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Dual Behavior of Masked *o*-Benzoquinones in Intermolecular Diels−Alder Reactions with Acyclic Dienes: A Rapid Entry to Polyfunctionalized Bicyclo[2.2.2]oct-5-en-2-ones and *cis*-Decalins

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The potentiality of the masked *o*-benzoquinones, i.e., 6,6-dimethoxy-2,4-cyclohexadienones **5**−**8**, to react both as dienes and dienophiles in their intermolecular reactions has been demonstrated. The masked *o*-benzoquinones (MOBs) **5**−**8** generated in situ from 2-methoxyphenols **1**−**4** underwent intermolecular Diels−Alder cycloadditions with acyclic 1,3-dienes **9a**−**e** to provide bicyclo[2.2.2]-octenones **10a**−**f**−**13a**−**f** along with *cis*-decalin derivatives **14a**−**f**−**17a**−**f** with regio- and stereoselectivity, except in the case of MOB **8**. The formation of *cis*-decalins in these Diels−Alder reactions illustrates the dienophilic character of MOBs, in addition to their general behavior as dienes. The ratio of the two cycloadducts obtained in each reaction as a result of the dual character of MOBs depends on the nature and/or position of the substituents on both the cyclohexadienone moiety and the added conjugated acyclic diene. All of the cycloadducts resulted from the diene property of MOBs in intermolecular Diels−Alder reactions smoothly underwent Cope rearrangement to furnish *cis*-decalins as sole products in excellent to quantitative yields.

Introduction

The decalin skeleton is one of the most prevalent structural motifs present in numerous natural products.[1−3] In paticular, the terpenoids, possessing the decalin moiety, display a wide variety of biological activities that may have medicinal potential.[2,3] Owing to their importance in nature, synthesis of decalins has become a major focal point of synthetic chemistry. The structural complexity of the isolated natural products demands the development of new and efficient strategies to construct stereochemically rich and multifunctional decalins. For this reason, there has been a great deal of interest in developing a multitude of methods for their synthesis, as reflected by the flurry of recent reports in this area by various groups including ours.[4−8]

Masked *o*-benzoquinones (MOBs) are valuable intermediates in organic synthesis.[9] The Diels−Alder reactions[10−12] of these linearly conjugated cyclohexadienones[9,13] offer rapid construction of complex polycyclic frameworks including bicyclic and tricyclic ring systems with high selectivities. Over the years, we have been working on the chemistry of MOBs, and their synthetic

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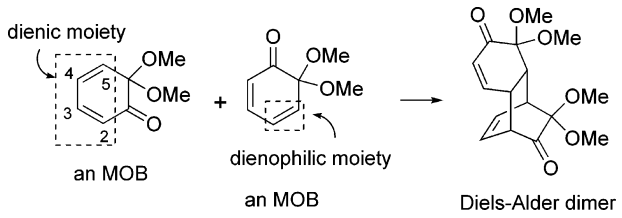
SCHEME 1



potential has been exploited.[9,14] The MOBs, by virtue of their structure, can react as both diene and dienophile which render them to involve in self-dimerization via Diels−Alder reaction (Scheme 1). MOBs and related cyclohexa-2,4-dien-2-ones generally participate as 4π-components; however, their dienophilicity has been unveiled recently by us[6,7b] and others.[8,15,16] When forced by their structure, MOBs exhibited dienophilic character in intramolecular Diels−Alder reactions.[7b,8] It occurred to us that if MOBs, being dual role players, participate in the [4 + 2] cycloadditions with acyclic 1,3-dienes, easy access to potentially useful polyfunctional bicyclo[2.2.2]-oct-5-en-2-ones[1c,12,17] and *cis*-decalins could be achieved. We now report herein full details of such reactions,[6] together with the results of our studies on the variation of the diene and dienophilic properties of MOBs with the nature and position of the substituents on both the cyclohexadienone core and the added conjugated acyclic dienes.

Results and Discussion

(a) Diels−Alder Reactions. 2-Methoxyphenols methyl vanillate (**1**), methyl syringate (**2**), methyl isovanillate (**3**), and creosol (2-methoxy-4-methylphenol, **4**) were chosen for the study of intermolecular Diels−Alder reactions of their MOBs with unactivated acyclic dienes viz, 1,3-butadiene (**9a**), *trans*-piperylene (**9b**), 1-acetoxy-1,3-butadiene (**9c**), 2,3-dimethyl-1,3-butadiene (**9d**), and isoprene (**9e**). All the acyclic dienes were used from commercial sources except 1,3-butadiene (**9a**), which was generated in situ from sulfolene.[18] The oxidation of methyl vanillate (**1**) in methanol was first carried out by adding diacetoxyiodobenzene (DAIB) in methanol at −20 °C to generate MOB **5** in the presence of in situ generated **9a**. The reaction mixture was stirred for 1 h followed by usual workup and chromatography (method A) to furnish bicyclo[2.2.2]octenone **10a** in 62% yield along with the *cis*-decalin **14a** in 17% yield (Scheme 2, Table 1). When the MOB **5** was allowed to react with other acyclic dienes **9b**, **9c**, and **9d**, the relative yields of the *cis*-decalin products **14b**, **14c**, and **14d** were substantially increased, presumably due to the enhanced diene character of **9b**, **9c**, and **9d** caused by the additional electron-donating group(s) in the dienes. It is interesting to note that the Diels−Alder reactions of MOB **5** with acyclic dienes **9a**−**d** are highly regio- and stereoselective and those of unsymmetrical acyclic dienes **9b** and **9c** are chemoselective. Contrary to this, the Diels−Alder reaction of MOB **5** with isoprene (**9e**) was found to be nonchemoselective. The two double bonds in **9e** were equally prone to act as dienophiles resulting in the formation of the mixture of two separable bicyclo[2.2.2]octenones **10e** and **10f** along with the two *cis*-decalins **14e** and **14f** (Scheme 3).

Taking the electron-deficient nature of the diene moiety in MOB **5** into account, we then considered the MOB **6** bearing an electron-releasing methoxy group at the position 2 (Scheme 2). We first carried out the Diels−Alder reaction of MOB **6** with the parent diene **9a**. Predictably, diene **9a** was not active enough to compel the MOB **6** to act as a dienophile, as a result of which only bicyclo[2.2.2]octenone **11a** was isolated in 24% yield along with the 6% of *exo*-adduct **11a′**. In contrast, MOB **6** showed dienophilicity along with the dienic character when the Diels−Alder reactions were carried out with other dienes **9b** and **9c**, furnishing *cis*-decalins **15b** and **15c**. In these cases also, bicyclo[2.2.2]octenones of *exo*-stereochemistry **11b′** and **11c′** were isolated along with the endo adducts **11b** and **11c**. On the other hand, the Diels−Alder reaction of MOB **6** with the diene **9d** furnished exclusively *cis*-decalin product **15d** in 81% yield presumably due to the suppressed diene character of MOB **6** and the two electron-releasing methyl groups of the symmetrical 1,3-butadiene **9d**. In other words, the methoxycarbonyl-activated C4−C5 double bond of MOB **6** acts as a dienophile contributor for the electron-rich acyclic diene **9d**. The Diels−Alder reaction of MOB **6** with

SCHEME 2

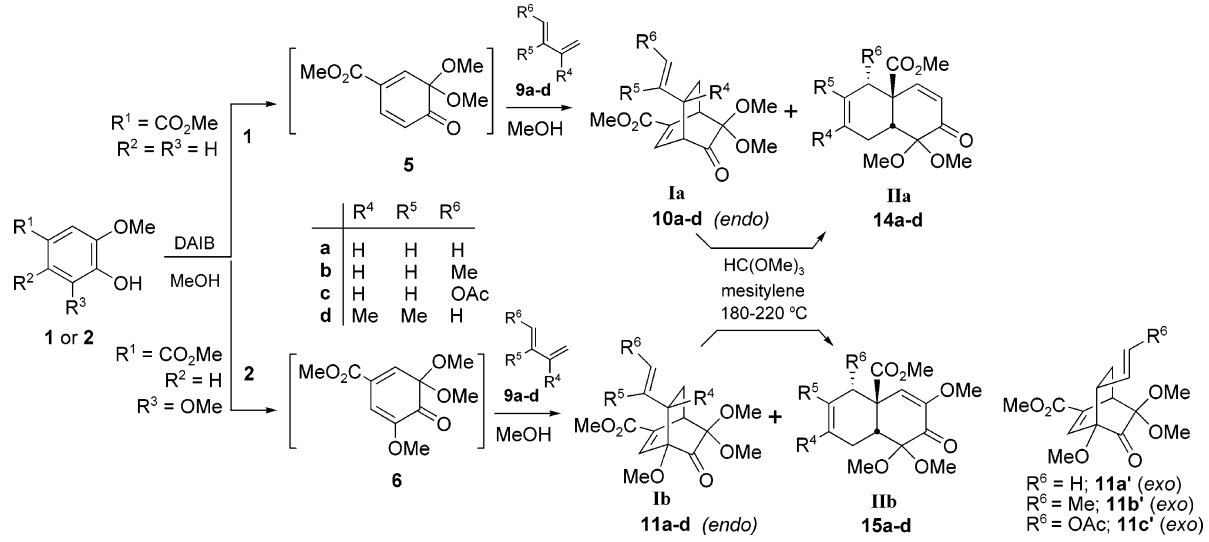


TABLE 1. Intermolecular Diels–Alder Reactions of Masked *o*-Benzoquinones 5–8 with Acyclic Dienes 9a–e

