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Intramolecular Diels−Alder Reactions of Brominated Masked *o*-Benzoquinones. A Detour Method To Synthesize Highly Functionalized Oxatricyclic [*m*.3.1.0] Ring Systems from 2-Methoxyphenols

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Intramolecular Diels−Alder (IMDA) reactions of masked *o*-benzoquinones (MOBs) **5a**−**d** to **7a**−**d** and **17a**−**d** to **19a**−**d** generated in situ from 2-methoxyphenols **2**−**4** and **14**−**16**, respectively, in the presence of alkenols **1a**−**d**, resulting in highly functionalized oxatricyclic [*m*.3.1.0] ring systems are described. The MOBs **5a**−**d** to **7a**−**d** underwent the IMDA reactions to furnish the adducts **8a**−**d**, **10a**−**d**, and **12a**−**d** (direct method) in poor yields with the concomitant formation of considerable amounts of unexpected byproducts **9a**−**d**, **11a**−**d**, and **13a**−**d**, respectively. To avoid the formation of byproducts and to improve the yields of the desired cycloadducts, a detour method comprising sequential bromination of 2-methoxyphenols **2**−**4**, tandem oxidative acetalization−Diels−Alder reaction, and debromination has been developed. The oxidation of bromophenols **14**−**16** in the presence of alkenols **1a**−**d** produced the corresponding MOBs **17a**−**d** to **19a**−**d**, which underwent cycloaddition to afford the cycloadducts **20a**−**d** to **22a**−**d**, respectively, as sole products in good to high yields in a highly regio- and stereoselective manner. Treatment of the bromoadducts **20a**−**d** to **22a**−**d** with tributylammonium formate−palladium reagent produced the corresponding debrominated products **8a**−**d**, **10a**−**d**, and **12a**−**d** in high to excellent yields. In general, the latter oxatricycles were obtained in higher overall yields via the detour method than those via the direct method.

Introduction

The intramolecular Diels−Alder (IMDA) reaction has been proved to be a very useful strategy in the regio- and stereoselective construction of highly substituted bicyclic and polycyclic ring systems.[1] The advantages of an intramolecular reaction over its intermolecular counterpart are well documented.[2] One important difference is that the decreased entropic demands in IMDA reactions often render them to proceed under milder conditions with higher reaction rates. Second, the reduction in the degrees of freedom of the unimolecular transition state often results in superior selectivities when compared to the intermolecular reactions.

Masked *o*-benzoquinones (MOBs),[3] a highly reactive class of 6,6-dialkoxycyclohexa-2,4-dienones, can be generated in situ by the oxidation of the corresponding 2-methoxyphenols with hypervalent iodine reagents in MeOH. When MeOH is replaced by an alkenol during the oxidation of 2-methoxyphenols, thus formed MOBs bearing an alkene moiety tethered through an acetal would undergo tandem IMDA reaction under appropriate reaction conditions to furnish various highly functionalized oxatricycles[4] that are useful synthons for polysubstituted *cis*-decalins,[5] variously fused triquinanes,[6] and bicyclo[4.2.2]decenones.[5f] Recently, highly functionalized tricyclic [*m*.2.2.0] ring systems were achieved via diastereoselective IMDA reactions of MOBs in our laboratories.[7] On the other hand, the IMDA adducts can undergo interesting and useful photochemical reactions, such as oxadi-π-methane rearrangement[8] to provide a variety of compounds with potential synthetic utility.[6b,9] The IMDA adducts obtained from analogous tandem processes were employed as advanced intermediates in the formal synthesis of (±)-reserpine[10] and the total syntheses of a clerodane diterpenic acid[11] and (±)-pallescensin B[12] in our laboratories. In addition to our efforts, various IMDA adducts of MOBs have been employed as key intermediates in the total syntheses of (±)-xestoquinone[5d,13] and (±)-halenoquinone.[14] Very recently, the synthesis of the

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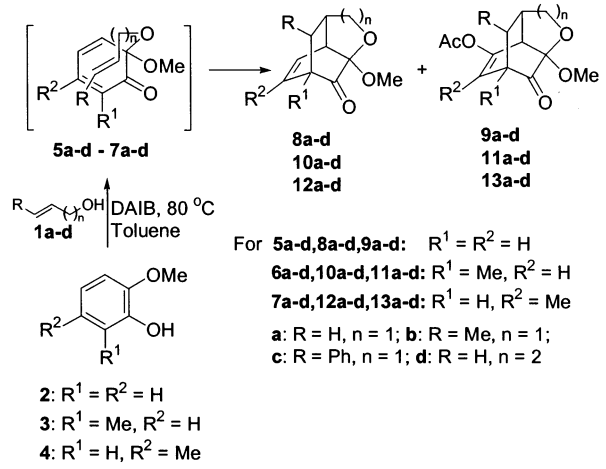
SCHEME 1



carbocyclic core of CP-263,114 was accomplished by employing a tandem phenolic oxidation−IMDA sequence as one of the key steps.[15] It is also worth mentioning that the IMDA reactions of 2-pyrones, homodienes structurally related to MOBs, tethered with unsymmetrically substituted alkynes and alkenes[16] were employed as key steps in the total syntheses of several alkaloids[17] and physiologically important vitamin D_3 analogues.[18]

We have previously developed an unprecedented methodology[4] involving in situ tethering of an alkenol to a diene system through acetal formation as an efficient route to furnish a oxatricyclic ring system. Several easily accessible 2-methoxyphenols were oxidized by (diacetoxyiodo)benzene (DAIB) in the presence of alkenols **1a**−**d** to generate MOBs that underwent IMDA reaction smoothly to provide highly functionalized oxatricycles in moderate to high yields. However, the IMDA reactions of the MOBs derived from the parent 2-methoxyphenol (guaiacol, **2**) were found to be less efficient in this methodology. To improve the yields of the desired cycloadducts, a detour method that was developed recently in this laboratory for the intermolecular Diels−Alder reactions of the MOBs[19] is now extended to the intramolecular strategies as well. This protocol comprises sequential bromination of 2-methoxyphenols **2**−**4**, tandem oxidative acetalization−Diels−Alder reaction, and debromination and has been proved quite successful. We report herein the details of this detour method to synthesize highly functionalized oxatricycles **8a**−**d**, **10a**−**d**, and **12a**−**d**.

