Tandem Oxidative Acetalization−Intramolecular Diels−Alder Reactions of 2-Methoxyphenols. Simple Synthesis of Bicyclo[2.2.2]octenone Derivatives

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Received February 8, 1999

Intramolecular Diels−Alder reactions of in situ generated masked *o*-benzoquinones are described. Oxidation of methyl vanillate (**2**) in the presence of allyl alcohol (**1a**), *trans*-crotyl alcohol (**1b**), cinnamyl alcohol (**1c**), and homoallyl alcohol (**1d**) resulted in the formation of masked *o*-benzoquinones **8a**−**d** that underwent intramolecular Diels−Alder reactions under reaction conditions to furnish adducts **14a**−**d** in 53−75% yields. This tandem oxidative acetalization−intramolecular Diels−Alder process was extended to other 2-methoxyphenols such as 2-methoxy-4-methylphenol (**3**), guaicol (**4**), methyl isovanillate (**5**), methyl syringate (**6**), and 2,6-dimethoxy-4-methylphenol (**7**) to obtain adducts **15a**−**d**, **16a**−**c**, **17a**−**d**, **18a**−**d**, and **19a**−**d**, respectively. While intramolecular Diels−Alder reactions of the masked *o*-benzoquinones **10a**, **12d**, and **13d** were found to be less efficient, the masked *o*-benzoquinones **9a**−**d**, **10b**, **10c**, **11a**−**d**, **12a**−**c**, and **13a**−**c** furnished the desired products in 38−80% yields. Masked *o*-benzoquinones **21a**−**d** generated from **2** and substituted acrylic acids **20a**−**d** underwent intramolecular Diels−Alder reactions to provide the tricyclic lactones **22a**−**d** in 32−40% yields.

Introduction

The Diels−Alder reaction has become one of the most frequently employed carbon−carbon bond-forming reactions in organic synthesis, since it provides easy access to a wide variety of cyclic systems, usually with predictable stereochemistry.[1,2] Its versatility has been further enhanced with the introduction of its intramolecular version, i.e., the intramolecular Diels−Alder reaction,[3] which stands out from the intermolecular reaction both in aesthetic sense and usefulness.[4] The reaction requires efficient designing and stitching together of the two reacting moieties prior to the reaction. It produces a minimum of two rings in a highly regioselective and stereocontrolled manner. The advantages offered by intramolecular reactions over their intermolecular counterparts have generated much interest in finding ways to intramolecularize the reactions.[5] Attempts toward intramolecularization of a variety of reactions including Diels−Alder reactions using disposable tethers have resulted in considerable success.[6,7]

In recent years, "domino" or "tandem" processes have gained considerable importance as a means to achieve synthesis of molecules with high complexity in a rapid and efficient manner.[8−10] As evidenced by a large number of reports in recent literature, the intramolecular Diels−Alder reactions are among the few that are commonly employed in combination with other reactions in domino/tandem processes.[11] In tandem processes, synthesis of the triene precursors required for intramolecular Diels−Alder reactions has been generally achieved via one of two strategies: (i) in situ tethering of diene and alkene via alkylation, acylation, condensation, etc.; (ii) in situ generation of either diene or alkene via oxidation, elimination, retrogradation, etc.[8,9]

We have found that oxidation of 2-methoxyphenols in methanol with (diacetoxy)iodobenzene (DAIB) or [bis-(trifluoroacetoxy)]iodobenzene (BTIB) produces unstable *o*-benzoquinone monodimethylacetals, which are generically called as masked *o*-benzoquinones (MOBs).[12,13]

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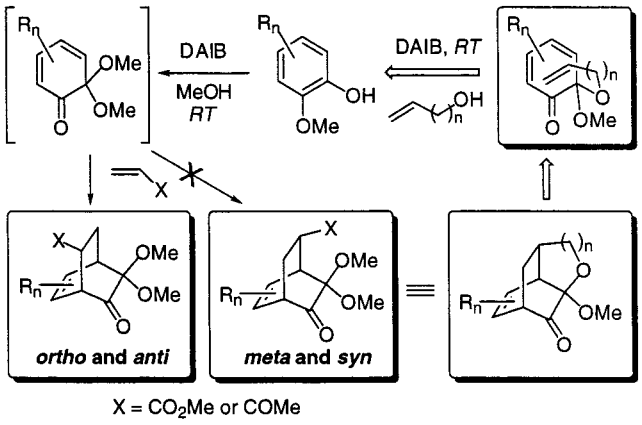
10.1021/jo990232k CCC: $18.00
Published on Web 05/01/1999

Scheme 1



These MOBs readily undergo dimerization under reaction conditions.[14] However, if MOBs are generated in the presence of electron-deficient dienophiles they readily undergo highly regio- and stereoselective intermolecular Diels−Alder reactions to furnish exclusively ortho and anti adducts (with respect to keto group), i.e., functionalized bicyclo[2.2.2]octenones (Scheme 1).[12] Bicyclo[2.2.2]-octenones and their derivatives are useful synthons that are convertible into polysubstituted cyclohexanes,[15] bicyclo-[3.2.1]octenones,[16] bicyclo[4.2.0]octenones,[17,18] tricyclo-[3.3.0.0^{2,8}]octanones,[18] variously fused triquinanes,[19] *cis*-decalins,[20] and bicyclo[4.2.2]decenones.[20a]

It was believed that the oxidation of a 2-methoxyphenol, if carried out in the presence of an alkenol in an inert solvent, would result in the formation of a 2,4-cyclohexadienone tethered to an alkene and thus formed MOB would undergo a tandem intramolecular cycloaddition under appropriate reaction conditions (Scheme 1). If such a tandem process could be developed, it would meet some of the aforementioned highly desirable criteria. Furthermore, it could also be seen from Scheme 1 that such a process would provide an easy access to bicyclo[2.2.2]-octenone derivatives with a distinct regio- and stereochemistry that could be considered as equivalents of hitherto not obtained meta and syn adducts of intermolecular Diels−Alder reactions of MOBs. In fact, it was found to be the case.[12a] Hence, a novel tandem oxidative acetalization−intramolecular Diels−Alder approach to the synthesis of highly functionalized 4-oxatricyclo-[4.3.1.0^{3,7}]decenones and 4-oxatricyclo[4.4.1.0^{3,8}]undecenones has been developed.

It is pertinent to mention that there are quite a few precedents for the intramolecular Diels−Alder reactions of 2,4-cyclohexadienones tethered to alkene moieties with all-carbon or heteroatom containing spacers, prepared by means of lengthy sequences of reactions.[21−26] Notable and shortest among them is the Yates approach, which provides tricyclic lactones in low yields via Wessely oxidation of phenols with lead tetraacetate in the presence of substituted acrylic acids followed by cycloaddition of thus formed acrylates upon heating.[26] In the present case also, the tethering has been achieved in a similar manner by an oxidation reaction but through an acetal. However, in the present cases the cycloaddition proceeds smoothly under oxidation reaction conditions not requiring change of solvent or temperature. To the best of our knowledge, in an intramolecular Diels−Alder reaction such in situ tethering of alkene moiety to diene through acetal formation is unprecedented. We herein describe the details of our studies on these tandem processes.[12a]

Results and Discussion

Masked *o*-benzoquinone (MOB) **8a**, generated via oxidation of methyl vanillate (**2**) in the presence of allyl alcohol (**1a**) using DAIB in dichloromethane at room temperature, underwent intramolecular cycloaddition under these conditions to provide the tricyclic compound **14a** in 75% yield (Scheme 2, Table 1). No attempt was made to isolate the MOB **8a** since MOBs are known to dimerize in concentrated solutions. Then this reaction was extended to other alkenols such as *trans*-crotyl alcohol (**1b**), cinnamyl alcohol (**1c**), and homoallyl alcohol (**1d**) to generate MOBs **8b**−**d**. While the MOBs **8b** and **8d** furnished the expected products **14b** and **14d**, respectively, in 74% yield, the MOB **8c** gave the desired adduct **14c** only in 53% yield.

