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Diels−Alder Cycloaddition and Ring-Closing Metathesis: A Versatile, Stereoselective, and General Route to Embellished Bridged Bicyclic Systems, Carbocyclic Framework of Secoatisanes, and Homologues

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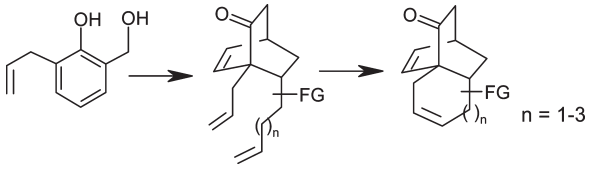
Received June 15, 2009



A general and stereoselective methodology for the synthesis of bridged bicyclic octenones having various types of alkenyl chains and a tricyclic framework of secoatisanes and higher analogues is reported. In situ generation and cycloaddition of 2-allyl-6,6-spiroepoxycyclohexadienones with ethyl acrylate gave bicyclo[2.2.2]octanes having an allyl group at the bridgehead and other chemically distinguishable functionality in a regio- and stereoselective fashion. Selective manipulation of adducts led to the introduction of other olefinic chain of variable lengths at the carbon adjacent to the bridge head. Ring-closing metathesis in bicyclooctanes having olefin tethers provided an efficient route to tricyclic systems having bicyclo[2.2.2]octane framework having spiro-fused six-, seven-, and eight-membered rings.

Introduction

Atisanes and secoatisanes constitute an important class of diterpenoids that have generated significant interest by virtue of their complex molecular architecture containing a spiro-fused bicyclo[2.2.2]octane framework and diverse biological properties.[1−3] Serofendic acid A **1**, a member of a unique class of atisane diterpenoids, recently isolated from lipophilic extracts of fetal calf serum has been found to possess neuroprotective activity.[2] While atisanes type diterpenoids are known for long time, seco-atisanes **2a**−**c** (Figure 1) having tricyclo[6.2.2.0^{1,6}]dodecane framework of type **3** were isolated recently from Chinese mangrove *Exoecaria*.[3] The tricyclo[6.2.2.0^{1,6}]dodecane core is also present in the molecular structure of platencin **2d**, which was recently isolated from *Stereptomyces plantecis*.[4] Platencin, a potent inhibitor of FabH and FabF,[2] has also stimulated intense interest on account of its biological activity and unusual structure.[5] While there are no synthetic studies toward recently isolated secoatisanes, only a few routes to atisanes

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Published on Web 07/17/2009 DOI: 10.1021/jo901279g

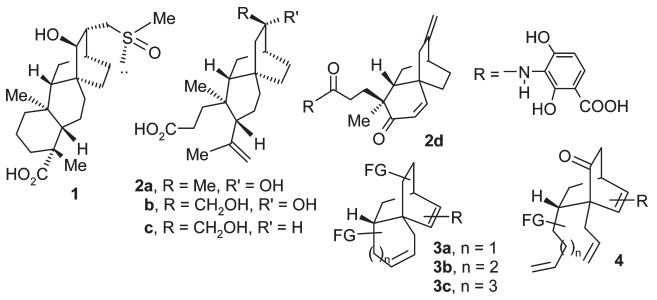


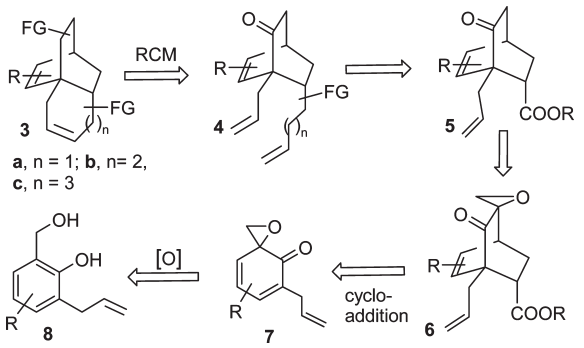
FIGURE 1. Serofendic acid A **1**, secoatisanes **2a**−**c**, platencin **2d**, and potential intermediates **3** and **4**.

diterpenoids have been developed.[6−9] Some of these employed a double Michael addition to create spiro-annulated bicyclo[2.2.2]octane system,[8a−c] whereas others used indirect methods.[6,9]

Recently, there has been an upsurge of interest in the development of new methods involving reactive intermediates arising as a result of oxidative dearomatization such as *o*-quinols, cyclohexadienone ketals, and spiroepoxycyclohexa-2,4-dienones, and the chemistry of these species has provided efficient methodology for the synthesis of a variety of molecular architectures.[10−12]

In view of the limited routes available for the construction of tricyclo[6.2.2.0^{1,6}]dodecane framework and our continuing interest[11] in the development of new methods employing 6,6-spiroepoxycyclohexadienones, we considered developing a new and general route to functionalized tricyclo-[6.2.2.0^{1,6}]dodecanes of type **3a** as well as the higher homologues of type **3b**,**c** having medium rings fused to the bridged bicyclooctane framework. It was envisaged that a ring-closing metathesis reaction in appropriately designed bridged bicyclic compounds of type **4** would provide a general and flexible entry to annulated bicyclooctenones of type **3**. The crucial precursor of type **4** was thought to be derived from the functionalized bicyclo[2.2.2]octenones of type **5**. The precursor **5** was thought to be prepared from the aromatic precursor **8** via its transformation to spiroepoxycyclohexadienone **7**, cycloaddition, and subsequent manipulation of the adduct **6** (Scheme 1).

SCHEME 1



There are several interesting features of our strategy. For example, the allylic chain at the bridgehead in crucial precursor **4** is derived from the starting aromatic precursor **8**. The other olefinic tether will be introduced by manipulation of the *endo* ester group in **5**, thus keeping both the tethers in appropriate stereochemical disposition required for the ring-closing metathesis. Furthermore, the bridged bicyclic precursor **4** is generated via manipulation of the adduct **6** which is endowed with easily distinguishable functionalities and rapidly assembled from a simple aromatic precursors of type **8**.

We wish to report herein a general and stereoselective methodology for the synthesis of embellished bicyclo[2.2.2]octanes of type **4** having various types olefinic tethers from simple aromatic precursors, and their ring-closing metathesis leading to functionalized tricyclo-[6.2.2.0^{1,6}]dodecanes **3a** and their homologues **3b**,**c** having medium rings.

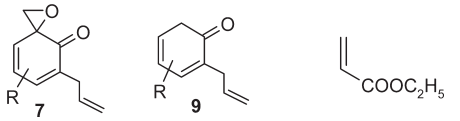


FIGURE 2. Cyclohexa-2,4-dienones and potential dienophile.

Results and Discussion

Synthesis of the Bicyclic Systems of Type 4 Endowed with Olefinic Tethers. Conceptually, the bicyclic systems of type **4** may be accessible via a direct cycloaddition of cyclohexa-2,4-dienones such as **9** with ethyl acrylate followed by further manipulation. However, cyclohexadienones of type **9** are not accessible as these are keto tautomers of the corresponding phenols. We therefore employed the 6,6-spiroepoxycyclohexa-2,4-dienone **7**, which may be generated by the oxidative dearomatization of *o*-hydroxymethyl phenols and its cycloaddition with acrylate and manipulation of the resulting adduct for the synthesis of bridged bicyclic systems of type **4**.

Thus, the *o*-hydroxymethyl phenols **12a**,**b** were easily prepared from *p*-cresol **10a** and salicyldehyde **10b**, respectively. Allylation of *p*-cresol followed by Claisen rearrangement gave **11a** which upon hydroxymethylation readily gave the known[11b] compound **12a** in good yield (Scheme 2). Similarly, the aldehyde **11b** was prepared from salicyldehyde[13] and reduced with sodium borohydride to give the hydroxymethyl phenol **12b**.

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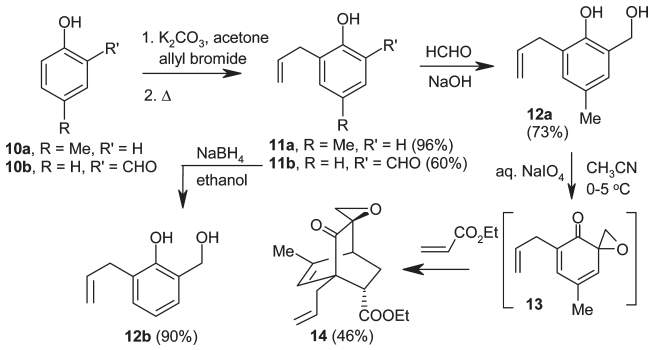
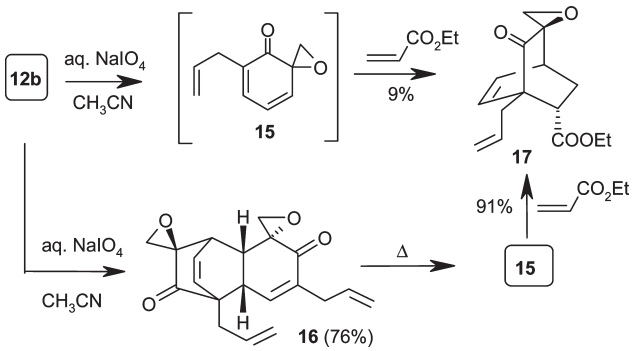
SCHEME 2



SCHEME 3



A solution of 6-allyl-2-hydroxymethyl-4-methylphenol **12a** in acetonitrile containing ethyl acrylate was oxidized with aqueous sodium *m*-periodate,[14] following a procedure developed in our laboratory,[15] to give the *endo* adduct **14** in reasonably good yield as a result of regio- and stereoselective cycloaddition of in situ generated cyclohexa-2,4-dienone **13** and ethyl acrylate (Scheme 2).

However, oxidation of the precursor **12b** under similar conditions gave the desired adduct **17** in very poor yield (9%), and the dimer **16** was obtained as a major product. The structure of dimer **16** was deduced from its spectral features and further confirmed through single-crystal X-ray diffraction (Supporting Information). It appears that the formation of the dimer **16** is presumably due to the relatively faster rate of intermolecular cycloaddition as compared to **13** which has a methyl group at C-4. In view of the above, it was thought that in situ generation of the cyclohexadienone **15** via retro Diels−Alder reaction of the dimer **16** and subsequent interception with ethyl acrylate under thermal activation might lead to the formation of the desired adduct **17**. Therefore, the dimer **16** was prepared by the oxidation of **12b** and heated in the presence of ethyl acrylate. Indeed, chromatography of the reaction mixture furnished the desired adduct **17** in excellent yield (91%) (Scheme 3).

The structure of both adducts was deduced from their spectral data and comparison. Thus, the IR spectrum of adduct **14** showed a broad absorption band at 1736 cm^{-1} for the carbonyl groups of α-epoxy ketone and the ester group. The ^1H NMR (300 MHz) spectrum displayed characteristic signals at δ 5.92−5.78 (m, 1H), 5.13−5.04 (m, 2H), and 5.64 (s with structure, 1H) for olefinic protons of the allyl moiety and the β-proton of β,γ-enone group, respectively. The methylene protons of ester were observed at δ 4.12 (q, J = 6 Hz, 2H). The protons of the oxirane ring showed a characteristic signals at δ 3.15 as part of an AB system (J_{AB} = 6 Hz) and 2.92 (part of an AB system, J_{AB} = 6 Hz). It further exhibited a signal at δ 2.85 (dd with structure, J_1 = 12 Hz, J_2 = 6 Hz, 1H). The methine proton attached to the α-carbon of ester showed signals at δ 2.65 (dd with structure, J_1 = 10 Hz, J_2 = 6 Hz, 1H), 2.50−2.33 (m, 3H). It further showed signals at δ 1.94 (s with structure, 3H), 1.82 (ddd, J_1 = 12 Hz, J_2 = 6 Hz, J_3 = 3 Hz, 1H), 1.26 (t, J = 6 Hz, 3H, CH_3). The ^{13}C NMR (75 MHz) spectrum exhibited characteristic signals at δ 203.9 and 172.9 for the carbonyl groups present in the ethano bridge and ester groups, respectively. In addition, signals were observed at δ 143.4, 134.0, 122.7, 118.2 for four olefinic carbons. Other carbons showed their signals at δ 60.7, 57.6, 54.2 52.5, 44.0, 43.3 34.1, 28.7, 20.6, and 14.1. The aforementioned spectral features clearly suggested the structure of adduct **14**. The orientation of the oxirane ring was suggested on the basis of the general tendencies of spiroepoxycyclohexadienones during their cycloaddition and comparison of the spectral features of related compounds.[11,14] This stereogenic center is inconsequential as it will be lost during further transformations. The adduct **17** also displayed similar spectral characteristics.

The presence and disposition of carbonyl, oxirane, and ester functionalities in the aforementioned adducts provided a unique opportunity for their selective manipulation and elaboration to the desired bicyclic systems. Thus, treatment of the epoxyketone **14** with activated zinc in aqueous methanol containing ammonium chloride furnished the β-keto alcohol **18** in excellent yield (92%) as a *syn*/*anti* mixture (^1H NMR spectrum) (Scheme 4). The β-keto alcohol **18** thus obtained was oxidized with Jones' reagent to the corresponding acid, which upon decarboxylation gave the desired compound **19**. Similarly, the adduct **17** was also converted into the ketoester **21**. The structures of all the compounds were fully consistent with their data. In order to introduce the other olefinic tether in the bicyclic compound **19** and **21**, conversion of ester groups into aldehydes was required. Hence, the carbonyl group in **19** was protected, and the resulting ketal ester **22** was reduced with lithium aluminum hydride to give the alcohols **23** in excellent yield (Scheme 4). Various reagents were explored for the oxidation of **23** into the aldehyde **24**. The alcohol **23** was readily oxidized with PCC;[16] however, deprotection of the ketal group was found to occur. After considerable experimentation, TPAP-NMO[17] was found to be the best reagent for the oxidation of **23** as it furnished the aldehyde **24** quantitatively without any problem. Similarly, the ketal ester **25** was also transformed into aldehyde **27** (Scheme 4).

