[3 + 4] and [3 + 5] Annulation Reactions of α-(Phenylthio) Dicarbonyl Electrophiles with Bis(trimethylsilyl) Enol Ethers: Synthesis of Highly Functionalized Medium Ring Carbocycles

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The [3 + 4] and [3 + 5] annulations of bis(trimethylsilyl) enol ethers with 1,4- and 1,5-dicarbonyl electrophiles bearing α-phenylthio substituents leads to the formation of bicyclic [3.2.1] and [3.3.1] ethers with good regiochemical and stereochemical control. Subsequent oxidation of the phenylthio moiety followed by reduction with SmI_2 constitutes a high-yielding and regioselective process for cleavage of the bridging ether linkage. The overall strategy provides a synthetic pathway for the synthesis of highly functionalized medium ring carbocycles.

Introduction

The synthesis of seven-[1] and eight-membered[2] rings remains a significant synthetic challenge to organic chemists. In particular, general methods which permit the formation of highly functionalized medium ring systems from two separate acyclic subunits remain scarce. When a requirement for stereochemical control at all of the stereocenters about the newly formed ring is imposed, even fewer viable methods emerge. Among these, the Lewis acid promoted [3 + 4] and [3 + 5] annulations of 1,4- and 1,5-dicarbonyl electrophiles **1** with the bis(trimethylsilyl) enol ether **2** and related analogues appears to be among the more versatile. This method provides highly functionalized bicyclic and tricyclic ethers **3** (Scheme 1).[3] Excellent control over the regiochemistry and stereochemistry in the annulations can be achieved by reliance upon a neighboring group participation mechanism involving a rigid oxocarbenium ion intermediate. The general features of this annulation reaction have been outlined previously,[3] and applications of the method to the construction of the natural products (+)-dactylol[4] and (±)-furanether B[5] have been demonstrated.

Although the bicyclic and tricyclic ethers resulting from the [3 + 4] and [3 + 5] annulation reactions are themselves useful structural entities, the annulation reaction could constitute a general approach to the synthesis of seven- and eight-membered carbocycles when combined with an efficient and regioselective process for cleaving the ether. Herein is reported the realization of a high-yielding operation which achieves this objective.

Results and Discussion

In assessing the diverse approaches that could be applied to the critical ether cleavage, a versatile, regioselective method was sought that would also tolerate the functionality placed in the ring systems by the annulation process. Retention of stereochemistry in the cleavage was also desirable, ruling out methods that proceed by S_N1 mechanisms. Among the many potential methods considered for ether cleavage in the annulated products, a reductive elimination process was deemed the most appropriate means to unveil the carbocycle.[6] In order to construct bicyclic ether systems capable of undergoing the various reductive cleavage manifolds (Scheme 2), it was necessary to introduce a suitable moiety (X) into the dicarbonyl precursors and ultimately into the annulation product itself.

Among the several possibilities for appropriate functional groups, the phenylthio group (X = SPh) was thought to be the most versatile. Easily incorporated within carbonyl substrates, the phenylthio group is readily oxidized to the corresponding sulfone, which can in turn be efficiently reduced by established protocols. Rapid access to several substrates was achieved *via* a two-step approach. Addition of [(phenylthio)methyl]-lithium[7] to several lactones **5** at −78 °C (Scheme 3) provided the hydroxy ketones **6** in moderate to good yields.[8] These compounds exist as mixtures of both open-

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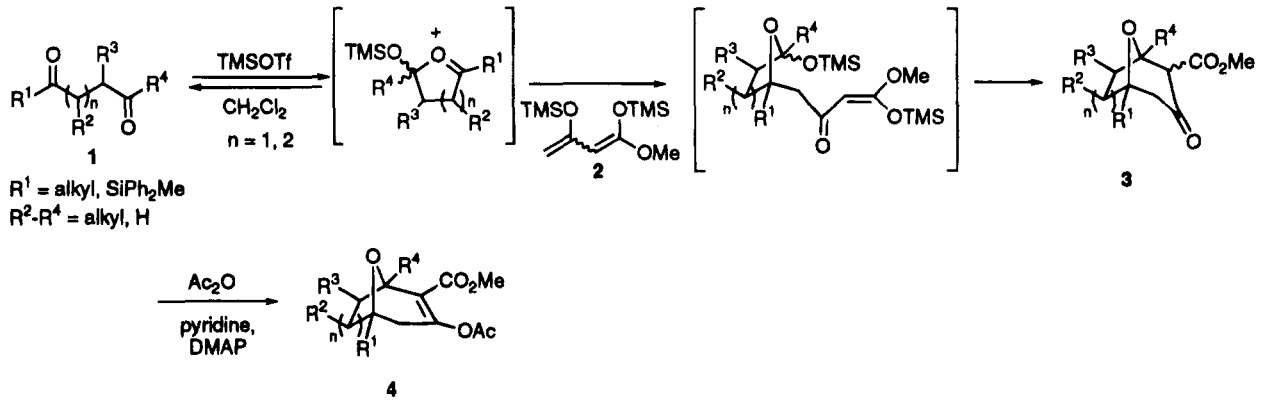
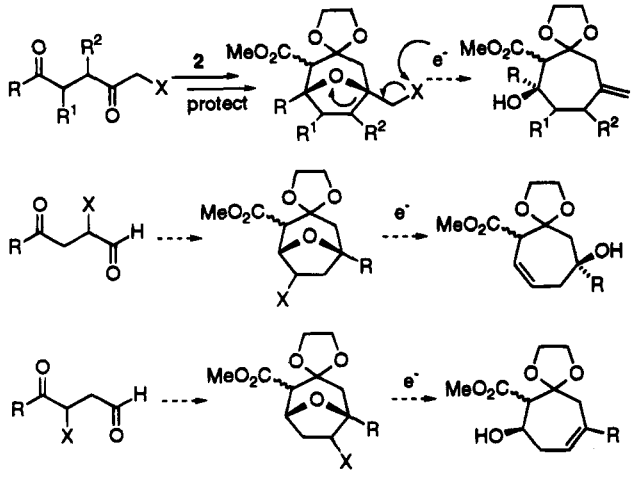
0022-3263/95/1960-8382$09.00/0

Scheme 1



Scheme 2



chain and hemiketal forms (**6** and **7**, respectively). Swern oxidation of such mixtures[9] provided the required 1,4-keto aldehydes **1**. This protocol failed when applied to hydroxy ketone **6b**. In this case, use of the Dess–Martin reagent[10] provided **1b** in good overall yield.

Syntheses of substrates **1e** and **1f** (Scheme 4) in which the phenylthio substituent was placed between the two carbonyl groups were achieved in several steps. Addition of the trimethylsilyl enol ether of acetone[11] to methyl α-chloro-α-(phenylthio)acetate[12] in the presence of $ZnBr_2$ provided keto ester **8e** in good yield. Protection of **8e** as the dioxolane furnished **9e**, which upon reduction of the ester and Swern oxidation provided aldehyde **10e** in excellent overall yield. Attempted cleavage of the dioxolane with PPTS[13] under several different reaction conditions resulted in recovery of starting material only. However, treatment with aqueous HCl in THF overnight provided a good yield of the desired **1e**. The isomeric substrate **1f** was prepared in a similar fashion from the known methyl 4-oxo-3-(phenylthio)pentanoate (**8f**).[14]

The results of the [3 + 4] and [3 + 5] annulations of the dicarbonyl substrates **1** with bis(trimethylsilyl) enol ether **2** are presented in Table 1. Moderate to good yields of bicyclic ethers **3** were isolated. Because compounds of type **3** exist as a mixture of keto–enol tautomers, derivatization to the enol acetates **4** was necessary to determine regioselectivities and diastereoselectivities. A range of keto aldehyde substrates (entries 1–6) was first studied. The following points are of importance: (a) For the [3 + 4] annulations TMSOTf was employed as the catalyst. This Lewis acid gave poor results in the [3 + 5] annulation (entry 2), and $TrSbCl_6$ was used instead in that case. (b) The annulations are completely regioselective, with initial nucleophilic attack occurring at the more hindered ketone carbonyl, implying the involvement of a neighboring group participation mechanism. (c) The diastereoselectivity was excellent when the internal substituent was adjacent to the aldehyde in the starting material (entries 3 and 5) but suffered somewhat when placed next to the ketone (entries 4 and 6) as expected by earlier observations.[3] Poor regioselectivity was noted in the annulation of diketone **1g** (entry 7), but regioselectivity improved significantly when enough steric discrimination was created between the two carbonyl moieties as in substrate **1h** (entry 8). In the latter case, the mechanism of the annulation dictates that the carbalkoxy and (phenylthio)methyl substituents in **3h** will be adjacent to one another on the ring in the final product.[15]

Oxidation of the annulated thioethers to the corresponding sulfones was required for the eventual reductive cleavage reaction. Protection of the ketone as the ketal was necessary during both the oxidation of the thioethers and the subsequent reductive cleavage. Reaction of **3a** with ethylene glycol in the presence of an acid catalyst afforded a separable 1:1 mixture of **11ai** and **11aii** in 83% yield (eq 1). However, attempted protection of the other keto esters in the same manner provided low yields of the desired products even after reaction over several days. The propensity of keto esters **3** to exist in their respective enol forms was thought to be responsible for the poor results. To eliminate this problem, decarboxylation[16] of a number of the keto esters was effected to provide ketones **12** in good yield (71–78%). Ketone carbonyl protection in the manner described above now

(8) Generating [(phenylthio)methyl]lithium by treatment of (phenylthio)methane with *n*-BuLi/triethylenediamine in THF followed by subsequent addition to γ-butyrolactone **5a** in THF at −40 °C has been reported to give **6a** in only 25% yield: Yamagiwa, S.; Hoshi, N.; Sato, H.; Uda, H.; Kosugi, H. *J. Chem. Soc., Perkin Trans. 1* **1978**, 214.

(9) Mancuso, A. J.; Swern, D. *Synthesis* **1981**, 165.

(10) (a) Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4155. For a more efficient synthesis of the Dess–Martin reagent, see: Ireland, R. E.; Longbin, L. *J. Org. Chem.* **1993**, *58*, 2899.

(11) Walshe, N. D. A.; Goodwin, G. B. T.; Smith, G. C.; Woodward, F. E. *Organic Syntheses*; Wiley: New York, 1993; Collect. Vol. VIII, p 1.

(12) Lee, T. V.; Okonkwo, J. O. *Tetrahedron Lett.* **1983**, *24*, 323.

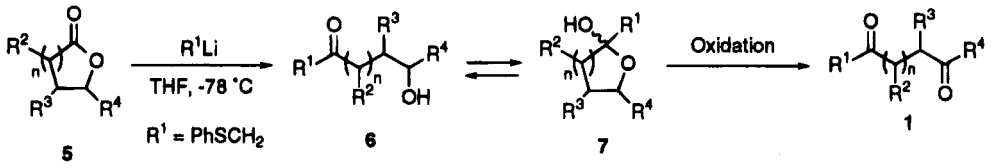
(13) Sterzycki, R. *Synthesis* **1979**, 724.

(14) Brownbridge, P.; Egert, E.; Hunt, P. G.; Kennard, O.; Warren, S. *J. Chem. Soc., Perkin Trans 1* **1981**, 2751.

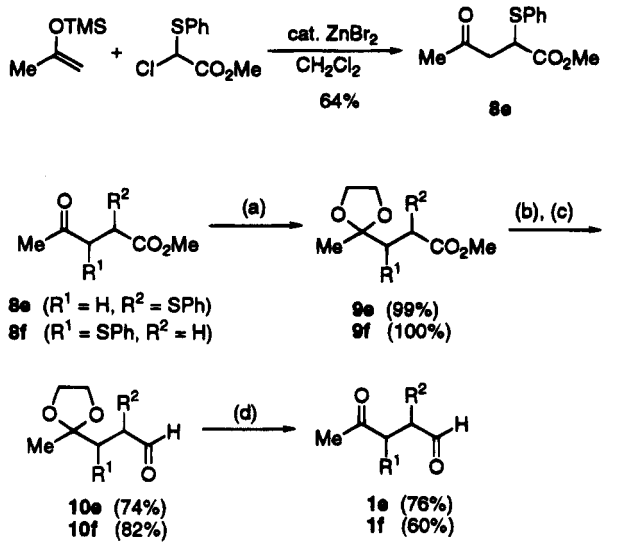
(15) The regiochemistry observed in this annulation was determined by desulfurization of **4h** with Raney Ni/EtOH which provided the known enol acetate.[3b] The properties of this compound (NMR, GC, TLC) were identical to those of an authentic sample.

(16) Krapcho, A. P.; Lovey, A. J. *Tetrahedron Lett.* **1973**, *14*, 957.

Scheme 3

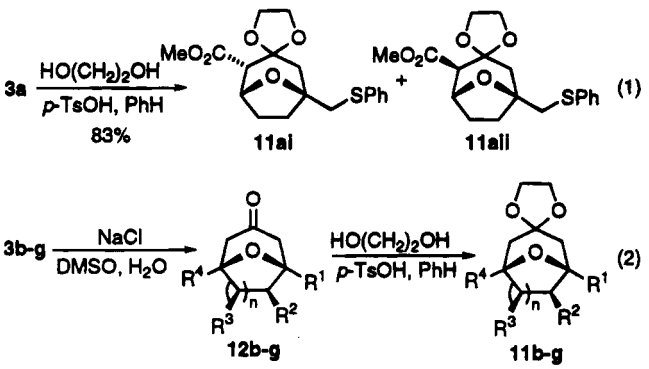


Scheme 4[a]

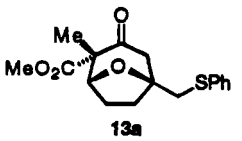


[a] (a) $HO(CH_2)_2OH$, PhH, *p*-TsOH; (b) $LiAlH_4$, THF, 0 °C; (c) $(COCl)_2$, DMSO, CH_2Cl_2, −78 °C then Et_3N, −78 °C to rt; (d) HCl, THF, H_2O.

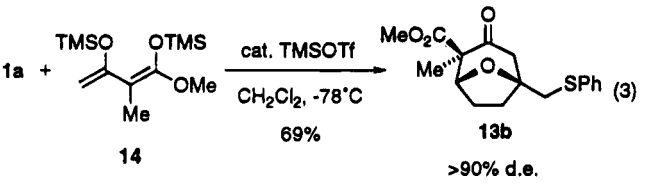
proceeded to afford **11** in essentially quantitative yield (eq 2, Table 2).



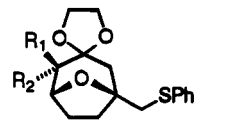
An alternative way around this difficulty was to alkylate the keto ester, thus removing the offending enolizable center. Hence, treatment of **3a** with NaH/MeI provided **13a** as a single isomer. Exclusive exo approach of electrophiles to the less hindered side of such enolates has been established previously.[3c] It is interesting that



13b, which possesses the opposite stereochemistry at the quaternary ester stereogenic center of **13a**, can be accessed as a >20:1 mixture of diastereoisomers in 69% yield by annulation of **1a** with the 2-substituted bis(trimethylsilyl) enol ether **14** (eq 3).[17]



Protection of **13a** and **13b** (ethylene glycol, H^+, PhH) proceeded slowly over several days to furnish the respective dioxolanes **11i** and **11j**. Starting material was always present and recovered in these reactions. A single attempt was made to convert **13b** to **11j** under the conditions of Noyori,[18] which also resulted in poor conversion.



