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Studies on the Photochemical Rearrangements of Enantiomerically Pure, Polysubstituted, and Variously Annulated Bicyclo[2.2.2]octenones

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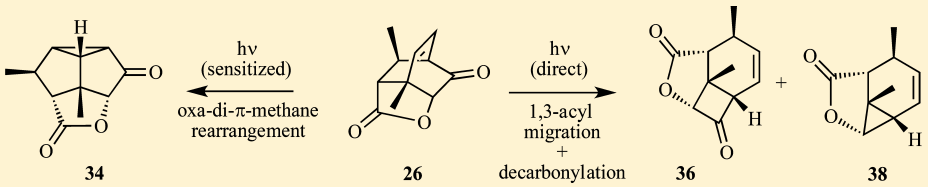
Supporting Information

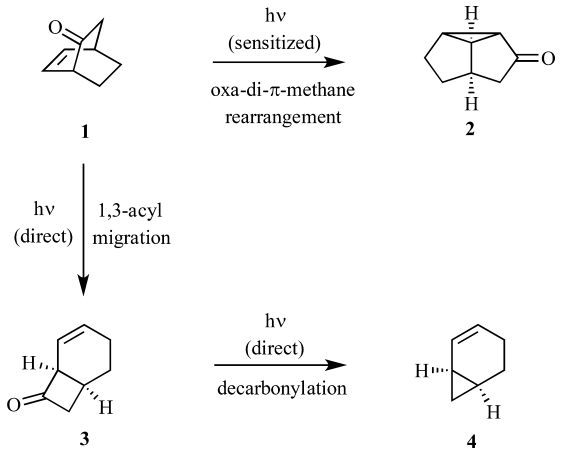


ABSTRACT: A series of enantiomerically pure bicyclo[2.2.2]octenones, including the lactone-annulated system **26**, has been prepared by engaging derivatives of an enzymatically derived and homochiral *cis*-1,2-dihydrocatechol in inter- or intra-molecular Diels–Alder reactions. Systems such as **26** readily participate in photochemically promoted oxa-di-π-methane rearrangement or 1,3-acyl migration processes to give products such as diquinane **34** or mixtures of cyclobutanone **36** and cyclopropane **38**, respectively.

INTRODUCTION

Bicyclo[2.2.2]octenones including the parent system **1** (Scheme 1) are excellent substrates for certain photochemically promoted rearrangement reactions.[1] Specifically, on irradiation in the presence of photosensitizers such as acetophenone they participate in oxa-di-π-methane rearrangements and, so affording, via a triplet pathway, cyclopropannulated diquinanes such as **2**. In contrast, on direct irradiation they engage, now via a singlet pathway, in a 1,3-acyl migration reaction (Givens rearrangement) to give bicyclo[4.2.0]oct-4-en-7-ones such as **3**. Upon sustained irradiation, photoproduct **3** and many of its derivatives can undergo decarbonylation to give the corresponding Δ^2-norcarene, e.g. **4**.

Scheme 1. Oxa-di-π-methane, 1,3-Acyl Migration, and Photodecarbonylation Reactions of the Parent Bicyclo[2.2.2]octenone (1)



The capacity to effectively exploit these valuable transformations is contingent on having ready access to bicyclo[2.2.2]octenones, especially enantiomerically pure ones. While various methods are available for the synthesis of such systems,[2] a particularly useful approach involves the facially selective intermolecular cycloaddition of dienophiles to enantiomerically pure *cis*-1,2-dihydrocatechols such as **5** (Figure 1) that are readily obtained through the whole-cell biotransformation of the corresponding arene (toluene in the case of compound **5**).[3] Indeed, we have exploited such adducts in the photochemically mediated total synthesis of a range of sesquiterpenoid natural products including various triquinanes,[4] protoilludanes,[5] and the structure assigned to a sterpurene.[6] In seeking to extend such studies for the purposes of preparing new molecular scaffolds, including those of use in drug discovery, we became interested in establishing the degree to which the bicyclo[2.2.2]octenone framework could be substituted and/or annulated and continue to engage in the above-

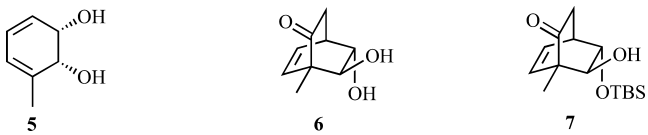


Figure 1. Homochiral *cis*-1,2-dihydrocatechol **5** and the derived bicyclo[2.2.2]octenone-based photosubstrates **6** and **7**.

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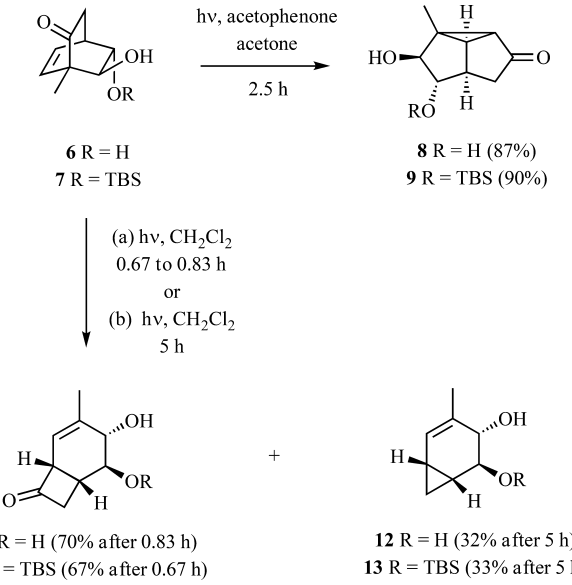
mentioned photochemical processes. Herein, we detail research that serves to emphasize the remarkable extent to which these processes can be applied in a reliable fashion.

In connection with our recently reported studies[7] on the synthesis of the sorbicillinoid-derived isolate rezishanone C, we prepared,[7] using intermolecular Diels–Alder cycloaddition processes, the oxygenated bicyclo[2.2.2]octenones **6** and **7** in gram quantities from *cis*-1,2-dihydrocatechol **5**. Accordingly, compounds **6** and **7** became the substrates used in the opening stages of the present work.

RESULTS AND DISCUSSION

Independent irradiation (using a medium-pressure mercury lamp) of an acetone solution of each of compounds **6** and **7** held in a round-bottomed flask made from borosilicate glass and containing ca. 1.4 molar equiv of acetophenone (Scheme 2) afforded the anticipated oxa-di-π-methane rearrangement

Scheme 2. Photochemical Behaviors of Bicyclo[2.2.2]octenones 6 and 7 under Either Direct Irradiation or Photosensitized Conditions



6 R = H
7 R = TBS

8 R = H (87%)
9 R = TBS (90%)

10 R = H (70% after 0.83 h)
11 R = TBS (67% after 0.67 h)

12 R = H (32% after 5 h)
13 R = TBS (33% after 5 h)

products **8** (87% or 98% brsm) and **9** (90% or 99% brsm), respectively. All of the spectral data acquired on compounds **8** and **9** were entirely consistent with the assigned structures, but final confirmation of these followed from single-crystal X-ray analyses (see the Experimental Section and Supporting Information for details).

When dichloromethane solutions of substrates **6** and **7** were subjected to direct irradiation for brief periods (less than 1 h) with the same type of lamp then the anticipated Givens rearrangement products **10** (70% or 84% brsm) and **11** (67%), respectively, were obtained. Upon sustained irradiation (5 h) of the same substrates, significant quantities of the corresponding decarbonylated systems **12** (32%) and **13** (33%) were obtained along with reduced amounts of the corresponding and chromatographically separable cyclobutenones. Once again, all of the spectroscopic data acquired on compounds **10**–**13** were in accord with the assigned structures, but those of the first and the last of these were confirmed by single-crystal X-ray analysis.

Establishing the impact of various modes of ring-fusion on the capacity of bicyclo[2.2.2]octenones to engage in oxa-di-π-methane and 1,3-acyl migration reactions was another topic of interest. Therefore, building upon our earlier studies[8] on the assembly of the relevant frameworks through the intramolecular Diels–Alder (IMDA) reactions of crotonate esters derived from *cis*-1,2-dihydrocatechols, compound **5** was converted (Scheme 3) into the diesters **14** (81%) and **15** (74%) under previously established[8] conditions. When each of compounds **14** and **15** was heated in refluxing toluene they engaged in the two possible modes of cycloaddition and thus giving rise to the corresponding pair of adducts, viz. lactones **16** (40% from **14**), **17** (41% from **15**), **18** (26% from **14**), and **19** (12% from **15**), that could be separated from one another by conventional chromatographic means. The remaining ester residues within each of adducts **18** and **19** were cleaved by standard methods and the resulting alcohols **20** (74%) and **21** (76%) oxidized to the corresponding ketones **22** (86%) and **23** (82%), respectively, using the Dess–Martin periodinane.[9] Similarly, esters **16** and **17** were cleaved using potassium carbonate in methanol and the product alcohols **24** (79%) and **25** (94%), respectively, oxidized to the corresponding ketones, namely, compounds **26** (94%) and **27** (78%). Single-crystal X-ray analyses were conducted on compounds **23** and **27**, details of which are presented in the Experimental Section and SI.

The oxa-di-π-methane rearrangement of the lactone-annulated bicyclo[2.2.2]octenones **22** and **23** took place readily when acetone solutions of each of these was irradiated in the presence of acetophenone (Scheme 4). By such means the cyclopropane-annulated oxatriquinanes **28** (40%) and **29** (43%) were obtained. In contrast, direct irradiation of substrates **22** and **23** led to the corresponding mixtures of cyclobutanones **30** (up to 75%) and **31** (up to 73%), respectively, as well as their decarbonylated counterparts **32** (up to 37%) and **33** (up to 52%), respectively. The structures of compounds **30** and **32** were confirmed by single-crystal X-ray analyses.

Equivalent studies on the photochemical behaviors of the isomeric lactone annulated bicyclo[2.2.2]octenones **26** and **27** (Scheme 5) led to analogous outcomes. Specifically, the anticipated oxatriquinanes **34** (45%) and **35** (49%) were obtained on photosensitized irradiation of these substrates while direct irradiation afforded mixtures of cyclobutanones **36** (up to 70%) and **37** (up to 71%) as well as their decarbonylated congeners **38** (up to 35%) and **39** (up to 40%), respectively. The structures of compounds **34**, **35**, **36**, and **38** were each confirmed by single-crystal X-ray analyses.

It is worth noting that both the substrates and the photoproducts shown in Scheme 5 are pseudoenantiomers of their counterparts shown in Scheme 4. Thus, for example, if each of compounds **30** (Scheme 4) and **36** (Scheme 5) lacked the two methyl groups then they would be enantiomers. Accordingly, the protocols just described provide a means by which the single enantiomeric form of starting material **5** can be converted into either enantiomeric form of a range of relatively complex molecular frameworks.

In seeking to establish the effects of alternate modes of ring fusion and other substituents on the capacity of bicyclo[2.2.2]-octenones to engage in photochemically promoted rearrangements, the behaviors of various polyhydro-4,7-ethanoindenone derivatives were explored. The routes shown in Scheme 6 were used to prepare these cyclopentannulated systems. Thus, the previously described[4d] tricyclic system **40**, prepared by a reaction sequence involving an initial Diels–Alder cycloaddition reaction between 2-cyclopenten-1-one and the

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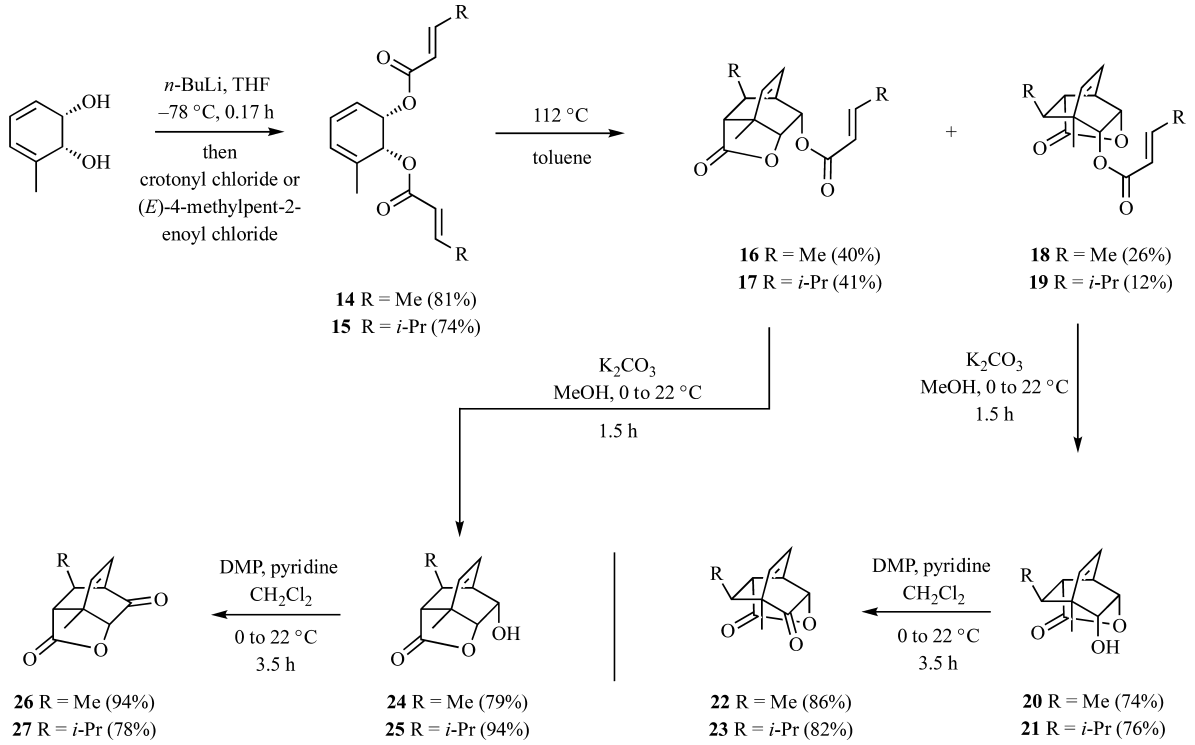
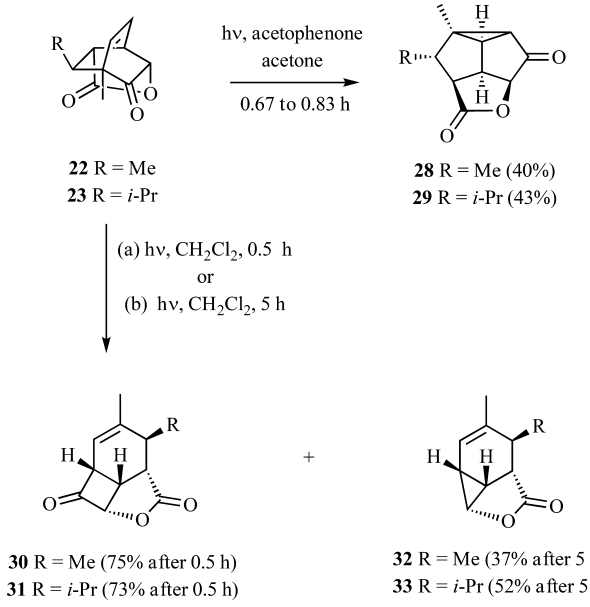
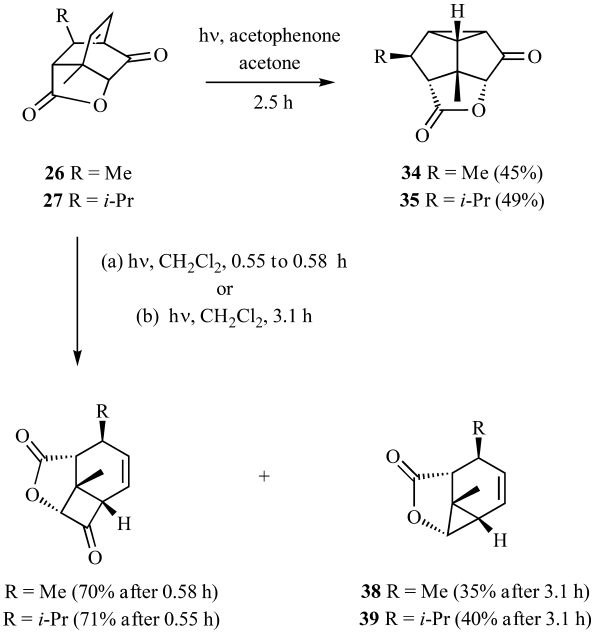
Scheme 3. Synthesis of Lactone-Annulated Bicyclo[2.2.2]octenones 22, 23, 26, and 27



Scheme 4. Photochemical Behaviors of Bicyclo[2.2.2]octenones 22 and 23 under Either Direct Irradiation or Sensitized Conditions



Scheme 5. Photochemical Behaviors of Bicyclo[2.2.2]octenones 26 and 27 under Either Direct Irradiation or Sensitized Conditions



acetonide derived from *cis*-diol **5**, was reduced with $LiAlH_4$, and the previously reported[4d,5b] alcohol **41** (39%) obtained in pure form after chromatographic separation from its coproduced epimer.[4d,5b] Compound **41**, the structure of which was confirmed by single-crystal X-ray analysis, was acetylated under standard conditions to give ester **42** (97%), and the acetonide moiety associated with this last compound was hydrolyzed by treating a methanol/water solution of it with acidified AG-50W-X8 resin. The product diol **43** (97%) was selectively oxidized using the sterically demanding oxammonium salt derived from *p*-TsOH·H_2O-promoted disproportionation of 4-acetamido-TEMPO,[10] and thus producing acyloin **44** (97%) that was also subjected to single-crystal X-ray analysis. Compound **44** was converted into derivatives **45** (91%), **46** (77%), **47** (82%), and **48** (93%) by standard methods, while samarium iodide mediated deoxygenation of benzoate **48** also allowed for the preparation of bicyclo[2.2.2]-octenone **49** (85%). Once again, the structures of compounds **45**, **47**, and **48** were confirmed by single-crystal X-ray analyses.