Results and Discussion

The IMDA reactions of MOBs **5a**−**d** to **7a**−**d** generated from the 2-methoxyphenols **2**−**4** in the presence of alkenols **1a**−**d**, respectively, are outlined in Scheme 1, and the results are summarized in Table 1. Initial investigations are conducted on the MOB **5a** that was generated in situ from guaiacol (**2**) in the presence of allyl alcohol (**1a**) using DAIB in CH_2Cl_2. At room temperature, the MOB **5a** underwent intramolecular cycloaddition to provide the tricyclic compound **8a** in 33% yield.[4a] When the IMDA reaction was attempted at 80 °C (method A), the cycloadduct **8a** was obtained in 28% yield along with an unexpected IMDA adduct **9a**, bearing acetoxy function in 18% yield. Subsequently, this reaction was extended to other alkenols such as *trans*-crotyl alcohol (**1b**), cinnamyl alcohol (**1c**), and homoallyl alcohol (**1d**) to produce IMDA adducts via the in situ generated MOBs **5b**−**d**. While the MOBs **5b** and **5c** yielded the expected products **8b** and **8c** in 44 and 72% yields, respectively, at room temperature, the MOB **5d** could not provide the desired product **8d**.[4a] On the other hand, the reactions of **2** with **1b**−**d** at 80 °C afforded the cycloadducts **8b**, **8c**, and **8d** albeit in low yields, along with the side products **9b**, **9c**, and **9d** via the MOBs **5b**−**d**, respectively (Scheme 1, Table 1).

To evaluate the effect of electron-donating substituents present on the C_2 and C_3 of cyclohexadienone moiety on these IMDA reactions, 2-methoxy-6-methylphenol (**3**) and 2-methoxy-5-methylphenol (**4**) were oxidized in the presence of alkenols **1a**−**d**. Surprisingly, 2-methoxyphenols **3** and **4** did not provide the corresponding cycloadducts in the presence of alkenols **1a**−**d** at room temperature. However, as shown in Table 1, at 80 °C, the MOB **6a** generated from phenol **3** and allyl alcohol (**1a**) underwent cycloaddition to produce the desired adduct **10a** in 38% yield with the concomitant formation of **11a** in 19% yield (entry 9). In addition to these two cycloadducts, two other minor products, viz. 1,4-benzoquinone **23**[20] and 4-acetoxyphenol **24**, were also isolated in 3 and 6% yields, respectively (Scheme 2). The MOBs **6b**, **6c**, and **6d** exhibited similar reactivity furnishing a total of four products in each case. On the other hand, the MOBs **7a**−**d** generated at 80 °C from 2-methoxyphenol **4** and alkenols **1a**−**d** underwent cycloaddition to produce the desired adducts **12a**−**d** along with the corresponding 8-acetoxy cycloadducts **13a**−**d**, respectively (Table 1). Thus, the cycloadditions of the MOBs **5a**−**d** to **7a**−**d** were found to be inefficient and appear to have no synthetic value, except in the case of MOB **5c**, which provided the desired product **8c** in 72% yield (Table 1, entry 5). No attempt was made to isolate the MOBs **5a**−**d** to **7a**−**d** since this type of MOBs were known to dimerize when concentrated.

Plausible reaction pathways leading to the formation of the products **23**, **24**, **10d**, and **11d** from 2-methoxyphenol **3** in the presence of alkenol **1d**, for instance, are depicted in Scheme 2. The initial interaction of **3** with the oxidant DAIB leads to the intermediate **25**, which subsequently takes part in the reaction through two possible pathways A and B. In path A, a tandem oxidative acetalization−IMDA reaction sequence starting from **25** results in the tricyclic derivative **10d**. In path B, acetic acid, generated from the oxidant, reacts with **25** to provide 4-acetoxy-2,5-cyclohexadienone **26**, which aromatizes to give the corresponding phenol **24**. Subsequently, 2-methoxyphenol **24** undergoes DAIB-mediated oxidative acetalization in the presence of alkenol **1d** to furnish the oxatricyclic derivative **11d** via the MOB **27**. The other minor byproduct *p*-benzoquinone **23** may arise from the oxidation of **24** and/or **26** (Scheme 2).