Oxidation of the sulfides **11** to the sulfones **15** with *m*-CPBA was rapid (<1 h) and proceeded in excellent yield (Table 3). The substrates were now poised for the reductive elimination reaction which would unveil the seven- and eight-membered carbocycles. Treatment of β-hydroxy and β-acetoxy sulfones with SmI_2 in the presence of HMPA has been shown to effect the reductive cleavage of such compounds more efficiently than Na/Hg.[19] When sulfone **15ai** was treated with 5 equiv of SmI_2 in the presence of HMPA in THF at room temperature, **16ai** was obtained in 60% yield (Table 3, entry 1). Thin layer chromatographic analysis of the reaction mixture indicated that some starting material remained after the reaction had decolorized, which suggested that more reductant was needed. Thus, treatment of **15ai** under similar conditions using 5.5 equiv of SmI_2 afforded an optimized 86% yield of **16ai**. The reaction was complete in less than 10 min. Little or no reduction of the ester group or retro aldol cleavage occurred under the reaction conditions. The isomeric sulfone **15aii** (entry 2), when treated under the same conditions, provided only **16aii** without any epimerization. The other external olefins (entries 3−7) were formed cleanly by reduction of the respective sulfones. The internal olefins **16e** and **16f** were obtained in good yields from the sulfones **15e** and **15f**. It is interesting to note that in the case of **15e**, although reduction of the sulfone was rapid, ring-opening required 45 min.

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(18) Tsunoda, T.; Suzuki, M.; Noyori, R. *Tetrahedron Lett.* **1980**, *21*, 1357.

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Table 1. Lewis Acid Promoted [3 + 4] and [3 + 5] Annulations of α-Phenylthio-Substituted 1,4- and 1,5-Dicarbonyl Substrates 1 with 2

entry	substr	prod	n	R^1	R^2	R^3	R^4	% isoltd yield (3)[a] [% isoltd yield (4)]	diastereoselectivity[b] (regioselectivity)
1	**1a**	**3a**	1	$PhSCH_2$	H	H	H	71 [90]	(>200:1)
2	**1b**	**3b**	2	$PhSCH_2$	H	H	H	75 [93]	(>200:1)
3	**1c**	**3c**	1	$PhSCH_2$	H	Me	H	52 [95]	>200:1
4	**1d**	**3d**	1	$PhSCH_2$	Me	H	H	50 [90]	1.8:1
5	**1e**	**3e**	1	Me	H	PhS	H	70 [92]	>200:1
6	**1f**	**3f**	1	Me	PhS	H	H	63 [82]	11:1
7	**1g**	**3g**	1	$PhSCH_2$	H	H	Me	73 [79]	(1.3:1)
8	**1h**	**3h**	1	*i*-Pr	H	H	$PhSCH_2$	58 [70]	(1:42)

[a] Refers to yields of purified products. All of these compounds have been fully characterized spectroscopically (^1H NMR, ^{13}C NMR, IR), and elemental composition has been established by combustion analysis and/or high-resolution mass spectrometry. [b] Diastereoselectivities and regioselectivities were determined either by NMR or fused silica capillary GC analysis after derivatization to the corresponding enol acetates **4**.

Table 2. Decarboxylation and Protection of Annulated Products

substr	n	R^1	R^2	R^3	R^4	% isolated yield[a] **12**	**11**
3b	2	$PhSCH_2$	H	H	H	79	100
3c	1	$PhSCH_2$	H	Me	H	71	100
3d	1	Me	H	SPh	H	73	100
3e	1	Me	SPh	H	H	78	100
3f	1	$PhSCH_2$	H	H	Me	74	92

[a] Refers to yields of products homogeneous by TLC and NMR. All of these compounds have been fully characterized spectroscopically (^1H NMR, ^{13}C NMR), and elemental composition has been established by combustion analysis and/or high-resolution mass spectrometry.

An additional appealing feature of the sulfone moiety in the bicyclic ether is that further elaboration by alkylation can readily be achieved prior to cleavage. For example, treatment of **15i** with LDA/MeI provided **15k** as a *ca.* 4:1 mixture of isomers (Scheme 5). Reduction of **15k** under the standard conditions provided **16k** as a 1.3:1 mixture of olefinic isomers in 65% yield.

Conclusions

In summary, a highly versatile approach to the stereocontrolled synthesis of seven- and eight-membered rings has been developed. The method relies upon [3 + 4] and [3 + 5] annulations of nucleophilic bis(trimethylsilyl) enol ethers with thioether-substituted dicarbonyl dielectrophiles. The phenylthio group can be easily incorporated within the dicarbonyl dielectrophiles required for the annulation reactions. The annulation process creates bicyclic ethers in a highly regioselective and stereoselective manner, with the level of selectivity for each substrate readily predicted on the basis of the cyclic oxocarbenium ion intermediate. These annulated products are amply endowed with functionality, and thus further elaboration of the ring system is readily accomplished. The steric bias afforded by the bicyclic ethers permits excellent stereoselectivity in further alkylation and carbonyl addition reactions. Finally, the reductive cleavage described can be accomplished at three different points about the ring, adding an extra dimension of flexibility to the overall process. The combination of these steps results in a highly versatile route to seven- and eight-membered rings. Using this approach, substitution at each of the positions about the resulting ring can be accomplished. Stereochemical control can be achieved as well, and thus the process represents a highly general means for the construction of systems otherwise quite difficult to access.

Experimental Section

Reagents. THF was distilled immediately prior to use from benzophenone ketyl under Ar. Dichloromethane was freshly distilled from CaH_2. *m*-CPBA was purified according to the literature procedure.[20] Standard benchtop techniques were employed for handling air-sensitive reagents.[21]

β-Methyl-γ-butyrolactone (5c). To a solution of methyl 2-methyl-3-[(trimethylsilyl)oxy]-1-cyclopropanecarboxylate[22] (2.33 g, 11.5 mmol) in dry methanol (12 mL) at 0 °C was added KBH_4[23] (0.62 g) in portions. After stirring for 1 h, the mixture was warmed to rt and then stirred overnight. To the mixture at 0 °C were added 50% H_2SO_4 (9 mL) and then water (20 mL) to obtain a clear solution. After standing overnight the mixture was extracted with $CHCl_3$, and the combined organic extract was dried over $MgSO_4$. Concentration followed by Kugelrohr distillation (ot 65–75 °C at 20 mmHg) provided 0.912 g (79%) of the title compound: ^1H NMR (400 MHz, $CDCl_3$) δ 4.39 (dd, J = 8.8, 7.1 Hz, 1H), 3.85 (dd, J = 8.8, 6.3 Hz, 1H), 2.58–2.69 (m, 1H), 2.08–2.18 (m, 2H), 1.14 (d, J = 6.4 Hz, 3H).

General Procedure for the Addition of [(Phenylthio)methyl]lithium to Lactones 5. *n*-BuLi (1.6 M in hexanes, 1.05 equiv) was added dropwise to a stirred solution of (phenylthio)methane (1 equiv) and DABCO (1 equiv) in THF (1.5 mL/mmol) under argon at 0 °C. After stirring for 1 h, the solution of [(phenylthio)methyl]lithium was cannulated dropwise into a solution of **5** (1 equiv) in THF (0.5 mL/mmol) at −78 °C. After stirring for 2 h, the mixture was warmed to 0 °C, and the reaction was quenched with saturated aqueous NH_4Cl. The mixture was diluted with ethyl acetate, washed with water and then brine, and dried over $MgSO_4$. Concentration followed by flash chromatography provided **6**. The products sometimes contained minor impurities but further purification was not attempted because of thermal instability.

4-Oxo-5-(phenylthio)pentanol (6a). Addition of [(phenylthio)methyl]lithium to γ-butyrolactone **5a** (6.44 g, 75 mmol) by the general procedure followed by flash chromatography (3:2 hexanes/ethyl acetate) provided 9.40 g (60%) of the title compound as a white solid which existed in solution as a mixture of open-chain and hemiketal forms: mp 46–47 °C (hexanes) (lit.[8] mp 38–39 °C); IR (Nujol mull) 3650, 1700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) open-chain form δ 7.14–7.43 (m, 5H), 3.68 (s, 2H), 3.58 (q, J = 5.8 Hz, 2H), 2.71 (t, J = 6.9 Hz, 2H), 1.77–1.84 (m, 2H), 1.60 (t, J = 5.2 Hz, 1H); hemiketal form δ 7.14–7.47 (m, 5H), 4.00–4.06 (m, 1H), 3.85–3.92 (m, 1H), 3.36 (d, J = 13.5 Hz, 1H), 3.27 (d, J = 13.5 Hz, 1H), 3.08 (br s, 1H), 1.87–2.17 (m, 4H); LRMS (EI) m/z 210 (30), 192 (29), 124 (100).

5-Oxo-6-(phenylthio)hexanol (6b). Addition of [(phenylthio)methyl]lithium to δ-valerolactone **5b** (7.50 g, 75 mmol) by the general procedure provided 15.97 g (95%) of the title compound as a white solid which existed in solution as a mixture of open-chain and hemiketal forms. The crude

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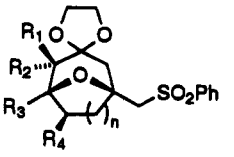
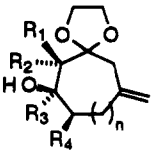
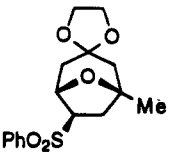
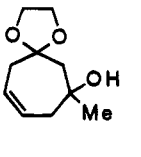
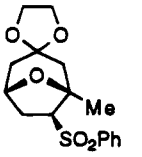
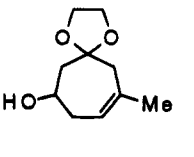
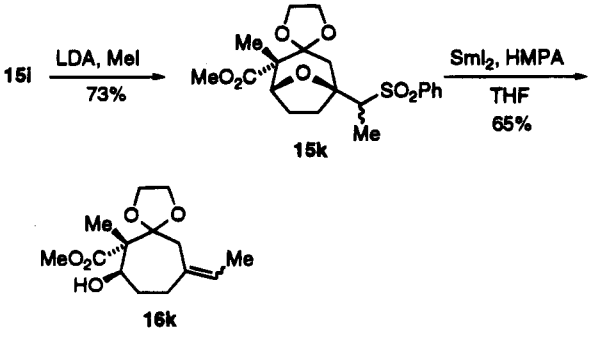
(21) Brown, H. C. *Organic Syntheses via Boranes*; Wiley: New York, 1975.
(22) Reissig, H. U.; Reichelt, I.; Kunz, T. *Org. Synth.* **1993**, *71*, 189.
(23) Grimm, E. L.; Reissig, H.-U. *J. Org. Chem.* **1985**, *50*, 242.

Table 3. Oxidation of Sulfides and Reductive Cleavage of the Resulting Sulfones

entry	sulfide substrate	sulfone (% isolated yield)[a,b]	ring cleavage product (% isolated yield)[a,c]
	(n, R_1, R_2, R_3, R_4)		
1	**11ai** (1, H, CO_2Me, H, H)	**15ai** (93)	**16ai** (86)
2	**11aii** (1, CO_2Me, H, H, H)	**15aii** (96)	**16aii** (81)
3	**11b** (2, H, H, H, H)	**15b** (85)	**16b** (77)
4	**11c** (1, H, H, H, Me)	**15c** (92)	**16c** (84)
5	**11g** (1, H, H, Me, H)	**15g** (98)	**16g** (79)
6	**11i** (1, Me, CO_2Me, H, H)	**15i** (66)[d]	**16i** (81)
7	**11j** (1, CO_2Me, Me, H, H)	**15j** (96)	**16j** (79)
8	**11e**	 **15e** (92)	 **16e** (77)
9	**11f**	 **15f** (92)	 **16f** (80)

[a] Refers to yields of purified materials. All products have been fully characterized spectroscopically (^1H, ^{13}C NMR, IR), and elemental composition has been established by combustion analysis and/or high-resolution mass spectrometry. [b] Typical oxidation procedure: 2.1-2.2 equiv *m*-CPBA, CH_2Cl_2, rt, 1h. [c] Typical cleavage conditions : 5.5 equiv SmI_2, 25 equiv HMPA, THF, rt, 10-45 min. [d] Overall yield from ketone **13a**.

Scheme 5



compound was used without further purification: IR (neat) 3208, 1704 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) open-chain form δ 7.10–7.41 (m, 5H), 3.53–3.65 (m, 4H), 2.61 (t, J = 7.0 Hz, 2H), 1.40–1.70 (m, 5H); hemiketal form δ 7.10–7.41 (m, 5H), 3.87–3.95 (m, 1H), 3.60–3.65 (m, 1H), 3.31 (d, J = 13.6 Hz, 1H), 3.13–3.15 (m, 1H), 2.98 (d, J = 13.6 Hz, 1H), 1.73–1.90 (m, 2H), 1.40–1.70 (m, 4H); LRMS (EI) m/z 224 (20), 206 (100).

2-Methyl-4-oxo-5-(phenylthio)pentanol (6c). Addition of [(phenylthio)methyl]lithium to β-methyl-γ-butyrolactone **5c** (0.720 g, 7.2 mmol) by the general procedure followed by flash chromatography (7:3 hexanes/ethyl acetate) provided 0.700 g (43%) of the title compound which existed in solution mainly as the open-chain form: IR (neat) 3444, 1769, 1709, 1583 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) open-chain form δ 7.10–7.50 (m, 5H), 3.68 (s, 2H), 3.48–3.55 (m, 1H), 3.31–3.39 (m, 1H), 2.71 (dd, J = 16.9, 6.8 Hz, 1H), 2.49 (dd, J = 16.9, 6.4 Hz, 1H), 2.15–2.25 (m, 1H), 1.50 (t, J = 5.8 Hz, 1H), 0.88 (d, J = 6.9 Hz, 3H); HRMS calcd for $C_{12}H_{16}O_2S$ 224.0871, found 224.0861; LRMS (EI) m/z 224 (50), 206 (100).

3-Methyl-4-oxo-5-(phenylthio)pentanol (6d). Addition of [(phenylthio)methyl]lithium to α-methyl-γ-butyrolactone **5d** (4.00 g, 40 mmol) by the general procedure followed by flash chromatography (7:3 hexanes/ethyl acetate) provided 6.49 g (72%) of the title compound which existed in solution mainly as a single hemiketal form: IR (neat) 3433, 1770, 1707, 1583 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) hemiketal form δ 7.00–7.50 (m, 5H), 3.83 (dt, J = 8.3, 3.2 Hz, 1H), 3.57 (q, J = 8.3 Hz, 1H), 3.11 (d, J = 13.5 Hz, 1H), 3.04 (d, J = 13.5 Hz, 1H), 2.89 (br s, 1H), 1.55–1.85 (m, 3H), 0.98 (d, J = 6.7 Hz, 3H); HRMS calcd for $C_{12}H_{16}O_2S$ 224.0871, found 224.0859; LRMS (EI) m/z 224 (50), 206 (100).