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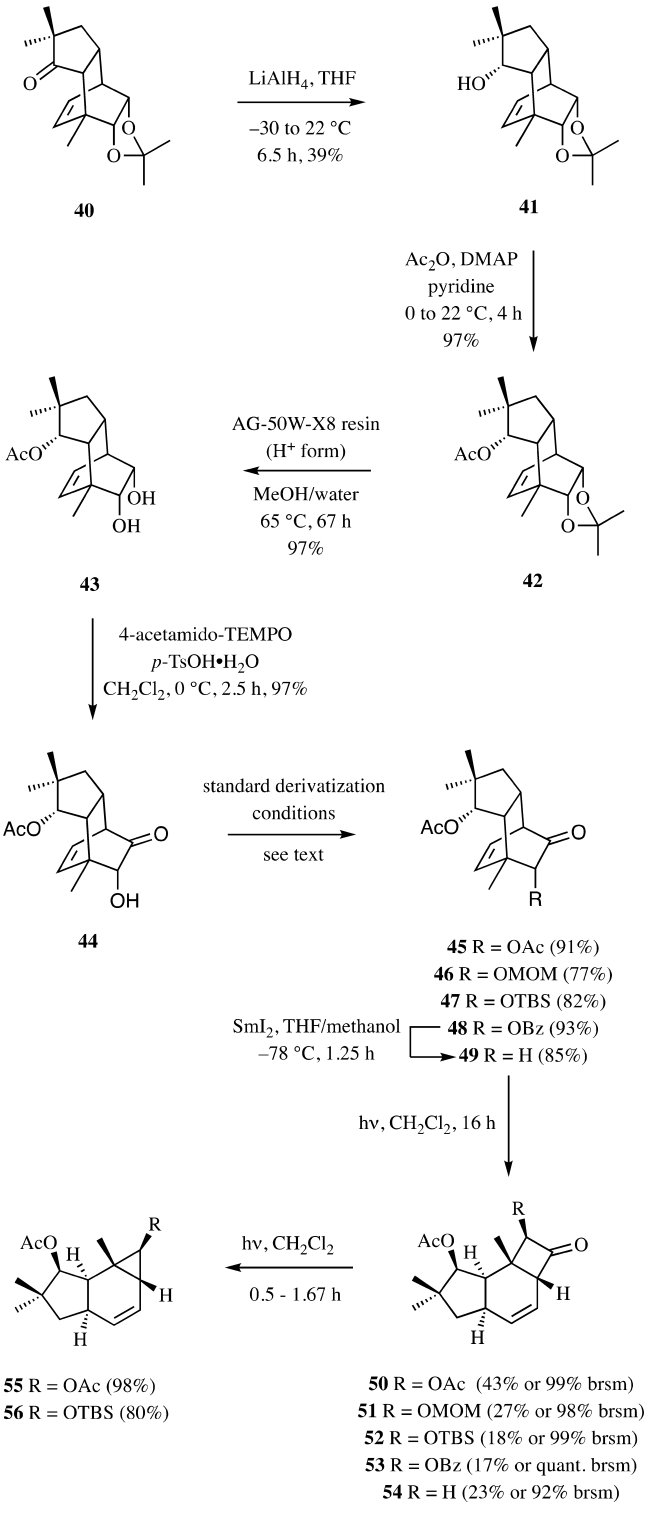
Scheme 6. Synthesis of Cyclopentannulated Bicyclo[2.2.2]octenones 45−49 and Their Photochemical Behaviors under Direct Irradiation Conditions

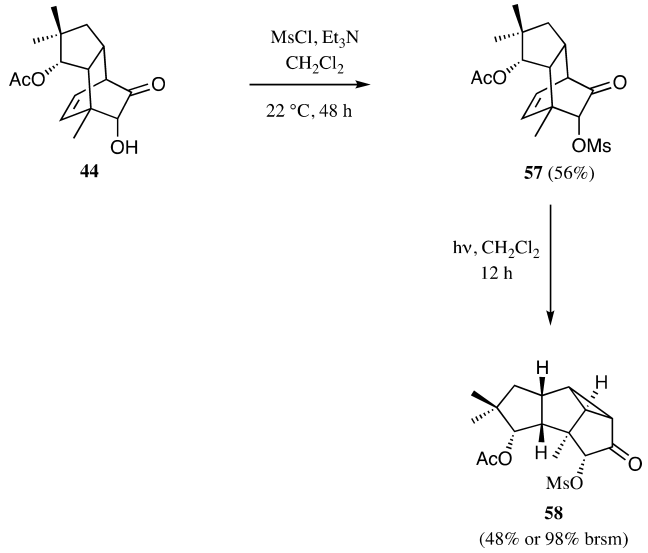


On direct irradiation of dichloromethane solutions of each of compounds **45**−**49** they engaged in 1,3-acyl migration reactions to give the cyclobutanones **50** (43% or 99% brsm), **51** (27% or 98% brsm), **52** (18% or 99% brsm), **53** (17% or quant brsm), and **54** (23% or 92% brsm), respectively. Irradiation of compounds **50** and **47** led to cyclopropanes **55** (98%) and **56** (80%), respectively. The structures of all of these photoproducts were determined through comprehensive spectroscopic analyses. In particular, the infrared spectrum of each of cyclobutanones **50**−**54** exhibited a characteristic carbonyl absorption band in the range 1778−1792 cm^{-1} as well as a carbonyl carbon resonance above δ 200 ppm in the corresponding ^{13}C NMR spectrum. The structure of compound **53** was confirmed by single-crystal X-ray analysis.

Given our extensive earlier studies[4] on the oxa-di-π-methane rearrangements of substrates very closely related to compounds **45**−**49**, we have not subjected these to photosensitized irradiation but would fully expect them to behave in a similar manner and thus leading to the corresponding cyclopropannulated triquinanes.

In contrast to outcomes noted above (Scheme 6), when the mesylate **57** (Scheme 7), which was readily prepared in 56% yield from acyloin **44**, was subjected (as a solution in dichloromethane) to direct irradiation it engaged in an oxa-di-π-methane rearrangement reaction rather than a 1,3-acyl migration reaction and so affording the cyclopentannulated and stereochemically pure triquinane **58** in 48% yield (or 98% yield brsm). The configuration at the carbon bearing the mesyloxy group is tentatively assigned as illustrated although the alternate one cannot be discounted as a result of the intervention of a photoepimerization process.[4b−d] The precise origins of this seemingly anomalous behavior of sulfonate ester **57** remain unclear at the present time and serve to highlight the very limited understanding of the photochemical properties of such systems.[11] These matters are the subject of ongoing studies in our laboratories.

Scheme 7. Synthesis and Anomalous Photochemical Behavior of the Mesyloxy-Substituted Bicyclo[2.2.2]octenone 57



CONCLUSIONS

The studies reported here have established that a wide range of extensively substituted and variously annulated bicyclo[2.2.2]-octenones are capable of engaging in either oxa-di-π-methane or 1,3-acyl migration reactions depending upon the mode of photoactivation (sensitized vs direct irradiation). The 1,3-acyl migration reactions leading to the isomeric cyclobutanones can be followed by rapid photodecarbonylation processes to

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coproduce the corresponding (but normally readily separable) cyclopropanes. A noteworthy feature of the photochemical behaviors of the annulated bicyclo[2.2.2]octenones studied here is that the mode of ring fusion (annulation) can have a significant impact on the rates of both types of processes. Thus, for example, the lactone-annulated systems **22**, **23**, **26**, and **27** appear to engage in more rapid 1,3-acyl migration reactions than their cyclopentannulated counterparts **45**−**49**. The same could be said of the corresponding oxa-di-π-methane process, especially when the outcomes of our earlier studies[4] are taken into account. That is to say, the lactone annulated compounds just mentioned also appear to participate in more rapid triplet-sensitized rearrangement reactions than their cyclopentannulated counterparts. The origins of these variations are the subject of ongoing studies, the outcomes of which will be reported in due course.

EXPERIMENTAL SECTION

General Experimental Procedures. Unless otherwise specified, proton (^{1}H) and carbon (^{13}C) NMR spectra were recorded at 18 °C in base-filtered $CDCl_3$ on a spectrometer operating at 400 MHz for proton and 100 MHz for carbon nuclei. ^{1}H NMR data are recorded as follows: chemical shift (δ) [multiplicity, coupling constant(s) J (Hz), relative integral] where multiplicity is defined as s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet or combinations of the above. In relevant cases, the signal due to residual $CHCl_3$ appearing at δ_H 7.26 and the central resonance of the $CDCl_3$ "triplet" appearing at δ_C 77.0 were used to reference ^{1}H and ^{13}C NMR spectra, respectively. Samples were analyzed by infrared spectroscopy (ν_{max}) as thin films on KBr plates. Optical rotations were recorded using the sodium D-line (589 nm) in a cell with a path length of 1 dm, at the concentrations indicated and in the specified solvent at 22 °C. Specific rotations were then calculated in the usual manner. Low- and high-resolution electron impact (EI) mass spectra were recorded on a double focusing, triple sector machine. Low- and high-resolution ESI mass spectra were recorded on a triple-quadrupole mass spectrometer operating in positive ion mode. Melting points are uncorrected. Analytical thin layer chromatography (TLC) was performed on aluminum-backed 0.2 mm thick silica gel 60 F_{254} plates. Eluted plates were visualized using a 254 nm UV lamp and/or by treatment with a suitable dip followed by heating. These dips included phosphomolybdic acid/ceric sulfate/sulfuric acid (conc)/water (37.5 g: 7.5 g: 37.5 g: 720 mL), potassium permanganate/potassium carbonate/5% sodium hydroxide aqueous solution/water (3 g: 20 g: 5 mL: 300 mL), and *p*-anisaldehyde or vanillin/sulfuric acid (conc)/ethanol (15 g: 2.5 mL: 250 mL). Flash chromatographic separations were carried out following protocols defined by Still et al.[12] with silica gel 60 (40−63 μm) as the stationary phase and using the AR- or HPLC-grade solvents indicated. The melting points of solids purified by such means were recorded directly (ie after they had crystallized from the concentrated chromatographic fractions). Starting materials, reagents, drying agents, and other inorganic salts were generally commercially available and were used as supplied. Tetrahydrofuran (THF), methanol, and dichloromethane were dried using a solvent purification system that is based upon a technology originally described by Grubbs et al.[13] Where necessary, reactions were performed under a nitrogen atmosphere.

Specific Chemical Transformations. *(2a′R,3S,4S,4aR)-3,4-Dihydroxy-2b-methylhexahydrocyclopropa[cd]pentalen-2(1H)-one (**8**).* A deoxygenated solution of compound **6**[7] (94 mg, 0.56 mmol) and acetophenone (90 μL, 0.77 mmol) in acetone (100 mL) maintained under nitrogen was subjected to irradiation with a Hanovia 450 W medium-pressure mercury-vapor lamp for 2.5 h and then cooled and concentrated under reduced pressure to give a yellow oil. This material was subjected to flash column chromatography (silica, 1:1 → 1:0 v/v ethyl acetate/40−60 petroleum ether gradient elution) to afford two fractions, A and B.

Concentration of fraction A (R_f = 0.3 in ethyl acetate) afforded the starting compound **6** (10 mg, 11% recovery) as a colorless, crystalline solid that was identical, in all respects, with an authentic sample.

Concentration of fraction B (R_f = 0.1 in ethyl acetate) afforded compound **8** (82 mg, 87% or 98% brsm) as a white, crystalline solid: mp = 169−171 °C; $[\alpha]_D$ = +71.4 (*c* 1.0, methanol); ^{1}H NMR (400 MHz, CD_3OD) δ 4.15 (d, J = 2.6 Hz, 1H), 3.74 (s, 1H), 2.81 (t, J = 5.0 Hz, 1H), 2.72 (m, 1H), 2.42 (m, 1H), 2.08 (m, 1H), 1.82 (d, J = 5.0 Hz, 1H), 1.37 (s, 3H) (signals due to O−H group protons not observed); ^{13}C NMR (100 MHz, CD_3OD) δ 217.3, 88.2, 86.3, 47.8, 47.0, 46.3(0), 46.2(8), 44.2, 21.5; IR ν_{max} 3356, 2962, 2904, 1706, 1693, 1290, 1040, 898 cm^{-1}; MS (ESI, + ve) m/z 191 [(M + Na)$^+$, 100]; HRMS m/z (M + Na)$^+$ calcd for $C_9H_{12}O_3Na$ 191.0684, found 191.0685.

*(2a′R,3S,4S,4aR)-4-((tert-Butyldimethylsilyl)oxy)-3-hydroxy-2b-methylhexahydrocyclopropa[cd]pentalen-2(1H)-one (**9**).* A deoxygenated solution of compound **7**[7] (158 mg, 0.56 mmol) and acetophenone (90 μL, 0.77 mmol) in acetone (100 mL) maintained under nitrogen was subjected to irradiation with a Hanovia 450 W medium-pressure mercury-vapor lamp for 2.5 h. The cooled reaction mixture was concentrated under reduced pressure to give a clear, yellow oil, and this was subjected to flash column chromatography (silica, 1:9 → 3:7 v/v ethyl acetate/40−60 petroleum ether gradient elution) to afford two fractions, A and B.

Concentration of fraction A (R_f = 0.4 in 3:7 v/v ethyl acetate/40−60 petroleum ether) afforded compound **7** (13 mg, 8% recovery) as a colorless crystalline solid that was identical, in all respects, with an authentic sample.

Concentration of fraction B (R_f = 0.2 in 3:7 v/v ethyl acetate/40−60 petroleum ether) afforded compound **9** (143 mg, 90% or 99% brsm) as a white, crystalline solid: mp = 99−100 °C; $[\alpha]_D$ = +41.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (800 MHz, $CDCl_3$) δ 4.20 (d, J = 2.5 Hz, 1H), 3.81 (s, 1H), 2.76 (t, J = 5.1 Hz, 1H), 2.66 (m, 1H), 2.38 (m, 1H), 2.13 (d, J = 17.9 Hz, 1H), 1.86 (d, J = 5.0 Hz, 1H), 1.79 (broad s, 1H), 1.35 (s, 3H), 0.90 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 213.3, 86.8, 85.8, 45.3, 45.0(4), 44.9(8), 44.4, 42.2, 24.9, 20.4, 17.2, − 5.6; IR ν_{max} 3351, 2957, 2929, 2886, 2857, 1719, 1254, 1092, 867, 836, 771 cm^{-1}; MS (ESI, + ve) m/z 305 [(M + Na)$^+$, 100], 283 [(M + H)$^+$, 30]; HRMS m/z (M + Na)$^+$ calcd for $C_{15}H_{26}O_3SiNa$ 305.1549, found 305.1548.

*(1R,2S,3S,6R)-2,3-Dihydroxy-4-methylbicyclo[4.2.0]oct-4-en-7-one (**10**).* A magnetically stirred and deoxygenated solution of compound **6** (100 mg, 0.59 mmol) in dichloromethane (100 mL) maintained under nitrogen was subjected to direct irradiation with a Hanovia 450 W medium-pressure mercury-vapor lamp for 0.83 h. The cooled reaction mixture was concentrated under reduced pressure to give a yellow solid that was subjected to flash column chromatography (silica, 2:3 → 1:0 v/v ethyl acetate/40−60 petroleum ether gradient elution) to afford two fractions, A and B.

Concentration of fraction A (R_f = 0.4 in ethyl acetate) afforded compound **10** (70 mg, 70% or 84% brsm) as a white, crystalline solid: mp = 83−85 °C; $[\alpha]_D$ = −234.4 (*c* 1.0, MeOH); ^{1}H NMR (400 MHz, CD_3OD) δ 5.40 (m, 1H), 3.96 (d, J = 6.9 Hz, 1H), 3.88 (m, 1H), 3.47 (t, J = 7.5 Hz, 1H), 3.24 (m, 1H), 2.98 (m, 1H), 2.57 (m, 1H), 1.81 (s, 3H) (signals due to O−H group protons not observed); ^{13}C NMR (100 MHz, CD_3OD) δ 209.0, 140.2, 116.7, 76.2, 73.6, 61.0, 50.1, 30.2, 20.0; IR ν_{max} 3391, 2882, 1769, 1066, 1047, 1014, 884 cm^{-1}; MS (ESI, + ve) m/z 223 [(M + MeOH + Na)$^+$, 40], 191 [(M + Na)$^+$, 100]; HRMS m/z (M + Na)$^+$ calcd for $C_9H_{12}O_3Na$ 191.0684, found 191.0684.

Concentration of fraction B (R_f = 0.3 in ethyl acetate) afforded compound **6** (14 mg, 14% recovery) as a colorless, crystalline solid that was identical, in all respects, with an authentic sample.

