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Dual Behavior of Masked *o*-Benzoquinones in Intramolecular Diels−Alder Reactions. Expedient Synthesis of Highly Functionalized *cis*-Decalins from 2-Methoxyphenols

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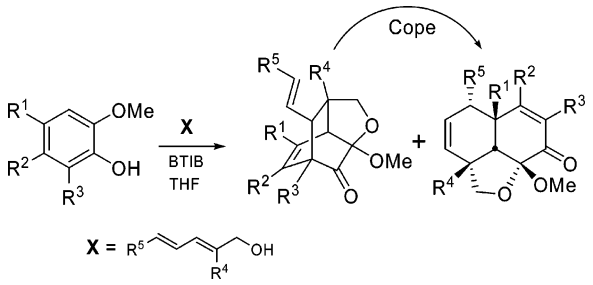

The potential dual behavior as dienes and dienophiles of the diene moieties of masked *o*-benzoquinones (MOBs) **10a**−**e**−**12a**−**e**, generated upon oxidation of 2-methoxyphenols **1**−**3** with BTIB in the presence of appropriate dienols, in their intramolecular Diels−Alder (IMDA) reactions has been examined. The IMDA reactions of MOBs **10a**−**d**, **11a**,**b**,**d**, and **12a**,**b**,**d** resulted in highly functionalized oxatricyclic compounds **18a**−**d**, **19a**,**b**,**d,** and **20a**,**b**,**d**, respectively, with concomitant formation of *cis*-decalin derivatives **21a**−**d**, **22a**,**b**,**d,** and **23a**,**b**,**d** in a highly regio- and stereoselective manner. However, the MOBs **10e**−**12e** provided exclusively oxatricyclic compounds **18e**−**20e**. The formation of *cis*-decalins in these IMDA reactions illustrates the dienophilic character of MOBs, in addition to their 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 2,4-dienol. The majority of the cycloadducts resulted from the diene property of MOBs in intramolecular Diels−Alder reactions smoothly underwent Cope rearrangement to furnish *cis*-decalins as sole products in excellent to quantitative yields that provides a short and efficient entry to polyfunctionized *cis*-decalins from 2-methoxyphenols. Furthermore, the variation of dienophilic and diene characters of MOBs in the IMDA reactions with the electron-donating or electron-withdrawing substituent of both cyclohexadienone moiety and the added conjugated acyclic diene or 2,4-dienol has been studied in detail.

Introduction

The Diels−Alder reaction has become one of the most commonly used paradigms in organic chemistry. It has been enjoying widespread use in organic synthesis owing to its ability of forming two bonds in a cyclohexenyl system and simultaneous creation of up to four stereogenic centers in a highly stereoselective and predictable manner.[1−3] Furthermore, the Diels−Alder reaction is considered as one of the most efficient reactions in terms of atom economy and broad versatility.[4] Particularly, the intramolecular version, i.e., the intramolecular Diels−Alder (IMDA) reaction, is a versatile tool for the rapid construction of polycyclic ring systems with high degree of structural and stereochemical complexity.[3,5] The advantages of an intramolecular reaction over its inter-

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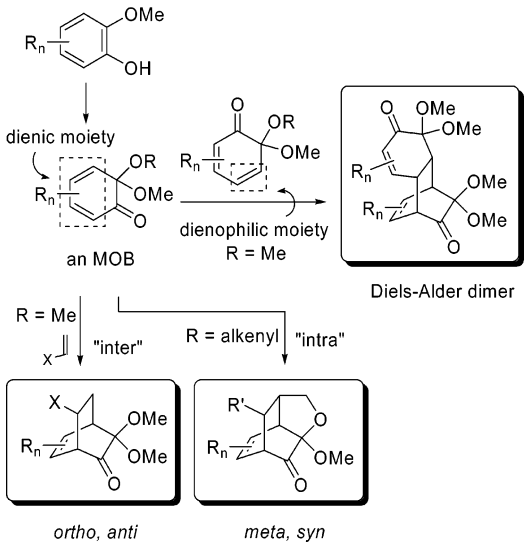
molecular counterpart are well documented in terms of milder reaction conditions, superior reactivity due to favorable entropy considerations, and hightened regioselectivities due to constraints posed by the connecting chain.[6] The IMDA reactions are commonly employed in combination with other reactions in tandem processes.[7] The synthesis of triene precursors required for IMDA reactions is achieved either by (i) in situ tethering of 4π- and 2π-components via alkylation, acylation, and condensation or (ii) in situ generation of either diene or alkene via oxidation, elimination, and retrogradation.[8,9]

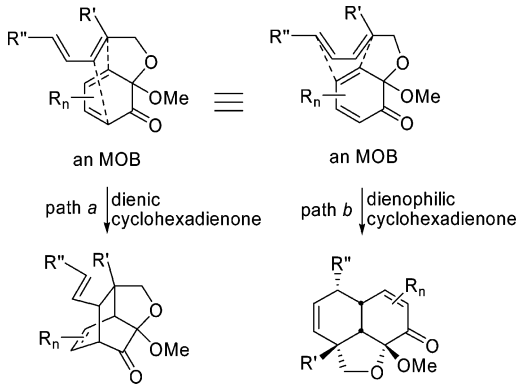
6,6-Dialkoxycyclohexa-2,4-dienones, named as masked *o*-benzoquinones (MOBs)[10a,c] by us, are very reactive cyclic conjugated dienones and readily undergo self-dimerization via Diels−Alder cycloaddition between a dienic MOB and a dienophilic MOB.[11,12a] It was found that oxidation of simple and readily accessible 2-methoxyphenols in methanol with diacetoxyiodobenzene (DAIB) or bis(trifluoroacetoxy)iodobenzene (BTIB) produce highly reactive MOBs.[10c,13,14] We successfully employed MOBs as exclusive 4π-partners in intermolecular Diels−Alder reactions by trapping them with various olefinic dienophiles to furnish bicyclo[2.2.2]oct-5-en-2-one derivatives with complete *ortho*,*anti*-selectivity[12] (the substituent on the dienophile is adjacent and anti to the carbonyl function of the bicyclo[2.2.2]octenone moiety). The IMDA reaction of MOBs, generated in situ by oxidation of 2-methoxyphenols in the presence of allylic and homoallylic alcohols in a tandem oxidative acetalization process, provides oxacyclic compounds with complete *meta*,*syn*-selectivity[15] (with respect to the carbonyl group present in the Diels−Alder adduct) (Scheme 1).

The capacity of the cyclohexa-2,4-dienone unit of MOBs to react as a dienophile component in both inter-[16] and intramolecular[17] Diels−Alder cycloadditions has been

SCHEME 1



SCHEME 2. Dual Behavior of MOBs in IMDA Reactions



encountered in our laboratories. Simultaneously, dienophilic reactivity of MOBs in the IMDA reaction was reported in the total synthesis of naphthofurans and phenanthrofurans[18a] and (±)-xestoquinone.[18b] An *o*-quinol acetate was employed as a dienophile in the Diels−Alder reactions with Brassard's diene to provide functionally rich naphthalenes which were key intermediates in the syntheses of helically chiral molecules.[19] Based on this background, we are interested in employing cyclohexa-2,4-dienone moiety of MOB as dienophile for the construction of highly functionalized *cis*-decalins. We now report herein full details of dual nature of MOBs in their IMDA reactions, together with the results of our studies on the variation of the dienic and dienophilic properties of MOBs with the nature and position of the substituents on both the cyclohexadienone moiety and the tethered acyclic 2,4-dienic unit[17] (Scheme 2). The cycloadducts obtained from the dienic MOB and dienophilic tether

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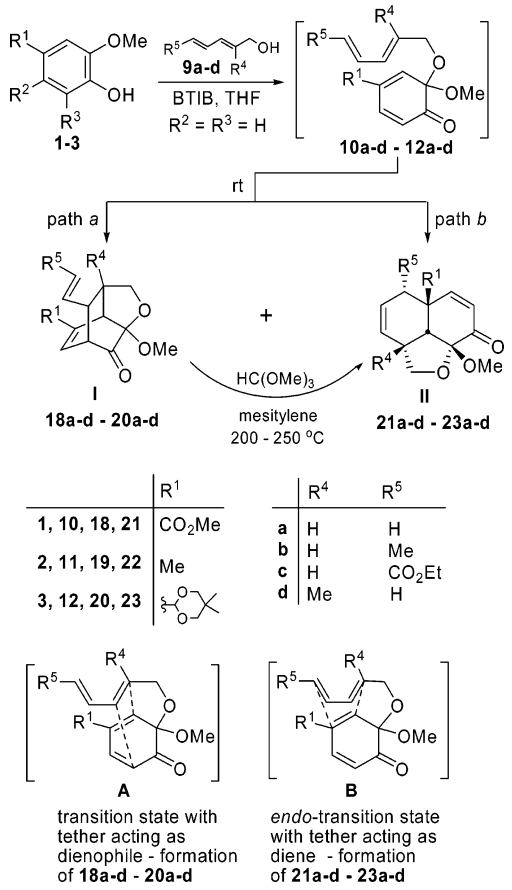
SCHEME 3



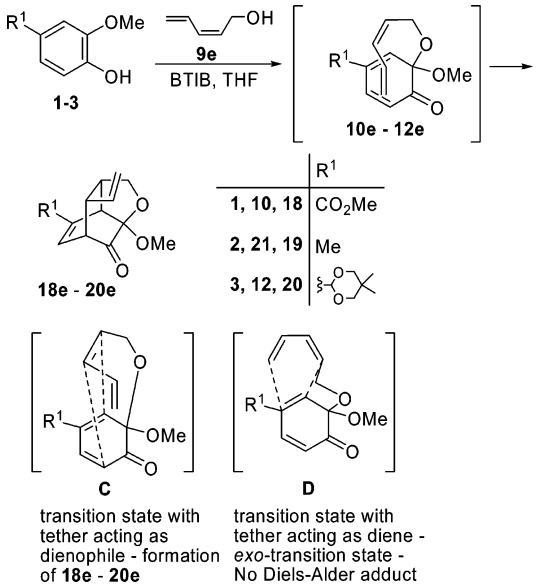
smoothly underwent the Cope rearrangement to provide the highly functionalized *cis*-decalins.

Results and Discussion

(a) Intramolecular Diels–Alder Reactions. The IMDA reactions of MOBs **10a**–**e**–**12a**–**e** generated from the 2-methoxyphenols **1**–**3** in the presence of 2,4-dienols **9a**–**e**, respectively, as outlined in Schemes 3 and 4 were first examined and the results are summarized in Table 1. It may be noted that the 2-methoxyphenols in these cases are all bearing the substituent (methoxycarbonyl, methyl and 5,5-dimethyl-1,3-dioxanyl) at the C-4 position. The reason for such selection is that the resulting *cis*-decalins obtained in the Diels–Alder reactions would possess substitution at the fused position, as most of the decalin-containing natural products have angular substitutions.

Initial investigations were conducted on the MOB **10a** which was generated in situ from methyl vanillate (**1**) in the presence of *trans*-penta-2,4-dienol (**9a**)[20] using BTIB in THF. At room temperature, the MOB **10a**, exhibiting the dual behavior both as a diene (Scheme 3, simplified transition-state structure A) and a dienophile (Scheme 3, simplified transition-state structure B), underwent IMDA reactions to provide the tricyclic compound **18a** and *cis*-decalin derivative **21a** each in 31% isolated yields. Subsequently, this reaction was extended to various 2,4-dienols **9b**–**e**. The reason for choosing such 2,4-dienols

SCHEME 4



is to understand the factors affecting the dual nature of MOBs with these electronically different tethers in the IMDA reactions. Thus, sorbyl alcohol (**9b**), which was expected to have more dienic character, *trans*-5-ethoxycarbonylpenta-2,4-dienol (**9c**),[20] where the presence of an ethoxycarbonyl group increases the dienophilic nature of this tether, were tested along with **9d**. Consequently, the MOBs **10b**–**d** which were generated in situ by the BTIB-mediated oxidation of 2-methoxyphenol **1** in the presence of dienols **9b**–**d**, produced a pair of expected products **18b**, **21b**; **18c**, **21c**; and **18d**, **21d**, respectively. The IMDA reactions of MOBs **10a**,**c**,**d** produced a 1:1 mixture of the corresponding oxatricyclic product **18a**, **18c**, and **18d** and *cis*-decalin **21a**, **21c**, and **21d**, while the MOB **10b** derived from sorbyl alcohol and 2-methoxyphenol **1** gave *cis*-decalin **21b** as the major product. The combined yields of the cycloadducts obtained from the dual reactivity of MOBs are good. Under similar conditions, the MOB **10e** generated from methyl vanillate and *cis*-penta-2,4-dienol (**9e**)[20] could provide only the oxatricyclic compound **18e** (Scheme 4). In the case of MOB **10e**, if the tether were to act as a diene, then its approach to the dienophilic part of cyclohexa-2,4-dienone should be an *endo*-approach in the transition state which is an unfavorable pathway due to ring strain. The other possible reaction pathway should be an *exo*-approach which is not observed, probably due to the high energy associated in the transition state (Scheme 4, simplified transition-state structure D). Consequently, the only other preference is the formation of cycloadduct **18e** (Scheme 4, simplified transition-state structure C). For compound **18e**, though with a 1,5-diene unit, the two double bonds (one terminal and the other being the internal double bond) have a fixed and unfavorable configuration for the Cope rearrangement to occur.