In order to introduce the alkenyl chains, the aldehydes **24** and **27** were treated with various Grignard reagents. Thus, reaction of aldehyde **24** with vinylmagnesium bromide gave the alcohols **28a** and **28b**, the former being a major product,

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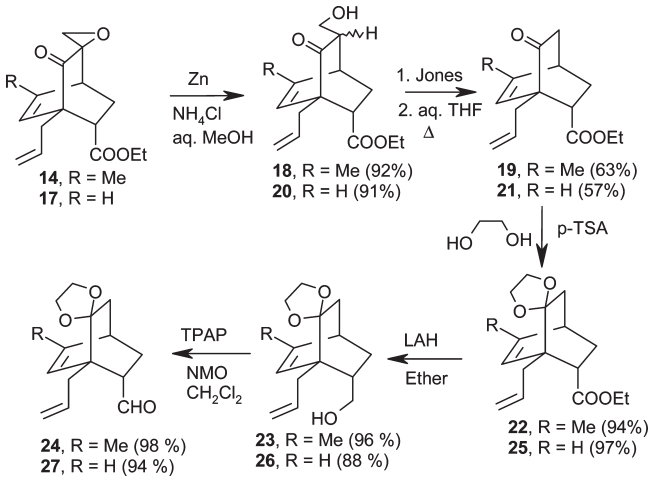
SCHEME 4

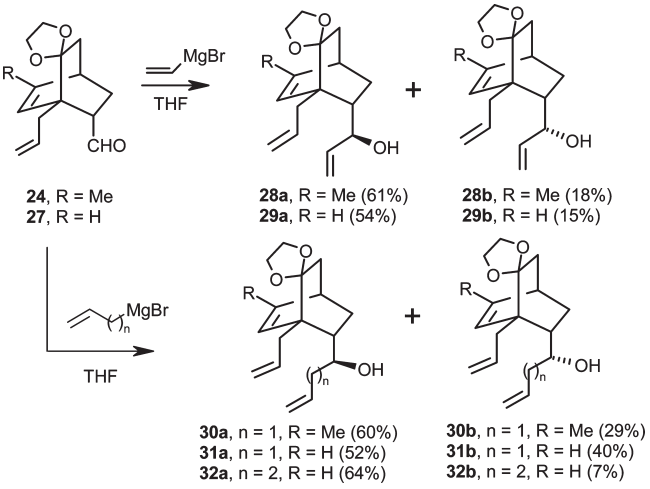


in addition to a small amount of the reduced product **23**. Similar reaction of **27** with vinylmagnesium bromide also furnished the alcohols **29a**,**b** containing **29a** as major product. The addition of allylmagnesium bromide to **24** also gave diastereomeric alcohols **30a** and **30b** in excellent yield. Similarly, the reaction of aldehyde **27** with allyl- and butenylmagnesium bromides furnished the alcohols **31a**,**b** and **32a**,**b**, respectively (Scheme 5). The structure of these alcohols was deduced by comparison of their spectral features and further transformations (vide infra). Further, the alcohol **28b** was oxidized with MnO_2 to the ketone **33.** Removal of the ketal group in compound **30b** gave the keto alcohol **34**, which was oxidized to furnish the dione **35**. Similarly, hydrolysis of the compound **32a** gave **36** which upon oxidation with PCC gave the dione **37** (Scheme 6).

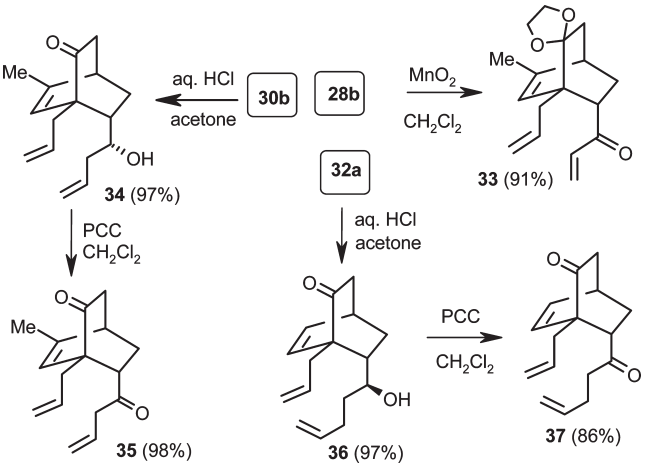
It may be mentioned that bridged bicyclic systems endowed with olefinic tethers are not readily accessible and the aforementioned methodology provides a general and stereoselective synthesis of such systems. The methodology is general, flexible, and readily adaptable. After the bridged bicyclo[2.2.2]octenones **28**−**37** appropriately disposed with olefinic tethers were synthesized, their ring-closing metathesis reaction was examined as described below.

Studies on Ring-Closing Metathesis: Synthesis of Functionalized Tricyclo[6.2.2.0^{1,6}]dodecanes, Tricyclo[7.2.2.0^{1,7}]tridecanes, and Tricyclo[8.2.2.0^{1,8}]tetradecanes. Ring-closing metathesis has proved to be a general and versatile method for the formation of various types of rings.[18,19] A large number of examples dealing with ring-closing metathesis on a variety of precursors

SCHEME 5



SCHEME 6



are known, and enumerable applications in synthesis are continuously being reported.[20−22] Studies on ring-closing metathesis and related reactions on bridged bicyclo[2.2.2]octanes are, however, limited. This is presumably due to lack of methods leading to bridged polycyclic systems endowed with appropriately disposed alkenyl chains. Recently, Phillips and co-workers have developed ROM−RCM in bridged bicyclo[2.2.2]octanes and employed in the synthesis of the natural product.[22] The ring-closing metathesis, though very general, the steric, conformational, and geometric factors, and the functionality in the substrates govern the cyclization in a subtle fashion, and they often produce oligomers resulting from olefin polymerization (intermolecular RCM). The bicyclic compounds **28**−**37** which contain two olefinic tethers and a C═C bond in the bicyclo[2.2.2]octane framework may also undergo reactions such as ring-opening−ring-closing metathesis, especially

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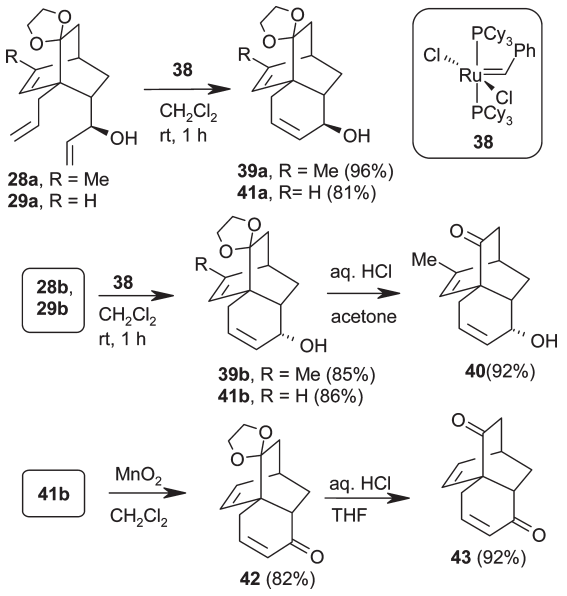
SCHEME 7



between the tether at the methine carbon and the C=C double bond in the ethano bridge, and oligomerization, in addition to the desired cyclization. Keeping this in mind, we explored the ring-closing metathesis in **28**−**37**.

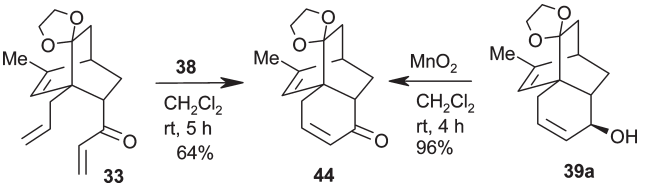
Thus, a solution of compound **28a** in CH_2Cl_2 was treated with first-generation Grubbs' catalyst (**38**) at ambient temperature, which led to a smooth reaction and furnished the tricyclic keto alcohol **39a** in excellent yield. Similarly, treatment of **28b** and **29a**,**b** furnished the corresponding cyclized products **39b** and **41a**,**b**, respectively, in very good yields (Scheme 7). The product **39b** was hydrolyzed with aq HCl to give the hydroxy ketone **40** in excellent yield. Further, the ketal alcohol **41b** was transformed into the keto ketal **42** which upon removal of the protecting group furnished the dione **43** (Scheme 7).

The structures of all the products were suggested by their ^1H NMR and ^{13}C NMR spectra and comparison of their spectral features. The stereostructure of the keto alcohol **40** was further confirmed through single-crystal X-ray diffraction studies (see the Supporting Information) which also proved the structures of its precursors, especially the stereochemical orientation of the hydroxyl group in **28b** and **39b**. The structure and stereochemistry of other products were deduced by comparison of their spectral features with those of **28b** and **39b**.

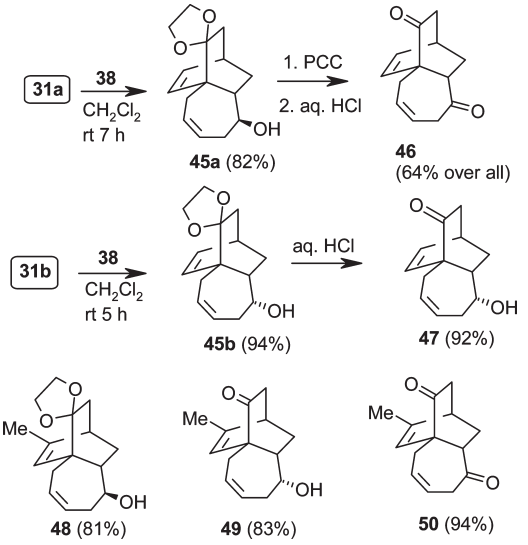
Ring-closing metathesis of the trienone **33** was also examined. Thus, a solution of **33** in dichloromethane was treated with the catalyst **38**. The reaction was sluggish as compared to the aforementioned substrates. After the reaction mixture was stirred for 5 h followed by chromatography, the product **44** was isolated in moderate yield (65%) (Scheme 8). The compound **44** was also prepared by oxidation of the ketal alcohol **39a** with MnO_2. The sluggishness of the keto ketal **33** toward ring-closing metathesis could be due to geometrical constraints imposed by the presence of a conjugated carbonyl group in one of the tethers.

The bicyclic compounds **30a**, **31a**,**b**, and **34** were also subjected to ring-closing metathesis. First, a solution of the compound **31a** in dichloromethane was stirred with Grubbs'

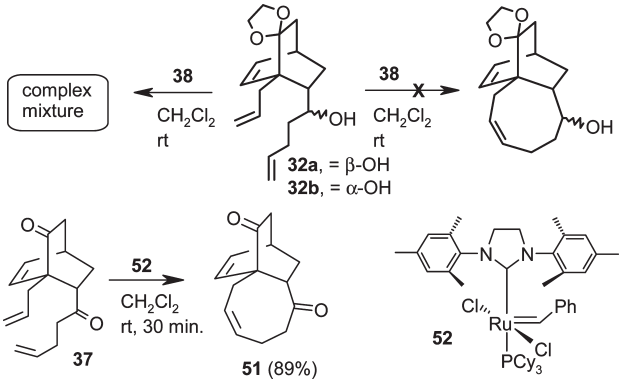
SCHEME 8



SCHEME 9



SCHEME 10



first-generation catalyst **38**, which furnished the cyclized product **45a** having a seven-membered ring annulated to bicyclo[2.2.2]octane framework, in excellent yield. The ketal alcohol **45a** was converted into the dione **46** via PCC oxidation and hydrolysis of the ketal group (Scheme 9). Ring-closing metathesis of the compound **31b** also gave the tricyclic compound **45b** which upon hydrolysis furnished the keto alcohol **47**. Similarly, the ketal alcohol **30a** and keto alcohol **34** underwent smooth ring-closing metathesis to give the corresponding tricyclic compounds **48** and **49**, respectively, in excellent yield. Further, the keto alcohol **49** was oxidized with PCC to give the dione **50** (Scheme 9).

The structures of all the products were deduced from their spectral features and comparison. The stereochemical disposition of hydroxyl groups in **45a** and **49** was further confirmed through a single-crystal X-ray structure (see the

Supporting Information). This also confirmed the structure of the preceding intermediates including the Grignard addition products **31a**, **30b**, and their congeners.

The construction of eight-membered rings is generally considered to be difficult due to conformational, steric, and entropic factors.[23] Though a number of rings of various sizes have been prepared by ring-closing metathesis, the formation of medium and larger rings depend on various factors including the functional groups, in a subtle fashion. In view of this, it was interesting to examine the ring-closing metathesis of compounds **32a**,**b** which would lead to formation of eight-membered rings. Thus, compounds **32a** and **32b** were treated with Grubbs' first-generation catalyst **38**. However, in both cases, a complex mixture of products was obtained from which we could not isolate the desired compound. Hence, ring-closing metathesis was attempted on the dione **37**. It was indeed gratifying to note that the treatment of **37** with Grubbs' second-generation catalyst **52** ensued a smooth reaction and furnished the tricyclic dienedione **51** having an eight-membered ring annulated to the bridged bicyclic octane framework, in excellent yield (Scheme 10).