*(1R,2S,3S,6R)-2-((tert-Butyldimethylsilyl)oxy)-3-hydroxy-4-methylbicyclo[4.2.0]oct-4-en-7-one (**11**).* A magnetically stirred and deoxygenated solution of compound **7** (100 mg, 0.35 mmol) in dichloromethane (100 mL) maintained under nitrogen was subjected to direct irradiation with a Hanovia 450 W medium-pressure mercury-vapor lamp for 0.67 h. The cooled reaction mixture was concentrated under reduced pressure to give a pale-yellow oil. This was subjected to

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flash column chromatography (silica, 1:9 v/v ethyl acetate/40−60 petroleum ether elution) to give, after concentration of the appropriate fractions (R_f = 0.6 in 3:7 v/v ethyl acetate/40−60 petroleum ether), compound **11** (67 mg, 67%) as a white, crystalline solid: mp = 67−69 °C; $[\alpha]_D$ = −139.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.38 (m, 1H), 4.04 (d, *J* = 7.0 Hz, 1H), 3.86 (m, 1H), 3.57 (t, *J* = 7.7 Hz, 1H), 3.24 (m, 1H), 2.94 (m, 1H), 2.57 (m, 1H), 2.18 (broad s, 1H), 1.82 (s, 3H), 0.90 (s, 9H), 0.13 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.0, 138.4, 115.1, 77.9, 73.4, 60.6, 50.2, 29.9, 25.9, 19.1, 18.3, − 3.8, − 4.2; IR ν_{max} 3499, 2954, 2930, 2857, 1779, 1126, 1087, 836 cm^{-1}; MS (ESI, + ve) *m*/*z* 337 [(M + MeOH + Na)$^+$, 30], 305 [(M + Na)$^+$, 100]; HRMS *m*/*z* (M + Na)$^+$ calcd for $C_{15}H_{26}O_3SiNa$ 305.1549, found 305.1554.

*(1R,2S,3S,6R)-4-Methylbicyclo[4.1.0]hept-4-ene-2,3-diol (**12**).* A magnetically stirred and deoxygenated solution of compound **6** (100 mg, 0.59 mmol) in dichloromethane (100 mL) maintained under a nitrogen atmosphere was subjected to direct irradiation with a Hanovia 450 W medium-pressure mercury-vapor lamp for 5 h. The cooled reaction mixture was concentrated under reduced pressure to give a brown oil that was subjected to flash column chromatography (silica, 1:4 → 1:1 v/v ethyl acetate/40−60 petroleum ether gradient elution) to afford two fractions, A and B.

Concentration of fraction A (R_f = 0.6 in ethyl acetate) afforded compound **12** (27 mg, 32%) as a pale-yellow oil: $[\alpha]_D$ = +93.2 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 (m, 1H), 4.04−3.99 (complex m, 2H), 1.92 (broad s, 2H), 1.76 (s, 3H), 1.48−1.35 (complex m, 2H), 1.03 (m, 1H), 0.64 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 130.3, 127.8, 73.3, 70.1, 21.4, 19.6, 18.7, 11.0; IR ν_{max} 3367, 2920, 1445, 1260, 1048, 1001, 724 cm^{-1}; MS (EI, 70 eV) *m*/*z* 140 ($M^{\bullet+}$, 30), 122 [$(M - H_2O)^{\bullet+}$, 60], 93 (100), 79 (90), 77 (70), 70 (60), 55 (60); HRMS *m*/*z* $M^{\bullet+}$ calcd for $C_8H_{12}O_2$ 140.0837, found 140.0842.

Concentration of fraction B (R_f = 0.4 in ethyl acetate) afforded compound **10** (48 mg, 48%) as a white, crystalline solid that was identical, in all respects, with an authentic sample.

*(1R,2S,3S,6R)-2-((tert-Butyldimethylsilyl)oxy)-4-methylbicyclo-[4.1.0]hept-4-en-3-ol (**13**).* A magnetically stirred and deoxygenated solution of compound **7** (100 mg, 0.35 mmol) in dichloromethane (100 mL) maintained under a nitrogen atmosphere was subjected to irradiation with a Hanovia 450 W medium-pressure mercury-vapor lamp for 5 h. The cooled reaction mixture was concentrated under reduced pressure to give a brown oil that was subjected to flash column chromatography (silica, 1:9 → 1:4 v/v ethyl acetate/40−60 petroleum ether gradient elution) to afford two fractions, A and B.

Concentration of fraction A (R_f = 0.7 in 3:7 v/v ethyl acetate/40−60 petroleum ether) afforded compound **13** (30 mg, 33%) as a colorless, crystalline solid: mp = 32−33 °C; $[\alpha]_D$ = +35.3 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71 (m, 1H), 4.08 (d, *J* = 5.9 Hz, 1H), 3.59 (m, 1H), 1.97 (broad s, 1H), 1.74 (s, 3H), 1.33−1.17 (complex m, 2H), 0.99−0.94 (complex m, 1H), 0.92 (s, 9H), 0.32 (m, 1H), 0.14 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.4, 124.7, 75.1, 74.0, 26.0, 19.6, 19.3, 18.7, 18.3, 12.0, − 4.1, − 4.6; IR ν_{max} 3458, 2929, 2857, 1254, 1075, 1003, 835, 775 cm^{-1}; MS (EI, 70 eV) *m*/*z* 239 [$(M - CH_3^{\bullet})^+$, 30], 211 (35), 197 [$(M - C_4H_9^{\bullet})^+$, 35], 105 (60), 75 (100), 73 (95); HRMS *m*/*z* $(M - CH_3^{\bullet})^+$ calcd for $C_{13}H_{23}O_2Si$ 239.1467, found 239.1468.

Concentration of fraction B (R_f = 0.6 in 3:7 v/v ethyl acetate/40−60 petroleum ether) afforded compound **11** (33 mg, 33%) as a colorless, crystalline solid that was identical, in all respects, with an authentic sample.

*(1S,2R)-3-Methylcyclohexa-3,5-diene-1,2-diyl (2E,2′E)-Bis(but-2-enoate) (**14**).* A magnetically stirred solution of (1*S*,2*R*)-3-methylcyclohexa-3,5-diene-1,2-diol (**5**) (2.40 g, 19.0 mmol) in dry THF (284 mL) was cooled to −78 °C and then treated, dropwise over 0.5 h, with *n*-BuLi (12.5 mL of a 1.6 M solution in hexane, 20.0 mmol). The resulting solution was stirred at −78 °C for 0.17 h and then treated with crotonoyl chloride (1.80 mL, 19.02 mmol) over 0.33 h. The resulting solution was stirred for 2 h at −78 °C and then treated, dropwise over 0.5 h, with *n*-BuLi (12.5 mL of a 1.6 M solution in hexane, 20.0 mmol). After 0.17 h, another portion of crotonoyl chloride (1.80 mL, 19.02 mmol) was added over 0.33 h, and then stirring of the recation mixture was continued at −78 °C for 1 h. The ensuing mixture was warmed to 22 °C and then quenched with $NaHCO_3$ (96 mL of a saturated aqueous solution) before being diluted with diethyl ether (390 mL). The separated organic phase was washed with NH_4Cl (1 × 96 mL of a saturated aqueous solution) and then dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue thus obtained was subjected to flash column chromatography to give, after concentration of the appropriate fractions (R_f = 0.5 in 1:4 v/v ethyl acetate/40−60 petroleum ether), compound **14** (4.04 g, 81%) as a pale-yellow oil. The spectral data recorded on this material matched those reported previously.[8]

*(1S,2R)-3-Methylcyclohexa-3,5-diene-1,2-diyl (2E,2′E)-Bis(4-methylpent-2-enoate) (**15**).* A magnetically stirred solution of (1*S*,2*R*)-3-methylcyclohexa-3,5-diene-1,2-diol (**5**) (2.40 g, 19.02 mmol) in dry THF (284 mL) was cooled to −78 °C and then treated, dropwise over 0.5 h, with *n*-BuLi (12.5 mL of a 1.6 M solution in hexane, 20.0 mmol). The resulting solution was stirred at −78 °C for 0.17 h and then treated, dropwise over 0.33 h, with (*E*)-4-methylpent-2-enoyl chloride[14] (2.50 mL, 19.02 mmol). The ensuing mixture was stirred at −78 °C for 2 h and again treated, dropwise over 0.5 h, with *n*-BuLi (12.5 mL of a 1.6 M solution in hexane, 20.0 mmol). After 0.17 h, further (*E*)-4-methylpent-2-enoyl chloride (1.80 mL, 19.02 mmol) was added, again dropwise over 0.33 h, and stirring was continued at −78 °C for 1 h. The reaction mixture was then allowed to warm to 22 °C before being quenched with $NaHCO_3$ (96 mL of a saturated aqueous solution) and diluted with diethyl ether (390 mL). The separated organic phase was washed with NH_4Cl (1 × 96 mL of a saturated aqueous solution), dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue thus obtained was subjected to flash column chromatography to give, after concentration of the appropriate fractions (R_f = 0.6 in 1:4 v/v ethyl acetate/40−60 petroleum ether), compound **15** (4.47 g, 74%) as a pale-yellow oil: $[\alpha]_D$ = +71.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98−6.88 (complex m, 2H), 6.06 (m, 1H), 5.88 (broadened d, *J* = 5.2 Hz, 1H), 5.81−5.72 (complex m, 3H), 5.62 (s, 2H), 2.43 (m, 2H), 1.84 (s, 3H), 1.05−1.02 (complex m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 166.3, 156.5, 156.2, 134.7, 126.6, 123.0, 121.9, 118.3, 118.1, 69.5, 68.0, 31.1, 31.0, 21.3, 21.2, 19.8 (two signals obscured or overlapping); IR ν_{max} 2963, 1717, 1651, 1297, 1260, 1157, 982, 859 cm^{-1}; MS (ESI, + ve) *m*/*z* 341 [(M + Na)$^+$, 100]; HRMS *m*/z: (M + Na)$^+$ calcd for $C_{19}H_{26}O_4Na$ 341.1729, found 341.1728.

*3a,8-Dimethyl-2-oxo-2,3,3a,6,7,7a-hexahydro-3,6-methanobenzofuran-7-yl (E)-But-2-enoate (**16**) and 6,8-Dimethyl-2-oxo-2,3,3a,6,7,7a-hexahydro-3,6-methanobenzofuran-7-yl (E)-But-2-enoate (**18**).* A magnetically stirred solution of compound **14** (4.04 g, 15.40 mmol) in toluene (97 mL) maintained under a nitrogen atmosphere was heated at reflux for 24 h then cooled to 22 °C and concentrated under reduced pressure. The resulting yellow oil was subjected to flash chromatography (silica, 1:19 v/v ethyl acetate/40−60 petroleum ether elution) to give two fractions, A and B.

Concentration of fraction A [R_f = 0.2(5) in 1:4 v/v ethyl acetate/40−60 petroleum ether] afforded compound **16** (1.62 g, 40%) as a white, crystalline solid, mp = 45−47 °C. The spectral data recorded on this material matched those reported previously.[8]

Concentration of fraction B (R_f = 0.2 in 1:4 v/v ethyl acetate/40−60 petroleum ether) afforded compound **18** (1.06 g, 26%) as a clear, colorless oil. The spectral data recorded on this material matched those reported previously.[8]

*8-Isopropyl-3a-methyl-2-oxo-2,3,3a,6,7,7a-hexahydro-3,6-methanobenzofuran-7-yl (E)-4-Methylpent-2-enoate (**17**) and 8-Isopropyl-6-methyl-2-oxo-2,3,3a,6,7,7a-hexahydro-3,6-methanobenzofuran-7-yl (E)-4-Methylpent-2-enoate (**19**).* A magnetically stirred solution of compound **15** (4.47 g, 14.04 mmol) in toluene (88 mL) maintained under a nitrogen atmosphere was heated at reflux for 72 h then cooled to 22 °C, and concentrated under reduced pressure. The resulting yellow oil was subjected to flash chromatography (silica, 1:19 v/v ethyl acetate/40−60 petroleum ether elution) to afford two fractions, A and B.

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Concentration of fraction A (R_f = 0.4 in 1:4 v/v ethyl acetate/40−60 petroleum ether) afforded compound **17** (1.83 g, 41%) as a white, crystalline solid: mp = 69−71 °C; $[\alpha]_D$ = −115.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (dd, *J* = 15.7 and 6.5 Hz, 1H), 6.38 (t, *J* = 7.6 Hz, 1H), 5.84 (m, 2H), 4.37 (dd, *J* = 6.7 and 2.2 Hz, 1H), 4.24 (d, *J* = 6.7 Hz, 1H), 2.98 (m, 1H), 2.47 (m, 1H), 1.93−1.88 (complex m, 2H), 1.40 (s, 3H), 1.27 (m, 1H), 1.08 (s, 3H), 1.06 (s, 3H), 0.97 (d, *J* = 6.5 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.3, 166.5, 156.8, 133.1, 132.2, 117.9, 77.3, 70.6, 49.7, 46.9, 45.1, 38.8, 31.1, 30.5, 21.3, 21.2, 20.9, 20.8, 20.7; IR ν_{max} 2962, 1783, 1717, 1264, 1160, 1038, 1009, 902 cm^{-1}; MS (EI, 70 eV) *m*/*z* 318 ($M^{\bullet+}$, 5), 156 (15), 133 (10), 97 (100), 69 (10), 41 (20); HRMS *m*/*z* $M^{\bullet+}$ calcd for $C_{19}H_{26}O_4$ 318.1831, found 318.1834.

Concentration of fraction B [R_f = 0.3(5) in 1:4 v/v ethyl acetate/40−60 petroleum ether] afforded compound **19** (537 mg, 12%) as a clear, colorless oil: $[\alpha]_D$ = +176.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (dd, *J* = 15.7 and 6.5 Hz, 1H), 6.09 (d, *J* = 8.2 Hz, 1H), 6.00 (dd, *J* = 8.2 and 6.6 Hz, 1H), 5.83 (dd, *J* = 15.7 and 1.5 Hz, 1H), 4.57 (m, 1H), 4.05 (d, *J* = 6.7 Hz, 1H), 3.45 (m, 1H), 2.47 (m, 1H), 2.30 (m, 1H), 2.16 (m, 1H), 2.01 (m, 1H), 1.24 (s, 3H), 1.08 (s, 3H), 1.06 (s, 3H), 0.99 (d, *J* = 6.9 Hz, 3H), 0.61 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.7, 166.7, 156.8, 140.3, 124.6, 117.8, 74.4, 72.9, 48.0, 42.2, 40.6, 40.2, 31.1, 27.4, 22.8, 21.3, 21.2, 19.9, 19.1; IR ν_{max} 2961, 1786, 1718, 1264, 1158, 1027, 982, 907 cm^{-1}; MS (EI, 70 eV) *m*/*z* 318 ($M^{\bullet+}$, 5), 205 (5), 97 (100), 69 (15), 41 (25); HRMS *m*/*z* $M^{\bullet+}$ calcd for $C_{19}H_{26}O_4$ 318.1831, found 318.1832.

*7-Hydroxy-6,8-dimethyl-3a,6,7,7a-tetrahydro-3,6-methanobenzofuran-2(3H)-one (**20**).* A magnetically stirred solution of compound **18** (918 mg, 3.50 mmol) in methanol (55 mL) maintained at 0 °C was treated, in one portion, with potassium carbonate (242 mg, 1.75 mmol). The ensuing mixture was stirred at 0 °C for a further 0.5 h and then warmed to 22 °C, stirred at this temperature for 1 h, and then recooled to 0 °C and treated with water (30 mL) before being concentrated under reduced pressure. The residue thus obtained was extracted with ethyl acetate (3 × 100 mL), and the combined organic phases were then dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The resulting light-yellow oil was subjected to flash column chromatography (silica, 3:7 → 1:1 v/v ethyl acetate/40−60 petroleum ether gradient elution) to give, after concentration of the appropriate fractions (R_f = 0.1 in 3:7 v/v ethyl acetate/40−60 petroleum ether), compound **20** (503 mg, 74%) as a white, crystalline solid: mp = 114−116 °C; $[\alpha]_D$ = +67.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.06−6.00 (complex m, 2H), 4.39 (t, *J* = 6.0 Hz, 1H), 3.43 (m, 1H), 3.26 (t, *J* = 6.7 Hz, 1H), 2.23 (d, *J* = 6.8 Hz, 1H), 2.11 (m, 1H), 2.01 (d, *J* = 4.5 Hz, 1H), 1.25 (s, 3H), 0.89 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.9, 141.2, 124.2, 74.9, 71.9, 46.9, 44.1, 40.4, 36.5, 18.8, 17.3; IR ν_{max} 3417, 2968, 1760, 1750, 1184, 1102, 1015, 713 cm^{-1}; MS (ESI, + ve) *m*/*z* 217 [$(M + Na)^+$, 100]; HRMS *m*/*z* $(M + Na)^+$ calcd for $C_{11}H_{14}O_3Na$ 217.0841, found 217.0844.

*7-Hydroxy-8-isopropyl-6-methyl-3a,6,7,7a-tetrahydro-3,6-methanobenzofuran-2(3H)-one (**21**).* A magnetically stirred solution of compound **19** (1.11 g, 3.50 mmol) in methanol (55 mL) maintained at 0 °C was treated, in one portion, with potassium carbonate (242 mg, 1.75 mmol). After being kept for 0.5 h at 0 °C, the reaction mixture was warmed to 22 °C, maintained at this temperature for 1 h, and then recooled to 0 °C and treated with water (30 mL) before being concentrated under reduced pressure. The residue thus obtained was extracted with ethyl acetate (3 × 100 mL), and the combined organic phases were then dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give a light-yellow oil. This material was subjected to flash column chromatography (silica, 3:17 → 3:7 v/v ethyl acetate/40−60 petroleum ether gradient elution) and gave, after concentration of the appropriate fractions (R_f = 0.3 in 3:7 v/v ethyl acetate/40−60 petroleum ether), compound **21** (590 mg, 76%) as a white solid: mp = 120−122 °C; $[\alpha]_D$ = +100.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.09 (d, *J* = 8.1 Hz, 1H), 5.93 (m, 1H), 4.35 (m, 1H), 3.43 (m, 1H), 3.12 (d, *J* = 6.9 Hz, 1H), 2.28 (m, 1H), 2.03−1.95 (complex m, 2H), 1.26 (s, 3H), 0.97 (d, *J* = 6.7 Hz, 3H), 0.60 (d, *J* = 6.7 Hz, 3H) (signal due to O−H group proton not observed); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.3, 141.8, 123.3, 74.8, 72.9, 47.6, 44.0, 40.2 (3), 40.1 (7), 27.3, 22.7, 19.8, 18.8; IR ν_{max} 3425, 2958, 1765, 1170, 1100, 978, 723 cm^{-1}; MS (ESI, + ve) *m*/*z* 467 [$(2M + Na)^+$, 30], 245 [$(M + Na)^+$, 100], 223 [$(M + H)^+$, 70]; HRMS *m*/*z* $(M + Na)^+$ calcd for $C_{13}H_{18}O_3Na$ 245.1154, found 245.1156.