For evaluating the effect of electron-donating substituent on the C_4 of cyclohexadienone moiety on these IMDA reactions, creosol (**2**) was oxidized in the presence of 2,4-dienols **9a**–**e**. The increase in the dienic character of MOBs **11a**–**e** is clear from Table 1; the major product is oxatricyclic compound formed via path *a* in the IMDA reactions of **11a**,**b**,**d**, whereas **11c**, in which dienol tether

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TABLE 1. Intramolecular Diels–Alder Reactions of Masked *o*-Benzoquinones 10a–e–12a–e

				Diels–Alder reaction[a]					Cope rearrangement of **I**				
				addition	after	adducts/yield[d] (%)			*T*	time	yield[d] of **II** (%)		
entry	phenol	dienol[a]	MOB	time[b]/*T* (°C)	addition[c] (h)	**I**	**II**	**I**:**II**[e]	(°C)	(h)	from **I**[f]	total	method C[g]
1	**1**	**9a**	**10a**	10 min/rt	6	**18a**/31	**21a**/31	1:1	200	8	92	60	50
2		**9b**	**10b**	10 min/rt	6	**18b**/16	**21b**/42	1:3	200	10	93	57	55
3		**9c**	**10c**	10 min/rt	6	**18c**/35	**21c**/35	1:1	200	24	0	35	30
4		**9d**	**10d**	10 min/rt	6	**18d**/25	**21d**/25	1:1	220	10	92	48	48
5		**9e**	**10e**	10 min/rt	6	**18e**/47	**21e**/0	1:0	200	24	0	0	0
6	**2**	**9a**	**11a**	10 min/rt	6	**19a**/40	**22a**/20	2:1	200	8	93	57	62
7		**9b**	**11b**	10 min/rt	6	**19b**/46	**22b**/16	3:1	200	8	95	60	72
8		**9c**	**11c**	10 min/rt	6	**19c**/61	**22c**/0	1:0	200	8	45	28	23
9		**9d**	**11d**	10 min/rt	6	**19d**/34	**22d**/9	4:1	250	6	75	35	35
10		**9e**	**11e**	10 min/rt	6	**19e**/52	**22e**/0	1:0	200	24	0	0	0
11	**3**	**9a**	**12a**	10 min/rt	6	**20a**/57	**23a**/19	3:1	200	8	100	76	60
12		**9b**	**12b**	10 min/rt	6	**20b**/60	**23b**/10	6:1	220	8	93	66	73
13		**9c**	**12c**	10 min/rt	6	**20c**/42	**23c**/0	1:0	200	8	41	17	0
14		**9d**	**12d**	10 min/rt	6	**20d**/18	**23d**/2	9:1	250	8	80	16	13
15		**9e**	**12e**	10 min/rt	6	**20e**/36	**23e**/0	1:0	220	24	0	0	0

[a] Diels–Alder reactions were carried out according to method A using 10 equiv of the appropriate dienol. [b] Time period during which BTIB in THF was added to the reaction mixture containing the appropriate 2-methoxyphenol and dienol in THF. [c] Time period for which the reaction mixture was allowed to stir at rt after the complete addition of BTIB. [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** were carried out according to method B. [g] In method C, the crude mixture of Diels–Alder adducts **I** and **II** was as such subjected to Cope rearrangements.

TABLE 2. Intramolecular Diels–Alder Reactions of Masked *o*-Benzoquinones 13a–c–17a–c

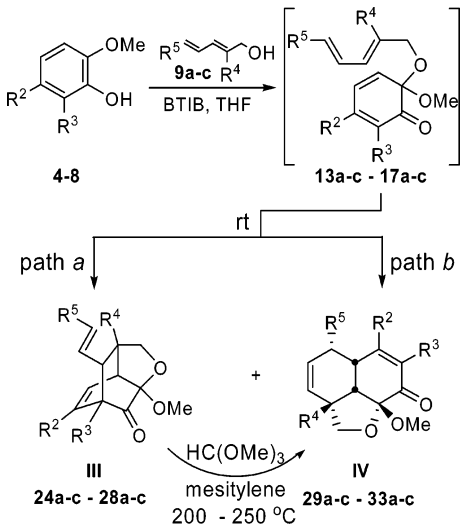
				Diels–Alder reaction[a]					Cope rearrangement of **III**[f]			
				addition	after	adducts/yield[d] (%)			*T*[f]	time	yield[d] of **IV**(%)	
entry	phenol	dienol[a]	MOB	time[b]/*T* (°C)	addition[c] (h)	**III**	**IV**	**III**:**IV**[e]	(°C)	(h)	from **III**	total
1	**4**	**9a**	**13a**	10 min/rt	6	**24a**/13	**29a**/12	1:1	200	8	94	25
2		**9b**	**13b**	10 min/rt	6	**24b**/ 31	**29b**/31	1:1	200	10	99	62
3		**9c**	**13c**	10 min/rt	6	**24c**/18	**29c**/0	1:0	200	24	0	0
4[g]	**5**	**9a**	**14a**	10 min/rt	6	**25a**/5	**30a**/7	1:1	200	8	89	12
5[h]		**9b**	**14b**	10 min/rt	6	**25b**/31	**30b**/11	3:1	200	8	99	42
6		**9c**	**14c**	10 min/rt	6	**25c**/0	**30c**/0		200	8		0
7[i]	**6**	**9a**	**15a**	10 min/rt	6	**26a**/0	**31a**/0		200	8		0
8[j]		**9b**	**15b**	10 min/rt	6	**26b**/12	**31b**/0	1:0	200	24	0	0
9		**9c**	**15c**	10 min/rt	6	**26c**/0	**31c**/0		250	6		0
10[k]	**7**	**9a**	**16a**	10 min/rt	6	**27a**/6	**32a**/6	1:1	200	8	96	12
11		**9b**	**16b**	10 min/rt	6	**27b**/6	**32b**/6	1:1	200	8	94	12
12		**9c**	**16c**	10 min/rt	6	**27c**/0	**32c**/0		220	8		0
13[l]	**8**	**9a**	**17a**	10 min/rt	6	**28a**/6	**33a**/6	1:1	200	8	85	11
14		**9b**	**17b**	10 min/rt	6	**28b**/28	**33b**/19	2:1	200	8	86	43
15		**9c**	**17c**	10 min/rt	6	**28c**/0	**33c**/0		220	8	85	0

[a] Diels–Alder reactions were carried out according to method A with 10 equiv of the appropriate dienol. [b] Time period during which BTIB in THF was added to the reaction mixture containing the appropriate 2-methoxyphenol and dienol in THF. [c] Time period for which the reaction mixture was allowed to stir at rt after the complete addition of BTIB. [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 **III** were carried out according to method B. [g] In IMDA reaction of entry 4, in addition to the products **25a** and **30a**, oxidation product **34** was also isolated in 30% yield. [h] In IMDA reaction of entry 5, in addition to the products **25b** and **30b**, oxidation product **35** was also isolated in 15% yield. [i] In IMDA reaction of entry 7, instead of expected products **26a** and **31a**, oxidation product **36** was also isolated in 20% yield. [j] In IMDA reaction of entry 8, in addition to **26b**, oxidation product **37** was also isolated in 9% yield. [k] In IMDA reaction of entry 10, in addition to the products **27a** and **32a**, oxidation product **38** was also isolated in 20% yield. [l] In IMDA reaction of entry 13, in addition to the products **28a** and **33a**, oxidation product **39** was also isolated in 25% yield.

is electron-poor, brings **19c** exclusively with no traces of **22c**. A similar trend was observed from the IMDA reactions of MOBs **12a–e** generated from 2-methoxyphenol **3** and dienols **9a–e** resulting in the formation of cycloadducts **20a–e** and **23a–e**. In these cases, it may be noted that the product resulted from the diene character of MOB (path *a*) is still predominant due to the steric and electronic effects exerted by the bulky ketal group present on the C-4 position of cyclohexadienone moiety. The MOBs **10e–12e** where the dienol tether uses its *cis* double bond in the IMDA reaction consequently led to the oxatricycles **18e–20e** via path *a* exclusively as predicted.

To study the variation of dienophilic and diene characters of the MOBs with the position and the nature of the substituent on the MOBs as well as 2,4-dienols, the IMDA reactions of MOBs **13a–c–17a–c** were performed. The vehicles chosen for our study are unsubstituted 2-methoxyphenol (guaiacol, **4**), 2-methoxyphenols with electron-donating and withdrawing substituents at position 6 (**5**, **7**), and position 5 (**6**, **8**), respectively, and 2,4-dienols **9a–c**. Initially, the oxidation of **4** with BTIB in THF was carried out at room temperature in the presence of the dienol **9a** to generate the MOB **13a**. When the IMDA reaction of MOB **13a** reached completion, after 6 h at the room temperature, the usual workup followed

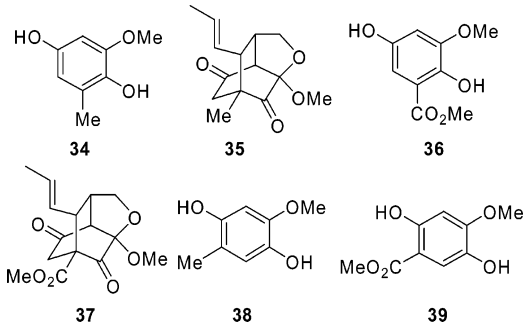
SCHEME 5



	R^2	R^3
4, 13, 24, 29	H	H
5, 14, 25, 30	H	Me
6, 15, 26, 31	H	CO_2Me
7, 16, 27, 32	Me	H
8, 17, 28, 33	CO_2Me	H

	R^4	R^5
a	H	H
b	H	Me
c	H	CO_2Et

CHART 1



by silica gel column chromatography (method A) provided 1:1 ratio of products **24a** and **29a** in poor yield (25% total yield, Table 2 and Scheme 5). Similar results were obtained in the unimolecular reactions of **14a**, **16a**, and **17a** leading to the oxatricyclic compounds **25a**, **27a**, and **28a** and *cis*-decalin compounds **30a**, **32a**, and **33a**, respectively, in a 1:1 ratio. These oxatricyclic compounds were accompanied by the corresponding *p*-hydroquinones **34**, **38,** and **39** in 20−30% yield (entries 4, 10, and 13, Table 2, Chart 1). The reaction of methyl *o*-vanillate (**6**) with **9a** gave the *p*-hydroquinone **36** instead of the expected cycloadducts. The electron-releasing methyl group substituted 2-methoxyphenols **5** and **7** with **9b** gave the products in 3:1 and 1:1 ratios; however, 2-methoxyphenol **5** also furnished oxidation product **35** in 15% yield. On the other hand, the reactions of dienol **9c** with **5** and **7** provided no cycloadducts. When electron-poor 2-methoxyphenols **6** and **8** were subjected to oxidation in the presence of 2,4-dienols **9a**−**c** followed by the IMDA reactions, instead of the formation of cycloadducts, **6** with **9a** gave oxidation product **36** in 20% yield, while **8** gave a 1:1 mixture of cycloadducts along with oxidation product **39** in 25% yield. MOB **15b** gave exclusively **26b** following path *a* along with 9% of oxidation product **37**, while **17b** provided a 2:1 mixture of cycloadducts. It is interesting to note that **6** and **8** did not afford **26c**, **31c**, and **28c**, **33c**, respectively. The formation of all the unexpected products **34**−**39** can be attributed to the absence of a substitution on oxidation-prone C-4 of these 2-methoxyphenols (**5**−**8**). Similar oxidation at position-4 was observed during our recent study on IMDA reactions of MOBs derived from 2-methoxyphenols and allyl alcohols.[15a]

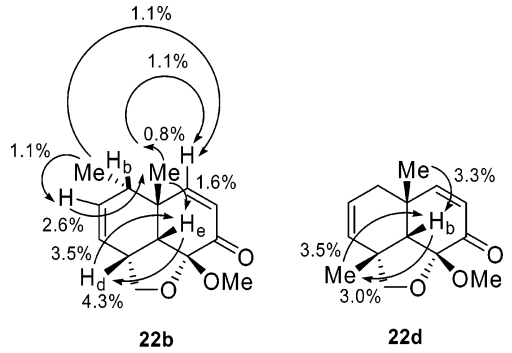
The formation of *cis*-decalins in method A needs further comment as they could in principle have resulted in two ways: either by (i) direct Diels−Alder reactions, in which MOB moieties behave as dienophiles, or (ii) a tandem process involving Diels−Alder reaction in which MOB moieties serve as dienes and Cope rearrangements. All of our cases transforming bicyclo[2.2.2]octenones (**18**−**20** and **24**−**28**) into *cis*-decalins (**21**−**23** and **29**−**33**) took place at elevated temperatures as in cases of usual Cope rearrangements (see the later discussion). To check the possibility that CF_3CO_2H formed during the course of reaction may catalyze the Cope rearrangement although it seems quite improbable, we treated bicyclo[2.2.2]-octenones **19b** and **24b** with CF_3CO_2H (10 equiv) and dienol **9b** (10 equiv) in dry THF at room temperature for 24 h. No *cis*-decalins were observed, and the reactants remained unchanged during the reaction period; thus, we believe that the present dual Diels−Alder reactions are kinetically controlled reactions. Consequently, the second possibility could be ruled out since Cope rearrangements require elevated temperatures.