Conclusion

In summary, a new, general, and stereoselective methodology for the synthesis of bicyclo[2.2.2]octenones annulated with functionalized six-, seven-, and eight-membered rings has been developed. The key features of the methodology are the cycloaddition of 2-allyl-6,6-spiroepoxycyclohexa-2,4-dienones with ethyl acrylate and ring-closing metathesis. The cycloaddition of 2-allyl-6,6-spiroepoxycyclohexa-2,4-dienones with ethyl acrylate gives bicyclo[2.2.2]octanes disposed with chemically distinguishable functional groups. Regioselective manipulation of functional groups permitted introduction of various types of olefinic tethers in the desired stereochemical orientation. Interestingly, the present methodology creates structural, functional, and stereochemical complexity in the very first step of the synthesis from readily available aromatic precursors, which is one of the important aspects of design and development of methodology.[24,25]

Experimental Section

2-Allyl-6-hydroxymethylphenol (12b). To a solution of the aldehyde **11b** (10 g, 61.7 mmol) in methanol−H_2O (4:1, 125 mL) was added sodium borohydride (2.34 g, 61.5 mmol) at ∼5 °C, and the reaction mixture was stirred for 1 h. The reaction mixture was diluted with water (5 mL), and then dilute HCl (2 mL, 50%) was added slowly. Methanol was removed under reduced pressure, water (10 mL) was added to the residue and extracted with ethyl acetate (3 × 60 mL), and the combined extract was washed with brine and dried on sodium sulfate. Removal of solvent followed by chromatography on silica gel [petroleum ether−ethyl acetate (90:10)] gave the compound **12b** as a thick liquid (9.11 g, 90%). IR (film) ν_{max}: 3367 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.32 (s, 1H); 7.09 (d, J = 7.3 Hz, 1H); 6.93 (d, J = 7.3 Hz, 1H); 6.79 (m, 1H); 6.07−5.97 (m, 1H); 5.14−5.08 (m, 2H); 4.85 (br s, 2H); 3.42 (d, J = 6.2 Hz, 2H); 2.2 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.0, 136.8, 130.1, 127.1, 126.2, 124.7, 120.0, 115.9, 64.5, 34.3. HRMS (ESI) (m/z): found 187.0747 $[M + Na]^+$, calcd for $C_{10}H_{12}O_2Na$ 187.0735.

(1*S,2*S**,4*S**,5*R**)-Ethyl 1-Allyl-5-spirooxirane-6-oxo-8-methylbicyclo[2.2.2]oct-7-ene-2-carboxylate (14).** To a solution of 2-allyl-4-methyl-6-hydroxymethylphenol **12a** (10 g, 56 mmol) in acetonitrile (200 mL) cooled at ∼0 °C was added ethyl acrylate (30 mL, excess) followed by the addition of a saturated solution of sodium metaperiodate (40 g, 187 mmol in 70 mL water) dropwise over a period of 2 h. After the reaction mixture was stirred in an ice bath for 3 h, it was further stirred overnight at ambient temperature (∼28 °C). The reaction mixture was saturated with sodium chloride and filtered through a Celite pad. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3 × 50 mL). The combined extract was washed with brine and dried. The solvent was evaporated under reduced pressure, and the residue was chromatographed on silica gel. Elution with petroleum ether-ethyl acetate (90:10) gave the compound **14** (7.13 g, 46%) as a colorless liquid. IR (neat) ν_{max}: 1736 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.92−5.78 (m, 1H), 5.64 (s with structure, 1H), 5.13−5.04 (m, 2H), 4.12 (q, J = 6 Hz, 2H), 3.15 (part of an AB system, J_{AB} = 6 Hz, 1H), 2.92 (part of an AB system, J_{AB} = 6 Hz, 1H), 2.85 (dd with structure, J_1 = 12 Hz, J_2 = 6 Hz, 1H), 2.65 (dd with structure, J_1 = 10 Hz, J_2 = 6 Hz, 1H), 2.50−2.33 (merged m, 3H), 1.94 (s with structure, 3H), 1.82 (ddd, J_1 = 12 Hz, J_2 = 6 Hz, J_3 = 3 Hz, 1H), 1.26 (t, 3H, J = 6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 203.9, 172.9, 143.4, 134.0, 122.7, 118.2, 60.7, 57.6, 54.2, 52.5, 44.0, 43.3, 34.1, 28.7, 20.6, 14.1. HRMS (ESI) (m/z): found 299.1250 $[M + Na]^+$, calcd for $C_{16}H_{20}O_4Na$ 299.1259.

(1*S,2*S**,6*R**,7*R**,8*R**,9*R**)-6,9-Bis-spiroepoxy-1,4-diallyltricyclo[6.2.2.0^{2,7}]dodec-3,11-diene-5,10-dione (16).** To a solution of the *o*-hydroxymethylphenol **12b** (13 g, 79.26 mmol) in acetonitrile (200 mL) was added a solution of $NaIO_4$ (56 g, 261 mmol) in water (200 mL) dropwise at ∼10 °C in 2 h. The reaction mixture was then stirred for 3 h at ambient temperature. The reaction mixture was filtered on a Celite bed to remove inorganic salts. The organic layer was separated from the filtrate, and the aqueous layer was extracted with ethyl acetate (3 × 50 mL). The organic extracts were combined and washed with brine (50 mL) and dried over sodium sulfate. Removal of solvent gave a solid which was recrystallized from petroleum ether−ethyl acetate (85:15) to give the compound **16** (9.75 g, 76%) as a solid. Mp: 147−149 °C. IR (film) ν_{max}: 3442, 3348, 1731, 1684, 1645 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 6.63−6.57 (dd, J_1 = 8 Hz, J_2 = 7 Hz, 1H), 6.53 (d, J = 5 Hz, 1H), 6.08−5.92 (m, 1H), 5.84−5.7 (merged m, 2H), 5.26−5.04 (merged m, 4H), 3.34 (dd, J_1 = 5 Hz, J_2 = 9 Hz, 1H), 3.16 (part of an AB system, J_{AB} = 6 Hz, 1H), 3.09−2.92 (complex m, 2H), 2.92 (part of an AB system, J_{AB} = 6 Hz, 1H), 2.92−2.88 (m, 1H), 2.86−2.81 (AB system, J_{AB} = 6 Hz, 2H), 2.78−2.70 (m, 2H), 2.55−2.46 (dd, J_1 = 15 Hz, J_2 = 7.5 Hz, 1H), ^{13}C NMR (75 MHz, $CDCl_3$): δ 204.5, 192.5, 141.6, 140.0, 134.3, 133.6, 133.55, 118.9, 117.5, 58.9, 58.5, 57.8, 57.7, 53.8, 40.8, 39.9, 39.5, 34.0, 33.7. HRMS (ESI) (m/z): found 325.1453 $[M + H]^+$, calcd for $C_{20}H_{21}O_4$ 325.1440.

Crystal data of 16: $C_{20}H_{20}O_4$, M 324.36, space group, triclinic, P-1, a = 8.663(2) Å, b = 9.548(3) Å, c = 10.915(3) Å, λ = 0.7107 Å, α = 90.92(2)°, β = 94.53(2)°, γ = 116.86(3)°, U 801.5(4) Å^3, Z = 2, D_c = 1.344 mg/m^3, T = 293(2) K, F(000) = 344, size = 0.33 × 0.28 × 0.23 mm. Reflections collected/unique 2818/2305 [R(int) = 0.0202], final R indices [$I > 2\sigma(I)$] R1 = 0.0319, wR2 = 0.0823. R indices (all data) R1 = 0.0397, wR2 = 0.0846.

(1*S,2*S**,4*S**,5*R**)-Ethyl 1-Allyl-5-spirooxirane-6-oxobicyclo-[2.2.2]oct-7-ene-2-carboxylate (17).** A mixture of the dimer **16** (10 g, 30.8 mmol) in *o*-dichlorobenzene (50 mL) and ethyl acrylate (20 mL, excess) was heated at 110 °C for 7 h. It was charged on a column of silica gel. Elution with petroleum ether ethyl acetate (96:4) removed the *o*-dichlorobenzene and unreacted ethyl

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acrylate. Further elution with petroleum ether/ethyl acetate (90:10) gave the epoxy ketone **17** (14.8 g, 91%) as a colorless liquid. IR (neat) ν_{max}: 1735 cm-1. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.60−6.56 (dd, J_1 = 8.2 Hz, J_2 = 6.6 Hz, 1H), 6.10 (d, J = 8.2 Hz, 1H), 5.94−5.81 (m, 1H), 5.14−5.06 (m, 2H), 4.13 (q, J = 7 Hz, 2H), 3.17 (part of an AB system, J_{AB} = 6.2 Hz, 1H), 2.91−2.85 (m, merged with AB system, J_{AB} = 6.2 Hz, 2H), 2.74−2.66 (dd, J_1 = 14 Hz, J_2 = 6.6 Hz, 1H), 2.65−2.60 (m, 1H), 2.55−2.40 (m, 2H), 1.84−1.80 (ddd, J_1 = 14 Hz, J_2 = 6 Hz, J_3 = 5 Hz, 1H), 1.27 (t, J = 7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 203.9, 172.8, 133.9, 133.6, 131.0, 118.5, 60.9, 57.7, 54.4, 53.3, 43.5, 38.0, 34.1, 29.4, 14.2. HRMS (ESI) (m/z): found 263.1294 $[M + H]^+$, calcd for $C_{15}H_{19}O_4$ 263. 1283.

Ethyl 1-Allyl-5-hydroxymethyl-8-methyl-6-oxobicyclo[2.2.2]oct-7-ene-2-carboxylate (18). To a solution of the adduct **14** (7.8 g, 28.2 mmol) in MeOH−H_2O (5:1, 120 mL) were added zinc (activated 56 g, excess) and NH_4Cl (9 g, 168 mmol). The reaction mixture was stirred at ambient temperature (∼30 °C). After completion of the reaction (TLC, 8 h), the reaction mixture was filtered on a Celite bed and washed with ethyl acetate (3 × 20 mL). The filtrate was concentrated under vacuum; the residue was diluted with water (50 mL) and extracted with ethyl acetate (4 × 40 mL). The combined extract was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo, and the residue was chromatographed on silica gel. Elution with petroleum ether−ethyl acetate (80:20) gave the β-keto alcohol **18** as a liquid (*syn*/*anti* mixture, 7.22 g, 92%). IR (neat) ν_{max}: 3490, 1719 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.91−5.76 (m, 1H), 5.55 (s with structure, 1H), 5.11−5.0 (m, 2H), 4.10 (q, J = 6 Hz, 2H), 3.85−3.76 (m, 1H), 3.64 (br s, 1H), 2.77−2.69 (m, 1H), 2.67−2.49 (m, 3H), 2.37−2.15 (m, 3H), 1.92 (two s with structure, total 3H), 1.66−1.55 (m, 1H), 1.24 (t, J = 6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 212.8, 173.0, 146.7, 134.5, 121.3, 118.0, 62.7, 60.7, 54.4, 49.1, 44.3, 39.6, 34.0, 27.6, 20.1, 14.1 (signals due to major isomer). HRMS (ESI) (m/z): found 279.1600 $[M + H]^+$, calcd for $C_{16}H_{23}O_4$ 279.1596.

(1*S,2*S**,4*R**) Ethyl 1-Allyl-8-methyl-6-oxobicyclo[2.2.2]oct-7-ene-2-carboxylate (19).** To a solution of the β-keto alcohol **18** (2 g, 7.2 mmol) in acetone (50 mL) at ∼5 °C was added freshly prepared Jones' reagent dropwise. After completion of the reaction (TLC), acetone was removed under vacuum. The residue was diluted with water (20 mL) and extracted with ethyl acetate (4 × 30 mL). The extract was combined and dried on anhydrous Na_2SO_4, and the solvent was removed under vacuum to give the carboxylic acid, which was subjected to decarboxylation without further purification. The carboxylic acid thus obtained was dissolved in THF−H_2O mixture (1:1, 40 mL) and refluxed for 12 h. The reaction mixture was saturated with sodium chloride, and the organic layer was separated. The aqueous layer was extracted with ether (3 × 30 mL), and the organic layers were combined and dried on anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the product was chromatographed on silica gel. Elution with petroleum ether−ethyl acetate (97:3) gave the title compound **19** as a colorless liquid (1.12 g, 63%). IR (neat) ν_{max}: 1737, 1727 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.95−5.80 (m, 1H), 5.52 (s, 1H), 5.11−5.00 (m, 2H), 4.10 (q, J = 6 Hz, 2H), 2.77−2.68 (m, 2H), 2.58 (d of part of an AB system, J_{AB} = 14 Hz, J_2 = 7 Hz, 1H), 2.41 (d of part of an AB system, J_{AB} = 14 Hz, J_2 = 7 Hz, 1H), 2.19−2.02 (m, 3H), 1.89 (s, 3H), 1.77−1.64 (m, 1H, merged with signal due to H_2O present in $CDCl_3$), 1.24 (t, J = 6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 209.9, 173.4, 145.7, 134.8, 121.4, 117.6, 60.5, 53.8, 43.1, 39.3, 37.2, 34.1, 32.2, 20.1, 14.1. HRMS (ESI) (m/z): found 249.1501 $[M+H]^+$, calcd for $C_{15}H_{21}O_3$ 249.1491.

(1*S,2*S**,4*R**) Ethyl 1-Allyl-6-oxobicyclo[2.2.2]oct-7-ene-2-carboxylate (21).** To a solution of the adduct **17** (9.8 g, 37.40 mmol) in MeOH−H_2O (5:1, 180 mL) were added zinc (activated 70 g, excess) and NH_4Cl (11 g, 205 mmol, excess). The reaction mixture was stirred at ambient temperature (∼30 °C). After completion of the reaction (TLC, 8 h), it was filtered through a Celite bed and washed with ethyl acetate (30 mL). The filtrate was concentrated under vacuum; the residue was diluted with water (50 mL) and extracted with ethyl acetate (4 × 50 mL). The combined extract was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum, and the residue was purified by column chromatography. Elution with petroleum ether−ethyl acetate (75:25) gave the β-keto alcohol **20** as a liquid (*syn*/*anti* mixture, 9 g, 91%). IR (neat) ν_{max}: 3418, 1716, 1639 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.66 and 6.50 (each of these dd, J_1 = 8.4 Hz, J_2 = 6.9 Hz, total 1H), 6.00−5.80 (merged m, total 2H), 5.12−5.05 (m, 2H), 4.12 (two merged q, J = 7 Hz, 2H), 3.85−3.54 (m, 2H), 3.05−2.90 (m, total 1H), 2.84−2.50 (m, total 2H), 2.48−2.20 (cluster of m, 4H), 1.80−1.60 (m merged with signal due to H_2O present in $CDCl_3$, 1H), 1.25 (two merged t, J = 7 Hz, total 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.4, 173.1, 137.2, 134.4, 129.4, 118.1, 62.6, 60.8, 54.3, 49.5, 43.7, 34.2, 34.0, 28.2, 14.2 (signals due to major isomer). HRMS ESI (m/z): found 265.1448 $[M + H]^+$, calcd for $C_{15}H_{21}O_4$ 265.1440.