The MOBs **9a**−**d**, obtained by the oxidation of 2-methoxy-4-methylphenol (**3**) in the presence of alkenols **1a**−**d**, exhibited similar behavior. MOBs **9a** and **9b** provided the desired products **15a** and **15b** in 77% and 70% yields, respectively, under the reaction conditions. The MOB **9c** unlike **8c** underwent cycloaddition smoothly to furnish the compound **15c** in high yield. MOB **9d** derived from **3** and **1d** afforded the desired product **15d** only in 39% yield (Scheme 2, Table 1).

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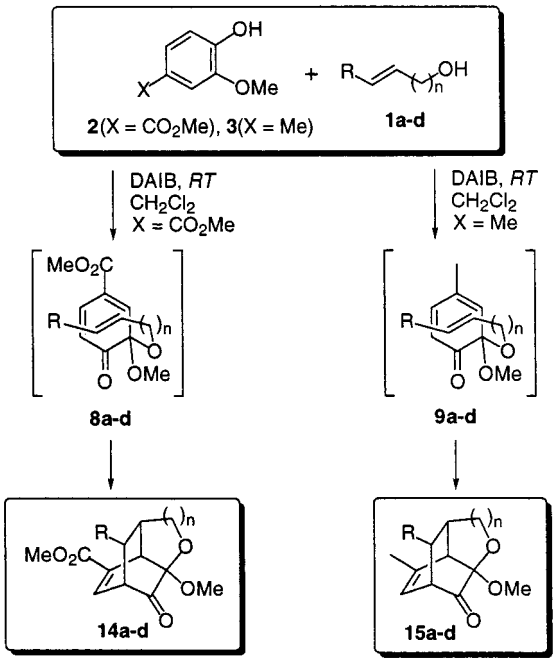
Scheme 2



a: R = H, n = 1; **b:** R = Me, n = 1; **c:** R = Ph, n = 1; **d:** R = H, n = 2

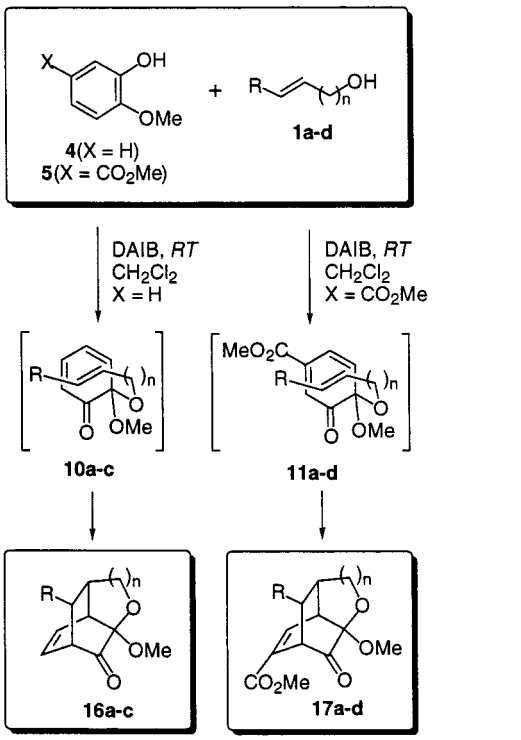
Table 1. Intramolecular Diels–Alder Reactions of Masked *o*-Benzoquinones

entry	phenol	alkene	MOB	product	yield (%)
1	**2**	**1a**	**8a**	**14a**	75
2		**1b**	**8b**	**14b**	74
3		**1c**	**8c**	**14c**	53
4		**1d**	**8d**	**14d**	74
5	**3**	**1a**	**9a**	**15a**	77
6		**1b**	**9b**	**15b**	70
7		**1c**	**9c**	**15c**	80
8		**1d**	**9d**	**15d**	39
9	**4**	**1a**	**10a**	**16a**	30
10		**1b**	**10b**	**16b**	44
11		**1c**	**10c**	**16c**	72
12	**5**	**1a**	**11a**	**17a**	64
13		**1b**	**11b**	**17b**	56
14		**1c**	**11c**	**17c**	39
15		**1d**	**11d**	**17d**	38
16	**6**	**1a**	**12a**	**18a**	75
17		**1b**	**12b**	**18b**	56
18		**1c**	**12c**	**18c**	52
19		**1d**	**12d**	**18d**	29
20	**7**	**1a**	**13a**	**19a**	58
21		**1b**	**13b**	**19b**	40
22		**1c**	**13c**	**19c**	49
23		**1d**	**13d**	**19d**	15
24	**2**	**20a**	**21a**	**22a**	40
25		**20b**	**21b**	**22b**	40
26		**20c**	**21c**	**22c**	35
27		**20d**	**21d**	**22d**	32

It may be noted that the MOBs described so far have got substituents on the C_4 of cyclohexadienone moiety and in some cases at the alkene terminus also. To ascertain the effect of substituents present on cyclohexadienone moiety on these intramolecular cycloaddition reactions, 2-methoxyphenols such as guaicol (**4**), methyl isovanillate (**5**), methyl syringate (**6**), and 2,6-dimethoxy-4-methylphenol (**7**) were oxidized in the presence of alkenols **1a**–**d** under the usual conditions (Schemes 3 and 4, Table 1).

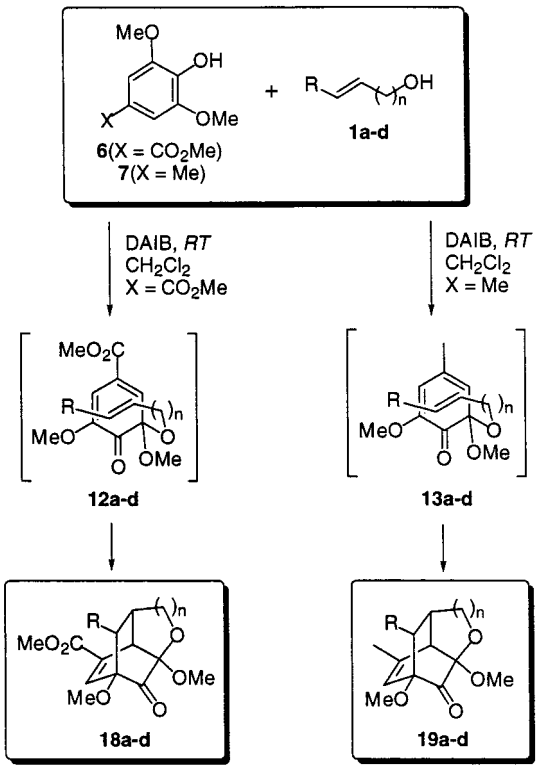
MOB **10a** generated from **4** and **1a**, with no substituent on the dienone moiety, underwent intramolecular cycloaddition to provide the desired product **16a** in 30% yield. Efforts made to improve the yield were unsuccessful. It is interesting to note that the parent MOB, i.e., 6,6-dimethoxy-2,4-cyclohexadienone derived from guaicol (**4**), has not been shown to undergo any intermolecular Diels–Alder reaction except self-dimerization. However, the MOBs **10b** and **10c** were raised from phenol **4** and

Scheme 3



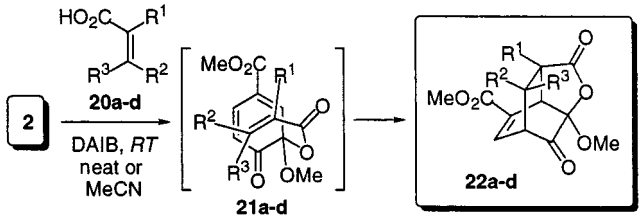
a: R = H, n = 1; **b:** R = Me, n = 1; **c:** R = Ph, n = 1; **d:** R = H, n = 2

Scheme 4



a: R = H, n = 1; **b:** R = Me, n = 1; **c:** R = Ph, n = 1; **d:** R = H, n = 2

Scheme 5



a: $R^1 = R^2 = R^3 = H$; **b:** $R^1 = Me$, $R^2 = R^3 = H$
c: $R^2 = Me$, $R^1 = R^3 = H$; **d:** $R^1 = H$, $R^2 = R^3 = Me$

alkenols **1b** and **1c**. The MOB **10b** provided the expected product **16b** in 44% yield. Interestingly, **10c** provided the desired product **16c** in a high yield of 72% (Scheme 3). On the other hand, the reaction of **4** and **1d** was found to be quite complex, and no desired product could be observed in the ^1H NMR spectrum of the crude reaction mixture.