From the foregoing IMDA reactions of all MOBs conducted in the present study, the following empirical rules can be proposed regarding the variation of dienophilicity and diene character of the MOBs as a function of their substitution pattern and also of the added 2,4-dienols.

(1) When the cyclohexadienone moiety of MOB acts as a diene in the IMDA reaction, oxatricyclic compound will be formed, whereas if the former acts as a dienophile, *cis*-decalin product will be obtained. If R^1 is an electron-withdrawing (methoxycarbonyl) group as in MOBs **10a**−**e**, the relative diene character of the MOB will be diminished and the dienophilicity of the double bond to the ester carbonyl group will be enhanced and as a result, the yield of the *cis*-decalin product will be either predominant or in comparable with the corresponding oxatricyclic product (Table 1, entries 2−5). If R^1 is a methyl group, MOB becomes electron-rich and hence exhibits diene character. Consequently, the major product will be the oxatricyclic compound (Table 1, entries 6−10), probably due to the electronic effect. If R^1 is a ketal group, the product resulted from the diene character will be still predominant (Table 1, entries 11−15) presumably because of the electronic effect and to some extent steric effect.

(2) It may be noted that the IMDA reactions of MOBs **10e**−**12e** (Scheme 4) tethered with *cis*-penta-2,4-dienol, (Table 1, entries 5, 10, 15) furnished exclusively the oxatricyclic compounds **18e**−**20e**, respectively. The effect of ring strain prevents the *cis*-penta-2,4-dienyl moiety from behaving as a diene to give the *cis*-decalin products.

CHART 2. NOE Enhancements of the Cycloadducts 22b and 22d



(3) The absence of substitution at an oxidation-prone site, C-4, of these 2-methoxyphenols furnished lower yields of the desired products along with the concomitant production of side products (Table 2, 2-methoxyphenols **4**−**8**). At this point we are unable to explain the reaction of dienol **9c** with 2-methoxyphenols **5**−**8** which provided only messy noncharactarizable reaction products.

(4) In a nutshell, from the foregoing discussion, we can propose that the optimum dienophilicity and high selectivity of MOB can be obtained through constellation of an electron-withdrawing group at position 4 of the 2,4-cyclohexadienone unit and an alkyl group at position 5 of the 2,4-dienol (Table 1, entry 2).

(b) Structural Determination of Products. The structures of all of the new compounds were established by using spectroscopic methods including IR, ^{1}H and ^{13}C NMR, and low and high-resolution mass spectroscopy. Elemental analyses were conducted only for the solid compounds **19b** and **19d** and could obtain satisfactory results. For most of the adducts in both of their 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 IR spectra of all the cycloadducts showed strong absorptions at 1730−1749 cm^{-1}, characteristic of the carbonyl group adjacent to the α-methoxy and cyclic ether functionality.[15]

The ^{1}H NMR (400 MHz) spectra of the crude reaction mixtures resulted from the IMDA reactions of the MOBs did not show the peaks corresponding to the other isomeric cycloadducts indicating that the cycloaddition took place in a highly regio- and stereoselective manner. The regio- and stereochemical assignments of the oxatricyclic compounds were made by comparing the coupling patterns and coupling constants of the various protons with those of the analogous IMDA adducts, whose regio- and stereochemistry were earlier determined unambiguously in our laboratories.[15] In addition, the stereochemistry of the *cis*-decalins **22b**, and **22d** were further confirmed with the help of difference in nuclear Overhauser enhancement (NOE) experiments (Chart 2). In the case of **22b**, saturation of bridged methyl protons gave rise to an increase in the signal intensity of H_b (0.8%) and H_e (1.6%) that proves their assigned stereochemistry with respect to the bridged methyl group, while saturation of H_d brought about significant NOE in the H_e (3.5%), similarly saturation of H_e gave rise to enhancement in the signal intensity of H_d (4.2%). Thus it is clear that H_d with H_e and bridged methyl group are of *cis*-relationship. In the case of **22d**, saturation of the bridged methyl protons gave rise to an increase in signal intensity of bridged proton H_b (3.3%) while saturation of H_b brought about significant NOE in the methyl (3.0%) group present at the fused junction of 6 and five-membered ring. Similarly when methyl was saturated gave rise to enhancement in the signal intensity of H_b (3.5%) thus confirming these groups are of *cis*-relationship to each other. In the cases of the remaining decalins, the stereochemical assignments were based on analogy of the coupling patterns.

(c) Cope Rearrangement of the Cycloadducts. The majority of the oxatricyclic compounds obtained from IMDA reactions underwent Cope rearrangement smoothly when heated to 200−250 °C in mesitylene with the addition of 1 equiv of molar ratio of $HC(OMe)_3$ to remove traces of water present if any (method B). For Cope rearrangement to occur, the basic requirement is proximity of the two double bonds involved in the reaction. Thus, IMDA adducts **18e**−**20e** did not undergo Cope rearrangement as predicted, in view of their *anti*-stereochemistry. To make the whole transformation simple, the crude Diels−Alder reaction mixtures were concentrated using a Kugelrohr apparatus after the usual workup and the residues were dissolved in mesitylene and heated to 200−250 °C (method C) to obtain decalins as sole products in high yields (Table 1). Surprisingly, the oxatricyclic compound **18c** did not undergo Cope rearrangement in method B. Unlike anionic oxy-Cope rearrangement, Cope rearrangement is a reversible reaction. During the course of reaction, the equilibrium shifts toward the thermodynamically more stable product. The oxatricyclic compound **18c** is presumably more stable than **21c**, and consequently, we could not observe any **21c** when subjected to the usual Cope rearrangement conditions. To check our reasoning and the possible presence of **21c** during the course of above reaction, we checked the ^{1}H NMR of crude reaction mixture of **18c** when subjected to Cope reaction conditions for 2, 4, and 8 h but failed to observe any **21c**, and hence, we propose compound **18c** to be more favorable and thermodynamically more stable compound. To confirm our analysis that **18c** is more stable, when *cis*-decalin **21c** was heated at 200 °C for 8 h, oxatricyclic compound **18c** could be isolated in 88% yield suggesting that indeed **18c** is more stable than **21c**. A similar fate was observed with compound **26b**, which could not undergo Cope rearrangement to provide compound **31b**. In a special case when compound **19c** was heated to 200 °C in mesitylene for 8 h, a mixture of **22c** and **19c** in a 1:1 ratio was obtained. To verify the presence of **19c** in the reaction is from the reverse Cope rearrangement, compound **22c** was heated to 200 °C in mesitylene for 8 h again only to observe 1:1 mixture of **22c** and **19c** confirming the usual trend of Cope rearrangement.

The strain imparted by the tricyclo[4.3.1.0^{3,7}] system in the adducts **24b**, **25b**, **27b**, and **28b** is diminished after the smooth Cope rearrangement to provide the *cis*-decalins **26b**, **30b**, **32b**, and **33b**, respectively (Table 2). It is noteworthy that the thermal transformations of the

cycloadducts examined are in conformity with the general tendency of 1,5-dienes toward Cope rearrangement.[22−24]

Conclusion

In summary, we have presented herein the dual behavior of MOBs in the IMDA reactions with a series of examples. A general and short route (one or two pots) to highly functionalized *cis*-decalins with complete stereocontrol up to five stereocenters is developed. Our methodology demonstrates the utilization of commercially available or easily accessible 2-methoxyphenols in the synthesis of potentially useful *cis*-decalins. The observed experimental results led us to derive 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 dienol in the IMDA reactions. The cycloadducts obtained from the dienic MOB and dienophilic tether smoothly underwent the Cope rearrangement to provide the highly functionalized *cis*-decalins. As exemplified, biologically active marine metabolites (±)-xestoquinone and its 9,10-methoxy derivatives were synthesized by this methodology.[13c] Heterocycles related to viridin were also synthesized on the same lines.[18b] This methodology brings the structurally complex natural products within relatively simple reach. Extension of this protocol in the synthesis of decalin-based natural products is currently in progress in our laboratories.

Experimental Section

Methyl (1*S,3*R**,6*R**,7*S**,10*R**)-3-methoxy-2-oxo-10-ethenyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-8-carboxylate (18a):** colorless liquid; IR (film) 2856, 1750, 1715, 1628, 1439, 1256, 1020 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (m, 1H), 2.80 (apparent d, J = 7.8 Hz, 1H), 3.36 (dd, J = 3.0, 7.2 Hz, 1H) 3.48 (s, 3H), 3.78 (s, 3H), 3.85 (d, J = 8.4 Hz, 1H), 4.02 (dd, J = 2.2, 4.4 Hz, 1H), 4.19 (dd, J = 3.6, 8.4 Hz, 1H), 5.03 (dd, J = 1.2, 10.6 Hz, 1H), 5.05 (dd, J = 1.2, 16.6 Hz, 1H), 5.54 (ddd, J = 7.8, 10.6, 16.6 Hz, 1H), 7.13 (dd, J = 2.2, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.5, 42.4, 46.6, 51.1, 52.2, 52.5, 73.4, 99.2, 116.4, 132.7, 137.4, 137.5, 164.2, 199.4; MS (70 eV) *m/z* (relative intensity) 264 (M^+, 4), 232 (90), 221 (5), 204 (84), 190 (69), 172 (77), 159 (30), 145 (100), 117 (82), 105 (17); HRMS (EI) calcd for $C_{14}H_{16}O_5$ (M^+) 264.0989, found 264.0975.

Methyl (1*S,3*R**,6*R**,7*S**,10*S**)-3-methoxy-2-oxo-10-[(*E*)-1-propenyl]-4- oxatricyclo[4.3.1.0^{3,7}]dec-8-ene-8-carboxylate (18b):** colorless liquid; IR (film) 2943, 1748, 1716, 1439, 1255, 1110, 1069 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.64 (dd, J = 1.4, 6.4 Hz, 1H), 2.34 (ddd, J = 2.0, 3.6, 4.4 Hz, 1H), 2.78 (apparent d, J = 8.4 Hz, 1H), 3.33 (dd, J = 2.4, 5.2 Hz, 1H), 3.58 (s, 3H), 3.72 (s, 3H), 3.87 (d, J = 8.0 Hz, 1H), 4.03 (dd, J = 2.2, 4.4 Hz, 1H), 4.20 (dd, J = 3.6, 8.0 Hz, 1H), 5.17 (ddd, J = 1.4, 8.4, 13.3 Hz, 1H), 5.53 (dq, J = 6.4, 13.3 Hz, 1H), 7.19 (dd, J = 2.2, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.8, 41.3, 43.1, 46.0, 51.0, 52.2, 53.0, 73.4, 98.2, 127.3, 130.4, 130.5, 137.7, 164.3, 198.8; MS (70 eV) *m/z* (relative intensity) 250 (M^+ − CO, 22), 235 (10), 219 (5), 203 (12), 59 (80), 186 (25), 158 (53), 129 (6), 115 (73), 91 (100); HRMS (EI) calcd for $C_{15}H_{18}O_5$ (M^+) 278.1154, found 278.1149.

Ethyl (*E*)-3-{(1*R,2*S**,3*S**,6*R**,7*R**)-6-methoxy-8-(methoxycarbonyl)-10-oxo-5-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-yl}-2-propenoate (18c):** colorless liquid; IR (film) 2953, 1753, 1714, 1650, 1436, 1258, 1037 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (t, J = 6.8 Hz, 3H), 2.44 (apparent dd, J = 1.6, 4.4 Hz, 1H), 2.96 (apparent dd, J = 2.4, 8.6 Hz, 1H), 3.42 (dd, J = 2.8, 6.8 Hz, 1H), 3.50 (s, 3H), 3.80 (s, 3H), 3.89 (d, J = 7.6 Hz, 1H), 4.06 (dd, J = 1.6, 8.4 Hz, 1H), 4.10−4.30 (m, 3H), 5.84 (d, J = 15.6 Hz, 1H), 6.60 (dd, J = 8.6, 15.6 Hz, 1H), 7.15 (dd, J = 2.0, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 41.6, 42.4, 45.2, 51.2, 51.5, 52.3, 60.7, 73.1, 99.2, 122.9, 133.4, 136.6, 146.4, 164.0, 165.7, 198.3; MS (70 eV) *m/z* (relative intensity) 264 (M^+ − CO, 100), 250 (10), 234 (41), 218 (7), 189 (59), 177 (11), 159 (64), 145 (64), 130 (42), 124 (20); HRMS (EI) calcd for $C_{17}H_{20}O_7$ 336.1210, found 336.1209.