The β-keto alcohol **20** thus obtained was oxidized and subjected to decarboxylation as follows. Thus, a solution of the β-keto alcohol **20** (4 g, 15.15 mmol) in acetone (120 mL) was oxidized with a freshly prepared Jones' reagent at ∼5 °C. After completion of the reaction (TLC), acetone was removed under vacuum. The residue was diluted with water (25 mL) and extracted with ethyl acetate (5 × 20 mL). The combined extract was dried over anhydrous sodium sulfate. Solvent was removed under vacuum, and the resulting β-keto acid was dissolved in a THF−H_2O mixture (1:1, 100 mL) and refluxed for 12 h. The reaction mixture was then saturated with sodium chloride, and the organic layer was separated. The aqueous layer was extracted with ether (3 × 30 mL), and the organic layers were combined and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the product was purified by column chromatography on silica gel. Elution with petroleum ether−ethyl acetate (97:3) gave the title compound **21** as a colorless liquid (2.0 g, 57%). IR (neat) ν_{max}: 1726 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.56 (dd, J_1 = 8.2 Hz, J_2 = 6.4 Hz, 1H), 6.00 (d, J = 8.2 Hz, 1H), 5.94−5.82 (m, 1H), 5.10−5.00 (m, 2H), 4.13 (q, J = 7 Hz, 2H), 3.05−3.00 (m, 1H), 2.75 (dd, J_1 = 10 Hz, J_2 = 7 Hz, 1H), 2.62 (d of part of an AB system, J_{AB} = 14 Hz, J_2 = 7.6 Hz, 1H), 2.48 (d of part of an AB system, J_{AB} = 14 Hz, J_2 = 7.6 Hz, 1H), 2.20−2.10 (m, 3H), 1.80−1.70 (m, 1H), 1.27 (t, J = 7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.9, 173.3, 136.2, 134.7, 129.7, 118.0, 60.7, 54.0, 42.6, 39.8, 34.1, 33.0, 31.9, 14.2. HRMS ESI (m/z): found 235.1329 $[M+H]^+$, calcd for $C_{14}H_{19}O_3$ 235.1334.

(1*S,2*S**,4*R**)-Ethyl 1-Allyl-7-spiro(1,3-dioxalane)-5-methylbicyclo-[2.2.2]oct-5-ene-2-carboxylate (22).** To a mixture of ethylene glycol (1 mL, excess), *p*-toluenesulfonic acid (0.05 g), and benzene (15 mL) dried in a Dean−Stark apparatus was added a solution of the keto ester **19** (1.0 g, 4.03 mmol) in dry benzene. The reaction mixture was refluxed for 4 h. It was cooled, and a saturated solution of sodium bicarbonate (20 mL) was slowly added. The benzene layer was separated, and the aqueous layer was extracted with ether (3 × 20 mL). The combined organic layer was washed with brine and dried on anhydrous sodium sulfate. The solvent was removed under vacuum, and the resulting product was chromatographed on silica gel [petroleum ether−ethyl acetate (98:2)] to give the ketal ester **22** as a liquid (1.1 g, 94%). IR (neat) ν_{max}: 1734 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.06−5.91 (m, 1H), 5.63 (s with structure, 1H), 5.01−4.90 (m, 2H), 4.03 (q, J = 7.1 Hz, 2H), 3.92−3.80 (br s, 4H), 3.25−3.05 (m, 1H), 2.51−2.40 (m, 3H), 2.02−1.90 (m, 1H), 1.84 (s with structure, 3H), 1.70−1.65 (m, 2H), 1.56−1.45 (m, 1H), 1.21(t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.2, 142.8, 136.5, 124.6, 115.1, 114.1, 64.3, 64.2, 59.9, 47.1, 42.6, 42.0, 36.3, 34.6, 32.3,

19.9, 14.0. HRMS (ESI) (m/z): found 293.1765 $[M + H]^+$, calcd for $C_{17}H_{25}O_4$ 293.1753.

(1*S,4*R**,6*S**)-1-Allyl-7-spiro(1,3-dioxalane)-6-hydroxymethyl-3-methylbicyclo[2.2.2]oct-2-ene (23).** To a stirred suspension of lithium aluminum hydride (0.100 g, 2.63 mmol) in ether (25 mL) was added dropwise a solution of ketal ester **22** (0.8 g, ~2.73 mmol) in dry ether (15 mL) at ~5 °C, and the reaction mixture was stirred at ambient temperature. After completion of the reaction (TLC), the reaction mixture was cooled, and excess lithium aluminum hydride was destroyed by addition of ethyl acetate (2 mL) followed by aqueous sodium hydroxide solution (20 mL). It was further stirred for 2 h, and then the organic layer was separated. The aqueous layer was extracted with ether (3 × 20 mL). The combined organic layer was washed with brine and dried on anhydrous sodium sulfate. Removal of solvent followed by chromatography of the product on silica gel [(petroleum ether−ethyl acetate (80:20)] furnished the ketal alcohol **23** as a colorless liquid (0.657 g, 96%). IR (neat) ν_{max}: 3424, 1635 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 6.20−6.00 (m, 1H), 5.50 (s, 1H), 5.10−4.95 (m, 2H), 3.86 (br s, 4H), 3.71 (dd, J_1 = 10.2 Hz, J_2 = 3.5 Hz, 1H), 3.34 (dd, J_1 = 10.2 Hz, J_2 = 7.5 Hz, 1H), 2.70−2.50 (m, 1H), 2.50−2.30 (m, 3H), 1.98−1.6 (singlet merged with m and signal due to H_2O in $CDCl_3$, 6H), 1.42−1.20 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.6, 137.0, 125.0, 115.2, 114.8, 64.9, 64.1, 46.5, 42.4, 38.6, 36.2 34.3, 30.6, 20.0. HRMS (ESI) (m/z): found 273.1476 $[M + Na]^+$, calcd for $C_{15}H_{22}O_3Na$ 273.1467.

(1*S,2*S**,4*R**)-1-Allyl-7-spiro(1,3-dioxalane)-5-methylbicyclo-[2.2.2]oct-5-ene-2-carbaldehyde (24).** To a stirred solution of ketal alcohol **23** (2.0 g, 8 mmol) in dichloromethane (100 mL), NMO (1 g, 8.5 mmol), and powdered 4 Å molecular sieves (3.5 g) was added TPAP (100 mg, 0.28 mmol) at room temperature under nitrogen atmosphere. After completion of reaction (TLC, 12 h), it was filtered through a small pad of silica gel, and the filtrate was concentrated under vacuum. Chromatography of the residue (petroleum ether−ethyl acetate, 98:2) furnished the aldehyde **24** as a colorless liquid (1.95 g, 98%). IR (neat) ν_{max}: 1717, 1637 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 9.40 (d, J = 4 Hz, 1H), 6.06- 5.94 (m, 1H), 5.67 (s, 1H), 5.09−5.00 (m, 2H), 3.97−3.80 (m, 4H), 3.05−2.96 (m, 1H), 2.54−2.50 (m, 3H), 1.91−1.55 (s merged with m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.8, 145.3, 135.8, 124.3, 117.1, 113.8, 64.5, 50.7, 46.8, 42.8, 36.4, 34.8, 27.5, 20.1. HRMS (ESI) (m/z): found 271.1304 $[M + Na]^+$, calcd for $C_{15}H_{20}O_3Na$ 271.1310.

(1*S,2*S**,4*R**)-Ethyl 1-Allyl-7-spiro(1,3-dioxalane)bicyclo-[2.2.2]oct-5-ene-2-carboxylate (25).** To a mixture of ethylene glycol (2 mL, excess), *p*-toluenesulfonic acid (0.03 g), and benzene (30 mL) dried in a Dean−Stark apparatus was added a solution of the keto ester **21** (1.3 g, 5.55 mmol) in dry benzene. The reaction mixture was refluxed for 4 h, after which time it was cooled, poured into a saturated solution of sodium bicarbonate (30 mL) and crushed ice, and stirred vigorously. The benzene layer was separated, and the aqueous layer was extracted with ether (2 × 20 mL). The combined organic layer was washed with saturated sodium bicarbonate (2 × 20 mL) and dried over anhydrous sodium sulfate. Removal of solvent followed by chromatography on silica gel [petroleum ether−ethyl acetate (94:6)] gave the ketal ester **25** as a colorless liquid (1.5 g, 97%). IR (neat) ν_{max}: 1735 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 6.40 (dd, J_1 = 8.1 Hz, J_2 = 6.6 Hz, 1H), 6.07 (d, J = 8.1 Hz, 1H), 6.5−5.95 (m, 1H), 5.01−4.93 (m, 2H), 4.04 (q, J = 7.3 Hz, 2H), 3.90−3.86 (m, 4H), 3.10 (dd, J_1 = 9.6 Hz, J_2 = 5.3 Hz, 1H), 2.70 (m, 1H), 2.57−2.50 (m, 2H), 2,07−2.00 (m, 1H), 1.68 (m, 2H), 1.56−1.50 (m, 1H), 1.27 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.3, 136.5, 134.1, 132.9, 115.6, 113.9, 76.5, 64.6, 64.3, 60.2, 46.8, 42.5, 42.0, 34.7, 33.3, 30.9, 14.2. HRMS (ESI) (m/z): found 279.1596 $[M + H]^+$, calcd for $C_{16}H_{23}O_4$ 279.1596.

(1*S,4*R**,6*S**)-1-Allyl-7-spiro(1,3-dioxalane)-6-hydroxymethylbicyclo[2.2.2]oct-2-ene (26).** A solution of ketal ester **25** (1.3 g, 4.67 mmol) in dry ether (20 mL) was slowly added to a stirred suspension of lithium aluminum hydride (0.260 g, 6.84 mmol) in ether (30 mL) at ~5 °C. After completion of the reaction (TLC), the reaction mixture was worked up as described previously and the product was chromatographed on silica gel. Elution with petroleum ether−ethyl acetate (80:20) furnished the ketal alcohol **26** as a liquid (0.97 g, 88%). IR (neat) ν_{max}: 3421, 2942 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 6.35 (dd, J_1 = 8.3 Hz, J_2 = 6.4 Hz, 1H), 6.17−6.05 (m, 1H), 5.94 (d, J = 8.3 Hz, 1H), 5.12−4.95 (merged m, 2H), 3.85−3.82 (m, 4H), 3.72 (dd J_1 = 12.5 Hz, J_2 = 7.5 Hz, 1H), 1.96−1.88 (m, 1H), 1.74−1.62 (m, 2H), 1.36−1.22 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.1, 135.6, 133.4, 115.6, 114.6, 65.1, 64.3, 64.2, 46.5, 43.0, 38.2, 34.4, 31.5, 30.8. HRMS (ESI) (m/z): found 237.1484 $[M + H]^+$, calcd for $C_{14}H_{21}O_3$ 237.1491.

(1*S,2*S**,4*R**)-1-Allyl-7-spiro(1,3-dioxalane)bicyclo[2.2.2]oct-5-ene-2-carbaldehyde (27).** To a stirred mixture of ketal alcohol **26** (1.5 g, 6.35 mmol), NMO (1.28 g, 10.98 mmol), and powdered 4 Å molecular sieves (3 g) in dichloromethane (100 mL) was added TPAP (0.080 g, 0.22 mmol) at room temperature under nitrogen atmosphere. After completion of reaction (TLC, 12 h), it was filtered through a small pad of silica gel. The filtrate was concentrated, and the product was chromatographed on silica gel (petroleum ether−ethyl acetate, 90:10) to give the aldehyde **27** as a colorless liquid (1.40 g, 94%). IR (neat) ν_{max}: 1718 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 9.4 (d, J = 6 Hz, 1H), 6.48 (dd, J_1 = 8.4 Hz, J_2 = 6.6 Hz, 1H), 6.09 (d, J = 8.4 Hz, 1H), 6.05−5.95 (m, 1H), 5.09−5.03 (m, 2H), 3.90−3.85 (m, 4H), 3.06−3.00 (m, 2H), 2.78−2.76 (m, 1H), 2.60−2.55 (m, 2H), 1.94−1.88 (m, 1H), 1.78−1.55 (m, merged with signal due to H_2O present in $CDCl_3$, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.5, 136.2, 135.6, 132.2, 117.4, 113.4, 64.6, 50.0, 46.4, 43.1, 34.7, 30.8, 28.1. HRMS (ESI) (m/z): found 235.1337 $[M + H]^+$, calcd for $C_{14}H_{19}O_3$ 235.1334.