On the other hand, MOB **11a** generated from phenol **5** and alkenol **1a**, with a methoxycarbonyl substituent on C_3 of the cyclohexadienone moiety, underwent efficient cycloaddition to produce the desired adduct **17a** in 64% yield. While MOB **11b** provided the desired adduct **17b** in a good yield of 56%, the cycloaddition of **11c** and **11d** was found to be relatively inefficient and furnished the adducts **17c** and **17d** in 39% and 38% yield, respectively (Scheme 3, Table 1).

The MOBs **12a**−**d** generated from phenol **6** and alkenols **1a**−**d**, with two substituents on the cyclohexadienone moiety, also exhibited similar reactivity. The intramolecular cycloaddition of MOB **12a** proceeded with high efficiency to furnish the desired adduct **18a** in 75% yield. The reactions of **12b** and **12c** with substituents on alkene terminus also furnished the corresponding adducts **18b** and **18c** in 56% and 52% yield. As expected, the MOB **12d** underwent inefficient cycloaddition to afford the adduct **18d** in only 29% yield (Scheme 4, Table 1). On the other hand, the MOBs **13a**−**d** derived from **7** and **1a**−**d** underwent cycloadditions with relatively low efficiency. MOBs **13a**−**c** furnished the corresponding adducts **19a**−**c** in 40−58% yield. The adduct **19d** was obtained in a very low yield of 15% from MOB **13d**.

The possibility of employing alkenoic acids in place of alkenols was also explored. Oxidation of **2** in acrylic acid **20a** with DAIB afforded the desired lactone **22a** in 40% yield. In a similar fashion, methacrylic acid (**20b**), *trans*-crotonic acid (**20c**), and β,β-dimethylacrylic acid (**20d**) were employed to generate MOBs **21b**−**d**, which underwent intramolecular cycloaddition to provide adducts **22b**−**d** in moderate yields (Scheme 5). It is pertinent to mention that Yates and Auksi obtained the adducts in roughly the same yields in a similar modified Wessely oxidative acyloxylation of 2-methylphenols followed by cycloaddition processes developed by them.[26]

The structures of all the new compounds were unambiguously determined by their IR, ^1H and ^{13}C NMR, and low- and high-resolution mass spectral analyses. The majority of the Diels−Alder adducts provided satisfactory elemental analyses. The stereochemical assignments in compounds **14c** were based on its $^1H-^1H$ COSY and NOESY spectral analyses. The NOESY spectrum of **14c** showed NOE correlations between H_{5a} and H_{10} and the ortho protons of the phenyl group and H_9, indicating their proximity. These correlations confirm that the phenyl

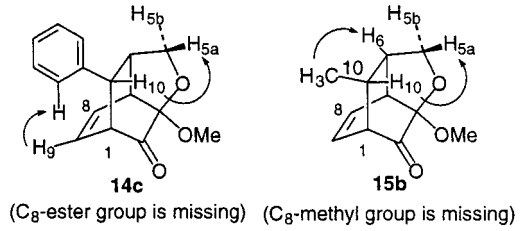


Figure 1. NOESY correlations.

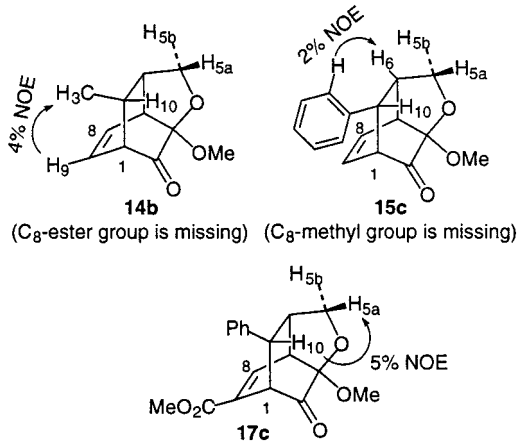
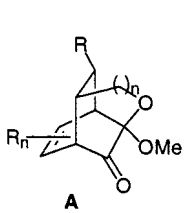


Figure 2. NOE enhancements.

group in **14c** is oriented syn to the vinyl bridge and anti to the ether ring. Similarly, the NOESY spectrum of **15b** indicated the proximity of H_{10} and H_{5a} and C_{10}-methyl protons and H_6, confirming the assigned stereochemistry (Figure 1). On the other hand, about 4% NOE was observed in the signal corresponding to vinyl proton upon irradiation of C_{10}-methyl protons of **14b** indicating syn relationship between them. NOE experiments on **15c** and **17c** confirmed the stereochemical assignments (Figure 2). In the remaining compounds, the stereochemical assignments were based on coupling constants and on analogy.

Unambiguous determination of the structures of products of these intramolecular Diels−Alder reactions makes clear the fact that the relative stereochemistry around the alkene double bond is transmitted to the product. Although there exist precedents for the formation of regioisomers in the intramolecular cycloadditions of certain 2,4-cyclohexadienones that are tethered at C_6 to alkenes by two- and three-carbon spacers,[23d,e] in the present cases only single products were produced and the products of type **A** were never observed.



The relatively low yields of the adducts **15d**, **17d**, **18d**, and **19d**, however, clearly indicate that the intramolecular cycloadditions of the corresponding MOBs **9d**, **11d**, **12d**, and **13d** that contain three-atom spacers are less facile when compared to MOBs with two-atom spacers derived from the corresponding phenols and allyl alcohol (**1a**). The increased entropic demands with increase in

the length of the spacer could be one of the possible reasons for the lower efficieny of these cycloadditions. However, MOB **8d** provided the desired adduct **14d** in a high yield of 74% probably due to optimal reactivity of cyclohexadienone moiety.