5-Oxo-6-(phenylthio)hexan-2-ol (6g). Addition of [(phenylthio)methyl]lithium to γ-valerolactone **5g** (3.75 g, 38 mmol) by the general procedure followed by flash chromatography (2:1 hexanes/ethyl acetate) provided 4.60 g (55%) of the title compound which existed in solution as a mixture of one major hemiketal form and an open-chain form: IR (neat) 3400, 3058, 2969, 2928, 1711 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) major hemiketal form δ 7.14–7.43 (m, 5H), 4.30–4.39 (m, 1H), 3.34 (d, J = 13.4 Hz, 1H), 3.24 (d, J = 13.4 Hz, 1H), 1.45–2.25 (m, 5H), 1.18 (d, J = 6.2 Hz, 3H); open-chain form δ 7.14–7.43 (m, 5H), 3.70–3.77 (m, 1H), 3.68 (s, 2H), 3.05 (s, 1H), 2.71 (t,

J = 7.1 Hz, 2H), 1.99–2.10 (m, 2H), 1.15 (d, J = 6.3 Hz, 3H); HRMS calcd for $C_{12}H_{16}O_2S$ 224.0871, found 224.0864; LRMS (EI) m/z 224 (5), 206 (100).

2-Methyl-6-oxo-7-(phenylthio)heptan-3-ol (6h). Addition of [(phenylthio)methyl]lithium to γ-isopropyl-γ-butyrolactone **5h**[24] (0.870 g, 6.80 mmol) by the general procedure followed by flash chromatography (2:1 hexanes/ethyl acetate) provided 0.932 g (54%) of the title compound which existed in solution as a mixture of two major hemiketal forms and an open-chain form: IR (neat) 3422, 1748, 1713 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) major hemiketal form δ 7.13–7.48 (m, 5H), 3.91 (apparent q, J = 6.9 Hz, 1H), 3.33 (d, J = 13.6 Hz, 1H), 3.21 (d, J = 13.6 Hz, 1H), 3.05 (d, J = 0.7 Hz, 1H), 1.54–2.13 (m, 5H), 0.80–0.92 (m, 6H); minor hemiketal form δ 7.13–7.48 (m, 5H), 3.62–3.68 (m, 1H), 3.31 (d, J = 13.5 Hz, 1H), 3.22 (d, J = 13.5 Hz, 1H), 2.92 (d, J = 0.6 Hz, 1H), 1.54–2.13 (m, 5H), 0.80–0.92 (m, 6H); open-chain form δ 7.13–7.48 (m, 5H), 4.07–4.14 (m, 1H), 3.70 (s, 2H), 2.74 (t, J = 7.0 Hz, 2H), 1.54–2.13 (m, 4H), 0.80–0.92 (m, 6H); HRMS calcd for $C_{14}H_{20}O_2S$ 252.1184, found 252.1186; LRMS (EI) m/z 252 (10), 234 (100).

General Procedure for Swern Oxidations.[9] To a stirred solution of $(COCl)_2$ (1.1 equiv) in CH_2Cl_2 (2.4 mL/mmol **6**) under argon at −78 °C was added DMSO (2.2 equiv). After 5 min a solution of **6** (1 equiv) in CH_2Cl_2 (1.2 mL/mmol **6**) was added dropwise. After stirring for an additional 15 min, Et_3N (4.4 equiv) was added and the mixture was warmed to rt. Water was added, and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2, and the combined organic layers were washed with water, saturated aqueous $NaHCO_3$ and then brine and dried over $MgSO_4$. Concentration followed by flash chromatography provided **1**.

4-Oxo-5-(phenylthio)pentanal (1a). Swern oxidation of **6a** (4.416 g, 21.0 mmol) by the general procedure followed by flash chromatography (7:3 hexanes/ethyl acetate) provided 2.463 g (56%) of the title compound: IR (neat) 3058, 2904, 2832, 2728, 1712 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 1H), 7.17–7.34 (m, 5H), 3.73 (s, 2H), 2.86–2.91 (m, 2H), 2.71–2.77 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.6, 200.1, 134.5, 129.4, 129.1, 126.8, 43.7, 37.6, 32.6; HRMS calcd for $C_{11}H_{12}SO_2$ 208.0558, found 208.0570; LRMS (EI) m/z 208 (40), 123 (100).

2-Methyl-4-oxo-5-(phenylthio)pentanal (1c). Swern oxidation of **6c** (0.693 g, 3.1 mmol) by the general procedure followed by flash chromatography (3:1 hexanes/ethyl acetate) provided 0.438 g (64%) of the title compound: IR (neat) 1722, 1714, 1583 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.17–7.34 (m, 5H), 3.71 (s, 2H), 3.02 (dd, J = 17.7, 7.3 Hz, 1H), 2.85–2.29 (m, 1H), 2.58 (dd, J = 17.7, 5.5 Hz, 1H), 1.10 (d, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.5, 203.0, 134.5, 129.5, 129.1, 126.1, 43.9, 41.9, 40.9, 13.4; HRMS calcd for $C_{12}H_{14}O_2S$ 222.0715, found 222.0708; LRMS (EI) m/z 222 (100).

3-Methyl-4-oxo-5-(phenylthio)pentanal (1d). Swern oxidation of **6d** (5.50 g, 24.6 mmol) by the general procedure followed by flash chromatography (3:1 hexanes/ethyl acetate) provided 1.83 g (34%) of the title compound: IR (neat) 1715, 1583 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.66 (s, 1H), 7.15–7.35 (m, 5H), 3.84–3.95 (m, 2H), 3.28–3.39 (m, 1H), 2.95 (dd, J = 18.7, 8.9 Hz, 1H), 2.50 (dd, J = 18.7, 4.7 Hz, 1H), 1.12 (d, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.3, 200.2, 135.0, 129.3, 129.1, 126.7, 47.3, 43.0, 38.1, 17.0; HRMS calcd for $C_{12}H_{14}O_2S$ 222.0715, found 222.0708; LRMS (EI) m/z 222 (100).

6-(Phenylthio)-2,5-hexanedione (1g). Swern oxidation of **6g** (1.00 g, 4.5 mmol) by the general procedure followed by flash chromatography (2:1 hexanes/ethyl acetate) provided 0.62 g (63%) of the title compound: IR (neat) 3058, 2966, 2906, 1713 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.15–7.35 (m, 5H), 3.73 (s, 2H), 2.78–2.85 (m, 2H), 2.67–2.73 (m, 2H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.8, 204.3, 134.8, 129.4, 129.1, 126.8, 43.9, 37.3, 34.2, 29.8; HRMS calcd for $C_{12}H_{14}O_2S$ 222.0715, found 222.0722; LRMS (EI) m/z 222 (30), 123 (30), 99 (100).

(24) Fukuzawa, S.; Nakanishi, A.; Fujinami, T.; Shizuyoshi, S. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1669.

2-Methyl-7-(phenylthio)-3,6-heptanedione (1h). Swern oxidation of **6h** (1.458 g, 5.79 mmol) by the general procedure followed by flash chromatography (3:1 hexanes/ethyl acetate) provided 0.255 g (18%) of the title compound: IR (neat) 1712, 1674 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.15–7.33 (m, 5H), 3.75 (s, 2H), 2.79–2.84 (m, 2H), 2.70–2.75 (m, 2H), 2.56–2.64 (m, 1H), 1.09 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.7, 204.2, 134.8, 129.1, 128.9, 126.5, 43.8, 40.4, 34.1, 34.0, 18.0; HRMS calcd for $C_{14}H_{18}O_2S$ 250.1028, found 250.1040; LRMS (EI) m/z 250 (100).

5-Oxo-6-(phenylthio)hexanal (1b). To a solution of Dess–Martin periodinane[10] (3.956 g, 9.33 mmol) in CH_2Cl_2 (38 mL) under argon was added a solution of **6b** (1.902 g, 8.49 mmol) in CH_2Cl_2 (12 mL). After stirring for 50 min, the solution was diluted with Et_2O and poured into saturated aqueous $NaHCO_3$ containing 16.2 g of $Na_2S_2O_3 \cdot 5H_2O$. After stirring for a further 5 min, the layers were separated and the organic layer was washed with saturated aqueous $NaHCO_3$, water, and then brine and dried over $MgSO_4$. Concentration followed by flash chromatography (2:1 hexanes/ethyl acetate) provided 1.364 g (72%) of the title compound: IR (neat) 1714 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.69 (t, J = 1.3 Hz, 1H), 7.17–7.33 (m, 5H), 3.64 (s, 2H), 2.65 (t, J = 7.0 Hz, 2H), 2.40 (dt, J = 7.3, 1.3 Hz, 2H), 1.81–1.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.7, 201.6, 134.6, 129.6, 129.2, 126.9, 43.7, 42.7, 39.2, 16.0; HRMS calcd for $C_{12}H_{14}O_2S$ 222.0715, found 222.0720; LRMS (EI) m/z 222 (100).

Methyl 4-Oxo-3-(phenylthio)pentanoate (8e). To a solution of acetone trimethylsilyl enol ether[11] (5.72 g, 44 mmol) and methyl α-chloro-α-(phenylthio)acetate[12] (8.70 g, 40.2 mmol) in CH_2Cl_2 (240 mL) under argon was added anhydrous zinc bromide (0.90 g, 4.0 mmol). After 5.5 h, the mixture was washed with water and then brine and dried over $MgSO_4$. Concentration followed by flash chromatography (6:1 hexanes/ethyl acetate) provided 6.10 g (64%) of the title compound: IR (neat) 1732, 1716 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40–7.49 (m, 2H), 7.25–7.35 (m, 3H), 4.02 (dd, J = 10.2, 4.4 Hz, 1H), 3.66 (s, 3H), 3.11 (dd, J = 18.1, 10.2 Hz, 1H), 2.80 (dd, J = 18.1, 4.5 Hz, 1H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.2, 171.9, 133.8, 132.0, 129.0, 128.6, 52.4, 45.3, 44.5, 29.8; HRMS calcd for $C_{12}H_{14}O_3S$ 238.0644, found 238.0650; LRMS (EI) m/z 238 (40), 206 (100).

General Procedure for the Protection of Ketones as Ketals. A mixture of the ketone or keto ester (1 equiv), ethylene glycol (2–10 equiv), and catalytic p-TsOH in benzene was heated to reflux in a Dean–Stark apparatus for 24–60 h. The mixture was diluted with ether, washed with saturated aqueous $NaHCO_3$, water, and then brine, and dried over $MgSO_4$. Concentration provided the crude dioxolane.

Methyl 4-Oxo-2-(phenylthio)pentanoate, Ethylene Acetal (9e). Protection of **8e** (6.10 g, 25.6 mmol) by the general procedure (24 h, 2 equiv of ethylene glycol) provided the crude title compound in 100% yield: IR (neat) 1738 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42–7.46 (m, 2H), 7.26–7.34 (m, 3H), 3.83–3.94 (m, 4H), 3.80 (dd, J = 11.4, 2.7 Hz, 1H), 3.60 (s, 3H), 2.48 (dd, J = 14.3, 11.4 Hz, 1H), 2.10 (dd, J = 14.3, 2.7 Hz, 1H), 1.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 133.0, 132.8, 128.9, 128.0, 108.5, 64.7, 64.6, 52.0, 45.7, 41.2, 24.2; HRMS calcd for $C_{14}H_{18}O_4S$ 282.0926, found 282.0931; LRMS (EI) m/z 282 (100).

Methyl 4-Oxo-3-(phenylthio)pentanoate, Ethylene Acetal (9f). Protection of **8f** (4.587 g, 19.3 mmol) by the general procedure (24 h, 2 equiv of ethylene glycol) provided the crude title compound in 100% yield: IR (neat) 1738 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46–7.52 (m, 2H), 7.18–7.31 (m, 3H), 3.82–4.00 (m, 4H), 3.76 (dd, J = 8.0, 6.4 Hz, 1H), 3.63 (s, 3H), 2.52 (dd, J = 15.9, 8.0 Hz, 1H), 2.81 (dd, J = 15.9, 6.4 Hz, 1H), 1.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 135.5, 131.5, 128.9, 127.0, 110.8, 65.2, 65.1, 53.0, 51.7, 36.6, 21.8; HRMS calcd for $C_{14}H_{18}O_4S$ 282.0926, found 282.0914; LRMS (EI) m/z 282 (60), 161 (100).

General Procedure for the Reduction of Esters to the Corresponding Alcohol. To a suspension of $LiAlH_4$ (0.78 equiv) in THF (2.0 mL/mmol hydride) at 0 °C under argon was added dropwise a solution of **9** (1 equiv) in the same volume of THF. After 30 min at 0 °C, the mixture was treated sequentially with water (3.5 μL/mmol hydride), 15% NaOH

(3.5 μL/mmol hydride), and water (12.7 μL/mmol hydride). The mixture was filtered, concentrated, and purified by flash chromatography (1:1 hexanes/ethyl acetate) to provide the alcohol.

5-Hydroxy-4-(phenylthio)butan-2-one, Ethylene Acetal. Reduction of **9e** (7.14 g, 25.3 mmol) by the general procedure provided 5.165 g (80%) of the title compound: IR (neat) 3444 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40–7.44 (m, 2H), 7.20–7.32 (m, 3H), 3.92–4.00 (m, 4H), 3.59–3.69 (m, 2H), 3.35–3.44 (m, 1H), 2.98 (t, J = 6.7 Hz, 1H), 2.11 (dd, J = 14.9, 4.1 Hz, 1H), 1.98 (dd, J = 14.9, 8.6 Hz, 1H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.8, 132.3, 129.0, 127.3, 109.3, 64.8, 64.7, 64.4, 46.4, 41.4, 24.0; HRMS calcd for $C_{13}H_{18}O_3S$ 254.0977, found 254.0969; LRMS (EI) m/z 254 (100).

5-Hydroxy-3-(phenylthio)butan-2-one, Ethylene Acetal. Reduction of **9f** (5.514 g, 19.3 mmol) by the general procedure provided 4.240 g (87%) of the title compound: IR (neat) 3430 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 7.2 Hz, 2H), 7.15–7.30 (m, 3H), 3.80–4.05 (m, 6H), 3.37 (dd, J = 9.6, 4.1 Hz, 1H), 2.07–2.18 (m, 1H), 1.90 (dd, J = 6.3, 5.3 Hz, 1H), 1.72–1.82 (m, 1H), 1.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 131.3, 128.9, 126.7, 111.6, 65.2, 65.1, 60.7, 55.1, 34.1, 21.8; HRMS calcd for $C_{13}H_{18}O_3S$ 254.0977, found 254.0991; LRMS (EI) m/z 254 (100).

2-Methyl-2-[3-oxo-2-(phenylthio)propyl]-1,3-dioxolane (10e). Swern oxidation of 5-hydroxy-4-(phenylthio)-butan-2-one, ethylene acetal (5.147 g, 20.3 mmol) by the general procedure followed by flash chromatography (4:1 hexanes/ethyl acetate) provided 4.691 g (92%) of the title compound: IR (neat) 1715 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.08 (d, J = 5.9 Hz, 1H), 7.37–7.42 (m, 2H), 7.24–7.32 (m, 3H), 3.80–3.95 (m, 3H), 3.71–3.76 (m, 1H), 3.67 (ddd, J = 11.5, 5.9, 3.5 Hz, 1H), 2.27 (dd, J = 14.6, 11.5 Hz, 1H), 2.16 (dd, J = 14.6, 3.5 Hz, 1H), 1.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.4, 132.9, 131.5, 129.0, 128.2, 108.4, 65.0, 64.2, 51.5, 38.8, 24.6; HRMS calcd for $C_{13}H_{16}O_3S$ 252.0820, found 252.0826; LRMS (EI) m/z 252 (5), 87 (100).

