Cyclopropyl Building Blocks for Organic Synthesis, 38[◇]

Highly Functionalized Bicyclo[3.2.1]octane Derivatives from Readily Available 2′-Alkoxytricyclo[3.2.1.0^{2,7}]octanes: Building Blocks for Terpenes, Part I☆

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2′-Alkoxytricyclo[3.2.1.0^{2,7}]octanes **4-R** are obtained in good to excellent yields from methyl 2-chloro-2-cyclopropylideneacetate (**3**) and the dienolates derived from the 3-alkoxycyclohex-2-enones **1-R** and **2-R**, by a cascade of two consecutive Michael additions and a γ-elimination. Compounds **4-R** are transformed to the correspondingly substituted bicyclo[3.2.1]octanecarboxylates **5** by treatment with acid. 2′-Methoxytricyclooctanes **4a−d-Me** are readily deprotonated to give chelation-stabilized cyclopropyllithium derivatives **6-Me**, which react with electrophiles to yield the 7′-substituted tricyclo[3.2.1.0^{2,7}]octanes **4f−i-Me** (61−66%). By acidic workup of such reaction mixtures, or subsequent treatment of the isolated products **4f−i-Me** with acid, efficient transformation to the correspondingly substituted bicyclo[3.2.1]octanecarboxylates **5** is observed.

The bicyclo[3.2.1]octane ring system is a key structural component in a large variety of tri- and tetracyclic sesqui- and diterpenes and their metabolites.[2] The basic skeleton has frequently been constructed by intramolecular alkylation,[3] ring expansion,[4] and aldol reaction.[5] The facile formation of tricyclo[3.2.1.0^{2,7}]octane derivatives upon cascade cycloaddition[6] of methyl 2-chloro-2-cyclopropylideneacetate (**3**), which is readily available in three steps from ethylene and tetrachlorocyclopropene,[7] with cyclohexa-1,3-dienolates Li-**1R**, prompted us to investigate such compounds further and to look at their subsequent transformations to highly functionalized bicyclic skeletons. The 2′-alkoxy-substituted derivatives **4** are of particular interest, as they contain a vicinally "push-pull"-type substituted cyclopropane unit,[8] and can therefore undergo an acid-catalyzed retro-aldol reaction to give functionalized bicyclo[3.2.1]octane derivatives **5**, some of which appear to be potential precursors to spirocyclopropane analogues of terpenoid natural products.

A number of lithium cyclohexadienolates Li-**1-R**, generated from the corresponding 3-alkoxycyclohex-2-enones **1-R** with lithium diisopropylamide (LDA), reacted with the α-chloroacrylate **3** to give the tricyclic γ-oxo esters **4-R** in good yields.[9] The enones, **1b-Me** and **1d-Bu**, were obtained by alkylation of the dienolates from **1a-Me** and **1c-Bu** with, respectively, methyl iodide and allyl bromide.

Enone **2-Bzl** was prepared by *C*-allylation of cyclohexane-1,3-dione and subsequent *O*-benzylation, demonstrating an option for additional functionalization of the tricyclo[3.2.1.0^{2,7}]octanes **4-R** at C-5′ and C-7′. Treatment of the tricyclic γ-oxo esters **4-R** with an acid (HCl, CF_3COOH, *p*-TsOH) in dichloromethane afforded the 2′,6′-dioxobicyclo[3.2.1]octanecarboxylates **5** in excellent yields (51−98%). Moreover, this two-step process, consisting of a cascade of two consecutive Michael additions followed by γ-elimination, and then subsequent retrograde aldol reaction under acidic hydrolytic conditions, could easily be carried out in one pot.

Kinetic Acidity of the Tricyclic Oxo Ester 4-R and the Reaction of 6-Me with Electrophiles

Deprotonation of the tricyclic γ-oxo ester **4-Me** with LDA in THF occurred only at C-7′. This could be shown by the constitution of the isolated products after quenching of **6-Me** with electrophiles. Thus, alkylation and silylation with methyl iodide and chlorotrimethylsilane gave **4f-Me** and **4g-Me**, in 61% and 66% yield, respectively.

It is quite remarkable, since it cannot lead to a regularly stabilized enolate,[10] that the tricyclic γ-oxo ester **4c-Me** is so easily deprotonated, even though the carbonyl group at C-6′ exerts its usual electron-withdrawing effect and thereby

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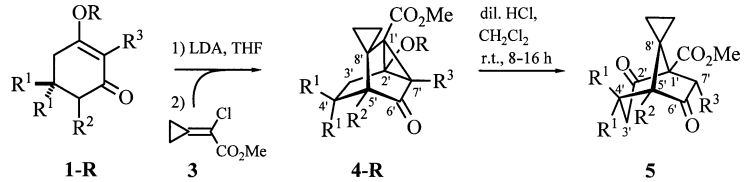
  1434−193X/98/0303−0441 $ 17.50+.50/0

Scheme 1

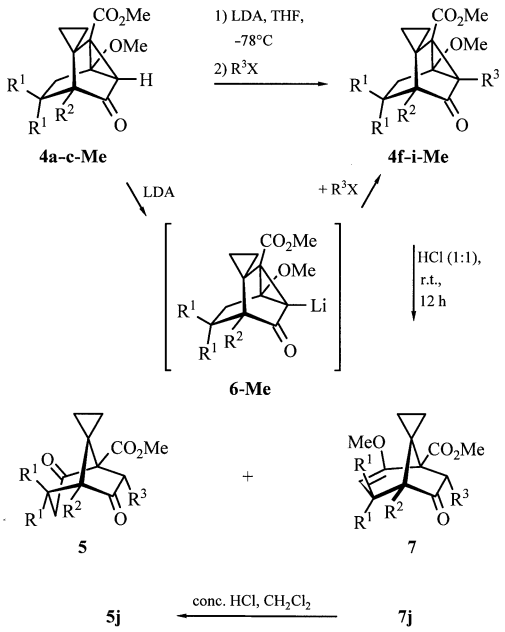


1-R **3** **4-R** **5**

2-R (R = Bzl, R^1, R^2 = H, R^3 = allyl)

1-R, 4-R	a	a	b	c	c	c	c	c	d	e	5a	b	c	d	e
R	Me	Et	Me	Me	Et	*i*Pr	allyl	Bu	Bu	Bzl	–	–	–	–	–
R^1	H	H	H	Me	Me	Me	Me	Me	Me	H	H	H	Me	Me	H
R^2	H	H	Me	H	H	H	H	H	allyl	H	H	Me	H	allyl	H
R^3	H	H	H	H	H	H	H	H	H	allyl	H	H	H	H	allyl
Yield (%)	59	60	82	83	58	71	66	72	61	29	quant.	96	91	99	51

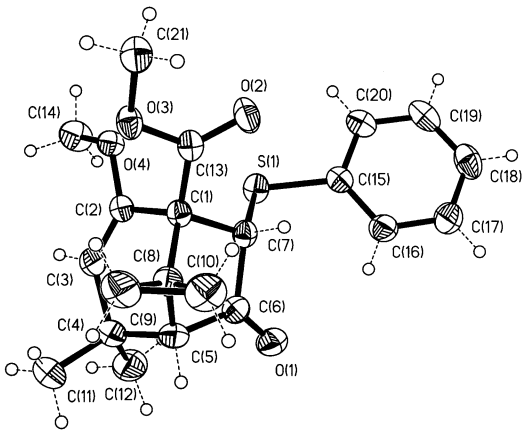
Scheme 2



	R^1	R^2	R^3	Yield (%)
4f-Me	Me	H	Me	61
4g-Me	Me	H	TMS	66
4h-Me	Me	H	allyl	0
4i-Me	Me	H	SPh	0
5f	Me	H	Me	94
5g	Me	H	TMS	80
5j	H	Me	SPh	99
7g	Me	H	TMS	18
7i	Me	H	SPh	69
7j	H	Me	SPh	73
7k	H	H	SPh	13

increases the kinetic acidity of the adjacent cyclopropylic proton. Of at least equal importance, however, is the alkoxy group on the cyclopropane ring, which can stabilize the lithiated species by chelation.[11] It was rather surprising, though, that the allyl derivative **4h-Me** could not be isolated in pure form as it completely decomposed during attempted column chromatography, when employing either ordinary or flash silica gel as an adsorbent. However, it was possible to prepare the allyl-substituted **4e-Bzl** directly from the enone **2-Bzl** and chloroacrylate **3** if acidic workup conditions were avoided. Under acidic conditions the tricyclic compound **4e-Bzl** rearranged easily to give the diketone **5e.** Treatment of the tricyclic γ-oxo esters **4a-Me**, **4b-Me**, **4c-Me** with LDA, followed by quenching the corresponding lithio derivatives with diphenyl disulfide, afforded the β-*endo*-phenylsulfanyl-substituted γ-oxo esters **7i–k** in good yields with the exception of **7k**. The configuration of **7i** was confirmed by X-ray crystal structure analysis (Figure 1). The methyl enol ether moiety in the bicyclic β-oxo sulfide **7j** easily could be cleaved by treatment with HCl in dichloromethane.

Figure 1. Molecular structure of compound **7i** in the crystal, the thermal ellipsoids are drawn at the 50% probability level[12]

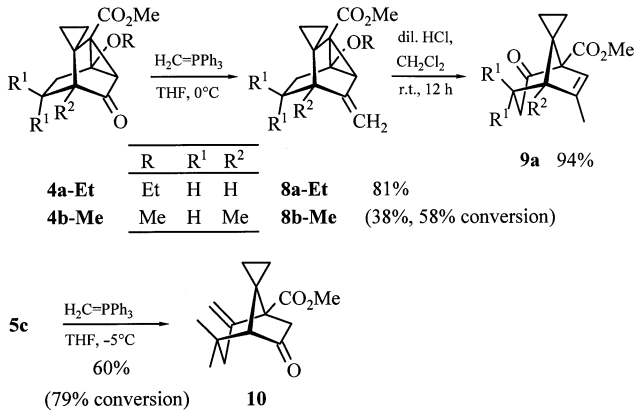


Reactivity of the Carbonyl Groups in the γ-Oxo Esters 4-R and 7

The Wittig olefination (2.5 equiv. of methylenetriphenylphosphorane were used) of the tricyclic γ-oxo esters **4a-Et**, **4b-Me** afforded the 6-methylene tricycles **8a-Et** and **8b-Me** in 81% and 38% isolated yields, respectively, while compound **4c-Me**, with its two methyl substituents on C-4′,

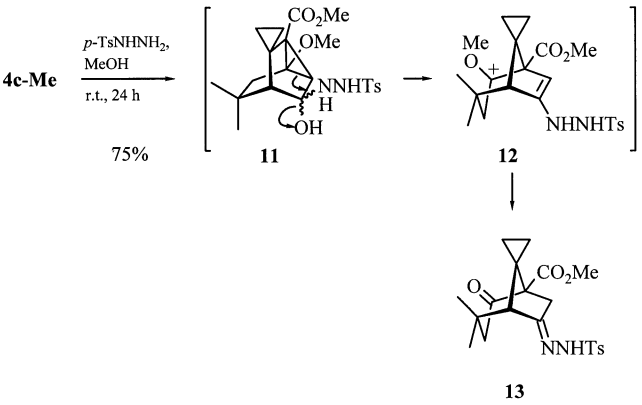
did not react at all when treated with the ylide, even for prolonged times. Apparently, the attack of the methylenephosphorane is blocked by the 4′-*endo*-methyl group. Treatment of the 6′-methylene-2′-methoxytricyclo[3.2.1.0^{2,7}]octane **8a-Et** with dilute HCl afforded the 6′-methyl-2′-oxobicyclo[3.2.1]oct-6′-ene-1′-carboxylate **9a** in a 94% yield. Quite surprisingly, the 2,6-dioxobicyclo[3.2.1]octane-1-carboxylate **5c** reacted completely regioselectively with the Wittig ylide at −10°C, and gave only the 2′-methylene-6′-oxobicyclo[3.2.1]octane-1′-carboxylate **10** in a 60% yield.

Scheme 3



Treatment of the tricyclic γ-oxo ester **4c-Me** with *p*-tosylhydrazine in methanol afforded the bicyclic hydrazone **13** (75%). Most probably the intermediate **11,** formed upon addition of *p*-tosylhydrazine to the carbonyl group of **4c-Me**, undergoes opening of the three-membered ring to yield the oxo compound **13** via the intermediate **12**.

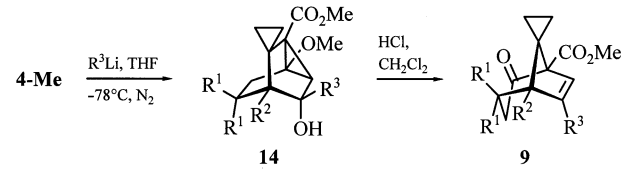
Scheme 4



Furthermore, treatment of the tricyclic γ-oxo esters **4-R** with an organolithium reagent yielded the *endo*-alcohols **14** in moderate to excellent yields. Undoubtedly, only one diastereomer was formed in all cases, and the *endo* configuration at C-6′ is reflected by the appearance of two signals for cyclopropyl protons at δ = −0.8 and −0.2 for the alcohol **14n**.