(1*S,4*R**,6*S**)-1-Allyl-7-spiro(1,3-dioxalane)-3-methyl-6-[(*S**)-1-hydroxyprop-2-enyl]bicyclo[2.2.2]oct-2-ene (28a) and (1*S**,4*R**,6*S**)-1-Allyl-7-spiro(1,3-dioxalane)-3-methyl-6-[(*R**)-1-hydroxyprop-2-enyl]bicyclo[2.2.2]oct-2-ene (28b).** To a stirred solution of aldehyde **24** (0.2 g, 0.8 mmol) in dry THF (15 mL) at ~0 °C was added dropwise a solution of vinylmagnesium bromide (3.2 mL, 3.2 mmol) and the mixture stirred at ambient temperature (2 h). The reaction mixture was cooled, and saturated ammonium chloride solution (5 mL) was added dropwise and further stirred for 1 h. The reaction mixture was extracted with ether (3 × 20 mL) and dried over anhydrous sodium sulfate. The solvent was removed, and the resulting product was chromatographed on silica gel. Elution with petroleum ether−ethyl acetate (88:12) first gave the less polar alcohol **28a** (0.135 g, 61%) as a colorless liquid. IR (neat) ν_{max}: 3437, 1636 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 6.18−6.03 (m, 1H), 5.78−5.64 (merged m, 2H), 5.20 (dt, J_1 = 18 Hz, J_2 = 2 Hz, 1H), 5.13−4.19 (merged m, 3H), 4.60 (br m, 1H), 3.93−3.83(m, 4H), 2.65 (m of a d of part of an AB system, J_{AB} = 15 Hz, J_2 = 7 Hz, 1H), 2.51 (m of a d of part of an AB system, J_{AB} = 15 Hz, J_2 = 8 Hz, 1H), 2.46−2.39 (m, 2H), 1.84 (d, J = 2 Hz, 3H), 1.71−1.58 (m merged with signal due to water present in $CDCl_3$, 4H), 1.45−1.43 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5, 140.1, 136.9, 125.1, 115.7, 115.1, 114.0, 71.2, 64.3, 64.2, 47.1, 42.3, 40.5, 36.7, 34.2, 27.0, 20.2. HRMS (ESI) (m/z): found 299.1624 $[M + Na]^+$, calcd for $C_{17}H_{24}O_3Na$ 299.1623.

Further elution with petroleum ether−ethyl acetate (85:15) furnished the more polar product **28b** (0.040 g, 18%) as a colorless liquid. IR (neat) ν_{max}: 3421, 1622 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 6.20−6.10 (m, 1H), 5.76−5.68 (m, 1H), 5.39 (br s, 1H), 5.17−4.9 (m, 4H), 4.43−4.40 (m, 1H), 3.89−3.83 (m, 4H), 2.7−2.58 (m, 2H), 2.48−2.30 (m, 2H), 1.84−1.58 (s merged with m, 7H), 1.36−1.22 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.7, 139.1, 137.7, 126.1, 115.3, 115.1, 114.8, 73.4, 64.3, 64.1, 46.7, 42.5, 41.7, 36.3, 34.7, 27.6, 20.0. HRMS (ESI) (m/z): found 299.1620 $[M + Na]^+$, calcd for $C_{17}H_{24}O_3Na$ 299.1623.

Continued elution with petroleum ether−ethyl acetate (80:20) gave the reduced alcohol **23** (0.015 g, 7%).

(1*S,4*R**,6*S**)-1-Allyl-7-spiro(1,3-dioxalane)-6-[(*S**)-1-hydroxyprop-2-enyl]bicyclo[2.2.2]oct-2-ene (29a) and (1*S**,4*R**,6*S**)-1-Allyl-7-spiro(1,3-dioxalane)-6-[(*R**)-1-hydroxyprop-2-enyl]bicyclo-[2.2.2]oct-2-ene (29b).** To a stirred solution of aldehyde **27** (0.7 g, 3 mmol) in dry THF (20 mL) at ∼0 °C was added dropwise a solution of vinylmagnesium bromide (12 mL, 12 mmol) and the mixture stirred at ambient temperature (2.5 h). The reaction mixture was worked up as described above, and the product was chromatographed on silica gel. Elution with petroleum ether−ethyl acetate (90:10) first gave the less polar alcohol **29a** (0.420 g, 54%) as a colorless liquid. IR (neat) ν_{max}: 3487, 1635 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 6.42 (dd, $J_1 = 8$ Hz, $J_2 = 7$ Hz, 1H), 6.18−6.06 (m, 2H), 5.74 (ddd, $J_1 = 16.4$ Hz, $J_2 = 11.7$ Hz, $J_3 = 3$ Hz, 1H), 5.20 (m of d, $J = 16.4$ Hz, 1H), 5.14−5.00 (cluster of m, 3H), 4.60−4.55(m, 1H), 3.91−3.85(m, 4H), 2.74−2.64(m, 2H), 2.54(m of part of an AB system, $J_{AB} = 14.8$ Hz, 1H), 2.43−2.37(m, 1H), 1.74−1.64(m, 3H), 1.44 (d, $J = 4.5$ Hz, 1H), 1.42−1.34 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.1, 136.7, 136.2, 133.5, 115.8, 114.8, 114.1, 71.2, 64.3, 64.1, 46.8, 42.5, 39.8, 34.0, 30.8, 27.8. HRMS (ESI) (*m*/*z*): found 285.1465 $[M+Na]^+$, calcd for $C_{16}H_{22}O_3Na$ 285.1467.

Further elution with petroleum ether−ethyl acetate (85:15) gave the alcohol **29b** as a colorless liquid (0.115 g, 15%). IR (neat) ν_{max}: 3446, 1635 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 6.28 (dd, $J_1 = 8.3$ Hz, $J_2 = 6.4$ Hz, 1H), 6.24−6.12 (m, 1H), 5.84 (d, $J = 8.8$ Hz, 1H), 5.82−5.72 (m, 1H), 5.22−4.98 (merged m, 4H), 4.46−4.40 (m, 1H), 3.91−3.86 (m, 4H), 2.74−2.62 (m, 3H), 2.46 (dd, $J_1 = 15$ Hz, $J_2 = 7$ Hz, 1H), 1.84−1.76 (m, 1H), 1.74−1.62 (merged m, 3H), 1.48 (br s, 1H), 1.40−1.32 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.2, 137.5, 134.1, 133.7, 115.6, 114.9, 73.6, 64.3, 64.0, 46.4, 42.7, 40.6, 34.6, 30.6, 28.5. HRMS (ESI) (*m*/*z*): found 285.1465 $[M + Na]^+$, calcd for $C_{16}H_{22}O_3Na$ 285.1467.

Continued elution with petroleum ether−ethyl acetate (80:20) gave the reduced alcohol **26** (0.090 g, 13%).

(1*S,4*R**,6*S**)-1-Allyl-7-spiro(1,3-dioxalane)-3-methyl-6-[(*S**)-1-hydroxybut-3-enyl]bicyclo[2.2.2]oct-2-ene (30a) and (1*S**,4*R**,6*S**)-1-Allyl-7-spiro(1,3-dioxalane)-3-methyl-6-[(*R**)-1-hydroxybut-3-enyl]bicyclo[2.2.2]oct-2-ene (30b).** To a suspension of magnesium (freshly activated, 0.40 g, 16.6 mmol) in dry ether (10 mL) was added a crystal of iodine. A dilute solution of allyl bromide (0.6 mL, 6.8 mmol) in ether (25 mL) was added very slowly over ∼1 h under vigorous stirring. The solution was further stirred for 1 h and then added to a solution of the ketal aldehyde **24** (0.4 g, 1.61 mmol) in dry ether (10 mL) at 0 °C. After addition of the Grignard reagent, the reaction mixture was further stirred for 2 h at ambient temperature. The reaction mixture was cooled in ice bath, and a saturated solution of ammonium chloride (10 mL) was added dropwise and stirred for 0.5 h. The organic layer was separated, and the aqueous layer was extracted with ether (3 × 20 mL). The combined extract was washed with brine (30 mL) and dried over anhydrous sodium sulfate. Removal of solvent gave the crude product which was chromatographed on silica gel. Elution with petroleum ether−ethyl acetate (90:10) gave the alcohol **30a** (0.280 g, 60%) as a colorless liquid. IR (film) ν_{max}: 3547, 1638 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 6.10−5.98 (m, 1H), 5.86−5.74 (m, 1H), 5.62 (br s, 1H), 5.12−4.96 (m, 4H), 4.10−4.05 (m, 1H), 3.90−3.80 (m, 4H), 2.60 (d of part of an AB system, $J_{AB} = 17.1$ Hz, $J_2 = 7.6$ Hz, 1H), 2.50−2.42 (m, 2H), 2.36−2.28 (m, 1H), 2.22−2.12 (m, 1H), 2.06−1.98 (m, 1H), 1.82 (d, $J = 1.5$ Hz, 3H), 1.76−1.63 (m, 3H), 1.58−1.50 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.9, 136.8, 135.4, 124.8, 117.0, 115.7, 115.1, 70.2, 64.3, 64.2, 47.0, 42.2, 40.3, 39.6, 36.6, 34.2, 26.5, 20.3. HRMS (ESI) (*m*/*z*): found 313.1782 $[M + Na]^+$, calcd for $C_{18}H_{26}O_3Na$ 313.1780.

Further elution with petroleum ether−ethyl acetate (82:18) furnished the lower alcohol **30b** (0.136 g, 29%) as a colorless liquid. IR (film) ν_{max}: 3410, 1622 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 6.2−6.01 (m, 1H), 5.88−5.68 (m, 1H), 5.48 (s, 1H), 5.20−4.86 (m, 4H), 3.83 (br s, 5H), 2.70−2.34 (m, 4H), 2.16−1.91 (m, 1H), 1.90−1.42 (s merged with m, total 8H), 1.38−1.20 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3 + CCl_4$): δ 142.7, 137.6, 135.7, 125.5, 118.0, 115.3, 114.8, 71.0, 64.1, 63.9, 46.7, 42.2, 40.9, 37.7, 36.3, 34.6, 28.5, 20.1. HRMS (ESI) (*m*/*z*): found 313.1779 $[M + Na]^+$, calcd for $C_{18}H_{26}O_3Na$ 313.1780. Continued elution with petroleum ether−ethyl acetate (80:20) gave the alcohol **23** (0.036 g, 9%).

(1*S,4*R**,6*S**)-1-Allyl-7-spiro(1,3-dioxalane)-6-[(*S**)-1-hydroxybut-2-enyl]bicyclo[2.2.2]oct-2-ene (31a) and (1*S**,4*R**,6*S**)-1-Allyl-7-spiro(1,3-dioxalane)-6-[(*R**)-1-hydroxybut-3-enyl]bicyclo-[2.2.2]oct-2-ene (31b).** To magnesium (freshly activated, 0.4 g, 16.6 mmol) in dry ether (10 mL) and a crystal of iodine was added a dilute solution of allyl bromide (0.6 mL, 6.8 mmol) in ether (25 mL) very slowly over 1 h under vigorous stirring at ∼5 °C. It was further stirred for 2 h. A solution of the ketal aldehyde **27** (0.4 g, 1.7 mmol) in dry ether (10 mL) was added to the reaction mixture at 0 °C. The reaction mixture was further stirred for 1 h at ambient temperature. The mixture was quenched with a saturated solution of ammonium chloride (10 mL) and further stirred for 0.5 h. The reaction mixture was worked up as described before and the product was chromatographed on silica gel. Elution with petroleum ether−ethyl acetate (87:13) gave the alcohol **31a** (0.245 g, 52%) as a colorless liquid. IR (neat) ν_{max}: 3547 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 6.42 (dd, $J_1 = 8.1$ Hz, $J_2 = 6.3$ Hz, 1H), 6.14−6.00 (merged m, 2H), 5.86−5.72 (m, 1H), 5.12−4.98 (m, 4H), 4.06 (t, $J = 6.6$ Hz, 1H), 3.90−3.85 (m, 4H), 2.74−2.58 (m merged with m of an AB system, 2H), 2.50 (d of part of AB system, $J_{AB} = 15.5$ Hz, $J_2 = 7.7$ Hz, 1H), 2.38−2.30 (m, 1H), 2.26−2.00 (m, 2H), 1.82−1.62 (m, 3H), 1.54−1.46 (m, 1H), 1.40 (br s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.8, 136.4, 135.2, 133.3, 117.3, 115.7, 114.8, 70.1, 64.3, 64.1, 46.8, 42.4, 40.4, 39.1, 34.0, 30.8, 27.4. HRMS (ESI) (*m*/*z*): found 277.1815 $[M + H]^+$, calcd for $C_{17}H_{25}O_3$ 277.1804.

Further elution with petroleum ether−ethyl acetate (85:15) furnished the lower alcohol **31b** (0.190 g, 40%) as a colorless liquid. IR (film) ν_{max}: 3435, 1637 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 6.33 (dd, $J_1 = 8$ Hz, $J_2 = 6.6$ Hz, 1H), 6.19−6.08 (m, 1H), 5.96 (d, $J = 8$ Hz, 1H), 5.86−5.75 (m, 1H), 5.13−4.95 (merged m, 4H), 3.93−3.84 (m, 5H), 2.70−2.56 (m, 3H), 2.53−2.44 (m, 1H), 2.10−2.02 (m, 1H), 1.96−1.78 (m, 2H), 1.72−1.53 (m overlapped with signal due to H_2O present in $CDCl_3$, 3H), 1.38−1.28 (complex m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.5, 135.7, 134.6, 133.1, 118.1, 71.2, 64.3, 64.0, 46.6, 42.5, 40.4, 38.1, 34.5, 30.7, 29.2. HRMS (ESI) (*m*/*z*): found 299.1632 $[M + Na]^+$, calcd for $C_{17}H_{24}O_3Na$ 299.1634. Continued elution with petroleum ether−ethyl acetate (80:20) gave the alcohol **26** (0.01 g, 2%).