2-Methyl-2-[3-oxo-1-(phenylthio)propyl]-1,3-dioxolane (10f). Swern oxidation of 5-hydroxy-3-(phenylthio)-butan-2-one, ethylene acetal (4.240 g, 16.7 mmol) by the general procedure followed by flash chromatography (3:1 hexanes/ethyl acetate) provided 3.966 g (94%) of the title compound: IR (neat) 1719 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.67 (t, J = 1.9 Hz, 1H), 7.45–7.52 (m, 2H), 7.21–7.33 (m, 3H), 3.81–4.00 (m, 4H), 3.78 (t, J = 6.8 Hz, 1H), 2.79 (ddd, J = 16.8, 6.9, 2.3 Hz, 1H), 2.62 (ddd, J = 16.8, 6.6, 1.7 Hz, 1H), 1.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 134.9, 132.1, 129.1, 127.4, 110.7, 65.2, 64.9, 51.6, 45.1, 22.2; HRMS calcd for $C_{13}H_{16}O_3S$ 252.0820, found 252.0822; LRMS (EI) m/z 252 (100).

General Procedure for Dioxolane Deprotection. To a solution of **10** in THF (4.5 mL/mmol) was added 5–10% aqueous HCl (2.3 mL/mmol). After stirring for 24 h, the mixture was washed with water and then brine and dried over $MgSO_4$. Concentration followed by rapid flash chromatography (5:1 hexanes/ethyl acetate) provided **1**.

4-Oxo-2-(phenylthio)pentanal (1e). Deprotection of **10e** (0.811 g, 3.22 mmol) with 5% aqueous HCl by the general procedure provided 0.507 g (76%) of the title compound: IR (neat) 1714 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.60 (s, 1H), 7.38–7.43 (m, 2H), 7.28–7.33 (m, 3H), 4.02–4.07 (m, 1H), 3.00 (dd, J = 18.1, 8.8 Hz, 1H), 2.73 (dd, J = 18.1, 4.8 Hz, 1H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.9, 193.5, 134.3, 130.5, 129.3, 129.0, 51.1, 41.9, 30.0; HRMS calcd for $C_{11}H_{12}O_2S$ 208.0558, found 208.0557; LRMS (EI) m/z 208 (60), 137 (100).

4-Oxo-3-(phenylthio)pentanal (1f). Deprotection of **10f** (0.511 g, 2.0 mmol) with 10% aqueous HCl by the general procedure provided 0.252 g (60%) of the title compound: IR (neat) 1714, 1652 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.68 (s, 1H), 7.37–7.42 (m, 2H), 7.30–7.35 (m, 3H), 4.05 (dd, J = 9.5, 4.4 Hz, 1H), 3.10 (dd, J = 18.6, 9.5 Hz, 1H), 2.78 (dd, J = 18.6, 4.4 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.6, 199.0, 134.2, 130.9, 129.3, 129.0, 49.7, 44.7, 28.1; HRMS calcd for $C_{11}H_{12}O_2S$ 208.0558, found 208.0558; LRMS (EI) m/z 208 (40), 137 (100).

General Procedure for the Annulation of α-(Phenylthio) 1,4-Dicarbonyl Substrates 1a and 1c–h. A 0.1 M solution of TMSOTf (30 mol %) in CH_2Cl_2 was added to a 0.1 M solution of **1** (1 equiv) in CH_2Cl_2 at −78 °C under argon. After 3 min, a 0.1 M solution of **2** (1.2 equiv) was added dropwise down the inside of the flask over 10–15 min. The reaction mixture was stirred for 2.5–6 h, and then the reaction was quenched by addition of a pH = 7.0 phosphate buffer. After the mixture was warmed to rt, the layers were separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic extracts were dried over $MgSO_4$ and concentrated. Purification by flash chromatography provided **3**.

4-(Methoxycarbonyl)-1-[(phenylthio)methyl]-8-oxabicyclo[3.2.1]octan-3-one (3a). Following the general procedure, **1a** (0.360 g, 1.73 mmol) was annulated for 2.5 h to provide, after flash chromatography (5:1 hexanes/ethyl acetate), 0.377 g (71%) of the title compound as a mixture of keto–enol tautomers: IR (neat) 1738, 1716, 1660, 1652, 1621 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.33 (s, 0.39H, enol), 7.35–7.41 (m, 2H total), 7.23–7.40 (m, 2H total), 7.15–7.22 (m, 1H total), 5.02 (d, J = 8.0 Hz, 0.39H, enol), 4.95 (d, J = 5.7 Hz, 0.46H, exo), 4.80 (dd, J = 6.7, 4.2 Hz, 0.15H, endo), 3.75 (s), 3.74 (s), 3.73 (s, 3H total), 3.23–3.32 (m, 2H total), 3.15 (s, 0.46H, exo), 2.91 (dd, J = 15.0, 1.8 Hz, 0.46H, exo), 1.65–2.76 (overlapping m, 5.69 H total); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4, 201.1, 170.0, 169.4, 168.3, 167.9, 136.7, 136.2, 129.9, 129.7, 129.6, 129.0, 128.97, 128.92, 126.5, 126.3, 103.4, 84.9, 84.3, 81.3, 77.7, 72.7, 62.7, 61.4, 52.6, 52.1, 52.0, 51.4, 43.6, 43.0, 42.9, 41.6, 36.1, 34.1, 33.7, 33.0, 28.9, 27.8; HRMS calcd for $C_{16}H_{18}O_4S$ 306.0926, found 306.0924; LRMS (EI) m/z 306 (100). Anal. Calcd for $C_{16}H_{18}O_4S$: C, 62.75; H, 5.88. Found: C, 62.91; H, 6.23.

(1*R,5*S**,6*S**)-4-(Methoxycarbonyl)-6-methyl-1-[(phenylthio)methyl]-8-oxabicyclo[3.2.1]octan-3-one (3c).** Following the general procedure, **1c** (1.122 g, 5.05 mmol) was annulated for 5 h to provide, after flash chromatography (4:1 hexanes/ethyl acetate), 0.838 g (52%) of the title compound as a mixture of keto–enol tautomers: IR (neat) 1738, 1715, 1660, 1652, 1622, 1614 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ enol form 11.60 (br s, 1H), 7.15–7.45 (m, 5H), 4.50 (s, 1H), 3.74 (s, 3H), 3.20–3.30 (m, 2H), 2.75 (dd, J = 17.9, 1.3 Hz, 1H), 2.29–2.39 (m, 1H), 2.14 (d, J = 17.9 Hz, 1H), 2.02 (dd, J = 13.1, 8.3 Hz, 1H), 1.50–1.55 (m, 1H), 1.09 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 169.1, 136.8, 129.4, 128.9, 126.2, 103.5, 81.7, 78.3, 52.1, 51.5, 43.9, 42.2, 41.2, 21.3; HRMS calcd for $C_{17}H_{20}O_4S$ 320.1082, found 320.1074; LRMS (EI) m/z 320 (100). Anal. Calcd for $C_{17}H_{20}O_4S$: C, 63.75; H, 6.25; S, 10.00. Found: C, 63.88; H, 6.38; S, 9.77.

(1*R,5*R**,7*S**)-4-(Methoxycarbonyl)-7-methyl-1-[(phenylthio)methyl]-8-oxabicyclo[3.2.1]octan-3-one (3d).** Following the general procedure, **1d** (1.940 g, 8.7 mmol) was annulated for 6 h to provide, after flash chromatography (4:1 hexanes/ethyl acetate), 2.037 g (52%) of the title compound as a mixture of keto–enol tautomers/diastereoisomers. The proton NMR was difficult to assign because of overlapping of signals from several isomers (see supporting information): IR (neat) 1738, 1732, 1716, 1660, 1622 cm^{-1}; HRMS calcd for $C_{17}H_{20}O_4S$ 320.1082, found 320.1066; LRMS (EI) m/z 320 (100). Anal. Calcd for $C_{17}H_{20}O_4S$: C, 63.75; H, 6.25; S, 10.00. Found: C, 64.08; H, 6.49; S, 10.42.

(1*R,5*S**,6*R**)-4-(Methoxycarbonyl)-1-methyl-7-(phenylthio)-8-oxabicyclo[3.2.1]octan-3-one (3e).** Following the general procedure, **1e** (1.438 g, 6.90 mmol) was annulated for 5 h to provide, after flash chromatography (5:1 hexanes/ethyl acetate), 1.478 g (70%) of the title compound: IR (neat) 1742, 1716, 1660, 1652, 1622 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ enol form 11.58 (br s, 1H), 7.39–7.45 (m, 2H), 7.18–7.32 (m, 3H), 4.76 (s, 1H), 3.70–3.76 (m, 1H), 3.58 (s, 3H), 2.59 (d, J = 18.0 Hz, 1H), 2.39 (dd, J = 14.1, 8.4 Hz, 1H), 2.12 (d, J = 18.0 Hz, 1H), 1.66–1.70 (m, 1H), 1.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 169.7, 136.0, 130.7, 128.7, 126.5, 102.3, 79.7, 76.8, 54.5, 51.2, 43.1, 42.7, 26.8; HRMS calcd for $C_{16}H_{18}O_4S$ 306.0926, found 306.0921; LRMS (EI) m/z 306 (100). Anal. Calcd for $C_{16}H_{18}O_4S$: C, 62.75; H, 5.88; S, 10.46. Found: C, 62.60; H, 5.98; S, 10.62.

(1*R,5*R**,7*S**)-4-(Methoxycarbonyl)-1-methyl-7-(phenylthio)-8-oxabicyclo[3.2.1]octan-3-one (3f).** Following the general procedure, **1f** (0.480 g, 2.31 mmol) was annulated for 5 h to provide, after flash chromatography (5:1

hexanes/ethyl acetate), 0.446 g (63%) of the title compound as a mixture of keto–enol tautomers: IR (neat) 1738, 1732, 1715, 1660, 1651, 1622 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ enol form 11.60 (br s, 1H), 7.15–7.34 (m, 5H), 4.89 (d, J = 6.0 Hz, 1H), 3.75 (s, 3H), 3.60–3.70 (m, 1H), 2.69 (d, J = 18.1 Hz, 1H), 2.43–2.53 (m, 1H), 2.19 (d, J = 18.1 Hz, 1H), 2.04–2.12 (m, 1H), 1.47 (s, 3H); HRMS calcd for $C_{16}H_{18}O_4S$ 306.0926, found 306.0929; LRMS (EI) m/z 306 (80), 165 (100). Anal. Calcd for $C_{16}H_{18}O_4S$: C, 62.75; H, 5.88. Found: C, 62.74; H, 6.11.

4-(Methoxycarbonyl)-5-methyl-1-[(phenylthio)methyl]-8-oxabicyclo[3.2.1]octan-3-one and Regioisomer (3g). Following the general procedure, **1g** (1.94 g, 8.7 mmol) was annulated for 6 h to provide, after flash chromatography (4:1 hexanes/ethyl acetate), 2.037 g (73%) of the title compound as a mixture of keto–enol tautomers/regioisomers. The proton NMR was difficult to assign because of overlapping of signals from several isomers (see supporting information): IR (neat) 1738, 1732, 1714, 1682, 1651, 1633 cm^{-1}; HRMS calcd for $C_{17}H_{20}O_4S$ 320.1082, found 320.1072; LRMS (EI) m/z 320 (100). Anal. Calcd for $C_{17}H_{20}O_4S$: C, 63.75; H, 6.25; S, 10.00. Found: C, 63.54; H, 6.53; S, 9.96.

1-Isopropyl-4-(methoxycarbonyl)-5-[(phenylthio)-methyl]-8-oxabicyclo[3.2.1]octan-3-one (3h). Following the general procedure, **1h** (0.238 g, 0.95 mmol) was annulated for 5 h to provide, after flash chromatography (7:1 hexanes/ethyl acetate), 0.192 g (58%) of the title compound as a mixture of epimers: IR (neat) 1738, 1715 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) major isomer δ 7.12–7.40 (m, 5H), 3.64 (s, 3H), 3.49 (s, 1H), 3.40 (d, J = 13.4 Hz, 1H), 3.36 (d, J = 13.4 Hz, 1H), 2.84 (d, J = 14.6 Hz, 1H), 2.35 (d, J = 14.6 Hz, 1H), 1.60–2.10 (m, 5H), 0.92 (d, J = 6.8 Hz, 3H), 0.87 (d, J = 6.6 Hz, 3H); HRMS calcd for $C_{19}H_{24}O_4S$ 348.1395, found 348.1406; LRMS (EI) m/z 348 (100). Anal. Calcd for $C_{19}H_{24}O_4S$: C, 65.52; H, 6.90; S, 9.20. Found: C, 65.73; H, 7.09; S, 8.77.

(1*R,4*S**,5*S**)-4-(Methoxycarbonyl)-4-methyl-1-[(phenylthio)methyl]-8-oxabicyclo[3.2.1]octan-3-one (13b).** Following the general procedure, **1a** (0.753 g, 3.62 mmol) was annulated with 1,3-bis[(trimethylsilyl)oxy]-1-methoxy-2-methylbuta-1,3-diene[17] (**14**) for 4 h to provide, after flash chromatography (5:1 hexanes/ethyl acetate), 0.795 g (69%) of the title compound as a >20:1 mixture of diastereomers: IR (neat) 1715 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31–7.39 (m, 2H), 7.22–7.28 (m, 2H), 7.14–7.19 (m, 1H), 4.75 (d, J = 7.7 Hz, 1H), 3.71 (s, 3H), 3.23 (s, 2H), 2.94 (dd, J = 14.9, 2.0 Hz, 1H), 2.45 (d, J = 14.9 Hz, 1H), 1.98–2.09 (m, 1H), 1.59–1.86 (m, 3H), 1.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.3, 172.4, 136.3, 129.8, 128.9, 126.4, 84.6, 81.8, 62.1, 52.6, 51.1, 42.8, 33.6, 24.9, 15.5; HRMS calcd for $C_{17}H_{20}O_4S$ 320.1082, found 320.1087; LRMS (EI) m/z 320 (100). Anal. Calcd for $C_{17}H_{20}O_4S$: C, 63.75; H, 6.25; S, 10.00. Found: C, 63.97; H, 6.51; S, 9.61.

General Procedure for the Annulation of α-(Phenylthio) 1,5-Dicarbonyl Substrates. A 0.007 M solution of $TrSbCl_6$ (6.5 mol %) in CH_2Cl_2 was added dropwise over 5 min to a 0.1 M solution of **1** (1 equiv) in CH_2Cl_2 at −78 °C. After stirring for 2 min, a 0.1 M solution of freshly distilled **2** (1.2 equiv) in CH_2Cl_2 was added dropwise down the side of the flask over 5 min. After stirring at −78 °C for 2.5 h, the mixture was warmed to rt and the volatiles were removed *in vacuo*. The residue was subjected to flash chromatography to provide **3**.

3-Hydroxy-4-(methoxycarbonyl)-1-[(phenylthio)methyl]-9-oxabicyclo[3.3.1]non-3-ene (3b). Following the general procedure, **1b** (0.955 g, mmol) was annulated for 2.5 h to provide, after flash chromatography (7:1 hexanes/ethyl acetate), 1.028 g (75%) of the title compound which existed in solution predominantly as the enol form: IR (neat) 1739, 1715, 1661, 1626 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 11.93 (s, 1H), 7.33–7.39 (m, 2H), 7.21–7.28 (m, 2H), 7.12–7.18 (m, 1H), 4.83 (d, J = 2.9 Hz, 1H), 3.73 (s, 3H), 3.15 (d, J = 12.9 Hz, 1H), 3.03 (d, J = 12.9 Hz, 1H), 2.77 (d, J = 18.8 Hz, 1H), 2.20 (d, J = 18.8 Hz, 1H), 1.45–2.00 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 170.1, 137.0, 129.5, 128.9, 126.1, 99.4, 72.8, 67.8, 51.4, 47.6, 36.5, 36.4, 28.2, 15.5; HRMS calcd for $C_{17}H_{20}O_4S$ 320.1082, found 320.1069; LRMS (EI) m/z 320 (100). Anal. Calcd for $C_{17}H_{20}O_4S$: C, 63.75; H, 6.25; S, 10.00. Found: C, 64.11; H, 6.46; S, 9.63.