Based on our detour method recently developed in the case of intermolecular Diels−Alder reactions,[19] we envi-

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TABLE 1. Intramolecular Diels–Alder Reactions of Masked *o*-Benzoquinones 5a–d, 6a–d, and 7a–d Derived from 2-Methoxyphenols 2, 3, and 4, Respectively (Direct Method)[a]

				reaction conditions		products	
entry	phenol	alkenol	MOB	addition[c] time (h)/*T* (°C)	after addition[d] time (h)/*T* (°C)	yield (%)	yield (%)
1[e]	**2**	**1a**	**5a**	4/rt	8/rt	**8a**/33	**9a**/0
2		**1a**	**5a**	1/80	1/80	**8a**/28	**9a**/18
3[e]		**1b**	**5b**	4/rt	8/rt	**8b**/44	**9b**/0
4		**1b**	**5b**	1/80	1/80	**8b**/25	**9b**/16
5[e]		**1c**	**5c**	4/rt	8/rt	**8c**/72	**9c**/0
6		**1c**	**5c**	1/80	1/80	**8c**/38	**9c**/32
7		**1d**	**5d**	4/rt	8/rt	**8d**/0	**9d**/0
8		**1d**	**5d**	1/80	1/80	**8d**/17	**9d**/10
9[f]	**3**[g]	**1a**	**6a**	1/80	1/80	**10a**/38	**11a**/19
10[f]		**1b**	**6b**	1/80	1/80	**10b**/36	**11b**/18
11[f]		**1c**	**6c**	1/80	1/80	**10c**/21	**11c**/10
12[f]		**1d**	**6d**	1/80	1/80	**10d**/4	**11d**/39
13	**4**[g]	**1a**	**7a**	1/80	1/80	**12a**/26	**13a**/17
14		**1b**	**7b**	1/80	1/80	**12b**/26	**13b**/10
15		**1c**	**7c**	1/80	1/80	**12c**/15	**13c**/10
16		**1d**	**7d**	1/80	1/80	**12d**/3	**13d**/10

[a] Reactions in entries 2, 4, and 6–15 were carried out following method A. [b] Five equivalents of alkenols was used in method A. [c] Time during which 2-methoxyphenol (**2**, **3**, or **4**) was added to a mixture of alkenol **1** and DAIB in toluene. [d] Time for which the reaction mixture was stirred after the complete addition of 2-methoxyphenol (**2**, **3**, **4**) and reaction temperature. [e] Results in entries 1, 3, and 5 were taken from ref 4a for comparison. [f] In addition to the products mentioned in the table, **23** and **24** were also isolated during the reactions in entries 9, 10, 11, and 12 in yields of 3, 6; 2, 6; 10, 5; and 3, 6%, respectively. [g] Phenols **3** and **4** did not react with alkenols **1a–d** at room temperature.

sioned that the incorporation of a readily removable bromo substitution at the position-4 of MOBs **5a–d** to **7a–d** would prevent the formation of the undesired side products and self-dimerization of MOBs. In fact, the introduction of a bromine atom has been found useful earlier in the cases of 2-pyrones where the resultant brominated pyrones reacted with both electron-poor and electron-rich dienophiles via normal and inverse-electron-demand Diels–Alder cycloadditions with good stereocontrol.[21] Thus, we have examined the IMDA reactions of MOBs **17a–d** to **19a–d** obtained from the bromophenols **14–16**, respectively, in the presence of the alkenols **1a–d** (Scheme 3 and Table 2). The requisite 4-bromophenols **14–16**[19a] were readily accessed by the bromination (NBS/AcOH) of the corresponding 2-methoxyphenols using a modified literature procedure.[22] The oxidation of 4-bromophenol **14** with DAIB in CH_2Cl_2 carried out at 0 °C in the presence of allyl alcohol reached completion within 10 min to provide MOB **17a**. The crude MOB **17a** was subjected to the IMDA reaction by heating in dry toluene at 80 °C for 12 h (method B). The usual workup followed by silica gel column chromatography yielded the pure cycloadduct **20a** in 58%. To investigate the generality of this reaction, it was extended to other alkenols **1b–d** to obtain the corresponding cycloadducts **20b–d** in 70, 78, and 38% yields, respectively. Similarly, the MOBs **18a–d** and **19a–d** produced in the analogous manner by the oxidation of the bromophenols **15** and **16** in the presence of alkenols **1a–d** furnished the expected products **21a–d** and **22a–d**, respectively. All the MOBs **17a–d** to **19a–d** were generated in situ, and no attempt was made to isolate them. The ^{1}H NMR (400 MHz) spectra of the crude reaction mixtures resulted from the IMDA reactions of the latter MOBs did not show the peaks corresponding to the isomeric cycloadducts indicating that the cycloaddition proceeded in a highly regio- and stereoselective manner.

As evidenced from the yields incorporated in Tables 1 and 2, the IMDA reactions of the MOBs **17a–d** to **19a–d** with bromo substitution are more facile than their corresponding nonbrominated counterparts **5a–d** to **7a–d**. This may be due to the bulkiness of the bromine atom at the 4-position of 4-bromo-2-methoxyphenols that hinders the ipso attack of AcOH to prevent the side reactions and thus increases the yields of the IMDA reactions of brominated MOBs **17a–d** to **19a–d**. Furthermore, the introduction of a bromine atom at the 4-position retards the self-dimerization of MOBs as we have observed in the cases of intermolecular Diels–Alder reactions[19] and