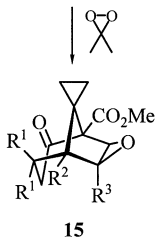
The alcohols **14** could be easily transformed into 6′-alkyl-2′-oxobicyclo[3.2.1]oct-6′-enes **9** by treatment with conc. HCl in dichloromethane. The epoxidation of the bicyclo[3.2.1]octenones **9** with dimethyldioxirane[13] gave the *exo*-

Scheme 5



Starting Material	R^1	R^2	R^3		Yield 14 (%)		Yield (%) 9	15
4b-Me	H	Me	Me	**l**	95	**l**	71	91
4c-Me	Me	H	Me	**m**	54			
4c-Me	Me	H	Ph	**n**	66	**n**	86	98
4c-Me	Me	H	$HC(SPh)_2$	**o**	44			
4c-Me	Me	H	≡–OH	**p**	65			
4a-Et	H	H	Me			**a**[a]		37

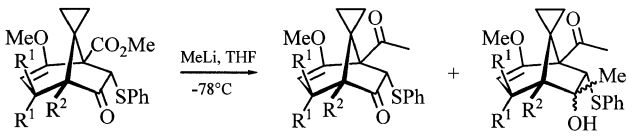
[a] See Scheme 3.



epoxides **15** in good yields. Epoxide **15n** was also detected (TLC) after treatment of the alkene **9n** with *m*-chloroperbenzoic acid (*m*-CPBA), but the attempted removal of *m*-chlorobenzoic acid, and excess peracid by washing with $NaHCO_3$ solution, led to complete decomposition.

Reaction of the methyl 2′-methoxy-7′-phenylsulfanyl-6′-oxobicyclo[3.2.1]oct-2′-ene-1-carboxylate **7i** with methyllithium occurred exclusively with addition at the ester function, instead of the desired addition at the C-6′ carbonyl group. However, the bridgehead methyl ketone derivative **16j** does add methyllithium at the C-6′ carbonyl group to form the desired alcohol **17j**, albeit with low diastereoselectivity (4:1), whilst the 4′,4′-dimethyl-substituted derivative **16i** did not react with methyllithium under these conditions.

Scheme 6

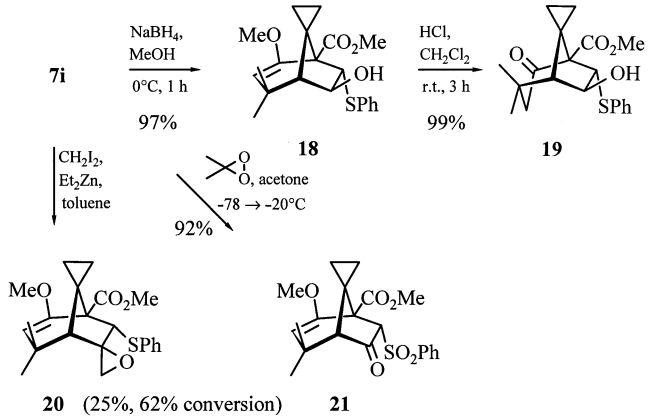


Starting Material	R^1	R^2	Yield (%)		Yield (%)
7i	Me	H	**16i**	93	**17i** 0
7j	H	Me	**16j**	62	**17j** 28

Reduction of the bicyclic γ-oxo ester **7i** with excess sodium tetrahydridoborate proceeded smoothly to give the *exo*-alcohol **18** in quantitative yield. Upon treatment of **18** with an acid its enol ether functionality was cleaved, affording the ketone **19** in a 99% yield. When the bicyclic γ-oxo ester **7i** was treated with a solution of dimethyldioxirane in acetone, only its phenylsulfanyl group was oxidized to afford the β-oxo sulfone **21** in a 92% yield, which means that no epoxidation at the electron-rich double bond occurred under the reaction conditions (−78 to −20°C). It is conceivable that the two methyl groups on C-4 prevent an attack on the double bond, at least at low temperature. In

line with this, the enol ether moiety in the bicyclic γ-oxo ester **7i** was not cyclopropanated with diiodomethane/diethylzinc; attack of this reagent occurred only at the carbonyl group to yield the epoxide **20** (40%, 62% conversion). The bridgehead methyl-substituted γ-oxo ester **7j** did not react with diiodomethane/diethylzinc under the same conditions.

Scheme 7



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Experimental Section

THF was dried over sodium/benzophenone and distilled prior to use. All reactions with moisture- and air-sensitive compounds were performed in flame-dried glassware under a positive pressure of nitrogen. Reaction mixtures were stirred magnetically unless otherwise indicated. Air- and moisture-sensitive liquids and solutions were transferred by syringe or cannula into reaction vessels through rubber septa. Reaction product solutions and chromatography fractions were concentrated using a Büchi rotary evaporator at ca. 20 Torr. − ^{1}H NMR and ^{13}C NMR: Bruker WM 250 and AM 250 at 250 and 62.9 MHz, respectively. − IR: Bruker IFS (FT) spectrophotometer and Zeiss Spektralphotometer IMR-25. − UV: Zeiss DMR 10. − MS: Varian MAT 311 A and Finnigan MAT CH 7, EI, 70 eV, low and high resolution. − GC: GC 8000 Series, Fisons Instruments, capillary column: DB 1, 10 m, methylsilicon rubber, nitrogen as carrier gas. − M. p. (not corrected): Büchi-SMP-20. − TLC: DC-aluminum foil, silica gel 60 F_{254}, Merck, Darmstadt. − Column chromatography: Silica gel 60, 0.063−0.200 mm (70−220 mesh ASTM), Merck, Darmstadt. − Short-path distillation: Kugelrohr GKR-50, Büchi, Buchs, Switzerland. Temperatures are path temperatures. − Elemental analyses: Mikroanalytisches Laboratorium des Institutes für Organische Chemie der Universität Göttingen and Mikroanalytisches Laboratorium der Universität Stuttgart.

General Procedure for the Preparation of Tricyclo[3.2.1.0^{2,7}]-octanones **4-R**: A 1.66−3.03 M solution of *n*-butyllithium in hexane or cyclohexane was slowly added to a cooled (−10°C), stirred solution of dry diisopropylamine (1.40−5.50 ml) in anhydrous THF (10−40 ml) under N_2. The resulting solution was stirred at −10°C for 30 min, cooled to −78°C, and a solution of the 3′-alkoxycyclohex-2′-enone **1-R** (10−37.5 mmol) in anhydrous THF (10−20 ml) was added over 10 min. The resulting solution was stirred at −78°C for 30 min and a solution of methyl 2-chloro-2-cyclopropylideneacetate (**3**) (10−36.5 mmol) in anhydrous THF (10−20 ml) was added within 10 min. The resulting solution was stirred overnight. Saturated NH_4Cl solution (10 ml) was added, the organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (3 × 30 ml), and the combined organic layers were washed with brine (2 × 50 ml) and dried ($MgSO_4$). The solvent was evaporated and the residue was either chromatographed on silica gel (eluent: CH_2Cl_2), or crystallized from cold pentane, to afford the pure tricyclo[3.2.1.0^{2,7}]octanone **4-R**.

Methyl 2′-Methoxy-6′-oxospiro[cyclopropane-1,8′-tricyclo-[3.2.1.0^{2,7}]octane]-1′-carboxylate (**4a-Me**): From 1.26 g (10 mmol) of 3-methoxycyclohex-2-enone (**1a-Me**) and 1.46 g (10 mmol) of **3**. Yield 1.40 g (59%), colorless crystals, m. p. 79−80°C (hexane). − IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1}, 1720, 1440, 1345, 1265, 1220, 1150, 1095, 1030, 880. − ^{1}H NMR ($CDCl_3$): δ = 0.38−0.52 (m, 2 H), 0.64 (m, 1 H), 1.18 (m, 1 H), 1.48 (m, 1 H), 1.60 (m, 1 H), 1.90 (m, 1 H), 2.34 (m, 2 H), 2.62 (d, *J* = 1.7 Hz, 1 H), 3.28 (s, 3 H), 3.60 (s, 3 H). − ^{13}C NMR ($CDCl_3$): δ = 5.0, 9.3, 19.3, 22.8, 24.4, 41.0, 46.2, 50.1, 51.9, 55.3, 75.9, 165.9, 207.5. − MS (70 eV); *m/z* (%): 236 (52) [M$^+$], 208 (100), 193 (42), 177 (23), 165 (24), 161 (34), 149 (83), 133 (22), 122 (41), 117 (37), 105 (29), 91 (50), 77 (28). − $C_{13}H_{16}O_4$ (236.3): calcd. C 66.09, H 6.83; found C 66.04, H 6.78.

Methyl 2′-Ethoxy-6′-oxospiro[cyclopropane-1,8′-tricyclo[3.2.1.0^{2,7}]-octane]-1′-carboxylate (**4a-Et**): From 1.40 g (10 mmol) of 3-ethoxycyclohex-2-enone (**1a-Et**) and 1.46 g (10 mmol) of **3**. Yield 1.49 g (60%), colorless oil, b. p. 110°C (< 0.01 Torr). − ^{1}H NMR ($CDCl_3$): δ = 0.50 (m, 2 H), 0.73 (m, 1 H), 1.09 (t, ^3J = 7.0 Hz, 3 H), 1.25 (m, 1 H), 1.52 (quint, ^3J = 2.1 Hz, 1 H), 1.63 (m, 1 H), 1.92 (m, 1 H), 2.32 (ddd, *J* = 13.9, 11.1, 3.2 Hz, 1 H), 2.47 (ddd, *J* = 13.9, 10.6, 6.1 Hz, 1 H), 2.70 (d, *J* = 1.7 Hz, 1 H), 3.47 (m, 1 H), 3.63 (m, 1 H), 3.64 (s, 3 H). − ^{13}C NMR ($CDCl_3$): δ = 5.1, 9.4, 15.2, 20.5, 23.0, 24.4, 41.5, 46.0, 50.3, 51.8, 63.8, 75.5, 166.1, 207.8. − MS (70 eV); *m/z* (%): 250 (26) [M$^+$], 222 (100), 193 (61), 165 (28), 163 (56), 135 (52), 107 (24), 105 (38), 91 (41), 77 (22). − Attempted purification by distillation under reduced pressure yielded mixtures of **4a-Et** and **5a**.

Methyl 2′-Methoxy-5′-methyl-6′-oxospiro[cyclopropane-1,8′-tricyclo[3.2.1.0^{2,7}]octane]-1′-carboxylate (**4b-Me**): From 2.80 g (20 mmol) of 3-methoxy-6-methylcyclohex-2-enone (**1b-Me**) and 2.93 g (20 mmol) of **3**. Yield 4.10 g (82%), colorless crystals, m. p. 88−89°C (hexane). − IR (KBr): $\tilde{\nu}$ = 2932 cm^{-1}, 1734, 1457, 1436, 1341, 1288, 1235, 1157, 1060, 1024. − ^{1}H NMR ($CDCl_3$): δ = 0.38 (m, 1 H), 0.52 (m, 2 H), 0.56 (s, 3 H), 1.22 (m, 1 H), 1.41 (m, 1 H), 1.67 (m, 1 H), 2.27−2.49 (m, 2 H), 2.69 (s, 1 H), 3.35 (s, 3 H), 3.67 (s, 3 H). − ^{13}C NMR ($CDCl_3$): δ = 3.6, 5.9, 12.8, 19.6, 27.2, 31.0, 39.9, 45.7, 51.8, 55.2, 75.5, 166.1, 209.0. − MS (70 eV); *m/z* (%): 250 (26) [M$^+$], 222 (82), 207 (55), 193 (17), 191 (79), 179 (24), 175 (30), 163 (100), 147 (28), 135 (18), 131 (33), 119 (16), 105 (27), 91 (41), 77 (22). − $C_{14}H_{18}O_4$ (250.3): calcd. C 67.18, H 7.25; found C 67.30, H 7.39.

Methyl 2′-Methoxy-4′,4′-dimethyl-6′-oxospiro[cyclopropane-1,8′-tricyclo[3.2.1.0^{2,7}]octane]-1′-carboxylate (**4c-Me**): From 5.78 g (37.5 mmol) of 3-methoxy-5,5-dimethylcyclohex-2-enone (**1c-Me**) and 5.35 g (36.5 mmol) of **3**. Yield 8.00 g (83%), colorless crystals, m. p. 89−90°C (hexane). − IR (KBr): $\tilde{\nu}$ = 2995 cm^{-1}, 1734, 1438, 1349, 1243, 1223, 1187, 1167, 1129, 1062. − ^{1}H NMR ($CDCl_3$): δ = 0.29 (m, 1 H), 0.42 (m, 1 H), 0.85 (m, 1 H), 0.86 (s, 3 H), 1.10 (d, *J* = 1.4 Hz, 1 H), 1.16 (s, 3 H), 1.44 (m, 1 H), 2.07 (d, *J* = 13.7

Hz, 1 H), 2.33 (d, J = 13.7 Hz, 1 H), 2.54 (d, J = 1.4 Hz, 1 H), 3.28 (s, 3 H), 3.63 (s, 3 H). − ^{13}C NMR ($CDCl_3$): δ = 6.5, 7.5, 23.0, 29.72, 29.74, 34.0, 35.8, 39.3, 45.7, 52.0, 55.1, 60.6, 73.9, 166.2, 206.4. − MS (70 eV); *m/z* (%): 264 (11) [M^+], 236 (27), 222 (67), 205 (27), 189 (36), 177 (53), 161 (45), 154 (38), 122 (36), 98 (100), 91 (22), 68 (59). − $C_{15}H_{20}O_4$ (264.3): calcd. C 68.16, H 7.63; found C 68.45, H 7.60.

