1 H), 5.28-5.16 (m, 2H), 3.42-3.32 (m, 2 H), 2.66-2.55 (m, 1 H), 1.95-1.38 (m, 17 H). ^{13}C NMR ($CDCl_3$) δ 206.0 (s), 130.95 (d, J=157 Hz), 119.5 (t, J=156 Hz), 80.55 (s), 58.3 (d, J=132 Hz), 42.7 (t, J=133 Hz), 40.8 (d, J =138 Hz), 27.2 (t, J=126 Hz), 26.4 (t, J=121 Hz), 25.6 (t, J=121 Hz), 24.97 (t, J=126 Hz), 24.07 (t, J=122 Hz), 24.0 (t, J=122 Hz), 22.9 (t, J=126 Hz), 22.3 (t, J=129 Hz). IR (neat) 1786 (s, C=O) cm^{-1}. MS *m/e* (rel. intensity) 256 (2), 254 (5, M$^+$), 219 (14, M$^+$-Cl), 177 (10), 161 (10), 137 (23), 112 (16), 98 (60), 79 (83), 55 (100). HRMS calcd for $C_{15}H_{23}{}^{35}ClO$ (M$^+$): 254.1437. Found: 254.1437.

(*1RS,2RS,4SR,5SR,6SR*)-4-(3'-Propenyl)-4-chlorotricyclo[4.2.1.0^{2,5}]nonan-3-one (16). Following the general procedure above, treatment of **6** (875 mg, 4.2 mmol) with allyltributyltin (2.6 mL, 8.4 mmol) and AIBN (140 mg) in 10 mL of benzene afforded 563 mg (64%) of **16**. ^{1}H NMR ($CDCl_3$) δ 5.94-5.73 (m, 1 H), 5.32-5.14 (m, 2 H), 3.19 (d, J_{ab}=6.6 Hz, 1 H), 2.65-2.52 (m, 3 H), 2.33 (d, J_{ab}=6.6 Hz, 1 H), 1.78-1.00 (m, 7 H). ^{13}C NMR ($CDCl_3$) δ 207.3, 131.9, 121.0, 81.7, 58.4, 51.0, 45.3, 38.8, 35.5, 35.0, 28.1, 27.8. IR (neat) 1786 (s, C=O) cm^{-1}. MS *m/e* (rel. intensity) 212 (1), 210 (4, M$^+$), 175 (18), 147 (24), 128 (34), 105 (52), 91 (100), 77 (49). HRMS calcd for $C_{12}H_{15}O$ (M$^+$-Cl): 175.1123. Found: 175.1123.

(*1SR,6RS,8SR*)-3,4-Cyclopentyl-8-(3'-propenyl)-8-chlorobicyclo[4.2.0]oct-3-en-7-one (17). Following the general procedure above, treatment of **7** (1.97 g, 8.5 mmol) with allyltributyltin (5.26 mL, 16.0 mmol) and AIBN (280 mg) in 20 mL of benzene afforded 843 mg (42%) of **17**. ^{1}H NMR ($CDCl_3$) δ 5.92-5.72 (m, 1 H), 5.30-5.04 (m, 2 H), 3.62 (m, 1 H), 2.91 (m, 1 H), 2.82-1.70 (m, 12 H). ^{13}C NMR ($CDCl_3$) δ 207.6 (s), 133.4 (s), 133.1 (s), 131.1 (d, J=157 Hz), 120.0 (t, J=154 Hz), 80.0 (s), 53.1 (d, J=137 Hz), 42.8 (t, J=124 Hz), 36.1 (t, J=129 Hz), 35.7 (d, J=142 Hz), 35.7 (t, J=130 Hz), 23.8 (t, J=129 Hz), 22.7(t, J=131 Hz), 21.4 (t, J=130 Hz). IR (neat) 1788 (s, C=O) cm^{-1}. MS *m/e* (rel. intensity) 238 (4), 236 (12, M$^+$), 201 (8, M$^+$-Cl), 159 (18), 136 (43), 117 (47), 91 (100). HRMS calcd for $C_{14}H_{17}{}^{35}ClO$: 236.0968. Found: 236.0968.