General Procedure for the Acetylation of the Bicyclic Ethers. A mixture of **3** (*ca.* 0.3 mmol), pyridine (3 mL), Ac_2O (0.4 mL), and catalytic DMAP was stirred for 1–4 days. The mixture was then diluted with Et_2O, washed with 1 M HCl, saturated aqueous $NaHCO_3$, water, and then brine, and dried over $MgSO_4$. Concentration followed by flash chromatography provided **4**.

3-Acetoxy-4-(methoxycarbonyl)-1-[(phenylthio)methyl]-8-oxabicyclo[3.2.1]oct-3-ene (4a). Acetylation of **3a** (0.090 g, 0.29 mmol) by the general procedure followed by flash chromatography (3:1 hexanes/ethyl acetate) provided 0.092 g (90%) of the title compound: IR (neat) 1770, 1722, 1715, 1660 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33–7.39 (m, 2H), 7.21–7.27 (m, 2H), 7.13–7.17 (m, 1H), 5.01 (d, J = 5.3 Hz, 1H), 3.68 (s, 3H), 3.24 (q, J = 13.0 Hz, 2H), 2.73 (d, J = 17.8 Hz, 1H), 2.20 (d, J = 17.8 Hz, 1H), 2.16 (s, 3H), 2.05–2.14 (m, 2H), 1.90–1.96 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 163.3, 154.5, 136.6, 129.6, 128.9, 126.3, 122.0, 81.7, 74.1, 51.6, 43.3, 42.0, 36.1, 33.8, 20.8; HRMS calcd for $C_{18}H_{20}O_5S$ 348.1031, found 348.1015; LRMS (EI) m/z 348 (100). Anal. Calcd for $C_{18}H_{20}O_5S$: C, 62.07; H, 5.75; S, 9.20. Found: C, 62.05; H, 5.98; S, 9.31.

3-Acetoxy-4-(methoxycarbonyl)-1-[(phenylthio)methyl]-9-oxabicyclo[3.3.1]non-3-ene (4b). Acetylation of **3b** (0.189 g, 0.59 mmol) by the general procedure followed by flash chromatography (6:1 hexanes/ethyl acetate) provided 0.200 g (93%) of the title compound, which crystallized slowly: mp 87–88 °C; IR (neat) 1761, 1722, 1672 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33–7.39 (m, 2H), 7.23–7.29 (m, 2H), 7.14–7.19 (m, 1H), 4.96 (d, J = 3.7 Hz, 1H), 3.70 (s, 3H), 3.15 (d, J = 12.7 Hz, 1H), 3.05 (d, J = 12.7 Hz, 1H), 2.69 (d, J = 18.9 Hz, 1H), 2.22 (d, J = 18.9 Hz, 1H), 2.21 (s, 3H), 1.58–2.02 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 163.2, 156.0, 137.0, 129.5, 128.9, 126.1, 118.3, 73.2, 69.6, 51.6, 47.2, 37.3, 36.4, 27.4, 20.8, 15.4; LRMS (EI) m/z 362 (100). Anal. Calcd for $C_{19}H_{22}O_5S$: C, 62.98; H, 6.08; S, 8.84. Found: C, 63.12; H, 6.31; S, 8.46.

(1*R,5*S**,6*S**)-3-Acetoxy-4-(methoxycarbonyl)-6-methyl-1-[(phenylthio)methyl]-8-oxabicyclo[3.2.1]oct-3-ene (4c).** Acetylation of **3c** (0.099 g, 0.31 mmol) by the general procedure followed by flash chromatography (4:1 hexanes/ethyl acetate) provided 0.107 g (95%) of the title compound: IR (neat) 1761, 1723, 1661 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34–7.36 (m, 2H), 7.22–7.26 (m, 2H), 7.13–7.16 (m, 1H), 4.57 (s, 1H), 3.68 (s, 3H), 3.26 (d, J = 13.0 Hz, 1H), 3.22 (d, J = 13.0 Hz, 1H), 2.69 (d, J = 17.6 Hz, 1H), 2.47–2.51 (m, 1H), 2.10–2.17 (m, 5H), 1.51 (d, J = 12.9 Hz, 1H), 1.08 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 163.4, 154.1, 136.6, 129.3, 128.9, 126.2, 121.8, 82.0, 79.6, 51.7, 44.0, 43.5, 42.3, 41.6, 21.3, 20.8; HRMS calcd for $C_{19}H_{22}O_5S$ 362.1188, found 362.1170; LRMS (EI) m/z 362 (100). Anal. Calcd for $C_{19}H_{22}O_5S$: C, 62.98; H, 6.08. Found: C, 62.88; H, 6.25.

(1*R,5*R**,7*S**)-3-Acetoxy-4-(methoxycarbonyl)-7-methyl-1-[(phenylthio)methyl]-8-oxabicyclo[3.2.1]oct-3-ene (4d).** Acetylation of **3d** (0.101 g, 0.32 mmol) by the general procedure followed by flash chromatography (4:1 hexanes/ethyl acetate) provided 0.103 g (90%) of the title compound as a 1.8:1 mixture of diastereomers by NMR: IR (neat) 1766, 1722, 1715, 1667 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ major diastereomer 7.34–7.37 (m, 2H), 7.23–7.28 (m, 2H), 7.14–7.18 (m, 1H), 4.97 (d, J = 6.3 Hz, 1H), 3.69 (s, 3H), 3.31 (d, J = 12.5 Hz, 1H), 3.13 (d, J = 12.5 Hz, 1H), 2.91 (d, J = 18.1 Hz, 1H), 2.33–2.48 (m, 2H), 2.01–2.18 (m, 4H), 1.64–1.73 (m, 1H), 1.08 (d, J = 6.5 Hz, 3H); δ minor diastereomer 7.34–7.37 (m, 2H), 7.23–7.28 (m, 2H), 7.14–7.18 (m, 1H), 4.92 (d, J = 6.7 Hz, 1H), 3.69 (s, 3H), 3.24–3.25 (m, 2H), 2.73 (d, J = 18.5 Hz, 1H), 2.33–2.48 (m, 2H), 2.01–2.18 (m, 4H), 1.64–1.73 (m, 1H), 1.19 (d, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 168.2, 163.23, 163.20, 154.6, 154.5, 136.8, 136.7, 129.2, 128.94, 128.90, 126.2, 126.1, 123.2, 122.0, 84.1, 82.4, 73.2, 72.7, 51.6, 46.4, 43.3, 42.6, 41.8, 41.1, 39.7, 39.6, 35.6, 20.9, 20.8, 17.4, 17.3; HRMS calcd for $C_{19}H_{22}O_5S$ 362.1188, found 362.1180; LRMS (EI) m/z 362 (100). Anal. Calcd for $C_{19}H_{22}O_5S$: C, 62.98; H, 6.08; S, 8.84. Found: C, 62.85; H, 6.29; S, 9.10.

(1*R,5*S**,6*R**)-3-Acetoxy-4-(methoxycarbonyl)-1-methyl-7-(phenylthio)-8-oxabicyclo[3.2.1]oct-3-ene (4e).** Acetylation of **3e** (0.092 g, 0.30 mmol) by the general procedure followed by flash chromatography (4:1 hexanes/ethyl acetate)

provided 0.096 g (92%) of the title compound as a white solid as a >200:1 mixture by GC analysis: mp 84–85 °C; IR (neat) 1766, 1723, 1660, 1652 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43–7.48 (m, 2H), 7.21–7.32 (m, 3H), 4.85 (s, 1H), 3.89 (dd, J = 8.5, 2.2 Hz, 1H), 3.47 (s, 3H), 2.57 (d, J = 17.3 Hz, 1H), 2.49–2.53 (m, 1H), 2.18 (s, 3H), 2.05 (d, J = 17.3 Hz, 1H), 1.67–1.74 (m, 1H), 1.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 162.5, 155.7, 135.4, 131.4, 128.7, 126.8, 120.5, 79.8, 78.1, 54.8, 51.2, 43.3, 43.1, 26.3, 20.7; HRMS calcd for $C_{18}H_{20}O_5S$ 348.1031, found 348.1035; LRMS (EI) m/z 348 (100). Anal. Calcd for $C_{18}H_{20}O_5S$: C, 62.07; H, 5.75; S, 9.20. Found: C, 61.93; H, 6.08; S, 9.04.

(1*R,5*R**,7*S**)-3-Acetoxy-4-(methoxycarbonyl)-1-methyl-7-(phenylthio)-8-oxabicyclo[3.2.1]oct-3-ene (4f).** Acetylation of **3f** (0.102 g, 0.33 mmol) by the general procedure followed by flash chromatography (4:1 hexanes/ethyl acetate) provided 0.095 g (82%) of the title compound as an 11:1 mixture of diastereomers: IR (neat) 1770, 1723, 1715, 1666 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) major diastereomer δ 7.24–7.33 (m, 4H), 7.15–7.18 (m, 1H), 4.99 (d, J = 6.2 Hz, 1H), 3.86 (t, J = 8.2 Hz, 1H), 3.71 (s, 3H), 2.64–2.70 (m, 2H), 2.11–2.22 (m, 5H), 1.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 163.1, 154.3, 136.2, 129.6, 129.0, 126.3, 121.5, 81.7, 72.2, 51.7, 51.6, 45.9, 44.7, 22.9, 20.9; HRMS calcd for $C_{18}H_{20}O_5S$ 348.1031, found 348.1020; LRMS (EI) m/z 348 (90), 273 (100). Anal. Calcd for $C_{18}H_{20}O_5S$: C, 62.07; H, 5.75; S, 9.20. Found: C, 61.90; H, 5.91; S, 9.32.

3-Acetoxy-4-(methoxycarbonyl)-5-methyl-1-[(phenylthio)methyl]-8-oxabicyclo[3.2.1]oct-3-ene and Regioisomer (4g). Acetylation of **3g** (0.207 g, 0.65 mmol) by the general procedure followed by flash chromatography (4:1 hexanes/ethyl acetate) provided 0.185 g (79%) of the title compound as a 1.3:1 mixture of regioisomers: IR (neat) 1756, 1714, 1658 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.08–7.41 (m, 5H total), 3.71 and 3.57 (s, 3H total), 3.15–3.40 (m, 2H total), 2.76 (d, J = 17.1 Hz, 0.43H), 2.66 (d, J = 17.4 Hz, 0.57H), 2.46–2.52 (m, 1H total), 1.93–2.20 (m, 6H total), 1.79–1.88 (m, 1H total), 1.43 and 1.38 (s, 3H total); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 165.0, 164.6, 152.8, 150.5, 137.2, 136.6, 129.6, 129.5, 128.8, 128.5, 126.2, 125.9, 125.8, 124.0, 83.6, 81.2, 81.0, 79.5, 51.5, 43.4, 43.3, 42.7, 41.2, 41.1, 39.9, 36.5, 34.8, 26.3, 21.3, 20.7, 20.6; HRMS calcd for $C_{19}H_{22}O_5S$ 362.1188, found 362.1203; LRMS (EI) m/z 362 (100). Anal. Calcd for $C_{19}H_{22}O_5S$: C, 62.98; H, 6.08; S, 8.84. Found: C, 62.94; H, 6.29; S, 8.88.

3-Acetoxy-1-isopropyl-4-(methoxycarbonyl)-5-[(phenylthio)methyl]-8-oxabicyclo[3.2.1]oct-3-ene (4h). Acetylation of **3h** (0.079 g, 0.23 mmol) by the general procedure followed by flash chromatography (5:1 hexanes/ethyl acetate) provided 0.062 g (70%) of the title compound as a 42:1 mixture of isomers by GC analysis: IR (neat) 1766, 1711 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38–7.42 (m, 2H), 7.22–7.28 (m, 2H), 7.13–7.17 (m, 1H), 3.70 (d, J = 13.2 Hz, 1H), 3.64 (s, 3H), 3.38 (d, J = 13.2 Hz, 1H), 2.63 (d, J = 17.2 Hz, 1H), 2.48–2.53 (m, 1H), 2.19 (s, 3H), 2.05 (d, J = 17.2 Hz, 1H), 1.80–2.00 (m, 4H), 0.92 (d, J = 6.8 Hz, 3H), 0.87 (d, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 164.8, 153.6, 137.3, 129.7, 128.5, 125.8, 124.2, 84.7, 83.4, 51.6, 40.8, 39.8, 39.5, 35.7, 31.8, 20.8, 17.2, 16.5; HRMS calcd for $C_{21}H_{26}O_5S$ 390.1501, found 390.1516; LRMS (EI) m/z 390 (85), 207 (100). Anal. Calcd for $C_{21}H_{26}O_5S$: C, 64.62; H, 6.67; S, 8.21. Found: C, 64.75; H, 6.96; S, 7.74.

General Procedure for the Hydrolysis and Decarboxylation of β-Keto Esters.[16] A mixture of **3** (1 equiv) and NaCl (2 equiv) in DMSO (1.5 mL/mmol) and water (6 equiv) was heated to 140 °C under argon and stirred for a further 1.5 h. Water was added periodically during the reaction to replace that lost by evaporation. The mixture was cooled and then partitioned between Et_2O and water. The organic layer was washed with water and then brine and dried over $MgSO_4$. Concentration followed by flash chromatography provided **12**.

1-[(Phenylthio)methyl]-9-oxabicyclo[3.3.1]nonan-3-one (12b). Decarboxylation of **3c** (0.550 g, 1.72 mmol) by the general procedure followed by flash chromatography (6:1 hexanes/ethyl acetate) provided 0.356 g (79%) of the title compound: IR (neat) 1713 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34–7.39 (m, 2H), 7.22–7.28 (m, 2H), 7.13–7.19 (m, 1H), 4.53–4.58 (m, 1H), 3.19 (d, J = 13.1 Hz, 1H), 3.02 (d, J = 13.1 Hz, 1H), 2.69–2.76 (m, 2H), 2.40 (dd, J = 15.9, 1.6 Hz, 1H), 2.31 (d, J = 17.0 Hz, 1H), 1.85–1.96 (m, 1H), 1.52–1.75 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.3, 136.9, 129.5, 128.9, 126.2, 75.3, 70.2, 49.2, 47.1, 45.0, 35.0, 29.7, 16.4; HRMS calcd for $C_{15}H_{18}O_2S$ 262.1028, found 262.1041; LRMS (EI) m/z 262 (100). Anal. Calcd for $C_{15}H_{18}O_2S$: C, 68.70; H, 6.87; S, 12.21. Found: C, 69.06; H, 7.15; S, 12.00.