*6,8-Dimethyl-3a,7a-dihydro-3,6-methanobenzofuran-2,7-(3H,6H)-dione (**22**).* A magnetically stirred solution of compound **20** (466 mg, 2.40 mmol) in dry dichloromethane (78 mL) maintained at 0 °C under an atmosphere of nitrogen was treated with pyridine (1.2 mL, 15.05 mmol) and then Dess−Martin periodinane (1.83 g, 4.32 mmol). After a further 0.5 h, the reaction mixture was warmed to 22 °C, maintained at this temperature for 3 h, and then poured into water (100 mL) and extracted with dichloromethane (3 × 100 mL). The combined organic phases were washed with NaOH (1 × 100 mL of a 1 M aqueous solution) and then HCl (1 × 100 mL of a 1 M aqueous solution) before being dried ($MgSO_4$), filtered, and then concentrated under reduced pressure. The residue thus obtained was subjected to flash column chromatography (silica, 1:9 → 3:17 v/v ethyl acetate/40−60 petroleum ether gradient elution) to give, after concentration of the appropriate fractions (R_f = 0.3 in 3:7 v/v ethyl acetate/40−60 petroleum ether), compound **22** (397 mg, 86%) as a white, crystalline solid: mp = 121−124 °C; $[\alpha]_D$ = +518.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.32 (dd, *J* = 8.1 and 6.5 Hz, 1H), 6.02 (d, *J* = 8.1 Hz, 1H), 4.15 (dd, *J* = 5.0 and 1.0 Hz, 1H), 3.66 (m, 1H), 2.37 (d, *J* = 5.0 Hz, 1H), 2.21 (m, 1H), 1.32 (s, 3H), 1.02 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.5, 177.8, 136.7, 128.3, 73.9, 53.8, 47.1, 41.3, 40.9, 16.1, 15.2; IR ν_{max} 2976, 2937, 1785, 1736, 1159, 989, 837, 713 cm^{-1}; MS (ESI, + ve) *m*/*z* 247 [$(M + MeOH + Na)^+$, 100], 215 [$(M + Na)^+$, 20]; HRMS *m*/*z* $(M + MeOH + Na)^+$ calcd for $C_{12}H_{16}O_4Na$ 247.0946, found 247.0946.

*8-Isopropyl-6-methyl-3a,7a-dihydro-3,6-methanobenzofuran-2,7(3H,6H)-dione (**23**).* A magnetically stirred solution of compound **21** (533 mg, 2.40 mmol) in dry dichloromethane (78 mL) maintained at 0 °C under an atmosphere of nitrogen was treated with pyridine (1.2 mL, 15.05 mmol) and then the Dess−Martin periodinane (1.83 g, 4.32 mmol). After a further 0.5 h the reaction mixture was warmed to 22 °C, stirred at this temperature for 3 h, and then poured into water (100 mL) and extracted with dichloromethane (3 × 100 mL). The combined organic phases were washed with NaOH (1 × 100 mL of a 1 M aqueous solution) then HCl (1 × 100 mL of a 1 M aqueous solution) before being dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue thus obtained was subjected to flash column chromatography (silica, 3:17 → 3:7 v/v ethyl acetate/40−60 petroleum ether gradient elution) and gave, after concentration of the appropriate fractions (R_f = 0.3 in 3:7 v/v ethyl acetate/40−60 petroleum ether), compound **23** (433 mg, 82%) as a white, crystalline solid: mp = 114−116 °C; $[\alpha]_D$ = +396.1 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.19 (dd, *J* = 8.1 and 6.6 Hz, 1H), 6.04 (m, 1H), 4.12 (dd, *J* = 5.0 and 1.1 Hz, 1H), 3.67 (m, 1H), 2.64 (m, 1H), 2.11 (m, 1H), 1.99 (m, 1H), 1.36 (s, 3H), 1.01 (d, *J* = 6.9 Hz, 3H), 0.72 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.7, 178.5, 136.8, 127.3, 73.9, 53.6, 51.7, 40.9, 40.4, 28.2, 22.8, 20.0, 15.3; IR ν_{max} 2961, 1802, 1786, 1734, 1151, 1002, 981, 899 cm^{-1}; MS (ESI, + ve) *m*/*z* 275 [$(M + MeOH + Na)^+$, 100], 243 [$(M + Na)^+$, 40]; HRMS *m*/*z* $(M + MeOH + Na)^+$ calcd for $C_{14}H_{20}O_3Na$ 275.1259, found 275.1251.

*7-Hydroxy-3a,8-dimethyl-3a,6,7,7a-tetrahydro-3,6-methanobenzofuran-2(3H)-one (**24**).* A magnetically stirred solution of compound **16** (918 mg, 3.50 mmol) in methanol (55 mL) maintained at 0 °C under an atmosphere of nitrogen was treated, in one portion, with potassium carbonate (242 mg, 1.75 mmol). After a further 0.5 h, the reaction mixture was warmed to 22 °C, stirred at this temperature for 1 h, and then recooled to 0 °C and treated with water (30 mL) before being concentrated under reduced pressure. The residue thus obtained was extracted with ethyl acetate (3 × 100 mL), and the combined organic phases were then dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give a light-yellow oil. This material was subjected to flash column chromatography (silica, 1:4 → 3:7 v/v ethyl acetate/40−60 petroleum ether gradient elution) and gave, after concentration of the appropriate fractions (R_f = 0.2 in 3:7 v/v ethyl

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acetate/40−60 petroleum ether), compound **24** (538 mg, 79%) as a white, crystalline solid: mp = 146−148 °C; $[\alpha]_D$ = +15.8 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.36 (t, *J* = 7.6 Hz, 1H), 5.81 (dd, *J* = 7.6 and 1.0 Hz, 1H), 3.98 (d, *J* = 6.9 Hz, 1H), 3.57 (dd, *J* = 6.9 and 2.2 Hz, 1H), 2.68 (m, 1H), 2.47 (m, 2H), 1.68 (s, 1H), 1.39 (s, 3H), 0.93 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.0, 135.4, 130.8, 79.0, 69.0, 52.2, 45.2, 45.0, 33.1, 21.1, 20.1; IR ν_{max} 3402, 2964, 1740, 1347, 1182, 1085, 992, 948, 713, 703 cm^{-1}; MS (ESI, + ve) *m*/*z* 217 [$(M + Na)^+$, 100%]; HRMS *m*/*z* $(M + Na)^+$ calcd for $C_{11}H_{14}O_3Na$ 217.0841, found 217.0842.

*7-Hydroxy-8-isopropyl-3a-methyl-3a,6,7,7a-tetrahydro-3,6-methanobenzofuran-2(3H)-one (**25**).* A magnetically stirred solution of compound **17** (1.11 g, 3.50 mmol) in methanol (55 mL) maintained at 0 °C under an atmosphere of nitrogen was treated, in one portion, with potassium carbonate (242 mg, 1.75 mmol). After a further 0.5 h at 0 °C, the reaction mixture was warmed to 22 °C, stirred at this temperature for 1 h, and then recooled to 0 °C and treated with water (30 mL) before being concentrated under reduced pressure. The ensuing mixture was extracted with ethyl acetate (3 × 100 mL), and the combined organic phases were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue thus obtained was subjected to flash column chromatography (silica, 3:7 → 1:1 v/v ethyl acetate/40−60 petroleum ether gradient elution) and gave, after concentration of the appropriate fractions (R_f = 0.2 in 3:7 v/v ethyl acetate/40−60 petroleum ether), compound **25** (732 mg, 94%) as a white, crystalline solid: mp = 60−61 °C; $[\alpha]_D$ = +2.8 (*c* 0.9, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.35 (t, *J* = 8.3 Hz, 1H), 5.78 (dd, *J* = 8.3 and 1.2 Hz, 1H), 3.99 (d, *J* = 6.9 Hz, 1H), 3.54 (dd, *J* = 6.9 and 2.3 Hz, 1H), 2.89 (m, 1H), 2.48 (broad s, 1H), 1.85 (m, 2H), 1.38 (s, 3H), 1.25 (m, 1H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.1, 134.6, 131.1, 79.3, 68.9, 49.7, 46.4, 44.9, 41.7, 30.7, 21.1, 20.8(0), 20.7(6); IR ν_{max} 3452, 2962, 1778, 1166, 1117, 993, 706 cm^{-1}; MS (ESI, + ve) *m*/*z* 245 [$(M + Na)^+$, 40], 223 [$(M + H)^+$, 100], 205 (50), 159 (100), 109 (90), 90 (70); HRMS *m*/*z* $(M + H)^+$ calcd for $C_{13}H_{19}O_3$ 223.1334, found 223.1331.

*3a,8-Dimethyl-3a,7a-dihydro-3,6-methanobenzofuran-2,7-(3H,6H)-dione (**26**).* A magnetically stirred solution of compound **24** (466 mg, 2.40 mmol) in dry dichloromethane (78 mL) maintained at 0 °C under an atmosphere of nitrogen was treated with pyridine (1.2 mL, 15.05 mmol) and then the Dess−Martin periodinane (1.83 g, 4.32 mmol). After being kept at 0 °C for a further 0.5 h, the reaction mixture was warmed to 22 °C and maintained at this temperature for 3 h before being poured into water (100 mL) and extracted with dichloromethane (3 × 100 mL). The combined organic phases were washed with NaOH (1 × 100 mL of a 1 M aqueous solution) and HCl (1 × 100 mL of a 1 M aqueous solution) and then dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue thus obtained was subjected to flash column chromatography (silica, 1:9 → 3:17 v/v ethyl acetate/40−60 petroleum ether gradient elution) and gave, after concentration of the appropriate fractions (R_f = 0.3 in 3:7 v/v ethyl acetate/40−60 petroleum ether), compound **26** (434 mg, 94%) as a white, crystalline solid: mp = 135−136 °C; $[\alpha]_D$ = −445.7 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.37 (t, *J* = 7.5 Hz, 1H), 6.13 (dd, *J* = 7.5 and 1.0 Hz, 1H), 3.75 (s, 1H), 3.27 (dd, *J* = 6.7 and 3.1 Hz, 1H), 2.59 (m, 1H), 1.98 (s, 1H), 1.47 (s, 3H), 1.02 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 177.7, 134.5, 130.4, 78.5, 54.0, 51.9, 46.5, 37.2, 19.9, 18.4; IR ν_{max} 2964, 1788, 1742, 1312, 1161, 995, 875, 723 cm^{-1}; MS (ESI, + ve) *m*/*z* 247 [$(M + MeOH + Na)^+$, 100]; HRMS *m*/*z* $(M + MeOH + Na)^+$ Calcd for $C_{12}H_{16}O_3Na$ 247.0946, found 247.0943.

*8-Isopropyl-3a-methyl-3a,7a-dihydro-3,6-methanobenzofuran-2,7(3H,6H)-dione (**27**).* A magnetically stirred solution of compound **25** (533 mg, 2.40 mmol) in dry dichloromethane (78 mL) maintained at 0 °C under an atmosphere of nitrogen was treated with pyridine (1.2 mL, 15.05 mmol) and then the Dess−Martin periodinane (1.83 g, 4.32 mmol). After a further 0.5 h at 0 °C, the reaction mixture was warmed to 22 °C and then stirred at this temperature for 3 h before being poured into water (100 mL) and extracted with dichloromethane (3 × 100 mL). The combined organic phases were washed with NaOH (1 × 100 mL of a 1 M aqueous solution) and HCl (1 × 100 mL of a 1 M aqueous solution) then dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue thus obtained was subjected to flash column chromatography (silica, 1:9 → 3:17 v/v ethyl acetate/40−60 petroleum ether gradient elution) and gave, after concentration of the appropriate fractions (R_f = 0.5 in 3:7 v/v ethyl acetate/40−60 petroleum ether), compound **27** (413 mg, 78%) as a white, crystalline solid: mp = 121−123 °C; $[\alpha]_D$ = −332.5 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.37 (t, *J* = 8.2 Hz, 1H), 6.09 (dd, *J* = 8.2 and 1.1 Hz, 1H), 3.77 (s, 1H), 3.49 (dd, *J* = 6.7 and 3.1 Hz, 1H), 2.19 (s, 1H), 1.93 (dd, *J* = 10.2 and 2.5 Hz, 1H), 1.47 (s, 3H), 1.42 (m, 1H), 1.00 (d, *J* = 6.5 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.4, 177.7, 134.8, 129.8, 78.8, 51.1, 50.2, 49.4, 46.2, 29.2, 20.6, 20.4, 19.9; IR ν_{max} 2968, 17909, 1775, 1741, 1160, 985, 713 cm^{-1}; MS (ESI, + ve) *m*/*z* 275 [$(M + MeOH + Na)^+$, 100], 221 [$(M + H)^+$, 10]; HRMS *m*/*z* $(M + MeOH + Na)^+$ calcd for $C_{14}H_{20}O_3Na$ 275.1259, found 275.1260.

*(1a*S*,1a′*R*,3a*S*,4*S*,4a*R*,4a′*R*)-4,4a-Dimethylhexahydro-1H-cyclopropa[3,4]pentaleno[1,6-bc]furan-1,3(1aH)-dione (**28**).* A deoxygenated and magnetically stirred solution of compound **22** (108 mg, 0.56 mmol) and acetophenone (90 μL, 0.77 mmol) in acetone (100 mL) maintained under a nitrogen atmosphere was subjected to irradiation with a Hanovia 450 W medium-pressure mercury-vapor lamp for 0.83 h. The reaction mixture was then cooled and concentrated under reduced pressure to give a brown oil that was subjected to flash column chromatography (silica, 3:17 → 3:7 v/v ethyl acetate/40−60 petroleum ether gradient elution). Concentration of the appropriate fractions (R_f = 0.3 in 1:1 v/v ethyl acetate/40−60 petroleum ether) then gave compound **28** (44 mg, 40%) as a pale-yellow oil: $[\alpha]_D$ = +5.1 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 4.57 (dd, *J* = 9.0 and 2.2 Hz, 1H), 3.59 (m, 1H), 2.80 (t, *J* = 8.0 Hz, 1H), 2.60 (m, 1H), 2.45 (m, 1H), 1.98 (m, 1H), 1.30 (d, *J* = 7.2 Hz, 3H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9, 176.8, 82.4, 57.2, 46.1, 45.1, 45.0, 44.7, 38.1, 19.5, 18.4; IR ν_{max} 2969, 2928, 1779, 1726, 1192, 1152, 1054, 1031, 983 cm^{-1}; MS (ESI, + ve) *m*/*z* 215 [$(M + Na)^+$, 100]; HRMS *m*/*z* $(M + Na)^+$ calcd for $C_{11}H_{12}O_3Na$ 215.0684, found 215.0687.

*(1a*S*,1a′*R*,3a*S*,4*S*,4a*S*,4a′*R*)-4-Isopropyl-4a-methylhexahydro-1H-cyclopropa[3,4]pentaleno[1,6-bc]furan-1,3(1aH)-dione (**29**).* A deoxygenated and magnetically stirred solution of compound **23** (123 mg, 0.56 mmol) and acetophenone (90 μL, 0.77 mmol) in acetone (100 mL) maintained under a nitrogen atmosphere was subjected to irradiation with a Hanovia 450 W medium-pressure mercury-vapor lamp for 0.67 h. The reaction mixture thus formed was cooled and concentrated under reduced pressure to give a yellow oil that was subjected to flash column chromatography (silica, 3:17 → 1:3 v/v ethyl acetate/40−60 petroleum ether gradient elution). Concentration of the appropriate fractions (R_f = 0.4 in 1:1 v/v ethyl acetate/40−60 petroleum ether) then gave compound **29** (53 mg, 43%) as a white, crystalline solid: mp = 107−109 °C; $[\alpha]_D$ = −7.6 (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 4.60 (dd, *J* = 8.9 and 2.0 Hz, 1H), 3.61 (m, 1H), 3.10 (dd, *J* = 8.5 and 6.5 Hz, 1H), 2.62 (m, 1H), 2.38 (m, 1H), 2.15 (m, 1H), 1.88 (m, 1H), 1.27 (s, 3H), 1.05 (d, *J* = 6.9 Hz, 3H), 0.97 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9, 177.4, 82.5, 55.0, 47.8, 46.6, 45.6, 44.0, 38.3, 29.2, 22.1, 19.5, 17.0; IR ν_{max} 2963, 1780, 1728, 1196, 1150, 1049, 983 cm^{-1}; MS (EI, 70 eV) *m*/*z* 220 ($M^{\bullet+}$, 25), 153 (40), 149 (90), 133 (40), 105 (60), 93 (100), 91 (70), 84 (60), 77 (50), 59 (70); HRMS *m*/*z* $M^{\bullet+}$ calcd for $C_{13}H_{16}O_3$ 220.1099, found 220.1092.