(*1RS,5RS,7SR*)-2,3-Benzo-7-(3'-propenyl)-7-chlorobicyclo[3.2.0]heptan-6-one (18). Following the general procedure above, treatment of **8** (2.26 g, 10.0 mmol) with allyltributyltin (6.2 mL, 20.0 mmol) and AIBN (400 mg) in 10 mL of benzene afforded 1.57 g (67%) of **18**. ^{1}H NMR ($CDCl_3$) δ 7.33-7.20 (m, 4 H), 6.06-5.87 (m, 1 H), 5.36-5.27 (m, 2 H), 4.12 (m, 2 H). 3.42-3.07 (m, 2 H), 2.90 (d, J=6.9 Hz, 2 H). ^{13}C NMR ($CDCl_3$) δ 206.2 (s), 143.3 (s), 139.1 (s), 131.0 (d, J=160 Hz, 2 overlapping C), 128.0 (d, J=161 Hz), 126.6 (d, J=157 Hz), 125.0 (d, J=157 Hz), 120.2 (t, J=158 Hz), 81.3 (s), 57.9 (d, J=144 Hz), 50.3 (d, J=149 Hz), 42.4 (t, J=127 Hz), 34.4 (t, J=135 Hz). IR (neat) 1792 (s, C=O) cm^{-1}. MS *m/e* (rel. intensity) 234 (1), 232 (3, M$^+$), 197 (3, M$^+$-Cl), 169 (14), 141 (36), 128 (33), 116 (100). HRMS calcd for $C_{14}H_{13}{}^{35}ClO$: 232.0655. Found: 232.0655.

(*1RS,6RS,8SR*)-2,3-Benzo-8-(3'-propenyl)-8-chlorobicyclo[4.2.0]heptan-7-one (19). Following the general procedure above, treatment of **9** (2.40 g, 10.0 mmol) with allyltributyltin (4.7 mL, 14.0 mmol) and AIBN (400 mg) in 10 mL of benzene afforded 1.07 g (44%) of **19**. ^{1}H NMR ($CDCl_3$) δ 7.35 7.18 (m, 2 H), 7.18-7.10 (m, 1 H), 7.10-7.04 (m, 1 H), 6.06-5.89 (m, 1 H), 5.38-5.30 (m, 2 H), 3.87 (d, J=2.0 Hz, 2 H), 2.86 -2.79 (m, 2 H), 2.71-2.49 (m, 2 H), 2.32 (m, 1 H), 1.68-1.55 (m, 1 H). ^{13}C NMR ($CDCl_3$) δ 207.5 (s), 137.2 (s), 132.9 (s), 130.6 (d, J=155 Hz), 130.5 (d, J=168 Hz), 128.3 (d, J=166 Hz), 126.7 (d, J=168 Hz), 125.9 (d, J=161 Hz), 120.2 (t, J=157 Hz), 80.1 (s), 54.2 (d, J=139 Hz), 42.0 (t, J=126 Hz), 41.2 (d, J=139 Hz), 27.3 (t, J=128 Hz), 21.6 (t, J=132 Hz). IR (neat) 1786 (s, C=O) cm^{-1}. MS *m/e* (rel. intensity) 248 (1), 246 (4, M$^+$), 211 (2, M$^+$-Cl), 179 (4), 177 (8), 141 (18), 130 (100), 115 (62), 91 (10), 77 (18), 55 (58). HRMS calcd for $C_{15}H_{15}{}^{35}ClO$: 246.0811. Found: 246.0830.

Allyl Cyclobutanone 20. Following the general procedure above, treatment of **10** (960 mg, 3.6 mmol) with allyltributyltin (2.3 mL, 5.5 mmol) and AIBN (70 mg) in 3.6 mL of benzene afforded 530 mg (54%) of **20**. ^{1}H NMR ($CDCl_3$) δ 7.75 (d, J=8.0 Hz, 1 H), 7.72 (d, J=8.0 Hz, 1 H), 7.56 (t, J=8.0 Hz, 1 H), 7.51 (t, J=8.0 Hz, 1 H), 7.43 (d, J=8.0 Hz, 1 H), 7.41 (d, J=8.0 Hz, 1 H), 6.12-5.96 (m, 1 H), 5.42 (s, 1 H), 5.40 (d, J=6.0 Hz, 1 H), 5.21 (d, J=6.9 Hz, 1 H), 4.58-4.53 (d, J=6.9 Hz, 1 H), 3.00-2.94 (d, J=6.9 Hz, 2 H). ^{13}C NMR ($CDCl_3$) δ 200.5 (s), 140.4 (s), 139.6 (s), 137.6 (s), 131.5 (s), 130.3 (d, J=156 Hz), 128.0 (d, J=160 Hz), 127.7 (d, J=159 Hz), 124.1 (d, J=161 Hz, 2 overlapping C), 123.4 (d, J=161 Hz), 120.6 (t, J=157 Hz), 120.3 (d, J=162 Hz), 78.0 (s), 66.6 (d, J=148 Hz), 49.2 (d, J=148 Hz), 42.1 (t, J=133 Hz). IR (neat) 1790 (s, C=O) cm^{-1}. MS *m/e* (rel. intensity) 270 (11), 268 (33, M$^+$), 233 (19, M$^+$-Cl), 205 (78), 203 (30), 164 (18), 152 (10), 126 (2), 101 (11). HRMS calcd for $C_{17}H_{13}{}^{35}ClO$: 268.0655. Found: 268.0661.