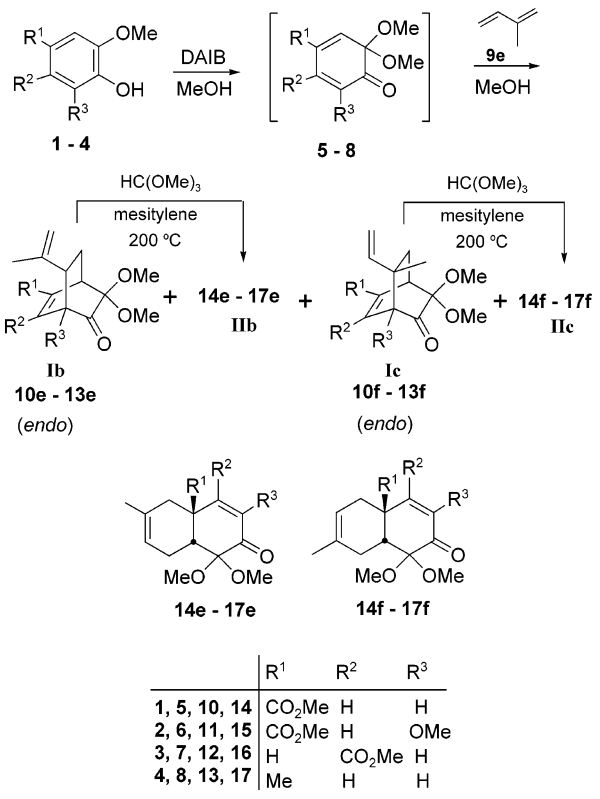
				Diels–Alder reaction[a]					Cope rearrangement of **I**[f]			
						adducts/yield[d](%)						
entry	phenol	MOB	diene[a]	addition time[b]/*T* (°C)	after addition[c]	**I**	**II**	**I**/**II**[e]	*T* (°C)	time (h)	yield[d] of **II** (%)	total yield of **II** (%)
1	**1**	**5**	**9a**	5 min/−20	1 h	**10a**/62	**14a**/17	4:1	200	8	86	70
2			**9b**	3 h/50	10 min	**10b**/55	**14b**/25	2:1	200	50	91[i]	
3			**9c**	5 min/80	10 min	**10c**/62	**14c**/34	2:1	180	40	87	88
4			**9d**	3 h/80	10 min	**10d**/29	**14d**/53	1:2	220	24	95	81
5			**9e**	3 h/50	1 h	**10e**/39	**14e**/15	3:1	200	24	95	52
						10f/15	**14f**/15	1:1	200	24	90	29
6[g]	**2**	**6**	**9a**	2 h/−20	30 min	**11a**/24	**15a**/0	1:0	200	8	78	19
7[g]			**9b**	3 h/50	10 min	**11b**/64	**15b**/11	6:1	180	24	85[i]	
8[g]			**9c**	30 min/80	10 min	**11c**/61	**15c**/16	4:1	200	40	91	72
9			**9d**	3 h/80	10 min	**11d**/0	**15d**/81	0:1				81
10			**9e**	3 h/50	2 h	**11e**/27	**15e**/3	9:1	200	24	91	28
						11f/18	**15f**/6	3:1	200	24	94	
11	**3**	**7**	**9a**	2 h/−20	8 h	**12a**/17	**16a**/0	1:0	200	8	90	15
12			**9b**	6 h/50	10 min	**12b**/81	**16b**/0	1:0	200	50	87[i]	
13			**9c**	2 h/80	10 min	**12c**/64	**16c**/14	5:1	200	40	89	71
14			**9d**	5 h/80	10 min	**12d**/56	**16d**/14	4:1	220	24	86	62
15			**9e**	3 h/50	6 h	**12e**/55	**16e**/0	1:0	200	20	80	44
						12f/9	**16f**/0	1:0	200	20	95	9
16	**4**	**8**	**9a**	5 min/−20	12 h	−/39[h]						
17			**9b**	5 min/rt	48 h	−/45[h]						
18			**9c**	5 min/rt	48 h	−/60[h]						
19			**9d**	5 min/rt	48 h	**13d**/34	**17d**/12	3:1	220	24	98	45
20			**9e**	5 min/rt	48 h	**13e**/45	**17e**/5	9:1	200	24	87	44
						13f/7	**17f**/1	7:1	200	24	92	7

[a] Diels–Alder reactions were carried out following method A using 10 equiv of the acyclic diene. Considerable amount of dimer of the corresponding MOB was isolated in entries 6, 10, 11, and 15–20. [b] Time during which DAIB in MeOH was added to the reaction mixture containing a 2-methoxyphenol and an acyclic diene in MeOH. [c] Time for which the reaction mixture was allowed to stir after the complete addition of DAIB. [d] Yields are of isolated products. [e] Ratio of the products was determined by the ^{1}H NMR spectrum of the crude reaction mixture and adjusted to the nearest whole number. [f] Cope rearrangements of **I** in entries 1–20 were carried out following method B. [g] In the Diels–Alder Reaction of MOB **6** with dienes **9a**, **9b**, and **9c** the exo-adducts **11a′**, **11b′**, and **11c′** were also isolated in 6, 16, 19% yields, respectively. [h] An inseparable mixture of two bicyclo[2.2.2]octenones was obtained. [i] Yields based on the consumed starting material.

isoprene (**9e**) provided cycloadducts **11e** and **11f** along with the *cis*-decalins **15e** and **15f** indicating the lack of chemoselectivity as in the case of cycloaddition of **9e** with MOB **5** (Scheme 3).

To evaluate the effect of the position of an electron-withdrawing group such as methoxycarbonyl as in the present case, MOB **7** generated from methyl isovanillate (**3**) was then taken for the study of its Diels–Alder reactivity with the acyclic dienes under consideration (Scheme 4). Surprisingly, the dienophilicity of the MOB **7** was completely absent in the presence of dienes **9a**, **9b**, and **9e** resulting in the formation of only bicyclo[2.2.2]-octenones **12a**, **12b**, and **12e**, respectively. As in the previous cases, due to the lack of chemoselectivity, the cycloadduct **12f** was also formed in 9% yield along with **12e** in the Diels–Alder reaction of MOB **7** and the diene **9e**. However, in the Diels–Alder reactions with the dienes **9c** and **9d**, the dienophilicity of MOB **7** was exhibited to an extent resulting in the formation of *cis*-decalins **16c** and **16d** along with the cycloadducts **12c** and **12d**, respectively. Thus, the decrease in the dienophilicity of the MOB **7** with the change of the position of

SCHEME 3



the electron-withdrawing group from the postion 4 to 3 in the MOBs is clearly demonstrated. This decrease in

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SCHEME 4

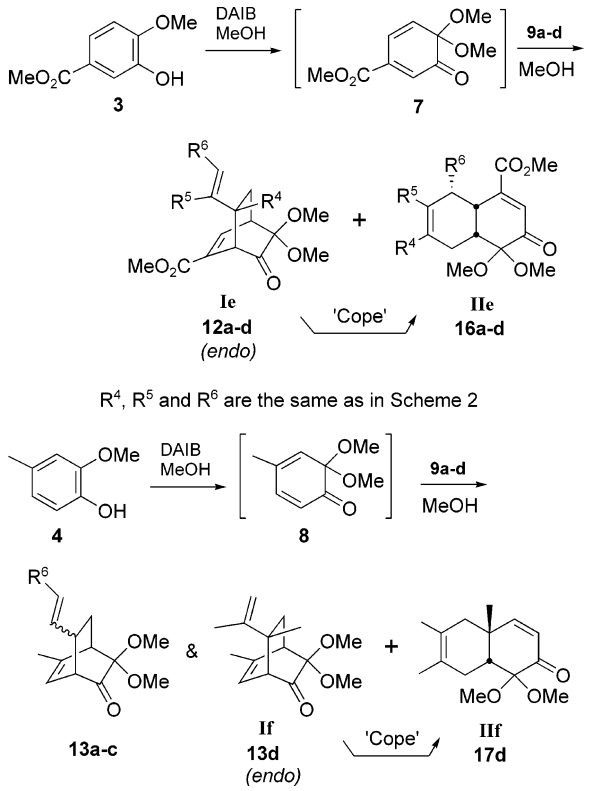
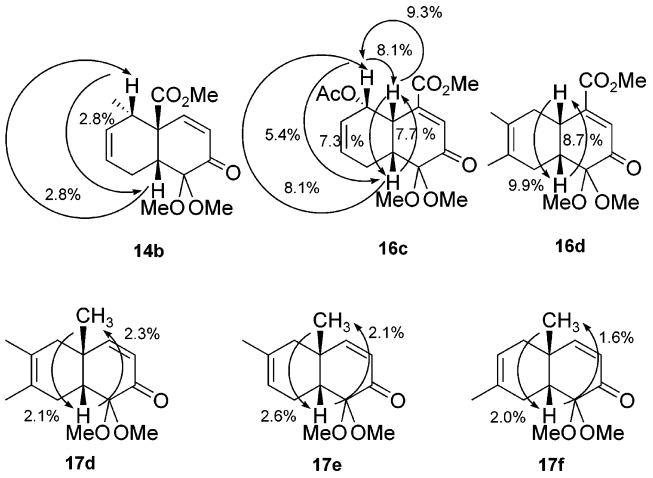


CHART 1. NOE Enhancements of 14b, 16c, and 17d−f



the dienophilicity of MOB **7** may probably be attributed to the cross-conjugation which reinforces the diene character.

To study the variation of the diene and dienophilic characters of MOB with the presence of electron-donating group at position-4, creosol (**4**) was selected (Scheme 4). The corresponding MOB **8** generated in situ showed very poor selectivity, providing inseparable mixtures of only bicyclo[2.2.2]octenones in the Diels−Alder reactions with the dienes **9a**, **9b**, and **9c**, indicating the complete absence of dienophilic character of the MOB **8**. However, with 2,3-dimethyl-1,3-butadiene (**9d**), MOB **8** furnished bicyclo[2.2.2]octenone **13d** and *cis*-decalin **17d** in 34 and 12% yields, respectively, while the Diels−Alder reaction with the diene **9e** furnished a pair of bicyclo[2.2.2]-octenones **13e** and **13f** and *cis*-decalins **17e** and **17f**, as in the cases of aforementioned MOBs. In a nutshell, the presence of electron-releasing methyl group at the position 4 of the MOB **8** enhances the diene character, possibly due to hyperconjugation of the methyl group with the cyclohexa-2,4-diene ring.

As evidenced by the ^{1}H NMR (400 MHz) spectra of the crude reaction mixtures devoid of the peaks corresponding to the minor isomer(s), all the foregoing cycloadditions proceeded in a highly regio- and stereoselective manner, except in the case of MOB **8.** The Diels−Alder reactions of MOBs **5**−**8** with isoprene (**9e**) also suffered from the lack of chemoselectivity.

The structures of all the compounds were established by IR, ^{1}H and ^{13}C NMR, DEPT, and low- and high-resolution mass spectral analyses. For most of the adducts in both low-resolution and high-resolution mass spectra recorded in electron impact mode (70 eV), the peaks corresponding to the molecular ion could not be seen; instead, the peaks corresponding to $M^+ - 28$ were observed, indicating the facile extrusion of CO from the molecular ions.

The regio- and stereochemistry of all the isolated bicyclo[2.2.2]octenones **10**−**13** are in line with the literature precedents.[19,20] The *endo*-stereochemistry of the aforementioned bicyclo[2.2.2]octenones was proved through their ability to undergo the Cope rearrangement. Furthermore, the regio- and stereochemistry of the *cis*-decalins **14b**, **16c**,**d**, and **17d**−**f** were determined using nuclear Overhauser enhancement (NOE) experiments (Chart 1). For the remaining compounds, the stereochemical assignments were based on the pattern of coupling constants and on analogy.

From the results (Table 1) of the intermolecular Diels−Alder reactions of MOBs **5**−**8** with the acyclic dienes **9a**−**e** and the above discussion, it is quite obvious that these MOBs exhibit dual behavior as dienophiles and dienes. The extent of dienophilicity or the diene character apparently depends on the nature and/or position of the substituent present on the MOB and also on the structure of the added acyclic diene. For instance, the dienophile character of the Δ^4 double bond of the 2,4-dienone moiety of MOB **5** increased with an electron-withdrawing (methoxycarbonyl) group at the position 4, and hence, MOB **5** showed optimum reactivity. However, the dienophilicity of all the MOB **5**−**8** is gradually increasing as we move from the acyclic dienes **9a** to **9d** as evidenced from the ratios of the cycloadducts obtained (Table 1). Hence, we can conclude that the presence of an electron-donating group on the acyclic diene compel the MOBs to act more as dienophiles. On the other hand, the electron-withdrawing group present at the position 3 of MOB **7** diminishes its dienophilicity due to cross-conjugation. Similarly, the electron-donating (methyl) group at position 4 of MOB **8** enhances the diene character, probably via hyperconjugation. Moreover, MOB **8** showed very poor selectivity as revealed by the mixture of two bicyclo-[2.2.2]octenones obtained with each of the dienes **9a**−**c**.