*(2a*S*,2a′*R*,3a*R*,6*S*,6a*S*)-5,6-Dimethyl-2a*^{1}*,3a,6,6a-tetrahydro-1H-cyclobuta[cd]isobenzofuran-1,3(2aH)-dione (**30**).* A deoxygenated and magnetically stirred solution of compound **22** (100 mg, 0.52 mmol) in dichloromethane (100 mL) maintained under a nitrogen atmosphere was subjected to irradiation with a Hanovia 450 W medium-pressure mercury-vapor lamp for 0.5 h. The reaction thus obtained was then cooled and concentrated under reduced pressure to give a yellow solid. Subjection of this material to flash column chromatography (silica, 1:4 → 3:7 v/v ethyl acetate/40−60 petroleum ether gradient elution) gave, after concentration of the appropriate fractions (R_f = 0.2 in 3:7 v/v ethyl acetate/40−60 petroleum ether),

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compound **30** (75 mg, 75%) as a white, crystalline solid: mp = 161−163 °C; $[\alpha]_D$ = −344.2 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 5.37 (m, 1H), 5.33 (m, 1H), 3.93 (m, 1H), 3.48 (m, 1H), 2.97 (dd, *J* = 10.0 and 2.1 Hz, 1H), 2.67 (m, 1H), 1.78 (s, 3H), 1.19 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.3, 177.5, 140.6, 112.9, 89.8, 58.8, 43.3, 33.9, 26.8, 23.0, 19.8; IR ν_{max} 2968, 1782, 1256, 1148, 1141, 1130, 1004 cm^{-1}; MS (ESI, + ve) *m*/*z* 247 [(M + MeOH + Na)$^+$, 100]; HRMS *m*/*z* (M + MeOH + Na)$^+$ calcd for $C_{12}H_{16}O_3Na$ 247.0946, found 247.0945.

(2aS,2a′R,3aR,6S,6aS)-6-Isopropyl-5-methyl-2a′,3a,6,6a-tetrahydro-1H-cyclobuta[cd]isobenzofuran-1,3(2aH)-dione (**31**). A deoxygenated and magnetically stirred solution of compound **23** (100 mg, 0.45 mmol) in dichloromethane (100 mL) maintained under nitrogen was subjected to irradiation with a Hanovia 450 W medium-pressure mercury-vapor lamp for 0.5 h. The reaction mixture thus obtained was cooled and concentrated under reduced pressure to give a yellow oil. Subjection of this material to flash column chromatography (silica, 1:4 → 3:7 v/v ethyl acetate/40−60 petroleum ether gradient elution) gave, after concentration of the appropriate fractions (R_f = 0.2 in 3:7 v/v ethyl acetate/40−60 petroleum ether), compound **31** (73 mg, 73%) as a clear, colorless oil: $[\alpha]_D$ = −163.3 (*c* 0.7, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 5.47 (s, 1H), 5.27 (dd, *J* = 6.4 and 4.0 Hz, 1H), 3.88 (m, 1H), 3.43 (m, 1H), 3.08 (dd, *J* = 10.1 and 1.4 Hz, 1H), 2.45 (d, *J* = 3.9 Hz, 1H), 1.90 (m, 1H), 1.79 (s, 3H), 1.06 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.4, 178.7, 138.9, 114.7, 89.1, 59.4, 45.9, 38.1, 30.8, 28.3, 24.5, 21.6, 19.6; IR ν_{max} 2963, 1782, 1168, 1147, 1131, 1005, 838 cm^{-1}; MS (ESI, + ve) *m*/*z* 275 [(M + MeOH + Na)$^+$, 100], 221 [(M + H)$^+$, 25]; HRMS *m*/*z* (M + MeOH + Na)$^+$ calcd for $C_{14}H_{20}O_3Na$ 275.1259, found 275.1260.

(2aS,2a′R,3S,5aR,5bR)-3,4-Dimethyl-2a′,3,5a,5b-tetrahydrocyclopropa[cd]isobenzofuran-2(2aH)-one (**32**). A deoxygenated and magnetically stirred solution of compound **22** (100 mg, 0.52 mmol) in dichloromethane (100 mL) maintained under a nitrogen atmosphere was irradiated with a Hanovia 450 W medium-pressure mercury-vapor lamp for 5 h. The ensuing reaction mixture was cooled to ca. 22 °C then concentrated under reduced pressure to give a brown oil. Subjection of this material to flash column chromatography (silica, 1:9 → 3:7 v/v ethyl acetate/40−60 petroleum ether gradient elution) gave two fractions, A and B.

Concentration of fraction A (R_f = 0.5 in 3:7 v/v ethyl acetate/40−60 petroleum ether) afforded compound **32** (32 mg, 37%) as a colorless, crystalline solid: mp = 73−75 °C; $[\alpha]_D$ = −102.8 (*c* 0.4, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 5.34 (s, 1H), 4.33 (dd, *J* = 6.3 and 5.4 Hz, 1H), 2.89 (dd, *J* = 7.7 and 3.0 Hz, 1H), 2.23 (m, 1H), 1.95 (m, 1H), 1.69 (s, 3H), 1.46 (m, 1H), 1.21 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3, 142.7, 112.7, 60.5, 44.7, 35.9, 22.4, 18.7, 17.8, 11.6; IR ν_{max} 2965, 1773, 1453, 1150, 1086, 1074, 922, 794 cm^{-1}; MS (ESI, + ve) *m*/*z* 187 [(M + Na)$^+$, 100]; HRMS *m*/*z* (M + Na)$^+$ calcd for $C_{10}H_{12}O_2Na$ 187.0735, found 187.0735.

Concentration of fraction B (R_f = 0.2 in 3:7 v/v ethyl acetate/40−60 petroleum ether) afforded compound **30** (28 mg, 28%) as a white solid that was identical with an authentic sample.

(2aS,2a′R,3S,5aR,5bR)-3-Isopropyl-4-methyl-2a′,3,5a,5b-tetrahydrocyclopropa[cd]isobenzofuran-2(2aH)-one (**33**). A deoxygenated and magnetically stirred solution of compound **23** (100 mg, 0.45 mmol) in dichloromethane (100 mL) maintained under a nitrogen atmosphere was subjected to irradiation with a Hanovia 450 W medium-pressure mercury-vapor lamp for 1.5 h. The ensuing mixture was cooled then concentrated under reduced pressure to give a brown oil. Subjection of this material to flash column chromatography (silica, 1:9 → 3:7 v/v ethyl acetate/40−60 petroleum ether gradient elution) afforded two fractions, A and B.

Concentration of fraction A (R_f = 0.6 in 3:7 v/v ethyl acetate/40−60 petroleum ether) gave compound **33** (45 mg, 52%) as a clear, colorless oil: $[\alpha]_D$ = −29.8 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 5.45 (s, 1H), 4.33 (m, 1H), 3.03 (dd, *J* = 7.7 and 2.4 Hz, 1H), 2.02−1.88 (complex m, 3H), 1.71 (s, 3H), 1.45 (m, 1H), 1.06 (d, *J* = 6.5 Hz, 3H), 0.98 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.1, 141.1, 114.8, 61.4, 47.6, 40.3, 30.7, 24.2, 21.7, 19.9, 18.0, 13.5; IR ν_{max} 2960, 1769, 1149, 1127, 1087, 933, 781 cm^{-1}; MS (ESI, + ve) *m*/*z* 215 [(M + Na)$^+$, 100]; HRMS *m*/*z* (M + Na)$^+$ calcd for $C_{12}H_{16}O_2Na$ 215.1048, found 215.1048.

Concentration of fraction B (R_f = 0.2 in 3:7 v/v ethyl acetate/40−60 petroleum ether) afforded compound **31** (25 mg, 25%) as a white solid that was identical with an authentic sample.

(1aR,1a′S,3aR,4S,4a^{1}R)-1a′,4-Dimethylhexahydro-1H-cyclopropa[3,4]pentaleno[1,6-bc]furan-1,3(1aH)-dione (**34**). A deoxygenated and magnetically stirred solution of compound **26** (108 mg, 0.56 mmol) and acetophenone (90 μL, 0.77 mmol) in acetone (100 mL) maintained under nitrogen was subjected to irradiation with a Hanovia 450 W medium-pressure mercury-vapor lamp for 2.5 h. The ensuing reaction mixture was cooled then concentrated under reduced pressure to give a yellow oil. Subjection of this material to flash column chromatography (silica, 3:17 → 3:7 v/v ethyl acetate/40−60 petroleum ether gradient elution) gave, after concentration of the appropriate fractions (R_f = 0.3 in 1:1 v/v ethyl acetate/40−60 petroleum ether), compound **34** (49 mg, 45%) as a white, crystalline solid: mp = 154−156 °C, $[\alpha]_D$ = +68.6 (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 4.21 (s, 1H), 2.55−2.47 (complex m, 3H), 2.18 (m, 1H), 1.97 (m, 1H), 1.54 (s, 3H), 1.38 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9, 176.5, 87.7, 64.3, 55.0, 42.6, 40.3, 38.0, 35.6, 22.6, 20.8; IR ν_{max} 2970, 1781, 1726, 1238, 1163, 1033, 884, 874 cm^{-1}; MS (ESI, + ve) *m*/*z* 247 [(M + MeOH + Na)$^+$, 20], 215 [(M + Na)$^+$, 100], 193 (30); HRMS *m*/*z* (M + Na)$^+$ calcd for $C_{11}H_{12}O_3Na$ 215.0684, found 215.0676.

(1aR,1a′S,3aR,4S,4a′R)-4-Isopropyl-1a′-methylhexahydro-1H-cyclopropa[3,4]pentaleno[1,6-bc]furan-1,3(1aH)-dione (**35**). A deoxygenated and magnetically stirred solution of compound **27** (123 mg, 0.56 mmol) and acetophenone (90 μL, 0.77 mmol) in acetone (100 mL) maintained under a nitrogen atmosphere was irradiated with a Hanovia 450 W medium-pressure mercury-vapor lamp for 2.5 h. The cooled reaction mixture was concentrated under reduced pressure to give a yellow oil and this subjected to flash column chromatography (silica, 3:17 → 1:3 v/v ethyl acetate/40−60 petroleum ether gradient elution). Concentration of the appropriate fractions (R_f = 0.5 in 1:1 v/v ethyl acetate/40−60 petroleum ether) then gave compound **35** (60 mg, 49%) as a white, crystalline solid: mp = 102−103 °C; $[\alpha]_D$ = +83.8 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 4.22 (s, 1H), 2.72 (d, *J* = 6.4 Hz, 1H), 2.41 (t, *J* = 4.0 Hz, 1H), 2.22−2.15 (complex m, 2H), 2.08 (m, 1H), 1.94 (m, 1H), 1.53 (s, 3H), 1.03 (d, *J* = 3.0 Hz, 3H), 1.02 (d, *J* = 3.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.1, 176.8, 87.6, 59.1, 54.6, 53.7, 37.4, 37.3, 35.5, 32.9, 20.6, 20.2, 19.4; IR ν_{max} 2961, 1790, 1781, 1732, 1240, 1160, 1047, 889 cm^{-1}; MS (ESI, + ve) *m*/*z* 275 [(M + MeOH + Na)$^+$, 20], 243 [(M + Na)$^+$, 100]; HRMS *m*/*z* (M + Na)$^+$ calcd for $C_{13}H_{16}O_3Na$ 243.0997, found 243.0993.

(2aR,2a′S,3aS,6S,6aR)-2a′,6-Dimethyl-2a′,3a,6,6a-tetrahydro-1H-cyclobuta[cd]isobenzofuran-1,3(2aH)-dione (**36**). A deoxygenated and magnetically stirred solution of compound **26** (100 mg, 0.52 mmol) in dichloromethane (100 mL) maintained under a nitrogen atmosphere was irradiated with a Hanovia 450 W medium-pressure mercury-vapor lamp for 0.58 h then cooled and concentrated under reduced pressure to give a yellow solid. Subjection of this material to flash column chromatography (silica, 1:4 → 3:7 v/v ethyl acetate/40−60 petroleum ether gradient elution) then gave, after concentration of the appropriate fractions (R_f = 0.2 in 3:7 v/v ethyl acetate/40−60 petroleum ether), compound **36** (70 mg, 70%) as a white, crystalline solid: mp = 100−101 °C; $[\alpha]_D$ = +220.5 (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 6.02 (m, 1H), 5.69 (dd, *J* = 10.0 and 4.0 Hz, 1H), 4.82 (d, *J* = 4.0 Hz, 1H), 3.60 (m, 1H), 2.93 (m, 1H), 2.66 (s, 1H), 1.70 (s, 3H), 1.23 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1, 177.7, 132.6, 119.1, 93.5, 63.8, 48.5, 35.5, 30.1, 24.9, 21.2; IR ν_{max} 2965, 1779, 1191, 1096, 997, 744, 725 cm^{-1}; MS (ESI, + ve) *m*/*z* 247 [(M + MeOH + Na)$^+$, 100%]; HRMS *m*/*z* (M + MeOH + Na)$^+$ calcd for $C_{12}H_{16}O_3Na$ 247.0946, found 247.0947.

(2aR,2a′S,3aS,6S,6aR)-6-Isopropyl-2a′-methyl-2a′,3a,6,6a-tetrahydro-1H-cyclobuta[cd]isobenzofuran-1,3(2aH)-dione (**37**). A deoxygenated and magnetically stirred solution of compound **27** (100 mg, 0.45 mmol) in dichloromethane (100 mL) maintained under a

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nitrogen atmosphere was irradiated with a Hanovia 450 W medium-pressure mercury-vapor lamp for 0.55 h then cooled and concentrated under reduced pressure to give a yellow solid. Subjection of this material to flash column chromatography (silica, 1:4 → 3:7 v/v ethyl acetate/40−60 petroleum ether gradient elution) then gave, after concentration of the appropriate fractions (R_f = 0.2 in 3:7 v/v ethyl acetate/40−60 petroleum ether), compound **37** (71 mg, 71%) as a white, crystalline solid: mp = 96−98 °C; $[\alpha]_D$ = +196.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.11 (m, 1H), 5.73 (dd, *J* = 10.1 and 3.6 Hz, 1H), 4.79 (d, *J* = 3.6 Hz, 1H), 3.56 (m, 1H), 2.95 (d, *J* = 1.7 Hz, 1H), 2.43 (t, *J* = 8.0 Hz, 1H), 1.68 (s, 3H), 1.66−1.60 (complex m, 1H), 1.09 (d, *J* = 6.6 Hz, 3H), 1.01 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 178.5, 131.8, 120.0, 93.5, 64.2, 44.8, 42.6, 35.9, 33.1, 24.1, 21.4, 21.3; IR ν_{max} 2964, 1782, 1471, 1293, 1193, 1000, 722 cm^{-1}; MS (ESI, + ve) *m*/*z* 527 [(2M + 2MeOH + Na)$^+$, 15], 275 [(M + MeOH + Na)$^+$, 100], 221 [(M + H)$^+$, 15]; HRMS *m*/*z* (M + MeOH + Na)$^+$ calcd for $C_{14}H_{20}O_3Na$ 275.1259, found 275.1257.

*(2aR,2a′S,3S,5aS,5bS)-2a′,3-Dimethyl-2a^1,3,5a,5b-tetrahydrocyclopropa[cd]isobenzofuran-2(2aH)-one (**38**).* A deoxygenated and magnetically stirred solution of compound **26** (100 mg, 0.52 mmol) in dichloromethane (100 mL) maintained under a nitrogen atmosphere was irradiated with a Hanovia 450 W medium-pressure mercury-vapor lamp for 3.1 h then cooled and concentrated under reduced pressure to give a brown oil. Subjection of this material to flash column chromatography (silica, 1:9 → 3:7 v/v ethyl acetate/40−60 petroleum ether gradient elution) then gave two fractions, A and B.

Concentration of fraction A (R_f = 0.5 in 3:7 v/v ethyl acetate/40−60 petroleum ether) afforded compound **38** (30 mg, 35%) as a colorless, crystalline solid: mp = 40−42 °C; $[\alpha]_D$ = +152.0 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.95 (dd, *J* = 9.9 and 6.0 Hz, 1H), 5.66 (dd, *J* = 9.9 and 4.5 Hz, 1H), 4.03 (d, *J* = 5.6 Hz, 1H), 2.65 (s, 1H), 2.54 (m, 1H), 1.39 (s, 3H), 1.35 (m, 1H), 1.22 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.7, 134.8, 119.4, 65.2, 49.3, 31.7, 23.5, 20.6, 19.3, 18.9; IR ν_{max} 2962, 2929, 1783, 1769, 1143, 1090, 846, 750 cm^{-1}; MS (EI, 70 eV) *m*/*z* 164 ($M^{+\bullet}$, 20%), 121 (30), 107 (100), 91 (70), 77 (25), 65 (15); HRMS *m*/*z* $M^{\bullet+}$ calcd for $C_{10}H_{12}O_2$ 164.0837, found 164.0835.

Concentration of fraction B (R_f = 0.2 in 3:7 v/v ethyl acetate/40−60 petroleum ether) afforded compound **36** (32 mg, 32%) as a white, crystalline solid that was identical, in all respects, with an authentic sample.

*(2aR,2a′S,3S,5aS,5bS)-3-Isopropyl-2a′-methyl-2a′,3,5a,5b-tetrahydrocyclopropa[cd]isobenzofuran-2(2aH)-one (**39**).* A deoxygenated and magnetically stirred solution of compound **27** (100 mg, 0.45 mmol) in dichloromethane (100 mL) maintained under a nitrogen atmosphere was irradiated with a Hanovia 450 W medium-pressure mercury-vapor lamp for 3.1 h then cooled and concentrated under reduced pressure to give a brown oil. Subjection of this material to flash column chromatography (silica, 1:9 → 3:7 v/v ethyl acetate/40−60 petroleum ether elution) then gave two fractions, A and B.

Concentration of fraction A (R_f = 0.6 in 3:7 v/v ethyl acetate/40−60 petroleum ether) afforded compound **39** (35 mg, 40%) as a yellow oil, $[\alpha]_D$ = +166.7 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.02 (dd, *J* = 9.9 and 6.1 Hz, 1H), 5.70 (dd, *J* = 9.9 and 4.2 Hz, 1H), 4.02 (d, *J* = 5.5 Hz, 1H), 2.92 (s, 1H), 2.02 (m, 1H), 1.79 (m, 1H), 1.36 (s, 3H), 1.34 (m, 1H), 1.05 (d, *J* = 6.6 Hz, 3H), 0.99 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.2, 134.0, 120.3, 65.5, 46.0, 43.8, 32.3, 23.7, 21.8, 20.9, 20.1, 19.3; IR ν_{max} 2966, 2872, 1778, 1148, 1092, 834, 752 cm^{-1}; MS (ESI, + ve) *m*/*z* 215 [(M + Na)$^+$, 100%]; HRMS *m*/*z* (M + Na)$^+$ calcd for $C_{12}H_{16}O_2Na$ 215.1048, found 215.1047.