Preparation of Halides

General Procedure for Hydrobromination. (*1SR,5RS,7SR*)-7-(3'-Bromopropyl)-7-chlorobicyclo[3.2.0]hept-2-en-6-one (21). A solution of 109 mg of **11** (0.6 mmol) in 30 mL of hexanes in a Pyrex phtolysis tube was degassed in the water bath of a sonicator (Branson 2200, 117 V-50/60 Hz, 175.5 W) for 10-20 min. The mixture was then irradiated with a Q-Beam, Max Million spotlight (Brinkman) while HBr was bubbling through the glass frit in the bottom of the photolysis tube. The reaction was complete within 0.5-1 h. After ether extraction, flash chromatography (30:1 hexanes-ether) of the crude product afforded 131 mg of **21** (83%). The spectra of **21** agree well with those of a sample prepared independently.[1b]

(*1SR,6RS,8SR*)-8-(3'-Bromopropyl)-3-chlorobicyclo[4.2.0]octan-7-one (22). Following the general procedure above, treatment of **12** (150 mg, 0.75 mmol) with HBr afforded 202 mg (97%) of **22**. ^{1}H NMR ($CDCl_3$) δ 3.52-3.27 (m, 3 H), 2.43 (q, J=8.1 Hz, 1 H), 2.22-0.95 (m, 11 H), 0.83 (m, 1 H).

^{13}C NMR ($CDCl_3$) δ 203.9, 81.6, 51.3, 37.8, 35.4, 33.0, 28.2, 25.0, 21.5, 21.4, 20.5. IR (neat) 1785 (s, C=O) cm^{-1}. MS *m/e* (rel. intensity) 280 (1, M$^+$), 245 and 243 (8, M$^+$-Cl), 217 and 215 (17), 201 (45), 135 (29), 91 (63), 79 (100). HRMS calcd for $C_{11}H_{16}{}^{79}BrO$ (M$^+$-Cl): 243.0385. Found: 243.0356.

(*1SR,6RS,8SR*)-2-Oxa-8-(3'-bromopropyl)-3-chlorobicyclo[4.2.0]octan-7-one (23). Following the general procedure above, treatment of **13** (200 mg, 1.0 mmol) with HBr afforded 154 mg (55%) of **23**. ^{1}H NMR ($CDCl_3$) δ 4.22 (d, *J*=6.0 Hz, 1 H), 4.02-3.88 (m, 1 H), 3.52-3.31 (m, 4 H), 2.27-2.03 (m, 4 H), 1.82-1.63 (m, 2 H), 1.63-1.45 (m, 2 H). ^{13}C NMR ($CDCl_3$):δ 202.7 (s), 80.2 (s), 69.7 (d, *J*=167 Hz), 64.9 (t, *J*=146 Hz), 51.6 (d, *J*=133 Hz), 35.4 (t, *J*=133 Hz), 33.1 (t, *J*=153 Hz), 27.8 (t, *J*=131 Hz), 21.3 (t, *J*=126 Hz), 18.6 (t, *J*=130 Hz). IR (neat) 1792 (s, C=O) cm^{-1}. MS *m/e* (rel. intensity) 282 (<1, M$^+$), 247 and 245 (43, M$^+$-Cl), 219 and 217 (6), 203 and 201 (4), 84 (85), 55 (100). HRMS calcd for $C_{10}H_{14}BrO_2$ (M$^+$-Cl): 245.0177. Found: 245.0167.