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(b) Cope Rearrangement of the Cycloadducts. It was remakable to observe the formation of two types of adducts in the aforementioned intermolecular Diels−Alder reactions that arose from the dual behavior of the corresponding MOBs. Consequently, formation of the cycloadducts **10**−**13** and **14**−**17** provided excellent opportunity to ascertain the role of MOBs and the origin of the adducts as to whether these are obtained as a result of primary cycloaddition or one is an artifact of the other. The *cis*-decalins could result from either direct Diels−Alder reactions, in which MOBs behave as dienophiles or from tandem processes involving Diels−Alder reactions, in which MOBs act as dienes and the resultant vinylbicyclo[2.2.2]octenones then undergo the Cope rearrangement. To ascertain the actual pathway, the bicyclo[2.2.2]octenones **11b** and **12d** were subjected to heating at 80 °C in MeOH containing AcOH and the corresponding diene in the appropriate proportions for 3 h. In the case of **11b**, the crude reaction mixture was found to contain compounds **11b** and **15b** in a 97:3 ratio with the help of ^{1}H NMR spectroscopy. On the other hand, compound **12d** remained unchanged. We therefore believe that the decalins are generally primary products, and not artifacts. Therefore, the present dual Diels−Alder reactions are kinetically controlled reactions since the Cope rearrangement requires higher temperatures. In view of the above, Cope rearrangement of the bicyclo[2.2.2]octenones **10**−**13** obtained from the intermolecular Diels−Alder reactions of our present study has been taken up. Gratifyingly, in all cases, the bicyclo[2.2.2]octenones **10**−**13** when heated to 180−220 °C in mesitylene (method B), underwent Cope rearrangement smoothly, furnishing the corresponding *cis*-decalins **14**−**17** in very high yields (Table 1). It is note worthy that the thermal transformations of the cycloadducts examined are in conformity with the general tendency of 1,5-dienes toward Cope rearrangement in which the position of equilibrium is influenced by the substitution pattern,[21] ring strain,[22] and conjugation.[23]

Conclusion

In summary, we have demonstrated the dual behavior of MOBs with a series of examples. Also, we could deduce some empirical rules regarding the variation of the diene and dienophilic characters of MOBs with their substitution pattern as well as the structure of the added acyclic diene in intermolecular Diels−Alder reactions. The bicyclooctenones smoothly underwent the Cope rearrangement to provide the highly functionalized *cis*-decalins. To our delight, the study of this set of reactions led to the development of a simple, potential, very short (one or two steps) and stereocontrolled route to highly functionalized *cis*-decalins with three stereocenters. The application of this methodology in the total synthesis of decalin-based natural products is underway in our laboratories.

Experimental Section

General Procedure for the Diels−Alder Reactions of MOBs. Method A. In a preheated/precooled bath was placed a flask containing 2-methoxyphenol (**1**−**4**, 2.0 mmol, 1.0 equiv) and an acyclic diene (**9a**−**e**, 20 mmol, 10 equiv) in methanol (8 mL). Subsequently, DAIB (2.4 mmol, 1.2 equiv) in methanol (6 mL) was added under nitrogen atmosphere (see Table 1, for time of addition of DAIB and for other reaction conditions). The reaction mixture was stirred for a period of time, and then MeOH and excess diene were removed and the residue was dissolved in CH_2Cl_2 (20 mL). The solution was washed with saturated aq $NaHCO_3$ and brine and dried ($MgSO_4$). Removal of the solvent followed by silica gel column chromatography with EtOAc/hexanes as eluent furnished the pure cycloadducts. The ratio of the cycloadducts **I** and **II** was determined by ^{1}H NMR analysis of the crude reaction mixture.

General Procedure for Cope Rearrangement. Method B. To a solution of **I** (0.5 mmol) in mesitylene (2.5 mL) was added trimethyl orthoformate (0.5 mmol), and the resulting mixture was degassed with argon for 30 min. The reaction mixture was then heated for a period of time (see Table 1 for the duration of heating and temperature), cooled to room temperatue, and concentrated using a Kugelrohr apparatus. The residue thus obtained was purified by silica gel column chromatography using 15% EtOAc in hexanes as eluent to furnish the pure *cis*-decalin derivative as sole product.

Methyl (1*R,4*R**,8*S**)-6,6-dimethoxy-5-oxo-8-vinylbicyclo[2.2.2]oct-2-ene-2-carboxylate (10a):** colorless liquid; IR (film) 1735, 1728 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17 (ddd, J = 2.8, 6.0, 13.2 Hz, 1H), 2.34 (ddd, J = 3.2, 6.8, 13.2 Hz, 1H), 2.89 (apparent dd, J = 6.0, 8.0 Hz, 1H), 3.27 (dd, J = 1.6, 6.8 Hz, 1H), 3.28 (s, 3H), 3.34 (s, 3H), 3.71 (s, 3H), 3.72 (apparent dd, J = 2.8, 3.2 Hz, 1H), 4.95 (d, J = 10.4 Hz, 1H), 5.00 (d, J = 16.8 Hz, 1H), 5.50 (ddd, J = 8.0, 10.4, 16.8 Hz, 1H), 7.05 (dd, J = 2.0, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.3, 38.1, 39.6, 49.6, 50.5, 52.0, 52.4, 93.5, 115.1, 129.6, 139.1, 143.8, 164.3, 200.9; MS (70 eV) *m*/*z* (relative intensity) 238 (M^+ − CO, 100), 207 (11), 191 (63), 179 (49), 163 (32), 147 (19), 105 (21), 103 (20), 91 (16), 59 (35); HRMS (EI) calcd for $C_{14}H_{18}O_5$ (M^+ − CO) 238.1225, found 238.1199.

Methyl (1*R,4*S**,8*S**)-6,6-dimethoxy-5-oxo-8-[(*E*)-1-propenyl]bicyclo[2.2.2]oct-2-ene-2-carboxylate (10b):** colorless liquid; IR (film) 1742, 1716 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.14 (ddd, J = 2.9, 6.0, 13.2 Hz, 1H), 1.59 (dd, J = 1.5, 6.6 Hz, 3H), 2.29 (ddd, J = 3.1, 9.7, 13.2 Hz, 1H), 2.79−2.86 (m, 1H), 3.24 (dd, J = 1.8, 6.6 Hz, 1H), 3.27 (s, 3H), 3.34 (s, 3H), 3.69 (ddd, J = 1.9, 2.9, 3.1 Hz, 1H), 3.79 (s, 3H), 5.09 (ddq, J = 1.5, 8.5, 15.1 Hz, 1H), 5.44 (ddq, J = 0.8, 6.6, 15.1 Hz, 1H), 7.06 (ddd, J = 0.8, 1.9, 6.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.6, 27.9, 38.4, 38.6, 49.9, 50.2, 52.0, 55.4, 93.3, 125.9, 132.8, 135.7, 137.8, 164.4, 201.1; EIMS *m*/*z* (relative intensity) 280 (M^+, 0.2), 253 (15), 252 (100), 205 (26), 193 (14), 177 (11), 145 (8), 117 (10), 105 (8), 91 (9); HRMS calcd for $C_{15}H_{20}O_5$ (M^+) 280.1311, found 280.1329.

Methyl (1*R,4*S**,8*S**)-8-[(*E*)-2-acetoxy-1-ethenyl]-6,6-dimethoxy-5-oxobicyclo[2.2.2]oct-2-ene-2-carboxylate (10c):** colorless liquid; IR (film) 1759, 1715 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 (ddd, J = 2.8, 5.5, 13.3 Hz, 1H), 2.08 (s, 3H), 2.36 (ddd, J = 2.8, 9.6, 13.3 Hz, 1H), 2.86−2.93 (m, 1H), 3.24 (dd, J = 1.4, 6.6 Hz, 1H), 3.27 (s, 3H), 3.34 (s, 3H), 3.71 (ddd, J = 1.9, 2.8, 2.8 Hz, 1H), 3.79 (s, 3H), 5.11 (dd, J = 9.6, 12.2 Hz, 1H), 7.05 (dd, J = 1.9, 6.6 Hz, 1H), 7.11 (d, J = 12.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 28.1, 33.9, 38.5, 49.9, 50.2, 52.0, 55.1, 93.1, 116.4, 135.1, 136.0, 138.3, 164.1, 167.7, 200.2; EIMS *m*/*z* (relative intensity) 324 (M^+, 0.2), 297 (17), 296 (100), 253 (25), 237 (17), 189 (14), 179 (16), 91 (12),

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75 (13), 43 (33); HRMS calcd for $C_{15}H_{20}O_6$ ($M^+ - 28$) 296.1260, found 296.1249.

Methyl (1*R,4*R**,5*R**)-5-isopropenyl-7,7-dimethoxy-5-methyl-8-oxobicyclo[2.2.2]oct-2-ene-2-carboxylate (10d):** colorless solid; mp 78−79 °C (from EtOAc−hexanes); IR (film) 1741, 1716 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.18 (s, 3H), 1.68 (d, J = 1.2 Hz, 3H), 1.74 (dd, J = 3.2, 13.3 Hz, 1H), 1.91 (dd, J = 2.8, 13.3 Hz, 1H), 3.29 (s, 3H), 3.34 (d, J = 6.4 Hz, 1H), 3.37 (s, 3H), 3.68 (ddd, J = 2.0, 2.8, 3.2 Hz, 1H), 3.75 (s, 3H), 4.59 (apparent s, 1H), 4.70 (apparent q, J = 1.2 Hz, 1H), 7.09 (dd, J = 2.0, 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8, 27.6, 32.2, 38.6, 44.6, 49.7, 50.0, 51.9, 58.9, 93.5, 110.1, 135.7, 137.9, 149.9, 164.5, 202.5; EIMS m/z (relative intensity) 294 (M^+, 1), 266 (100), 251 (22), 219 (29), 191 (23), 159 (22), 131 (20), 105 (22), 91 (34), 59 (23); HRMS calcd for $C_{16}H_{22}O_5$ (M^+) 294.1468, found 294.1458. Anal. Calcd for $C_{16}H_{22}O_5$: C, 65.29; H, 7.53. Found: C, 65.19; H, 7.54.