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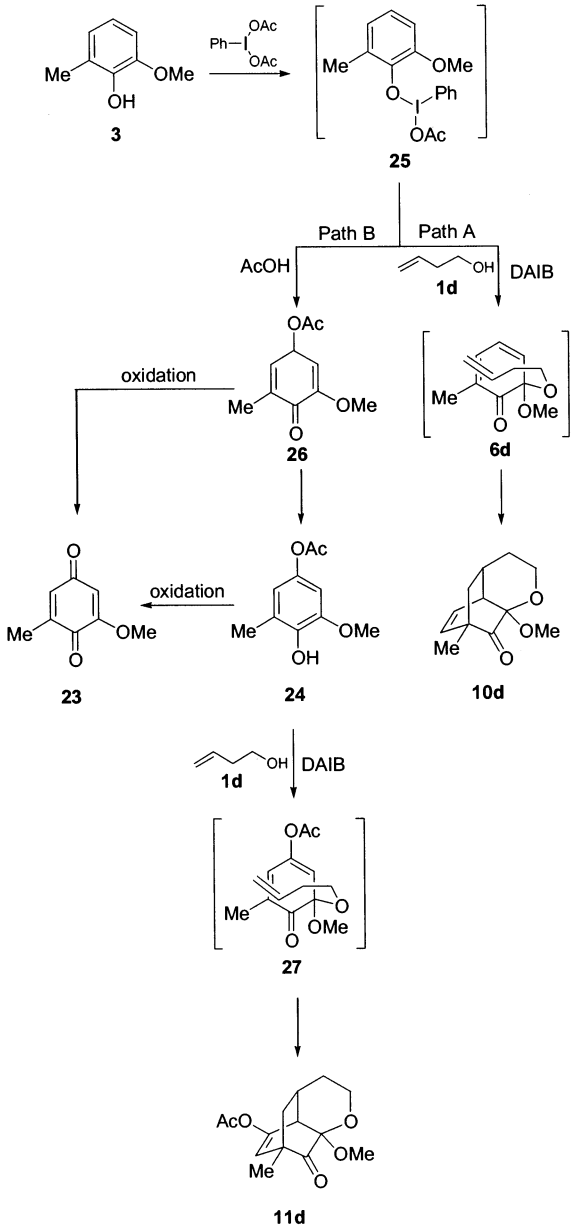
SCHEME 2



thus increases the yields of the IMDA reactions of brominated MOBs. It may also be noted that the adducts **8d**, **10d**, and **12d** (Table 1, entries 7, 8, 12, and 16) and **20d** − **22d** (Table 2, entries 4, 8, and 12) with one more carbon ($n = 2$) in the tether of their corresponding MOBs are obtained in relatively lower yields. This is in agreement with our earlier observation in the cases of IMDA reactions of other MOBs.[4a]

The cycloadducts **20a**−**d** to **22a**−**d** were then subjected to debromination using tributylammonium formate−palladium reagent [Bu_3N, HCO_2H/$Pd(PPh_3)_2Cl_2$][19a,23] to obtain the corresponding debrominated products **8a**−**d**, **10a**−**d**, and **12a**−**d** in high to excellent yields (Table 2). Thus, we have achieved the latter cycloadducts via the detour method in higher overall yields than those obtained via the direct method in one step in all cases but one (**8c**, entry 3). It is especially worth mentioning that there is 12-fold and 13-fold increase in the overall yields of the cycloadducts **10d** (entry 8) and **12d** (entry 12), respectively, via the detour method.

SCHEME 3

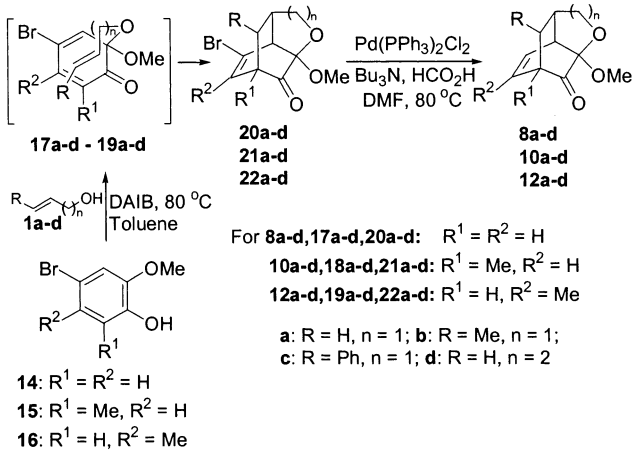


TABLE 2. Intramolecular Diels−Alder Reactions of Masked 4-Bromo-*o*-benzoquinones 17a−d, 18a−d, and 19a−d Derived from 2-Methoxyphenols 14, 15, and 16, Respectively (Detour Method)[a]

entry	phenol	alkenol[b]	MOB	adduct/ yield (%)	product[c]/ yield (%)	overall yield detour[d]	overall yield direct
1	**14**	**1a**	**17a**	**20a**/58	**8a**/91	51	33[e]
2		**1**b	**17b**	**20b**/70	**8b**/96	65	44[e]
3		**1c**	**17c**	**20c**/78	**8c**/90	68	72[e]
4		**1d**	**17d**	**20d**/38	**8d**/88	32	17
5	**15**	**1a**	**18a**	**21a**/73	**10a**/85	56	38
6		**1b**	**18b**	**21b**/74	**10b**/92	62	36
7		**1c**	**18c**	**21c**/79	**10c**/91	65	21
8		**1d**	**18d**	**21d**/62	**10d**/86	48	4
9	**16**	**1a**	**19a**	**22a**/60	**12a**/80	47	26
10		**1b**	**19b**	**22b**/73	**12b**/88	63	26
11		**1c**	**19c**	**22c**/75	**12c**/89	65	15
12		**1d**	**19d**	**22d**/46	**12d**/87	39	3

[a] Reactions in entries 4−12 were carried out following method B (MOBs were stirred in toluene at 80 °C for 12 h, see the Experimental Section). [b] Five equivalents of alkenols were used in method B. [c] Debrominated products were obtained from method C. [d] Overall yield of three steps: bromination, tandem oxidative acetalization−Diels−Alder reaction, and debromination. [e] Results were taken from ref 4a for comparison.

The structures of all the new compounds were established by spectroscopic methods including IR, ^1H and ^{13}C NMR, and low- and high-resolution mass. For the majority of the cycloadducts, satisfactory elemental analyses were obtained. 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 specta of all the cycloadducts showed strong absorptions at 1730−1749 cm^{-1}, characteristic of the carbonyl group adjacent to the α-methoxyl and cyclic ether functionality.[4a] The IR spectra of **9a**−**d**, **11a**−**d**, and **13a**−**d** showed additional absorption at 1746−1764 cm^{-1} corresponding to the carbonyl of the enol acetate.