(1*S,4*R**,6*S**)-1-Allyl-7-spiro(1,3-dioxalane)-6-[(*S**)-1-hydroxypent-4-enyl]bicyclo[2.2.2]oct-2-ene (32a) and (1*S**,4*R**,6*S**)-1-Allyl-7-spiro(1,3-dioxalane)-6-[(*R**)-1-hydroxypent-4-enyl]bicyclo-[2.2.2]oct-2-ene (32b).** To magnesium (freshly activated, 0.360 g, 15 mmol) in dry THF (10 mL) and a crystal of iodine, a dilute solution of 4-bromobutene (0.8 mL, 8 mmol) in THF (25 mL) was added very slowly over ∼1 h under vigorous stirring, at 5 °C. It was further stirred for 1 h. To this was added a solution of the ketal aldehyde **27** (0.350 g, 1.49 mmol) in dry THF (10 mL) at ∼0 °C. The reaction mixture was further stirred for 2 h at ambient temperature. Usual workup as described earlier followed by chromatography on silica gel [petroleum ether−ethyl acetate 85:15] gave the alcohol **32a** (0.28 g, 64%) as a colorless liquid. IR (neat) ν_{max}: 3564 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 6.43 (dd, $J_1 = 8$ Hz, $J_2 = 6.6$ Hz, 1H), 6.13- 6.02 (merged m, 2H), 5.87−5.76 (m, 1H), 5.10−4.93 (m, 4H), 4.04−3.82 (m, 5H), 2.74−2.68 (m, 1H), 2.63 (d of part of AB system, $J_{AB} = 15.6$ Hz, $J_2 = 7.0$ Hz, 1H), 2.50 (d of part of AB system, $J_{AB} = 15.6$ Hz, $J_2 = 7.0$ Hz, 1H),

2.34−2.28 (m, 1H), 2.20−2.00 (m, 2H), 1.80−1.63 (merged m, 3H), 1.55−1.45 (m, 2H), 1.38−1.30 (m, 1H), 1.27 (d, $J = 3.6$ Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 136.6, 136.4, 133.1, 115.6, 114.6, 114.5, 69.8, 64.1, 63.9, 46.7, 42.3, 39.5, 34.8, 33.8, 30.7, 30.1, 27.3. HRMS (ESI) (m/z): found 291.1959 $[M + H]^+$, calcd for $C_{18}H_{27}O_3$ 291.1960.

Continued elution with petroleum ether−ethyl acetate (80:20) gave the lower alcohol **32b** (0.030 g, 7%) as a colorless liquid. IR (neat) ν_{max}: 3432 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.31 (dd, $J_1 = 8.2$ Hz, $J_2 = 7.05$ Hz, 1H), 6.18- 6.07 (merged m, 1H), 5.93 (d, $J = 8.2$ Hz, 1H), 5.88−5.77 (m, 1H), 5.08−4.4 (m, 4H), 3.86 (br m, 5H), 2.69−2.54 (m, 3H), 2.46−2.38 (m, 1H), 2.30−2.18 (m, 1H), 2.12−2.00 (m, 1H), 1.84−1.76 (m, 1H), 1.73−1.60 (m merged with signal due to H_2O, 2H), 1.40−1.20 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.0, 137.5, 134.5, 133.4, 115.2, 115.1, 115.0, 72.2, 64.3, 64.0, 46.6, 42.6, 41.3, 34.6, 32.3, 30.8, 30.6, 29.2. HRMS ESI (m/z): found 313.1775 $[M + Na]^+$, calcd for $C_{18}H_{26}O_3Na$ 313.1780.

(1*S,2*S**,4*R**)-1-Allyl-5-methyl-7-spiro(1,3-dioxalane)-2-[prop-2-en-1-one]bicyclo[2.2.2]oct-5-ene (33).** A suspension of the ketal alcohol **28b** (0.1 g, 0.36 mmol) and freshly prepared MnO_2 (1 g, excess) in dichloromethane (30 mL) was stirred at ambient conditions for 24 h. The suspension was filtered on a Celite bed, and the solvent was removed. The crude product was chromatographed on silica gel [(petroleum ether−ethyl acetate (80:20)] to give the product **33** (0.09 g, 91%) as a colorless liquid. IR (neat) ν_{max}: 1701 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.24 (dd, $J_1 = 17.5$ Hz, $J_2 = 10$ Hz, 1H), 6.10 (dd, $J_1 = 17.5$ Hz, $J_2 = 1.5$ Hz, 1H), 5.90−5.79 (m, 1H), 5.70−5.56 (m, 2H), 4.81 (m of d, $J = 12.1$ Hz, 2H), 3.84−3.80 (br m, 4H), 3.41 (dd, $J_1 = 10.1$ Hz, $J_2 = 6.2$ Hz, 1H), 2.46−2.38 (m, 3H), 2.0−1.9 (m, 1H), 1.76 (d, $J = 2$ Hz, 3H), 1.68−1.60 (m, 2H), 1.31−1.23 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.2, 141.7, 136.8, 136.6, 127.4, 126.3, 115.9, 114.5, 64.4, 64.2, 47.3, 46.8, 42.2, 36.5, 34.5, 31.9, 19.9. HRMS (ESI) (m/z): found 297.1468 $[M + Na]^+$, calcd for $C_{17}H_{22}O_3Na$ 297.1467.

(1*S,4*R**,7*S**)-1-Allyl-5-methyl-7-[(*R**)-1-hydroxybut-3-enyl]-bicyclo[2.2.2]oct-5-en-2-one (34).** To an ice-cold solution of ketal alcohol **30b** (1.0 g, 3.4 mmol) in acetone−water (4:1, 50 mL) was added concentrated hydrochloric acid (2 mL), and the reaction mixture was stirred at ambient temperature. After completion of reaction (3 h, TLC), the reaction mixture was neutralized with solid $NaHCO_3$ and acetone was removed. To the residue were added water (20 mL) and ether (50 mL), and the organic layer was separated. The aqueous layer was extracted with ether (2 × 20 mL), and the combined organic layer was dried over anhydrous sodium sulfate. Removal of solvent followed by chromatography on silica gel (petroleum ether−ethyl acetate, 80:20) furnished the keto alcohol **34** (0.82 g, 97%) as a colorless liquid. IR (neat) ν_{max}: 3455, 1722 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.01−5.70 (m, 2H), 5.39 (s, 1H), 5.24−4.88 (m, 4H), 3.83 (br s, 1H), 2.66 (s with structure, 1H), 2.46 (d, $J = 6.9$ Hz, 2H), 2.30−2.02 (m, 4H), 2.0−1.8 (m, 5H), 1.64 (br s, 1H), 1.58−1.42 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3 + CCl_4$): δ 210.6, 145.7, 135.9, 135.0, 121.9, 118.7, 117.4, 70.5, 54.7, 42.2, 39.0, 37.7, 36.7, 34.5, 28.5, 20.2. HRMS (ESI) (m/z): found 269.1526 $[M+Na]^+$, calcd for $C_{16}H_{22}O_2Na$ 269.1517.

(1*S,4*R**,7*S**)-1-Allyl-5-methyl-7-(1-oxobut-3-enyl)bicyclo[2.2.2]-oct-5-en-2-one (35).** A suspension of the keto alcohol **34** (0.5 g, 2.03 mmol) and PCC (0.650 g, 3 mmol) in CH_2Cl_2 (30 mL) was stirred under ambient conditions for 24 h. The reaction mixture was filtered through a Celite bed, solvent was removed in vacuo, and the resulting product was chromatographed. Elution with petroleum ether−ethyl acetate (90:10) furnished the diketone **35** (0.49 g, 98%) as a colorless liquid. IR (neat) ν_{max}: 1722 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.79−6.70 (m, 1H), 5.99 (dd, $J_1 = 15$ Hz, $J_2 = 2$ Hz, 1H), 5.83−5.69 (m, 1H), 5.49 (s, 1H), 4.95- 4.87 (m, 3H), 3.08−2.94 (m, 1H), 2.66 (br s, 1H), 2.42 (d of part of an AB system, $J_{AB} = 13$ Hz, $J_2 = 7$ Hz, 1H), 2.37 (d of part of an AB system, $J_{AB} = 13$ Hz, $J_2 = 7$ Hz, 1H), 2.13−1.95 (m, 4H), 1.85−1.76 (m merged with s, 5H), 1.60−1.40 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.6, 198.9, 144.8, 143.3, 135.1, 131.9, 122.4, 117.9, 54.5, 46.9, 39.6, 37.4, 34.0, 32.1, 20.2, 18.5. HRMS (ESI) (m/z): found 245.1547 $[M + H]^+$, calcd for $C_{16}H_{21}O_2$ 245.1542.

(1*S,4*R**,7*S**)-1-Allyl-7-[(*S**)-1-hydroxypent-4-enyl]bicyclo-[2.2.2]oct-5-en-2-one (36).** To a solution of **32a** (0.14 g, 0.48 mmol) in acetone−water (20 mL, 4:1) was added aq HCl (0.2 mL) at ∼10 °C. The reaction mixture was stirred at ambient temperature for 6 h. Acetone was removed, and the aqueous residue was extracted with ethyl acetate (3 × 15 mL). The combined extract was washed with aq sodium bicarbonate followed by brine and dried on anhydrous sodium sulfate. The solvent was removed, and the product was chromatographed on silica gel. Elution with petroleum ether−ethyl acetate (88:12) gave the keto alcohol **36** (0.115 g, 97%) as a colorless liquid. IR (neat) ν_{max}: 3468, 1714 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.53 (dd, $J_1 = 8.1$ Hz, $J_2 = 6.6$ Hz, 1H), 6.02−5.90 (merged m, 2H), 5.85−5.74 (m, 1H), 5.20−4.94 (m, 4H), 4.00−3.99 (m, 1H), 2.98−2.97 (m, 1H), 2.64−2.48 (m, 2H), 2.20−1.82 (m, 4H), 1.96−1.82 (m, 2H), 1.72−1.48 (m, merged with signal due to H_2O present in $CDCl_3$, 2H), 1.40−1.30 (m, 1H), 1.22(d, $J = 4$ Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.4, 138.2, 137.3, 135.2, 129.7, 117.9, 115.0, 69.7, 54.3, 41.1, 39.4, 34.9, 33.6, 31.3, 30.1, 27.1. HRMS (ESI) (m/z): found 247.1700 $[M + H]^+$, calcd for $C_{16}H_{23}O_2$ 247.1698.

(1*S,4*R**,7*S**)-1-Allyl-7-(1-oxopent-4-enyl)bicyclo[2.2.2]oct-5-en-2-one (37).** To a solution of compound **36** (0.100 g, 0.40 mmol) in CH_2Cl_2 (15 mL) was added PCC (0.22 g, 1 mmol), and the reaction mixture was stirred at ambient temperature for 5 h, after which time it was filtered through a column of silica gel which gave the dione **37** (0.085 g, 86%) as a colorless liquid. IR (neat) ν_{max}: 1716 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.43 (dd, $J_1 = 8$ Hz, $J_2 = 6.6$ Hz, 1H), 6.02 (d, $J = 8$ Hz, 1H), 5.91−5.72 (m, 2H), 5.05−4.95 (m, 4H), 3.04−2.98 (m, 1H), 2.91 (dd, $J_1 = 10$ Hz, $J_2 = 6.6$ Hz, 1H), 2.65−2.44 (m, 4H), 2.32−2.14 (m, 5H), 1.54−1.46 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.1, 208.2, 137.1, 135.2, 135.0, 131.2, 117.9, 115.5, 54.4, 48.0, 42.9, 39.8, 33.8, 32.5, 31.9, 27.4. HRMS (ESI) (m/z) found 245.1537 $[M + H]^+$, calcd for $C_{16}H_{21}O_2$ 245.1542.

(1*S,6*S**,8*R**)-11-Spiro(1,3-dioxalane)-9-methyl-5(*S**)-hydroxy-tricyclo[6.2.2.0^{1,6}]dodeca-3,9-diene (39a).** To a degassed solution of diene **28a** (0.030 g, 0.10 mmol) in dichloromethane (15 mL) was added Grubbs' catalyst **38** (5 mg, 0.006 mmol), and the reaction mixture was stirred at ambient temperature under nitrogen for 1 h. Removal of solvent followed by chromatography of the residue on silica gel [petroleum ether−ethyl acetate (70:30)] gave the title compound **39a** as a colorless liquid (0.025 g, 96%). IR (neat) ν_{max}: 3429, 1657 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.77 (m of d, $J = 10.5$ Hz, 1H), 5.63 (m of d, $J = 10.5$ Hz, 1H), 5.51 (br m, 1H), 3.95−3.80 (m, 4H), 3.60−3.53 (m, 1H), 2.47 (m, 1H), 2.30 (m of part of an AB system, $J_{AB} = 18$ Hz, 1H), 2.13 (m of part of an AB system, $J_{AB} = 18$ Hz, 1H), 1.98−1.84 (m, 2H), 1.80(d, $J = 1.4$ Hz, 3H), 1.73 (d of part of an AB system, $J_{AB} = 12$ Hz, $J_2 = 3$ Hz, 1H), 1.61 (t of part of an AB system, $J_{AB} = 12$ Hz, $J_2 = 3$ Hz, 1H), 1.48−1.38 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 130.9, 127.3, 127.1, 114.1, 74.2, 64.9, 64.6, 45.7, 43.2, 41.3, 36.7, 30.0, 28.2, 20.0. HRMS (ESI) (m/z): found 271.1307 $[M + Na]^+$, calcd for $C_{15}H_{20}O_3Na$ 271.1310.