It is important to note that the substituents at the alkene terminus have a bearing effect on these intramolecular cycloadditions. From Table 1, it is also clear that the presence of a substituent on the cyclohexadienone moiety of MOB is of utmost importance for these cycloadditions to be efficient. When compared to the MOBs **11a**−**d** with a methoxycarbonyl substituent on C_3 of the 2,4-cyclohexadienone moiety derived from phenol **5**,[27] the presence of an electron-withdrawing or -releasing substituent on C_4, as in the case of MOBs **8a**−**d** or **9a**−**d**, increases the efficiency of these cycloadditions probably due to the absence of steric repulsions. On the other hand, substituents on C_2 of the cyclohexadienone moiety of MOBs in general reduce the efficiency of these intramolecular cycloadditions, which is evident from the yields of the adducts **18a**−**d** and **19a**−**d**.[27]

In conclusion, these tandem processes provide an easy access to highly functionalized bicyclo[2.2.2]octenones, making use of inexpensive and readily available starting materials. Since the diene and alkene are tethered in situ, from a practical point of view these reactions are quite simple. More importantly, the tethering being through an acetal situated next to a keto group has been repeatedly shown to be disposable in nature.[15,28,29] It can be disconnected by reduction with samarium diiodide[30] or can be hydrolyzed with aqueous acetic acid.[31] Furthermore, these reactions were employed as the key steps in the methodologies developed for the synthesis of several synthetically useful compounds such as *cis*-decalins, bicyclo[4.2.2]decenones, and bicyclo[3.3.0.0^{2,8}]octanone derivatives.[17a,32] These tandem processes were also successfully employed as one of the key steps in the formal synthesis of (±)-reserpine[15] and the total syntheses of a clerodane diterpenic acid[28] and pallescensin B.[29] Quite recently, this reaction has been extended to alka-2,4-dienols, wherein highly substituted *cis*-decalins were obtained.[33]

Experimental Section

General Procedures. Unless stated otherwise, reagents were obtained from commercial sources and used without further purification. Allyl alcohol, *trans*-crotyl alcohol, and homoallyl alcohol were distilled from anhydrous potassium carbonate prior to use. Acrylic acid and methacrylic acid were distilled from hydroquinone prior to use. All reactions were performed under a nitrogen atmosphere in anhydrous solvents, which were dried prior to use following standard procedures. Reactions were monitored by thin-layer chromatography carried out on 0.25 mm E. Merck silica gel plates (60F-254) using 7% ethanolic phosphomolybdic acid as developing agent. The product composition of each reaction was determined by the ^{1}H NMR (400 MHz) spectrum of the crude reaction mixture. Standard column chromatography was performed using 230−400 mesh silica gel obtained from E. Merck. Melting points are uncorrected. IR spectra were recorded as films on NaCl plates. ^{1}H and ^{13}C NMR spectra were recorded at 300 or 400 MHz and 75 or 100 MHz, respectively, in $CDCl_3$ and chemical shifts are reported in δ (ppm) using solvent resonance as the internal reference. Mass spectra were recorded by the NSC Instrumentation Center at Hsinchu, Taiwan. Elemental analyses were performed by the NSC Instrumentation Center at Taichung, Taiwan.

General Procedures for Tandem Oxidative Acetalization−Diels−Alder Reactions. For the Reactions of Phenols 2−7 with Alkenols 1a−d. To a flask containing a mixture of DAIB (2.0 g, 6.0 mM) and alkenol (25 mM) in dry dichloromethane (8 mL) at room temperature was added a solution of a phenol (5 mM) in dry dichloromethane (8 mL) during 1 h (2 h for phenols **6** and **7** and 4 h for phenol **4**) using a syringe pump. The contents of the flask were stirred for a further 8 h. Then all the volatile materials were removed under reduced pressure. Thus obtained residue was dissolved in dichloromethane, and the solution was washed successively with saturated sodium bicarbonate and brine. The organic layer was dried over anhydrous sodium sulfate and concentrated. The crude product was purified by column chromatography on silica gel using 20−40% ethyl acetate in hexanes as eluent.

(1*S,3*R**,6*R**,7*R**)-3-Methoxy-8-methoxycarbonyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (14a).** This was prepared from phenol **2** and allyl alcohol: yield 75%; mp 66−67 °C; IR (film) 2941, 1737 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82 (dd, J = 10.0, 2.1 Hz, 1H), 1.93 (d, J = 10.0 Hz, 1H), 2.55 (dd, J = 4.5, 3.7 Hz, 1H), 3.34 (dt, J = 7.1, 2.1 Hz, 1H), 3.49 (s, 3H), 3.78 (s, 3H), 3.80 (d, J = 8.1 Hz, 1H), 4.01 (dd, J = 4.5, 2.1 Hz, 1H), 4.17 (dd, J = 8.1, 3.7 Hz, 1H), 7.26 (dd, J = 7.1, 2.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.3, 34.9, 41.2, 46.2, 50.9, 52.1, 73.5, 99.7, 133.0, 139.5, 164.5, 200.4; MS (EI, 75 eV) *m*/*z* (relative intensity) 210 (M^+ − CO, 88), 195 (88), 163 (75), 91 (100), 59 (46); HRMS (EI) calcd for $C_{12}H_{14}O_5$ (M^+) 238.0841, found 238.0820. Anal. Calcd for $C_{12}H_{14}O_5$: C, 60.50; H, 5.92. Found: C, 60.35; H, 5.96.

(1*S,3*R**,6*R**,7*R**,10*R**)-3-Methoxy-8-methoxycarbonyl-10-methyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (14b).** This was prepared from phenol **2** and *trans*-crotyl alcohol: yield 74%; IR (film) 2948, 1706 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (d, J = 7.2 Hz, 3H), 2.03 (br s, 1H), 2.25 (dq, J = 4.4, 3.1 Hz, 1H), 3.22 (dd, J = 7.0, 2.9 Hz, 1H), 3.46 (s, 3H), 3.77 (s, 3H), 3.80 (d, J = 8.1 Hz, 1H), 3.96 (dd, J = 4.4, 2.0 Hz, 1H), 4.14 (dd, J = 8.1, 3.1 Hz, 1H), 7.14 (dd, J = 7.0, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.1, 37.2, 41.3, 43.8, 51.0, 52.2, 53.5, 73.5, 98.9, 132.3, 137.6, 164.3, 200.4; MS (EI, 12 eV) *m*/*z* (relative intensity) 224 (M^+-CO, 100), 209 (87), 177 (75), 105 (89), 91 (50); HRMS (EI) calcd for $C_{12}H_{16}O_4$ (M^+ − CO) 224.1049, found 224.1046.

(1*S,3*R**,6*R**,7*R**,10*R**)-3-Methoxy-8-methoxycarbonyl-10-phenyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (14c).** This was prepared from phenol **2** and cinnamyl alcohol: yield 53%; mp 100−102 °C; IR (film) 2999, 1751, 1720 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.85−2.86 (br, 1H), 3.43 (br, 1H), 3.51 (dd, J = 6.8, 2.8 Hz, 1H), 3.53 (s, 3H), 3.95 (s, 3H), 3.96 (d, J = 8.3 Hz, 1H), 4.17 (dd, J = 4.3, 2.0 Hz, 1H), 4.27 (dd, J = 8.3, 3.3 Hz, 1H), 7.00−7.11 (m, 3H), 7.24−7.27 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 41.6, 44.0, 47.0, 51.0, 52.1, 54.2, 73.8, 99.1, 127.1, 127.7, 128.3, 133.2, 137.0, 141.0, 164.24, 199.4; MS (EI, 75 eV) *m*/*z* (relative intensity) 286 (M^+ − CO, 88), 271 (31), 167 (46), 117 (100), 91 (50); HRMS (EI) calcd for $C_{18}H_{18}O_5$ (M^+) 314.1178, found 314.1166. Anal. Calcd for $C_{18}H_{18}O_5$: C, 68.78; H, 5.77. Found: C, 68.80; H, 5.78.