1-(3'-Bromopropyl)-1-chlorospiro[3.5]nonan-2-one (24). Following the general procedure above, treatment of **14** (110 mg, 0.50 mmol) with HBr afforded 87 mg (60%) of **24**. The spectra obtained for **24** agree well with those of a sample prepared independently.[1c]

12-(3'-Bromopropyl)-12-chlorobicyclo[8.2.0]tetradecan-11-one (25). Following the general procedure above, treatment of **15** (280 mg, 1.1mmol) with HBr afforded 160 mg (50%) of **25**. ^{1}H NMR ($CDCl_3$) δ 3.50-3.33 (m, 2 H), 3.22 (m, 1 H), 2.22-2.08 (m, 3 H), 2.08-1.89 (m, 4 H), 1.78-1.61 (m, 4 H), 1.61-1.30 (m, 10H). ^{13}C NMR ($CDCl_3$) δ 206.4 (s), 81.8 (s), 63.4 (d, *J*=131 Hz), 47.4 (d, *J*=134 Hz), 35.8 (t, *J*=134 Hz), 33.1 (t, *J*=152 Hz), 30.5 (t, *J*=128 Hz), 27.8 (t, *J*=137 Hz), 27.1 (t, *J*=131 Hz), 25.9 (t, *J*=140 Hz), 25.5 (t, *J*=128 Hz, two overlapping C), 25.1 (t, *J*=137 Hz), 24.9 (t, *J*=128 Hz), 24.5 (t, *J*=128 Hz). IR (neat) 1784 (s, C=O) cm^{-1}. MS *m/e* (rel. intensity) 338 (<1), 336 (2), 334 (1.5, M$^+$), 281 (6), 236 (12), 201 (31), 177 (21), 137 (56), 131 (43), 98 (91), 55 (100). HRMS calcd for $C_{14}H_{24}{}^{79}Br^{35}ClO$: 334.0699. Found: 334.0699.

(*1RS,2RS,4SR,5SR,6SR*)-4-(3'-Bromopropyl)-4-chlorotricyclo[4.2.1.0^{2,5}]nonan-3-one (26). Following the general procedure above, treatment of **16** (210 mg, 1.0 mmol) with HBr afforded 268 mg (92%) of **26**. ^{1}H NMR ($CDCl_3$) δ 3.45 (m, 2 H), 3.27 (m, 1 H), 2.57 (br s, 2 H), 2.29 (d, *J*=6.6 Hz, 1 H), 2.20-2.18 (m, 4 H), 1.78-1.11 (6 H). ^{13}C NMR ($CDCl_3$) δ 207.3 (s), 78.3 (s), 64.1 (d, *J*=147 Hz), 47.0 (d, *J*=148 Hz), 38.6 (d, *J*=154 Hz), 38.2 (d, *J*=146 Hz), 36.3 (t, *J*=130 Hz), 35.2 (t, *J*=148 Hz), 33.2 (t, *J*=152 Hz), 28.1 (t, *J*=134 Hz), 27.3 (t, *J*=129 Hz), 26.9 (t, *J*=128 Hz). IR (neat) 1784 (s, C=O) cm^{-1}. MS *m/e* (rel. intensity) 294 (1), 292 (4), 290 (4, M$^+$), 257 and 255 (16, M$^+$-Cl), 227 (36), 210 (25), 183 (23), 153 (12), 119 (35), 91 (100). HRMS calcd for $C_{12}H_{16}{}^{79}Br^{35}ClO$: 290.0073. Found: 290.0031.

(*1SR,6RS,8SR*)-3,4-Cyclopentyl-8-(3'-iodopropyl)-8-chlorobicyclo[4.2.0]oct-3-en-7-one (27). To a solution of 200 mg of **17** (0.9 mmol) in 5 mL of THF was added a 4.0 mL solution of 0.5 M 9-

BBN (2.0 mmol) in THF at 0 °C. The reaction mixture was warmed to 25 °C and kept at this temperature for 1 h and then 685 mg of iodine (2.7 mmol) was added followed by a 3 N methanol solution of NaOMe (0.9 mL). Ether workup of the reaction mixture gave 156 mg (50%) of **27**. ^{1}H NMR ($CDCl_3$) δ 3.72 (m, 1 H), 3.22 (m, 2 H), 2.88 (m, 1 H), 2.47 (m, 2 H), 2.38-1.98 (m, 10 H), 1.80 (m, 2 H). ^{13}C NMR ($CDCl_3$) δ 207.4 (s), 133.4 (s), 133.3 (s), 80.8 (s), 53.1 (d, J=141 Hz), 39.7 (t, J=125 Hz), 37.2 (d, J=131 Hz), 36.3 (t, J=128 Hz), 35.8 (t, J=129 Hz), 28.4 (t, J=131 Hz), 23.7 (t, J=129 Hz), 22.9 (t, J=132 Hz), 21.5 (t, J=129 Hz), 6.0 (t, J=151 Hz). IR (neat) 1786 (s, C=O) cm^{-1}. MS *m/e* (rel. intensity) 366 (12), 364 (35, M$^+$), 322 (83), 301 (63), 287 (98), 239 (4), 237 (12, M$^+$-Cl), 201 (10), 159 (42), 131 (83), 117 (50), 120 (100).