Methyl 2′-Ethoxy-4′,4′-dimethyl-6′-oxospiro[cyclopropane-1,8′-tricyclo[3.2.1.0^{2,7}]octane]-1′-carboxylate (**4c-Et**): From 1.68 g (10 mmol) of 3-ethoxy-5,5-dimethylcyclohex-2-enone **1c-Et** and 1.46 g (10 mmol) of **3**. Yield 1.60 g (58%), colorless crystals, m. p. 84−86°C (hexane). − IR (KBr): $\tilde{\nu}$ = 2990 cm^{-1}, 2963, 1734, 1722, 1432, 1369, 1342, 1238, 1079. − ^{1}H NMR ($CDCl_3$): δ = 0.22 (m, 1 H), 0.39 (m, 1 H), 0.81 (s, 3 H), 0.82 (m, 1 H), 0.98−1.05 (m, 4 H), 1.11 (s, 3 H), 1.41 (m, 1 H), 2.00 (d, J = 13.7 Hz, 1 H), 2.33 (d, J = 13.7 Hz, 1 H), 2.52 (m, 1 H), 3.35−3.55 (m, 2 H), 3.58 (s, 3 H). − ^{13}C NMR ($CDCl_3$): δ = 6.4, 7.4, 15.1, 22.9, 29.6 (2 signals), 34.0, 36.8, 39.6, 45.3, 51.7, 60.6, 63.5, 73.2, 166.2, 206.4. − MS (70 eV); *m/z* (%): 278 (30) [M^+], 250 (100), 235 (64), 222 (64), 229 (27), 207 (28), 191 (69), 175 (56), 163 (33), 161 (36), 147 (48), 135 (42), 119 (34), 105 (55), 91 (40), 83 (33), 77 (33). − $C_{16}H_{22}O_4$ (278.3): calcd. C 69.04, H 7.97; found C 69.03 H, 7.91.

Methyl 2′-Isopropyloxy-4′,4′-dimethyl-6′-oxospiro[cyclopropane-1,8′-tricyclo[3.2.1.0^{2,7}]octane]-1′-carboxylate (**4c-iPr**): From 1.82 g (10 mmol) of 3-isopropyloxy-5,5-dimethylcyclohex-2-enone (**1c-iPr**) and 1.46 g (10 mmol) of **3**. Yield 2.07 g (71%). − ^{1}H NMR ($CDCl_3$): δ = 0.26 (m, 1 H), 0.43 (m, 1 H), 0.85 (m, 1 H), 0.86 (s, 3 H), 1.03−1.12 (m, 7 H), 1.15 (s, 3 H), 1.47 (m, 1 H), 2.05 (d, J = 13.8 Hz, 1 H), 2.38 (d, J = 13.8 Hz, 1 H), 2.65 (br. s, 1 H), 3.61 (s, 3 H), 3.82 (sept, J = 6.2 Hz, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 6.6, 7.5, 22.9, 23.0, 23.6, 29.8, 29.9, 33.9, 38.7, 39.8, 45.1, 51.7, 60.8, 71.4, 73.0, 166.3, 206.9.

Methyl 2′-Allyloxy-4′,4′-dimethyl-6′-oxospiro[cyclopropane-1,8-tricyclo[3.2.1.0^{2,7}]octane]-1-carboxylate (**4c-allyl**): From 1.70 g (9.4 mmol) of 3-allyloxy-5,5-dimethylcyclohex-2-enone (**1c-allyl**) and 1.46 g (10 mmol) of **3**. Yield 1.82 g (66%), colorless crystals, m. p. 82−84°C (hexane). − IR (KBr): $\tilde{\nu}$ = 3078 cm^{-1}, 2965, 2932, 1724, 1457, 1435, 1373, 1340, 1234, 1191, 1130, 912. − ^{1}H NMR ($CDCl_3$): δ = 0.28 (m, 1 H), 0.45 (m, 1 H), 0.86 (m, 1 H), 0.86 (s, 3 H), 1.11 (d, J = 1.3 Hz, 1 H), 1.16 (s, 3 H), 1.47 (m, 1 H), 2.07 (d, J = 13.7 Hz, 1 H), 2.39 (d, J = 13.7 Hz, 1 H), 2.61 (d, J = 1.3 Hz, 1 H), 3.62 (s, 3 H), 3.90−4.08 (m, 2 H), 5.07−5.22 (m, 2 H), 5.79 (m, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 6.6, 7.5, 23.0, 29.7, 34.1, 37.0, 39.7, 45.3, 51.9, 60.7, 69.0, 73.4, 116.8, 133.5, 166.2, 206.4. − MS (70 eV); *m/z* (%): 290 (5) [M^+], 262 (19), 249 (31), 222 (65), 189 (55), 165 (32), 161 (38), 147 (22), 133 (31), 119 (27), 105 (15), 91 (18), 83 (100). − $C_{17}H_{22}O_4$ (290.4): calcd. C 70.32, H 7.64; found C 70.99, H 8.00.

Methyl 2′-Butyloxy-4′,4′-dimethyl-6′-oxospiro[cyclopropane-1,8′-tricyclo[3.2.1.0^{2,7}]octane]-1′-carboxylate (**4c-Bu**): From 1.96 g (10 mmol) of 3-butyloxy-5,5-dimethylcyclohex-2-enone (**1c-Bu**) and 1.46 g (10 mmol) of **3**. Yield 2.20 g (72%), colorless crystals, m. p. 50−51°C (hexane). − IR (KBr): $\tilde{\nu}$ = 3079 cm^{-1}, 2944, 2948, 2871, 1730, 1461, 1437, 1369, 1236, 1197, 1084, 969, 886. − ^{1}H NMR ($CDCl_3$): δ = 0.25 (m, 1 H), 0.42 (m, 1 H), 0.81−0.91 (m, 7 H), 1.09 (d, J = 1.5 Hz, 1 H), 1.15 (s, 3 H), 1.23−1.29 (m, 2 H), 1.38−1.48 (m, 3 H), 2.05 (d, J = 13.7 Hz, 1 H), 2.35 (d, J = 13.7 Hz, 1 H), 2.56 (d, J = 1.5 Hz, 1 H), 3.32 (dt, J = 8.8, 6.5 Hz, 1 H), 3.54 (dt, J = 8.8, 5.9 Hz, 1 H), 3.61 (s, 3 H). − ^{13}C NMR ($CDCl_3$): δ = 6.5, 7.5, 13.6, 19.0, 23.0, 29.7 (2 signals), 31.6, 34.0, 36.8, 39.7, 45.5, 51.8, 60.7, 67.7, 73.3, 166.3, 206.6. − MS (70 eV); *m/z* (%): 306 (35) [M^+], 278 (85), 249 (18), 228 (34), 207 (29), 191 (25), 190 (40), 189 (22), 168 (19), 165 (11), 163 (37), 162 (30), 147 (36), 134 (23), 119 (17), 107 (23), 105 (19), 91 (20), 83 (100). − $C_{18}H_{26}O_4$ (306.4): calcd. C 70.56, H 8.55; found C 70.38, H 8.58.

Methyl 5′-Allyl-2′-butyloxy-4′,4′-dimethyl-6′-oxospiro[cyclopropane-1,8′-tricyclo[3.2.1.0^{2,7}]octane]-1′-carboxylate (**4d-Bu**): From 1.11 g (4.70 mmol) of cyclohexenone **1d-Bu** and 0.73 g (5.00 mmol) of **3**. Yield 1.00 g (58%), colorless oil, b. p. 155°C (0.1 Torr). − IR (KBr): $\tilde{\nu}$ = 2958 cm^{-1}, 1728, 1437, 1369, 1346, 1237, 1222, 1123. − ^{1}H NMR ($CDCl_3$): δ = 0.34 (m, 1 H), 0.71−0.89 (m, 8 H), 1.04 (s, 3 H), 1.22−1.46 (m, 5 H), 1.78 (m, 1 H), 2.00 (m, 1 H), 1.96 (d, J = 13.5 Hz, 1 H), 2.45 (d, J = 13.5 Hz, 1 H), 2.60 (s, 1 H), 3.31 (m, 1 H), 3.57 (m, 1 H), 3.62 (s, 3 H), 4.90−4.97 (m, 2 H), 5.97 (m, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 4.1, 5.6, 13.7, 19.0, 25.1, 27.7, 29.8 (2 signals), 31.6, 38.0, 38.4, 39.7, 45.3, 51.8, 52.7, 67.8, 72.2, 115.9, 136.2, 166.2, 207.4. − MS (70 eV); *m/z* (%): 346 (10) [M^+], 318 (31), 289 (18), 259 (25), 258 (30), 234 (26), 230 (18), 208 (16), 207 (23), 206 (39), 203 (22), 191 (14), 187 (23), 175 (27), 165 (16), 159 (15), 147 (28), 145 (18), 131 (15), 119 (18), 117 (17), 105 (14), 91 (29), 83 (100).

2-Allyl-3-benzyloxycyclohex-2-enone (**2-Bzl**): A mixture of 2.00 g (13.1 mmol) of 2-allylcyclohexane-1,3-dione[14], 1.66 g (13.1 mmol) of benzyl chloride, and 0.314 g (13.1 mmol) of sodium hydride in 25 ml of anhydrous DMF was stirred overnight and kept at 70°C for 3 h. The solvent was removed under reduced pressure, the residue treated with 50 ml of water and the product extracted with ether (3 × 50 ml). The dried ($MgSO_4$) organic phases were concentrated and the residue distilled (kugelrohr 170°C/0.04 Torr). Yield 2.51 g (79%). The product crystallized on standing, m. p. 58−60°C. − ^{13}C NMR ($CDCl_3$): δ = 20.9 (t), 25.6 (t), 26.5 (t), 36.3 (t), 69.2 (t), 115.9 (t), 118.0 (s), 126.9 (d), 128.2 (d), 128.6 (d), 136.4 (s,d), 171.5 (s), 197.8 (s). − $C_{16}H_{18}O_2$ (242.3): calcd. C 79.31, H 7.49; found C 79.06, H 7.64.

Methyl 7′-Allyl-2′-benzyloxy-6′-oxospiro[cyclopropane-1,8′-tricyclo[3.2.1.0^{2,7}]octane]-1′-carboxylate (**4e-Bzl**): To a solution of 0.482 g (2.0 mmol) of **2-Bzl** in 20 ml of anhydrous THF was added, as above, LDA (2.2 mmol) at −78°C and after 30 min a solution of 0.293 g (2 mmol) of **3** in 2 ml of anhydrous THF. The reaction mixture was allowed to warm to room temp. (with stirring overnight) and poured into a saturated aqueous solution of ammonium chloride (50 ml). It was extracted with ether (3 × 50 ml), the organic phases were dried ($MgSO_4$) and concentrated. The residue was chromatographed on silica gel (diethyl ether/petroleum ether, 1:1). Yield 0.203 g (29%) of **4e-Bzl**, colorless crystals, m. p. 111−112°C, and 0.107 g of **5e**. − IR (KBr): $\tilde{\nu}$ = 3100 cm^{-1}, 3080, 2960, 1730, 1605, 1285, 1260, 795, 760. − ^{1}H NMR ($CDCl_3$): δ = 0.45−0.80 (m, 3 H), 1.30 (m, 1 H), 1.55−1.80 (m, 3 H), 1.97 (m, 1 H), 2.55−2.95 (m, 3 H), 3.62 (s, 3 H), 4.60−4.70 (m, 2 H), 5.00−5.20 (m, 2 H), 6.03 (m, 1 H), 7.20−7.40 (m, 5 H). − $C_{22}H_{24}O_4$ (352.4): calcd. C 74.98, H 6.86; found C 75.14, H 6.86. − The title compound decomposes on standing to give **5e**.

General Procedure for the Preparation of Bicyclo[3.2.1]octanediones **5**: A mixture of 0.71−7.84 mmol of methyl 2′-alkoxy-6′-oxospiro[cyclopropane-1,8′-tricyclo[3.2.1.0^{2,7}]octane]-1′-carboxylate **4** in CH_2Cl_2 (10−20 ml) and dilute (1:1) hydrochloric acid (10−20 ml) was stirred at room temp. for 8−16 h. The organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (3 × 20 ml), and the combined organic phases were dried ($MgSO_4$). The solvent was evaporated to afford the pure bicyclo[3.2.1]octanediones **5**.

Methyl 2′,6′-Dioxospiro[cyclopropane-1,8′-bicyclo[3.2.1]octane]-1′-carboxylate (**5a**): From 520 mg (2.20 mmol) of **4a-Me**. Yield 490 mg (quant.), m. p. 86−87°C (hexane). − IR (KBr): $\tilde{\nu}$ =

2953 cm^{-1}, 1746, 1708, 1437, 1263, 1226, 1179, 1136, 1067. − ^1H NMR ($CDCl_3$): δ = 0.55−0.60 (m, 2 H), 0.75 (m, 1 H), 1.29 (m, 1 H), 2.00−2.05 (m, 3 H), 2.51−2.58 (m, 2 H), 2.70 (d, *J* = 19.2 Hz, 1 H), 3.10 (d, *J* = 19.2 Hz, 1 H), 3.71 (s, 3 H). − ^{13}C NMR ($CDCl_3$): δ = 4.3, 9.2, 25.4, 29.9, 34.1, 45.9, 51.9, 53.6, 63.7, 167.5, 203.8, 213.1. − MS (70 eV); *m/z* (%): 222 (72) [M^+], 194 (23), 190 (39), 162 (44), 135 (23), 134 (39), 107 (23), 93 (18), 91 (49), 79 (40), 77 (29), 55 (100). − $C_{12}H_{14}O_4$ (222.2): calcd. C 64.85, H 6.35; found C 64.76, H 6.27. − Similarly, 1.96 g (7.83 mmol) of **4a-Et** was hydrolysed for 12 h. Yield 1.74 g (quant.) of **5a**.