The regio- and stereochemical assignments of the unknown cylcoadducts were made by comparing the

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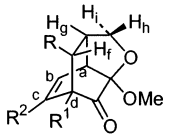
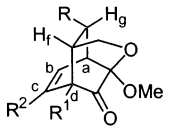
CHART 1



meta and *syn*
10b, 12c



ortho and *syn*
(Not formed)

cycloadduct	R	R^1	R^2	coupling constant (*J* in Hz)				
				H_a-H_g	H_c-H_f	H_d-H_f	H_g-H_i	H_g-H_h
10b	H	Me	H	4.7	1.3	#	3.2	0
12c	H	H	Me	4.4	#	3.6	3.6	0

#: Not applicable.

coupling patterns and coupling constants of the various protons with those of the analogous IMDA adducts, whose regio- and stereochemistries were earlier determined unambiguously in our laboratories.[4a] For the cycloadduct **10b** (R^1 = Me, R^2 = H), for instance, the observed long-range *W*-type coupling between H_c and H_f (J = 1.3 Hz) confirms that the methyl group is oriented syn to the vinyl bridge and anti to the ether ring, supporting the assigned regiochemistry, which is further corroborated by the coupling between H_g and H_i (J = 3.2 Hz). Similarly, the coupling patterns of H_a–H_g and H_d–H_f (Chart 1) in cycloadduct **12c** (R^1 = H, R^2 = Me) are diagnostic for the meta regiochemistry (with respect to the carbonyl function), ruling out the alternate structures that result from ortho regiochemistry. The proposed regiochemistry gains additional support by the existence of H_g–H_i coupling (J = 3.6 Hz) for the adduct **12c**. It may be noted that there is no coupling between H_g and H_h for the adducts **10a** and **12c** presumably due to their orthogonal relationship. In the remaining cycloadducts also, the stereochemical assignments were based on the similar analogy of the coupling patterns.

The structural assignments of **20a**–**d** to **22a**–**d** were based on the spectroscopic methods and the chemical transformation into the corresponding debrominated products **8a**–**d**, **10a**–**d**, and **12a**–**d**. The coupling patterns in the ^{1}H NMR spectra of **20a**–**d** to **22a**–**d** are analogous to those observed in case of **8a**–**d**, **10a**–**d**, and **12a**–**d**, respectively.

Conclusion

In conclusion, we have developed a new and efficient detour method comprising sequential bromination of 2-methoxyphenols **2**–**4**, tandem oxidative acetalization–Diels–Alder reaction, and debromination to synthesize highly functionalized oxatricyclic [*m*.3.1.0] ring systems. The MOBs **17a**–**d** to **19a**–**d** generated in situ from 2-methoxyphenols **14**–**16**, respectively, in the presence of alkenols **1a**–**d**, underwent highly regio- and stereoselective IMDA reactions to furnish exclusively meta, syn-adducts (with respect to carbonyl group) **20a**–**d** to **22a**–**d**. The introduction of a bromine atom at position-4 of the 2-methoxyphenols served the purpose of achieving higher overall yields of the oxatricycles **8a**–**d**, **10a**–**d**, and **12a**–**d** via the detour method than those obtained via the direct method. In addition, the vinyl bromides **20a**–**d** to **22a**–**d** can act as potential substrates for the syntheses of higher olefins by organometallic coupling reactions. The evaluation of the synthetic utility of the bromoadducts **20a**–**d** to **22a**–**d** is underway in our laboratory.

Experimental Section

General Methods. For general details and instrumentation, see our previous publication.[4a]

General Procedures for Tandem Oxidative Acetalization–Diels–Alder Reactions. (i) The Reactions of Phenols 2–4 with Alkenols 1a–d. Method A. To a suspension of DAIB (1.8 mM, 1.2 equiv) and an alkenol (7.5 mM, 5 equiv) in toluene (1.2 mL) was added a solution of phenol (**2**, **3** or **4**, 1.5 mM, 1 equiv) in toluene (2 mL) at 80 °C during 1 h using a syringe pump under nitrogen atmosphere. Stirring was continued for 1 h at the same temperature. The reaction mixture was then cooled to rt, washed successively with saturated $NaHCO_3$ and brine, and extracted with EtOAc. The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated, and the residue was purified by silica gel column chromatography with EtOAc/hexanes as eluent to furnish the pure cycloadducts (**8a**–**d** to **13a**–**d**).

(ii) The Reactions of Phenols 14–16 with Alkenols 1a–d. Method B. To a flask containing a mixture of DAIB (1.2 mM, 1.2 equiv) and an alkenol (5.0 mM, 5 equiv) in dry CH_2Cl_2 (5 mL) was added slowly a solution of phenol (**14**, **15**, or **16**, 1.0 mM, 1 equiv) in dry CH_2Cl_2 (5 mL) at 0 °C under nitrogen atmosphere. The contents were then stirred for 10 min. The volatiles were removed under reduced pressure, and the residue was dissolved in dry toluene (10 mL). After being stirred at 80 °C for 12 h, the reaction mixture was cooled to rt and concentrated under reduced pressure, and the residue was purified by silica gel column chromatography using EtOAc/hexanes as eluent to furnish the pure cycloadduct (**20a**–**d** to **22a**–**d**).