Methyl (1*R,4*S**,8*R**)-8-isopropenyl-6,6-dimethoxy-5-oxobicyclo[2.2.2]oct-2-ene-2-carboxylate (10e):** colorless liquid; IR (film) 1750, 1708 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.24 (ddd, J = 3.0, 6.9, 13.1 Hz, 1H), 1.64 (s, 3H), 2.31 (ddd, J = 3.0, 9.8, 13.1 Hz, 1H), 2.79−2.85 (m, 1H), 3.29 (s, 3H), 3.36 (s, 3H), 3.38 (dd, J = 1.6, 6.8 Hz, 1H), 3.69 (ddd, J = 2.0, 3.0, 3.0 Hz, 1H), 3.78 (s, 3H), 4.61−4.63 (m, 1H), 4.69−4.72 (m, 1H), 7.07 (ddd, J = 0.8, 2.0, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 26.8, 38.5, 41.1, 50.0, 50.1, 51.9, 53.4, 93.2, 110.9, 135.7, 137.0, 145.6, 164.3, 200.7; EIMS m/z (relative intensity) 280 (M^+, 4), 252 (100), 205 (44), 117 (41), 105 (34), 91 (55), 77 (40), 59 (55), 41 (41), 15 (36); HRMS calcd for $C_{14}H_{20}O_4$ ($M^+ - 28$) 252.1362, found 252.1356.

Methyl (1*R,4*R**,5*S**)-7,7-dimethoxy-5-methyl-8-oxo-5-vinylbicyclo[2.2.2]oct-2-ene-2-carboxylate (10f):** colorless liquid; IR (film) 1741, 1717 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.18 (s, 3H), 1.62 (dd, J = 3.3, 13.5 Hz, 1H), 1.91 (dd, J = 2.4, 13.5 Hz, 1H), 3.04 (d, J = 6.6 Hz, 1H), 3.28 (s, 3H), 3.37 (s, 3H), 3.70 (ddd, J = 2.2, 2.4, 3.3 Hz, 1H), 3.78 (s, 3H), 4.88 (d, J = 17.2 Hz, 1H), 4.90 (dd, J = 0.4, 10.6 Hz, 1H), 5.64 (dd, J = 10.6, 17.2 Hz, 1H), 7.06 (dd, J = 2.2, 6.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.4, 33.2, 38.8, 41.7, 49.7, 50.1, 51.9, 60.4, 93.5, 111.8, 136.6, 137.8, 145.7, 164.5, 201.7; EIMS m/z (relative intensity) 280 (M^+, 0.4), 252 (100), 237 (31), 205 (54), 193 (36), 177 (24), 145 (22), 117 (30), 105 (21), 91 (30); HRMS calcd for $C_{14}H_{20}O_4$ ($M^+ - 28$) 252.1362, found 252.1358.

Methyl (1*R,4*S**,8*S**)-4,6,6-trimethoxy-5-oxo-8-vinylbicyclo[2.2.2]oct-2-ene-2-carboxylate (11a):** colorless liquid; IR (film) 1756, 1719 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.29 (ddd, J = 3.0, 5.0, 13.4 Hz, 1H), 2.37 (ddd, J = 2.8, 9.5, 13.4 Hz, 1H), 2.93 (ddd, J = 5.0, 8.3, 9.5 Hz, 1H), 3.28 (s, 3H), 3.36 (s, 3H), 3.55 (s, 3H), 3.65 (dd, J = 2.8, 3.0 Hz, 1H), 3.80 (s, 3H), 5.07 (d, J = 18.0 Hz, 1H), 5.07 (d, J = 18.0 Hz, 1H), 5.54 (ddd, J = 8.3, 9.2, 18.0 Hz, 1H), 7.06 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.5, 37.5, 42.8, 49.8, 50.4, 52.2, 54.0, 86.6, 93.4, 116.8, 136.0, 137.2, 137.6, 163.9, 200.0; MS (70 eV) m/z (relative intensity) 268 (M^+ − CO, 14), 253 (100), 237 (26), 221 (26), 193 (82), 161 (23), 151 (12), 153 (20), 91 (32), 59 (32); HRMS (EI) calcd for $C_{15}H_{20}O_6$ (M^+) 296.1260, found 296.1279.

Methyl (1*R,4*R**,8*R**)-4,6,6-trimethoxy-5-oxo-8-vinylbicyclo[2.2.2]oct-2-ene-2-carboxylate (11a′):** colorless liquid; IR (film) 1756, 1713 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.83−1.87 (m, 2H), 2.69 (ddd, J = 6.0, 9.4, 9.8 Hz, 1H), 3.27 (s, 3H), 3.36 (s, 3H), 3.50 (s, 3H), 3.64 (dt, J = 2.0, 2.8 Hz, 1H), 3.80 (s, 3H), 5.09−5.15 (m, 2H), 5.55 (ddd, J = 9.4, 10.6, 16.6 Hz, 1H), 7.25 (d, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.7, 37.4, 44.5, 49.6, 50.3, 52.1, 53.6, 87.4, 94.0, 118.0, 135.9, 136.7, 137.6, 164.0, 199.3; EIMS m/z (relative intensity) 296 (M^+, 4), 268 (90), 253 (100), 237 (20), 221 (45), 193 (82), 161 (24), 135 (20), 91 (25), 59 (22); HRMS calcd for $C_{15}H_{20}O_6$ (M^+) 296.1260, found 296.1277.

Methyl (1*R,4*R**,8*S**)-4,6,6-trimethoxy-5-oxo-8-[(*E*)-1-propenyl]bicyclo[2.2.2]oct-2-ene-2-carboxylate (11b):** colorless liquid; IR (film) 1756, 1725 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.23 (ddd, J = 3.1, 5.3, 13.4 Hz, 1H), 1.63 (dd, J = 1.6, 6.4 Hz, 3H), 2.35 (ddd, J = 3.1, 9.6, 13.4 Hz, 1H), 2.87 (apparent ddd, J = 5.3, 9.1, 9.6 Hz, 1H), 3.27 (s, 3H), 3.35 (s, 3H), 3.54 (s, 3H), 3.62 (ddd, J = 2.0, 3.1, 3.1 Hz, 1H), 3.80 (s, 3H), 5.12 (ddq, J = 1.6, 9.1, 15.2 Hz, 1H), 5.48 (dq, J = 6.4, 15.2 Hz, 1H), 7.05 (dd, J = 1.6, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.9, 29.1, 37.4, 41.8, 49.8, 50.3, 52.1, 53.8, 87.1, 93.4, 127.6, 130.5, 135.8, 137.5, 163.9, 200.2; EIMS m/z (relative intensity) 310 (M^+, 2), 282 (25), 267 (25), 208 (17), 207 (100), 199 (23), 191 (19), 175 (48), 171 (20), 59 (15); HRMS calcd for $C_{15}H_{22}O_5$ ($M^+ - 28$) 282.1467, found 282.1465.

Methyl (1*R,4*R**,8*R**)-4,6,6-trimethoxy-5-oxo-8-[(*E*)-1-propenyl]bicyclo[2.2.2]oct-2-ene-2-carboxylate (11b′):** colorless solid; mp 85−86 °C (from EtOAc−hexanes); IR (film) 1756, 1715 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.65 (dd, J = 1.6, 6.4 Hz, 3H), 1.76−1.87 (m, 2H), 2.66 (apparent ddd, J = 6.1, 9.5, 9.7 Hz, 1H), 3.27 (s, 3H), 3.37 (s, 3H), 3.48 (s, 3H), 3.62 (ddd, J = 2.0, 3.0, 3.0 Hz, 1H), 3.80 (s, 3H), 5.13 (ddq, J = 1.6, 9.5, 15.0 Hz, 1H), 5.51 (ddq, J = 0.8, 6.4, 15.0 Hz, 1H), 7.24 (d, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.1, 27.3, 37.4, 43.6, 49.5, 50.4, 52.1, 53.4, 87.5, 94.1, 128.6 128.9, 136.5, 137.7, 164.0, 199.4; EIMS m/z (relative intensity) 283 (17), 282 (M^+ − 28, 100), 267 (92), 251 (18), 235 (38), 207 (73), 175 (25), 115 (15), 91 (17), 59 (37); HRMS calcd for $C_{15}H_{22}O_5$ (M^+ − 28) 282.1467, found 282.1479. Anal. Calcd for $C_{16}H_{22}O_6$: C, 61.92; H, 7.15. Found: C, 61.91; H, 7.27.

Methyl (1*R,4*R**,8*S**)-8-[(*E*)-2-acetoxy-1-ethenyl]-4,6,6-trimethoxy-5-oxobicyclo[2.2.2]oct-2-ene-2-carboxylate (11c):** colorless liquid; IR (film) 1759, 1718 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.26 (ddd, J = 3.0, 5.2, 13.4 Hz, 1H), 2.08 (s, 3H), 2.41 (ddd, J = 2.9, 9.8, 13.4 Hz, 1H), 2.90 (apparent ddd, J = 5.2, 9.7, 9.8 Hz, 1H), 3.28 (s, 3H), 3.35 (s, 3H), 3.54 (s, 3H), 3.65 (ddd, J = 2.0, 2.9, 3.0 Hz, 1H), 3.80 (s, 3H), 5.15 (dd, J = 9.7, 12.4 Hz, 1H), 7.04 (dd, J = 1.6, 2.0 Hz, 1H), 7.13 (d, J = 12.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.6, 29.0, 37.3, 37.7, 49.8, 50.3, 52.2, 53.9, 86.7, 93.3, 114.2, 136.3, 136.9, 137.0, 163.7, 167.7, 199.8; EIMS m/z (relative intensity) 354 (M^+, 2), 326 (100), 311 (46), 251 (32), 209 (52), 177 (28), 149 (18), 117 (15), 77 (20), 43 (49); HRMS calcd for $C_{17}H_{22}O_8$ (M^+) 354.1310, found 354.1310.

Methyl (1*R,4*R**,8*R**)-8-[(*E*)-2-acetoxy-1-ethenyl]-4,6,6-trimethoxy-5-oxobicyclo[2.2.2]oct-2-ene-2-carboxylate (11c′):** colorless solid; mp 122−123 °C (from EtOAc−hexanes); IR (film) 1757, 1716 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.80−1.92 (m, 2H), 2.08 (s, 3H), 2.66 (dddd, J = 0.6, 5.6, 10.1, 10.4 Hz, 1H), 3.28 (s, 3H), 3.37 (s, 3H), 3.49 (s, 3H), 3.65 (ddd, J = 2.0, 3.0, 3.0 Hz, 1H), 3.81 (s, 3H), 5.15 (dd, J = 10.1, 12.2 Hz, 1H), 7.15 (dd, J = 0.6, 12.2 Hz, 1H), 7.25 (d, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.6, 27.4, 37.4, 39.3, 49.6, 50.4, 52.2, 53.6, 87.1, 93.9, 112.3, 136.9, 137.2, 137.5, 163.8, 167.8, 199.1; EIMS m/z (relative intensity) 354 (M^+, 1), 326 (100), 311 (35), 279 (35), 251 (54), 220 (28), 211 (42), 209 (52), 117 (22), 43 (37); HRMS calcd for $C_{17}H_{22}O_8$ (M^+) 354.1315, found 354.1300. Anal. Calcd for $C_{17}H_{22}O_8$: C, 57.62; H, 6.26. Found: C, 57.55; H, 6.27.