(1*R,5*S**,6*S**)-6-Methyl-1-[(phenylthio)methyl]-8-oxabicyclo[3.2.1]octan-3-one (12c).** Decarboxylation of **3c** (0.334 g, 1.04 mmol) by the general procedure followed by flash chromatography (6:1 hexanes/ethyl acetate) provided 0.193 g (71%) of the title compound: IR (neat) 1715 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36–7.41 (m, 2H), 7.24–7.29 (m, 2H), 7.15–7.19 (m, 1H), 4.24 (d, J = 5.3 Hz, 1H), 3.21–3.31 (m, 2H), 2.60–2.69 (m, 2H), 2.37 (d, J = 15.4 Hz, 1H), 2.30 (d, J = 15.6 Hz, 1H), 2.11–2.21 (m, 1H), 2.06 (dd, J = 12.8, 8.8 Hz, 1H), 1.48 (ddd, J = 12.8, 3.6, 2.9 Hz, 1H), 1.09 (d, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.0, 136.6, 129.5, 129.0, 126.3, 84.0, 81.9, 52.9, 48.1, 43.5, 42.9, 38.6, 22.1; HRMS calcd for $C_{15}H_{18}O_2S$ 262.1028, found 262.1021; LRMS (EI) m/z 262 (100). Anal. Calcd for $C_{15}H_{18}O_2S$: C, 68.70; H, 6.87. Found: C, 68.71; H, 6.97.

(1*R,5*S**,6*R**)-1-Methyl-6-(phenylthio)-8-oxabicyclo-[3.2.1]octan-3-one (12e).** Decarboxylation of **3e** (0.800 g, 2.61 mmol) by the general procedure followed by flash chromatography (6:1 hexanes/ethyl acetate) provided 0.470 g (73%) of the title compound: mp 73–74 °C; IR (neat) 1709 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.17–7.31 (m, 5H), 4.54 (d, J = 5.2 Hz, 1H), 3.58 (dd, J = 8.7, 4.8 Hz, 1H), 2.65 (dd, J = 15.6, 5.2 Hz, 1H), 2.47 (d, J = 15.5 Hz, 1H), 2.31–2.40 (m, 2H), 2.27 (d, J = 15.5 Hz, 1H), 1.66 (ddd, J = 13.9, 4.8, 2.2 Hz, 1H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.2, 135.3, 130.3, 129.0, 126.8, 82.1, 80.8, 54.4, 49.7, 48.0, 43.7, 26.2; HRMS calcd for $C_{14}H_{16}O_2S$ 248.0871, found 248.0861; LRMS (EI) m/z 248 (100). Anal. Calcd for $C_{14}H_{16}O_2S$: C, 67.74; H, 6.45; S, 12.90. Found: C, 68.04; H, 6.68; S, 12.86.

(1*R,5*S**,7*S**)-1-Methyl-7-(phenylthio)-8-oxabicyclo-[3.2.1]octan-3-one (12f).** Decarboxylation of **3f** (0.650 g, 2.12 mmol) by the general procedure followed by flash chromatography (6:1 hexanes/ethyl acetate) provided 0.387g (73%) of the title compound along with a small amount of the epimer 0.027 g (5%): major diastereomer IR (neat) 1715 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.15–7.30 (m, 5H), 4.70 (t, J = 6.3 Hz, 1H), 3.68 (dd, J = 8.7, 5.7 Hz, 1H), 2.65 (dd, J = 15.5, 4.7 Hz, 1H), 2.56 (d, J = 15.5 Hz, 1H), 2.42 (dd, J = 15.5, 1.4 Hz, 1H), 2.38 (dd, J = 13.9, 8.7 Hz, 1H), 2.23 (d, J = 15.5 Hz, 1H), 2.11–2.21 (m, 1H), 1.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9, 135.7, 129.9, 129.0, 126.5, 83.8, 73.5, 56.1, 51.9, 47.7, 40.7, 23.1; HRMS calcd for $C_{14}H_{16}O_2S$ 248.0871, found 248.0870; LRMS (EI) m/z 248 (100). Anal. Calcd for $C_{14}H_{16}O_2S$: C, 67.74; H, 6.45; S, 12.90. Found: C, 68.16; H, 6.52; S, 12.93.

5-Methyl-1-[(phenylthio)methyl]-8-oxabicyclo[3.2.1]-octan-3-one (12g). Decarboxylation of **3g** (0.675 g, 2.1 mmol) by the general procedure followed by flash chromatography (5:1 hexanes/ethyl acetate) provided 0.407 g (74%) of the title compound: IR (neat) 1715 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.40 (m, 2H), 7.23–7.30 (m, 2H), 7.14–7.20 (m, 1H), 3.26 (AB q, J = 13.2 Hz, 2H), 2.61 (dd, J = 15.1, 2.1 Hz, 1H), 2.44 (d, J = 15.1 Hz, 1H), 2.39 (dd, J = 15.2, 1.3 Hz, 1H), 2.31 (dd, J = 15.2, 1.3 Hz, 1H), 1.93–2.04 (m, 1H), 1.75–1.87 (m, 3H), 1.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 136.7, 129.7, 129.0, 126.3, 83.3, 81.8, 54.0, 51.9, 43.5, 36.8, 35.1, 26.2; HRMS calcd for $C_{15}H_{18}O_2S$ 262.1028, found 262.1036; LRMS (EI) m/z 262 (100). Anal. Calcd for $C_{15}H_{18}O_2S$: C, 68.70; H, 6.87; S, 12.21. Found: C, 68.32; H, 7.05; S, 12.45.

(1*R,4*R**,5*S**)-4-(Methoxycarbonyl)-4-methyl-1-[(phenylthio)methyl]-8-oxabicyclo[3.2.1]octan-3-one (13a).** A solution of **3a** (0.839 g, 2.74 mmol) in THF (9 mL) was added dropwise to a stirred suspension of NaH (60% dispersion in mineral oil, 0.122 g, 3.05 mmol) in THF (6 mL) under argon. After 15 min MeI (0.778 g, 5.48 mmol) was added and the mixture was stirred for 3 h at rt. The mixture was diluted with Et_2O, washed with water and then brine, and dried over $MgSO_4$. Concentration followed by flash chromatography (3:1 hexanes/ethyl acetate) and Kugelrohr distillation (ot 160–165 °C at 0.2 mmHg) provided 0.702 g (80%) of the title com-

pound: IR (neat) 1738, 1714 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36–7.41 (m, 2H), 7.25–7.29 (m, 2H), 7.16–7.20 (m, 1H), 4.40–4.44 (m, 1H), 3.73 (s, 3H), 3.29 (d, J = 13.4 Hz, 1H), 3.23 (d, J = 13.4 Hz, 1H), 2.94 (d, J = 15.6 Hz, 1H), 2.34 (d, J = 15.6 Hz, 1H), 2.15–2.22 (m, 2H), 1.77–1.87 (m, 2H), 1.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.9, 171.0, 136.3, 129.8, 129.0, 126.5, 84.2, 80.9, 61.9, 52.2, 48.8, 43.1, 33.8, 28.2, 21.0; LRMS (EI) m/z 320 (100). Anal. Calcd for $C_{17}H_{20}O_4S$: C, 63.75; H, 6.25; S, 10.00. Found: C, 63.86; H, 6.48; S, 9.77.

(1*R,4*R**,5*S**)-4-(Methoxycarbonyl)-1-[(phenylthio)methyl]-8-oxabicyclo[3.2.1]octan-3-one, Ethylene Acetal (11ai) and (1*R**,4*S**,5*S**)-4-(Methoxycarbonyl)-1-[(phenylthio)methyl]-8-oxabicyclo[3.2.1]octan-3-one, Ethylene Acetal (11aii).** Protection of **3a** (0.567 g, 1.85 mmol) by the general procedure (48 h, 10 equiv of ethylene glycol) followed by flash chromatography (4:1 hexanes/ethyl acetate) provided 0.277 g (43%) of **11ai** [IR (neat) 1728 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33–7.38 (m, 2H), 7.23–7.28 (m, 2H), 7.13–7.19 (m, 1H), 4.63 (dd, J = 7.4, 3.6 Hz, 1H), 3.96–4.04 (m, 1H), 3.83–3.94 (m, 3H), 3.68 (s, 3H), 3.24 (AB q, J = 12.8 Hz, 2H), 3.12 (d, J = 3.6 Hz, 1H), 2.43–2.52 (m, 1H), 2.00–2.19 (m, 2H), 1.90 (s, 2H), 1.70 (dt, J = 12.3, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 137.0, 129.3, 128.9, 126.0, 107.5, 82.4, 75.9, 65.5, 63.9, 53.0, 51.6, 45.8, 43.6, 32.3, 27.6; HRMS calcd for $C_{18}H_{22}O_5S$ 350.1188, found 350.1172; LRMS (EI) m/z 350 (100). Anal. Calcd for $C_{18}H_{22}O_5S$: C, 61.71; H, 6.29; S, 9.14. Found: C, 61.50; H, 6.48; S, 8.82.], followed by 0.258 g (40%) of **11aii** [IR (neat) 1732 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32–7.37 (m, 2H), 7.22–7.27 (m, 2H), 7.12–7.17 (m, 1H), 4.58 (d, J = 7.8 Hz, 1H), 3.82–3.99 (m, 4H), 3.70 (s, 3H), 3.23 (AB q, J = 12.8 Hz, 2H), 2.62 (s, 1H), 2.35 (dd, J = 13.4, 1.0 Hz, 1H), 2.08–2.23 (m, 2H), 1.97–2.07 (m, 1H), 1.87 (dd, J = 13.4, 0.8 Hz, 1H), 1.66–1.76 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 137.1, 129.2, 128.8, 125.9, 106.1, 82.3, 76.8, 64.4, 63.7, 54.7, 51.7, 43.6, 43.1, 31.4, 29.2; HRMS calcd for $C_{18}H_{22}O_5S$ 350.1188, found 350.1173; LRMS (EI) m/z 350 (100). Anal. Calcd for $C_{18}H_{22}O_5S$: C, 61.71; H, 6.29; S, 9.14. Found: C, 62.11; H, 6.41; S, 8.87.].

1-[(Phenylthio)methyl]-9-oxabicyclo[3.3.1]nonan-3-one, Ethylene Acetal (11b). Protection of **12b** (0.290 g, 1.11 mmol) by the general procedure (18 h, 10 equiv of ethylene glycol) provided the crude title compound in 100% yield: ^1H NMR (400 MHz, $CDCl_3$) δ 7.32–7.37 (m, 2H), 7.21–7.26 (m, 2H), 7.10–7.15 (m, 1H), 4.29–4.35 (m, 1H), 3.87–3.96 (m, 4H), 3.06 (s, 2H), 2.18–2.30 (m, 1H), 2.14 (ddd, J = 14.0, 8.6, 1.8 Hz, 1H), 2.02 (dd, J = 14.2, 1.8 Hz, 1H), 1.78–1.89 (m, 2H), 1.70 (dd, J = 14.0, 1.9 Hz, 1H), 1.40–1.65 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 129.0, 128.8, 125.7, 107.1, 72.2, 68.0, 64.3, 63.7, 48.2, 41.6, 37.4, 34.0, 28.9, 14.9; HRMS calcd for $C_{17}H_{22}O_3S$ 306.1290, found 306.1286; LRMS (EI) m/z 306 (100).

(1*R,5*R**,6*S**)-6-Methyl-1-[(phenylthio)methyl]-8-oxabicyclo[3.2.1]octan-3-one, Ethylene Acetal (11c).** Protection of **12c** (0.151 g, 0.58 mmol) by the general procedure (24 h, 10 equiv of ethylene glycol) provided the crude title compound in 100% yield: ^1H NMR (400 MHz, $CDCl_3$) δ 7.32–7.36 (m, 2H), 7.21–7.26 (m, 2H), 7.11–7.16 (m, 1H), 3.97 (d, J = 3.4 Hz, 1H), 3.91–3.96 (m, 2H), 3.77–3.85 (m, 2H), 3.20 (d, J = 12.5 Hz, 1H), 3.13 (d, J = 12.5 Hz, 1H), 2.44–2.55 (m, 2H), 1.96 (dd, J = 13.8, 4.3 Hz, 1H), 1.90 (d, J = 13.7 Hz, 1H), 1.82 (dd, J = 13.7, 1.4 Hz, 1H), 1.72 (d, J = 13.8 Hz, 1H), 1.24–1.30 (m, 1H), 1.02 (d, J = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 129.2, 128.8, 125.8, 107.0, 82.5, 82.1, 64.5, 63.1, 44.9, 44.2, 41.8, 40.3, 36.5, 22.6; HRMS calcd for $C_{17}H_{22}O_3S$ 306.1290, found 306.1294; LRMS (EI) m/z 306 (100).

(1*R,5*S**,6*R**)-1-Methyl-6-(phenylthio)-8-oxabicyclo-[3.2.1]octan-3-one, Ethylene Acetal (11e).** Protection of **12e** (0.399 g, 1.61 mmol) by the general procedure (24 h, 10 equiv of ethylene glycol) provided the crude title compound in 100% yield: ^1H NMR (400 MHz, $CDCl_3$) δ 7.14–7.31 (m, 5H), 4.31 (d, J = 3.5 Hz, 1H), 4.10 (dd, J = 8.5, 4.2 Hz, 1H), 3.91–4.01 (m, 2H), 3.80–3.87 (m, 2H), 2.78 (dd, J = 13.1, 8.5 Hz, 1H), 2.00 (dd, J = 14.0, 4.4 Hz, 1H), 1.70–1.85 (m, 3H), 1.45–1.51 (m, 1H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 129.4, 128.9, 126.0, 106.6, 80.9, 80.7, 64.5, 63.3, 48.2, 46.5, 42.9, 40.5, 26.8; HRMS calcd for $C_{16}H_{20}O_3S$ 292.1133, found 292.1136; LRMS (EI) m/z 292 (100).

(1*R,5*S**,7*S**)-1-Methyl-7-(phenylthio)-8-oxabicyclo-[3.2.1]octan-3-one, Ethylene Acetal (11f).** Protection of **12f** (0.300 g, 1.21 mmol) by the general procedure (24 h, 10 equiv of ethylene glycol) provided the crude title compound in 100% yield: ^1H NMR (400 MHz, $CDCl_3$) δ 7.23–7.34 (m, 4H), 7.11–7.16 (m, 1H), 4.46 (dd, J = 7.9, 4.0 Hz, 1H), 4.23 (dd, J = 8.8, 5.3 Hz, 1H), 3.94–4.04 (m, 2H), 3.81–3.86 (m, 2H), 2.78 (dd, J = 13.0, 8.8 Hz, 1H), 1.90–2.03 (m, 3H), 1.85 (dd, J = 13.8, 1.8 Hz, 1H), 1.65–1.71 (m, 1H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 128.9, 128.8, 125.6, 106.7, 82.1, 73.4, 64.6, 63.2, 50.0, 48.3, 39.9, 39.7, 23.7; HRMS calcd for $C_{16}H_{20}O_3S$ 292.1133, found 292.1140; LRMS (EI) m/z 292 (100).

5-Methyl-1-[(phenylthio)methyl]-8-oxabicyclo[3.2.1]-octan-3-one, Ethylene Acetal (11g). Protection of **12g** (0.319 g, 1.22 mmol) by the general procedure (24 h, 10 equiv of ethylene glycol) followed by flash chromatography (3:1 hexanes/ethyl acetate) provided 0.341 g (92%) of the title compound: IR (neat) 3057, 2968, 2922, 2879, 1081 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32–7.37 (m, 2H), 7.21–7.27 (m, 2H), 7.10–7.16 (m, 1H), 3.93–3.98 (m, 2H), 3.79–3.84 (m, 2H), 3.17 (AB q, J = 12.4 Hz, 2H), 2.13–2.25 (m, 2H), 1.90 (dd, J = 12.1, 1.4 Hz, 1H), 1.75–1.85 (m, 3H), 1.72 (dd, J = 13.5, 1.5 Hz, 1H), 1.54–1.65 (m, 1H), 1.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 129.1, 128.8, 125.8, 107.5, 82.0, 80.6, 64.5, 63.2, 46.5, 44.2, 44.0, 35.5, 33.8, 26.8; HRMS calcd for $C_{17}H_{22}O_3S$ 306.1290, found 306.1292; LRMS (EI) m/z 306 (100). Anal. Calcd for $C_{17}H_{22}O_3S$: C, 66.67; H, 7.19; S, 10.46. Found: C, 66.43; H, 7.37; S, 10.72.