Methyl (1*S,3*R**,6*R**,7*S**,10*S**)-3-methoxy-6-methyl-2-oxo-10-ethenyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-ene-8-carboxylate (18d):** colorless liquid; IR (film) 2950, 1748, 1740, 1620, 1430, 1012 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (s, 3H), 2.83 (dd, J = 2.6, 9.6 Hz, 1H), 3.32 (dd, J = 2.6, 6.8 Hz, 1H) 3.48 (s, 3H), 3.70 (d, J = 1.6 Hz, 1H), 3.78 (s, 3H), 3.80 (d, J = 8.0 Hz, 1H), 3.86 (d, J = 8.0 Hz, 1H), 5.03 (d, J = 10.0 Hz, 1H), 5.06 (d, J = 17.4 Hz, 1H), 5.44 (ddd, J = 9.6, 10.0, 17.4 Hz, 1H), 7.21 (dd, J = 2.0, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.7, 46.4, 48.2, 50.8, 51.0, 52.2, 53.7, 80.6, 99.6, 117.7, 132.7, 135.7, 137.7, 164.4, 199.0; MS (70 eV) *m/z* (relative intensity) 250 (M^+ − CO, 100), 235 (60), 218 (27), 209 (13), 203 (60), 190 (72), 177 (22), 159 (34), 149 (22), 138 (13), 129 (24); HRMS (EI) calcd for $C_{15}H_{18}O_5$ 278.1154, found 278.1133.

Methyl (1*S,3*R**,6*R**,7*S**,10*S**)-3-methoxy-2-oxo-10-ethenyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-ene-8-carboxylate (18e):** colorless liquid; IR (film) 2988, 1747, 1716, 1628, 1438, 1263, 1044 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.47 (apparent dd, J = 8.2, 9.6 Hz, 1H), 2.56 (ddt, J = 3.6, 3.8, 9.6 Hz, 1H), 3.24 (dd, J = 1.6, 7.0 Hz, 1H), 3.50 (s, 3H), 3.79 (s, 3H), 3.97 (dd, J = 3.6, 8.4 Hz, 1H), 3.99 (dd, 3.6, 8.4 Hz, 1H), 4.05 (dd, J = 2.2, 6.2 Hz, 1H), 5.18 (d, J = 17.0 Hz, 1H), 5.21 (d, J = 10.6 Hz, 1H), 5.72 (ddd, J = 8.0, 10.6, 17.0 Hz, 1H) 7.29 (dd, J = 2.2, 7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.5, 42.0, 42.3, 51.0, 51.3, 52.2, 67.7, 99.8, 118.1, 132.5, 135.1, 139.5, 164.4, 199.4; MS (70 eV) *m/z* (relative intensity) 236 (M^+ - CO, 100), 235 (55), 221 (64), 204 (41), 159 (74), 182 (7), 177 (38), 161 (40), 145 (28), 117 (53); HRMS (EI) calcd for $C_{14}H_{16}O_5$ (M^+) 264.0998, found 264.0995.

(1*S,3*R**,6*R**,7*S**,10*R**)-3-Methoxy-8-methyl-10-ethenyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (19a):** colorless liquid; IR (film) 2983, 2908, 1741, 1639, 1443, 1261, 1088 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.92 (s, 3H), 2.31 (m, 1H), 2.70 (apparent d, J = 7.8 Hz, 1H), 3.05 (dd, J = 3.2, 7.0 Hz, 1H), 3.15 (dd, 2.0, 4.4 Hz, 1H), 3.51 (s, 3H), 3.84 (d, 8.2 Hz, 1H), 4.13 (d, J = 3.6, 8.2 Hz, 1H), 4.98 (d, J = 10.4 Hz, 1H), 5.02 (d, J = 16.4 Hz, 1H), 5.61 (ddd, J = 7.8, 10.4, 16.4 Hz, 1H), 5.77 (d, J = 7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 42.7, 46.7, 47.7, 51.4, 73.7, 100.3, 115.5, 119.9, 138.7, 139.1, 200.8; MS (70 eV) *m/z* (relative intensity) 192 (M^+ - CO, 47), 177 (5), 151 (5), 133 (36), 125 (64), 117 (58), 105 (62), 91 (100), 77 (42), 65 (31), 194 (9); HRMS (EI) calcd for $C_{13}H_{16}O_3$ (M^+) 220.1099, found 220.1103.

(1*S,3*R**,6*R**,7*S**,10*R**)-3-Methoxy-8-methyl-10-[(*E*)-1-propenyl]-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (19b):** colorless solid; mp 70−71 °C (from EtOAc−hexanes); IR (film) 2945, 2883, 1743, 1683, 1440, 1022 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.57 (dd, J = 1.8, 6.0 Hz, 3H), 1.86 (d, J = 1.6 Hz, 3H), 2.17 (apparent ddd, J = 1.6, 3.2, 4.4 Hz, 1H), 2.58 (apparent ddd, J = 1.6, 2.8, 8.6 Hz, 1H), 2.94 (dd, J = 2.8, 6.8 Hz, 1H), 3.05 (dd, J = 2.8, 4.4 Hz, 1H), 3.45 (s, 3H), 3.76 (d, J

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= 8.0 Hz, 1H), 4.05 (dd, *J* = 3.2, 8.0 Hz, 1H), 5.19 (ddq, *J* = 1.8, 8.6, 14.8 Hz, 1H), 5.41 (dq, *J* = 6.0, 14.8 Hz, 1H), 5.74 (ddq, *J* = 1.6, 2.8, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.8, 21.2, 43.3, 45.9, 47.6, 51.3, 51.9, 73.7, 100.2, 120.0, 126.1, 131.4, 138.8, 201.1; MS (70 eV) *m/z* (relative intensity) 206 (M^+ − CO, 100), 159 (4), 147 (39), 125 (50), 119 (44), 105 (43), 91 (37), 77 (16), 59 (9), 39 (12); HRMS (EI) calcd for $C_{13}H_{18}O_2$ (M^+ − CO) 206.1307, found 206.1308. Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77, H, 7.74. Found: C, 71.68, H, 7.80.

Ethyl (*E*)-3-{(1*R,2*S**,3*S**,6*R**,7*R**)-6-methoxy-8-methyl-10-oxo-5-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-yl}-2-propenoate (19c):** colorless liquid; IR (film) 2951, 1744, 1716, 1648, 1451, 1286, 1032 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.91 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H), 2.83 (apparent d, *J* = 8.8 Hz, 1H), 3.07 (dd, *J* = 3.0, 6.2 Hz, 1H), 3.15 (apparent dd, *J* = 1.6, 3.6 Hz, 1H), 3.49 (s, 3H), 4.11 (dd, *J* = 3.2, 8.6 Hz, 1H), 3.81 (d, *J* = 8.6 Hz, 1H), 4.11 (dd, *J* = 3.2, 8.6 Hz, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 5.80 (d, *J* = 6.2 Hz, 1H), 5.81 (d, *J* = 6.2 Hz, 1H), 6.68 (dd, *J* = 8.8, 15.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 21.3, 42.5, 45.3, 47.8, 50.4, 51.5, 73.4, 100.0, 120.0, 122.1, 139.8, 149.7, 166.06, 166.08, 199.7; MS (70 eV) *m/z* (relative intensity) 264 (M^{+-}- CO, 100), 250 (10), 234 (41), 218 (7), 189 (59), 177 (11), 159 (64), 145 (64), 130 (42), 124 (20); HRMS (EI) calcd for $C_{16}H_{20}O_5$ (M^+) 292.1300, found 292.1301.

(1*S,3*R**,6*R**,7*R**,10*S**)-3-Methoxy-6,8-dimethyl-10-ethenyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (19d):** colorless solid; mp 122−123 °C (from EtOAc−hexanes); IR (film) 2955, 2876, 1732, 1630, 1436, 1042 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (s, 3H), 1.90 (t, *J* = 1.6 Hz, 3H), 2.71 (dd, *J* = 2.6, 8.2 Hz, 1H), 2.80 (d, *J* = 2.2 Hz, 1H), 3.00 (dd, *J* = 2.6, 6.8 Hz, 1H), 3.50 (s, 3H), 3.76 (s, 2H), 5.00 (dd, *J* = 2.6, 8.2 Hz, 1H), 5.07 (dd, *J* = 1.6, 17.4 Hz, 1H), 5.55 (dd, *J* = 8.2, 8.2, 17.4 Hz, 1H), 5.87 (ddd, *J* = 1.6, 2.2, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.7, 22.2, 46.5, 50.8, 51.3, 52.5, 54.8, 80.9, 100.7, 116.9, 120.0, 136.7, 139.1, 200.5; MS (70 eV) *m/z* (relative intensity) 206 (M^+ - CO, 50), 165 (21), 159 (9), 147 (100), 131 (62), 124 (38), 120 (10), 119 (48), 105 (25); HRMS (EI) calcd for $C_{14}H_{18}O_3$ 234.1254, found 234.1257. Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.67; H, 7.81.

(1*S,3*R**,6*R**,7*S**,10*S**)-3-Methoxy-8-methyl-10-[(*E*)-1-propenyl]-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (19e):** colorless liquid; IR (film) 2940, 1742, 1638, 1441, 1325, 1169, 1084 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.89 (d, *J* = 1.8 Hz, 3H), 2.42 (apparent dd, *J* = 8.4, 10.0 Hz, 1H), 2.51 (ddd, *J* = 3.2, 3.6, 10.0 Hz, 1H), 2.91 (dd, *J* = 1.6, 6.8 Hz, 1H), 3.12 (dd, *J* = 2.0, 4.0 Hz, 1H), 3.51 (s, 3H), 3.86 (dd, *J* = 3.2, 8.4 Hz, 1H), 3.89 (d, *J* = 8.4 Hz, 1H), 5.14 (dd, *J* = 0.4, 9.4 Hz, 1H), 5.13 (dd, *J* = 0.4, 18.0 Hz, 1H), 5.73 (ddd, *J* = 8.0, 9.4, 18.0 Hz, 1H), 5.96 (ddd, *J* = 1.8, 2.0, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 38.8, 43.5, 48.3, 50.3, 51.4, 68.0, 100.9, 117.1, 123.2, 136.4, 138.9, 200.8; MS (70 eV) *m/z* (relative intensity) 220 (M^+, 2), 192 (100), 177 (14), 164 (33), 159 (8), 145 (5), 133 (60), 124 (18), 117 (25), 105 (12); HRMS (EI) calcd for $C_{13}H_{16}O_3$ (M^+) 220.1099, found 220.1104.

(1*S,3*R**,6*R**,7*S**,10*S**)-8-(5,5-Dimethyl-1,3-dioxan-2-yl)-3-methoxy-10-ethenyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (20a):** colorless liquid; IR (film) 2925, 1747, 1638, 1467, 1392, 1016 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.76 (s, 3H), 1.24 (s, 3H), 2.38 (apparent d, *J* = 2.8 Hz, 1H), 2.75 (apparent d, *J* = 8.2 Hz, 1H), 3.19 (dd, *J* = 3.2, 6.8 Hz, 1H), 3.53 (m, 5H), 3.60−3.70 (m, 3H), 3.86 (d, *J* = 8.2 Hz, 1H), 4.18 (dd, *J* = 3.6, 8.2 Hz, 1H), 4.96 (s, 1H), 5.03 (dd, *J* = 1.6, 10.0 Hz, 1H), 5.06 (dd, *J* = 1.6, 17.0 Hz, 1H), 5.64 (ddd, *J* = 8.4, 10.0, 17.0 Hz, 1H), 6.19 (dd, *J* = 1.6, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 23.0, 30.1, 41.2, 43.0, 46.8, 50.4, 51.2, 73.4, 77.1 (CH_2 × 2), 100.0, 100.2, 115.8, 124.0, 138.2, 139.7, 200.3; MS (70 eV) *m/z* (relative intensity) 320 (M^+, 4), 292 (5), 261 (8), 234 (3), 208 (10), 174 (8), 161 (4), 145 (9), 131 (3), 110 (100); HRMS (EI) calcd for $C_{18}H_{24}O_5$ (M^+) 320.1624, found 320.1614.

(1*S,3*R**,6*R**,7*S**,10*R**)-8-(5,5-Dimethyl-1,3-dioxan-2-yl)-3-methoxy-10-[(*E*)-1-propenyl]-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (20b):** colorless liquid; IR (film) 2920, 1746, 1464, 1391, 1187, 1103, 1024 cm^{-1};^{1}H NMR (300 MHz, $CDCl_3$) δ 0.77 (s, 3H), 1.21 (s, 3H), 1.63 (dd, *J* = 1.5, 6.7 Hz, 3H), 2.20−2.40 (m, 1H), 2.68 (apparent d, *J* = 8.6 Hz, 1H), 3.20 (dd, *J* = 3.0, 6.8 Hz, 1H), 3.40−3.60 (m, 2H), 3.52 (s, 3H), 3.66 (s, 3H), 3.84 (d, *J* = 8.1 Hz, 1H), 4.16 (dd, *J* = 3.3, 8.1 Hz, 1H), 4.96 (s, 1H), 5.24 (ddq, *J* = 1.5, 8.6, 14.8 Hz, 1H), 5.50 (dq, *J* = 6.7, 14.8 Hz, 1H), 6.19 (dd, *J* = 1.8, 8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.9, 21.8, 23.0, 30.1, 41.2, 43.6, 46.1, 50.4, 51.8, 73.5, 77.4 (CH_2 × 2), 100.0, 109.3, 124.2, 126.5, 131.0, 139.5, 200.7; MS (70 eV) *m/z* (relative intensity) 333 (M^+ − 1, 8), 305 (50), 275 (8), 249 (10), 206 (8), 146 (6), 126 (7), 114 (100); HRMS (EI) calcd for $C_{19}H_{26}O_5$ (M^+) 334.1782, found 334.1779.