General Procedure for the Debromination of Cycloadducts. Method C.[19a,23] To the bromo compound (**20a**–**d** to **22a**–**d**, 0.5 mM) were added successively Bu_3N (1.5 mM, 3 equiv), HCO_2H (1.0 mM, 2 equiv), and $Pd(PPh_3)_2Cl_2$ (0.025 mM, 0.05 equiv) in dry DMF (1.0 mL) under nitrogen atmosphere. The contents were then heated at 80 °C for 16 h. The reaction mixture was cooled to room temperature, diluted with EtOAc, and worked up as usual. The thus obtained residue was subjected to silica gel column chromatography (EtOAc/hexanes) to afford the pure product (**8a**–**d**, **10a**–**d**, **12a**–**d**). Yields are given Table 2.

(1*S,3*R**,6*R**,7*R**)-3-Methoxy-4-oxatricyclo[4.3.1.0^{3,7}]-dec-8-en-2-one (8a).**[4a] Following the general procedure (method A), MOB **5a**, generated in situ from phenol **2** and allyl alcohol (**1a**), was reacted and the crude residue was subjected to column chromatography (EtOAc/hexanes = 1:2) to afford **8a** (28% yield) as a colorless solid.

(1*R,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 (8b).**[4a] Following the general procedure (method A), MOB **5b** generated in situ from phenol **2** and *trans*-crotyl alcohol (**1b**) was reacted and the crude residue was subjected to column chromatography (EtOAc/hexanes = 1:2) to furnish **8b** (25% yield) as a colorless liquid.

(1*R,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 (8c).**[4a] Following the general procedure (method A), MOB **5c** generated in situ from phenol **2** and cinnamyl alcohol (**1c**) was reacted and the crude residue was subjected to column chromatography (EtOAc/hexanes = 1:3) to afford **8c** (38% yield) as a colorless solid: mp 129–131 °C (from EtOAc–hexanes).

(1*S,3*R**,7*S**,8*R**)-3-Methoxy-4-oxatricyclo[5.3.1.0^{3,8}]-undec-9-en-2-one (8d).** Following the general procedure (method A), MOB **5d** generated in situ from phenol **2** and homoallyl alcohol (**1d**) was reacted and the crude residue was subjected to column chromatography (EtOAc/hexanes = 1:4)

to provide **8d** (17% yield) as a colorless solid: IR (film) 2946, 1736 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.37 (ddd, J = 8.0, 6.8, 1.6 Hz, 1H), 6.20 (ddd, J = 8.0, 6.4, 1.6 Hz, 1H), 3.90 (apparent dd, J = 12.4, 5.6 Hz, 1H), 3.61 (ddd, J = 13.2, 13.2, 2.8 Hz, 1H), 3.41 (s, 3H), 3.13 (m, 1H), 2.74−2.71 (m, 1H), 2.26 (m, 1H), 1.96−1.88 (m, 1H), 1.65 (ddd, J = 13.6, 3.2, 3.2 Hz, 1H), 1.55 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.5, 134.0, 128.2, 93.2, 60.7, 50.9, 48.2, 43.2, 30.1, 29.1, 27.6; MS (EI, 70 eV) *m/z* (relative intensity) 166 (M^+ − CO, 100), 138 (29), 113 (14), 107 (17), 91 (24) 79 (76); HRMS (EI) calcd for $C_{11}H_{14}O_3$ (M^+) 194.0943, found 194.0940.

(1*S,3*R**,6*R**,7*S**)-3-Methoxy-2-oxo-4-oxatricyclo-[4.3.1.0^{3,7}]dec-8-en-8-yl acetate (9a):** colorless solid obtained in 18% yield; mp 79−80 °C (from CH_2Cl_2−hexanes); IR (film) 2969, 1764, 1742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.88 (dd, J = 7.6, 3.0 Hz, 1H), 4.10 (dd, J = 8.2, 3.6 Hz, 1H), 3.77 (d, J = 8.2 Hz, 1H), 3.51 (s, 3H), 3.21 (dd, J = 4.4, 3.0 Hz, 1H), 3.15 (ddd, J = 7.6, 2.8, 2.8 Hz, 1H), 2.80−2.76 (m, 1H), 2.16 (s, 3H), 1.96−1.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.2, 168.5, 149.2, 111.7, 99.7, 73.4, 51.2, 46.4, 43.7, 35.5, 31.3, 20.7; MS (EI, 70 eV) *m/z* (relative intensity) 238 (M^+, 6), 210 (13), 209 (49), 193 (17), 167 (41) 99 (100); HRMS (EI) calcd for $C_{12}H_{14}O_5$ (M^+) 238.0841, found 238.0846.

(1*S,3*R**,6*R**,7*S**,10*R**)-3-Methoxy-10-methyl-2-oxo-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-8-yl acetate (9b):** colorless solid (16% yield); mp 87−89 °C (from CH_2Cl_2−hexanes); IR (film) 2975, 1763, 1739 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.71 (dd, J = 7.4, 2.6 Hz, 1H), 4.08 (dd, J = 8.0, 3.2 Hz, 1H), 3.80 (d, J = 8.0 Hz, 1H), 3.51 (s, 3H), 3.16 (dd, J = 4.0, 2.6 Hz, 1H), 3.02 (dd, J = 7.4, 3.2 Hz, 1H), 2.28−2.26 (m, 1H), 2.16 (s, 4H), 1.03 (d, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.6, 168.8, 148.7, 109.1, 99.1, 73.5, 51.5, 50.9, 46.9, 44.4, 37.3, 28.8, 18.5; MS (EI, 70 eV) *m/z* (relative intensity) 252 (M^+, 3), 224 (5), 181 (16), 165 (14), 151 (10) 57 (100); HRMS (EI) calcd for $C_{12}H_{14}O_5$ (M^+) 252.0998, found 252.0988.