(1*S,3*R**,7*S**,8*R**)-3-Methoxy-9-methoxycarbonyl-4-oxatricyclo[5.3.1.0^{3,8}]undec-9-en-2-one (14d).** This was prepared from phenol **2** and homoallyl alcohol: yield 74%; mp

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72−73 °C; IR (film) 2960, 1754, 1725 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.52 (dt, J = 13.8, 2.7 Hz, 1H), 1.69 (dt, J = 13.8, 3.2 Hz, 1H), 1.88−1.98 (m, 2H), 2.27 (dt, J = 11.2, 3.5 Hz, 1H), 3.29 (dt, J = 6.6, 2.8 Hz, 1H), 3.31 (s, 3H), 3.36 (dd, J = 11.2, 2.0 Hz, 1H), 3.57 (dt, J = 12.7, 2.7 Hz, 1H), 3.72 (s, 3H), 3.89 (dd, J = 12.7, 5.8 Hz, 1H), 7.13 (dd, J = 6.6, 2.0 Hz, 1H); ^{13}C NMR(100 MHz, $CDCl_3$) δ 27.7, 28.8, 29.7, 42.3, 49.0, 50.9, 51.9, 60.8, 92.6, 137.2, 137.6, 164.4, 205.7; MS (EI, 75 eV) *m*/*z* (relative intensity) 224 (M^+ − CO, 100), 177 (55), 105 (52); HRMS (EI) calcd for $C_{12}H_{16}O_4$ (M^+ − CO) 224.1049, found 224.1043. Anal. Calcd for $C_{13}H_{16}O_5$: C, 61.90; H, 6.39. Found: C, 61.89; H, 6.43.

(1*S,3*R**,6*R**,7*R**)-3-Methoxy-8-methyl-4-oxatricyclo-[4.3.1.0^{3,7}]dec-8-en-2-one (15a).** This was prepared from phenol **3** and allyl alcohol: yield 77%; mp 46−47 °C; IR (film) 2943, 1738 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.70−1.81 (m, 2H), 1.84 (d, J = 1.7 Hz, 3H), 2.44−2.49 (m, 1H), 3.00 (ddd, J = 6.2, 4.1, 2.6 Hz, 1H), 3.09 (dd, J = 4.5, 2.8 Hz, 1H), 3.46 (s, 3H), 3.72 (d, J = 8.0 Hz, 1H), 4.06 (dd, J = 8.0, 3.4 Hz, 1H), 5.87 (ddq, J = 6.2, 2.8, 1.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.0, 31.2, 34.9, 45.1, 47.5, 50.9, 73.7, 100.6, 122.4, 139.1, 201.5; MS (EI, 12 eV) *m*/*z* (relative intensity) 194 (M^+, 1), 166 (54), 125 (100), 91 (48); HRMS (EI) calcd for $C_{11}H_{14}O_3$ (M^+) 194.0943, found 194.0949. Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 68.13; H, 7.30.

(1*S,3*R**,6*R**,7*R**,10*R**)-3-Methoxy-8,10-dimethyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (15b).** This was prepared from phenol **3** and *trans*-crotyl alcohol: yield 70%; mp 103−104 °C; IR (film) 2934, 1736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.92 (d, J = 7.0 Hz, 3H), 1.90 (d, J = 1.5 Hz, 3H), 1.93 (br s, 1H), 2.14 (m, 1H), 2.90 (dd, J = 6.7, 3.3 Hz, 1H), 3.07 (dd, J = 4.4, 2.0 Hz, 1H), 3.49 (s, 3H), 3.78 (d, J = 7.9 Hz, 1H), 4.06 (dd, J = 7.9, 3.2 Hz, 1H), 5.78 (ddq, J = 6.7, 2.0, 1.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.6, 21.1, 36.7, 43.9, 47.3, 51.1, 52.2, 73.8, 99.9, 119.5, 138.5, 201.6; MS (EI, 70 eV) *m*/*z* (relative intensity) 180 (M^+ − CO, 77), 125 (100), 121 (70), 105 (36), 93 (30); HRMS (EI) calcd for $C_{11}H_{16}O_2$ (M^+ − CO) 180.1150, found 180.1147. Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H: 7.74. Found: C, 69.24; H, 7.78.

(1*S,3*R**,6*R**,7*R**,10*R**)-3-Methoxy-8-methyl-10-phenyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (15c).** This was prepared from phenol **3** and cinnamyl alcohol: yield 80%; mp 116−118 °C; IR (film) 2949, 1745 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.00 (d, J = 1.5 Hz, 3H), 2.77 (br s, 1H), 3.18 (dd, J = 6.7, 2.9 Hz, 1H), 3.28 (dd, J = 4.4, 2.1 Hz, 1H), 3.33 (br s, 1H), 3.55 (s, 3H), 3.93 (d, J = 8.0 Hz, 1H), 4.19 (dd, J = 8.0, 3.2 Hz, 1H), 5.63 (ddq, J = 6.7, 2.1, 1.5 Hz, 1H), 7.00−7.02 (m, 2H), 7.20−7.28 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.3, 44.2, 47.3, 48.2, 51.4, 53.3, 74.2, 100.3, 119.6, 126.8, 128.0, 128.3, 139.6, 142.1, 200.7; MS (EI, 75 eV) *m*/*z* (relative intensity) 243 (19), 242 (M^+-CO, 100), 183 (65), 125 (51), 91 (40); HRMS (EI) calcd for $C_{17}H_{19}O_3$ (M^+ + 1) 271.1334, found 271.1338. Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.46; H, 6.72.

(1*S,3*R**,7*S**,8*R**)-3-Methoxy-9-methyl-4-oxatricyclo-[5.3.1.0^{3,8}]undec-9-en-2-one (15d).** This was prepared from phenol **3** and homoallyl alcohol: yield 39%; IR (film) 2923, 1734 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.48 (ddd, J = 13.5, 2.9, 1.6 Hz, 1H), 1.56 (dt, J = 13.5, 3.0 Hz, 1H), 1.84 (d, J = 1.7 Hz, 3H), 1.78−1.88 (m, 2H), 2.12−2.22 (m, 1H), 2.45 (dd, J = 3.2, 2.0 Hz, 1H), 2.93 (dd, J = 7.3, 3.0 Hz, 1H), 3.35 (s, 3H), 3.54 (dt, J = 12.6, 2.8 Hz, 1H), 3.82 (ddd, J = 12.6, 6.7, 1.3 Hz, 1H), 5.72 (ddq, J = 7.3, 2.0, 1.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2, 27.3, 29.7, 30.2, 47.8, 48.5, 51.1, 60.6, 93.3, 120.0, 144.2, 208.3; MS (EI, 75 eV) *m*/*z* (relative intensity) 181 (40), 180 (M^+ − CO, 100), 165 (46), 93 (45); HRMS (EI) calcd for $C_{12}H_{16}O_3$ (M^+) 208.1099, found 208.1089.

(1*S,3*R**,6*R**,7*R**)-3-Methoxy-4-oxatricyclo[4.3.1.0^{3,7}]-dec-8-en-2-one (16a).** This was prepared from phenol **4** and allyl alcohol: yield 30%; IR (film) 2936, 1744 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.71−1.78 (m, 2H), 2.42 (m, 1H), 3.07 (m, 1H), 3.26 (m, 2H), 3.39 (s, 3H), 3.69 (d, J = 8.0 Hz, 1H), 4.02 (dd, J = 8.0, 3.3 Hz, 1H), 6.12 (ddd, J = 9.4, 5.5, 2.2 Hz, 1H), 6.23 (ddd, J = 9.4, 6.7, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.7, 35.2, 42.3, 45.5, 50.9, 73.6, 100.3, 129.4, 130.7, 201.5; MS (EI, 15 eV) *m*/*z* (relative intensity) 152 (M^+ − CO, 81), 111 (50), 93 (100), 91 (63), 87 (56), 51 (53); HRMS (EI) calcd for $C_{10}H_{12}O_3$ (M^+ − CO) 152.0837, found 152.0837.