Ethyl (*E*)-3-{(1*R,2*S**,3*S**,6*R**,7*R**)-8-(5,5-dimethyl-1,3-dioxan-2-yl)-6-methoxy-10-oxo-5-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-yl}-2-propenoate (20c):** colorless liquid; IR (film) 2959, 1748, 1715, 1650, 1464, 1029 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.68 (s, 3H), 1.14 (s, 3H), 1.22 (t, *J* = 6.8 Hz, 3H), 2.30−2.40 (m, 1H), 2.83 (apparent d, *J* = 8.6 Hz, 1H), 3.15 (dd, *J* = 3.2, 6.8 Hz, 1H), 3.40−3.46 (m, 2H), 3.45 (s, 3H), 3.50−3.70 (m, 2H), 3.63 (dd, *J* = 1.8, 6.4 Hz, 1H), 3.77 (d, *J* = 8.4 Hz, 1H), 4.00−4.20 (m, 3H), 4.89 (s, 1H), 5.73 (d, *J* = 15.6 Hz, 1H), 6.13 (dd, *J* = 1.8, 6.8 Hz, 1H), 6.65 (dd, *J* = 8.6, 15.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 21.7, 22.9, 30.1, 41.2, 42.7, 45.3, 50.1, 50.3, 52.3, 60.4, 73.1, 76.9, 77.1, 99.9, 122.4, 123.4, 140.3, 147.3, 166.0, 199.1; MS (70 eV) *m/z* (relative intensity) 264 (M^+ - CO, 100), 250 (10), 234 (41), 218 (7), 189 (59), 177 (11), 159 (64), 145 (64), 130 (42), 124 (20); HRMS (EI) calcd for $C_{21}H_{28}O_7$ (M^+) 392.1836, found 392.1835.

(1*S,3*R**,6*R**,7*S**,10*S**)-8-(5,5-Dimethyl-1,3-dioxan-2-yl)-3-methoxy-6-methyl-10-ethenyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (20d):** colorless liquid; IR (film) 2948, 2882, 1732, 1674, 1460, 1014 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.72 (s, 3H), 0.95 (s, 3H), 1.19 (s, 3H), 2.75 (apparent d, *J* = 10.0 Hz, 1H), 3.12 (dd, *J* = 2.4, 6.7 Hz, 1H), 3.32 (d, *J* = 1.9 Hz, 1H), 3.46 (d, *J* = 9.0 Hz, 2H), 3.49 (s, 3H), 3.63 (d, *J* = 9.6 Hz, 2H), 3.80 (s, 2H), 4.91 (s, 1H), 4.99 (dd, *J* = 1.2, 10.0 Hz, 2H) 5.04 (dd, *J* = 1.2, 16.7 Hz, 1H), 5.52 (ddd, *J* = 10.0, 10.0, 16.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.9, 21.8, 22.9, 30.1, 46.3, 48.2, 50.4, 51.2, 52.5, 77.3, 81.0, 99.72, 99.74, 100.6, 116.9, 124.3, 136.6, 140.1, 200.0; MS (70 eV) *m/z* (relative intensity) 307 (66), 306 (100), 291 (14), 274 (17), 248 (14), 220 (62), 205 (7), 193 (32), 175 (12), 133 (18); HRMS (EI) calcd for $C_{19}H_{26}O_5$ (M^+) 334.1780, found 334.1795.

(1*S,3*R**,6*R**,7*S**,10*S**)-8-(5,5-Dimethyl-1,3-dioxan-2-yl)-3-methoxy-10-ethenyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (20e):** colorless liquid; IR (film) 2928, 1745, 1640, 1487, 1100, 1012 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.74 (s, 3H), 1.21 (s, 3H), 2.45 (apparent dd, *J* = 8.0, 10.0 Hz, 1H) 2.52 (1H, ddd, *J* = 3.2, 3.2, 10.0 Hz, 1H), 3.07 (dd, *J* = 1.6, 6.8 Hz, 1H), 3.50 (s, 3H), 3.40−3.70 (m, 5H), 3.94 (d, *J* = 3.2 Hz, 2H), 4.92 (s, 1H), 5.13 (d, *J* = 16.8 Hz, 1H), 5.15 (d, *J* = 10.2 Hz, 1H), 5.72 (ddd, *J* = 8.0, 10.2, 16.8 Hz, 1H), 6.17 (dd, *J* = 1.6, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 23.0, 30.2, 39.1, 41.9, 43.1, 50.0, 50.4, 67.7, 77.1, 77.2, 100.2, 100.5, 117.1, 127.1, 136.0, 139.3, 200.2; MS (70 eV) *m/z* (relative intensity) 292 (M^+, 100), 258 (8), 266 (8), 211 (10), 194 (9), 145(11), 133-(2); HRMS (EI) calcd for $C_{18}H_{24}O_3$ (M^+) 292.1714, found 292.1658.

Methyl (2a*R,5a*S**,8a*R**,8b*R**)-8a-methoxy-2a,5,5a,8,8a,8b-hexahydro-2*H*-benzo[*cd*]isobenzofuran-5a-carboxylate (21a)**: colorless liquid; IR (film) 2967, 1734, 1694, 1442, 1283, 1214, 1099, 1041 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.96 (ddd, *J* = 1.6, 3.6, 16.8 Hz, 1H), 2.61 (ddd, *J* = 6.0, 16.8 Hz, 1H), 3.15−3.20 (m, 1H), 3.27 (s, 3H), 3.41 (dd, *J* = 1.6, 9.2 Hz, 1H), 3.72 (s, 3H), 3.80 (dd, *J* = 2.8, 8.4 Hz, 1H), 4.13 (dd, *J* = 7.2, 8.4 Hz, 1H), 5.72 (dddd, *J* = 1.2, 3.4, 5.8, 10.0 Hz, 1H), 5.81 (ddd, *J* = 2.0, 4.0, 10.0 Hz, 1H), 6.09 (d, *J* = 10.2 Hz, 1H), 6.96 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$)

δ 35.3, 37.7, 47.6, 49.1, 50.3, 52.9, 73.2, 102.5, 124.5, 128.4, 130.1, 151.0, 173.7, 190.3; MS (70 eV) *m/z* (relative intensity) 264 (M^+, 5), 249 (12), 232 (97), 221 (6), 204 (84), 190 (73), 172 (82), 159 (30), 145 (100), 117 (91); HRMS (EI) calcd for $C_{14}H_{16}O_3$ (M^+) 264.0989, found 264.0988.

Methyl (2a*R,5*S**,5a*R**,8a*R**,8b*R**)-8a-methoxy-5-methyl-8-oxo-2a,5,5a,8,8a,8b-hexahydro-2*H*-benzo[*cd*]isobenzofuran-5a-carboxylate (21b):** colorless liquid; IR (film) 2938, 1731, 1693, 1446, 1383, 1235, 1046 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.11 (d, *J* = 7.2 Hz, 3H), 2.71 (ddd, *J* = 2.8, 4.6, 7.2 Hz, 1H), 3.00−3.12 (m, 1H), 3.31 (s, 3H), 3.43 (d, *J* = 10.0 Hz, 1H), 3.76 (dd, *J* = 4.0, 8.8 Hz, 1H), 3.83 (s, 3H), 4.24 (dd, *J* = 7.2, 8.8 Hz, 1H), 5.59 (ddd, *J* = 2.8, 7.2, 9.0 Hz, 1H), 5.77 (ddd, *J* = 2.4, 4.6, 9.0 Hz, 1H), 6.20 (d, *J* = 10.4 Hz, 1H), 6.88 (d, *J* = 10.4 HZ, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.9, 29.6, 37.8, 38.2, 51.0, 51.3, 51.4, 52.9, 71.0, 101.7, 129.4, 130.8, 132.6, 141.0, 174.5, 191.3; MS (70 eV) *m/z* (relative intensity) 278 (M^+, 4), 263 (12), 247 (18), 219 (9), 159 (16), 131 (26), 99 (100), 91 (18), 81 (16), 59 (9); HRMS (EI) calcd for $C_{15}H_{18}O_5$ (M^+) 278.1154, found 278.1141.

5-Ethyl-5a-methyl (2a*R,5*S**,5a*S**,8a*R**,8b*R**)-8a-methoxy-8-oxo-2a,5,5a,8a,8b-hexahydro-2*H*-benzo[*cd*]isobenzofuran-5,5a-dicarboxylate (21c):** colorless liquid; IR (film) 2953, 1732, 1711, 1646, 1437, 1093 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.27 (t, *J* = 6.8 Hz, 3H), 2.95−3.05 (m, 1H), 3.28 (dd, *J* = 0.8, 9.6 Hz, 1H), 3.32 (s, 3H), 3.65 (dd, *J* = 2.8, 6.4 Hz, 1H), 3.72 (dd, *J* = 4.8, 9.0 Hz, 1H), 3.80 (s, 3H), 4.20 (q, *J* = 6.8 Hz, 2H), 4.23 (dd, *J* = 6.4, 9.0 Hz, 1H), 5.83 (ddd, *J* = 2.8, 5.2, 9.4 Hz, 1H), 6.04 (ddd, *J* = 3.2, 6.4, 9.4 Hz, 1H), 6.15 (d, *J* = 10.4 Hz, 1H), 6.69 (dd, *J* = 0.8, 10.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 38.9, 48.9, 49.5, 51.9, 52.0, 52.3, 61.6, 73.1, 101.7, 126.3, 130.3, 132.1, 145.6, 170.5, 173.8, 191.4; MS (70 eV) *m/z* (relative intensity) 264 (M^+ − CO, 100), 250 (10), 234 (41), 218 (7), 189 (59), 177 (11), 159 (64), 145 (64), 130 (42), 124 (20); HRMS (EI) calcd for $C_{17}H_{20}O_7$ (M^+) 336.1209, found 336.1209.

Methyl (2a*R,5a*S**,8a*R**,8b*R**)-8a-methoxy-2a-methyl-8-oxo-2a,5,5a,8,8a, 8b-hexahydro-2*H*-benzo[*cd*]isobenzofuran-5a-carboxylate (21d):** colorless liquid; IR (film) 2955, 1732, 1688, 1436, 1042 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.32 (s, 3H), 1.87 (ddd, *J* = 2.2, 2.4, 16.4 Hz, 1H), 2.69 (ddd, *J* = 2.6, 6.3, 16.4 Hz, 1H), 3.15 (d, *J* = 2.4 Hz, 1H), 3.27 (s, 3H), 3.72 (s, 3H), 3.76 (d, *J* = 8.8 Hz, 1H), 3.84 (d, *J* = 8.8 Hz, 1H), 5.63 (dd, *J* = 2.2, 9.6 Hz, 1H), 5.69 (ddd, *J* = 2.6, 6.3, 9.6 Hz, 1H), 6.10 (d, *J* = 10.4 Hz, 1H), 6.97 (d, *J* = 10.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.0, 34.5, 43.2, 47.8, 50.0, 52.8, 56.0, 80.5, 103.4, 123.0, 128.2, 136.4, 151.6, 173.7, 189.8; MS (70 eV) *m/z* (relative intensity) 278 (M^+, 13), 246 (93), 232 (8), 218 (34), 205 (40), 197 (24), 186 (100), 176 (39), 158 (72), 145 (70); HRMS (EI) calcd for $C_{15}H_{18}O_5$ (M^+) 278.1154, found 278.1144.

(2a*R,5a*R**,8a*R**,8b*R**)-8a-Methoxy-5a-methyl-2a,5,5a,8,8a,8b-hexahydro-2*H*-benzo[*cd*]isobenzofuran-8-one (22a):** colorless liquid; IR (film) 2923, 1732, 1669, 1445, 1262, 1065 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.13 (s, 3H), 1.74 (d, *J* = 15.8 Hz, 1H), 1.90 (dd, *J* = 3.2, 15.8 Hz, 1H), 2.49 (d, *J* = 9.6 Hz, 1H), 2.94 (apparent dd, *J* = 7.6, 9.6 Hz, 1H), 3.21 (s, 3H), 3.66 (dd, *J* = 3.6, 8.8 Hz, 1H), 4.03 (dd, *J* = 7.6, 8.8 Hz, 1H), 5.60−5.70 (m, 2H), 5.92 (d, *J* = 10.0 Hz, 1H), 6.61 (d, *J* = 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.3, 35.3, 37.3, 37.7, 50.5, 53.4, 72.7, 102.9, 125.7, 127.0, 129.4, 159.1, 191.4; MS (70 eV) *m/z* (relative intensity) 220 (M^+, 11), 205 (90), 188 (36), 173 (10), 160 (58), 151 (26), 147 (100), 137 (5), 117 (57), 105 (48); HRMS (EI) calcd for $C_{13}H_{17}O_3$ (M^+) 220.1099, found 220.1095.