Methyl 5′-Methyl-2′,6′-dioxospiro[cyclopropane-1,8′-bicyclo[3.2.1]octane]-1′-carboxylate (**5b**): From 250 mg (1.00 mmol) of **4b-Me**. Yield 226 mg (96%), colorless crystals, m. p. 107−109°C (hexane). − IR (KBr): $\tilde{\nu}$ = 2962 cm^{-1}, 1743, 1707, 1436, 1319, 1235, 1225, 1038. − ^1H NMR ($CDCl_3$): δ = 0.40−0.67 (m, 3 H), 0.77 (s, 3 H), 1.27 (m, 1 H), 1.78−1.84 (m, 2 H), 2.43−2.64 (m, 2 H), 2.73 (d, *J* = 19.3 Hz, 1 H), 3.08 (d, *J* = 19.3 Hz, 1 H), 3.73 (s, 3 H). − ^{13}C NMR ($CDCl_3$): δ = 2.7, 5.6, 14.2, 32.4, 33.4, 34.6, 45.2, 50.4, 52.0, 63.0, 167.8, 203.9, 224.8. − MS (70 eV); *m/z* (%): 236 (75) [M^+], 208 (34), 205 (33), 204 (61), 180 (28), 177 (45), 176 (49), 149 (33), 148 (38), 134 (18), 133 (20), 122 (25), 120 (25), 107 (22), 105 (30), 93 (31), 91 (52), 79 (27), 77 (32), 55 (100). − $C_{13}H_{16}O_4$ (236.3): calcd. C 66.09, H 6.83; found C 66.15, H 6.73.

Methyl 4′,4′-Dimethyl-2′,6′-dioxospiro[cyclopropane-1,8′-bicyclo[3.2.1]octane]-1′-carboxylate (**5c**): From 2.048 g (7.76 mmol) of **4c-Me**. Yield 1.77 g (91%), m. p. 115−117°C ($CHCl_3$/hexane). − IR (KBr): $\tilde{\nu}$ = 3020 cm^{-1}, 2880, 1745, 1705, 1430, 1320, 1235, 1145, 1045. − ^1H NMR ($CDCl_3$): δ = 0.25 (m, 1 H), 0.43 (m, 1 H), 0.87 (m, 1 H), 0.98 (s, 3 H), 1.11 (s, 3 H), 1.56 (br. s, 1 H), 1.58 (m, 1 H), 2.26 (dd, *J* = 15.7, 1.1 Hz, 1 H), 2.35 (d, *J* = 15.7 Hz, 1 H), 2.60 (d, *J* = 19.1 Hz, 1 H), 2.89 (dd, *J* = 19.1, 1.1 Hz, 1 H), 3.62 (s, 3 H). − ^{13}C NMR ($CDCl_3$): δ = 7.2, 7.7, 27.6, 28.3, 29.0, 36.7, 45.8, 49.2, 52.0, 63.2, 64.0, 167.8, 204.5, 220.9. − MS (70 eV); *m/z* (%): 250 (47) [M^+], 194 (74), 166 (63), 138 (41), 105 (27), 91 (27), 83 (100), 79 (29). − $C_{14}H_{18}O_4$ (250.3): calcd. C 67.18, H 7.25; found C 67.26, H 7.17. − Hydrolysis of 278 mg (1.00 mmol) of **4c-Et** gave 233 mg (93%), hydrolysis of 290 mg (1.00 mmol) of **4c-allyl** 232 mg (92%), and hydrolysis of 306 mg (1.00 mmol) of **4c-Bu** 236 mg (94%) of **5c**, respectively. − Treatment of 292 mg (1.11 mmol) of γ-oxo ester **4c-Me** in 20 ml of CH_2Cl_2 with 1 ml of trifluoroacetic acid at room temp. for 1 d gave 275 mg (99%) of **5c**. − Hydrolysis with *p*-toluenesulfonic acid: A solution of 268 mg (1.01 mmol) of tricyclic γ-oxo ester **4c-Me** and 274 mg (1.44 mmol) of *p*-toluenesulfonic acid monohydrate in 20 ml of CH_2Cl_2 was stirred at room temp. for 2 d. The solvent was evaporated and the residue was chromatographed on silica gel (CH_2Cl_2) to afford **5c**. Yield 240 mg (95%) as colorless crystals.

Reaction of Tricyclic γ-Oxo Ester **4c-Me** *with Boron Trifluoride−Diethyl Ether:* A solution of 172 mg (0.65 mmol) of tricyclic ester **4c-Me** and 0.5 ml of boron trifluoride−diethyl ether in 20 ml of CH_2Cl_2 was stirred at room temp. for 1 h. The solvent was evaporated and the residue was chromatographed on silica gel (CH_2Cl_2) to give 150 mg (92%) of **5c**.

Methyl 5′-Allyl-4′,4′-dimethyl-2′,6′-dioxospiro[cyclopropane-1,8-bicyclo[3.2.1]octane]-1′-carboxylate (**5d**): From 245 mg (0.71 mmol) of **4d-Bu**. Yield 203 mg (99%), m. p. 109−111°C ($CHCl_3$/hexane). − IR (KBr): $\tilde{\nu}$ = 2947 cm^{-1}, 1733, 1716, 1635, 1456, 1314, 1250, 1033. − ^1H NMR ($CDCl_3$): δ = 0.19 (m, 1 H), 0.74−1.00 (m, 2 H), 0.92 (s, 3 H), 1.05 (s, 3 H), 1.51 (m, 1 H), 1.93 (dd, *J* = 16, 8.2 Hz, 1 H), 2.20 (d, *J* = 16 Hz, 1 H), 2.28−2.37 (m, 2 H), 2.62 (d, *J* = 19 Hz, 1 H), 2.91 (d, *J* = 19 Hz, 1 H), 3.62 (s, 3 H), 4.89−4.99 (m, 2 H), 5.68 (m, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 4.6, 6.5, 24.8, 25.3, 30.0, 32.0, 40.1, 46.5, 51.6, 51.9, 57.4, 63.7, 116.9, 135.1, 167.5, 204.0, 222.7. − MS (70 eV); *m/z* (%): 290 (11) [M^+], 259 (14), 231 (68), 206 (100), 189 (27), 174 (38), 161 (22), 147 (62), 146 (67), 133 (30), 119 (67), 105 (47), 91 (76), 83 (78). − $C_{17}H_{22}O_4$ (290.4): calcd. C 70.32, H 7.64; found C 70.22, H 7.63.

Methyl 7′-Allyl-2′,6′-dioxospiro[cyclopropane-1,8′-bicyclo[3.2.1]octane]-1′-carboxylate (**5e**): Acidic workup (2 N HCl, stirring overnight at 20°C) of **4e-Bzl** gave directly **5e** which was chromatographed on silica gel (diethyl ether/petroleum ether, 1:1). Yield 51%, m. p. 75−77°C. − IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}, 2985, 1735, 1715, 1640, 1260, 1100, 795, 750. − ^1H NMR ($CDCl_3$): δ = 0.45−0.70 (m, 3 H), 1.28 (m, 1 H), 2.05−2.15 (m, 3 H), 2.10−2.45 (m, 3 H), 2.78 (m, 1 H), 3.28 (m, 1 H), 3.75 (s, 3 H), 5.00−5.15 (m, 2 H), 6.00 (m, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 4.5, 9.4, 25.9, 28.7, 30.5, 35.8, 52.2, 52.6, 56.6, 68.9, 116.6, 135.6, 168.0, 205.4, 216.4. − $C_{15}H_{18}O_4$ (262.3): calcd. C 68.69, H 6.92; found C 68.59, H 6.87.

Methyl 2′-Methoxy-4′,4′,7′-trimethyl-6′-oxospiro[cyclopropane-1,8′-tricyclo[3.2.1.0^{2,7}]octane]-1′-carboxylate (**4f-Me**): A 3.03 M solution of butyllithium (0.66 ml, 2.0 mmol) in cyclohexane was slowly added to a cooled (−5°C), stirred solution of 0.30 ml (2.12 mmol) of anhydrous diisopropylamine in 5 ml of anhydrous THF under N_2. The resulting yellow solution was stirred at −10°C for 15 min, cooled to −78°C, and a solution of 510 mg (1.93 mmol) of **4c-Me** in 5 ml of anhydrous THF was added over 15 min. The resulting yellow solution was stirred at −78°C for 45 min and a solution of methyl iodide (0.5 ml) in anhydrous THF (5 ml) was added over 15 min. The resulting solution was stirred at −78°C for 30 min, and warmed to room temp. overnight. Water (20 ml) was added, the organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (3 × 20 ml) and the combined organic phases were dried ($MgSO_4$). The solvent was evaporated and the residue was chromatographed on silica gel (CH_2Cl_2) to afford 327 mg (61%) of **4f-Me**, colorless crystals, m. p. 91−92°C (hexane). − IR (KBr): $\tilde{\nu}$ = 2963 cm^{-1}, 1738, 1436, 1337, 1239, 1090, 1047, 1030. − ^1H NMR ($CDCl_3$): δ = 0.11−0.27 (m, 2 H), 0.74 (s, 3 H), 0.79 (m, 1 H), 1.06−1.18 (m, 2 H), 1.07 (s, 3 H), 1.29 (s, 3 H), 1.95 (d, *J* = 13.6 Hz, 1 H), 2.24 (d, *J* = 13.6 Hz, 1 H), 3.23 (s, 3 H), 3.54 (s, 3 H). − ^{13}C NMR ($CDCl_3$): δ = 5.4, 6.2, 7.3, 23.0, 29.6, 29.7, 33.7, 35.5, 43.3, 45.9, 51.4, 59.3, 73.0, 166.0, 208.4. − MS (70 eV); *m/z* (%): 278 (16) [M^+], 229 (8), 194 (15), 191 (11), 162 (12), 135 (13), 125 (50), 95 (100), 91 (12). − $C_{16}H_{22}O_4$ (278.4): calcd. C 69.04, H 7.97; found C 69.01, H 7.67.

Methyl 4′,4′,7′-Trimethyl-2′,6′-dioxospiro[cyclopropane-1,8′-bicyclo[3.2.1]octane]-1′-carboxylate (**5f**): A mixture of 324 mg (1.17 mmol) of **4f-Me** in 10 ml of CH_2Cl_2 and 10 ml of dilute (1:1) hydrochloric acid was stirred at room temp. for 12 h. The organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (2 × 20 ml) and the combined organic layers were dried ($MgSO_4$). The solvent was evaporated to afford 288 mg (94%) of **5f**, colorless crystals, m. p. 74−75°C ($CHCl_3$/hexane). − IR (KBr): $\tilde{\nu}$ = 2977 cm^{-1}, 1729, 1711, 1424, 1320, 1286, 1251, 1192, 1053. − ^1H NMR ($CDCl_3$): δ = 0.23−0.40 (m, 2 H), 0.95 (m, 1 H), 1.01 (s, 3 H), 1.15 (d, *J* = 7.2 Hz, 3 H), 1.18 (s, 3 H), 1.57 (m, 1 H), 1.67 (t, *J* = 1.4 Hz, 1 H), 2.03 (d, *J* = 16.8 Hz, 1 H), 2.40 (dd, *J* = 16.8, 1.4 Hz, 1 H), 3.05 (m, 1 H), 3.70 (s, 3 H). − ^{13}C NMR ($CDCl_3$): δ = 7.4, 8.2, 10.1, 27.8, 27.9, 29.4, 37.2, 51.3, 51.8, 52.1, 62.5, 68.5, 168.2, 204.2, 224.6. − MS (70 eV); *m/z* (%): 264 (14) [M^+], 233 (13), 208 (31), 205 (18), 180 (37), 165 (15), 152 (32), 122 (16), 119 (13), 83 (100). − $C_{15}H_{20}O_4$ (264.2): calcd. C 68.16, H, 7.63; found C 68.05, H 7.64.

Methyl 2′-Methoxy-4′,4′-dimethyl-7′-trimethylsilyl-6′-oxospiro[cyclopropane-1,8′-tricyclo[3.2.1.0^{2,7}]octane]-1′-carboxylate (**4g-**

Me): A 3.03 M solution of butyllithium (0.66 ml, 2.0 mmol) in cyclohexane was added slowly to a cooled (−5°C) and stirred solution of 0.28 ml (1.98 mmol) of diisopropylamine in 5 ml of anhydrous THF, under N_2. The resulting yellow solution was stirred at −10°C for 15 min, cooled to −78°C and a solution of 502 mg (1.90 mmol) of tricyclic γ-oxo ester **4c-Me** in 5 ml of anhydrous THF was added over 15 min. The resulting yellow solution was stirred at −78°C for 60 min, and a solution of 1.00 g (9.21 mmol) of chlorotrimethylsilane in 5 ml of anhydrous THF was added over 15 min and stirred at −78°C for 60 min. Water (20 ml) was added, the organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (3 × 20 ml) and the combined organic phases were dried ($MgSO_4$). The solvent was evaporated and the residue was chromatographed on silica gel (CH_2Cl_2) to afford 420 mg (66%) of **4g-Me**, colorless oil. − IR (KBr): $\tilde{\nu}$ = 2954 cm^{-1}, 1737, 1719, 1437, 1245, 1194, 1165. − ^1H NMR ($CDCl_3$): δ = 0.17 (s, 9 H), 0.27−0.33 (m, 2 H), 0.80−0.95 (m, 1 H), 0.84 (s, 3 H), 1.11 (m, 1 H), 1.14 (s, 3 H), 1.22 (br. s, 1 H), 2.04 (d, *J* = 13.7 Hz, 1 H), 2.33 (d, *J* = 13.7 Hz, 1 H), 3.31 (s, 3 H), 3.64 (s, 3 H). − ^{13}C NMR ($CDCl_3$): δ = −0.3, 6.7, 7.6, 23.6, 29.8, 30.2, 32.9, 36.6, 39.3, 50.2, 51.6, 55.1, 60.1, 76.0, 166.8, 210.5. − MS (70 eV); *m/z* (%): 336 (40) [M^+], 322 (100), 305 (11), 293 (25), 277 (25), 261 (17), 227 (13), 189 (12), 173 (6), 89 (16), 73 (20). − $C_{18}H_{28}O_4Si$ (336.5): calcd. C 64.25, H 8.39; found C 64.33, H 8.25.