(1*R,3*R**,6*R**,7*S**,10*R**)-3-Methoxy-2-oxo-10-phenyl-2-oxo-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-8-yl acetate (9c):** colorless needles (32% yield); mp 109−110 °C (from CH_2Cl_2−hexanes); IR (film) 2975, 1746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.27−7.25 (m, 5H), 5.52 (dd, J = 7.4, 2.8 Hz, 1H), 4.20 (dd, J = 8.4, 3.2 Hz, 1H), 3.93 (d, J = 8.4 Hz, 1H), 3.56 (s, 3H), 3.41 (dd, J = 4.0, 2.8 Hz, 1H), 3.35 (dd, J = 2.8, 2.8 Hz, 1H), 3.26 (dd, J = 7.4, 2.8 Hz, 1H), 3.16−3.14 (m, 1H), 2.24 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.7, 169.2, 150.0, 141.2, 128.4, 128.3, 127.0, 108.9, 99.3, 74.0, 52.4, 51.8, 47.7, 47.6, 44.8, 20.8; MS (EI, 70 eV) *m/z* (relative intensity) 286 (M^+ − CO, 28), 244 (38), 243 (38), 144 (45), 115 (51) 99 (100); HRMS (EI) calcd for $C_{17}H_{18}O_4$ (M^+ − CO) 286.1205, found 286.1203.

(1*S,3*R**,7*S**,8*S**)-3-Methoxy-2-oxo-4-oxatricyclo-[5.3.1.0^{3,8}]undec-9-en-9-yl acetate (9d):** colorless solid (10% yield); mp 128−129 °C (from CH_2Cl_2−hexanes); IR (film) 2976, 1757, 1730 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.76 (dd, J = 7.0, 6.4, 2.6 Hz, 1H), 3.89 (dddd, J = 12.8, 5.6, 1.2, 1.2 Hz, 1H), 3.56 (ddd, J = 12.8, 12.8, 2.4 Hz, 1H), 3.44 (s, 3H), 3.12 (ddd, J = 7.4, 3.0, 2.6 Hz, 1H), 2.74−2.69 (m, 1H), 2.61 (dd, J = 2.8, 2.6 Hz, 1H), 2.17 (s, 3H), 2.06 (ddd, J = 13.6, 11.6, 2.6 Hz, 1H), 1.91 (dddd, J = 13.6, 9.6, 5.6, 3.6 Hz, 1H), 1.64 (ddd, J = 13.6, 3.2, 3.0 Hz, 1H), 1.52−1.57 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.6, 168.9, 153.4, 109.8, 92.9, 60.7, 51.3, 47.6, 46.6, 29.7, 29.6, 27.7, 20.8; MS (EI, 70 eV) *m/z* (relative intensity) 252 (M^+, 2), 224 (5), 181 (17), 165 (21), 125 (18) 99 (100); HRMS (EI) calcd for $C_{12}H_{16}O_4$ (M^+ − CO) 224.1049, found 224.1039.

(1*S,3*R**,6*R**,7*R**)-3-Methoxy-1-methyl-4-oxatricyclo-[4.3.1.0^{3,7}]dec-8-en-2-one (10a).** Following the general procedure (method A), MOB **6a** generated in situ from phenol **3** and allyl alcohol (**1a**) was reacted and the crude residue was subjected to column chromatography (EtOAc/hexanes = 1:3) to give **10a** (38% yield) as a colorless liquid: IR (film) 2975, 1749 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.20 (dd, J = 8.2, 6.4 Hz, 1H), 5.97 (dd, J = 8.2, 1.7 Hz, 1H), 4.13 (dd, J = 8.0, 3.6 Hz, 1H), 3.80 (d, J = 8.0 Hz, 1H), 3.51 (s, 3H), 3.31 (ddd, J = 6.0, 4.6, 1.8 Hz, 1H), 2.58−2.53 (m, 1H), 1.78 (dd, J = 13.2, 10.0 Hz, 1H), 1.63 (d, J = 13.2 Hz, 1H), 1.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.6, 136.4, 129.2, 100.7, 74.1, 51.4, 47.2, 42.8, 38.9, 37.3, 16.8; MS (EI, 12 eV) *m/z* (relative intensity) 166 (M^+ − CO, 60), 151 (8), 134 (5), 125 (100), 119 (4), 107 (26), 91 (18), 79 (9), 74 (3), 43 (3); HRMS (EI) calcd for $C_{10}H_{14}O_2$ (M^+ − CO) 166.0994, found 166.0998.

(1*R,3*R**,6*R**,7*R**,10*R**)-3-Methoxy-1,10-dimethyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (10b).** Following the general procedure (method A), MOB **6b** generated in situ from phenol **3** and *trans*-crotyl alcohol (**1b**) was reacted and the crude residue was subjected to column chromatography (EtOAc/hexanes = 1:3) to afford **10b** (36% yield) as a colorless liquid: IR (film) 2971, 1739 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.21 (dd, J = 8.1, 6.5 Hz, 1H), 5.78 (ddd, J = 8.1, 1.3, 1.3 Hz, 1H), 4.11 (dd, J = 8.0, 3.2 Hz, 1H), 3.80 (d, J = 8.0 Hz, 1H), 3.51 (s, 3H), 3.25 (ddd, J = 6.5, 4.7, 1.3 Hz, 1H), 2.04 (ddd, J = 4.7, 3.2, 1.3 Hz, 1H), 1.80 (apparent m, ddq, J = 7.1, 1.3, 1.3 Hz, 1H), 1.27 (s, 3H), 0.95 (d, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.2, 133.3, 128.6, 100.0, 73.7, 51.4, 51.3, 46.4, 42.3, 16.6, 15.1; MS (EI, 70 eV) *m/z* (relative intensity) 180 (M^+ − CO, 100), 165 (15), 151 (6), 125 (16), 105 (14), 91 (27), 77 (22), 65 (15), 39 (23), 27 (11); HRMS (EI) calcd for $C_{11}H_{16}O_2$ (M^+ − CO) 180.1151, found 180.1167.