Concentration of fraction B (R_f = 0.2 in 3:7 v/v ethyl acetate/40−60 petroleum ether) afforded compound **37** (34 mg, 34%) as a white, crystalline solid that was identical, in all respects, with an authentic sample.

*(3aR,4R,4aR,5S,7aR,8S,8aS)-2,2,4,6,6-Pentamethyl-3a,4a,5,6,7,7a,8,8a-octahydro-4H-4,8-ethenoindeno[5,6-d][1,3]-dioxol-5-yl Acetate (**42**).* A magnetically stirred solution of compound **41**[4d,5b] (5.00 g, 17.96 mmol), acetic anhydride (3.40 mL, 35.97 mmol) and 4-(*N*,*N*-dimethylamino)pyridine (440 mg, 3.60 mmol) in triethylamine (7.50 mL, 53.8 mmol) was stirred at 0 °C for 2 h and then warmed to 22 °C and stirred at this temperature for another 2 h. After this time, NH_4Cl (50 mL of a saturated aqueous solution) was added to the reaction mixture, and the resulting suspension was extracted with dichloromethane (3 × 50 mL). The combined organic fractions were washed with water (2 × 50 mL) and brine (1 × 50 mL) before being dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue thus obtained was subjected to flash column chromatography (silica, 1:19 v/v ethyl acetate/40−60 petroleum ether elution) and gave, after concentration of the appropriate fractions (R_f = 0.3 in 1:9 v/v ethyl acetate/40−60 petroleum ether), compound **42** (5.58 g, 97%) as a white, crystalline solid: mp = 135−137 °C; $[\alpha]_D$ = +7.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86−5.80 (complex m, 2H), 4.98 (d, *J* = 6.1 Hz, 1H), 4.22 (dd, *J* = 7.2 and 3.1 Hz, 1H), 3.79 (d, *J* = 7.2 Hz, 1H), 2.75 (m, 1H), 2.22 (m, 1H), 2.07 (m, 1H), 2.04 (s, 3H), 1.37 (m, 2H), 1.32 (s, 3H), 1.27 (s, 3H), 1.14 (s, 3H), 0.95 (s, 3H), 0.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 137.3, 125.7, 109.1, 84.1, 81.0, 80.1, 49.7, 44.7, 42.0, 40.8, 40.0, 38.0, 25.6 (5), 25.6 (2), 25.2, 22.4, 21.6, 19.9; IR ν_{max} 2961, 2934, 1733, 1370, 1234, 1073, 723 cm^{-1}; MS (ESI, + ve) *m*/*z* 343 [(M + Na)$^+$, 100]; HRMS *m*/*z* (M + Na)$^+$ calcd for $C_{19}H_{28}O_4Na$ 343.1885, found 343.1884.

*(3S,3aR,4R,7S,7aR,8S,9R)-8,9-Dihydroxy-2,2,4-trimethyl-2,3,3a,4,7,7a-hexahydro-1H-4,7-ethanoinden-3-yl Acetate (**43**).* AG-50W-X8 resin (3.32 g of H^+ form) was added to a magnetically stirred solution of compound **42** in methanol/water (72 mL of a 5:1 v/v mixture) and the resulting suspension heated under reflux for 67 h and then cooled to 22 °C before being filtered through a sintered glass funnel. The filtrate was concentrated under reduced pressure and the residue thus obtained subjected to flash column chromatography (silica, 3:7 v/v ethyl acetate/40−60 petroleum ether elution). Concentration of the appropriate fractions (R_f = 0.1 in 3:7 v/v ethyl acetate/40−60 petroleum ether) gave compound **43** (1.80 g, 97%) as a white solid: mp = 73−74 °C; $[\alpha]_D$ = −2.3 (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.99−5.91 (complex m, 2H), 4.97 (d, *J* = 6.1 Hz, 1H), 3.88 (dd, *J* = 7.5 and 2.4 Hz, 1H), 3.40 (d, *J* = 7.5 Hz, 1H), 2.73 (m, 1H), 2.52 (broad s, 2H), 2.27 (m, 1H), 2.13 (m, 1H), 2.03 (s, 3H), 1.39 (m, 1H), 1.25 (t, *J* = 11.6 Hz, 1H), 1.15 (s, 3H), 0.93 (s, 3H), 0.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 138.8, 126.8, 81.6, 75.4, 71.7, 50.4, 44.1, 42.0, 41.5, 41.3, 40.8, 25.5, 22.3, 21.6, 19.6; IR ν_{max} 3394, 2965, 2932, 1732, 1374, 1240, 1057 cm^{-1}; MS *m*/*z* 583 [(2M + Na)$^+$, 5], 303 [(M + Na)$^+$, 100]; HRMS *m*/*z* (M + Na)$^+$ calcd for $C_{16}H_{24}O_4Na$ 303.1572, found 303.1577.

*(3S,3aR,4R,7S,7aS,9R)-9-Hydroxy-2,2,4-trimethyl-8-oxo-2,3,3a,4,7,7a-hexahydro-1H-4,7-ethanoinden-3-yl Acetate (**44**).* A magnetically stirred mixture of *p*-toluenesulfonic acid monohydrate (448 mg, 2.36 mmol) and 4-acetamido-TEMPO (502 mg, 2.35 mmol) in dichloromethane (10 mL) was maintained at 0 °C under a nitrogen atmosphere for 0.5 h and the resulting solution then added, dropwise over 2 h, to a magnetically stirred solution of compound **43** (300 mg, 1.07 mmol) in dichloromethane (10 mL) maintained at 0 °C. The ensuing mixture was stirred for a further 2 h at this temperature and then quenched with $NaHCO_3$ (50 mL of a saturated aqueous solution). The resulting suspension was extracted with dichloromethane (3 × 50 mL), and the combined organic phases were washed with water (2 × 50 mL) and brine (1 × 50 mL) before being dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue thus obtained was subjected to flash column chromatography (silica, 3:17 v/v ethyl acetate/40−60 petroleum ether elution) to give, after concentration of the appropriate fractions (R_f = 0.2 in 3:7 v/v ethyl acetate/40−60 petroleum ether), compound **44** (289 mg, 97%) as a white, crystalline solid: mp = 147−149 °C; $[\alpha]_D$ = +215.0 (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08 (d, *J* = 7.9 Hz, 1H), 5.92 (t, *J* = 7.9 Hz, 1H), 5.09 (d, *J* = 6.0 Hz, 1H), 3.34 (s, 1H), 3.15 (d, *J* = 6.0 Hz, 1H), 2.72−2.49 (complex m, 3H), 2.06 (s, 3H), 1.52 (dd, *J* = 12.2 and 7.4 Hz, 1H), 1.40 (t, *J* = 12.2 Hz, 1H), 1.22 (s, 3H), 1.00 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.0, 170.2, 142.2, 121.9, 81.1, 75.2, 51.8, 50.1, 44.8, 43.9, 41.7, 39.3, 25.6, 22.2, 21.6, 18.1; IR ν_{max} 3451, 3239, 2965, 1730, 1374, 1236, 1081, 1039

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cm^{-1}; MS (ESI, + ve) m/z 579 [$(2M + Na)^+$, 10], 301 [$(M + Na)^+$, 100]; HRMS m/z $(M + Na)^+$ calcd for $C_{16}H_{22}O_4Na$ 301.1416, found 301.1411.

*(3S,3aR,4R,7S,7aS,9R)-2,2,4-Trimethyl-8-oxo-2,3,3a,4,7,7a-hexahydro-1H-4,7-ethanoindene-3,9-diyl Diacetate (**45**).* A magnetically stirred solution of compound **44** (239 mg, 0.86 mmol), 4-(*N*,*N*-dimethylamino)pyridine (11 mg, 0.09 mmol), and triethylamine (180 μL, 1.29 mmol) in dichloromethane (10 mL) maintained at 0 °C under a nitrogen atmosphere was treated with acetic anhydride (97 μL, 1.03 mmol). The ensuing mixture was kept at 0 °C for 2 h and then at 22 °C for 16 h before being quenched with NH_4Cl (10 mL of a saturated aqueous solution). The resulting mixture was extracted with dichloromethane (2 × 20 mL), and the combined organic phases were washed with water (2 × 20 mL) and brine (1 × 20 mL) before being dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue thus obtained was subjected to flash column chromatography (silica, 3:17 v/v ethyl acetate/40−60 petroleum ether elution) and gave, after concentration of the appropriate fractions (R_f = 0.4 in 3:7 v/v ethyl acetate/40−60 petroleum ether), compound **45** (250 mg, 91%) as a white, crystalline solid: mp = 175−177 °C; $[\alpha]_D$ = +200.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.09 (d, *J* = 8.1 Hz, 1H), 5.97 (t, *J* = 8.1 Hz, 1H), 5.09 (d, *J* = 6.0 Hz, 1H), 4.85 (s, 1H), 3.17 (d, *J* = 6.0 Hz, 1H), 2.74 (m, 1H), 2.64 (dd, *J* = 10.6 and 6.0 Hz, 1H), 2.10 (s, 3H), 2.06 (s, 3H), 1.53 (dd, *J* = 12.2 and 7.3 Hz, 1H), 1.39 (t, *J* = 12.2 Hz, 1H), 1.05 (s, 3H), 1.01 (s, 3H), 0.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.2, 170.7, 170.1, 141.4, 122.2, 81.1, 74.2, 51.5, 50.7, 44.9, 42.6, 41.7, 39.6, 25.5, 22.2, 21.5, 20.7, 17.9; IR ν_{max} 2979, 2965, 2932, 1721, 1374, 1230, 1053, 1020 cm^{-1}; MS (ESI, + ve) m/z 663 [$(2M + Na)^+$, 20], 343 [$(M + Na)^+$, 100], 321 [$(M + H)^+$, 5]; HRMS m/z $(M + Na)^+$ calcd for $C_{18}H_{24}O_5Na$ 343.1521, found 343.1505.

*(3S,3aR,4R,7S,7aS,9R)-9-(Methoxymethoxy)-2,2,4-trimethyl-8-oxo-2,3,3a,4,7,7a-hexahydro-1H-4,7-ethanoinden-3-yl Acetate (**46**).* A magnetically stirred solution of compound **44** (280 mg, 1.00 mmol), chloromethyl methyl ether (122 μL, 1.60 mmol), tetra-*n*-butylammonium iodide (37 mg, 0.10 mmol), and *N*,*N*-diisopropylethylamine (348 μL, 2.00 mmol) in dichloromethane (5 mL) maintained under a nitrogen atmosphere was stirred at 22 °C for 48 h and then treated with NH_4Cl (10 mL of a saturated aqueous solution) and extracted with dichloromethane (2 × 20 mL). The combined organic phases were washed with water (2 × 20 mL) and brine (1 × 20 mL) before being dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue thus obtained was subjected to flash column chromatography (silica, 1:4 v/v ethyl acetate/40−60 petroleum ether elution) and gave, after concentration of the appropriate fractions (R_f = 0.3 in 1:4 v/v ethyl acetate/40−60 petroleum ether), compound **46** (251 mg, 77%) as a pale-yellow oil: $[\alpha]_D$ = +213.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.06 (d, *J* = 8.0 Hz, 1H), 5.90 (t, *J* = 8.0 Hz, 1H), 5.03 (d, *J* = 6.7 Hz, 2H), 4.59 (d, *J* = 6.7 Hz, 1H), 3.38 (s, 3H), 3.31 (s, 1H), 3.04 (d, *J* = 6.3 Hz, 1H), 2.61 (m, 1H), 2.46 (dd, *J* = 10.6 and 6.1 Hz, 1H), 2.03 (s, 3H), 1.46 (dd, *J* = 12.1 and 7.4 Hz, 1H), 1.35 (t, *J* = 12.1 Hz, 1H), 1.14 (s, 3H), 0.95 (s, 3H), 0.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.3, 170.1, 141.0, 121.5, 97.5, 81.1, 77.1, 56.3, 51.0, 50.7, 44.8, 43.2, 41.5, 40.2, 25.3, 22.1, 21.5, 18.4; IR ν_{max} 2966, 1731, 1372, 1239, 1150, 1035, 710 cm^{-1}; MS (ESI, + ve) m/z 667 [$(2M + Na)^+$, 5], 345 [$(M + Na)^+$, 100]; HRMS m/z $(M + Na)^+$ calcd for $C_{18}H_{26}O_5Na$ 345.1678, found 345.1665.

*(3S,3aR,4R,7S,7aS,9R)-9-((tert-Butyldimethylsilyl)oxy)-2,2,4-trimethyl-8-oxo-2,3,3a,4,7,7a-hexahydro-1H-4,7-ethanoinden-3-yl Acetate (**47**).* A magnetically stirred solution of compound **44** (400 mg, 1.44 mmol), *tert*-butyldimethylsilyl chloride (1.73 g, 11.48 mmol), and imidazole (980 mg, 14.39 mmol) in 1,2-dichloroethane (20 mL) kept under a nitrogen atmosphere was heated at reflux for 65 h and then cooled, quenched with NH_4Cl (10 mL of a saturated aqueous solution), and extracted with dichloromethane (2 × 40 mL). The combined organic phases were washed with water (2 × 40 mL) and brine (1 × 40 mL) before being dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue thus obtained was subjected to flash column chromatography (silica, 2:5:100 v/v/v ethyl acetate/dichloromethane/40−60 petroleum ether elution) and gave, after concentration of the appropriate fractions (R_f = 0.6 in 3:7 v/v ethyl acetate/40−60 petroleum ether), compound **47** (465 mg, 82%) as a white, crystalline solid: mp = 71−72 °C; $[\alpha]_D$ = +121.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.03 (d, *J* = 8.0 Hz, 1H), 5.87 (t, *J* = 8.0 Hz, 1H), 5.06 (d, *J* = 6.0 Hz, 1H), 3.27 (s, 1H), 3.02 (dd, *J* = 6.0 and 1.8 Hz, 1H), 2.62 (m, 1H), 2.42 (dd, *J* = 10.6 and 6.0 Hz, 1H), 2.06 (s, 3H), 1.51−1.37 (complex m, 2H), 1.12 (s, 3H), 0.99 (s, 3H), 0.86 (s, 12H), 0.10 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.5, 170.3, 141.7, 120.9, 81.4, 76.0, 51.1, 50.5, 44.9, 44.4, 41.7, 40.3, 26.0, 25.5, 22.3, 21.6, 19.0, 18.6, − 4.0, − 5.0; IR ν_{max} 2959, 2930, 2856, 1733, 1237, 1129, 1112, 1093, 858, 837, 778, 709 cm^{-1}; MS m/z 415 [$(M + Na)^+$, 100]; HRMS m/z $(M + Na)^+$ calcd for $C_{22}H_{36}O_4SiNa$ 415.2281, found 415.2275.

*(3S,3aR,4R,7S,7aS,9R)-3-Acetoxy-2,2,4-trimethyl-8-oxo-2,3,3a,4,7,7a-hexahydro-1H-4,7-ethanoinden-9-yl Benzoate (**48**).* A magnetically stirred solution of compound **44** (2.90 g, 10.42 mmol), 4-(*N*,*N*-dimethylamino)pyridine (127 mg, 1.04 mmol), and triethylamine (2.9 mL, 21.00 mmol) in dichloromethane (50 mL) maintained under a nitrogen atmosphere at 0 °C was treated with benzoyl chloride (1.50 mL, 12.50 mmol). The ensuing mixture was allowed to warm to and then stirred at 22 °C for 16 h before being quenched with NH_4Cl (50 mL of a saturated aqueous solution) and then extracted with dichloromethane (2 × 100 mL). The combined organic phases were washed with water (2 × 100 mL) and then brine (1 × 100 mL) before being dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue thus obtained was subjected to flash column chromatography (silica, 2:5:100 v/v/v ethyl acetate/dichloromethane/40−60 petroleum ether elution) and gave, after concentration of the appropriate fractions [R_f = 0.2(5) in 1:19 v/v ethyl acetate/40−60 petroleum ether], compound **48** (3.69 g, 93%) as a white, crystalline solid: mp = 134−136 °C; $[\alpha]_D$ = +196.0 (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.3 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.41 (t, *J* = 7.3 Hz, 2H), 6.20 (d, *J* = 8.1 Hz, 1H), 6.04 (t, *J* = 8.1 Hz, 1H), 5.12−5.10 (complex m, 2H), 3.23 (dd, *J* = 6.6 and 1.6 Hz, 1H), 2.80 (m, 1H), 2.72 (dd, *J* = 10.6 and 6.6 Hz, 1H), 2.07 (s, 3H), 1.55 (dd, *J* = 12.1 and 7.3 Hz, 1H), 1.43 (m, 1H), 1.11 (s, 3H), 1.02 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.0, 170.1, 166.2, 141.3, 133.4, 130.0, 129.5, 128.5, 122.4, 81.1, 74.4, 51.3, 50.7, 44.9, 42.9, 41.7, 39.7, 25.4, 22.2, 21.5, 18.0; IR ν_{max} 2967, 1722, 1268, 1238, 1108, 729, 706 cm^{-1}; MS (ESI, + ve) m/z 787 [$(2M + Na)^+$, 100], 405 [$(M + Na)^+$, 85]; HRMS m/z $(M + Na)^+$ calcd for $C_{23}H_{26}O_5Na$ 405.1678, found 405.1682.