Hydrolysis of **4g-Me**. − *Methyl 4′,4′-Dimethyl-7′-trimethylsilyl-2′,6′-dioxospiro[cyclopropane-1,8′-bicyclo[3.2.1]octane]-1′-carboxylate* (**5g**) *and Methyl 2′-Methoxy-4′,4′-dimethyl-7′-trimethylsilyl-6′-oxospiro[cyclopropane-1,8′-bicyclo[3.2.1]oct-2-ene]-1′-carboxylate* (**7g**): A mixture of 400 mg (1.19 mmol) of **4g-Me** in 20 ml of CH_2Cl_2 and 20 ml of dilute (1:1) hydrochloric acid was stirred at room temp. for 12 h. The organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (3 × 20 ml) and the combined organic phases were dried ($MgSO_4$). The solvent was evaporated and the residue was chromatographed on silica gel (CH_2Cl_2) to afford 308 mg (80%) of **5g** as an oil and 71 mg (18%) of **7g** as an oil.

5g: ^1H NMR ($CDCl_3$): δ = 0.06 (s, 9 H), 0.22−0.31 (m, 2 H), 0.91 (m, 1 H), 0.98 (s, 3 H), 1.11 (s, 3 H), 1.41 (m, 1 H), 1.59 (br. s, 1 H), 2.28 (d, *J* = 16.2 Hz, 1 H), 2.39 (dd, *J* = 16.2, 0.9 Hz, 1 H), 2.88 (t, *J* = 1.3 Hz, 1 H), 3.65 (s, 3 H). − ^{13}C NMR ($CDCl_3$): δ = −0.5, 7.4, 8.4, 28.1, 29.7, 31.4, 36.5, 50.2, 50.6, 52.0, 64.7, 67.3, 168.4, 204.8, 214.0.

7g: ^1H NMR ($CDCl_3$): δ = 0.00 (s, 9 H), 0.10−0.29 (m, 2 H), 0.90 (m, 1 H), 0.98 (s, 3 H), 1.13 (s, 3 H), 1.20 (m, 1 H), 1.58 (br.s, 1 H), 1.81 (d, *J* = 1.1 Hz, 1 H), 3.43 (s, 3 H), 3.60 (s, 3 H), 4.29 (s, 1 H). − ^{13}C NMR ($CDCl_3$): δ = −0.8, 7.5, 8.3, 29.1, 30.5, 32.6, 36.3, 51.5, 54.0, 55.1, 58.3, 64.6, 102.9, 154.7, 169.7, 216.8.

Reaction of Tricyclic γ-Oxo Ester **4a-Me** *with Diphenyl Disulfide.* − *Methyl 2′-Methoxy-6′-oxo-7′-phenylsulfanylspiro[cyclopropane-1,8′-bicyclo[3.2.1]oct-2′-ene]-1′-carboxylate* (**7k**): A 1.66 M solution of butyllithium (1.30 ml, 2.16 mmol) in hexane was slowly added to a cooled (−10°C) and stirred solution of 0.30 ml (2.12 mmol) of anhydrous diisopropylamine in 10 ml of anhydrous THF under N_2. The resulting colorless solution was stirred at −10°C for 30 min, cooled to −78°C, and a solution of 460 mg (1.95 mmol) of tricyclic γ-oxo ester **4a-Me** in 10 ml of anhydrous THF was added over 10 min. The resulting yellow solution was stirred at −78°C for 50 min and a solution of 880 mg (4.03 mmol) of diphenyl disulfide in 10 ml of anhydrous THF was added over 10 min. The resulting solution was stirred overnight. A saturated aqueous NH_4Cl solution (10 ml) was added, the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 20 ml). The combined organic phases were washed with brine (2 × 30 ml), dried ($MgSO_4$), concentrated, and the residue was chromatographed on silica gel (CH_2Cl_2) to afford 83 mg (13%) of **7k** as colorless prisms, m. p. 108−109°C (hexane). − IR (KBr): $\tilde{\nu}$ = 2952 cm^{-1}, 1751, 1736, 1647, 1287, 1251, 1234, 1202, 1111, 1067, 1040. − ^1H NMR ($CDCl_3$): δ = 0.40−0.68 (m, 3 H), 1.15 (m, 1 H), 2.06−2.11 (m, 2 H), 2.32 (ddd, *J* = 16.4, 4.6, 2.0 Hz, 1 H), 2.54 (ddd, *J* = 16.4, 5.1, 2.4 Hz, 1 H), 3.59 (s, 6 H), 4.44 (d, *J* = 0.9 Hz, 1 H), 4.60 (dd, *J* = 4.6, 2.4 Hz, 1 H), 7.20−7.32 (m, 3 H), 7.63−7.68 (m, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 4.5, 10.1, 28.4, 28.5, 51.9, 54.8, 59.4, 68.0, 92.5, 127.3, 128.7, 129.0, 132.7, 135.1, 156.1, 168.3, 223.9. − MS (70 eV); *m/z* (%): 344 (100) [M^+], 235 (22), 207 (51), 203 (8), 193 (9), 175 (20), 161 (9), 147 (12), 135 (8), 122 (6), 91 (7). − $C_{19}H_{20}O_4S$ (344.4): calcd. C 66.26, H 5.85; found C 66.28, H 5.75.

Methyl 2′-Methoxy-5′-methyl-6′-oxo-7′-phenylsulfanylspiro[cyclopropane-1,8′-bicyclo[3.2.1]oct-2′-ene]-1′-carboxylate (**7j**): A 2.34 M solution of butyllithium (0.90 ml, 2.11 mmol) in hexane was slowly added to a cooled (−10°C), stirred solution of 0.30 ml (2.12 mmol) of anhydrous diisopropylamine in 10 ml of anhydrous THF under N_2. The resulting colorless solution was stirred at −10°C for 30 min, cooled to −78°C and a solution of 0.485 g (1.94 mmol) of tricyclic oxo ester **4b-Me** in 10 ml of anhydrous THF was added over 10 min. The resulting red solution was stirred at −78°C for 30 min and a solution of 0.872 g (4.0 mmol) of diphenyl disulfide in 10 ml of anhydrous THF was added over 10 min. The resulting solution was stirred overnight. A saturated aqueous NH_4Cl solution (10 ml) was added, the organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (3 × 20 ml), and the combined organic phases were dried ($MgSO_4$). The solvent was evaporated and the residue was chromatographed on silica gel (CH_2Cl_2) to afford 510 mg (73%) of **7j**, colorless prisms, m. p. 120−122°C (hexane). − IR (KBr): $\tilde{\nu}$ = 2953 cm^{-1}, 2834, 1748, 1733, 1668, 1482, 1444, 1285, 1228, 1024, 744. − ^1H NMR ($CDCl_3$): δ = 0.23 (m, 1 H), 0.47 (m, 1 H), 0.67 (dt, *J* = 9.8, 5.6 Hz, 1 H), 0.77 (s, 3 H), 1.12 (dt, *J* = 9.8, 5.6 Hz, 1 H), 2.16−2.19 (m, 2 H), 3.57 (s, 3 H), 3.60 (s, 3 H), 4.36 (s, 1 H), 4.57 (dd, *J* = 4.1, 3.0 Hz, 1 H), 7.22−7.31 (m, 3 H), 7.63−7.68 (m, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 2.5, 5.0, 15.0, 31.6, 36.5, 49.1, 51.8, 54.8, 59.5, 66.7, 92.5, 127.3, 128.6, 132.9, 135.3, 156.1, 168.5, 225.5. − MS (70 eV); *m/z* (%): 358 (100) [M^+], 249 (13), 222 (58), 227 (9), 189 (22), 176 (8), 161 (19), 149 (9), 147 (9), 91 (8). − $C_{20}H_{22}O_4S$ (358.5): calcd. C 67.02, H 6.19; found C 66.87, H 6.24.

Methyl 2′-Methoxy-4′,4′-dimethyl-6′-oxo-endo-7′-phenylsulfanylspiro[cyclopropane-1,8′-bicyclo[3.2.1]oct-2′-ene]-1′-carboxylate (**7i**): A 2.34 M solution of butyllithium (0.90 ml, 2.11 mmol) in hexane was slowly added to a cooled (−10°C) and stirred solution of 0.30 ml (2.12 mmol) of anhydrous diisopropylamine in 10 ml of anhydrous THF under N_2. The resulting colorless solution was stirred at −10°C for 30 min, cooled to −78°C and a solution of 525 mg (1.99 mmol) of tricyclic γ-oxo ester **4c-Me** in 10 ml of anhydrous THF was added over 10 min. The resulting orange solution was stirred at −78°C for 30 min and a solution of 870 mg (3.99 mmol) of diphenyl disulfide in 10 ml of anhydrous THF was added over 10 min. The resulting solution was stirred overnight. A saturated aqueous NH_4Cl solution (10 ml) was added, the organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (3 × 20 ml) and the combined organic phases were dried ($MgSO_4$). The solvent was evaporated and the residue was chromatographed on silica gel to give 510 mg (69%) of **7i**, colorless prisms, m. p. 156−157°C (hexane). − IR (KBr): $\tilde{\nu}$ = 2953 cm^{-1}, 2834, 1748, 1733, 1668, 1482, 1444, 1285, 1228, 1024, 744. − ^1H NMR ($CDCl_3$): δ = 0.19−0.37 (m, 2 H), 0.99 (dt, *J* = 6, 5.8 Hz, 1 H),

1.09 (s, 3 H), 1.22 (s, 3 H), 1.39 (dt, J = 6, 5.8 Hz, 1 H), 1.74 (s, 1 H), 3.59 (s, 3 H), 3.60 (s, 3 H), 4.28 (d, J = 1.4 Hz, 1 H), 4.52 (s, 1 H), 7.22−7.32 (m, 3 H), 7.64−7.69 (m, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 7.3, 7.6, 27.9, 29.5, 30.3, 37.0, 51.9, 54.7, 59.7, 63.2, 65.3, 104.6, 127.3, 128.6, 132.7, 135.4, 153.3, 168.6, 221.4. − MS (70 eV); *m/z* (%): 372 (78) [M^+], 297 (18), 263 (28), 235 (84), 207 (29), 203 (31), 175 (37), 161 (22), 105 (20), 91 (37), 77 (23), 69 (26), 57 (75), 56 (89), 55 (43), 43 (79), 41 (100). − $C_{21}H_{24}O_4S$ (372.5): calcd. C 67.72, H 6.49; found C 67.92, H 6.51.

Methyl 5′-Methyl-2′,6′-dioxo-7′-phenylsulfanylspiro[cyclopropane-1,8′-bicyclo[3.2.1]octane]-1′-carboxylate (**5j**): A mixture of 169 mg (0.47 mmol) of **7j** and 10 ml of conc. hydrochloric acid in 10 ml of CH_2Cl_2 was stirred at room temp. for 4 h. The organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (2 × 20 ml) and the combined organic phases were dried ($MgSO_4$). The solvent was evaporated to afford 160 mg (99%) of **5j**, colorless crystals, m. p. 95−97°C (hexane). − IR (KBr): $\tilde{\nu}$ = 2921 cm^{-1}, 1748, 1734, 1710, 1696, 1457, 1436, 1012, 760. − ^{1}H NMR ($CDCl_3$): δ = 0.22 (m, 1 H), 0.46 (m, 1 H), 0.64 (m, 1 H), 0.80 (s, 3 H), 1.16 (m, 1 H), 1.81−1.89 (m, 2 H), 2.43−2.71 (m, 2 H), 3.52 (s, 3 H), 4.45 (s, 1 H), 7.27−7.32 (m, 3 H), 7.58−7.64 (m, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 2.6, 6.2, 14.8, 31.6, 34.8, 36.4, 49.6, 52.1, 60.6, 68.6, 128.2, 128.87, 128.89, 133.6, 166.6, 200.5, 224.0. − MS (70 eV); *m/z* (%): 344 [M^+]. − $C_{19}H_{20}O_4S$ (344.4): calcd. C 66.26, H 5.85; found C 66.80, H 5.85.

Wittig Reaction of Tricyclic γ-Oxo Ester **4a-Et**. − *Methyl 2′-Ethoxy-6′-methylenespiro[cyclopropane-1,8′-tricyclo[3.2.1.0^{2,7}]-octane-1′-carboxylate* (**8a-Et**): A 2.40 M solution of butyllithium (1.00 ml, 2.4 mmol) in cyclohexane was slowly added to a cooled (0°C) mixture of 900 mg (2.52 mmol) of methyltriphenylphosphonium bromide in 10 ml of anhydrous THF under N_2. After having stirred the mixture at 0°C for 60 min, a solution of 250 mg (1.00 mmol) of oxo ester **4a-Et** in 10 ml of anhydrous THF was added during 10 min. The resulting mixture was stirred overnight. Water (40 ml) was added, the organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (2 × 30 ml) and the combined organic phases were dried ($MgSO_4$). The solvent was evaporated and the residue was chromatographed on silica gel (CH_2Cl_2/pentane, 1:1) to afford 200 mg (81%) of **8a-Et** as a colorless oil. − ^{1}H NMR ($CDCl_3$): δ = 0.28 (m, 1 H), 0.43 (m, 1 H), 0.67 (m, 1 H), 1.06 (t, J = 7.0 Hz, 1 H), 1.15 (m, 1 H), 1.22 (d, J = 8.6 Hz, 1 H), 1.37 (m, 1 H), 1.45 (ddd, J = 11.7, 5.4, 2.6 Hz, 1 H), 1.53 (br. s, 1 H), 1.75 (m, 1 H), 2.15 (ddd, J = 13.7, 11.6, 3.7 Hz, 1 H), 2.37 (ddd, J = 13.7, 11.4, 5.4 Hz, 1 H), 2.80 (s, 1 H), 3.40 (m, 1 H), 3.52 (m, 1 H), 3.58 (s, 3 H), 4.65 (s, 1 H), 4.77 (s, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 4.8, 9.2, 15.4, 22.5, 25.7, 27.0, 38.8, 43.7, 47.4, 51.3, 62.8, 71.3, 101.7, 150.1, 168.2.