Methyl (1*R,4*R**,8*S**)-8-isopropenyl-4,6,6-trimethoxy-5-oxobicyclo[2.2.2]oct-2-ene-2-carboxylate (11e):** colorless liquid; IR (film) 1756, 1719 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.31 (ddd, J = 2.8, 6.9, 13.2 Hz, 1H), 1.58 (d, J = 0.8 Hz, 3H), 2.32 (ddd, J = 3.2, 9.9, 13.2 Hz, 1H), 3.03 (ddd, J = 1.2, 6.9, 9.9 Hz, 1H), 3.30 (s, 3H), 3.37 (s, 3H), 3.56 (s, 3H), 3.66 (ddd, J = 1.6, 2.8, 3.2 Hz, 1H), 3.80 (s, 3H), 4.78−4.81 (m, 2H), 7.10 (dd, J = 1.2, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.3, 28.4, 37.3, 45.0, 49.9, 50.0, 52.0, 54.0, 86.4, 93.1, 114.6, 134.9, 137.3, 143.9, 163.8, 199.2; EIMS m/z (relative intensity) 310 (M^+, 2), 283 (17), 282 (100), 267 (52), 251 (18), 235 (18), 207 (52), 193 (8), 175 (20), 123 (9); HRMS calcd for $C_{16}H_{22}O_6$ (M^+) 310.1417, found 310.1422.

Methyl (1*R,4*S**,5*S**)-4,7,7-trimethoxy-5-methyl-8-oxo-5-vinylbicyclo[2.2.2]oct-2-ene-2-carboxylate (11f):** colorless solid; mp 96−97 °C (from EtOAc−hexanes); IR (film) 1732, 1713 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.12 (s, 3H), 1.76 (dd, J = 3.6, 13.8 Hz, 1H), 1.90 (dd, J = 2.4, 13.8 Hz, 1H), 3.27 (s,

3H), 3.39 (s, 3H), 3.52 (s, 3H), 3.64 (ddd, J = 2.0, 2.4, 3.6 Hz, 1H), 3.81 (s, 3H), 4.92 (d, J = 16.8 Hz, 1H), 5.00 (d, J = 11.2 Hz, 1H), 5.78 (dd, J = 11.2, 16.8 Hz, 1H), 7.18 (d, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.1, 34.8, 37.6, 46.0, 49.6, 50.2, 52.1, 55.3, 90.8, 93.1, 113.4, 135.7, 137.1, 143.3, 164.0, 200.7; EIMS *m/z* (relative intensity) 310 (M^+, 57), 278 (48), 267 (41), 251 (100), 123 (79), 191 (32), 175 (27), 159 (25), 91 (19), 59 (18); HRMS calcd for $C_{16}H_{22}O_6$ (M^+) 310.1416, found 280.1407. Anal. Calcd for $C_{16}H_{22}O_6$: C, 61.92; H, 7.15. Found: C, 61.84; H, 7.16.

Methyl (1*R*,4R*,7S)-5,5-dimethoxy-6-oxo-7-vinylbicyclo[2.2.2]oct-2-ene-2-carboxylate (12a):** colorless liquid; IR (film) 1742, 1719 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.13 (ddd, J = 3.0, 9.6, 13.2 Hz, 1H), 2.22 (ddd, J = 2.8, 6.0, 13.2 Hz, 1H), 2.83 (apparent dd, J = 6.0, 7.2 Hz, 1H), 3.24 (m, 1H), 3.25 (s, 3H), 3.30 (s, 3H), 3.67 (dd, J = 2.0, 2.4 Hz, 1H), 3.70 (s, 3H), 4.90 (d, J = 10.4 Hz, 1H), 4.98 (d, J = 17.6 Hz, 1H), 5.44 (ddd, J = 7.2, 10.4, 17.6 Hz, 1H), 7.37 (dd, J = 7.2, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.2, 38.1, 39.6, 49.6, 50.4, 52.3, 93.4, 115.0, 129.5, 139.1, 143.8, 164.3, 137.2, 200.9; MS (70 eV) *m/z* (relative intensity) 238 (M^+ - CO, 100), 209 (26), 191 (44), 179 (42), 163 (42), 131 (33), 119 (23), 105 (72), 77 (71), 59 (71); HRMS (EI) calcd for $C_{14}H_{18}O_5$ ($M^+ - CO$) 238.1205, found 238.1201.

Methyl (1S*,4R*,7S*)-5,5-dimethoxy-6-oxo-7-[(*E*)-1-propenyl]bicyclo[2.2.2]oct-2-ene-2-carboxylate (12b): colorless liquid; IR (film) 1741, 1721 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10 (ddd, J = 2.8, 5.6, 13.2 Hz, 1H), 1.57 (ddd, J = 0.5, 1.6, 6.5 Hz, 3H), 2.23 (ddd, J = 3.0, 9.7, 13.2 Hz, 1H), 2.77−2.85 (m, 1H), 3.23 (ddd, J = 2.8, 3.0, 7.1 Hz, 1H), 3.27 (s, 3H), 3.32 (s, 3H), 3.65 (dd, J = 1.8, 1.8 Hz, 1H), 3.75 (s, 3H), 5.05 (ddq, J = 1.6, 8.2, 15.1 Hz, 1H), 5.44 (ddq, J = 1.0, 6.5, 15.1 Hz, 1H), 7.39 (dd, J = 1.8, 7.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.7, 26.9, 37.3, 39.6, 49.6, 50.4, 51.9, 52.8, 93.3, 125.9, 129.5, 131.9, 143.7, 164.3, 201.2; EIMS *m/z* (relative intensity) 280 (M^+, 1), 252 (100), 205 (20), 193 (18), 128 (26), 117 (27), 105 (20), 91 (37), 75 (25), 59 (39); HRMS calcd for $C_{15}H_{20}O_5$ (M^+) 280.1311, found 280.1312.

Methyl (1S*,4R*,7S*)-7-[(*E*)-2-acetoxy-1-ethenyl]-5,5-dimethoxy-6-oxobicyclo[2.2.2]oct-2-ene-2-carboxylate (12c): colorless liquid; IR (film) 1747, 1717 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (ddd, J = 3.0, 5.6, 13.3 Hz, 1H), 2.07 (s, 3H), 2.30 (ddd, J = 2.9, 9.8, 13.3 Hz, 1H), 2.85−2.92 (m, 1H), 3.25 (ddd, J = 2.9, 3.0, 7.0 Hz, 1H), 3.28 (s, 3H), 3.33 (s, 3H), 3.66 (dd, J = 1.9, 2.0 Hz, 1H), 3.76 (s, 3H), 5.08 (dd, J = 9.2, 12.4 Hz, 1H), 7.12 (dd, J = 0.8, 12.4 Hz, 1H), 7.42 (dd, J = 1.9, 7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 27.3, 33.2, 39.5, 49.7, 50.5, 52.1, 52.7, 93.3, 115.8, 129.5, 136.2, 144.2, 164.3, 167.9, 200.6; EIMS *m/z* (relative intensity) 324 (M^+, 0.2), 296 (75), 237 (59), 236 (23), 209 (21), 207 (21), 101 (21), 91 (34), 59 (22), 43 (100); HRMS calcd for $C_{15}H_{20}O_6$ (M^+ − 28) 296.1260, found 296.1257.

Methyl (1S*,4R*,7R*)-7-isopropenyl-5,5-dimethoxy-7-methyl-6-oxobicyclo[2.2.2]oct-2-ene-2-carboxylate (12d): colorless liquid; IR (film) 1739, 1715 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (s, 3H), 1.70 (d, J = 0.8 Hz, 3H), 1.79, 1.82 (ABX, J = 13.8, 3.0 Hz, 2H), 3.24 (dt, J = 3.0, 7.0 Hz, 1H), 3.29 (s, 3H), 3.35 (s, 3H), 3.72 (s, 3H), 3.75 (d, J = 1.6 Hz, 1H), 4.63 (apparent s, 1H), 4.69 (apparent d, J = 0.8 Hz, 1H), 7.29 (dd, J = 1.6, 7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.7, 27.5, 31.3, 39.7, 43.7, 49.5, 50.2, 51.8, 56.5, 93.5, 110.9, 131.9, 142.8, 149.1, 164.2, 202.3; EIMS *m/z* (relative intensity) 294 (M^+, 2), 266 (100), 251 (31), 219 (25), 209 (56), 207 (27), 197 (25), 101 (54), 91 (37), 59 (37); HRMS calcd for $C_{16}H_{22}O_5$ (M^+) 294.1468, found 294.1472.

Methyl (1S*,4R*,7R*)-7-isopropenyl-5,5-dimethoxy-6-oxobicyclo[2.2.2]oct-2-ene-2-carboxylate (12e): colorless liquid; IR (film) 1742, 1723 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (ddd, J = 2.8, 6.8, 13.2 Hz, 1H), 1.67 (s, 3H), 2.22 (ddd, J = 3.2, 9.6, 13.2 Hz, 1H), 2.78 (ddd, J = 1.6, 6.8, 9.6 Hz, 1H), 3.26−3.30 (m, 4H), 3.35 (s, 3H), 3.74 (s, 3H), 3.82 (dd, J = 1.6, 2.0 Hz, 1H), 4.63 (br s, 1H), 4.70 (br s, 1H), 7.38 (dd, J = 2.0, 7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 25.5, 39.5, 40.2, 49.7, 50.4, 51.0, 51.9, 93.3, 111.0, 129.6, 143.4, 145.1, 164.3, 201.0; EIMS *m/z* (relative intensity) 280 (M^+, 1), 252 (100), 209 (90), 205 (32), 193 (33), 117 (36), 101 (37), 91 (45), 75 (34), 59 (50); HRMS calcd for $C_{15}H_{20}O_5$ (M^+) 280.1311, found 280.1298.

Methyl (1S*,4R*,7S*)-5,5-dimethoxy-7-methyl-6-oxo-7-vinylbicyclo[2.2.2]oct-2-ene-2-carboxylate (12f): colorless liquid; IR (film) 1739, 1720 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17 (s, 3H), 1.60 (dd, J = 3.2, 13.6 Hz, 1H), 1.81 (dd, J = 2.0, 13.6 Hz, 1H), 3.14−3.27 (m, 1H), 3.27 (s, 3H), 3.34 (s, 3H), 3.44 (d, J = 1.2 Hz, 1H), 3.71 (s, 3H), 4.88 (d, J = 16.8 Hz, 1H), 4.89 (d, J = 11.2 Hz, 1H), 5.59 (dd, J = 11.2, 16.8 Hz, 1H), 7.33 (dd, J = 1.2, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.8, 32.2, 39.9, 40.9, 49.6, 50.4, 52.0, 58.1, 93.7, 112.3, 131.8, 142.9, 145.0, 164.3, 201.7; EIMS *m/z* (relative intensity) 252 ($M^+ - CO$, 100), 237 (21), 205 (28), 193 (33), 177 (24), 161 (14), 145 (18), 117 (27), 91 (40), 59 (32); HRMS calcd for $C_{14}H_{20}O_4$ ($M^+ - CO$) 252.1362, found 252.1360.