(2a*R,5*S**,5a*S**,8a*R**,8b*R**)-8a-Methoxy-5,5a-dimethyl-2a,5,5a,8,8a,8b-hexahydro-2*H*-benzo[*cd*]isobenzofuran-8-one (22b):** colorless liquid; IR (film) 2961, 2874, 1736, 1614, 1439, 1282, 1209, 1026 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.07 (d, *J* = 7.2 Hz, 3H), 1.32 (s, 3H), 2.00−2.20 (m, 1H), 2.66 (d, *J* = 10.0 Hz, 1H), 2.85−3.05 (m, 1H), 3.37 (s, 3H), 3.67 (dd, *J* = 4.4, 8.8 Hz, 1H), 4.17 (dd, *J* = 8.0, 8.8 Hz, 1H), 5.61 (ddd, *J* = 3.0, 6.4, 9.6 Hz, 1H), 5.67 (ddd, *J* = 2.0, 4.4, 9.6 Hz, 1H), 6.07 (d, *J* = 10.4 Hz, 1H), 6.63 (d, *J* = 10.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.6, 28.8, 37.7, 39.0, 39.5, 51.1, 54.3, 71.5, 102.8, 127.9, 129.1, 133.9, 154.8, 192.2; MS (70 eV) *m/z* (relative intensity) 234 (M^+, 10), 206 (40), 191 (5), 175 (11), 161 (29), 131 (42), 115 (47), 91 (95), 79 (72), 39 (100); HRMS (EI) calcd for $C_{14}H_{18}O_3$, (M^+) 234.1256, found 234.1255.

Ethyl (2a*R,5*S**,5a*R**,8a*R**,8b*R**)-8a-methoxy-5a-methyl-8-oxo-2a,5,5a,8,8a,8b-hexahydro-2*H*-benzo[*cd*]isobenzofuran-5-carboxylate (22c):** colorless liquid; IR (film) 2939, 1773, 1688, 1455, 1174, 1030 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.2 Hz, 3H), 1.40 (s, 3H), 2.73 (dd, *J* = 0.9, 10.5 Hz, 1H), 2.92 (dd, *J* = 2.5, 5.2 Hz, 1H), 2.98 (apparent ddd, *J* = 2.4, 3.0, 5.2 Hz, 1H), 3.41 (s, 3H), 3.58 (dd, *J* = 6.0, 9.0 Hz, 1H), 4.20−4.40 (m, 3H), 5.76 (ddd, *J* = 2.4, 5.2, 9.3 Hz, 1H), 5.88 (d, *J* = 10.5 Hz, 1H), 6.00 (d, *J* = 10.5 Hz, 1H), 6.86 (dd, *J* = 0.9, 10.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 28.5, 38.5, 39.6, 51.5, 51.8, 54.0, 60.1, 70.6, 102.5, 127.5, 128.0, 131.3, 153.5, 172.3, 192.5; MS (70 eV) *m/z* (relative intensity) 292 (M^+, 30), 264 (100), 234 (17), 219 (30), 210 (8), 204 (24), 186 (39), 176 (11), 158 (64), 145 (37); HRMS (EI) calcd for $C_{16}H_{20}O_5$ (M^+) 292.1311, found 292.1308.

(2a*R,5a*R**,8a*R**,8b*S**)-8a-Methoxy-2a,5a-dimethyl-2a,5,5a,8,8a,8b-hexahydro-2*H*-benzo[*cd*]isobenzofuran-8-one (22d):** colorless liquid; IR (film) 2926, 1738, 1690, 1455, 1042 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.19 (s, 3H), 1.26 (s, 3H), 1.78 (apparent ddd, *J* = 2.4, 2.8, 16.4 Hz, 1H), 1.99 (dd, *J* = 5.8, 16.4 Hz, 1H), 2.25 (d, *J* = 1.6 Hz, 1H), 3.24 (s, 3H), 3.70 (d, *J* = 8.4 Hz, 1H), 3.75 (d, *J* = 8.4 Hz, 1H), 5.60 (dd, *J* = 2.4, 10.0 Hz, 1H), 5.66 (ddd, *J* = 2.8, 5.8, 10.0 Hz, 1H), 6.00 (d, *J* = 10.0 Hz, 1H), 6.76 (d, *J* = 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.3, 27.5, 35.2, 37.3, 42.7, 50.0, 60.5, 79.4, 103.9, 123.3, 127.1, 134.5, 160.0, 190.7; MS (70 eV) *m/z* (relative intensity) 234 (M^+, 15), 219 (29), 206 (37), 187 (34), 176 (48), 174 (62), 161 (100), 147 (43), 133 (45), 131 (40); HRMS (EI) calcd for $C_{14}H_{18}O_3$ (M^+) 234.1256, found 234.1263.

(2a*R,5a*S**,8a*R**,8b*R**)-5a-(5,5-Dimethyl-1,3-dioxan-2-yl)-2a,5,5a,8,8a,8b-hexahydro-2*H*-benzo[*cd*]isobenzofuran-8-one (23a):** colorless liquid; IR (film) 2926, 1692, 1467, 1391, 1210, 1034 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.61 (s, 3H), 1.07 (s, 3H), 1.75 (dd, *J* = 2.6, 15.2 Hz, 1H), 2.34 (dd, *J* = 3.6, 15.2 Hz, 1H), 2.87 (apparent dd, *J* = 2.8, 6.8 Hz, 1H), 2.98 (d, *J* = 8.0 Hz, 1H), 3.18 (s, 3H), 3.30 (d, *J* = 10.0 Hz, 2H), 3.40−3.60 (m, 2H), 3.71 (dd, *J* = 2.8, 8.8 Hz, 1H), 4.02 (dd, *J* = 6.8, 8.8 Hz, 1H), 4.26 (s, 1H), 5.63−5.66 (m, 2H), 6.00 (d, *J* = 10.0 Hz, 1H), 6.94 (d, *J* = 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.2, 30.7, 37.6, 43.5, 47.5, 50.5, 72.8, 77.3 (CH_2 × 2), 102.7, 103.1, 125.7, 127.8, 130.0, 153.8, 191.3; MS (70 eV) *m/z* (relative intensity) 320 (M^+, 26), 319 (26), 292 (30), 277 (3), 261 (24), 208 (32), 193 (9), 175 (32), 144 (25), 115 (100); HRMS (EI) calcd for $C_{18}H_{24}O_5$ (M^+) 320.1624, found 320.1626.

(2a*R,5*S**,5a*R**,8a*R**,8b*R**)-5a-(5,5-Dimethyl-1,3-dioxan-2-yl)-8a-methoxy-5-methyl-2a,5,5a,8,8a,8b-hexahydro-2*H*-benzo[*cd*]isobenzofuran-8-one (23b):** colorless liquid; IR (film) 1692 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.66 (s, 3H), 0.90 (d, *J* = 7.2 Hz, 3H), 1.13 (s, 3H), 2.54 (apparent ddd, *J* = 2.0, 7.2, 9.2, 1H), 2.80−3.00 (m, 1H), 3.13 (d, *J* = 9.2 Hz, 1H), 3.24 (s, 3H), 3.35 (dd, *J* = 3.6, 11.0 Hz, 2H), 3.61 (dd, *J* = 3.6, 11.0 Hz, 2H), 3.78 (dd, *J* = 2.0, 8.4 Hz, 1H), 4.05 (dd, *J* = 7.2, 8.4 Hz, 1H), 4.38 (s, 1H), 5.61 (m, 2H), 6.16 (d, *J* = 9.6 Hz, 1H), 6.82 (d, *J* = 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.7, 21.6, 23.1, 30.2, 32.2, 37.5, 47.3, 47.7, 50.6, 72.5, 77.6 (CH_2 × 2), 103.1, 103.4, 128.9, 129.3, 133.2, 150.4, 191.2; MS (70 eV) *m/z* (relative intensity) 334 (M^+, 2), 305 (50), 272 (4), 251 (6), 205 (6), 172 (4), 158 (4), 144, (3), 114 (100); HRMS (EI) calcd for $C_{19}H_{26}O_5$ (M^+) 334.1782, found 334.1783.

Ethyl (2a*R,5*S**,5a*S**,8a*R**,8b*R**)-5a-(5,5-dimethyl-1,3-dioxanyl-2-yl)-8a-methoxy-2a-methyl-8-oxo-2a,5,5a,8,8a,8b-hexahydro-2*H*-benzo[*cd*]isobenzofuran-5-carboxylate (23c):** colorless liquid; IR (film) 2931, 1719, 1469, 1032 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.69 (s, 3H), 1.18 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H), 2.80−2.90 (m, 1H), 3.23 (d, *J* = 1.2

Hz, 1H), 3.34 (s, 3H), 3.39 (d, J = 11.6 Hz, 3H), 3.62 (dd, J = 2.4, 8.4 Hz, 1H), 3.64 (dd, J = 2.8, 6.4 Hz, 1H), 3.84 (dd, J = 3.2, 8.8 Hz, 1H), 4.00−4.20 (m, 3H), 4.53 (s, 1H), 5.70−5.90 (m, 2H), 6.12 (d, J = 10.4 Hz, 1H), 6.93 (d, J = 10.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 21.7, 23.2, 30.2, 39.4, 45.2, 47.8, 48.3, 51.2, 60.9, 71.5, 77.4, 77.5, 102.7, 103.8, 127.3, 129.6, 132.3, 147.9, 172.5, 192.3; MS (70 eV) *m/z* (relative intensity) 392 (M^+, 6), 364 (20), 319 (12), 277 (7), 233 (8), 210 (11), 173 (16), 145 (15), 115 (100), 69 (35); HRMS (EI) calcd for $C_{21}H_{28}O_7$ (M^+) 392.1835, found 392.1831.

(2a*R,5a*S**,8a*R**,8b*R**)-5a-(5,5-Dimethyl-1,3-dioxan-2-yl)-8a-methoxy-2a-methyl-2a,5,5a,8,8a,8b-hexahydro-2*H*-benzo[*cd*]isobenzofuran-8-one (23d):** colorless liquid; IR (film) 3026, 2955, 1688, 1606, 1436, 1042 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.70 (s, 3H), 1.16 (s, 3H), 1.22 (s, 3H), 1.69 (d, J = 15.8 Hz, 1H), 2.45 (dd, J = 4.4, 15.8 Hz, 1H), 2.81 (s, 1H), 3.23 (s, 3H), 3.36 (d, J = 11.6 Hz, 2H), 3.64 (d, J = 11.6 Hz, 1H), 3.73 (d, J = 8.4 Hz, 2H), 3.80 (d, J = 8.4 Hz, 2H), 4.37 (s, 1H), 5.62 (s, 1H), 6.08 (d, J = 10.4 Hz, 1H), 7.24 (d, J = 10.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 21.6, 23.1, 25.7, 30.2, 31.0, 42.8, 43.5, 50.0, 54.0, 77.4, 79.4, 101.6, 104.2, 123.5, 127.5, 135.1, 154.5, 190.9; MS (70 eV) *m/z* (relative intensity) 333 (M^+, 24), 319 (12), 303 (24), 289 (4), 275 (15), 217 (12), 208 (25), 189 (24), 175 (18), 115 (100); HRMS (EI) calcd for $C_{19}H_{26}O_5$ (M^+) 334.1780, found 334.1776.

(1*R,3*R**,6*S**,7*S**,10*S**)-3-Methoxy-10-vinyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (24a):** colorless liquid; IR (film) 2949, 1745, 1460, 1023 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (ddd, J = 1.6, 3.6, 4.4 Hz, 1H), 2.72 (apparent d, J = 8.0 Hz, 1H), 3.17 (ddd, J = 1.6, 2.8, 6.4 Hz, 1H), 3.32 (ddd, J = 1.6, 4.4, 6.4 Hz, 1H), 3.50 (s, 3H), 3.83 (d, J = 8.0 Hz, 1H), 4.13 (dd, J = 3.6, 8.0 Hz, 1H), 5.01 (d, J = 9.8 Hz, 1H), 5.05 (d, J = 17.0 Hz, 1H), 5.63 (ddd, J = 8.0, 9.8, 17.0 Hz, 1H), 6.18 (ddd, J = 1.6, 6.4, 8.0 Hz, 1H), 6.25 (ddd, J = 1.6, 6.4, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.06, 43.09, 46.4, 51.4, 51.9, 73.6, 99.9, 115.7, 128.3, 129.5, 138.4, 200.7; MS (70 eV) *m/z* (relative intensity) 178 (M^+ - CO, 76), 159 (12), 145 (9), 124 (18), 119 (88), 105 (31), 93 (12), 91 (100), 77 (47), 41 (44); HRMS (EI) calcd for $C_{11}H_{14}O_2$ (M^+ − CO) 178.0994, found 178.0987.

(1*R,3*R**,6*S**,7*S**,10*S**)-3-Methoxy-6-methyl-10-[(*E*)-1-propenyl]-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (24b):** colorless liquid; IR (film) 3063, 2950, 1744, 1686, 1461, 1094 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.62 (dd, J = 1.6, 6.8 Hz, 3H), 2.30−2.45 (m, 1H), 2.66 (apparent d, J = 8.2 Hz, 1H), 3.11 (ddd, J = 1.6, 3.2, 6.4 Hz, 1H), 3.30 (ddd, J = 2.2, 4.4, 6.4 Hz, 1H), 3.49 (s, 3H), 3.81 (d, J = 8.0 Hz, 1H), 4.11 (dd, J = 4.0, 8.0 Hz, 1H), 5.23 (ddd, J = 1.6, 8.2, 15.8 Hz, 1H), 5.49 (dq, J = 6.8, 15.8 Hz, 1H), 6.18 (ddd, J = 2.2, 6.4, 8.4 Hz, 1H), 6.23 (ddd, J = 1.6, 6.4, 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.8, 43.0, 43.7, 45.7, 51.3, 52.4, 73.7, 100.0, 126.4, 128.4, 129.3, 131.2, 201.1; MS (70 eV) *m/z* (relative intensity) 192 (M^+ - CO, 68), 174 (4), 163 (4), 145 (4), 117 (50), 105 (89), 91 (100), 77 (36), 65 (22); HRMS (EI) calcd for $C_{12}H_{16}O_2$ (M^+ − CO) 192.1150, found 192.1130.