Wittig Reaction of Tricyclic γ-Oxo Ester **4b-Me**. − *Methyl 2′-Methoxy-5′-methyl-6′-methylenespiro[cyclopropane-1,8′-tricyclo[3.2.1.0^{2,7}]octane]-1′-carboxylate* (**8b-Me**): Similarly prepared from a 2.34 M solution of butyllithium (1 ml, 2.34 mmol) in cyclohexane, 820 mg (2.30 mmol) of methyltriphenylphosphonium bromide in 10 ml of anhydrous THF, and a solution of 250 mg (1.00 mmol) of γ-oxo ester **4b-Me** in 10 ml THF, under N_2. Yield 94 mg (38%, 58% conversion) of **8b-Me**, as a colorless oil after flash column chromatography on silica gel (CH_2Cl_2). − ^{1}H NMR ($CDCl_3$): δ = 0.33 (m, 1 H), 0.47 (m, 1 H), 0.58 (s, 3 H), 1.13 (m, 1 H), 1.26 (m, 1 H), 1.58 (ddd, J = 12.5, 11.3, 3.7 Hz, 1 H), 2.17 (ddd, J = 13.6, 11.7, 3.7 Hz, 1 H), 2.35 (dddd, J = 13.6, 11.3, 5.8, 0.8 Hz, 1 H), 2.81 (s, 1 H), 3.28 (s, 3 H), 3.64 (s, 3 H), 4.61 (s, 1 H), 4.84 (s, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 3.3, 5.7, 16.1, 20.4, 29.5, 33.7, 37.5, 41.6, 43.9, 51.5, 54.6, 71.5, 99.8, 154.3, 168.2.

Methyl 6′-Methyl-2′-oxospiro[cyclopropane-1,8′-bicyclo[3.2.1]-oct-6′-ene]-1′-carboxylate (**9a**): A mixture of 190 mg (0.77 mmol) of methylenetricyclooctane **8a-Et** in 20 ml of CH_2Cl_2 and 20 ml of dilute (1:1) hydrochloric acid was stirred at room temp. for 12 h. The organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (3 × 20 ml) and the combined organic layers were dried ($MgSO_4$). The solvent was evaporated to afford 158 mg (94%) of **9a**, colorless oil, b.p. 110°C (0.01 Torr). − IR (KBr): $\tilde{\nu}$ = 2933 cm^{-1}, 1744, 1711, 1436, 1320, 1247, 1172, 1145, 1060, 822. − ^{1}H NMR ($CDCl_3$): δ = 0.43−0.59 (m, 2 H), 0.68 (m, 1 H), 1.05 (m, 1 H), 1.82 (m, 1 H), 1.88 (d, J = 1.6 Hz, 1 H), 1.95 (m, 1 H), 2.03 (m, 1 H), 2.42 (m, 1 H), 2.69 (m, 1 H), 3.68 (s, 3 H), 5.85 (dd, J = 3.2, 1.6 Hz, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 4.8, 9.1, 15.6, 22.9, 33.9, 36.2, 50.6, 51.4, 70.8, 124.9, 147.2, 167.8, 203.0. − MS (70 eV); *m/z* (%): 220 (31) [M^+], 202 (16), 188 (17), 164 (100), 133 (34), 132 (27), 105 (86), 91 (26). − $C_{13}H_{16}O_3$ (220.3): calcd. C 70.89, H 7.32; found C 70.82, H 7.34.

General Procedure for the Preparation of Methyl 2′-Oxo-6′-alkylspiro[cyclopropane-1,8′-bicyclo[3.2.1]oct-6′-ene]-1′-carboxylates **9** *from* **14**: A mixture of 0.61−1.32 mmol of the tertiary alcohol **14** in 10 ml of CH_2Cl_2 and 10 ml of hydrochloric acid was stirred at room temp. for 0.5−7.0 h. The organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (3 × 20 ml) and the combined organic phases were dried ($MgSO_4$). The solvent was evaporated to afford the bicyclo[3.2.1]octenes **9**.

Methyl 5′,6′-Dimethyl-2′-oxospiro[cyclopropane-1,8′-bicyclo-[3.2.1]oct-6′-ene]-1′-carboxylate (**9l**): From 162 mg (0.61 mmol) of alcohol **14l**. Yield 101 mg (71%), colorless crystals, m. p. 28°C (hexane). − IR (KBr): $\tilde{\nu}$ = 2954 cm^{-1}, 1744, 1711, 1436, 1262, 1237, 1175, 1043. − ^{1}H NMR ($CDCl_3$): δ = 0.30−0.45 (m, 2 H), 0.52 (m, 1 H), 0.69 (s, 3 H), 0.91 (m, 1 H), 1.61−1.73 (m, 2 H), 1.73 (s, 3 H), 2.31 (m, 1 H), 2.59 (m, 1 H), 3.61 (s, 3 H), 5.79 (s, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 2.9, 5.2, 13.1, 16.1, 30.6, 34.4, 38.1, 46.5, 51.3, 70.5, 123.8, 149.4, 167.9, 202.7. − MS (70 eV); *m/z* (%): 234 (40) [M^+], 206 (14), 202 (22), 178 (100), 175 (36), 163 (29), 147 (50), 133 (40), 119 (94), 105 (24), 91 (48), 77 (26). − $C_{14}H_{18}O_3$ (234.3): calcd. C 71.77, H 7.74; found C 71.62, H 7.63.

Methyl 4′,4′-Dimethyl-2′-oxo-6′-phenylspiro[cyclopropane-1,8′-bicyclo[3.2.1]oct-6′-en]-1′-carboxylate (**9n**): From 450 mg (1.32 mmol) of alcohol **14n**. Yield 350 mg (86%), colorless crystals, m. p. 126−128°C (hexane). − IR (KBr): $\tilde{\nu}$ = 2922 cm^{-1}, 1737, 1696, 1433, 1319, 1250, 1205, 1067, 762. − ^{1}H NMR ($CDCl_3$): δ = 0.39 (m, 1 H), 0.50 (m, 1 H), 0.74 (s, 3 H), 1.04 (m, 1 H), 1.26 (s, 3 H), 1.49 (m, 1 H), 2.31 (d, J = 16.3 Hz, 1 H), 2.45 (s, 1 H), 2.66 (d, J = 16.3 Hz, 1 H), 3.71 (s, 3 H), 6.70 (s, 1 H), 7.24−7.38 (m, 3 H), 7.47−7.50 (m, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 7.4, 9.3, 30.3, 30.4, 36.7, 37.5, 50.6, 51.7, 57.4, 71.2, 125.7, 126.9, 128.1, 128.5, 136.1, 150.4, 168.0, 203.3. − MS (70 eV); *m/z* (%): 310 (22) [M^+], 278 (9), 254 (25), 226 (100), 222 (24), 195 (20), 194 (34), 181 (8), 167 (39), 165 (24), 152 (11), 83 (11). − $C_{20}H_{22}O_3$ (310.4): calcd. C 77.39, H 7.14; found C 77.28, H 7.22.

Wittig Reaction of Bicyclo[3.2.1]octanedione **5c**. − *Methyl 4′,4′-Dimethyl-2′-methylene-6′-oxospiro[cyclopropane-1,8′-bicyclo-[3.2.1]octane]-1′-carboxylate* (**10**): A 2.85 M solution of butyllithium (1.00 ml, 2.85 mmol) in cyclohexane was slowly added to a cooled (−5°C) mixture of 1.02 g (2.86 mmol) of methyltriphenylphosphonium bromide in 10 ml of anhydrous THF under N_2. After stirring of the mixture continuously for 15 min at −5°C, a solution of 250 mg (1.00 mmol) of bicyclo[3.2.1]octanedione **5c** in 10 ml of anhydrous THF was added. The resulting mixture was stirred at −5°C for 45 min. Water (40 ml) was added, the organic layer was separated, the aqueous layer was extracted with CH_2Cl_2

(2 × 30 ml) and the combined organic phases were dried ($MgSO_4$). The solvent was evaporated and the residue was chromatographed on silica gel (CH_2Cl_2/pentane, 2:1) to afford 150 mg (60%, 79% conversion) of **10** as colorless needles, m. p. 47−48°C (hexane). − IR (KBr): $\tilde{\nu}$ = 2966 cm^{-1}, 1730, 1643, 1472, 1458, 1322, 1248, 1228, 1147, 1055. − ^1H NMR ($CDCl_3$): δ = 0.15 (ddd, *J* = 9.7, 5.9, 4.5 Hz, 1 H), 0.40 (ddd, *J* = 9.7, 5.9, 4.5 Hz, 1 H), 0.75 (m, 1 H), 0.95 (s, 3 H), 1.07 (s, 3 H), 1.22 (s, 1 H), 1.49 (m, 1 H), 2.05 (d, *J* = 14.5 Hz, 1 H), 2.18 (d, *J* = 14.5 Hz, 1 H), 2.49 (d, *J* = 18.7 Hz, 1 H), 2.83 (d, *J* = 18.7 Hz, 1 H), 3.66 (s, 3 H), 4.65 (d, *J* = 1.8 Hz, 1 H), 4.83 (d, *J* = 1.8 Hz, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 7.8, 8.3, 26.5, 27.5, 29.2, 36.0, 43.9, 47.4, 51.6, 56.2, 64.8, 109.9, 144.9, 170.9, 223.9. − MS (70 eV); *m/z* (%): 248 (58) [M^+], 220 (76), 205 (33), 189 (100), 177 (34), 161 (72), 149 (50), 145 (56), 133 (50), 132 (24), 131 (43), 119 (50), 117 (37), 105 (59), 91 (58), 79 (26), 77 (33). − $C_{15}H_{20}O_3$ (248.3): calcd. C 72.55, H 8.12; found C 72.51, H 8.16.

Reaction of Tricyclic Oxo Ester **4c-Me** *with p-Tosylhydrazine:* 264 mg (1.00 mmol) of tricyclic γ-oxo ester **4c-Me** was added to a solution of 220 mg (1.18 mmol) of *p*-toluenesulfonylhydrazine in 5 ml of methanol. The resulting solution was stirred at room temp. overnight. Water (5 ml) was added and the precipitate was filtered to afford hydrazone **13**. Yield 315 mg (75%), colorless crystals, m. p. 183−184°C (ethanol). − IR (KBr): $\tilde{\nu}$ = 3202 cm^{-1}, 2955, 1749, 1718, 1436, 1351, 1282, 1169. − ^1H NMR ($CDCl_3$): δ = 0.20 (m, 1 H), 0.54 (m, 1 H), 0.70 (m, 1 H), 1.00 (s, 6 H), 1.45 (s, 1 H), 1.51 (m, 1 H), 1.86 (d, *J* = 16.1 Hz, 1 H), 2.43 (s, 3 H), 2.48 (d, *J* = 16.1 Hz, 1 H), 2.53 (d, *J* = 18.8 Hz, 1 H), 2.84 (d, *J* = 18.8 Hz, 1 H), 3.64 (s, 3 H), 7.31 and 7.75 (AA′BB′ system, 4 H), 7.62 (br. s, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 7.7, 7.8, 22.5, 27.5, 28.1, 28.9, 35.4, 35.9, 47.3, 51.7, 57.8, 64.6, 128.1, 129.4, 135.1, 144.1, 158.3, 169.0, 221.9. − MS (70 eV); *m/z* (%): 418 (39) [M^+], 263 (40), 206 (14), 202 (13), 191 (59), 179 (13), 175 (23), 147 (42), 133 (22), 131 (22), 119 (25), 117 (29), 115 (24), 105 (24), 91 (100), 77 (29). − $C_{21}H_{26}N_2O_5S$ (418.5): calcd. C 60.27, H 6.26; found C 60.22, H 6.17.

General Procedure for the Preparation of Methyl 6′-Hydroxy-2′-methoxy-6′-alkylspiro[cyclopropane-1,8′-tricyclo[3.2.1.0^{2,7}]-octane]-1′-carboxylates **14**: A 1.56−1.60 M solution of alkyllithium (2.00 ml, 3.1−3.2 mmol) was slowly added to a cooled (−78°C) and stirred solution of the tricyclic γ-oxo ester **4-Me** (1−2 mmol) in anhydrous THF (10 ml) under N_2. The mixture was stirred for 1.5−12 h. Saturated aqueous NH_4Cl solution (10 ml) was added, the organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (2 × 30 ml) and the combined organic phases were dried ($MgSO_4$). The solvent was evaporated and the residue was either chromatographed on silica gel (CH_2Cl_2/EtOAc) or recrystallized from the appropriate solvent to afford the pure alcohols **14**.