(1*S,6*S**,8*R**)-11-Spiro(1,3-dioxalane)-9-methyl-5(*R**)-hydroxy-tricyclo[6.2.2.0^{1,6}]dodeca-3,9-diene (39b).** To a degassed solution of diene **28b** (0.110 g, 0.4 mmol) in dichloromethane (40 mL) was added Grubbs' catalyst **38** (17 mg, 0.02 mmol) and the mixture stirred at ambient temperature for 1 h under nitrogen. Removal of solvent followed by chromatography of the residue on silica gel [petroleum ether−ethyl acetate (90:10)] gave the title compound **39b** as a colorless liquid (0.084 g, 85%). IR (neat) ν_{max}: 3430 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.96−5.80 (m, 2H), 5.6 (br s, 1H), 3.99−3.80 (m 4H), 3.78−3.70 (m, 1H), 2.54−2.48 (br m, 1H), 2.46−2.35 (m, 1H), 2.35−2.21 (m, 2H), 2.06−1.97 (m, 1H), 1.82−1.72 (singlet merged with m, 4H), 1.66−1.58 (m, 2H), 1.34 (d, J=11.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 129.9, 127.7, 125.9, 113.8, 66.8, 64.9, 64.5, 43.5, 42.9, 36.9, 36.5, 27.8, 26.6, 20.2. HRMS (ESI) (m/z): found 271.1315 $[M + Na]^+$, calcd for $C_{15}H_{20}O_3Na$: 271.1310.

(1*S,6*S**,8*R**)-12-Methyl-5(*R**)-hydroxytricyclo[6.2.2.0^{1,6}]-dodeca-3,11-dien-10-one (40).** To a stirred solution of **39b** (0.110 g, 0.44 mmol) in acetone−water (4:1, 5 mL) was added concd HCl (0.1 mL). After completion of the reaction (3 h, TLC), the reaction mixture was neutralized by addition of solid $NaHCO_3$. Acetone was removed, and the residue was diluted with water and extracted with ether (2 × 15 mL). The combined organic extract was washed with saturated sodium bicarbonate (1 × 10 mL) and brine (1 × 10 mL) and dried over anhydrous sodium sulfate. Solvent was removed under vacuum, and the product was chromatographed on silica gel. Elution with petroleum ether−ethyl acetate (90:10) gave the title compound **40** (0.083 g, 92%) as a colorless solid. Mp: 122−124 °C. IR (film) ν_{max}: 3386, 1724 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.99−5.86 (m, 2H), 5.44 (s, 1H), 3.87−3.79 (m, 1H), 2.84−2.69 (m, 2H), 2.37−2.31 (m, 1H), 2.20−2.16 (m, 4H), 1.94−1.80 (singlet merged with m, 4H), 1.23 (d, J = 11.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 211.7, 149.5, 128.9, 127.3, 122.4, 66.3, 49.6, 41.1, 38.2, 37.2, 27.5, 27.4, 20.4. HRMS (ESI) (m/z): found 227.1042 $[M + Na]^+$, calcd for $C_{13}H_{16}O_2Na$ 227.1048.

Crystal data of 40: $C_{13}H_{16}O_2$, M 204.25, space group, triclinic, P-1, a = 8.1475(9) Å, b = 8.2598(17) Å, c = 8.4400(10) Å, λ = 0.71073 Å, α = 79.263(13)°, β = 70.219(10)°, γ = 80.475(12)°, U 519.41(14) Å^3, Z = 2, D_c = 1.300 mg/m^3, T = 293(2) K, F(000) = 218, size = 0.40 × 0.35 × 0.30 mm. Reflections collected/unique 1946/1811 [R(int) = 0.0339], final R indices [$I > 2\sigma(I)$] R1 = 0.0629, wR2 = 0.1698, R indices (all data) R1 = 0.0939, wR2 = 0.1912

(1*S,6*S**,8*R**)-11-Spiro(1,3-dioxalane)-5(*S**)-hydroxytricyclo-[6.2.2.0^{1,6}]dodeca-3,9-diene (41a).** To a degassed solution of diene **29a** (0.220 g, 0.83 mmol) in dichloromethane (50 mL) was added Grubbs' first-generation catalyst **38** (34 mg, 0.04 mmol), and the reaction mixture was stirred at ambient temperature under nitrogen for 2 h. Removal of solvent followed by chromatography on silica gel (petroleum ether−ethyl acetate, 85:15) gave **41a** (0.160 g, 81%) as a colorless liquid. IR (neat) ν_{max}: 3413, 1657 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.35 (dd, J_1 = 8.4 Hz, J_2 = 7 Hz, 1H), 5.92 (d, J = 8.4 Hz, 1H), 5.82−5.76 (m, 1H), 5.64 (m of d, J = 10 Hz, 1H), 3.94−3.80 (m, 4H), 3.60 (br m, 1H), 2.70 (br s, 1H), 2.34 (m of part of an AB system, J_{AB} = 17.5 Hz, 1H), 2.18 (m of part of an AB system, J_{AB} = 17.5 Hz, 1H), 2.00−1.89 (m, 2H), 1.74 (d of part of an AB system, J_{AB} = 12 Hz, J_2 = 2.4 Hz,1H), 1.65−1.58 (m merged with signal due to H_2O present in $CDCl_3$, 1H), 1.47−1.41 (m, 1H), 1.28−1.24 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.0, 134.7, 130.8, 126.8, 113.4, 73.5, 64.7, 64.4, 45.1, 43.5, 39.9, 30.8, 30.2, 27.7. HRMS (ESI) (m/z): found 235.1331 $[M + H]^+$, calcd for $C_{14}H_{19}O_3$ 235.1334.

(1*S,6*S**,8*R**)-11-Spiro(1,3-dioxalane)-5(*R**)-hydroxytricyclo-[6.2.2.0^{1,6}]dodeca-3,9-diene (41b).** To a degassed solution of diene **29b** (0.066 g, 0.25 mmol) in dichloromethane (25 mL) was added Grubbs' first-generation catalyst **38** (15 mg, 0.02 mmol) and the mixture stirred at ambient temperature under nitrogen for 3 h (TLC). Removal of solvent followed by chromatography on silica gel (petroleum ether−ethyl acetate, 85:15) gave **41b** (0.050 g, 86%) as a colorless liquid. IR (film) ν_{max}: 3465 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.45 (superimposed dd, J=8 Hz, 1H), 6.04 (d, J= 8.4 Hz, 1H), 5.95−5.82 (merged m, 2H), 3.98−3.84 (m, 4H), 3.83−3.76 (m, 1H), 2.80−2.74 (br m, 1H), 2.46−2.40 (m, 1H), 2.37−2.22 (m, 2H), 2.06−2.00 (m, 1H), 1.86−1.78 (m, 2H), 1.68−1.60 (m, 1H), 1.36 (d, J = 11.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.6, 134.2, 129.9, 127.7, 113.4, 66.9, 64.9, 64.6, 44.0, 42.6, 35.9, 31.2, 27.6, 27.2. HRMS (ESI) (m/z): found 235.1342 $[M + H]^+$, calcd for $C_{14}H_{19}O_3$ 235.1334.

(1*S,6*S**,8*R**)-11-Spiro(1,3-dioxalane)tricyclo[6.2.2.0^{1,6}]dodeca-3,9-dien-5-one (42).** To a solution of compound **41b** (0.030 g, 0.128 mmol) in CH_2Cl_2 (20 mL) was added MnO_2 (0.5 g, excess), and the reaction mixture was stirred at ambient temperature for 10 h (TLC). The suspension was filtered through a Celite bed and washed with CH_2Cl_2 (10 mL), and the solvent was removed. The resulting product was chromatographed on silica gel (petroleum ether−EtOAc, 85:15) to give **42** (0.024 g, 82%) as a colorless solid. Mp: 50−52 °C. IR (film) ν_{max}: 1679 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92 (ddd, J_1 = 9.9 Hz, J_2 = 5.9 Hz, J_3 = 2.2 Hz, 1H), 6.40 (superimposed dd, J = 8 Hz, 1H), 6.0 (dd, J_1 = 9.9 Hz, J_2 = 2 Hz, 1H), 5.88 (d, J=8 Hz, 1H), 3.98−3.88 (m, 4H), 2.92 (dd, J_1 = 10 Hz, J_2 = 6.4 Hz, 1H), 2.78−2.68 (merged m, 2H), 2.60 (d of part of an AB system, J_{AB} = 18 Hz, J_2 = 5.5 Hz, 1H), 2.17 (m of d, J = 13 Hz, 1H), 1.80−1.72 (m, 2H), 1.62 (m of d, J = 13 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.8, 147.1, 137.7, 132.7, 129.9, 113.0, 65.1, 65.0, 47.1, 45.6, 43.0, 30.4, 28.6. 26.1. HRMS (ESI) (m/z): found 233.1180 $[M + H]^+$, calcd for $C_{14}H_{17}O_3$ 233.1178.

(1*S,6*S**,8*R**)-Tricyclo[6.2.2.0^{1,6}]dodeca-3,11-diene-5,10-dione (43).** To a solution of **42** (0.015 g, 0.06 mmol) in acetone−water (10 mL, 4:1) was added aq HCl (10%, 0.03 mL) at ∼10 °C. The reaction mixture was stirred at ambient temperature for 10 h. Acetone was removed, and the aqueous residue was extracted with ethyl acetate (3 × 10 mL). The combined extract was washed with aq sodium bicarbonate followed by brine and dried on anhydrous sodium sulfate. Removal of solvent followed by chromatography on silica gel [petroleum ether−ethyl acetate 85:15] gave **43** (0.011 g, 92%) as a colorless solid.Mp: 113−115 °C. IR (neat) ν_{max}: 1715, 1682 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95 (dd, J_1 = 10 Hz, J_2 = 6 Hz, 1H), 6.56 (superimposed dd, J=7 Hz, 1H), 6.07 (d with structure, J=10 Hz, 1H), 5.81(d, J= 7 Hz, 1H), 3.11−3.00 (m, 2H), 2.70 (dd, J_1 = 10 Hz, J_2 = 5 Hz, 1H), 2.56 (dd, J_1 = 19.4 Hz, J_2 = 10 Hz, 1H). 2.42 (d with structure, J= 14.3 Hz, 1H), 2.16−2.12 (m, 2H), 1.88 (superimposed ddd, J_1 = 14.3 Hz, J_2 = 10 Hz, J_3 = 3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.9, 197.2, 146.6, 139.7, 130.1, 129.9, 54.5, 46.3, 40.6, 31.0, 28.7, 27.2. HRMS (ESI) (m/z): found 189.0912 $[M + H]^+$, calcd for $C_{12}H_{13}O_2$ 189.0916.

(1*S,6*S**,8*R**)-11-Spiro(1,3-dioxalane)-9-methyltricyclo[6.2.2.0^{1,6}]-dodeca-3,9-dien-5-one (44).** To a degassed solution of **33** (0.050 g, 0.18 mmol) in dichloromethane (40 mL) was added Grubbs' catalyst **38** (8 mg, 0.01 mmol) and the mixture stirred at ambient temperature for 5 h under nitrogen. Removal of solvent followed by chromatography of the residue on silica gel (petroleum ether−ethyl acetate, 98:2) gave the title compound **44** as a colorless liquid (28 mg, 64%). IR (film) ν_{max}: 1701 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.84 (ddd, J_1 = 8.2 Hz, J_2 = 5.9 Hz, J_3 = 2.4 Hz, 1H), 5.94 (m of d, J = 8.2 Hz, 1H), 5.40 (s with str, 1H), 3.95−3.8 (m, 4H), 2.81 (dd, J_1 = 9.5 Hz, J_2 = 3.7 Hz, 1H), 2.63 (superimposed dd of part of an AB system, J_{AB} = 19 Hz, J_2 = J_3 = 3 Hz, 1H), 2.50 (m of dd of part of an AB system, J_{AB} = 19 Hz, J_2 = 5.8 Hz, 1H), 2.42−2.36 (m, 1H), 2.09 (ddd, J_1 = 10.6 Hz, J_2 = 5 Hz, J_3 = 3.5 Hz, 1H), 1.73−1.60 (m merged with d, J = 1.5 Hz, total 5H), 1.55 (superimposed dd of d, J_1 = 13.3 Hz, J_2 = J_3 = 3.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.8, 146.9, 146.6, 129.8, 124.6, 113.3, 64.9, 64.8, 47.2, 46.1, 42.4, 35.9, 28.6, 25.5, 20.1. HRMS (ESI) (m/z): found 247.1344 $[M + H]^+$, calcd for $C_{15}H_{19}O_3$ 247.1334.

Preparation of Compound 44 by Oxidation of 39a. To a solution of compound **39a** (0.020 g, 0.072 mmol) in CH_2Cl_2 (20 mL) was added freshly prepared MnO_2 (0.200 g), and the reaction mixture was stirred for 4 h at ambient temperature. It was filtered on a Celite bed and washed with CH_2Cl_2 (15 mL). The filtrate was concentrated in vacuo, and the residue was chromatographed. Elution with petroleum ether−ethyl acetate

(70.30) gave the compound **44** as a colorless liquid (0.019 g, 96%) which was found to be identical with the compound prepared above.

(1*S,7*S**,9*R**)-12-Spiro(1,3-dioxalane)-(6*S**)-hydroxytricyclo-[7.2.2.0^{1,7}]trideca-3,10-diene (45a).** To a degassed solution of triene **31a** (0.190 g, 0.68 mmol) in dichloromethane (50 mL) was added Grubbs' first-generation catalyst **38** (28 mg, 0.03 mmol), and the reaction mixture was stirred at ambient temperature for 7 h under nitrogen. Removal of solvent followed by chromatography on silica gel (petroleum ether−ethyl acetate, 80:20) gave **45a** (0.140 g, 82%) as a colorless solid. Mp: 116−118 °C. IR (film) ν_{max}: 3413, cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.32 (dd, J_1 = 8.2 Hz, J_2 = 6.4 Hz, 1H), 6.01−5.90 (merged m, 2H), 5.84−5.75 (m, 1H), 3.92−3.85 (m, 4H), 3.06−2.96 (m, 1H), 2.64−2.24 (merged m, 6H), 2.06−1.94 (m, 1H), 1.74−1.58 (m, merged with broad s, 3H), 1.26−1.18 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.5, 132.3, 131.6, 128.4, 114.5, 73.4, 64.9, 64.6, 47.7, 47.3, 43.0, 35.7, 33.4, 30.3, 26.4. HRMS (ESI) (*m*/*z*): found 249.1502 [M + H]$^+$, calcd for $C_{15}H_{21}O_3$ 249.1491.