(1*R,4*R**,5*S**)-4-(Methoxycarbonyl)-4-methyl-1-[(phenylthio)methyl]-8-oxabicyclo[3.2.1]octan-3-one, Ethylene Acetal (11i).** Protection of **13a** (0.636 g, 1.99 mmol) by the general procedure (90 h, 10 equiv of ethylene glycol) provided 0.718 g of an inseparable 9:1 mixture of **11i** and **13a**. The crude product was used directly in the next step: IR (neat) 1732 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33–7.37 (m, 2H), 7.23–7.28 (m, 2H), 7.13–7.18 (m, 1H), 4.37 (d, J = 7.5 Hz, 1H), 3.86–4.04 (m, 4H), 3.66 (s, 3H), 3.17 (s, 2H), 2.32–2.41 (m, 1H), 2.01–2.13 (m, 2H), 1.94 (d, J = 13.9 Hz, 1H), 1.72 (d, J = 13.9 Hz, 1H), 1.60–1.70 (m, 1H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 137.1, 129.3, 128.8, 126.0, 109.5, 82.1, 80.9, 65.4, 63.9, 53.3, 51.4, 43.6, 42.5, 32.2, 28.3, 21.1; HRMS calcd for $C_{19}H_{24}O_5S$ 364.1344, found 364.1343; LRMS (EI) m/z 364 (30), 241 (100).

(1*R,4*R**,5*S**)-4-(Methoxycarbonyl)-4-methyl-1-[(phenylthio)methyl]-8-oxabicyclo[3.2.1]octan-3-one, Ethylene Acetal (11j).** Protection of **13b** (0.304 g, 0.95 mmol) by the general procedure (10 d, 20 equiv of ethylene glycol) followed by flash chromatography (4:1 hexanes/ethyl acetate) provided 0.161 g of recovered **13b** and 0.131 g of **11j** (81% based upon recovered **13b**): IR (neat) 1746, 1716 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33–7.35 (m, 2H), 7.22–7.26 (m, 2H), 7.12–7.16 (m, 1H), 4.34 (d, J = 7.9 Hz, 1H), 3.83–3.95 (m, 4H), 3.70 (s, 3H), 3.19 (s, 2H), 2.46 (d, J = 13.2 Hz, 1H), 2.24–2.28 (m, 1H), 2.09–2.14 (m, 1H), 1.81–1.87 (m, 2H), 1.70–1.74 (m, 1H), 1.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 137.1, 129.1, 128.7, 125.8, 108.3, 82.9, 82.2, 64.8, 64.4, 55.4, 51.8, 43.3, 43.0, 32.2, 25.6, 13.6; HRMS calcd for $C_{19}H_{24}O_5S$ 364.1344, found 364.1362; LRMS (EI) m/z 364 (100).

General Procedure for the Oxidation of Sulfides to Sulfones. To a solution of **11** (1 equiv) in CH_2Cl_2 (7 mL/mmol **11**) was added purified *m*-CPBA (2.2 equiv). After stirring for 1 h at rt, the mixture was diluted with CH_2Cl_2, washed with saturated aqueous $Na_2S_2O_3 \cdot 5H_2O$, saturated aqueous $NaHCO_3$, water, and then brine, and dried over $MgSO_4$. Concentration followed by flash chromatography (1:1 hexanes/ethyl acetate) afforded **15** as a white solid.

(1*R,4*R**,5*S**)-4-(Methoxycarbonyl)-1-[(phenylsulfonyl)methyl]-8-oxabicyclo[3.2.1]octan-3-one, Ethylene Acetal (15ai).** Oxidation of **11ai** (0.387 g, 1.11 mmol) by the general procedure provided 0.391 g (93%) of the title compound: mp 155–156 °C; IR (neat) 1728 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.88–7.92 (m, 2H), 7.61–7.67 (m, 1H), 7.52–7.57 (m, 2H), 4.35 (dd, J = 7.7, 3.7 Hz, 1H), 3.83–4.04 (m, 4H), 3.67 (s, 3H), 3.47 (d, J = 14.0 Hz, 1H), 3.34 (d, J = 14.0 Hz, 1H), 3.08 (d, J = 3.7 Hz, 1H), 2.44–2.53 (m, 1H), 2.30–2.38 (m, 1H), 2.26

(d, J = 13.9 Hz, 1H), 1.94–2.07 (m, 2H), 1.78–1.88 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 140.7, 133.7, 129.1, 127.8, 106.7, 80.0, 75.0, 65.4, 64.6, 63.8, 52.7, 51.6, 46.0, 32.7, 27.4; HRMS calcd for $C_{18}H_{22}O_7S$ 382.1086, found 382.1095; LRMS (EI) m/z 382 (10), 269 (100). Anal. Calcd for $C_{18}H_{22}O_7S$: C, 56.54; H, 5.76; S, 8.38. Found: C, 56.19; H, 5.97; S, 8.44.

(1*R,4*S**,5*S**)-4-(Methoxycarbonyl)-1-[(phenylsulfonyl)methyl]-8-oxabicyclo[3.2.1]octan-3-one, Ethylene Acetal (15aii).** Oxidation of **11aii** (0.115 g, 0.33 mmol) by the general procedure provided 0.120 g (96%) of the title compound as a glass: IR (neat) 1732 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.93 (m, 2H), 7.59–7.65 (m, 1H), 7.50–7.56 (m, 2H), 4.46 (d, J = 7.8 Hz, 1H), 3.79–4.01 (m, 4H), 3.67 (s, 3H), 3.58 (d, J = 14.0 Hz, 1H), 3.36 (d, J = 14.0 Hz, 1H), 2.59 (s, 1H), 2.35–2.47 (m, 2H), 2.12–2.23 (m, 2H), 1.94–2.05 (m, 1H), 1.82–1.92 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 140.7, 133.6, 129.1, 127.7, 105.2, 79.7, 75.7, 64.9, 64.4, 63.7, 54.6, 51.7, 43.2, 31.9, 29.1; HRMS calcd for $C_{18}H_{22}O_7S$ 382.1086, found 382.1084; LRMS (EI) m/z 382 (10), 269 (100). Anal. Calcd for $C_{18}H_{22}O_7S$: C, 56.54; H, 5.76; S, 8.38. Found: C, 56.57; H, 5.97; S, 8.48.

1-[(Phenylsulfonyl)methyl]-9-oxabicyclo[3.3.1]nonan-3-one, Ethylene Acetal (15b). Oxidation of **11b** (0.339 g, 1.11 mmol) by the general procedure provided 0.319 g (85%) of the title compound: mp 122–124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88–7.90 (m, 2H), 7.50–7.63 (m, 3H), 4.15–4.18 (m, 1H), 3.88–3.96 (m, 4H), 3.23–3.31 (m, 2H), 2.24–2.31 (m, 2H), 2.06–2.21 (m, 2H), 1.93–1.98 (m, 1H), 1.74–1.82 (m, 2H), 1.68 (dd, J = 14.1, 1.8 Hz, 1H), 1.50–1.59 (m, 1H), 1.40–1.43 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 133.3, 128.9, 127.5, 106.2, 71.4, 67.9, 67.5, 64.1, 63.5, 41.8, 37.2, 33.9, 28.4, 14.2; HRMS calcd for $C_{17}H_{22}O_5S$ 338.1188, found 338.1182; LRMS (EI) m/z 338 (2), 183 (100). Anal. Calcd for $C_{17}H_{22}O_5S$: C, 60.36; H, 6.51; S, 9.47. Found: C, 60.35; H, 6.92; S, 9.38.

(1*R,5*R**,6*S**)-6-Methyl-1-[(phenylsulfonyl)methyl]-8-oxabicyclo[3.2.1]octan-3-one, Ethylene Acetal (15c).** Oxidation of **11c** (0.176 g, 0.58 mmol) by the general procedure provided 0.178 g (92%) of the title compound: mp 151–152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88–7.94 (m, 2H), 7.59–7.65 (m, 1H), 7.50–7.57 (m, 2H), 3.88–4.00 (m, 3H), 3.78–3.85 (m, 2H), 3.46 (d, J = 14.0 Hz, 1H), 3.33 (d, J = 14.0 Hz, 1H), 2.67 (dd, J = 12.4, 8.7 Hz, 1H), 2.50–2.60 (m, 1H), 2.19 (dd, J = 13.6, 1.7 Hz, 1H), 1.95 (dd, J = 13.8, 4.3 Hz, 1H), 1.90 (dd, J = 13.8, 1.3 Hz, 1H), 1.67–1.73 (m, 1H), 1.42 (ddd, J = 12.4, 3.6, 2.0 Hz, 1H), 0.99 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 133.6, 129.1, 127.7, 106.1, 81.4, 80.3, 65.2, 64.4, 63.1, 45.1, 42.3, 40.3, 36.3, 22.7; HRMS calcd for $C_{17}H_{22}O_5S$ 338.1188, found 338.1171; LRMS (CI$^-$) m/z 337 (M – H)$^+$.

(1*R,5*S**,6*R**)-1-Methyl-6-(phenylsulfonyl)-8-oxabicyclo-[3.2.1]octan-3-one, Ethylene Acetal (15e).** Oxidation of **11e** (0.460 g, 1.58 mmol) by the general procedure provided 0.468 g (92%) of the title compound: mp 130–132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88–7.90 (m, 2H), 7.62–7.66 (m, 1H), 7.54–7.57 (m, 2H), 4.81 (d, J = 3.4 Hz, 1H), 4.11 (dd, J = 9.2, 5.1 Hz, 1H), 3.89–3.92 (m, 2H), 3.79–3.82 (m, 2H), 2.51 (dd, J = 13.3, 9.2 Hz, 1H), 1.90–1.98 (m, 2H), 1.67–1.72 (m, 3H), 1.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 133.7, 129.1, 128.9, 106.0, 81.0, 74.9, 68.2, 64.5, 63.4, 46.1, 40.1, 36.9, 26.0; HRMS calcd for $C_{16}H_{20}O_5S$ 324.1031, found 324.1034; LRMS (EI) m/z 324 (10), 309 (100). Anal. Calcd for $C_{16}H_{20}O_5S$: C, 59.26; H, 6.17; S, 9.88. Found: C, 58.83; H, 6.19; S, 9.66.

(1*R,5*S**,7*S**)-1-Methyl-7-(phenylsulfonyl)-8-oxabicyclo-[3.2.1]octan-3-one, Ethylene Acetal (15f).** Oxidation of **11f** (0.353 g, 1.21 mmol) by the general procedure provided 0.359 g (92%) of the title compound: mp 129–132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.89 (m, 2H), 7.59–7.64 (m, 1H), 7.50–7.57 (m, 2H), 4.50–4.55 (m, 1H), 4.12 (dd, J = 9.0, 7.0 Hz, 1H), 3.78–3.95 (m, 4H), 2.25–2.34 (m, 1H), 2.06 (dd, J = 12.5, 9.0 Hz, 1H), 1.90–1.97 (m, 2H), 1.77–1.82 (m, 4H), 1.55–1.61 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 133.3, 129.1, 128.1, 105.9, 81.7, 73.1, 66.6, 64.6, 63.2, 49.4, 39.2, 34.2, 22.7; HRMS calcd for $C_{16}H_{20}O_5S$ 324.1031, found 324.1047; LRMS (EI) m/z 324 (30), 309 (100). Anal. Calcd for $C_{16}H_{20}O_5S$: C, 59.26; H, 6.17; S, 9.88. Found: C, 59.04; H, 6.36; S, 9.89.

5-Methyl-1-[(phenylsulfonyl)methyl]-8-oxabicyclo[3.2.1]-octan-3-one, Ethylene Acetal (15g). Oxidation of **11g** (0.329 g, 1.08 mmol) by the general procedure provided 0.354 g (98%) of the title compound: mp 112–115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88–7.92 (m, 2H), 7.59–7.65 (m, 1H), 7.50–7.56 (m, 2H), 3.90–4.00 (m, 2H), 3.77–3.86 (m, 2H), 3.45 (d, J = 14.2 Hz, 1H), 3.38 (d, J = 14.2 Hz, 1H), 2.34 (ddd, J = 12.5, 9.8, 4.8 Hz, 1H), 2.13–2.21 (m, 2H), 1.94–2.05 (m, 1H), 1.82 (dd, J = 13.5, 1.3 Hz, 1H), 1.73 (d, J = 13.6 Hz, 1H), 1.67 (dd, J = 13.6, 1.3 Hz, 1H), 1.49–1.56 (m, 1H), 1.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 133.5, 128.9, 127.9, 106.7, 79.8, 79.4, 64.9, 64.5, 63.1, 46.4, 44.6, 35.2, 33.6, 26.4; HRMS calcd for $C_{16}H_{19}O_5S$ (M – CH_3)$^+$ 323.0953, found 323.0951; LRMS (CI$^-$) m/z 337 (M – H)$^+$. Anal. Calcd for $C_{17}H_{22}O_5S$: C, 60.36; H, 6.51; S, 9.47. Found: C, 60.32; H, 6.56; S, 9.07.

(1*R,4*R**,5*S**)-4-(Methoxycarbonyl)-4-methyl-1-[(phenylsulfonyl)methyl]-8-oxabicyclo[3.2.1]octan-3-one, Ethylene Acetal (15i).** Oxidation of **11i** (*ca.* 1.99 mmol) by the general procedure followed by flash chromatography (2:1 hexanes/ethyl acetate) provided 0.521 g (66% from **13a**) of the title compound: mp 116–118 °C; IR (neat) 1730 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88–7.92 (m, 2H), 7.60–7.66 (m, 1H), 7.51–7.57 (m, 2H), 4.25 (d, J = 7.8 Hz, 1H), 3.86–4.02 (m, 4H), 3.64 (s, 3H), 3.47 (d, J = 14.1 Hz, 1H), 3.33 (d, J = 14.1 Hz, 1H), 2.32–2.41 (m, 1H), 2.19–2.28 (m, 1H), 1.95–2.07 (m, 3H), 1.70 (dt, J = 12.2, 4.3 Hz, 1H), 1.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 140.6, 133.5, 129.0, 127.6, 108.6, 80.0, 79.4, 65.2, 64.6, 63.7, 53.0, 51.3, 42.3, 32.7, 27.9, 20.7; HRMS calcd for $C_{19}H_{24}O_7S$ 396.1243, found 396.1229; LRMS (EI) m/z 396 (15), 241 (100). Anal. Calcd for $C_{19}H_{24}O_7S$: C, 57.58; H, 6.06; S, 8.08. Found: C, 57.36; H, 6.23; S, 7.97.