*Methyl 6′-Hydroxy-5′,6′-dimethyl-2′-methoxyspiro[cyclopropane-1,8′-tricyclo[3.2.1.0^{2,7}]*octane]-1′-carboxylate (**14l**): From 365 mg (1.46 mmol) of **4b-Me** and 2.00 ml (3.12 mmol) of a 1.56 M solution of methyllithium in diethylether. Yield 370 mg (95%), colorless crystals, m. p. 78−80°C (hexane). − ^1H NMR ($CDCl_3$): δ = 0.11 (m, 1 H), 0.34 (s, 3 H), 0.36−0.45 (m, 2 H), 0.99 (m, 1 H), 1.14 (m, 1 H), 1.23 (s, 3 H), 1.71 (m, 1 H), 2.05−2.25 (m, 3 H), 2.16 (s, 1 H), 3.18 (s, 3 H), 3.56 (s, 3 H). − ^{13}C NMR ($CDCl_3$): δ = 2.5, 6.2, 13.3, 19.1, 24.7, 27.4, 27.7, 38.6, 39.8, 42.2, 51.3, 54.3, 68.2, 77.8, 168.4. − MS (70 eV); *m/z* (%): 266 (13) [M^+], 234 (55), 223 (28), 207 (20), 205 (22), 193 (29), 191 (100), 180 (22), 177 (20), 175 (59), 163 (34), 161 (23), 159 (16), 149 (22), 133 (22), 122 (19), 91 (24). − $C_{15}H_{22}O_4$ (266.3): calcd. C 67.65, H 8.33; found C 68.09, H 8.27.

Methyl 6′-Hydroxy-2′-methoxy-4′,4′,6′-trimethylspiro[cyclopropane-1,8′-tricyclo[3.2.1.0^{2,7}]octane]-1′-carboxylate (**14m**): From 528 mg (2.00 mmol) of **4c-Me** and 3.00 ml (4.68 mmol) of a 1.56 M solution of methyllithium in diethylether. Yield 300 mg (54%), colorless crystals, m. p. 96−98°C (hexane). − IR (KBr): $\tilde{\nu}$ = 3457 cm^{-1}, 2954, 1718, 1433, 1361, 1244, 1132, 1075, 963. − ^1H NMR ($CDCl_3$): δ = 0.29−0.35 (m, 2 H), 0.63 (s, 1 H), 0.73 (m, 1 H), 1.18 (s, 3 H), 1.24 (s, 3 H), 1.40 (m, 1 H), 1.55 (s, 3 H), 1.70 (s, 1 H), 2.09 (d, *J* = 13.1 Hz, 1 H), 2.09 (m, 1 H), 2.37 (d, *J* = 13.1 Hz, 1 H), 3.23 (s, 3 H), 3.62 (s, 3 H). − ^{13}C NMR ($CDCl_3$): δ = 9.4, 10.2, 25.5, 29.9, 32.1, 33.5, 34.2, 36.2, 36.5, 40.5, 51.7, 54.5, 56.6, 67.9, 80.1, 168.7. − MS (70 eV); *m/z* (%): 280 (1) [M^+], 248 (24), 237 (10), 209 (10), 205 (100), 177 (19), 169 (20), 145 (10), 105 (10), 91 (10).

Methyl 6′-Hydroxy-2′-methoxy-4′,4′-dimethyl-6′-phenylspiro[cyclopropane-1,8′-tricyclo[3.2.1.0^{2,7}]octane]-1′-carboxylate (**14n**): From 528 mg (2.00 mmol) of tricyclic oxo ester **4c-Me** and 2.00 ml (3.2 mmol) of a 1.60 M solution of phenyllithium in diethyl ether. Yield 450 mg (66%), colorless crystals, m. p. 131−133°C (hexane). − IR (KBr): $\tilde{\nu}$ = 3413 cm^{-1}, 2950, 1718, 1359, 1344, 1245, 1126, 1089, 1066, 764. − ^1H NMR ($CDCl_3$): δ = −0.82 (m, 1 H), −0.17 (m, 1 H), 0.46 (m, 1 H), 0.99 (br. s, 1 H), 1.20 (m, 1 H), 1.19 (s, 3 H), 1.42 (s, 3 H), 1.92 (s, 1 H), 2.08 (d, *J* = 13.1 Hz, 1 H), 2.54 (s, 1 H), 2.56 (d, *J* = 13.1 Hz, 1 H), 3.29 (s, 3 H), 3.69 (s, 3 H), 7.25−7.35 (m, 3 H), 7.56−7.60 (m, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 8.3, 9.8, 24.2, 31.9, 33.5, 33.7, 33.8, 36.5, 41.8, 51.8, 54.5, 58.0, 68.2, 83.1, 126.2, 127.4, 127.8, 147.5, 168.5. − MS (70 eV); *m/z* (%): 342 (7) [M^+], 310 (55), 282 (7), 266 (35), 251 (10), 237 (15), 227 (20), 205 (46), 196 (25), 169 (11), 167 (13), 105 (100), 77 (19). − $C_{21}H_{26}O_4$ (342.4): calcd. C 73.66, H 7.65; found C 73.81, H 7.75.

Methyl 6′-Hydroxy-2′-methoxy-4′,4′-dimethyl-6′-[bis(phenylsulfanyl)methyl]spiro[cyclopropane-1,8′-tricyclo[3.2.1.0^{2,7}]octane]-1′-carboxylate (**14o**): From 264 mg (1.00 mmol) of tricyclic oxo ester **4c-Me** and 2.3 mmol of bis(phenylsulfanyl)methyllithium in THF [prepared from a 2.34 M solution (1.00 ml, 2.34 mmol) of butyllithium and 534 mg (2.30 mmol) of bis(phenylsulfanyl)methane in 8 ml of THF at 0°C]. Yield 220 mg (44%), colorless crystals, m. p. 89−91°C (ethanol). − IR (KBr): $\tilde{\nu}$ = 3450−3330 cm^{-1}, 2929, 1710, 1472, 1437, 1363, 1344, 1248, 1082. − ^1H NMR ($CDCl_3$): δ = 0.22−0.37 (m, 2 H), 0.77 (dt, *J* = 9.9, 5.9 Hz, 1 H), 1.20 (s, 3 H), 1.31 (s, 3 H), 1.47 (dt, *J* = 9.9, 5.9 Hz, 1 H), 1.57 (s, 1 H), 2.03 (d, *J* = 13.2 Hz, 1 H), 2.44 (d, *J* = 13.2 Hz, 1 H), 2.75 (s, 1 H), 2.78 (br. s, 1 H), 3.23 (s, 3 H), 3.48 (s, 3 H), 5.11 (s, 1 H), 7.18−7.32 (m, 8 H), 7.42−7.46 (m, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 8.6, 9.4, 25.3, 31.7, 33.4, 34.1, 34.6, 36.2, 40.2, 51.4, 52.8, 54.4, 68.5, 71.8, 86.2, 127.2, 128.2, 128.8, 132.1, 133.1, 134.1, 135.9, 167.9. − MS (70 eV); *m/z* (%): 496 (30) [M^+], 464 (22), 387 (100), 381 (34), 355 (82), 327 (51), 277 (43), 271 (22), 245 (24), 231 (41), 227 (31), 205 (22), 189 (27), 177 (23), 161 (20), 145 (28), 122 (33), 109 (28), 91 (28), 83 (25), 77 (25), 57 (46). − $C_{28}H_{32}O_4S_2$ (496.7): calcd. C 67.71, H 6.49; found C 67.63, H, 6.47.

Methyl 6′-Hydroxy-6′-(1-hydroxypropyn-2-yl)-2′-methoxy-4′,4′-dimethylspiro[cyclopropane-1,8′-tricyclo[3.2.1.0^{2,7}]octane]-1′-carboxylate (**14p**): From 1.050 g (3.97 mmol) of tricyclic γ-oxo ester **4c-Me**, 524 mg (9.35 mmol) of propargyl alcohol (distilled from K_2CO_3 prior to use), and a 2.34 M solution of butyllithium (8.00 ml, 18.72 mmol) in hexane added at −78°C and slowly warmed to room temp. Yield 823 mg (65%), colorless oil. − ^1H NMR ($CDCl_3$): δ = 0.38 (m, 1 H), 0.54 (m, 1 H), 0.71 (m, 1 H), 1.00 (s, 1 H), 1.16 (s, 3 H), 1.23 (s, 3 H), 1.36 (m, 1 H), 1.96 (d, *J* = 13.2 Hz, 1 H), 2.34 (d, *J* = 13.2 Hz, 1 H), 2.50 (s, 1 H), 3.22 (s, 3 H), 3.36 (m, 1 H), 3.62 (s, 3 H), 4.28 (d, *J* = 3.9 Hz, 1 H). − ^{13}C NMR

($CDCl_3$): δ = 9.2, 10.6, 25.4, 31.6, 33.2, 33.5, 36.1, 36.4, 41.1, 50.8, 51.7, 54.4, 56.6, 67.5, 75.4, 82.0, 89.5, 168.5.

General Procedure for the Epoxidation of **9**: A 0.05−0.08 M solution of dimethyldioxirane (1.00−3.20 mmol) in acetone was added to a cooled (0°C) and stirred solution of 0.46−0.68 mmol of bicyclooctenes **9** in 10 ml of CH_2Cl_2. The resulting solution was stirred for 1−3 h. The solvent was evaporated and the residue was either chromatographed on silica gel (CH_2Cl_2) or recrystallized from an appropriate solvent to afford epoxides **15**.

exo-Epoxide **15a**: From 150 mg (0.68 mmol) of **9a** and 20 ml (1.0 mmol) of a 0.05 M solution of dimethyldioxirane. Yield 60 mg (37%), colorless crystals, m. p. 98−99°C (hexane). − IR (KBr): $\tilde{\nu}$ = 2964 cm^{-1}, 1741, 1706, 1438, 1316, 1276, 1254, 1070. − ^1H NMR ($CDCl_3$): δ = 0.27 (m, 1 H), 0.41 (m, 1 H), 0.72−0.77 (m, 2 H), 1.55 (s, 3 H), 1.69 (m, 1 H), 1.98−2.05 (m, 2 H), 2.43−2.49 (m, 2 H), 3.66 (s, 1 H), 3.68 (s, 3 H). − ^{13}C NMR ($CDCl_3$): δ = 1.4, 12.0, 14.6, 25.7, 27.1, 35.5, 46.8, 51.8, 60.2, 61.7, 69.0, 166.8, 202.8. − MS (70 eV); *m/z* (%): 236 (2) [M^+], 206 (18), 180 (37), 179 (100), 177 (23), 166 (22), 165 (49), 149 (27), 133 (15), 122 (15), 120 (22), 105 (25), 91 (35), 77 (24). − $C_{13}H_{16}O_4$ (236.3): calcd. C 66.09, H 6.83; found C 66.22, H 6.97.

exo-Epoxide **15l**: From 107 mg (0.46 mmol) of **9l** and 40 ml (3.2 mmol) of a 0.08 M solution of dimethyldioxirane. Yield 105 mg (91%), colorless crystals, m. p. 128−130°C (hexane). − IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1}, 1743, 1705, 1436, 1420, 1316, 1275, 1074, 1058. − ^1H NMR ($CDCl_3$): δ = 0.08 (m, 1 H), 0.50−0.57 (m, 2 H), 0.72 (m, 1 H), 0.72 (s, 3 H), 1.49 (s, 3 H), 1.74 (m, 1 H), 1.86 (m, 1 H), 2.45−2.50 (m, 2 H), 3.71 (s, 1 H), 3.72 (s, 3 H). − ^{13}C NMR ($CDCl_3$): δ = −0.1, 7.7, 12.3, 13.8, 28.9, 33.3, 36.0, 43.6, 51.9, 61.8, 62.5, 68.8, 167.0, 202.9. − MS (70 eV); *m/z* (%): 250 (7) [M^+], 235 (87), 229 (17), 203 (18), 193 (100), 179 (66), 163 (28), 147 (17), 133 (24), 119 (16), 105 (19), 91 (29), 77 (17). − $C_{14}H_{18}O_4$ (250.3): calcd. C 67.18, H 7.25; found C 67.13, H 7.32.

exo-Epoxide **15n**: From 165 mg (0.53 mmol) of **9n** and 25 ml (2.00 mmol) of a 0.08 M solution of dimethyldioxirane. Yield 170 mg (98%), colorless crystals, m. p. 152−153°C (hexane). − IR (KBr): $\tilde{\nu}$ = 3001 cm^{-1}, 1743, 1708, 1455, 1438, 1318, 1259, 1061, 745. − ^1H NMR ($CDCl_3$): δ = 0.51 (m, 1 H), 0.52 (s, 3 H), 0.63 (m, 1 H), 0.77 (m, 1 H), 1.17 (s, 3 H), 1.30 (m, 1 H), 2.08 (s, 1 H), 2.22 (d, *J* = 15.4 Hz, 1 H), 2.62 (d, *J* = 15.4 Hz, 1 H), 3.74 (s, 3 H), 4.54 (s, 1 H), 7.37−7.43 (m, 5 H). − ^{13}C NMR ($CDCl_3$): δ = 5.0, 11.8, 25.6, 30.2, 31.3, 39.5, 51.3, 52.0, 54.6, 60.0, 64.6, 68.0, 128.8, 128.9, 136.1, 167.0, 203.5. − MS (70 eV); *m/z* (%): 326 (41) [M^+], 243 (73), 242 (99), 227 (51), 225 (22), 222 (27), 220 (37), 193 (33), 182 (50), 165 (15), 153 (24), 141 (15), 128 (22), 115 (18), 105 (100), 91 (15), 83 (31), 77 (32). − $C_{20}H_{22}O_4$ (326.4): calcd. C 73.60, H 6.79; found C 73.65, H 6.88.