***(1RS,5RS,7SR)*-2,3-Benzo-7-(3'-iodopropyl)-7-chlorobicyclo[3.2.0]heptan-6-one (28).** To a solution of 60 mg of **18** (0.25 mmol) in 2 mL of THF was added a 0.5 mL solution of 0.5 M 9-BBN (0.25 mmol) in THF at 0 °C. After stirring at 0 °C for 30 min, GC-MS analysis of the reaction mixture showed the reaction was not complete. Another 0.5 mL (0.25 mmol) of 9-BBN solution was added. The reaction mixture was kept at 0 °C for an additional 30 min and then 191 mg of iodine (0.75 mmol) was added followed by a 250 µL of a 3 N methanol solution of NaOMe. The reaction mixture was extracted with ether. The combined organic layers were washed with 5% $Na_2S_2O_3$ and dried over $MgSO_4$. Removal of solvent gave 81 mg (90%) of **28**. ^{1}H NMR ($CDCl_3$) δ 7.36-7.25 (4 H), 4.17 (td, J=8.1, 1.4 Hz, 1 H), 4.06 (d, J=8.0 Hz, 1 H), 3.40-3.10 (m, 4 H), 3.29 (m, 2 H), 2.29 (m, 2 H). ^{13}C NMR ($CDCl_3$) δ 206.4 (s), 143.5 (s), 138.9 (s), 128.4 (d, J=161 Hz), 128.2 (d, J=161 Hz), 126.9 (d, J=161 Hz), 125.3 (d, J=162 Hz), 82.0 (s), 58.0 (d, J=144 Hz), 51.6 (d, J=149 Hz), 39.3 (t, J=132 Hz), 34.6 (t, J=133 Hz), 28.6 (t, J=134 Hz), 5.9 (t, J=153 Hz). IR (neat) 1790 (s, C=O) cm^{-1}. MS *m/e* (rel. intensity) 360 (1, M$^+$), 297 (16), 169 (11), 141 (34), 116 (100). HRMS calcd for $C_{14}H_{14}{}^{35}ClIO$: 359.9778. Found: 359.9778.

***(1RS,6RS,8SR)*-2,3-Benzo-8-(3'-bromopropyl)-8-chlorobicyclo[4.2.0]heptan-7-one (29).** Following the general procedure above, treatment of **19** (246 mg, 1.0 mmol) with HBr afforded 240 mg (78%) of **29**. ^{1}H NMR ($CDCl_3$) δ 7.27-7.18 (m, 4 H), 4.01-3.91 (m, 1 H), 3.81 (d, J=10.4 Hz, 1 H), 3.59-3.43 (m, 2 H), 2.77-2.56 (m, 2 H), 2.38-2.13 (m, 5 H), 1.70-1.54 (m, 1 H). ^{13}C NMR ($CDCl_3$) δ 207.6 (s), 137.4 (s), 132.8 (s), 130.6 (d, J=155 Hz), 128.6 (d, J=155 Hz), 127.0 (d, J=160 Hz), 126.1 (d, J=161 H), 81.0 (s), 54.2 (d, J=139 Hz), 42.7 (d, J=141 Hz), 36.7 (t, J=128 Hz), 33.0 (t, J=129 Hz), 27.4 (t, J=129 Hz, 2 overlapping C), 21.7 (t, J=131 Hz). IR (neat) 1788 (s, C=O) cm^{-1}. MS *m/e* (rel. intensity) 328 (<1, M$^+$), 265 and 263 (<1), 155 (14), 130 (100), 89 (10), 55 (56). MS (CI) *m/e* (rel. intensity) 331 (14), 329 (63), 327 (43, M$^+$ + H), 293 and 291 (8, M$^+$-Cl), 263 and 261 (5), 247 (12), 130 (100).