(1*S,3*R**,6*R**,7*R**,10*R**)-3-Methoxy-10-methyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (16b).** This was prepared from phenol **4** and *trans*-crotyl alcohol: yield 44%; IR (film) 2963, 1742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.95 (d, J = 7.0 Hz, 3H), 1.94 (br s, 1H), 2.18 (apparent q, J = 7.0 Hz, 1H), 3.03 (ddd, J = 6.3, 2.6, 1.7 Hz, 1H), 3.26 (ddd, J = 6.3, 4.4, 1.7 Hz, 1H), 3.48 (s, 3H), 3.79 (d, J = 8.0 Hz, 1H), 4.08 (dd, J = 8.0, 3.3 Hz, 1H), 6.15−6.24 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.7, 36.7, 42.9, 44.3, 51.2, 52.8, 73.7, 99.6, 128.0, 129.1, 201.7; MS (EI, 70 eV) *m*/*z* (relative intensity) 166 (M^+ − CO, 63), 151 (10), 133 (4), 119 (6), 111 (34), 107 (100), 91 (57), 79 (54), 74 (6), 59 (10); HRMS (EI) calcd for $C_{10}H_{14}O_2$ (M^+ − CO) 166.0994, found 166.0994.

(1*S,3*R**,6*R**,7*R**,10*R**)-3-Methoxy-10-phenyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (16c).** This was prepared from phenol **4** and cinnamyl alcohol: yield 72%; mp 129−131 °C; IR (film) 3060, 2945, 1738 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.7−2.79 (m, 1H), 3.28−3.30 (m, 1H), 3.36 (br s, 1H), 3.46−3.50 (m, 1H), 3.54 (s, 3H), 3.92 (d, J = 8.2 Hz, 1H), 4.20 (dd, J = 8.2, 3.3 Hz, 1H), 6.01 (ddd, J = 8.0, 6.6, 1.4 Hz, 1H), 6.39 (ddd, J = 8.0, 6.5, 1.3 Hz, 1H), 7.10−7.07 (m, 2H), 7.28−7.18 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.6, 44.6, 46.9, 51.4, 53.7, 74.1, 99.9, 126.9, 127.9, 128.1, 128.3, 130.1, 141.8, 200.7; MS (EI, 70 eV) *m*/*z* (relative intensity) 257 (M^+ + 1, 0.8), 228 (100), 169 (66), 91 (57); HRMS (EI) calcd for $C_{15}H_{16}O_2$ (M^+ − CO) 228.1150, found 228.1142. Anal. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.78; H, 6.31.

(1*S,3*R**,6*R**,7*R**)-3-Methoxy-9-methoxycarbonyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (17a).** This was prepared from phenol **5** and allyl alcohol: yield 64%; IR (film) 2938, 1746, 1706 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.80 (ddd, J = 13.5, 9.9, 2.1 Hz, 1H), 1.91 (ddd, J = 13.5, 3.1, 1.6 Hz, 1H), 2.53 (ddd, J = 9.9, 3.4, 3.1 Hz, 1H), 3.47 (m, 1H), 3.49 (s, 3H), 3.74 (s, 3H), 3.76 (m, 1H), 3.80 (d, J = 8.1 Hz, 1H), 4.15 (dd, J = 8.1, 3.4 Hz, 1H), 7.17 (dd, J = 6.7, 1.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.7, 35.7, 43.3, 44.6, 51.1, 51.9, 73.6, 99.8, 134.1, 139.0, 163.1, 200.4; MS (EI, 75 eV) *m*/*z* (relative intensity) 210 (M^+ − CO, 100), 169 (71), 119 (36), 91 (45); HRMS (EI) calcd for $C_{12}H_{14}O_5$ (M^+) 238.0842, found 238.0843.

(1*S,3*R**,6*R**,7*R**,10*R**)-3-Methoxy-9-methoxycarbonyl-10-methyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (17b).** This was prepared from phenol **5** and *trans*-crotyl alcohol: yield 56%; IR (film) 2952, 2880, 1736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.85 (d, J = 7.1 Hz, 3H), 1.95 (dd, J = 7.1, 2.5 Hz, 1H), 2.21 (m, 1H), 3.38−3.43 (m, 1H), 3.34 (s, 3H), 3.57 (m, 1H), 3.70 (s, 3H), 3.76 (d, J = 8.3 Hz, 1H), 4.09 (dd, J = 8.3, 3.4 Hz, 1H), 7.16 (dd, J = 6.8, 2.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.3, 36.6, 43.4, 44.3, 51.3, 51.7, 52.1, 73.6, 99.2, 131.5, 138.2, 163.8, 200.6; MS (EI, 75 eV) *m*/*z* (relative intensity) 224 (M^+ − CO, 100), 169 (34), 165 (34), 133 (44), 105 (80), 91 (47); HRMS (EI) calcd for $C_{12}H_{16}O_4$ (M^+ − CO) 224.1049, found 224.1052.

(1*S,3*R**,6*R**,7*R**,10*R**)-3-Methoxy-9-methoxycarbonyl-10-phenyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (17c).** This was prepared from phenol **5** and cinnamyl alcohol: yield 39%; mp 126−128 °C; IR (film) 2968, 1732 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.83 (br, 1H), 3.43 (br, 1H), 3.50 (s, 3H), 3.52 (s, 3H), 3.65 (dd, J = 7.0, 4.2 Hz, 1H), 3.85 (d, J = 1.9 Hz, 1H), 3.95 (d, J = 8.3 Hz, 1H), 4.25 (dd, J = 8.3, 3.4 Hz, 1H), 6.98−7.24 (m, 5H), 7.33 (dd, J = 7.0, 1.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 44.0, 44.4, 46.7, 51.5, 51.9, 52.7, 74.0, 99.5, 127.0, 127.6, 128.4, 131.3, 139.0, 140.5, 163.1, 199.7; MS (EI, 70 eV) *m*/*z* (relative intensity) 287 (24), 286 (M^+ − CO, 100), 195 (50), 169 (31), 167 (56); HRMS (EI) calcd for $C_{18}H_{18}O_5$ (M^+) 314.1154, found 314.1167. Anal. Calcd for $C_{18}H_{18}O_5$: C, 68.78; H, 5.77. Found: C, 68.52; H, 5.73.

(1*S,3*R**,7*S**,8*R**)-3-Methoxy-10-methoxycarbonyl-4-oxatricyclo[5.3.1.0^{3,8}]undec-9-en-2-one (17d).** This was prepared following procedure A from phenol **5** and homoallyl alcohol: yield 38%; mp 112−113 °C; IR (film) 2949, 1725 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.54 (dt, J = 13.7, 1.8 Hz, 1H), 1.69 (dt, J = 13.7, 3.1 Hz, 1H), 1.88−1.96 (m, 2H), 2.26 (m,

1H), 2.87 (dd, J = 6.9, 3.4 Hz, 1H), 3.34 (s, 3H), 3.58 (dt, J = 12.8, 2.7 Hz, 1H), 3.70−3.71 (m, 1H), 3.72 (s, 3H), 3.90 (dd, J = 12.8, 5.8 Hz, 1H), 7.32 (dd, J = 6.9, 1.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.4, 29.1, 29.5, 44.8, 47.5, 51.6, 52.0, 60.8, 92.6, 132.1, 143.6, 164.0, 205.7; MS (EI, 75 eV) m/z (relative intensity) 224 (M^+ − CO, 100), 105 (43), 93 (21), 77 (28); HRMS (EI) calcd for $C_{12}H_{16}O_4$ (M^+ − CO) 224.1049, found 224.1050. Anal. Calcd for $C_{13}H_{16}O_5$: C, 61.90; H, 6.39. Found: C, 61.93; H, 6.46.