Reaction of the Oxo Sulfide **7j** *with Methyllithium. − 1′-Acetyl-2′-methoxy-5′-methyl-6′-oxo-7′-phenylsulfanylspiro[cyclopropane-1,8′-bicyclo[3.2.1]oct-2′-ene]* (**16j**) *and 1′-Acetyl-6′-hydroxy-2′-methoxy-5′,6′-dimethyl-7′-phenylsulfanylspiro[cyclopropane-1,8′-bicyclo[3.2.1]oct-2′-ene]* (**17j**): A 1.56 M solution of methyllithium (1.80 ml, 2.81 mmol) in diethyl ether was slowly added to a cooled (−78°C) and stirred solution of 294 mg (0.82 mmol) of **7j** in 10 ml of anhydrous THF under N_2. The resulting solution was stirred overnight. Saturated aqueous NH_4Cl solution (10 ml) was added, the organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (3 × 20 ml) and the combined organic phases were dried ($MgSO_4$). The solvent was evaporated and the residue was chromatographed on silica gel (CH_2Cl_2) to afford 175 mg (62%) of **16j**, colorless crystals, and 81 mg (28%) of **17j**, oil.

16j: M. p. 120−122°C ($CHCl_3$/hexane). − IR (KBr): $\tilde{\nu}$ = 2896 cm^{-1}, 1744, 1709, 1661, 1480, 1354, 1256, 1229, 1046. − ^1H NMR ($CDCl_3$): δ = 0.28 (m, 1 H), 0.51−0.70 (m, 2 H), 0.77 (s, 3 H), 0.93 (m, 1 H), 2.11 (s, 3 H), 2.22−2.23 (m, 2 H), 3.60 (s, 3 H), 4.43 (s, 1 H), 4.66 (m, 1 H), 7.23−7.32 (m, 3 H), 7.64−7.67 (m, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 3.0, 5.4, 14.8, 29.8, 32.1, 36.6, 49.6, 54.5, 64.0, 65.6, 93.3, 127.2, 128.6, 132.4, 135.1, 156.3, 203.5, 226.0. − MS (70 eV); *m/z* (%): 342 (100) [M^+], 299 (4), 236 (6), 220 (22), 205 (36), 191 (12), 177 (13), 161 (10), 149 (19), 135 (5), 115 (10), 91 (17). − $C_{20}H_{22}O_3S$ (342.5): calcd. C 70.15, H 6.48; found C 70.20, H 6.46.

17j: ^1H NMR ($CDCl_3$): δ = 0.15 (m, 1 H), 0.36−0.54 (m, 2 H), 0.57 (s, 3 H), 0.72 (m, 1 H), 0.83 (s, 3 H), 1.92 (dd, *J* = 16.2, 4.8 Hz, 1 H), 2.03 (s, 3 H), 2.50 (dd, *J* = 16.2, 4.8 Hz, 1 H), 3.46 (s, 1 H), 3.53 (s, 3 H), 4.08 (s, 1 H), 4.65 (dd, *J* = 4.8, 2.4 Hz, 1 H), 7.24−7.32 (m, 3 H), 7.66−7.71 (m, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 2.5, 5.6, 16.1, 29.1, 29.8, 32.0, 34.1, 47.0, 54.1, 64.9, 68.5, 76.3, 94.3, 127.8, 128.8, 134.3, 155.3, 205.7.

Reaction of the Bicyclic Oxo Sulfide **7i** *with Methyllithium. − 1′-Acetyl-2′-methoxy-4′,4′-dimethyl-6′-oxo-7′-phenylsulfanylspiro-[cyclopropane-1,8′-bicyclo[3.2.1]oct-2′-ene]* (**16i**): A 1.56 M solution of methyllithium (2.0 ml, 3.12 mmol) in diethyl ether was slowly added to a cooled (−78°C) and stirred solution of 186 mg (0.50 mmol) of **7i** in 10 ml of anhydrous THF under N_2. The resulting solution was stirred for 20 h. Saturated aqueous NH_4Cl solution (10 ml) was added, the organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (3 × 20 ml) and the combined organic phases were dried ($MgSO_4$). The solvent was evaporated to afford 165 mg (93%), colorless crystals, m. p. 143−145°C (hexane). − IR (KBr): $\tilde{\nu}$ = 2974 cm^{-1}, 1735, 1708, 1653, 1481, 1242, 1102, 827, 791, 748, 695. − ^1H NMR ($CDCl_3$): δ = 0.28 (t, *J* = 8.0 Hz, 2 H), 1.06−1.22 (m, 2 H), 1.11 (s, 3 H), 1.26 (s, 3 H), 1.73 (br. s, 1 H), 2.11 (s, 3 H), 3.61 (s, 3 H), 4.37 (d, *J* = 1.2 Hz, 1 H), 4.60 (s, 1 H), 7.23−7.32 (m, 3 H), 7.63−7.67 (m, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 7.3, 7.9, 28.5, 29.5, 29.9, 30.4, 37.2, 54.5, 64.1, 64.4, 105.5, 127.2, 128.8, 132.1, 132.3, 135.3, 153.7, 203.5, 211.8. − MS (70 eV); *m/z* (%): 356 (39) [M^+], 247 (6), 229 (100), 191 (37), 175 (9), 163 (10), 161 (14), 149 (7), 145 (6), 105 (6), 91 (8). − $C_{21}H_{24}O_3S$ (356.5): calcd. C 70.76, H 6.79; found C 70.59, H 6.80.

Reduction of Bicyclic Oxo Sulfide **7i** *with $NaBH_4$. − Methyl 6′-Hydroxy-2′-methoxy-4′,4′-dimethyl-7′-phenylsulfanylspiro-[cyclopropane-1,8′-bicyclo[3.2.1]oct-2′-ene]-1′-carboxylate* (**18**): Sodium tetrahydroborate (3.00 g, 79 mmol) was slowly added to a cooled (0°C) and stirred solution of 372 mg (1.00 mmol) of **7i** in 30 ml of methanol. The resulting mixture was stirred for 1 h. Water (70 ml) was added, the mixture was extracted with CH_2Cl_2 (3 × 30 ml) and the combined organic phases were dried ($MgSO_4$). The solvent was evaporated to afford 364 mg (97%), colorless crystals, m. p. 141−143°C (hexane). − IR (KBr): $\tilde{\nu}$ = 3410 cm^{-1}, 2958, 1730, 1659, 1440, 1292, 1253, 1220, 1109. − ^1H NMR ($CDCl_3$): δ = 0.20−0.26 (m, 2 H), 0.89 (m, 1 H), 1.18 (s, 3 H), 1.27 (m, 1 H), 1.35 (s, 3 H), 1.51 (d, *J* = 5.1 Hz, 1 H), 3.31 (d, *J* = 7.5 Hz, 1 H), 3.55 (s, 3 H), 3.70 (s, 3 H), 4.51−4.62 (m, 3 H), 7.22−7.32 (m, 3 H), 7.54−7.58 (m, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 7.8, 8.2, 27.8, 29.8, 33.4, 37.6, 51.8, 54.2, 55.3, 60.1, 63.2, 71.8, 105.5, 126.8, 128.8, 131.1, 135.8, 152.5, 169.9. − MS (70 eV); *m/z* (%): 374 (81) [M^+], 359 (10), 343 (11), 327 (27), 265 (63), 235 (17), 233 (16), 207 (100), 191 (12), 175 (52), 163 (11), 161 (11), 149 (12), 123 (8). − $C_{21}H_{26}O_4S$ (374.5): calcd. C 67.35, H 7.00; found C 67.48, H 6.97.

Methyl 6′-Hydroxy-4′,4′-dimethyl-2′-oxo-7′-phenylsulfanylspiro-[cyclopropane-1,8′-bicyclo[3.2.1]octane]-1′-carboxylate (**19**): A

mixture of 364 mg (0.97 mmol) of **18** and 20 ml of conc. hydrochloric acid in 50 ml of CH_2Cl_2 was stirred at room temp. for 3 h. Ice (30 g) was added, the organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (3 × 20 ml) and the combined organic phases were dried ($MgSO_4$). The solvent was evaporated to afford 345 mg (99%), colorless crystals, m. p. 143−145°C (hexane). − IR (KBr): $\tilde{\nu}$ = 3485 cm^{-1}, 1724, 1712, 1484, 1439, 1259, 1204, 1110, 736, 690. − ^1H NMR ($CDCl_3$): δ = 0.13−0.27 (m, 2 H), 0.83 (m, 1 H), 1.11 (s, 3 H), 1.33 (s, 3 H), 1.44 (m, 1 H), 1.55 (dd, *J* = 5.9, 1.4 Hz, 1 H), 2.26 (dd, *J* = 16.2, 1.7 Hz, 1 H), 2.66 (d, *J* = 16.2 Hz, 1 H), 3.35 (d, *J* = 3.8 Hz, 1 H), 4.41 (d, *J* = 10.3 Hz, 1 H), 4.79 (m, 1 H), 7.26−7.36 (m, 3 H), 7.52−7.56 (m, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 8.3, 8.8, 28.2, 28.6, 31.0, 38.5, 51.4, 51.9, 55.0, 59.5, 69.9, 70.3, 127.9, 129.1, 132.1, 134.9, 168.1, 203.6. − MS (70 eV); *m/z* (%): 360 (56) [M^+], 250 (12), 229 (28), 191 (54), 178 (14), 166 (19), 150 (96), 138 (14), 135 (19), 119 (26), 110 (100), 91 (46), 83 (61), 77 (25). − $C_{20}H_{24}O_4S$ (360.5): calcd. C 66.64, H 6.71; found C 66.78, H 6.58.

Epoxide **20**: A 1.95 M solution of diethylzinc (2.9 ml, 5.66 mmol) in toluene was added within 5 min to a cooled (0°C) and stirred solution of 372 mg (1.00 mmol) of **7i** and 1.61 g (6.01 mmol) of diiodomethane in 20 ml of anhydrous toluene under N_2. The resulting solution was stirred at room temp. for 16 h. Water (120 ml) was added, the organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (3 × 50 ml), and the combined organic phases were washed with brine (3 × 100 ml) and dried ($MgSO_4$). The solvent was evaporated and the residue was chromatographed on silica gel (CH_2Cl_2/hexane, 1:1) to afford epoxide **20**. Yield 96 mg (25%), colorless crystals, m. p. 81−82°C (hexane). − IR (KBr): $\tilde{\nu}$ = 2908 cm^{-1}, 1741, 1625, 1290, 1266, 1243, 1222, 1147, 1093, 1068, 1054, 989, 715, 689. − ^1H NMR ($CDCl_3$): δ = 0.28 (m, 1 H), 0.42 (m, 1 H), 0.85 (m, 1 H), 0.89 (s, 3 H), 1.18 (s, 3 H), 1.34 (m, 1 H), 1.70 (s, 1 H), 3.47 (s, 3 H), 3.67 (s, 3 H), 4.02 (d, *J* = 1.1 Hz, 1 H), 5.16 (2d, *J* = 11.5 Hz, 2 H), 5.47 (s, 1 H), 7.22−7.32 (m, 3 H), 7.43−7.47 (m, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 8.1, 9.0, 29.3, 29.4, 35.5, 36.9, 51.5, 54.6, 57.5, 58.9, 73.0, 100.3, 106.1, 126.9, 128.9, 130.0, 135.6, 158.3, 161.4, 170.3. − MS (70 eV); *m/z* (%): 386 (6) [M^+], 371 (39), 277 (3), 249 (4), 235 (3), 203 (5), 189 (5), 163 (6), 123 (100), 77 (4). − $C_{22}H_{26}O_4S$ (386.5): calcd. C 68.37, H 6.78; found C 68.18, H 6.63.

Methyl 2′-Methoxy-4′,4′-dimethyl-6′-oxo-7′-phenylsulfonylspiro-[cyclopropane-1,8′-bicyclo[3.2.1]oct-2′-ene]-1′-carboxylate (**21**): A 0.08 M solution of dimethyldioxirane (50 ml, 4.00 mmol) in acetone was slowly added to a cooled (−78°C) and stirred solution of 250 mg (0.67 mmol) of **7i** in 20 ml of CH_2Cl_2 under N_2. The resulting mixture was stirred for 7 h (−78 to −20°C). The solvent was evaporated to afford 250 mg (92%), colorless crystals, m. p. 164−166°C (ethanol/hexane). − IR (KBr): $\tilde{\nu}$ = 2957 cm^{-1}, 1738, 1654, 1449, 1326, 1293, 1281, 1248, 1178, 1153, 1110. − ^1H NMR ($CDCl_3$): δ = 0.20−0.26 (m, 2 H), 1.01 (m, 1 H), 1.11 (s, 3 H), 1.18 (s, 3 H), 1.27 (m, 1 H), 1.72 (s, 1 H), 3.63 (s, 3 H), 3.71 (s, 3 H), 4.61 (d, *J* = 0.4 Hz, 1 H), 4.78 (d, *J* = 0.9 Hz, 1 H), 7.49−7.61 (m, 3 H), 7.97−8.01 (m, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 6.9, 7.7, 28.3, 28.7, 30.4, 37.2, 52.5, 55.5, 58.7, 63.9, 78.9, 106.1, 128.7, 129.0, 133.6, 141.1, 150.1, 167.8, 207.0. − MS (70 eV); *m/z* (%): 404 (17) [M^+], 391 (8), 390 (22), 389 (100), 230 (5), 207 (10), 175 (14), 57 (5), 44 (19). − $C_{21}H_{24}O_6S$ (404.5): calcd. C 62.36, H 5.98; found C 62.10, H 5.87.

☆ Dedicated to Professor *Hans Paulsen* on the occasion of his 75th birthday.

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[12] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100392. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [Fax: (internat.) +44 (0)1223 / 336-033, E-mail: deposit@ccdc.cam.ac.uk].

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