Bromide 30. Following the general procedure above, treatment of **20** (240 mg, 0.90 mmol) with HBr afforded 276 mg (89%) of **30**. ^{1}H NMR ($CDCl_3$) δ 7.75 (d, J=8.4 Hz, 1 H), 7.72 (d, J=8.4 Hz, 1

H), 7.57 (t, *J*=8.4 Hz, 1 H), 7.52 (t, *J*=8.4 Hz, 1 H), 7.43 (d, *J*=8.4 Hz, 1 H), 7.44 (d, *J*=8.4 Hz, 1 H), 5.30 (d, *J*=7.0 Hz, 1 H), 4.51 (d, *J*=7.0 Hz, 1H), 3.63-3.48 (m, 2 H), 2.49-2.38 (m, 2 H), 2.30-2.22 (m, 2 H). ^{13}C NMR ($CDCl_3$) δ 200.4 (s), 140.1 (s), 139.6 (s), 137.6 (s), 131.6 (s), 128.1 (d, *J*=161 Hz), 127.8 (d, *J*=160 Hz), 124.3 (d, *J*=161 Hz), 123.5 (d, *J*=161 Hz), 120.5 (d, *J*=161 Hz), 78.9 (s), 66.5 (d, *J*=147 Hz), 50.4 (d, *J*=148 Hz), 36.5 (t, *J*=125 Hz), 32.8 (t, *J*=151 Hz), 27.3 (t, *J*=130 Hz). IR (neat) 1790 (s, C=O) cm^{-1}. MS *m/e* (rel. intensity) 352 (<1), 350 (4), 348 (3, M^+), 312 (1), 287 (10), 233 (2), 205 (15), 181 (32), 152 (100), 126 (4), 101 (8). HRMS calcd for $C_{17}H_{14}{}^{79}Br^{35}ClO$: 347.9917. Found: 347.9917. X-ray analysis: see supplementary material.[11]

Ring Expansion of Cyclobutanones

Ring expansion of 21, see ref 1b.

Ring Expansion of 22. A mixture of 10 mg of **22** (0.036 mmol), 21 μL of Bu_3SnH (0.08 mmol) and 1 mg of AIBN in 2 mL of benzene was placed in an NMR tube and irradiated in a Rayonet photoreactor at 350 nm for 40 min. GC analysis of the reaction mixture showed ring expansion product **32**, ring attachment product, and direct reduction product in the ratio 57:31:12. After DBU workup,[10] flash chromatography (40:1 hexanes-ether) of the crude product afforded 3.0 mg (51%) of the ring expansion product **32**. The spectra obtained for **32** agreed well with those of a sample prepared independently.[1b]

General Procedure for Slow Addition of Bu_3SnH. Ring Expansion of 23. A solution of 128 μL of Bu_3SnH (0.48 mmol) and 3 mg AIBN (0.02 mmol) in 2 mL of benzene was added to a refluxing solution of 47 mg of **23** (0.17 mmol) in 2.5 mL of benzene over a period of 6 h. The reaction mixture was refluxed for an additional 1 h and then cooled to room temperature. After DBU workup, flash chromatography (50:1 hexanes-ether) of the crude product afforded 8 mg (28%) of ring expansion product **33** and a mixture of **33** and ring attachment product **34** (13 mg, 66:34, 46%). Data for **33**: ^1H NMR δ 3.99 (m, 1H), 3.79 (m, 1 H), 3.53 (td, *J*=9.8 and 2.8 Hz, 1 H), 2.76 (td, *J*=10.7 and 2.7 Hz, 1 H), 2.53 (m, 1 H), 2.14 (m, 2 H), 1.90-1.38 (m, 9 H). ^{13}C NMR ($CDCl_3$) δ 215.5 (s), 75.2 (d, *J*=144 Hz), 68.2 (t, *J*=142 Hz), 50.9 (d, *J*=125 Hz), 44.9 (t, *J*=129 Hz), 33.6 (t, *J*=128 Hz), 27.6 (t, *J*=130 Hz), 24.6 9 (t, *J*=126 Hz), 23.4 (t, *J*=128 Hz), 23.2 (t, *J*=128 Hz). IR (neat) 1694 (s, C=O) cm^{-1}. MS *m/e* (rel. intensity) 168 (11, M^+), 150 (7), 139 (4), 125 (17), 111 (21), 98 (47), 84 (47), 67 (19), 55 (100). HRMS calcd for $C_{10}H_{16}O_2$: 168.1150. Found: 168.1164.