*(1S,3aS,4S,7R,7aR)-2,2,7-Trimethyl-9-oxo-2,3,3a,4,7,7a-hexahydro-1H-4,7-ethanoinden-1-yl Acetate (**49**).* A magnetically stirred solution of compound **48** (3.30 g, 8.63 mmol) in deoxygenated THF/methanol (30 mL of a 9:1 v/v mixture) maintained at −78 °C under an argon atmosphere was treated, dropwise over 1 h, with samarium(II) iodide (ca. 250 mL of a 0.086 M solution in THF) at which point a dark-blue color persisted for 0.25 h. The resulting mixture was then quenched with NH_4Cl (100 mL of a saturated aqueous solution) and the ensuing suspension extracted with diethyl ether (2 × 100 mL). The combined organic phases were washed with HCl (2 × 50 mL of a 1 M aqueous solution) and brine (1 × 100 mL) before being dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The residue thus obtained was subjected to flash column chromatography (silica, 1:9 v/v diethyl ether/*n*-hexane elution) and gave, after concentration of the appropriate fractions [R_f = 0.4(5) in 1:9 v/v diethyl ether/*n*-hexane)], compound **49** (1.91 g, 85%) as a clear, colorless oil: $[\alpha]_D$ = +161.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.10 (d, *J* = 8.1 Hz, 1H), 5.86 (t, *J* = 8.1 Hz, 1H), 4.93 (d, *J* = 6.0 Hz, 1H), 2.96 (dd, *J* = 6.0 and 1.8 Hz, 1H), 2.60 (m, 1H), 2.46 (m, 1H), 1.98 (s, 3H), 1.79 (s, 2H), 1.38 (m, 1H), 1.26 (t, *J* = 11.5 Hz, 1H), 1.05 (s, 3H), 0.90 (s, 3H), 0.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.3, 170.0, 142.9, 123.0, 80.4, 53.6, 52.1, 47.7, 44.8, 42.0, 41.2, 39.2, 25.4, 22.2, 22.0, 21.4; IR ν_{max} 2965, 1726, 1373, 1239, 1069, 707 cm^{-1}; MS (ESI, + ve) m/z 547 [$(2M + Na)^+$, 10], 285 [$(M + Na)^+$, 100], 263 [$(M + H)^+$, 1]; HRMS m/z $(M + H)^+$ calcd for $C_{16}H_{23}O_3$ 263.1647, found 263.1649.

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*(1R,2aR,4aR,7S,7aR,7bS)-1-(Methoxymethoxy)-6,6,7b-trimethyl-2-oxo-2,2a,4a,5,6,7,7a,7b-octahydro-1H-cyclobuta[e]inden-7-yl Acetate (**50**).* A magnetically stirred solution of compound **45** (100 mg, 0.31 mmol) in dry, deoxygenated dichloromethane (30 mL) maintained under a nitrogen atmosphere was irradiated with a Hanovia 100 W medium-pressure mercury-vapor lamp (maintained at 5 °C) for 16 h. The reaction mixture was then cooled and concentrated under reduced pressure and the residue thus obtained subjected to flash column chromatography (silica, 1:19 v/v ethyl acetate/*n*-hexane elution) to afford two fractions, A and B.

Concentration of fraction A [R_f = 0.3(5) in 1:19 v/v ethyl acetate/*n*-hexane] gave compound **50** (43 mg, 43% or 99% brsm) as a clear, colorless oil: $[\alpha]_D$ = −157.0 (*c* 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.76 (m, 1H), 5.73 (m, 1H), 5.54 (m, 1H), 4.97 (d, *J* = 4.2 Hz, 1H), 3.02 (m, 1H), 2.96 (m, 1H), 2.87 (dd, *J* = 9.3 and 4.2 Hz, 1H), 2.14 (s, 3H), 2.06 (m, 1H), 1.98 (s, 3H), 1.51 (dd, *J* = 13.3 and 5.0 Hz, 1H), 1.09 (s, 3H), 1.03 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.3, 170.6, 169.9, 134.3, 117.2, 83.4, 83.2, 59.0, 45.4, 43.5, 42.8, 34.8, 34.7, 28.8, 24.3, 21.3, 20.5, 18.4; IR ν_{max} 2933, 2873, 1792, 1735, 1373, 1224, 1087 cm^{-1}; MS (ESI, + ve) *m*/*z* 375 [(M + MeOH + Na)$^+$, 20], 343 [(M + Na)$^+$, 100]; HRMS *m*/*z* (M + Na)$^+$ calcd for $C_{18}H_{24}O_5Na$ 343.1521, found 343.1520.

Concentration of the fraction B [R_f = 0.2(5) in 1:19 v/v ethyl acetate/*n*-hexane] gave compound **45** (56 mg, 56% recovery) as a colorless, crystalline solid that was identical, in all respects, with an authentic sample.

*(1R,2aR,4aR,7S,7aR,7bS)-1-(Methoxymethoxy)-6,6,7b-trimethyl-2-oxo-2,2a,4a,5,6,7,7a,7b-octahydro-1H-cyclobuta[e]inden-7-yl Acetate (**51**).* A magnetically stirred solution of compound **46** (100 mg, 0.31 mmol) in dry, deoxygenated dichloromethane (30 mL) maintained under a nitrogen atmosphere was irradiated with a Hanovia 100 W medium-pressure mercury-vapor lamp (maintained at 5 °C) for 16 h. The cooled reaction mixture was concentrated under reduced pressure and the residue thus obtained subjected to flash column chromatography (silica, 1:9 v/v ethyl acetate/*n*-hexane elution), thus affording two fractions, A and B.

Concentration of the fraction A [R_f = 0.3(5) in 1:9 v/v ethyl acetate/*n*-hexane] gave compound **51** (27 mg, 27% or 98% brsm) as a clear, colorless oil: $[\alpha]_D$ = −324.0 (*c* 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.70 (m, 1H), 5.55 (m, 1H), 5.00 (d, *J* = 4.1 Hz, 1H), 4.67 (m, 3H), 3.42 (s, 3H), 2.90 (m, 1H), 2.85 (m, 1H), 2.76 (dd, *J* = 9.4 and 4.1 Hz, 1H), 2.05 (m, 1H), 1.98 (s, 3H), 1.51 (dd, *J* = 13.2 and 5.2 Hz, 1H), 1.11 (s, 3H), 1.06 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.5, 170.7, 133.4, 118.0, 97.3, 89.4, 83.2, 58.5, 56.1, 45.4, 43.5, 43.2, 34.7, 34.4, 28.7, 24.2, 21.4, 18.5; IR ν_{max} 2962, 2933, 1787, 1733, 1373, 1240, 1110, 1067, 1012 cm^{-1}; MS (ESI, + ve) *m*/*z* 345 [(M + Na)$^+$, 100]; HRMS *m*/*z* (M + Na)$^+$ calcd for $C_{18}H_{26}O_5Na$ 345.1678, found 345.1672.

Concentration of the fraction B [R_f = 0.2(5) in 1:9 v/v ethyl acetate/*n*-hexane] gave compound **46** (71 mg, 71% recovery) as a clear, colorless oil that was identical, in all respects, with an authentic sample.

*(3S,3aR,4R,7S,7aS,9R)-9-((tert-Butyldimethylsilyl)oxy)-2,2,4-trimethyl-8-oxo-2,3,3a,4,7,7a-hexahydro-1H-4,7-ethanoinden-3-yl Acetate (**52**).* A magnetically stirred solution of compound **47** (100 mg, 0.25 mmol) in dry, deoxygenated dichloromethane (30 mL) maintained under a nitrogen atmosphere was irradiated with a Hanovia 100 W medium-pressure mercury-vapor lamp (maintained at 5 °C) for 16 h. The cooled reaction mixture was concentrated under reduced pressure and the residue thus obtained subjected to flash column chromatography (silica, 1:19 v/v ethyl acetate/*n*-hexane elution), thus thereby affording two fractions, A and B.

Concentration of the fraction A (R_f = 0.4 in 1:19 v/v ethyl acetate/*n*-hexane) gave compound **52** (18 mg, 18% or 99% brsm) as a clear, colorless oil: $[\alpha]_D$ = −189.0 (*c* 2.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.64 (m, 1H), 5.55 (m, 1H), 4.98 (d, *J* = 4.1 Hz, 1H), 4.71 (d, *J* = 2.8 Hz, 1H), 2.86−2.78 (complex m, 2H), 2.65 (dd, *J* = 9.3 and 4.1 Hz, 1H), 2.03 (m, 1H), 1.97 (s, 3H), 1.50 (dd, *J* = 13.2 and 5.1 Hz, 1H), 1.10 (s, 3H), 0.97 (s, 3H), 0.92 (s, 3H), 0.90 (s, 9H), 0.10 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.1, 170.6, 132.8, 118.7, 85.0, 83.3, 58.0, 45.5, 43.5, 43.2, 34.8, 34.5, 28.8, 25.8, 24.2, 21.3, 18.4, 18.2, − 4.6, − 4.9; IR ν_{max} 2958, 2931, 2859, 1788, 1736, 1239, 1108, 883, 838, 780 cm^{-1}; MS (ESI, + ve) *m*/*z* 415 [(M + Na)$^+$, 100], 393 [(M + H)$^+$, 5]; HRMS *m*/*z* (M + Na)$^+$ calcd for $C_{22}H_{36}O_4SiNa$ 415.2281, found 415.2284.

Concentration of the fraction B (R_f = 0.3 in 1:19 v/v ethyl acetate/*n*-hexane) gave compound **47** (81 mg, 81% recovery) as a colorless, crystalline solid that was identical, in all respects, with an authentic sample.

*(1R,2aR,4aR,7S,7aR,7bS)-7-Acetoxy-6,6,7b-trimethyl-2-oxo-2,2a,4a,5,6,7,7a,7b-octahydro-1H-cyclobuta[e]inden-1-yl Benzoate (**53**).* A magnetically stirred solution of compound **48** (100 mg, 0.26 mmol) in dry, deoxygenated dichloromethane (30 mL) maintained under a nitrogen atmosphere was irradiated with a Hanovia 100 W medium-pressure mercury-vapor lamp (maintained at 5 °C) for 16 h. The reaction mixture was then cooled and concentrated under reduced pressure and the residue so obtained subjected to flash column chromatography (silica, 1:19 v/v ethyl acetate/*n*-hexane elution), thus affording two fractions, A and B.

Concentration of the fraction A [R_f = 0.3(5) in 1:19 v/v ethyl acetate/*n*-hexane] gave compound **53** (17 mg, 17% or 100% brsm) as a colorless, crystalline solid: mp = 180−181 °C; $[\alpha]_D$ = −672.0 (*c* 1.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 5.97 (d, *J* = 2.8 Hz, 1H), 5.80 (m, 1H), 5.59 (m, 1H), 4.98 (d, *J* = 4.2 Hz, 1H), 3.10 (m, 1H), 3.04 (m, 1H), 2.97 (dd, *J* = 9.3 and 4.2 Hz, 1H), 2.08 (dd, *J* = 13.3 and 9.8 Hz, 1H), 1.99 (s, 3H), 1.53 (dd, *J* = 13.3 and 5.0 Hz, 1H), 1.12 (s, 3H), 1.10 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 170.6, 165.3, 134.3, 133.8, 130.1, 128.8, 128.7, 117.3, 83.6, 83.2, 59.2, 45.4, 43.5, 42.9, 35.1, 34.8, 28.8, 24.3, 21.3, 18.5; IR ν_{max} 2963, 2934, 2872, 1790, 1724, 1372, 1237, 1104, 709 cm^{-1}; MS (ESI, + ve) *m*/*z* 787 [(2M + Na)$^+$, 10], 437 [(M + MeOH + Na)$^+$, 50], 405 [(M + Na)$^+$, 100]; HRMS *m*/*z* (M + Na)$^+$ calcd for $C_{23}H_{26}O_5Na$ 405.1678, found 405.1670.

Concentration of the fraction B [R_f = 0.2(5) in 1:19 v/v ethyl acetate/*n*-hexane] gave compound **48** (83 mg, 83% recovery) as a colorless, crystalline solid that was identical, in all respects, with an authentic sample.

*(2aR,4aR,7S,7aR,7bS)-6,6,7b-Trimethyl-2-oxo-2,2a,4a,5,6,7,7a,7b-octahydro-1H-cyclobuta[e]inden-7-yl Acetate (**54**).* A magnetically stirred solution of compound **49** (100 mg, 0.38 mmol) in dry, deoxygenated dichloromethane (30 mL) maintained under a nitrogen atmosphere was irradiated with a Hanovia 100 W medium-pressure mercury-vapor lamp (maintained at 5 °C) for 16 h. The reaction mixture was then cooled and concentrated under reduced pressure and the ensuing residue subjected to flash column chromatography (silica, 1:19 v/v ethyl acetate/*n*-hexane elution), thus affording two fractions, A and B.

Concentration of the fraction A [R_f = 0.3(5) in 1:19 v/v ethyl acetate/*n*-hexane] gave compound **54** (23 mg, 23% or 92% brsm) as a clear, colorless oil, $[\alpha]_D$ = −254.0 (*c* 3.4, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73 (m, 1H), 5.48 (m, 1H), 4.97 (d, *J* = 4.2 Hz, 1H), 3.12 (dd, *J* = 16.2 and 2.1 Hz, 1H), 3.05 (m, 1H), 2.84 (m, 1H), 2.59 (dd, *J* = 9.2 and 4.3 Hz, 1H), 2.51 (dd, *J* = 16.2 and 6.0 Hz, 1H), 2.01 (dd, *J* = 13.2 and 9.7 Hz, 1H), 1.95 (s, 3H), 1.50 (dd, *J* = 13.2 and 4.8 Hz, 1H), 1.19 (s, 3H), 1.08 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.4, 170.7, 133.7, 118.2, 83.5, 64.1, 56.7, 45.7, 44.3, 43.4, 34.9, 29.0, 28.1, 25.5, 24.3, 21.3; IR ν_{max} 3020, 2966, 2871, 1778, 1731, 1373, 1239, 1020, 711 cm^{-1}; MS (ESI, + ve) *m*/*z* 285 [(M + Na)$^+$, 100]; HRMS *m*/*z* (M + Na)$^+$ calcd for $C_{16}H_{22}O_3Na$ 285.1467, found 285.1472.

Concentration of the fraction B (R_f = 0.3 in 1:19 v/v ethyl acetate/*n*-hexane) gave compound **49** (69 mg, 69% recovery) as a colorless, crystalline solid that was identical, in all respects, with an authentic sample.

*(1S,1aR,3aR,6S,6aR,6bR)-5,5,6b-Trimethyl-1,1a,3a,4,5,6,6a,6b-octahydrocyclopropa[e]indene-1,6-diyl Diacetate (**55**).* A magnetically stirred solution of compound **50** (40 mg, 0.12 mmol) in dry, deoxygenated dichloromethane (10 mL) maintained under a nitrogen atmosphere was irradiated with a Hanovia 450 W medium-pressure

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mercury-vapor lamp for 0.5 h. The reaction mixture was then cooled and concentrated under reduced pressure and the residue thus obtained subjected to flash column chromatography (silica, 1:9 v/v ethyl acetate/*n*-hexane elution). Concentration of the appropriate fractions [R_f = 0.6(5) in 1:9 v/v ethyl acetate/*n*-hexane] gave compound **55** (39 mg, 98%) as a clear, colorless oil: $[\alpha]_D$ = +167.0 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 (m, 1H), 5.22 (dd, *J* = 10.0 and 1.9 Hz, 1H), 5.04 (d, *J* = 3.9 Hz, 1H), 3.77 (d, *J* = 2.3 Hz, 1H), 2.82 (dd, *J* = 10.1 and 3.9 Hz, 1H), 2.64 (m, 1H), 2.05 (s, 3H), 2.00 (s, 3H), 1.90 (dd, *J* = 13.1 and 9.6 Hz, 1H), 1.33 (dd, *J* = 13.1 and 5.2 Hz, 1H), 1.22 (dd, *J* = 11.1 and 2.3 Hz, 1H), 1.06 (s, 6H), 0.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 171.1, 129.9, 123.1, 84.0, 63.4, 46.6, 42.8, 40.8, 35.4, 28.6, 24.3, 24.2, 22.1, 21.3, 20.9, 15.9; IR ν_{max} 3026, 2966, 2933, 2872, 1733, 1371, 1227 cm^{-1}; MS (ESI, + ve) *m*/*z* 347 [(M + MeOH + Na)$^+$, 100%], 331 [(M + K)$^+$, 20], 329 (50), 315 [(M + Na)$^+$, 60]; HRMS *m*/*z* (M + Na)$^+$ calcd for $C_{17}H_{24}O_4Na$ 315.1572, found 315.1570.

*(1S,1aR,3aR,6S,6aR,6bS)-1-((tert-Butyldimethylsilyl)oxy)-5,5,6b-trimethyl-1,1a,-3a,4,5,6,6a,6b-octahydrocyclopropa[e]inden-6-yl Acetate (**56**).* A magnetically stirred solution of compound **47** (100 mg, 0.25 mmol) in dry, deoxygenated dichloromethane (30 mL) maintained under a nitrogen atmosphere was irradiated with a Hanovia 450 W medium-pressure mercury-vapor lamp for 1.67 h. The reaction mixture was then cooled, concentrated under reduced pressure and the residue thus obtained subjected to flash column chromatography (silica, 1:19 v/v ethyl acetate/40−60 petroleum ether) to afford two fractions, A and B.