(1*R,3*R**,6*R**,7*R**)-1,3-Dimethoxy-8-methoxycarbonyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (18a).** This was prepared from phenol **6** and allyl alcohol: yield 75%; IR (film) 2961, 1731 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.97−2.09 (m, 2H), 2.65−2.68 (br, m, 1H), 3.51 (s, 3H), 3.58 (s, 3H), 3.82 (s, 3H), 3.92 (d, J = 8.3 Hz, 1H), 4.01 (dd, J = 4.8, 1.8 Hz, 1H), 4.24 (dd, J = 8.3, 3.8 Hz, 1H), 7.26 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.1, 35.0, 40.6, 51.1, 52.2, 53.5, 74.3, 83.1, 99.6, 131.3, 140.6, 163.8, 198.4; MS (EI, 12 eV) m/z (relative intensity) 269 (M^+ + 1, 23), 240 (M^+ − CO, 100), 180 (46), 121 (50), 59 (44); HRMS (EI) calcd for $C_{13}H_{16}O_6$ (M^+) 268.0947, found 268.0948.

(1*R,3*R**,6*R**,7*R**,10*R**)-1,3-Dimethoxy-8-methoxycarbonyl-10-methyl-3-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (18b).** This was prepared from phenol **6** and *trans*-crotyl alcohol: yield 56%; IR (film) 2949, 1732 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (d, J = 7.1 Hz, 3H), 2.17 (br t, J = 3.4 Hz, 1H), 2.36 (q, J = 7.1 Hz, 1H), 3.51 (s, 3H), 3.58 (s, 3H), 3.82 (s, 3H), 3.92−3.98 (m, 2H), 4.21 (dd, J = 8.2, 3.4 Hz, 1H), 7.07 (d, J = 1.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.4, 38.9, 40.3, 44.1, 51.0, 52.1, 53.3, 74.1, 86.5, 99.1, 130.3, 139.0, 163.7, 199.2; MS (EI, 12 eV) m/z (relative intensity) 254 (M^+ − CO, 100), 222 (34), 179 (37), 135 (35); HRMS (EI) calcd for $C_{14}H_{18}O_6$ (M^+) 282.1103, found 282.1112.

(1*R,3*R**,6*R**,7*R**,10*R**)-1,3-Dimethoxy-8-methoxycarbonyl-10-phenyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (18c).** This was prepared from phenol **6** and cinnamyl alcohol: yield 52%; IR (film) 3041, 2960, 1732 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.82−2.89 (br, 1H), 3.41 (br, 1H), 3.53 (s, 3H), 3.57 (s, 3H), 3.87 (s, 3H), 4.06 (d, J = 8.4 Hz, 1H), 4.16 (d, J = 4.8 Hz, 1H), 4.30 (dd, J = 9.4, 3.6 Hz, 1H), 7.00−7.l2 (m, 3H), 7.25−7.28 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.3, 46.3, 50.9, 51.3, 52.4, 54.3, 74.5, 86.8, 98.9, 127.4, 128.2, 129.1, 131.4, 138.2, 139.3, 163.9, 198.7; MS (EI, 12 eV) m/z (relative intensity) 316 (M^+ − CO, 100), 256 (54), 199 (87), 165 (80), 115 (70); HRMS (EI) calcd for $C_{18}H_{20}O_5$ (M^+ − CO) 316.1311, found 316.1300. Anal. Calcd for $C_{19}H_{20}O_6$: C, 66.27; H, 5.85. Found: C, 66.31; H, 5.90.

(1*R,3*R**,7*S**,8*R**)-1,3-Dimethoxy-9-methoxycarbonyl-4-oxatricyclo[5.3.1.0^{3,8}]undec-9-en-2-one (18d).** This was prepared from phenol **6** and homoallyl alcohol: yield 29%; mp 103−104 °C; IR (film) 2953, 1725 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.59 (dd, J = 11.3, 2.2 Hz, 1H), 1.76 (dd, J = 13.1, 2.8 Hz, 1H), 1.95−2.05 (m, 1H), 2.13 (dd, J = 25.4, 13.1 Hz, 1H), 2.40 (dt, J = 11.3, 3.5 Hz, 1H), 3.37−3.38 (m, 1H), 3.40 (s, 3H), 3.58 (s, 3H), 3.62−3.70 (m, 1H), 3.82 (s, 3H), 3.90−4.00 (m, 1H), 7.29 (d, J = 6.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.0, 29.4, 33.8, 41.8, 51.0, 52.1, 54.0, 60.7, 85.2, 92.7, 135.9, 138.0, 163.8, 203.8; MS (EI, 12 eV) m/z (relative intensity) 254 (M^+ − CO, 100), 239 (46), 135 (46), 59 (25); HRMS (El) calcd for $C_{14}H_{18}O_6$ (M^+) 282.1103, found 282.1108. Anal. Calcd for $C_{14}H_{18}O_6$: C, 59.57; H, 6.43. Found: C, 59.51; H, 6.50.

(1*R,3*R**,6*R**,7*R**)-1,3-Dimethoxy-8-methyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (19a).** This was prepared from phenol **7** and allyl alcohol: yield 58%; IR (film) 2925, 1747 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.90−2.02 (m, 2H), 1.92 (s, 3H), 2.59−2.63 (br m, 1H), 3.14 (dd, J = 4.6, 1.8 Hz, 1H), 3.53 (s, 6H), 3.88 (d, J = 8.2 Hz, 1H), 4.16 (dd, J = 8.2, 3.6 Hz, 1H), 5.91 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 34.7, 35.1, 47.0, 51.5, 52.9, 74.6, 82.0, 100.6, 124.5, 137.9, 199.4; MS (EI, 12 eV) m/z (relative intensity) 196 (M^+ − 28, 100), 181 (47), 155 (64), 137 (61); HRMS (EI) calcd for $C_{12}H_{16}O_4$ (M^+) 224.1049, found 224.1050.

(1*R,3*R**,6*R**,7*R**,10*R**)-1,3-Dimethoxy-8,10-dimethyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (19b).** This was prepared from phenol **7** and *trans*-crotyl alcohol: yield 40%; IR (film) 2939, 1752 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94 (d, J = 7.0 Hz, 3H), 1.93 (d, J = 1.6 Hz, 3H), 2.05−2.09 (m, 1H), 2.29 (m, 1H), 3.07 (dd, J = 4.4, 2.1 Hz, 1H), 3.52 (s, 3H), 3.53 (s, 3H), 3.91 (d, J = 8.1 Hz, 1H), 4.14 (dd, J = 8.1, 3.4 Hz, 1H), 5.69 (d, J = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.1, 20.9, 38.2, 44.5, 46.9, 51.6, 52.8, 74.6, 85.3, 100.3, 122.2, 136.8, 200.2; MS (EI, 12 eV) m/z (relative intensity) 210 (M^+ − CO, 100), 155 (49), 151 (39), 136 (28); HRMS (EI) calcd for $C_{13}H_{18}O_4$ (M^+) 238.1205, found 238.1200.

(1*R,3*R**,6*R**,7*R**,10*R**)-1,3-Dimethoxy-8-methyl-10-phenyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (19c).** This was prepared from phenol **7** and cinnamyl alcohol: yield 49%; IR (film) 2950, 1750 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.06 (d, J = 1.2 Hz, 3H), 2.77−2.80 (m, 1H), 3.26 (dd, J = 4.4, 2.4 Hz, 1H), 3.35 (s, 1H), 3.49 (s, 3H), 3.59 (s, 3H), 4.03 (d, J = 8.4 Hz, 1H), 4.22 (dd, J = 8.4, 3.2 Hz, 1H), 5.74 (d, J = 2.8 Hz, 1H), 7.08−7. 10 (m, 2H), 7.24−7.29 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2, 46.4, 47.7, 50.4, 51.8, 53.7, 74.8, 85.6, 100.1, 121.6, 127.0, 127.9, 129.3, 137.9, 140.3, 199.6; MS (EI, 12 eV) m/z (relative intensity) 272 (M^+ − CO, 77), 181 (83), 155 (100), 115 (33), 91 (48); HRMS (EI) calcd for $C_{18}H_{20}O_4$ (M^+) 300.1362, found 300.1380. Anal. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 71.97; H, 6.75.