Ring Expansion of 24. Following the general procedure above, treatment of **24** (26 mg, 0.088 mmol) with Bu_3SnH (71 μL, 0.26 mmol) and AIBN (2 mg) afforded 13.8 mg (87%) of **35**. ^1H NMR δ 2.51 (s, 2 H), 2.39 (t, *J*=6.5 Hz, 2 H), 1.77 (m, 2 H), 1.70-1.12 (14 H). ^{13}C NMR ($CDCl_3$) δ 21.5 (t, *J*=127

Hz), 24.2 (t, *J*=132 Hz), 24.4 (t, *J*=132 Hz), 26.2 (t, *J*=128 Hz), 29.7 (s), 37.4 (t, *J*=125 Hz), 43.0 (t, *J*=130 Hz), 44.0 (t, *J*=130 Hz), 53.0 (t, *J*=129 Hz), 214.6 (s). IR (neat) 1700 (s, C=O) cm^{-1}. MS *m/e* (rel. intensity) 180 (5, M^+), 162 (27), 137 (10), 122 (100), 107 (23), 95 (23). HRMS calcd for $C_{12}H_{20}O$: 180.1514. Found: 180.1524.

Ring Expansion of 25. Following the general procedure above, treatment of **25** (112 mg, 0.33 mmol) with Bu_3SnH (225 μL, 0.83 mmol) and AIBN (6 mg) afforded 30.0 mg (41%) of **36**. ^1H NMR δ 2.62-1.95 (4 H), 1.92-1.30 (22 H). ^{13}C NMR ($CDCl_3$) δ 216.8 (s), 56.0 (d), 41.8 (t), 38.9 (d), 34.6 (t), 32.6 (t), 28.5 (t), 28.2 (t), 26.0, 25.4, 24.9, 24.8, 24.7, 24.4, 23.7. IR (neat) 1700 (s, C=O) cm^{-1}. MS *m/e* (rel. intensity) 222 (7, M^+), 165 (15), 137 (12), 124 (14), 111 (100), 95 (28), 81 (32), 67 (50), 55 (84). HRMS calcd for $C_{15}H_{26}O$: 222.1984. Found: 222.1982.

Ring Expansion of 26. Following the general procedure above, treatment of **26** (150 mg, 0.51 mmol) with Bu_3SnH (329 μL, 1.1 mmol) and AIBN (17 mg) afforded 12 mg (13%) of ring expansion product **37** and a mixture of **37** and ring attachment product **38** (64:35, 69 mg, 76%). Data for **37**: ^1H NMR δ 2.62 (m, 1 H), 2.36 (m, 1 H), 1.90 (m, 2 H), 1.72 (m, 2 H), 1.70-0.95 (m, 8 H). ^{13}C NMR ($CDCl_3$) δ 212.9 (s), 59.5 (d, *J*=130 Hz), 45.2 (d, *J*=136 Hz), 44.1 (d, *J*=148 Hz), 43.7 (t, *J*=133 Hz), 37.3 (d, *J*=146 Hz), 34.6 (t, *J*=138 Hz), 31.6 (t, *J*=127 Hz), 29.8 (t, *J*=134 Hz), 27.8 (t, *J*=126 Hz), 27.8 (t, *J*=126 Hz), 23.7 (t, *J*=131 Hz). IR (neat) 1703 (s, C=O) cm^{-1}. MS *m/e* (rel. intensity): 178 (7, M^+), 160 (<1), 150 (3), 134 (3), 121 (8), 111 (100). HRMS calcd for $C_{12}H_{18}O$: 178.1358. Found: 178.1371.

Ring Expansion of 27. Following the general procedure above, treatment of **27** (75 mg, 0.20 mmol) with Bu_3SnH (114 μL, 0.5 mmol) and AIBN (8 mg) afforded 18.3 mg (45%) of **39**. ^1H NMR ($CDCl_3$) δ 2.75-2.52 (m, 2 H), 2.50-2.42 (m, 1 H), 2.35-1.53 (m, 17 H). ^{13}C NMR ($CDCl_3$) δ 215.9, 132.8, 132.5, 51.0, 43.9, 36.0, 35.7, 35.0, 33.2, 32.9, 27.9, 26.8, 24.3, 22.1. IR (neat) 1700 (s, C=O) cm^{-1}. MS *m/e* (rel. intensity) 204 (76, M^+), 186 (17), 175 (26), 157 (29), 147 (6), 131 (30), 117 (48), 105 (18), 91 (100). HRMS calcd for $C_{14}H_{20}O$: 204.1514. Found: 204.1558.