Concentration of the fraction A (R_f = 0.6 in 1:4 v/v ethyl acetate/40−60 petroleum ether) gave compound **56** (74 mg, 80% or 87% brsm) as a clear, colorless oil: $[\alpha]_D$ = −65.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR [400 MHz, $(CD_3)_2CO$] δ 5.92 (m, 1H), 5.11 (dd, *J* = 10.0 and 2.1 Hz, 1H), 5.01 (d, *J* = 4.1 Hz, 1H), 3.14 (d, *J* = 2.2 Hz, 1H), 2.78 (m, 1H), 2.63 (m, 1H), 1.95 (s, 3H), 1.89 (m, 1H), 1.30 (dd, *J* = 13.0 and 5.2 Hz, 1H), 1.09 (s, 3H), 1.06 (s, 3H), 0.97 (dd, *J* = 5.5 and 2.4 Hz, 1H), 0.90 (s, 9H), 0.87 (s, 3H), 0.10(1) (s, 3H), 0.09(8) (s, 3H); ^{13}C NMR [100 MHz, $(CD_3)_2CO$] δ 170.7, 128.9, 125.2, 84.4, 63.9, 47.3, 43.3, 41.9, 36.2, 28.9, 27.7, 26.2, 24.7, 23.1, 21.1, 18.6, 15.9, − 4.9 (one signal obscured or overlapping); IR ν_{max} 3021, 2958, 2930, 2859, 1734, 1240, 1153, 859, 835, 776 cm^{-1}; MS (ESI, + ve) *m*/*z* 387 [(M + Na)$^+$, 100]; HRMS *m*/*z* (M + Na)$^+$ calcd for $C_{21}H_{36}O_3SiNa$ 387.2331, found 387.2331.

Concentration of the fraction B (R_f = 0.5 in 1:4 v/v ethyl acetate/40−60 petroleum ether) gave compound **47** (8 mg, 8% recovery) as a white, crystalline solid that was identical, in all respects, with an authentic sample.

*(3S,3aR,4R,7S,7aS,9R)-2,2,4-Trimethyl-9-((methylsulfonyl)oxy)-8-oxo-2,3,3a,4,-7,7a-hexahydro-1H-4,7-ethanoinden-3-yl Acetate (**57**).* A magnetically stirred solution of compound **44** (280 mg, 1.01 mmol), methanesulfonyl chloride (94 μL, 1.21 mmol) and triethylamine (212 μL, 1.52 mmol) in dichloromethane (5 mL) maintained under a nitrogen atmosphere was stirred at 22 °C for 48 h and then quenched with NH_4Cl (10 mL of a saturated aqueous solution) before being extracted with dichloromethane (2 × 50 mL). The combined organic fractions were washed with water (2 × 50 mL) and brine (1 × 50 mL) and then dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue thus obtained was subjected to flash column chromatography (silica, 1:9 v/v ethyl acetate/40−60 petroleum ether elution) to give, after concentration of the appropriate fractions (R_f = 0.3 in 1:9 v/v ethyl acetate/40−60 petroleum ether), compound **57** (198 mg, 56%) as a light-yellow oil: $[\alpha]_D$ = +114.0 (*c* 4.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08 (d, *J* = 8.1 Hz, 1H), 5.95 (t, *J* = 8.1 Hz, 1H), 5.08 (d, *J* = 5.9 Hz, 1H), 4.31 (s, 1H), 3.19 (m, 1H), 3.17 (s, 3H), 2.69 (m, 1H), 2.58 (dd, *J* = 10.6 and 6.0 Hz, 1H), 2.05 (s, 3H), 1.53 (m, 1H), 1.39 (t, *J* = 12.0 Hz, 1H), 1.20 (s, 3H), 0.98 (s, 3H), 0.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.1, 170.0, 140.9, 121.9, 81.3, 81.0, 50.7, 50.2, 44.9, 42.7, 41.6, 39.5(1), 39.4(8), 25.3, 22.1, 21.5, 18.1; IR ν_{max} 2968, 1730, 1358, 1238, 1173, 965, 841 cm^{-1}; MS (ESI, + ve) *m*/*z* 735 [(2M + Na)$^+$, 15], 379 [(M + Na)$^+$, 100]; HRMS *m*/*z* (M + Na)$^+$ calcd for $C_{17}H_{24}O_6SNa$ 379.1191, found 379.1193.

*(1R,2a^{1}S,2cR,5S,5aR,5bR)-4,4,5b-Trimethyl-1-((methylsulfonyl)-oxy)-2-oxodeca-hydro-1H-cyclopenta[a]cyclopropa[cd]pentalen-5-yl Acetate (**58**).* A magnetically stirred solution of compound **57** (100 mg, 0.28 mmol) in dry, deoxygenated dichloromethane (30 mL) maintained under a nitrogen atmosphere was irradiated with a Hanovia 100 W medium-pressure mercury-vapor lamp (maintained at 5 °C) for 12 h. The reaction mixture was then cooled and concentrated under reduced pressure and the residue thus obtained subjected to flash column chromatography (silica, 1:9 v/v ethyl acetate/*n*-hexane elution) to afford two fractions, A and B.

Concentration of the fraction A [R_f = 0.4(5) in 1:9 v/v ethyl acetate/*n*-hexane] gave compound **58** (48 mg, 48% or 98% brsm) as a clear, colorless oil: $[\alpha]_D$ = +161.0 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.54 (s, 1H), 5.09 (d, *J* = 4.8 Hz, 1H), 3.05 (s, 3H), 2.85−2.72 (complex m, 2H), 2.50 (d, *J* = 4.8 Hz, 1H), 2.23 (s, 3H), 2.18 (s, 1H), 1.71 (d, *J* = 4.8 Hz, 1H), 1.59 (dd, *J* = 8.7 and 2.3 Hz, 2H), 1.07 (s, 3H), 0.97(2) (s, 3H), 0.96(7) (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.1, 170.2, 80.9, 78.8, 50.4, 45.2, 42.5, 42.4, 41.1, 39.3, 37.6, 36.1, 32.9, 25.1, 22.7, 22.5, 21.2; IR ν_{max} 2966, 2936, 2875, 1729, 1356, 1236, 1172, 917, 842 cm^{-1}; MS *m*/*z* 735 [(2M + Na)$^+$, 5], 379 [(M + Na)$^+$, 100]; HRMS *m*/*z* (M + Na)$^+$ calcd for $C_{17}H_{24}O_6SNa$ 379.1191, found 379.1189.

Concentration of the fraction B (R_f = 0.3 in 1:9 v/v ethyl acetate/*n*-hexane) gave compound **57** (50 mg, 50% recovery) as a clear, colorless oil that was identical, in all respects, with an authentic sample.

X-ray Crystallographic Studies. *Crystallographic Data. Compound **8**:* $C_9H_{12}O_3$, *M* = 168.19, *T* = 150 K, orthorhombic, space group $P2_12_12_1$, *Z* = 4, *a* = 7.3238(1) Å, *b* = 7.5553(1) Å, *c* = 14.5389(2) Å; *V* = 804.49(2) Å^3, D_x = 1.389 g cm^{-3}, 1585 unique data ($2\theta_{max}$ = 144.6°), *R* = 0.023 [for 1569 reflections with $I > 2.0\sigma(I)$]; R_w = 0.057 (all data), *S* = 1.00.

*Compound **9**:* $C_{15}H_{26}O_3Si$, *M* = 282.46, *T* = 150 K, monoclinic, space group *C*2, *Z* = 4, *a* = 18.9377(5) Å, *b* = 6.2442(1) Å, *c* = 14.6275(5) Å; β = 105.950(3)°; *V* = 1663.12(8) Å^3, D_x = 1.128 g cm^{-3}, 3042 unique data ($2\theta_{max}$ = 144.8°), *R* = 0.032 [for 2889 reflections with $I > 2.0\sigma(I)$]; R_w = 0.080 (all data), *S* = 0.99.

*Compound **10**:* $C_9H_{12}O_3$, *M* = 168.19, *T* = 150 K, orthorhombic, space group $P2_12_12_1$, *Z* = 8, *a* = 8.23350(7) Å, *b* = 8.68949(8) Å, *c* = 23.6396(2) Å; *V* = 1691.29(3) Å^3, D_x = 1.321 g cm^{-3}, 3334 unique data ($2\theta_{max}$ = 144.6°), *R* = 0.04 [for 3257 reflections with $I > 2.0\sigma(I)$]; R_w = 0.112 (all data), *S* = 1.01.

*Compound **13**:* $C_{14}H_{26}O_2Si$, *M* = 254.45, *T* = 150 K, orthorhombic, space group $P2_12_12$, *Z* = 8, *a* = 18.3637(1) Å, *b* = 14.1093(1) Å, *c* = 12.0122(1) Å; *V* = 3112.35(4) Å^3, D_x = 1.086 g cm^{-3}, 6159 unique data ($2\theta_{max}$ = 145.0°), *R* = 0.025 [for 6101 reflections with $I > 2.0\sigma(I)$]; R_w = 0.067 (all data), *S* = 1.01.

*Compound **23**:* $C_{13}H_{16}O_3$, *M* = 220.27, *T* = 150 K, orthorhombic, space group $P2_12_12_1$, *Z* = 4, *a* = 7.27015(5) Å, *b* = 11.05109(8) Å, *c* = 13.78627(9) Å; *V* = 1107.63(1) Å^3, D_x = 1.321 g cm^{-3}, 2186 unique data ($2\theta_{max}$ = 144.8°), *R* = 0.022 [for 2152 reflections with $I > 2.0\sigma(I)$]; R_w = 0.057 (all data), *S* = 1.01.

*Compound **27**:* $C_{13}H_{16}O_3$, *M* = 220.27, *T* = 200 K, monoclinic, space group $P2_1$, *Z* = 2, *a* = 7.2003(2) Å, *b* = 8.4682(2) Å, *c* = 9.4258(3) Å; β = 91.1279(17)°; *V* = 574.61(3) Å^3, D_x = 1.273 g cm^{-3}, 1778 unique data ($2\theta_{max}$ = 60.0°), *R* = 0.048 [for 1655 reflections with $I > 2.0\sigma(I)$]; R_w = 0.156 (all data), *S* = 1.03.

*Compound **30**:* $C_{11}H_{12}O_3$, *M* = 192.21, *T* = 150 K, monoclinic, space group $P2_1$, *Z* = 2, *a* = 8.4949(4) Å, *b* = 5.9702(2) Å, *c* = 9.3840(4) Å; β = 95.383(4)°; *V* = 473.82(3) Å^3, D_x = 1.347 g cm^{-3}, 1032 unique data ($2\theta_{max}$ = 144.8°), *R* = 0.045 [for 998 reflections with $I > 2.0\sigma(I)$]; R_w = 0.130 (all data), *S* = 1.03.

*Compound **32**:* $C_{10}H_{12}O_2$, *M* = 164.20, *T* = 150 K, orthorhombic, space group $P2_12_12_1$, *Z* = 4, *a* = 7.8054(1) Å, *b* = 9.7920(1) Å, *c* = 11.0580(1) Å; *V* = 845.17(2) Å^3, D_x = 1.290 g cm^{-3}, 1677 unique data ($2\theta_{max}$ = 144.6°), *R* = 0.022 [for 1645 reflections with $I > 2.0\sigma(I)$]; R_w = 0.057 (all data), *S* = 1.01.

*Compound **34**:* $C_{11}H_{12}O_3$, *M* = 192.21, *T* = 150 K, monoclinic, space group $P2_1$, *Z* = 2, *a* = 6.9303(2) Å, *b* = 7.7696(2) Å, *c* = 8.6272(2) Å; β = 92.403(2)°; *V* = 464.13(2) Å^3, D_x = 1.375 g cm^{-3},

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993 unique data ($2\theta_{max}$ = 145.2°), R = 0.037 [for 980 reflections with $I > 2.0\sigma(I)$]; R_w = 0.117 (all data), S = 1.04.

Compound **35**: $C_{13}H_{16}O_3$, M = 220.27, T = 150 K, orthorhombic, space group $P2_12_12_1$, Z = 4, a = 7.3877(1) Å, b = 7.8178(1) Å, c = 19.8494(2) Å; V = 1146.41(2) Å^3, D_x = 1.276 g cm^{-3}, 2267 unique data ($2\theta_{max}$ = 144.8°), R = 0.030 [for 2238 reflections with $I > 2.0\sigma(I)$]; R_w = 0.056 (all data), S = 1.00.

Compound **36**: $C_{11}H_{12}O_3$, M = 192.21, T = 150 K, orthorhombic, space group $P2_12_12_1$, Z = 4, a = 7.4666(2) Å, b = 12.0831(5) Å, c = 10.8645(4) Å; V = 980.19(6) Å^3, D_x = 1.302 g cm^{-3}, 1491 unique data ($2\theta_{max}$ = 58.4°), R = 0.047 [for 1303 reflections with $I > 2.0\sigma(I)$]; R_w = 0.108 (all data), S = 1.00.

Compound **38**: $C_{10}H_{12}O_2$, M = 164.20, T = 150 K, hexagonal, space group $P6_5$, Z = 6, a = 14.7787(4) Å, c = 7.6213(2) Å; V = 1441.56(7) Å^3, D_x = 1.135 g cm^{-3}, 1379 unique data ($2\theta_{max}$ = 58.8°), R = 0.045 [for 1283 reflections with $I > 2.0\sigma(I)$]; R_w = 0.111 (all data), S = 1.03.

Compound **41**: $C_{17}H_{26}O_3$, M = 278.39, T = 150 K, orthorhombic, space group $P2_12_12_1$, Z = 4, a = 6.26451(4) Å, b = 12.09608(9) Å, c = 20.26568(14) Å; V = 1535.65(2) Å^3, D_x = 1.204 g cm^{-3}, 3025 unique data ($2\theta_{max}$ = 144.6°), R = 0.024 [for 2974 reflections with $I > 2.0\sigma(I)$]; R_w = 0.062 (all data), S = 1.00.

Compound **44**: $C_{16}H_{22}O_4$, M = 278.35, T = 150 K, orthorhombic, space group $P2_12_12_1$, Z = 4, a = 6.4307(1) Å, b = 8.7685(1) Å, c = 26.1929(2) Å; V = 1476.95(3) Å^3, D_x = 1.252 g cm^{-3}, 2913 unique data ($2\theta_{max}$ = 144.8°), R = 0.024 [for 2859 reflections with $I > 2.0\sigma(I)$]; R_w = 0.063 (all data), S = 1.00.

Compound **45**: $C_{18}H_{24}O_5$, M = 320.39, T = 150 K, monoclinic, space group $P2_1$, Z = 2, a = 7.4300(3) Å, b = 9.7667(3) Å, c = 12.1277(3) Å; β = 92.279(3)°; V = 879.37(5) Å^3, D_x = 1.210 g cm^{-3}, 2377 unique data ($2\theta_{max}$ = 58.6°), R = 0.038 [for 2242 reflections with $I > 2.0\sigma(I)$]; R_w = 0.093 (all data), S = 1.02.

Compound **47**: $C_{22}H_{36}O_4Si$, M = 392.61, T = 150 K, orthorhombic, space group $P2_12_12_1$, Z = 4, a = 25.6494(7) Å, b = 14.1949(4) Å, c = 6.2343(2) Å; V = 2269.85(11) Å^3, D_x = 1.149 g cm^{-3}, 5914 unique data ($2\theta_{max}$ = 58.8°), R = 0.045 [for 5443 reflections with $I > 2.0\sigma(I)$]; R_w = 0.102 (all data), S = 1.04.

Compound **48**: $C_{23}H_{26}O_5$, M = 382.46, T = 150 K, orthorhombic, space group $P2_12_12_1$, Z = 4, a = 19.9195(6) Å, b = 11.6626(3) Å, c = 8.7386(2) Å; V = 2030.09(9) Å^3, D_x = 1.251 g cm^{-3}, 2980 unique data ($2\theta_{max}$ = 58.6°), R = 0.041 [for 2759 reflections with $I > 2.0\sigma(I)$]; R_w = 0.101 (all data), S = 1.03.

Compound **53**: $C_{23}H_{26}O_5$, M = 382.46, T = 150 K, orthorhombic, space group $P2_12_12_1$, Z = 4, a = 8.9344(2) Å, b = 15.4099(3) Å, c = 14.9268(3) Å; V = 2055.09(7) Å^3, D_x = 1.236 g cm^{-3}, 3065 unique data ($2\theta_{max}$ = 59.0°), R = 0.042 [for 2868 reflections with $I > 2.0\sigma(I)$]; R_w = 0.112 (all data), S = 1.04.

Structure Determination. Images for compound **27**, **36**, **38**, **45**, **47**, **48**, and **53** were measured on a diffractometer (Mo Kα, graphite monochromator, λ = 0.71073 Å) fitted with an area detector and the data extracted using the DENZO/Scalepack or CrysAlis package.[15] Images for compounds **8**, **9**, **10**, **13**, **23**, **30**, **32**, **34**, **35**, **41**, and **44** were measured on a diffractometer (Cu Kα, mirror monochromator, λ= 1.54184 Å) fitted with an area detector and the data extracted using the CrysAlis package.[16] The structure solutions for all six compounds were solved by direct methods (SIR92)[17] then refined using the CRYSTALS program package.[18] Atomic coordinates, bond lengths and angles, and displacement parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC nos. 1545223, 154224, 1545225, 1545226, 1545227, 1545228, 1545229, 1545230, 1545231, 1545232, 1545233, 1545234, 1545235, 1545236, 1545237, 1545238, 1545239 and 1545240). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b01243.

Anisotropic displacement ellipsoid plots from the single-crystal X-ray analyses of compounds **8**−**10**, **13**, **23**, **27**, **30**, **32**, **34**−**36**, **38**, **41**, **44**, **45**, **47**, **48**, and **53**; ^{1}H and ^{13}C NMR spectra of compounds **8**−**39** and **42**−**58** (PDF)

X-ray crystallographic data for compounds **8**−**10**, **13**, **23**, **27**, **30**, **32**, and **34** (CIF)

X-ray crystallographic data for compounds **35**, **36**, **38**, **41**, **44**, **45**, **47**, **48**, and **53** (CIF)

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Notes

The authors declare no competing financial interest.

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