Ethyl (*E*)-3-[(1*R,2*S**,3*S**,6*R**,7*S**)-6-methoxy-10-oxo-5-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-yl]-2-propenate (24c):** colorless liquid; IR (film) 2953, 1741, 1719, 1648, 1023 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (t, J = 7.2 Hz, 3H), 2.36 (apparent d, J = 4.4 Hz, 1H), 2.88 (apparent d, J = 8.4 Hz, 1H), 3.21 (ddd, J = 1.6, 2.8, 6.6 Hz, 1H), 3.37 (ddd, J = 1.4, 4.4, 6.8 Hz, 1H), 3.51 (s, 3H), 3.83 (d, J = 8.2 Hz, 1H), 4.17 (q, J = 7.2 Hz, 2H), 5.80−5.85 (m, 2H), 6.21 (ddd, J = 1.6, 6.8, 8.0 Hz, 1H), 6.31 (ddd, J = 1.4, 6.6, 8.0 Hz, 1H), 5.76 (dd, J = 8.4, 15.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 42.9, 43.1, 45.0, 50.9, 51.5, 60.6, 73.3, 99.8, 122.4, 128.0, 130.2, 147.5, 166.0, 199.6; MS (70 eV) *m/z* (relative intensity) 278 (M^+, 1), 250 (21), 236 (12), 163 (27), 145 (39), 117 (59), 91 (82), 77 (37), 43 (48), 18 (100); HRMS (EI) calcd for $C_{15}H_{18}O_5$ (M^+) 278.1146, found 278.1154.

(1*R,3*R**,6*S**,7*S**,10*S**)-3-Methoxy-1-methyl-10-vinyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (25a):** colorless liquid; IR (film) 2971, 1741, 1638, 1453, 1054 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (s, 3H), 2.26 (apparent d, J = 8.8 Hz, 1H), 2.31 (ddd, J = 1.6, 3.6, 4.6 Hz, 1H), 3.29 (ddd, J = 1.4, 4.6, 6.4 Hz, 1H), 3.49 (s, 3H), 3.82 (d, J = 8.0 Hz, 1H), 4.12 (dd, J = 3.6, 8.0 Hz, 1H), 5.04 (d, J = 16.0 Hz, 1H), 5.05 (d, J = 10.8 Hz, 1H), 5.62−5.64 (m, 1H), 5.77 (dd, J = 1.4, 8.0 Hz, 1H), 6.23 (dd, J = 6.4, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.3, 42.3, 45.2, 50.8, 51.3, 53.2, 73.6, 100.2, 116.8, 129.0, 136.6, 137.6, 202.2; MS (70 eV) *m/z* (relative intensity) 220 (M^+, 8), 192 (28), 189 (25), 162 (84), 147 (62), 131 (38), 117 (44), 91 (100), 77 (56), 65 (35); HRMS (EI) calcd for $C_{13}H_{16}O_3$ (M^+) 220.1100, found 220.1102.

(1*R,3*R**,6*S**,7*S**10*S**)-3-Methoxy-1-methyl-10-[(*E*)-1-propenyl]-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (25b):** colorless liquid; IR (film) 2969, 1741, 1450, 1039 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17 (s, 3H), 1.63 (dd, J = 1.6, 6.4 Hz, 3H), 2.19 (apparent d, J = 9.6 Hz, 1H), 2.26 (ddd, J = 1.6, 3.0, 4.4 Hz, 1H), 3.26 (ddd, J = 1.6, 4.4, 6.0 Hz, 1H), 3.47 (s, 3H), 3.80 (d, J = 8.0 Hz, 1H), 4.09 (dd, J = 3.6, 8.0 Hz, 1H), 5.14 (ddq, J = 1.6, 9.6, 15.0 Hz, 1H), 5.44 (dq, J = 6.4, 15.0 Hz, 1H), 5.76 (d, J = 8.0 Hz, 1H), 6.20 (dd, J = 6.8, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.4, 17.8, 42.1, 45.5, 51.0, 51.2, 52.1, 73.6, 100.2, 127.5, 128.7, 130.2, 133.7, 202.5; MS (70 eV) *m/z* (relative intensity) 206 (M^+ − CO, 100), 175 (6), 147 (41), 131 (37), 119 (57), 105 (63), 91 (70), 77 (29), 59 (19), 39 (28); HRMS (EI) calcd for $C_{14}H_{18}O_3$ (M^+) 234.1256, found 234.1241.

Methyl (1*S,3*R**,6*R**,7*S**,10*S**)-3-methoxy-2-oxo-10-[(*E*)-1-propenyl]-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-ene-1-carboxylat**e (26b):** colorless liquid; IR (film) 2953, 1754, 1733, 1675, 1438, 1016 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.57 (dd, J = 1.6, 6.8 Hz, 3H), 2.20−2.40 (m, 1H), 3.09 (apparent d, J = 9.0 Hz, 1H), 3.27 (ddd, J = 1.6, 4.4, 6.4 Hz, 1H), 3.50 (s, 3H), 3.78 (s, 3H), 3.90 (dd, J = 8.0, 8.2 Hz, 1H), 4.13 (dd, J = 3.2, 8.2 Hz, 1H), 5.10 (ddq, J = 1.6, 9.0, 15.2 Hz, 1H), 5.51 (dd, 6.8, 15.2 Hz, 1H), 6.26 (dd, J = 6.4, 8.4 Hz, 1H), 6.55 (dd, J = 1.6, 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.9, 43.5, 44.5, 48.8, 51.9, 52.4, 64.3, 73.5, 99.9, 128.0, 128.5, 128.7, 128.8, 168.7, 196.1; MS (70 eV) *m/z* (relative intensity) 278 (M^+, 10), 250 (100), 247 (22), 215 (54), 191 (33), 159 (49), 131 (59), 115 (22), 91 (24), 59 (9); HRMS (EI) calcd for $C_{15}H_{18}O_5$ (M^+) 278.1155, found 278.1160.

(1*S,3*R**,6*S**,7*S**,10*S**)-3-Methoxy-9-methyl-10-vinyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (27a):** colorless liquid; IR (film) 2957, 1742, 1672, 1654, 1442, 1026 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.81 (d, J = 1.6 Hz, 3H), 2.28 (apparent dd, J = 2.6, 4.4 Hz, 1H), 2.72 (apparent dd, J = 2.6, 8.0 Hz, 1H), 2.94 (dd, J = 2.0, 2.6 Hz, 1H), 3.23 (dd, J = 4.4, 6.4 Hz, 1H), 3.49 (s, 3H), 3.82 (d, J = 8.0 Hz, 1H), 4.11 (dd, J = 2.6, 8.0 Hz, 1H), 5.02 (d, J = 10.2 Hz, 1H), 5.07 (d, J = 17.0 Hz, 1H), 5.60 (ddd, J = 8.0, 10.2, 17.0 Hz, 1H), 5.84 (ddq, J = 1.6, 2.0, 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 41.9, 42.8, 46.1, 50.9, 57.2, 73.5, 100.1, 115.6, 121.2, 137.2, 137.9, 200.3; MS (70 eV) *m/z* (relative intensity) 192 (M^+ − CO, 78), 187 (7), 153 (10), 138 (14), 134 (100), 131 (23), 125 (40), 105 (62), 91 (69), 77 (42); HRMS (EI) calcd for $C_{12}H_{16}O_2$ (M^+ − CO) 192.1150, found 192.1148.

(1*S,3*R**,6*S**,7*S**,10*S**)-3-Methoxy-9-methyl-10-[(*E*)-1-propenyl]-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (27b):** colorless liquid; IR (film) 2953, 1741, 1440, 1022 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.61 (dd, J = 1.2, 6.4 Hz, 3H), 1.80 (d, J = 1.6 Hz, 3H), 2.19 (dd, J = 3.6, 4.4 Hz, 1H), 2.65 (apparent d, J = 8.4 Hz, 1H), 2.87 (dd, J = 1.6, 2.8 Hz, 1H), 3.19 (dd, J = 4.4, 6.4 Hz, 1H), 3.46 (s, 3H), 3.78 (d, J = 8.0 Hz, 1H), 4.07 (dd, J = 3.6, 8.0 Hz, 1H), 5.18 (ddq, J = 1.2, 8.4, 15.0 Hz, 1H), 5.49 (dq, J = 6.4, 15.0 Hz, 1H), 5.80 (ddq, J = 1.6, 1.6, 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.9, 21.6, 42.0, 43.6, 45.4, 51.1, 57.7, 73.7, 100.2, 121.2, 126.5, 130.8, 137.5, 200.8; MS (70 eV) *m/z* (relative intensity) 206 (M^+ − CO, 100), 191 (4),

147 (52), 131 (36), 119 (66), 105 (64), 91 (70), 77 (31), 59 (27), 39 (34); HRMS (EI) calcd for $C_{13}H_{18}O_2$ (M^+ − CO) 206.1298, found 206.1310.

Methyl (1*S,3*R**,6*S**,7*S**,10*S**)-3-methoxy-2-oxo-10-vinyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-ene-9-carboxylate (28a):** colorless liquid; IR (film) 3078, 2920, 1746, 1716, 1683, 1436, 1018 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35−2.45 (m, 1H), 2.80−2.90 (m, 1H), 3.49 (dd, J = 4.4, 6.8 Hz, 1H) 3.51 (s, 3H), 3.75 (s, 3H), 3.78 (dd, J = 1.9, 2.4 Hz, 1H), 3.88 (d, J = 8.4 Hz, 1H), 4.19 (dd, J = 3.6, 8.4 Hz, 1H), 5.03 (d, J = 10.4 Hz, 1H), 5.05 (d, J = 17.2 Hz, 1H), 5.52 (ddd, J = 7.2, 10.4, 17.2 Hz, 1H), 7.22 (dd, J = 1.9, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.6, 43.8, 50.7, 51.4, 52.1, 73.6, 99.4, 115.8, 131.9, 138.2, 138.4, 163.4, 199.5; MS (70 eV) *m/z* (relative intensity) 236 (M^+ − CO, 30), 221 (2), 177 (22), 169 (24), 145 (59), 117 (100), 91 (63), 77 (34), 59 (50), 41 (66); HRMS (EI) calcd for $C_{13}H_{16}O_4$ (M^+ − CO) 236.1049, found 236.1033.

Methyl (1*S,3*R**,6*S**,7*S**,10*S**)-3-methoxy-2-oxo-10-[(*E*)-1-propenyl]-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-ene-9-carboxylate (28b):** colorless liquid; IR (film) 2952, 1746, 1719, 1665, 1628, 1438, 1022 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.57 (d, J = 6.0 Hz, 3H), 2.20−2.40 (m, 1H), 2.74 (apparent d, J = 8.0 Hz, 1H), 3.46 (s, 3H), 3.72 (s, 3H), 3.83 (d, J = 8.0 Hz, 3H), 4.14 (dd, J = 3.6, 8.0 Hz, 1H), 5.08 (ddd, J = 1.6, 8.0, 15.4 Hz, 1H), 5.47 (dq, J = 6.0, 15.4 Hz, 1H), 7.20 (dd, J = 2.2, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.8, 43.6, 43.7, 45.0, 51.1, 52.1, 73.6, 99.4, 127.4, 129.7, 131.7, 138.6, 163.6, 200.1; MS (70 eV) *m/z* (relative intensity) 250 (M^+ - CO, 97), 247 (44), 198 (22), 191 (22), 159 (48), 131 (73), 115 (30), 91 (46), 59 (30), 43 (100); HRMS (EI) calcd for $C_{15}H_{18}O_5$ (M^+) 278.1154, found 278.1173.

(2a*R,5a*R**,8a*R**,8b*S**)-8a-Methoxy-2a,5,5a,8,8a,8b-hexahydro-2*H*-benzo[*cd*]isobenzofuran-8-one (29a):** colorless liquid; IR (film) 2963, 1686, 1605, 1455, 1019 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.70−1.80 (m, 1H), 2.23 (ddd, J = 5.2, 5.2, 16.4 Hz, 1H), 2.61−2.69 (m, 1H), 2.87 (dd, J = 8.0, 8.8 Hz, 1H), 3.10−3.14 (m, 1H), 3.34 (s, 3H), 3.73 (dd, J = 3.6, 8.4 Hz, 1H), 4.14 (dd, J = 8.0, 8.4 Hz, 1H), 5.83 (ddd, J = 1.8, 5.2, 10.0 Hz, 1H), 5.89 (ddd, J = 3.2, 5.6, 10.0 Hz, 1H), 6.08 (dd, J = 1.6, 10.0 Hz, 1H), 6.93 (dd, J = 5.2, 10.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.0, 32.8, 37.2, 46.7, 50.6, 74.4, 103.3, 127.3, 128.2, 129.9, 152.9, 191.5; MS (70 eV) *m/z* (relative intensity) 206 (M^+, 37), 178 (8), 175 (8), 148 (53), 117 (67), 105 (54), 91 (100), 77 (68), 51 (38); HRMS (EI) calcd for $C_{12}H_{14}O_3$ (M^+) 206.0943, found 206.0940.