(1R*,4R*,7R*)-7-Isopropenyl-3,3-dimethoxy-5,7-dimethylbicyclo[2.2.2]oct-5-en-2-one (13d): colorless liquid; IR (film) 1734 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.13 (s, 3H), 1.69 (d, J = 0.8 Hz, 3H), 1.71 (dd, J = 2.8, 13.2 Hz, 1H), 1.78 (dd, J = 2.8, 13.2 Hz, 1H), 1.84 (d, J = 2.0 Hz, 3H), 2.82 (dt, J = 2.0, 2.8 Hz, 1H), 3.05 (d, J = 6.4 Hz, 1H), 3.32 (s, 3H), 3.34 (s, 3H), 4.60 (apparent s, 1H), 4.70 (dq, J = 0.8, 0.8 Hz, 1H), 5.69 (ddq, J = 2.0, 2.0, 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.0, 21.0, 27.6, 32.4, 43.7, 43.9, 49.4, 50.3, 57.5, 94.3, 109.7, 120.1, 143.0, 150.7, 203.9; EIMS *m/z* (relative intensity) 250 (M^+, 4), 222 (79), 218 (62), 171 (100), 147 (40), 143 (29), 105 (32), 91 (43), 77 (46), 41 (29); HRMS calcd for $C_{15}H_{22}O_3$ (M^+) 250.1569, found 250.1564.

(1R*,4R*,7R*)-7-Isopropenyl-3,3-dimethoxy-5-methylbicyclo[2.2.2]oct-5- en-2-one (13e): colorless liquid; IR (film) 1738 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (ddd, J = 2.8, 7.2, 12.8 Hz, 1H), 1.65 (s, 3H), 1.88 (d, J = 1.6 Hz, 3H), 2.16 (ddd, J = 3.0, 9.6, 12.8 Hz, 1H), 2.69 (ddd, J = 1.6, 7.2, 9.6 Hz, 1H), 2.87 (ddd, J = 2.0, 2.8, 3.0 Hz, 1H), 3.07 (dd, J = 1.6, 6.4 Hz, 1H), 3.31 (s, 3H), 3.33 (s, 3H), 4.61−4.63 (m, 1H), 4.67−4.69 (m, 1H), 5.64−5.67 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 21.7, 26.8, 40.4, 43.9, 49.8, 50.3, 52.0, 94.1, 110.2, 117.9, 144.3, 146.5, 202.2; EIMS *m/z* (relative intensity) 236 (M^+, 4), 208 (93), 133 (50), 119 (28), 105 (31), 91 (47), 77 (28), 75 (45), 41 (100), 39 (53); HRMS calcd for $C_{14}H_{20}O_3$ (M^+) 236.1412, found 236.1398.

(1R*,4R*,7S*)-3,3-Dimethoxy-5,7-dimethyl-7-vinylbicyclo[2.2.2]oct-5-en-2-one (13f): colorless liquid; IR (film) 1736 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.13 (s, 3H), 1.53 (dd, J = 3.2, 13.4 Hz, 1H), 1.77 (dd, J = 2.0, 13.4 Hz, 1H), 1.87 (d, J = 1.6 Hz, 3H), 2.70 (d, J = 6.4 Hz, 1H), 2.82−2.84 (m, 1H), 3.31 (s, 3H), 3.32 (s, 3H), 4.86 (d, J = 17.2 Hz, 1H), 4.87 (d, J = 10.6 Hz, 1H), 5.64−5.70 (m, 1H), 5.71 (dd, J = 10.6, 17.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 26.1, 33.4, 40.9, 44.1, 49.5, 50.3, 59.3, 94.4, 110.9, 119.8, 143.9, 146.7, 203.4; EIMS *m/z* (relative intensity) 236 (M^+, 2), 208 (100), 193 (29), 177 (23), 153 (29), 133 (88), 119 (40), 105 (35), 91 (54), 75 (41); HRMS calcd for $C_{13}H_{20}O_2$ (M^+ − 28) 208.1464, found 208.1469.

Methyl (4aS*,8aR*)-1,1-dimethoxy-2-oxo-1,2,4a,5,8,8a-hexahydro-4a-naphthalenecarboxylate (14a): colorless solid (from EtOAc−hexanes); IR (film) 1732, 1698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.67 (dddd, J = 2.6, 5.6, 9.6, 17.2 Hz, 1H), 2.17 (dddd, J = 2.6, 4.6, 9.6, 17.2 Hz, 1H), 2.25 (ddd, J = 1.8, 6.0, 17.0 Hz, 1H), 2.57 (ddd, J = 2.4, 6.0, 17.0 Hz, 1H), 3.05 (s, 3H), 3.19 (ddd, J = 2.0, 9.6, 9.6 Hz, 1H), 3.27 (s, 3H), 3.68 (s, 3H), 5.60 (dtt, J = 2.6, 6.0, 10.0 Hz, 1H), 5.67 (ddddd, J = 1.8, 2.4, 4.6, 5.6, 10.0 Hz, 1H), 5.98 (d, J = 10.4 Hz, 1H), 6.58 (dd, J = 2.0, 10.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.2, 35.3, 39.5, 47.1, 47.8, 50.8, 52.2, 99.3, 122.7, 125.5, 127.6, 150.7, 175.7, 191.9; MS (70 eV) *m/z* (relative intensity) 266 (M^+, 15), 238 (26), 234 (7), 178 (51), 178 (28), 131 (27), 127 (51), 119 (100), 101 (55), 91 (4); HRMS (EI) calcd

for $C_{14}H_{18}O_5$ (M^+) 266.1154, found 266.1159. Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81. Found: C, 63.15; H, 6.76.

Methyl (4a*S,5*S**,8a*R**)-1,1-dimethoxy-5-methyl-2-oxo-1,2,4a,5,8,8a-hexahydro-4a-naphthalenecarboxylate (14b):** colorless solid; mp 106−107 °C (from EtOAc−hexanes); IR (film) 1732, 1696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.06 (d, J = 7.2 Hz, 3H), 1.63−1.73 (m, 1H), 2.16−2.26 (m, 1H), 2.73−2.82 (m, 1H), 3.09 (s, 3H), 3.21 (ddd, J = 2.0, 8.6, 9.4 Hz, 1H), 3.30 (s, 3H), 3.70 (s, 3H), 5.44 (ddt, J = 2.0, 2.2, 9.8 Hz, 1H), 5.56 (ddt, J = 3.4, 3.5, 9.8 Hz, 1H), 6.03 (d, J = 10.6 Hz, 1H), 6.79 (dd, J = 2.0, 10.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.6, 23.9, 37.0, 42.0, 47.9, 50.9, 51.3, 52.1, 99.5, 125.4, 128.3, 130.0, 145.5, 175.3, 192.1; EIMS *m*/*z* (relative intensity) 280 (M^+, 43), 169 (31), 133 (100), 129 (31), 127 (32), 115 (33), 105 (30), 101 (84), 91 (39), 59 (43); HRMS calcd for $C_{15}H_{20}O_5$ (M^+) 280.1311, found 280.1318. Anal. Calcd for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 64.2; H, 7.17.

Methyl (4a*S,5*S**,8a*R**)-5-acetoxy-1,1-dimethoxy-2-oxo-1,2,4a,5,8,8a-hexahydro-4a-naphthalenecarboxylate (14c):** colorless solid; mp 126−127 °C (from EtOAc−hexanes); IR (film) 1739, 1696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.72 (ddddd, J = 2.6, 3.0, 3.1, 9.1, 20.0 Hz, 1H), 2.09 (s, 3H), 2.24 (ddddd, J = 2.5, 2.9, 3.0, 8.5, 20.0 Hz, 1H), 3.09 (s, 3H), 3.30 (s, 3H), 3.31 (ddd, J = 1.9, 8.5, 9.1 Hz, 1H), 3.69 (s, 3H), 5.57 (dddd, J = 2.2, 2.5, 2.6, 10.2 Hz, 1H), 5.68 (dddd, J = 3.0, 3.1, 3.2, 10.2 Hz, 1H), 5.75−5.80 (m, 1H), 6.10 (d, J = 10.4 Hz, 1H), 7.02 (dd, J = 1.9, 10.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 23.8, 40.4, 48.0, 51.0, 51.1, 52.5, 73.5, 99.0, 125.7, 127.9, 128.7, 144.4, 169.6, 173.2, 191.6; EIMS *m*/*z* (relative intensity) 324 (M^+, 14), 265 (50), 236 (29), 233 (27), 194 (100), 189 (27), 135 (46), 131 (32), 101 (93), 43 (71); HRMS calcd for $C_{16}H_{20}O_7$ (M^+) 324.1209, found 324.1204. Anal. Calcd for $C_{16}H_{20}O_7$: C, 59.25; H, 6.22. Found: C, 59.06; H, 6.21.

Methyl (4a*S,8a*R**)-1,1-dimethoxy-6,7-dimethyl-2-oxo-1,2,4a,5,8,8a-hexahydro-4a-naphthalenecarboxylate (14d):** colorless solid; mp 119−120 °C (from EtOAc−hexanes); IR (film) 1734, 1697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.54 (s, 3H), 1.57−1.67 (m, 1H), 1.61 (s, 3H), 2.00−2.08 (m, 1H), 2.09 (apparent d, J = 16.4 Hz, 1H), 2.58−2.66 (m, 1H), 3.07 (s, 3H), 3.18 (ddd, J = 2.1, 8.2, 10.2 Hz, 1H), 3.30 (s, 3H), 3.69 (s, 3H), 5.97 (d, J = 10.2 Hz, 1H), 6.56 (dd, J = 2.1, 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.4, 18.9, 29.7, 40.4, 42.1, 47.7, 48.2, 50.8, 52.1, 99.5, 122.4, 124.5, 127.6, 150.6, 175.6, 191.9; EIMS *m*/*z* (relative intensity) 294 (M^+, 64), 262 (100), 203 (40), 175 (38), 155 (45), 147 (67), 146 (43), 101 (64), 91 (40), 59 (58); HRMS calcd for $C_{16}H_{22}O_5$ (M^+) 294.1468, found 294.1459. Anal. Calcd for $C_{16}H_{22}O_5$: C, 65.29; H, 7.53. Found: C, 65.21; H, 7.55.

Methyl (4a*S,8a*R**)-1,1-dimethoxy-6-methyl-2-oxo-1,2,-4a,5,8,8a-hexahydro-4a-naphthalenecarboxylate (14e):** colorless solid; mp 127−128 °C (from EtOAc−hexanes); IR (film) 1735, 1696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.61−1.73 (m, 4H), 2.06−2.22 (m, 2H), 2.54−2.62 (m, 1H), 3.07 (s, 3H), 3.13 (dt, J = 2.0, 9.0 Hz, 1H), 3.29 (s, 3H), 3.70 (s, 3H), 5.28−5.33 (m, 1H), 5.97 (d, J = 10.1 Hz, 1H), 6.57 (dd, J = 2.0, 10.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.2, 23.5, 39.1, 40.2, 47.8, 48.0, 50.8, 52.2, 99.4, 119.3, 127.5, 130.3, 150.5, 175.8, 191.9; EIMS *m*/*z* (relative intensity) 280 (M^+, 67), 249 (40), 248 (60), 221 (24), 189 (31), 161 (24), 141 (72), 133 (67), 129 (24), 101 (100); HRMS calcd for $C_{15}H_{20}O_5$ (M^+) 280.1311, found 280.1301. Anal. Calcd for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 64.23; H, 7.25.