Crystal data of 45a: $C_{30}H_{40}O_6$, M 496.2 (two molecules), space group, orthorhombic, *Pbca*, *a* = 8.424(3) Å, *b* = 23.69(5) Å, *c* = 25.47(9) Å, λ = 0.7107 Å, α = 90.00°, β = 90.00°, γ = 90.00°, *U* 5083(10) Å^3, *Z* = 8, D_c = 1.298 mg/m^3, *T* = 293(2) K, *F*(000) = 2144, size = 0.28 × 0.24 × 0.21 mm. Reflections collected/unique 4458/2142 [*R*(int) = 0.0882], final *R* indices [$I > 2\sigma(I)$] R1 = 0.0346, wR2 = 0.0465 R indices (all data) R1 = 0.0992, wR2 = 0.0526.

(1*S,7*S**,9*R**)-12-Spiro(1,3-dioxalane)-(6*R**)-hydroxytricyclo-[7.2.2.0^{1,7}]trideca-3,10-diene (45b).** To a degassed solution of diene **31b** (0.100 g, 0.36 mmol) in dichloromethane (40 mL) was added Grubbs' first-generation catalyst **38** (15 mg, 0.02 mmol) and the mixture stirred at ambient temperature for 5 h under nitrogen. Removal of solvent followed by chromatography on silica gel [petroleum ether−ethyl acetate (70:30)] gave **45b** (0.084 g, 94%) as a colorless liquid. IR (film) ν_{max}: 3430 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.40 (dd, J_1 = 8 Hz, J_2 = 6.6 Hz, 1H), 6.04−5.95 (m, 2H), 5.83−5.74 (m, 1H), 4.0−3.80 (merged m, 5H), 2.68−2.62 (m, 1H), 2.58−2.42 (m, 3H), 2.34−2.24 (m, 2H), 1.92−1.84 (m, 1H), 1.76−1.66 (m, 2H), 1.62−1.54 (m, 1H), 1.44−1.38 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.5, 132.1, 130.9, 129.4, 114.6, 71.4, 64.9, 64.6, 45.8, 43.2, 43.0, 33.5, 31.4, 30.4, 27.0. HRMS (ESI) (*m*/*z*): found 249.1497 [M + H]$^+$, calcd for $C_{15}H_{21}O_3$ 249.1490.

(1*S,7*S**,9*R**)-Tricyclo[7.2.2.0^{1,7}]trideca-3,12-dien-11-one (46).** To a solution of compound **45a** (0.110 g, 0.443 mmol) in CH_2Cl_2 (15 mL) were added PCC (0.382 g, 1.77 mmol) and sodium acetate (0.084 g, 1.02 mmol), and the reaction mixture was stirred at ambient temperature for 8 h (TLC) and then filtered through a column of silica gel to give a keto ketal (0.076 g, 69%) as a colorless liquid which was subjected to hydrolysis as described below.

To a solution of the keto ketal thus obtained (0.020 g, 0.081 mmol) in acetone−water (10 mL, 4:1) was added aq HCl (0.4 mL) at ∼10 °C. The reaction mixture was stirred at ambient temperature for 10 h. Acetone was removed, and the aqueous residue was extracted with ethyl acetate (3 × 10 mL). The combined extract was washed with aq sodium bicarbonate followed by brine and dried on anhydrous sodium sulfate. Removal of solvent followed by chromatography on silica gel [petroleum ether−ethyl acetate 90:10] gave **46** (0.015 g, 93%) as a colorless solid. Mp: 118−120 °C. IR (film) ν_{max}: 1702 (br) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.62 (dd, J_1 = 8 Hz, J_2 = 6.6 Hz, 1H), 6.11−6.02 (m, 1H), 5.88−5.81(m, 1H), 5.69(d, *J* = 8 Hz, 1H), 3.28 (dd, J_1 = 10 Hz, J_2 = 6.2 Hz, 1H), 3.20 (br d, *J* = 17.5 Hz), 3.06−2.96(merged m, 2H), 2.78 (dd, J_1 = 15 Hz, J_2 = 6.2 Hz, 1H), 2.34 (dd, J_1 = 15 Hz, J_2 = 6.2 Hz, 1H), 2.19−2.00 (merged m, 3H), 1.84−1.76 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.1, 207.3, 139.0, 129.7, 128.4, 125.3, 56.7, 47.1, 43.3, 38.8, 31.7, 28.5, 28.1. HRMS (ESI) (*m*/*z*): found 203.1082 [M + H]$^+$, calcd for $C_{13}H_{15}O_2$ 203.1072.

(1*S,7*S**,9*R**)-(6*R**)-Hydroxytricyclo[7.2.2.0^{1,7}]trideca-3,12-dien-11-one (47).** To a solution of compound **45b** (0.050 g, 0.2 mmol) in acetone−H_2O (15 mL, 4:1) was added concd HCl (0.8 mL) at 0−5 °C, and the reaction mixture was stirred for 8 h. The reaction mixture was neutralized with $NaHCO_3$, and acetone was removed under vacuum. The mixture was was diluted with water and extracted with ether (3 × 20 mL). The combined extract was washed with brine (10 mL) and dried. Solvent was removed in vacuo, and the product was chromatographed on silica gel [petroleum ether−ethyl acetate (82: 18)] to give the keto alcohol **47** (0.038 g, 92%) as a colorless liquid. IR (film) ν_{max}: 3420, 1714 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.54 (superimposed dd, J_1 = J_2 = 8 Hz, 1H), 6.05−5.96 (m, 1H), 5.87−5.77(m, 2H), 3.89 (br m, 1H), 2.99−2.93 (m, 1H), 2.66−2.48 (m, 2H), 2.44−2.34 (m, 1H), 2.32−1.94 (merged m, 5H), 1.88−1.80 (m, 1H), 1.41−1.38 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.9, 138.4, 130.4, 129.2, 128.6, 70.5, 52.1, 44.6, 39.9, 33.4, 30.8, 28.3. HRMS (ESI) (*m*/*z*): found 205.1237 [M + H]$^+$, calcd for $C_{13}H_{17}O_2$ 205.1229.

(1*S,7*S**,9*R**)-12-Spiro(1,3-dioxalane)-10-methyl-(6*S**)-hydroxytricyclo[7.2.2.0^{1,7}]trideca-3,10-diene (48).** To a degassed solution of compound **30a** (0.048 g, 0.16 mmol) in CH_2Cl_2 (30 mL) was added first-generation Grubbs' catalyst **38** (14 mg, 0.02 mmol), and the reaction mixture was stirred for 5 h at ambient temperature. Removal of solvent followed by chromatography on silica gel [petroleum ether−ethyl acetate (70:30)] gave the compound **48** (0.035 g, 81%) as a colorless liquid. IR (film) ν_{max}: 3430 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.00−5.584 (m, 1H), 5.81−5.74 (m, 1H), 5.50 (br s, 1H), 4.00−3.8 (m, 5H), 3.01−2.95 (m, 1H), 2.55−2.20 (m, 6H), 2.00−1.90 (m, 1H), 1.78 (d, *J* = 1.5 Hz, 3H), 1.74−1.64 (m, 2H), 1.26−1.18 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 131.7, 128.2, 124.3, 114.9, 73.5, 64.9, 64.6, 48.2, 47.9, 42.6, 35.9, 35.8, 32.8, 26.5, 20.2. HRMS (ESI) (*m*/*z*): found 285.1459 [M+Na]$^+$, calcd for $C_{16}H_{22}O_3Na$ 285.1467.

(1*S,7*S**,9*R**)-13-Methyl-(6R*)-hydroxy-tricyclo[7.2.2.0^{1,7}]-trideca-3,12-dien-11-one (49).** To a degassed solution of diene **34** (0.120 g, 0.48 mmol) in CH_2Cl_2 (50 mL) was added Grubbs' catalyst **38** (20 mg, 0.024 mmol) and stirred at ambient temperature for 8 h, under nitrogen. Removal of solvent followed by chromatography of the residue on silica gel [petroleum ether-ethyl acetate (90:10)] gave the title compound **49**, as a colorless solid (0.088 g, 83%), mp. 127−128 °C. IR (film) ν_{max}: 3433, 1719 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.01−5.94 (m, 1H), 5.83−5.74 (m, 1H), 5.39 (s, 1H), 3.90−3.81 (m, 1H), 2.70−2.65 (m, 1H), 2.60−2.48 (m, 2H), 2.35 (m of d, *J* = 16 Hz, 1H), 2.23 (dd, J_1 = 16 Hz, J_2 = 5 Hz, 1H), 2.19−2.08 (m, 3H), 1.98−1.70 (m, 1H), 1.88−1.76 (singlet merged with m, 4H), 1.44 (d, *J* = 9.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 212.0, 148.0, 130.4, 129.1, 120.5, 70.5, 51.8, 45.1, 39.6, 36.3, 33.4, 30.3, 28.4, 20.3. HRMS (ESI) (*m*/*z*): Found 219.1389 [M + H]$^+$, calcd for $C_{14}H_{19}O_2$ 219.1385.

Crystal data of 49: $C_{14}H_{18}O_2$, *M* 218.28, space group, triclinic, *P*-1, *a* = 8.1740(16) Å, *b* = 8.4240(6) Å, *c* = 8.5710(7) Å, λ = 0.70930 Å, α = 98.169(7)°, β = 100.674(10)°, γ = 90.637(10)°, *U* = 573.66(13) Å^3, *Z* = 2, D_c = 1.264 mg/m^3, *T* = 293(2) K, *F*(000) = 236, size = 0.35 × 0.20 × 0.15 mm. Reflections collected/unique 1820/1820 [*R*(int) = 0.0000], final *R* indices [$I > 2\sigma(I)$] R1 = 0.0347, wR2 = 0.0803. *R* indices (all data) R1 = 0.0420, wR2 = 0.0853.

(1*S,7*S**,9*R**)-13-Methyltricyclo[7.2.2.0^{1,7}]trideca-3,12-dien-11-one (50).** To a stirred solution of the keto alcohol **49** (0.060 g, 0.27 mmol) in dichloromethane (15 mL) were added PCC (0.148 g, 0.68 mmol) and molecular sieves (4 Å, previously dried) and the mixture stirred at ambient temperature until completion of the reaction (TLC, 1 h). The reaction mixture was filtered on a Celite bed and washed with ether (3 × 15 mL). The filtrate was concentrated under vacuum, and the product was chromatographed on silica gel [petroleum ether−ethyl acetate (90:10)] to

furnish the diketone **50** as a colorless solid (0.056 g, 94%). Mp: 100−102 °C. IR (film) ν_{max}: 1731 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 6.12−6.01 (m, 1H), 5.88−5.76 (m, 1H), 5.26 (br s, 1H), 3.30−3.22 (m, 2H), 2.98 (dd, $J_1 = 18$ Hz, $J_2 = 7.2$ Hz, 1H), 2.80−2.69 (merged m, 2H), 2.28 (dd, $J_1 = 15$ Hz, $J_2 = 6.6$ Hz, 1H), 2.15−2.05 (m, 2H), 2.05−1.95 (m, 1H), 1.88 (d, $J = 1.5$ Hz, 3H), 1.80−1.62 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 209.1, 207.1, 148.5, 129.7, 125.0, 120.4, 56.60, 47.6, 43.1, 38.21, 36.9, 28.0, 27.7, 20.1. HRMS (ESI) (*m*/*z*): found 217.1237 $[M + H]^+$, calcd for $C_{14}H_{17}O_2$ 217.1229.

(1*S,8*S**,10*R**)-Tricyclo[8.2.2.0^{1,8}]tetradeca-3,13-diene-7,12-dione (51).** To a degassed solution of diene **37** (0.048 g, 0.196 mmol) in dichloromethane (20 mL) was added second-generation Grubbs' catalyst **52** (8 mg, 0.01 mmol) and the mixture stirred at ambient temperature under nitrogen. Removal of solvent followed by chromatography on silica gel [petroleum ether−ethyl acetate (90:10)] gave **51** (0.038 g, 89%) as a colorless solid. Mp: 95−97 °C. IR (film) ν_{max}: 1722, 1701 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 6.62 (dd, $J_1 = 8.0$ Hz, $J_2 = 6.6$ Hz, 1H), 6.02−5.80 (m, 2H), 5.68 (d, $J = 8.0$ z, 1H), 3.17 (dd, $J_1 = 9.6$ Hz, $J_2 = 6.3$ Hz, 1H), 3.06−3.00 (m, 1H), 2.72−2.64 (dd, $J_1 = 13.2$ Hz, $J_2 = 6.3$ Hz, 1H), 2.58−2.26 (cluster of m, 5H), 2.17 (dd, $J_1 = 13.2$ Hz, $J_2 = 8.9$ Hz, 1H), 2.10−2.02 (br m, 1H), 2.00−1.92 (m, 1H), 1.82−1.72 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 214.4, 209.2, 138.3, 130.0, 128.8, 128.7, 53.2, 47.0, 45.4, 39.4, 33.3, 32.5, 28.9, 23.2. HRMS (ESI) (*m*/*z*): found 217.1221$[M + H]^+$, calcd for $C_{14}H_{17}O_2$ 217.1229.

Acknowledgment. We are grateful to the Department of Science and Technology for continuing financial support. P. K.S. thanks CSIR and B.C.S. thanks DST and CSIR New Delhi for fellowships. Thanks are due to DST for creating a national single-crystal X-ray facility.

Supporting Information Available: ^1H NMR and ^{13}C NMR spectra of compounds **12b**, **14**, **16**−**37**, and **39**−**51,** ORTEP diagrams of **16**, **40**, **45a**, and **49**, and CIF data of **16**, **40**, **45a**, and **49**. This material is available free of charge via the Internet at http://pubs.acs.org.