(1*R,4*S**,5*S**)-4-(Methoxycarbonyl)-4-methyl-1-[(phenylsulfonyl)methyl]-8-oxabicyclo[3.2.1]octan-3-one, Ethylene Acetal (15j).** Oxidation of **11j** (0.129 g, 0.35 mmol) by the general procedure followed by flash chromatography (1:1 hexanes/ethyl acetate) provided 0.134 g (96%) of the title compound: mp 90–93 °C; IR (neat) 1730 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.91 (m, 2H), 7.59–7.65 (m, 1H), 7.51–7.56 (m, 2H), 4.24 (d, J = 7.0 Hz, 1H), 3.81–3.98 (m, 4H), 3.65 (s, 3H), 3.53 (d, J = 14.0 Hz, 1H), 3.31 (d, J = 14.0 Hz, 1H), 2.48 (d, J = 13.4 Hz, 1H), 2.26–2.39 (m, 2H), 2.14 (d, J = 13.4 Hz, 1H), 1.79–1.91 (m, 2H), 1.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 140.7, 133.5, 129.1, 127.7, 107.6, 81.2, 80.3, 64.9, 64.7, 64.3, 55.3, 51.7, 43.1, 32.7, 25.5, 13.5; LRMS (EI) m/z 396 (15), 241 (100). Anal. Calcd for $C_{19}H_{24}O_7S$: C, 57.58; H, 6.06; S, 8.08. Found: C, 57.53; H, 6.24; S, 8.48.

General Procedure for Reductive Cleavage of Sulfones 15 with SmI_2. Diiodomethane (5.5 equiv) was added *via* syringe to a stirred suspension of Sm (6 equiv) in THF under argon. The resultant mixture was stirred at rt for 1.5 h to give a deep blue, 0.1 M solution of SmI_2 in THF. A 0.1 M solution of **15** (1 equiv) in THF was added dropwise, followed by the addition of HMPA (25 equiv). A purple solution formed, and the reaction was stirred at rt (10–40 min). Upon completion of the reaction as determined by thin layer chromatographic analysis, saturated aqueous NH_4Cl was added and the mixture was extracted with ethyl acetate. The organic layer was washed with water and then brine and dried over $MgSO_4$. Concentration followed by flash chromatography (2:1 hexanes/ethyl acetate) provided **16**.

(1*R,2*S**)-1-Hydroxy-2-(methoxycarbonyl)-5-methylenecycloheptan-3-one, Ethylene Acetal (16ai).** Reduction of **15ai** (0.115 g, 0.30 mmol) by the general procedure (10 min) provided 0.063 g (86%) of the title compound: IR (neat) 3478, 1732 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.80 (s, 1H), 4.69 (s, 1H), 4.17–4.26 (m, 1H), 3.96–4.05 (m, 1H), 3.79–3.94 (m, 3H), 3.68 (s, 3H), 2.98 (d, J = 9.3 Hz, 1H), 2.68 (d, J = 15.2 Hz, 1H), 2.51 (d, J = 15.2 Hz, 1H), 2.28–2.43 (m, 2H), 2.23 (br s, 1H), 1.99–2.09 (m, 1H), 1.65–1.76 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 144.0, 114.1, 108.2, 70.4, 65.0, 64.4, 61.3, 51.8, 45.9, 35.7, 30.9; LRMS (EI) m/z 242 (20), 211 (100). Anal. Calcd for $C_{12}H_{18}O_5$: C, 59.50; H, 7.44. Found: C, 59.46; H, 7.64.

(1*R,2*R**)-1-Hydroxy-2-(methoxycarbonyl)-5-methylenecycloheptan-3-one, Ethylene Acetal (16aii).** Reduction of **15aii** (0.154 g, 0.40 mmol) by the general procedure (10 min) provided 0.079 g (81%) of the title compound: IR

(neat) 3499, 1732 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.85 (s, 1H), 4.77 (s, 1H), 4.15–4.22 (m, 1H), 3.90–4.00 (m, 4H), 3.72 (s, 3H), 3.08 (d, J = 2.8 Hz, 1H), 3.02 (d, J = 6.7 Hz, 1H), 2.91 (d, J = 14.5 Hz, 1H), 2.43–2.51 (m, 2H), 2.23–2.31 (m, 1H), 2.01–2.11 (m, 1H), 1.73–1.83 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 143.6, 114.5, 109.1, 69.1, 65.0, 64.1, 57.6, 51.8, 45.3, 33.7, 30.6; HRMS calcd for $C_{12}H_{18}O_5$ 242.1154, found 242.1155; LRMS (EI) m/z 242 (20), 173 (100). Anal. Calcd for $C_{12}H_{18}O_5$: C, 59.50; H, 7.44. Found: C, 59.50; H, 7.72.

4-Hydroxy-5-methylenecyclooctan-3-one, Ethylene Acetal (16b). Reduction of **15b** (0.157 g, 0.46 mmol) by the general procedure (10 min) provided 0.071 g (77%) of the title compound: IR (neat) 3418 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.90 (s, 1H), 4.85 (s, 1H), 3.85–4.00 (m, 5H), 2.56 (s, 1H), 2.41 (d, J = 13.9 Hz, 1H), 2.29 (d, J = 13.9 Hz, 1H), 2.19 (t, J = 6.2 Hz, 2H), 2.00 (dd, J = 14.7, 7.2 Hz, 1H), 1.87–1.96 (m, 2H), 1.70–1.80 (m, 1H), 1.54–1.63 (m, 1H), 1.47–1.53 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 115.8, 110.2, 67.7, 64.5, 64.1, 43.3, 41.8, 38.2, 35.8, 22.4; HRMS calcd for $C_{11}H_{18}O_3$ 198.1256, found 198.1247; LRMS (EI) m/z 198 (15), 141 (100).

(1*R,2*S**)-2-Hydroxy-1-methyl-6-methylenecycloheptan-4-one, Ethylene Acetal (16c).** Reduction of **15c** (0.092 g, 0.27 mmol) by the general procedure (10 min) provided 0.045 g (84%) of the title compound as a white solid: mp 54–55 °C; IR (Nujol mull) 3418 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.84 (s, 1H), 4.76 (s, 1H), 3.89–3.98 (m, 4H), 3.79–3.83 (m, 1H), 2.78 (d, J = 7.6 Hz, 1H), 2.52–2.61 (m, 2H), 2.33 (dd, J = 14.9, 10.8 Hz, 1H), 2.20 (dd, J = 14.9, 3.8 Hz, 1H), 2.13 (dd, J = 14.5, 6.4 Hz, 1H), 1.89 (dd, J = 14.5, 2.5 Hz, 1H), 1.80–1.86 (m, 1H), 1.01 (d, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 114.4, 110.2, 71.7, 64.7, 63.7, 46.1, 43.2, 38.6, 38.2, 19.5; HRMS calcd for $C_{11}H_{18}O_3$ 198.1256, found 198.1247; LRMS (EI) m/z 198 (40), 154 (100). Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.67; H, 9.09. Found: C, 66.97; H, 9.18.

1-Hydroxy-1-methylcyclohept-5-ene-3-one, Ethylene Acetal (16e). Reduction of **15e** (0.114 g, 0.35 mmol) by the general procedure (45 min) provided 0.050 g (77%) of the title compound: IR (neat) 3526 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.74–5.84 (m, 2H), 3.88–3.99 (m, 4H), 3.66 (br s, 1H), 2.52 (d, J = 12.9 Hz, 1H), 2.30–2.39 (m, 3H), 2.02 (d, J = 14.3 Hz, 1H), 1.94 (d, J = 14.3 Hz, 1H), 1.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.5, 127.2, 108.0, 69.9, 64.8, 63.9, 51.5, 40.5, 37.3, 31.4; HRMS calcd for $C_{10}H_{16}O_3$ 184.1099, found 184.1100; LRMS (EI) m/z 184 (15), 126 (70), 43 (100).

4-Hydroxy-1-methylcyclohept-1-ene-6-one, Ethylene Acetal (16f). Reduction of **15f** (0.137 g, 0.42 mmol) by the general procedure (15 min) provided 0.062 g (80%) of the title compound: IR (neat) 3418 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.51 (t, J = 6.5 Hz, 1H), 3.85–4.00 (m, 5H), 2.45–2.53 (m, 2H), 2.39 (dd, J = 14.7, 7.6 Hz, 1H), 2.33 (d, J = 14.4 Hz, 1H), 2.25 (dd, J = 14.7, 6.2 Hz, 1H), 2.08 (d, J = 5.0 Hz, 2H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1, 120.9, 107.7, 67.0, 64.6, 64.3, 47.7, 42.4, 35.1, 26.9; HRMS calcd for $C_{10}H_{16}O_3$ 184.1099, found 184.1108; LRMS (EI) m/z 184 (15), 115 (100).

1-Hydroxy-1-methyl-5-methylenecycloheptan-3-one, Ethylene Acetal (16g). Reduction of **15g** (0.140 g, 0.41 mmol) by the general procedure (15 min) provided 0.065 g (79%) of the title compound: IR (neat) 3517 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.81 (s, 1H), 4.72 (s, 1H), 3.85–4.02 (m, 4H), 3.70 (br s, 1H), 2.48–2.66 (m, 3H), 2.23 (ddd, J = 15.6, 7.0, 2.8 Hz, 1H), 1.93 (d, J = 14.4 Hz, 1H), 1.87 (d, J = 14.4 Hz, 1H), 1.77–1.85 (m, 1H), 1.64–1.73 (m, 1H), 1.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 113.4, 110.0, 70.4, 65.0, 63.6, 49.3, 46.1, 40.9, 31.5, 30.1; HRMS calcd for $C_{11}H_{18}O_3$ 198.1256, found 198.1264; LRMS (EI) m/z 198 (15), 129 (100). Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.67; H, 9.09. Found: C, 66.31; H, 9.31.

(1*R,2*S**)-1-Hydroxy-2-(methoxycarbonyl)-2-methyl-5-methylenecycloheptan-3-one, Ethylene Acetal (16i).** Reduction of **15i** (0.082 g, 0.21 mmol) by the general procedure (10 min) provided 0.043 g (81%) of the title compound as a white solid: mp 108–109 °C; IR (Nujol mull) 3467, 1705 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.79 (s, 1H), 4.67 (s, 1H), 4.44–4.50 (m, 1H), 3.69–4.03 (m, 4H), 3.67 (s, 3H), 2.54–2.66 (m, 2H), 2.35–2.45 (m, 1H), 2.29 (ddd, J = 14.1, 6.7, 3.0 Hz, 1H), 2.12 (d, J = 6.6 Hz, 1H), 1.84–1.92 (m, 1H), 1.60–1.71 (m, 1H), 1.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 144.8, 113.2, 111.0, 72.9, 64.8, 64.4, 60.0, 52.0, 42.4, 33.3, 30.9, 12.5; HRMS calcd for $C_{13}H_{20}O_5$ 256.1311, found 256.1317; LRMS (EI) m/z 256 (30), 225 (100). Anal. Calcd for $C_{13}H_{20}O_5$: C, 60.94; H, 7.81. Found: C, 61.02; H, 8.12.

(1*R,2*R**)-1-Hydroxy-2-(methoxycarbonyl)-2-methyl-5-methylenecycloheptan-3-one, Ethylene Acetal (16j).** Reduction of **15j** (0.090 g, 0.23 mmol) by the general procedure (20 min) provided 0.046 g (79%) of the title compound: IR (neat) 3520, 1714 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.78 (s, 1H), 4.67 (s, 1H), 3.87–4.02 (m, 4H), 3.74–3.81 (m, 1H), 3.70 (s, 3H), 3.32 (d, J = 9.9 Hz, 1H), 2.77 (d, J = 15.6 Hz, 1H), 2.54 (d, J = 15.6 Hz, 1H), 2.39–2.47 (m, 1H), 2.23–2.31 (m, 1H), 1.91–2.05 (m, 2H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 144.8, 113.2, 110.6, 75.3, 65.1, 64.1, 58.6, 51.9, 43.8, 33.8, 30.9, 18.7; HRMS calcd for $C_{13}H_{20}O_5$ 256.1311, found 256.1306; LRMS (EI) m/z 256 (15), 225 (100). Anal. Calcd for $C_{13}H_{20}O_5$: C, 60.94; H, 7.81. Found: C, 61.20; H, 8.19.

(1*R,4*R**,5*S**)-4-(Methoxycarbonyl)-4-methyl-1-[1-(phenylsulfonyl)ethyl]-8-oxabicyclo[3.2.1]octan-3-one, Ethylene Acetal (15k).** *n*-BuLi (1.6 M in hexanes, 0.170 mL, 0.27 mmol) was added to a stirred solution of $(i\text{-}Pr)_2NH$ (0.028 g, 0.27 mmol) in THF (0.5 mL) at −78 °C under argon. After stirring for 60 min, a solution of **15i** (0.100 g, 0.25 mmol) in THF (0.5 mL) was added dropwise to form a yellow solution. After a further 60 min MeI (0.180 g, 1.27 mmol) was added and the mixture was warmed slowly to rt over 2 h. Water was added, and the mixture was extracted with ethyl acetate. The organic extract was washed with water and then brine and dried over $MgSO_4$. Concentration followed by flash chromatography (1:1 hexanes/ethyl acetate) afforded 0.076 g (73%) of the title compound as a 4:1 mixture of isomers: ^1H NMR (400 MHz, $CDCl_3$) major isomer δ 7.82–7.89 (m, 2H), 7.47–7.63 (m, 3H), 4.22 (d, J = 7.6 Hz, 1H), 3.86–4.00 (m, 4H), 3.61 (s, 3H), 3.33 (q, J = 7.0 Hz, 1H), 2.29–2.37 (m, 1H), 2.10–2.21 (m, 2H), 1.86–2.01 (m, 2H), 1.63–1.73 (m, 1H), 1.34 (s, 3H), 1.25 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) major isomer δ 173.8, 139.9, 133.4, 128.9, 128.5, 109.1, 82.3, 80.5, 66.9, 65.4, 63.9, 53.2, 51.4, 41.4, 30.8, 27.8, 20.9, 10.3; HRMS calcd for $C_{20}H_{26}O_7S$ 410.1399, found 410.1379; LRMS (EI) m/z 410 (15), 269 (100).

(*E*)- and (*Z*)-(1*R,2*S**)-5-(1′-Ethylene)-1-hydroxy-2-(methoxycarbonyl)-2-methylcycloheptan-3-one, Ethylene Acetal (16k).** Reduction of **15k** (0.070 g, 0.17 mmol) by the general procedure (5 min) provided 0.030 g (65%) of the title compound as a 1.3:1 mixture of olefinic isomers: IR (neat) 3498, 1732 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.29 (q, J = 6.4 Hz, 0.57H), 5.19 (q, J = 6.5 Hz, 0.43 H), 4.50–4.57 (m, 0.57H), 4.35–4.41 (m, 0.43H), 3.70–4.09 (m, 4H total), 3.68 (s, 3H total), 2.11–2.64 (m, 4H total), 1.56–1.95 (m, 2H total), 1.54 (d, J = 6.4 Hz, 1.7H), 1.48 (d, J = 6.5 Hz, 1.3H), 1.34 (s, 1.3H), 1.25 (s, 1.7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 174.1, 135.3, 134.4, 122.1, 121.6, 111.8, 111.2, 73.2, 73.0, 65.1, 64.7, 64.5, 64.2, 60.2, 59.6, 52.1, 51.9, 43.9, 37.2, 34.5, 32.1, 31.2, 24.1, 13.4, 13.1, 13.0, 12.1; HRMS calcd for $C_{14}H_{22}O_5$ 270.1467, found 270.1471; LRMS (EI) m/z 270 (100).

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Supporting Information Available: ^1H and ^{13}C spectra of compounds for which no elemental analysis was obtained (59 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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