(2a*R,5*S**,5a*S**,8a*R**,8b*S**)-8a-Methoxy-5-methyl-2a,5,5a,8,8a,8b-hexahydro-2*H*-benzo[*cd*]isobenzofuran-8-one (29b):** colorless liquid; IR (film) 3021, 2969, 1685, 1458, 1035 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 (d, J = 7.2 Hz, 3H), 2.35−2.42 (m, 1H), 2.80−3.10 (m, 3H), 3.35 (s, 3H), 3.67 (dd, J = 4.8, 8.6 Hz, 1H), 4.18 (dd, J = 8.0, 8.6 Hz, 1H), 5.67 (s, 2H), 6.15 (dd, J = 1.6, 10.2 Hz, 1H), 6.76 (dd, J = 6.6, 10.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.4, 32.7, 37.2, 37.3, 51.4, 72.2, 103.1, 129.4, 129.7, 133.7, 149.7, 192.1; MS (70 eV) *m/z* 220 (M^+, 100), 196 (33), 192 (49), 177 (7), 162 (22), 147 (21), 133 (8), 117 (5), 91 (7), 77 (6); HRMS (EI) calcd for $C_{13}H_{16}O_3$ (M^+) 220.1100, found 220.1095.

(2a*R,5a*R**,8a*R**,8b*S**)-8a-Methoxy-7-methyl-2a,5,5a,8,8a,8b-hexahydro-2*H*-benzo[*cd*]isobenzofuran-8-one (30a):** colorless liquid; IR (film) 2942, 1682, 1450, 1029 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.60−1.80 (m, 1H), 1.71 (s, 3H), 2.18 (ddd, J = 1.2, 5.6, 16.0 Hz, 1H), 2.50−2.54 (m, 1H), 2.84 (dd, J = 8.4, 8.8 Hz, 1H), 3.05−3.10 (m, 1H), 3.31 (s, 3H), 3.73 (dd, J = 3.6, 8.2 Hz, 1H), 4.13 (dd, J = 8.0, 8.2 Hz, 1H), 5.80 (ddd, J = 2.0, 6.4, 9.4 Hz, 1H), 5.87 (ddd, J = 2.8, 5.6, 9.4 Hz, 1H), 6.66 (dd, J = 1.6, 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.7, 30.4, 31.9, 37.3, 46.5, 50.4, 74.6, 103.6, 127.4, 129.6, 135.2, 147.3, 192.1; MS (70 eV) *m/z* (relative intensity) 220 (M^+, 6), 192 (75), 189 (27), 162 (49), 147 (36), 125 (62), 117 (54), 105 (59), 91 (100), 77 (46); HRMS (EI) calcd for $C_{13}H_{16}O_3$ (M^+) 220.1100, found 220.1105.

(2a*R,5*S**,5a*R**,8a*R**,8b*S**)-8a-Methoxy-5,7-dimethyl-2a,5,5a,8,8a,8b-hexa-hydro-2*H*-benzo[*cd*]isobenzofuran-8-one (30b):** colorless liquid; IR (film) 2959, 1677, 1460, 1058 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (d, J = 7.6 Hz, 3H), 1.83 (d, J = 2.0 Hz, 3H), 2.20−2.40 (m, 1H), 2.80−2.84 (m, 1H), 2.90−3.00 (m, 2H), 3.32 (s, 3H), 3.62 (dd, J = 4.4, 8.8 Hz, 1H), 4.16 (dd, J = 7.2, 8.8 Hz, 1H), 5.64 (m, 2H), 6.47 (dd, J = 2.0, 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.0, 17.5, 32.7, 35.8, 37.3, 46.9, 51.2, 72.5, 103.6, 128.9, 133.6, 136.6, 144.1, 192.7; MS (70 eV) *m/z* (relative intensity) 234 (M^+, 23), 203 (21), 189 (9), 176 (74), 129 (36), 101 (100), 99 (43), 91 (62), 81 (37), 77 (33); HRMS (EI) calcd for $C_{14}H_{18}O_3$ (M^+) 234.1256, found 234.1260.

(2a*R,5a*S**,8a*R**,8b*S**)-8a-Methoxy-6-methyl-2a,5,5a,8,8a,8b-hexahydro-2*H*-benzo[*cd*]isobenzofuran-8-one (32a):** colorless liquid; IR (film) 3039, 2942, 1681, 1634, 1437, 1026 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.55−1.70 (m, 1H), 2.00 (d, J = 1.2 Hz, 3H), 2.20−2.40 (m, 2H), 2.82 (ddd, J = 2.0, 7.2, 8.8 Hz, 1H), 3.05−3.15 (m, 1H), 3.26 (s, 3H), 3.77 (dd, J = 2.4, 8.2 Hz, 1H), 4.09 (dd, J = 7.6, 8.2 Hz, 1H), 5.79 (ddd, J = 2.8, 5.2, 10.4 Hz, 1H), 5.86 (ddd, J = 2.8, 5.2, 10.4 Hz, 1H), 5.89 (dq, J = 1.2, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.3, 29.9, 36.9, 38.2, 46.7, 50.0, 74.6, 102.9, 124.8, 126.8, 129.6, 165.4, 190.3; MS (70 eV) *m/z* (relative intensity) 220 (M^+, 14), 204 (6), 189 (55), 161 (47), 147 (60), 131 (52), 117 (51), 105 (43), 91 (100), 77 (53); HRMS (EI) calcd for $C_{13}H_{16}O_3$ (M^+) 220.1099, found 220.1093.

(2a*R,5*S**,5a*S**,8a*R**,8b*S**)-8a-Methoxy-5,6-dimethyl-2a,5,5a,8,8a,8b-hexahydro-2*H*-benzo[*cd*]isobenzofuran-8-one (32b):** IR (film) 3021, 2967, 1678, 1630, 1435, 1026 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.71 (s, 3H), 1.96 (s, 3H), 2.30−2.41 (m, 1H), 2.62 (dd, J = 6.0, 8.0 Hz, 1H), 2.82 (dd, J = 8.0, 10.0 Hz, 1H), 3.10−3.16 (m, 1H), 3.29 (s, 3H), 3.74 (dd, J = 2.8, 8.0 Hz, 1H), 4.08 (dd, J = 8.0, 8.8 Hz, 1H), 5.73 (dd, J = 6.0, 10.0 Hz, 1H), 5.97 (dd, J = 6.0, 10.0 Hz. 1H), 6.06 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.4, 23.2, 30.2, 35.7, 41.1, 46.2, 50.2, 74.3, 103.0, 127.1, 127.3, 132.5, 162.4, 189.9; MS (70 eV) *m/z* (relative intensity) 234 (M^+, 8), 206 (19), 203 (87), 175 (29), 161 (38), 143 (54), 133 (39), 105 (55), 91 (100), 77 (54); HRMS (EI) calcd for $C_{14}H_{18}O_3$ (M^+) 234.1256, found 234.1256.

Methyl (2a*R,5a*S**,8a*R**,8b*R**)-8a-methoxy-8-oxo-2a,5,5a,8,8a,8b-hexahydro-2*H*-benzo[*cd*]isobenzofuran-6-carboxylate (33a):** colorless liquid; IR (film) 2949, 1724, 1696, 1434, 1249, 1038 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.52−1.58 (m, 1H), 2.31 (ddd, J = 5.2, 6.4, 16.0 Hz, 1H), 2.87 (dd, J = 7.0, 8.8 Hz, 1H), 3.03 (ddd, J = 5.2, 7.0, 11.6 Hz, 1H), 3.10−3.20 (m, 1H), 3.22 (s, 3H), 3.83 (s, 3H), 3.86 (dd, J = 1.6, 8.0 Hz, 1H), 4.12 (dd, J = 7.2, 8.0 Hz, 1H), 5.80 (ddd, J = 2.4, 4.4, 9.8 Hz, 1H), 5.86 (ddd, J = 2.4, 6.4, 9.8 Hz, 1H), 6.85 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.0, 31.8, 37.0, 47.0, 49.8, 52.8, 74.7, 103.6, 126.9, 129.0, 132.5, 151.6, 165.9, 191.2; MS (70 eV) *m/z* (relative intensity) 264 (M^+ , 23), 249 (60), 233 (34), 205 (34), 176 (22), 145 (48), 117 (100), 115 (21), 99 (67), 91 (61); HRMS (EI) calcd for $C_{13}H_{16}O_4$ (M^+) 264.0094, found 264.0997.

Methyl (2a*R,5*S**,5a*S**,8a*R**,8b*S**)-8a-methoxy-5-methyl-8-oxo-2a,5,5a,8,8a,8b-hexahydro-2*H*-benzo[*cd*]isobenzofuran-6-carboxylate (33b):** colorless liquid; IR (film) 3021, 2953, 1721, 1695, 1621, 1436, 1019 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.68 (d, J = 6.8 Hz, 1H), 2.41 (ddd, J = 6.4, 6.8, 11.8 Hz, 1H), 2.84 (dd, J = 8.0, 11.8 Hz, 1H), 3.10−3.20 (m, 1H), 3.23 (s, 3H), 3.29 (dd, J = 4.8, 8.0 Hz, 1H), 3.80 (dd, J = 3.6, 8.8 Hz, 1H), 3.84 (s, 3H), 4.10 (dd, J = 8.0, 8.8 Hz, 1H), 5.70 (dd, J = 5.2, 10.0 Hz, 1H), 5.95 (dd, J = 6.4, 10.0 Hz, 1H), 6.98 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.7, 30.7, 35.0, 35.8, 46.3, 50.0, 52.8, 74.2, 103.6, 126.7, 132.7, 134.1, 148.9, 166.0, 190.9; MS (70 eV) *m/z* (relative intensity) 278 (M^+, 8), 263 (21), 250 (19), 247 (86), 219 (18), 187 (13), 159 (31), 131 (59), 115 (51), 99 (100); HRMS (EI) calcd for $C_{15}H_{18}O_5$ (M^+) 278.1154, found 278.1157.

(1*R,3*R**,6*R**,7*R**,10*R**)-3-Methoxy-1-methyl-10-[(*E*)-1-propenyl]-4-oxatricyclo[4.3.1.0^{3,7}]decane-2,8-dione (35):** colorless liquid; IR (film) 2970, 1740, 1450, 1023 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 (s, 3H), 1.71 (dd, J = 1.6, 6.4 Hz, 3H), 2.14 (dd, 1.6, 19.6 Hz, 1H), 2.30 (apparent d, J = 8.8 Hz, 1H), 2.52 (d, J = 19.6 Hz, 1H), 2.67 (dd, J = 3.6, 4.4 Hz, 1H), 3.27 (apparent d, J = 4.4 Hz, 1H), 3.48 (s, 3H), 3.83 (d, J = 8.0 Hz, 1H), 4.16 (dd, J = 3.6, 8.0 Hz, 1H), 5.34 (ddq, J = 1.6, 8.8, 15.2 Hz, 1H), 5.56 (dq, J = 6.4, 15.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.6, 18.1, 43.1, 44.8, 46.3, 47.5, 51.5, 55.6, 74.5, 104.1, 126.9, 130.6, 205.4, 206.5; MS (70 eV) *m/z* (relative intensity) 222 (M^+ − CO, 69), 194 (18), 167 (24), 153 (14), 147 (9), 121 (14), 99 (100), 79 (72), 71 (68), 41 (75) HRMS (EI) calcd for $C_{13}H_{18}O_3$ 222.1256, found 222.1253.

Methyl (1*S,3*R**,6*R**,7*S**,10*R**)-3-methoxy-2,8-dioxo-10-[(*E*)-1-propenyl]-4-oxatricyclo[4.3.1.0^{3,7}]decane-1-carboxylate (37):** colorless liquid; IR (film) 2954, 1757, 1731, 1438, 1044 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.67 (d, J = 5.6 Hz, 3H), 2.65−2.75 (m, 1H), 2.71 (dd, J = 1.6, 20.4 Hz, 1H), 2.91 (d, J = 20.4 Hz, 1H), 3.23 (apparent d, J = 8.0 Hz, 1H), 3.27 (d, J = 4.4 Hz, 1H), 3.52 (s, 3H), 3.79 (s, 3H), 3.94 (d, J = 8.0 Hz, 1H), 4.21 (dd, J = 3.2, 8.4 Hz, 1H), 5.37 (ddd, J = 1.6, 8.0, 15.2 Hz, 1H), 5.51 (dd, J = 6.8, 14.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.1, 39.1, 43.6, 44.0, 52.1, 52.7, 56.9, 59.2, 74.4, 104.0, 126.0, 131.1, 168.4, 199.2, 201.4; MS (70 eV) *m/z* (relative intensity) 292 (M^+, 6), 248 (34), 233 (22), 215 (100), 201 (52), 187 (64), 173 (33), 157 (78), 129 (10), 115 (67); HRMS (EI) calcd for $C_{15}H_{18}O_5$ (M^+) 292.0946, found 292.0951.

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Supporting Information Available: General remarks, general experimental procedures, and ^{1}H NMR spectra of all the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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