(1*R,3*R**,7*S**,8*R**)-1,3-Dimethoxy-9-methyl-4-oxatricyclo[5.3.1.0^{3,8}]undec-9-en-2-one (19d).** This was prepared from phenol **7** and homoallyl alcohol: yield 15%; IR (film) 2945, 1739 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.54−1.69 (m, 2H), 1.87−1.96 (m, 1H), 1.93 (s, 3H), 2.04 (t, J = 12 Hz), 2.33−2.38 (m, 1H), 2.47 (dd, J = 3.8, 2.4 Hz, 1H), 3.46 (s, 3H), 3.52 (s, 3H), 3.64 (td, J = 12.7, 2.4 Hz, 1H), 3.94 (dd, J = 12.7, 5.6 Hz, 1H), 5.89 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 27.6, 29.9, 34.4, 48.0, 51.3, 53.2, 60.5, 83.8, 93.4, 120.9, 143.2, 205.9; MS (EI, 12 eV) m/z (relative intensity) 238 (M^+, 2), 210 (M^+ − CO, 84), 181 (72), 123 (100), 91 (34); HRMS (EI) calcd for $C_{13}H_{18}O_4$ (M^+) 238.1205, found 238.1206.

(1*S,3*R**,6*R**,7*R**)-3-Methoxy-8-methoxycarbonyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-ene-2,5-dione (22a).** To a flask containing DAIB (0.43 g, 1.3 mM) in acrylic acid (3 mL) at room temperature was added a solution of phenol **2** (0.2 g, 1.1 mM) in acrylic acid (2 mL) during 1 h using a syringe pump. The reaction mixture was stirred further for 2 h. Then the reaction mixture was diluted with water and extracted with ethyl acetate. The organic layer was washed successively with saturated sodium bicarbonate solution and brine, dried over anhydrous sodium sulfate, and concentrated. The crude product was purified by column chromatography on silica gel using 25% ethyl acetate in hexanes as eluent to furnish the lactone **22a** (0.11 g, 40%) as a colorless oil: IR (film) 2920, 1734, 1718, 1700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.88 (ddd, J = 14.1, 10.3, 1.6 Hz, 1H), 2.35 (dd, J = 14.1, 2.9 Hz, 1H), 2.93 (dd, J = 10.3, 5.4 Hz, 1H), 3.54 (m, 1H), 3.59 (s, 3H), 3.78 (s, 3H), 4.40 (dd, J = 5.4, 2.2 Hz, 1H), 7.40 (dd, J = 7.1, 2.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.9, 39.2, 42.2, 47.6, 52.4, 52.9, 99.3, 131.7, 140.9, 163.5, 173.6, 195.7; MS (EI, 12 eV) m/z (relative intensity) 224 (M^+ − CO, 22), 138 (15), 137 (100); HRMS (EI) calcd for $C_{12}H_{12}O_6$ (M^+) 252.0634, found 252.0632.

(1*S,3*R**,6*R**,7*R**)-3-Methoxy-8-methoxycarbonyl-6-methyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-ene-2,5-dione (22b).** This was prepared in an analogous manner to the procedure described above for **22a** from phenol **2** and methacrylic acid to obtain compound **22b** (117 mg, 40%) as a colorless oil: IR (film) 3022, 1744, 1721 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (s, 3H), 1.44 (dd, J = 14.2, 2.1 Hz, 1H), 2.46 (dd, J = 14.2, 3.4 Hz, 1H), 3.46 (ddd, J = 7.0, 3.4, 2.0 Hz, 1H), 3.58 (s, 3H), 3.80 (s, 3H), 4.04 (d, J = 2.1 Hz, 1H), 7.42 (dd, J = 7.0, 2.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.2, 36.3, 44.9, 47.7, 48.3, 52.5, 52.9, 97.5, 131.9, 140.7, 163.8, 175.9, 195.8; MS (EI, 75 eV) m/z (relative intensity) 238 (M^+ − CO, 14), 151 (100), 119 (34), 91 (45), 84 (79); HRMS (EI) calcd for $C_{13}H_{14}O_6$ (M^+) 266.0790, found 266.0800.

(1*S,3*R**,6*R**,7*R**,10*R**)-3-Methoxy-8-methoxycarbonyl-10-methyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-ene-2,5-dione (22c).** To a flask containing a mixture of DAIB (0.42 g, 1.3 mM) and *trans*-crotonic acid (2.0 g, 23.26 mM) in acetonitrile (10 mL)

at room temperature was added a solution of phenol **2** (0.2 g, 1.1 mM) in acetonitrile (5 mL) during 1 h using syringe pump. The reaction mixture was stirred further for 2 h. Then acetonitrile was removed, and the residue was dissolved in ethyl acetate. The ethyl acetate solution was washed successively with saturated sodium bicarbonate solution and brine, dried over anhydrous sodium sulfate, and concentrated. The crude product was purified by column chromatography on silica gel using 25% ethyl acetate in hexanes as eluent to furnish the lactone **20c** (0.102 g, 35%) as a colorless oil: IR (film) 2961, 1740, 1725, 1715 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.99 (d, J = 7.0 Hz, 3H), 2.50 (d, J = 5.2 Hz, 1H), 2.69 (m, 1H), 3.49 (dd, J = 7.0, 3.1 Hz, 1H), 3.57 (s, 3H), 3.79 (s, 3H), 4.34 (dd, J = 5.2, 2.0 Hz, 1H), 7.26 (dd, J = 7.0, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.7, 36.2, 42.3, 47.2, 52.5, 52.9, 54.8, 98.7, 131.6, 138.9, 163.6, 173.1, 195.5; MS (EI, 12 eV) *m*/*z* (relative intensity) 238 (M^+ − CO, 59), 194 (5), 151 (100); HRMS (EI) calcd for $C_{13}H_{14}O_6$ (M^+) 266.0790, found 266.0781.

(1*S,3*R**,6*R**,7*R**)-3-Methoxy-8-methoxycarbonyl-10,10-dimethyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-ene-2,5-dione (22d).** This was prepared in an analogous manner to the procedure described above for **22c** from phenol **2** and β,β-dimethylacrylic acid to obtain compound **22d** (98 mg, 32%) as a colorless oil: IR (film) 2965, 1760, 1745, 1720 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.96 (s, 3H), 1.18 (s, 3H), 2.50 (d, J = 5.2 Hz, 1H), 3.19 (d, J = 7.2 Hz, 1H), 3.57 (s, 3H), 3.79 (s, 3H), 4.33 (dd, J = 5.2, 2.2 Hz, 1H), 7.29 (dd, J = 7.2, 2.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.5, 27.4, 39.8, 43.2, 51.1, 52.5, 52.7, 61.9, 98.6, 130.9, 140.3, 163.6, 171.6, 195.8; MS (EI, 75 eV) *m*/*z* (relative intensity) 280 (M^+, 8), 224 (16), 165 (50), 133 (16), 83 (100); HRMS (EI) calcd for $C_{14}H_{16}O_6$ (M^+) 280.0947, found 280.0948.

Acknowledgment. We thank the National Science Council (NSC) of the Republic of China for financial support of our research. P.D.R. thanks NSC for a postdoctoral fellowship.

Supporting Information Available: ^1H and ^{13}C NMR and DEPT spectra of compounds **14**−**19(a**−**d)** and **22a**−**d**, $^1H-^1H$ COSY and NOESY spectra of **14c**, and X-ray crystallographic data of compound **15b**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO990232K