Methyl (4a*S,8a*R**)-1,1-dimethoxy-7-methyl-2-oxo-1,2,-4a,5,8,8a-hexahydro-4a-naphthalenecarboxylate (14f):** colorless liquid; IR (film) 1735, 1698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.55−1.60 (m, 1H), 2.04 (dd, J = 8.0, 19.6 Hz, 1H), 2.24 (dd, J = 6.0, 16.8 Hz, 1H), 2.56 (dddd, J = 2.8, 2.8, 5.6, 16.8 Hz, 1H), 3.08 (s, 3H), 3.23 (ddd, J = 2.4, 8.0, 9.6 Hz, 1H), 3.30 (s, 3H), 3.69 (s, 3H), 5.35−5.40 (m, 1H), 5.98 (d, J = 10.4 Hz, 1H), 6.58 (dd, J = 2.4, 10.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.9, 28.0, 35.8, 40.2, 47.2, 47.9, 50.9, 52.3, 99.4, 117.2, 127.6, 133.0, 151.1, 175.9, 192.1; EIMS *m*/*z* (relative intensity) 280 (M^+, 30), 248 (39), 221 (17), 192 (31), 161 (33), 133 (100), 129 (56), 105 (49), 91 (77), 59 (40); HRMS calcd for $C_{15}H_{20}O_5$ (M^+) 280.1311, found 280.1293.

Methyl (4a*S,8a*R**)-1,1,3-trimethoxy-2-oxo-1,2,4a,5,8,-8a-hexahydro-4a-naphthalenecarboxylate (15a):** colorless liquid; IR (film) 1731, 1724 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.15−2.30 (m, 3H), 2.60 (ddd, J = 3.6, 6.4, 17.2 Hz, 1H), 3.08 (s, 3H), 3.18 (ddd, J = 2.0, 8.1, 9.0 Hz, 1H), 3.29 (s, 3H), 3.63 (s, 3H), 3.68 (s, 3H), 5.46 (d, J = 2.0 Hz, 1H), 5.60 (ddd, J = 3.2, 6.4, 10.0 Hz, 1H), 5.69 (ddddd, J = 2.0, 3.6, 6.4, 8.0, 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.2, 36.3, 39.3, 44.6, 48.2, 50.9, 52.3, 55.3, 99.8, 117.0, 122.9, 125.2, 149.3, 176.7, 187.0; MS (70 eV) *m*/*z* (relative intensity) 296 (M^+, 13), 264 (29), 237 (100), 209 (66), 205 (21), 177 (32), 145 (28), 119 (26), 101 (44), 91 (37); HRMS (EI) calcd for $C_{15}H_{20}O_6$ (M^+) 296.1260, found 296.1255.

Methyl (4a*S,5*S**,8a*R**)-1,1,3-trimethoxy-5-methyl-2-oxo-1,2,4a,5,8,8a-hexahydro-4a-naphthalenecarboxylate (15b):** colorless liquid; IR (film) 1731, 1712 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.04 (d, J = 8.4 Hz, 3H), 1.61−1.72 (m, 1H), 2.14−2.24 (m, 1H), 2.73−2.83 (m, 1H), 3.09 (s, 3H), 3.18 (ddd, J = 1.6, 8.0, 9.6 Hz, 1H), 3.29 (s, 3H), 3.64 (s, 3H), 3.68 (s, 3H), 5.42 (ddt, J = 2.0, 2.0, 10.0 Hz, 1H), 5.53 (ddt, J = 3.3, 3.4, 10.0 Hz, 1H), 5.63 (d, J = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.5, 23.8, 37.2, 41.5, 48.0, 48.6, 50.8, 51.9, 55.1, 99.7, 111.4, 124.9, 130.0, 149.8, 176.1, 187.1; EIMS *m*/*z* (relative intensity) 310 (M^+, 8), 282 (100), 267 (31), 251 (54), 223 (51), 219 (32), 199 (32), 171 (28), 159 (30), 101 (64); HRMS calcd for $C_{16}H_{22}O_6$ (M^+) 310.1418, found 310.1416.

Methyl (4a*S,5*S**,8a*R**)-5-acetoxy-1,1,3-trimethoxy-2-oxo-1,2,4a,5,8,8a-hexahydro-4a-naphthalenecarboxylate (15c):** colorless solid; mp 168−169 °C (from EtOAc−hexanes); IR (film) 1736, 1708 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.72 (ddddd, J = 2.4, 2.9, 3.2, 9.1, 20.0 Hz, 1H), 2.11 (s, 3H), 2.23 (ddddd, J = 2.4, 2.8, 3.0, 8.6, 20.0 Hz, 1H), 3.09 (s, 3H), 3.28 (ddd, J = 1.8, 8.6, 9.1 Hz, 1H), 3.29 (s, 3H), 3.67 (s, 3H), 3.69 (s, 3H), 5.56 (dddd, J = 1.9, 2.4, 2.4, 10.2 Hz, 1H), 5.65 (dddd, J = 3.0, 3.1, 3.2, 10.2 Hz, 1H), 5.77−5.80 (m, 1H), 5.86 (d, J = 1.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 23.8, 40.2, 48.3, 48.8, 51.0, 52.5, 55.4, 74.0, 99.4, 110.4, 125.8, 127.5, 150.2, 169.7, 174.0, 186.6; EIMS *m*/*z* (relative intensity) 354 (M^+, 5), 326 (30), 322 (66), 295 (72), 280 (48), 263 (37), 220 (43), 211 (26), 101 (34), 43 (100); HRMS calcd for $C_{17}H_{22}O_8$ (M^+) 354.1315, found 354.1286. Anal. Calcd for $C_{17}H_{22}O_8$: C, 57.62; H, 6.26. Found: C, 57.60; H, 6.27.

Methyl (4a*S,8a*R**)-1,1,3-trimethoxy-6,7-dimethyl-2-oxo-1,2,4a,5,8,8a-hexahydro-4a-naphthalenecarboxylate (15d):** colorless liquid; IR (film) 1740, 1710 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.50 (s, 3H), 1.52−1.66 (m, 4H), 1.97−2.06 (m, 2H), 2.59−2.68 (m, 1H), 3.07 (s, 3H), 3.15 (dt, J = 1.9, 9.0 Hz, 1H), 3.29 (s, 3H), 3.63 (s, 3H), 3.68 (s, 3H), 5.42 (d, J = 1.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.4, 18.9, 29.5, 39.9, 42.8, 45.4, 48.1, 50.8, 52.2, 55.3, 99.8, 117.0, 122.3, 123.6, 149.1, 176.7, 187.1; EIMS *m*/*z* (relative intensity) 324 (M^+, 14), 323 (14), 205 (35), 105 (39), 101 (47), 91 (57), 77 (38), 59 (76), 43 (100), 15 (39); HRMS calcd for $C_{17}H_{23}O_6$ ($M^+ - 1$) 323.1495, found 323.1495.

Methyl (4a*S,8a*R**)-1,1,3-trimethoxy-6-methyl-2-oxo-1,2,4a,5,8,8a-hexahydro-4a-naphthalenecarboxylate (15e):** colorless liquid; IR (film) 1732, 1708 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.64−1.74 (m, 1H), 1.67 (s, 3H), 2.03 (d, J = 16.8 Hz, 1H), 2.09−2.20 (m, 1H), 2.56−2.64 (m, 1H), 3.08 (s, 3H), 3.10 (dt, J = 2.0, 9.0 Hz, 1H), 3.29 (s, 3H), 3.64 (s, 3H), 3.69 (s, 3H), 5.27−5.31 (m, 1H), 5.43 (d, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.3, 23.5, 38.9, 41.1, 45.3, 48.1, 50.8, 52.2, 55.2, 99.8, 116.7, 118.7, 130.3, 149.1, 176.6, 186.9; EIMS *m*/*z* (relative intensity) 310 (M^+, 89), 295 (41), 278 (53), 251 (100), 250 (40), 223 (49), 191 (43), 175 (38), 101 (54), 59 (32); HRMS calcd for $C_{16}H_{22}O_6$ (M^+) 310.1417, found 310.1412.

Methyl (4a*S,8a*R**)-1,1,3-trimethoxy-7-methyl-2-oxo-1,2,4a,5,8,8a-hexahydro-4a-naphthalenecarboxylate (15f):** colorless solid; mp 114−115 °C (from EtOAc−hexanes); IR

(film) 1732, 1709 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.58 (s, 3H), 1.55−1.65 (m, 1H), 2.02 (dd, J = 8.0, 19.2 Hz, 1H), 2.18 (dd, J = 5.2, 16.8 Hz, 1H), 2.59 (dddd, J = 2.8, 4.4, 6.0, 16.8 Hz, 1H), 3.08 (s, 3H), 3.20 (ddd, J = 1.2, 8.0, 9.6 Hz, 1H), 3.29 (s, 3H), 3.63 (s, 3H), 3.68 (s, 3H), 5.37 (ddd, J = 2.0, 4.4, 5.2 Hz, 1H), 5.45 (d, J = 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.9, 28.0, 36.8, 40.0, 44.6, 48.2, 50.9, 52.3, 55.3, 99.9, 117.3, 132.4, 149.2, 176.9, 187.2; EIMS *m*/*z* (relative intensity) 310 (M^+, 16), 278 (20), 251 (68), 223 (91), 191 (52), 159 (60), 105 (61), 91 (70), 59 (69), 15 (100); HRMS calcd for $C_{16}H_{22}O_6$ (M^+) 310.1416, found 310.1418. Anal. Calcd for $C_{16}H_{22}O_6$: C, 61.92; H, 7.15. Found: C, 61.77; H, 7.54.

Methyl (4a*R,8a*S**)-4,4-dimethoxy-3-oxo-3,4,4a,5,8,8a-hexahydro-1-naphthalenecarboxylate (16a):** colorless solid; mp 128−129 °C (from EtOAc−hexanes); IR (film) 1724, 1699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.70−1.90 (m, 1H), 1.95−2.10 (m, 1H), 2.20−2.40 (m, 1H), 2.58 (ddd, J = 2.8, 6.0, 19.2 Hz, 1H), 2.72 (ddd, J = 4.0, 7.2, 8.8 Hz, 1H), 3.15 (s, 3H), 3.30 (s, 3H), 3.42 (ddd, J = 3.2, 6.8, 8.8 Hz, 1H), 3.79 (s, 3H), 5.59 (ddd, J = 2.8, 4.4, 10.0 Hz, 1H), 5.59 (ddd, J = 2.0, 6.0, 10.0 Hz, 1H), 6.39 (d, J = 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 26.7, 32.6, 37.4, 48.2, 50.8, 52.5, 99.4, 125.3, 125.5, 130.1, 151.9, 167.3, 193.3; MS (70 eV) *m*/*z* (relative intensity) 266 (M^+, 25), 251 (100), 235 (45), 207 (17), 179 (20), 140 (30), 115 (25), 101 (66), 91 (10), 59 (50); HRMS (EI) calcd for $C_{14}H_{18}O_5$ (M^+) 266.1154, found 266.1155. Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81. Found: C, 63.09; H, 6.82.