Ring Expansion of 28. Following the general procedure above, treatment of **28** (36 mg, 0.10 mmol) with Bu_3SnH (100 μL, 0.37 mmol) and AIBN (3 mg) afforded 12 mg (60%) of **40**. ^1H NMR ($CDCl_3$) δ 7.21-7.12 (4 H), 3.66 (dd, *J*=16.5, 8.2 Hz, 1 H), 3.57 (br t, *J*=8.2 Hz, 1 H), 3.43 (dd, *J*=16.5, 8.2 Hz, 1 H), 2.95 (dd, *J*=16.5, 8.2 Hz, 1 H), 2.65 (td, *J*=11.5, 2.7 Hz, 1 H), 2.51 (m, 1 H), 2.04-1.88 (m, 3 H), 1.84-1.32 (m, 3 H). ^{13}C NMR ($CDCl_3$)δ 212.8, 145.8, 141.2, 127.0, 126.6, 124.5, 124.1, 55.9, 46.4, 43.1, 33.8, 31.6, 29.1, 25.9. IR (neat) 1703 (s, C=O) cm^{-1}. MS *m/e* (rel. intensity) 200 (100, M^+), 182 (10), 171 (20), 157 (50), 143 (70), 130 (96), 116 (89). HRMS calcd for $C_{14}H_{16}O$: 200.1201. Found: 200.1201.

Ring Expansion of 29. Following the general procedure above, treatment of **29** (220 mg, 0.67 mmol) with Bu_3SnH (665 μL, 2.0 mmol) and AIBN (20 mg) afforded 70 mg (49%) of **41**. ^1H NMR

($CDCl_3$) δ 7.25-7.05 (m, 4 H), 3.45 (m, 1 H), 2.93-2.81 (m, 2 H), 2.81-2.55 (m, 2 H), 2.53-2.36 (m, 2 H), 2.06-1.40 (m, 7 H). ^{13}C NMR ($CDCl_3$) δ 214.3 (s), 141.2 (s), 136.1 (s), 129.6 (d, J=152 Hz), 128.7 (d, J=121 Hz), 126.0 (d, J=160 Hz), 125.8 (d, J=160 Hz), 51.3 (d, J=121 Hz), 41.9 (t, J=123 Hz), 40.0 (d, J=127 Hz), 36.6 (t, J=128 Hz), 30.6 (t, J=129 Hz), 29.0 (t, J=127 Hz), 26.6 (t, J=130 Hz), 19.9 (t, J=127 Hz). IR (neat) 1701 (s , C=O) cm^{-1}. MS *m/e* (rel. intensity) 214 (28, M^+), 198 (6), 172 (7), 157 (18), 130 (97), 129 (100), 115 (67), 104 (11), 91 (24), 55 (92), 41 (78). HRMS calcd for $C_{15}H_{18}O$: 214.1358. Found: 214.1342. X-ray analysis: see supplementary material.[11]

Ring Expansion of 30. Following the general procedure above, treatment of **30** (240 mg, 0.68 mmol) with Bu_3SnH (557 µL, 2.0 mmol) and AIBN (11 mg) afforded 12 mg (8%) of **42**, a mixture of **42** and **43** (52:48, 55 mg, 34%), and 35 mg (22%) of **43**. Data for **42**: ^1H NMR ($CDCl_3$) δ 7.68 (t, J=9.0 Hz, 2 H), 7.55-7.49 (m, 2 H), 7.33 (d, J=6.9 Hz), 1 H), 7.25 (d, J=6.3 Hz, 1 H), 4.73 (d, J=8.8 Hz, 1 H), 4.1 (m, 1 H), 2.48 (m, 1 H), 2.28 (m, 1 H), 2.15-1.96 (m, 2 H), 1.88-1.65 (m, 4 H). ^{13}C NMR ($CDCl_3$) δ 210.4 (s), 146.3 (s), 141.7 (s), 138.7 (s), 131.7 (s), 128.0 (d, J=160 Hz), 128.0 (d, J=160 Hz), 123.6 (d, J=162 Hz), 123.1 (d, J=161 Hz), 121.3 (d, J=162 Hz), 118.9 (d, J=158 Hz), 61.8 (d, J=133 Hz), 44.7 (d, J=134 Hz), 42.1 (t, J=131 Hz), 31.6 (t, J=125 Hz), 26.2 (t, J=128 Hz), 24.7 (t, J=129 Hz). IR (neat) 1705 (s , C=O) cm^{-1}. MS *m/e* (rel. intensity) 236 (56, M^+), 207 (13), 180 (43), 165 (100), 152 (51). HRMS calcd for $C_{17}H_{16}O$: 236.1201. Found: 236.1199.

Acknowledgment: This research was generously supported by the Institute for General Medical Sciences of the National Institutes of Health under grant GM 39825.

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(*Received in USA* 8 *August* 1994; *revised* 16 *September* 1994; *accepted* 19 *September* 1994)