Methyl (4a*R,8*S**,8a*S**)-4,4-dimethoxy-8-methyl-3-oxo-3,4,4a,5,8,8a-hexahydro-1-naphthalenecarboxylate (16b):** colorless liquid; IR (film) 1731, 1701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.03 (d, J = 8.0 Hz, 3H), 1.93 (ddddd, J = 2.3, 3.4, 3.4, 9.2, 19.2 Hz, 1H), 2.08 (ddddd, J = 2.3, 3.3, 3.3, 8.0, 19.2 Hz, 1H), 2.61−2.70 (m, 1H), 2.76 (ddd, J = 4.0, 8.0, 9.2 Hz, 1H), 3.16 (s, 3H), 3.29 (s, 3H), 3.44 (ddd, J = 2.8, 4.0, 5.2 Hz, 1H), 3.78 (s, 3H), 5.51 (dddd, J = 2.1, 2.3, 2.3, 9.9 Hz, 1H), 5.61 (dddd, J = 3.2, 3.3, 3.4, 9.9 Hz, 1H), 6.10 (d, J = 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.6, 22.1, 33.3, 38.9, 39.0, 48.4, 51.0, 52.3, 99.3, 125.0, 128.5, 131.6, 152.3, 168.6, 192.9; EIMS *m*/*z* (relative intensity) 280 (M^+, 29), 265 (100), 252 (49), 249 (36), 248 (26), 154 (43), 115 (26), 114 (21), 101 (57), 91 (22); HRMS calcd for $C_{15}H_{20}O_5$ (M^+) 280.1311, found 280.1307.

Methyl (4a*R,8*S**,8a*S**)-8-acetoxy-4,4-dimethoxy-3-oxo-3,4,4a,5,8,8a-hexahydro-1-naphthalenecarboxylate (16c):** colorless liquid; IR (film) 1731, 1702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.90 (ddddd, J = 2.9, 2.9, 3.2, 10.0, 19.5 Hz, 1H), 2.04−2.14 (m, 1H), 2.05 (s, 3H), 2.90 (ddd, J = 4.0, 7.8, 10.0 Hz, 1H), 3.15 (s, 3H), 3.31 (s, 3H), 3.80 (s, 3H), 3.86 (dddd, J = 1.0, 2.9, 4.0, 5.8 Hz, 1H), 5.54−5.59 (m, 1H), 5.60−5.64 (m, 1H), 5.75 (dddd, J = 3.1, 3.1, 3.2, 10.0 Hz, 1H), 6.03 (dd, J = 0.8, 2.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 21.9, 36.9, 37.3, 48.3, 50.9, 52.4, 70.0, 98.8, 126.9, 127.9, 128.0, 150.0, 168.1, 170.2, 192.3; EIMS *m*/*z* (relative intensity) 324 (M^+, 16), 265 (26), 264 (29), 237 (35), 236 (47), 161 (24), 145 (28), 101 (66), 59 (27), 43 (100); HRMS calcd for $C_{16}H_{20}O_7$ (M^+) 324.1209, found 324.1217.

Methyl (4a*R,8a*S**)-4,4-dimethoxy-6,7-dimethyl-3-oxo-3,4,4a,5,8,8a-hexahydro-1-naphthalenecarboxylate (16d):** colorless liquid; IR (film) 1727, 1699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.52 (s, 3H), 1.56 (s, 3H), 1.68−1.79 (m, 1H), 1.83−1.92 (m, 1H), 2.26−2.36 (m, 1H), 2.39−2.46 (m, 1H), 2.69 (ddd, J = 4.0, 7.2, 11.0 Hz, 1H), 3.15 (s, 3H), 3.31 (s, 3H), 3.36 (dddd, J = 2.4, 3.2, 4.0, 6.0 Hz, 1H), 3.79 (s, 3H), 6.37 (d, J = 3.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.6, 19.0, 27.7, 33.3, 33.5, 38.1, 48.1, 50.7, 52.3, 99.4, 123.8, 124.8, 129.7, 151.8, 167.3, 193.3; EIMS *m*/*z* (relative intensity) 294 (M^+, 25), 279 (37), 219 (14), 159 (17), 131 (16), 119 (17), 118 (20), 101 (100), 91 (22), 59 (16); HRMS calcd for $C_{16}H_{22}O_5$ (M^+) 294.1468, found 294.1472.

Methyl (4a*R,8a*S**)-4,4-dimethoxy-7-methyl-3-oxo-3,4,-4a,5,8,8a-hexahydro-1-naphthalenecarboxylate (16e):** colorless liquid; IR (film) 1726, 1699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.61 (s, 3H), 1.72−1.84 (m, 1H), 1.95−2.05 (m, 1H), 2.27 (apparent d, J = 18.4 Hz, 1H), 2.41 (apparent d, J = 18.4 Hz, 1H), 2.64 (ddd, J = 4.0, 7.2, 11.0 Hz, 1H), 3.15 (s, 3H), 3.29 (s, 3H), 3.42 (dddd, J = 2.3, 2.8, 4.0, 6.1 Hz, 1H), 3.79 (s, 3H), 5.25−5.29 (m, 1H), 6.36 (d, J = 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 23.4, 31.6, 33.3, 37.2, 48.1, 50.6, 52.3, 99.4, 119.0, 129.7, 132.9, 151.6, 167.2, 193.0; EIMS *m*/*z* (relative intensity) 280 (M^+, 73), 265 (100), 249 (26), 181 (30), 154 (23), 117 (28), 105 (27), 101 (69), 91 (37), 59 (29); HRMS calcd for $C_{15}H_{20}O_5$ (M^+) 280.1311, found 280.1321.

Methyl (4a*R,8a*S**)-4,4-dimethoxy-6-methyl-3-oxo-3,4,-4a,5,8,8a-hexahydro-1-naphthalenecarboxylate (16f):** colorless liquid; IR (film) 1725, 1699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.57 (s, 3H), 1.71 (dd, J = 10.4, 18.6 Hz, 1H), 1.87 (ddd, J = 1.2, 7.2, 18.6 Hz, 1H), 2.22−2.32 (m, 1H), 2.55 (apparent dd, J = 4.4, 18.4 Hz, 1H), 2.73 (ddd, J = 6.4, 7.2, 10.4 Hz, 1H), 3.15 (s, 3H), 3.31 (s, 3H), 3.37 (dddd, J = 2.8, 4.0, 4.4, 6.4 Hz, 1H), 5.37 (ddd, J = 1.2, 3.6, 4.8 Hz, 1H) 6.39 (d, J = 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.1, 26.3, 27.0, 32.5, 37.8, 48.1, 50.8, 52.4, 99.4, 119.7, 132.3, 133.0, 152.0, 167.3, 193.4; EIMS *m*/*z* (relative intensity) 280 (M^+, 100), 265 (95), 249 (48), 217 (42), 205 (31), 193 (29), 164 (45), 154 (41), 101 (90), 88 (49); HRMS calcd for $C_{15}H_{20}O_5$ (M^+) 280.1311, found 280.1310.

(4a*R,8a*R**)-1,1-Dimethoxy-4a,6,7-trimethyl-1,2,4a,5,8,-8a-hexahydro-2-naphthalenone (17d):** colorless liquid;. IR (film) 1689 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.32 (s, 3H), 1.51 (s, 3H), 1.58 (s, 3H), 1.73−1.83 (m, 1H), 1.86−1.99 (m, 2H), 2.06−2.14 (m, 1H), 2.37 (ddd, J = 1.8, 7.6, 9.4 Hz, 1H), 3.16 (s, 3H), 3.26 (s, 3H), 5.81 (d, J = 10.0 Hz, 1H), 6.51 (dd, J = 1.8, 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.3, 18.8, 30.2, 30.6, 37.9, 42.9, 46.7, 47.9, 50.2, 99.7, 124.0, 124.4, 125.7, 159.0, 192.9; EIMS *m*/*z* (relative intensity) 250 (M^+, 4), 190 (100), 175 (36), 159 (34), 147 (44), 119 (72), 91 (55), 77 (39), 67 (33), 41 (38); HRMS calcd for $C_{15}H_{22}O_3$ (M^+) 250.1569, found 250.1560.

(4a*R,8a*R**)-1,1-Dimethoxy-4a,6-dimethyl-1,2,4a,5,8,8a-hexahydro-2-naphthalenone (17e):** IR (film) 1687 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.35 (s, 3H), 1.64 (s, 3H), 1.84−1.96 (m, 2H), 2.01−2.13 (m, 2H), 2.32 (dt, J = 1.6, 8.2 Hz, 1H), 3.18 (s, 3H), 3.26 (s, 3H), 5.23−5.30 (m, 1H), 5.84 (d, J = 10.0 Hz, 1H), 6.56 (dd, J = 1.6, 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.2, 24.2, 30.4, 37.7, 41.7, 44.4, 48.1, 50.3, 99.8, 119.4, 125.7, 131.8, 158.9, 192.8; EIMS *m*/*z* (relative intensity) 236 (M^+, 20), 157 (51), 145 (28), 135 (27), 117 (33), 105 (45), 101 (100), 91 (56), 77 (34), 43 (48); HRMS calcd for $C_{14}H_{20}O_3$ (M^+) 236.1412, found 236.1423.

(4a*R,8a*R**)-1,1-Dimethoxy-4a,7-dimethyl-1,2,4a,5,8,8a-hexahydro-2-naphthalenone (17f):** colorless liquid; IR (film) 1689 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.32 (s, 3H), 1.57 (d, J = 0.8 Hz, 3H), 1.79 (dd, J = 8.3, 19.2 Hz, 1H), 1.95 (dd, J = 8.1, 19.2 Hz, 1H), 2.03−2.07 (m, 2H), 2.40 (ddd, J = 1.8, 8.1, 8.3 Hz, 1H), 3.18 (s, 3H), 3.27 (s, 3H), 5.32−5.36 (m, 1H), 5.84 (d, J = 10.1 Hz, 1H), 6.56 (dd, J = 1.8, 10.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.9, 28.8, 30.1, 37.0, 39.9, 42.6, 48.1, 50.3, 99.8, 118.9, 125.9, 133.0, 159.4, 192.9; EIMS *m*/*z* (relative intensity) 236 (M^+, 2), 159 (39), 143 (41), 117 (27), 105 (29), 101 (100), 91 (68), 77 (42), 55 (44), 43 (41); HRMS calcd for $C_{14}H_{20}O_3$ (M^+) 236.1412, found 236.1402.

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Supporting Information Available: ^1H NMR spectra for all the cycloadducts. This material is available free of charge via the Internet at http://pubs.acs.org.

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