(1*R,3*R**,6*S**,7*R**,10*S**)-3-Methoxy-1-methyl-10-phenyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (10c).** Following the general procedure (method A), MOB **6c** generated in situ from phenol **3** and cinnamyl alcohol (**1c**) was reacted and the crude residue was subjected to column chromatography (EtOAc/hexanes = 1:3) to furnish **10c** (21% yield) as a colorless solid: mp 136−137 °C (from EtOAc−hexanes); IR (film) 2973, 1740 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.19−7.09 (m, 5H), 6.21 (dd, J = 8.1, 6.6 Hz, 1H), 5.74 (dd, J = 8.1, 1.6 Hz, 1H), 4.20 (dd, J = 8.1, 3.4 Hz, 1H), 3.95 (d, J = 8.1 Hz, 1H), 3.57 (s, 3H), 3.51−3.48 (m, 1H), 2.88 (dd, J = 1.7, 1.7 Hz, 1H), 2.82 (apparent m, ddd, J = 4.4, 3.4, 1.7 Hz, 1H), 1.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.0, 141.6, 133.4, 129.9, 129.3, 128.1, 127.1, 100.2, 72.3, 52.9, 52.2, 51.6, 48.5, 43.4, 15.7; MS (EI, 70 eV) *m/z* (relative intensity) 242 (M^+ − CO, 23), 183 (28), 167 (29), 143 (30), 125 (95), 115 (41), 100 (43), 91 (100), 77 (36), 65 (30); HRMS (EI) calcd for $C_{17}H_{18}O_3$ (M^+) 270.1256, found 270.1262. Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.52, H, 6.72. Found: C, 75.44, H, 6.68.

(1*S,3*R**,7*S**,8*R**)-3-Methoxy-1-methyl-4-oxatricyclo-[5.3.1.0^{3,8}]undec-9-en-2-one (10d).** Following the general procedure (method A), MOB **6d** generated in situ from phenol **3** and homoallyl alcohol (**1d**) was reacted and the crude residue was subjected to column chromatography (EtOAc/hexanes = 1:4) to furnish **10d** (4% yield) as a colorless liquid: IR (film) 2944, 1730 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.40 (dd, J = 8.3, 6.5 Hz, 1H), 5.91 (ddd, J = 8.3, 1.6, 0.8 Hz, 1H), 3.94−3.92 (m, 1H), 3.60 (ddd, J = 13.2, 12.7, 2.9 Hz, 1H), 3.43 (s, 3H), 2.73 (ddd, J = 6.5, 3.5, 1.5 Hz, 1H), 2.37−2.31 (m, 1H), 1.97−1.88 (m, 1H), 1.83 (dd, J = 13.5, 11.6 Hz, 1H), 1.56−1.50 (m, 1H), 1.42 (dd, J = 13.5, 3.0 Hz, 1H), 1.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.3, 133.9, 133.8, 93.6, 60.8, 51.0, 49.5, 42.3, 37.4, 30.3, 29.3, 17.0; MS (EI, 70 eV) *m/z* (relative intensity) 180 (M^+ − CO, 65), 165 (18), 152 (14), 137 (23), 120 (20), 105 (28), 93 (100), 87 (20), 79 (22), 59 (12); HRMS (EI) calcd for $C_{11}H_{16}O_2$ (M^+ − CO) 180.1151, found 180.1140.

(1*S,3*R**,6*R**,7*S**)-3-Methoxy-1-methyl-2-oxo-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-8-yl acetate (11a):** colorless solid (19% yield); mp 78−80 °C (from EtOAc−hexanes); IR (film) 2969, 1764, 1742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.57 (d, J = 2.8 Hz, 1H), 4.13 (dd, J = 8.0, 3.6 Hz 1H), 3.80 (d, J = 8.0 Hz, 1H), 3.53 (s, 3H), 3.23 (dd, J = 4.4, 2.8 Hz, 1H), 2.85 (apparent m, ddd, J = 10.0, 4.4, 3.6 Hz, 1H), 2.18 (s, 3H), 1.94 (dd, J = 13.2, 10.0 Hz, 1H), 1.64 (d, J = 13.2 Hz, 1H), 1.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.5, 168.7, 149.1, 117.0, 100.3, 74.0, 51.7, 46.8, 45.9, 39.4, 37.3, 20.9, 17.1; MS (EI, 12 eV) *m/z* (relative intensity) 224 (M^+ − CO, 12), 181

(33), 165 (16), 150 (17), 141 (19), 123 (17), 108 (11), 99 (100), 79 (11), 65 (5); HRMS (EI) calcd for $C_{12}H_{16}O_4$ (M^+ − CO) 224.1048, found 224.1040. Anal. Calcd for $C_{12}H_{16}O_4$: C, 61.90, H, 6.39. Found: C, 61.93, H, 6.40.

(1*R,3*R**,6*R**,7*S**,10*R**)-3-Methoxy-1,10-dimethyl-2-oxo-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-8-yl acetate (11b):** colorless liquid (18% yield); IR (film) 2942, 1763, 1739 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.39 (dd, J = 2.8, 0.8 Hz, 1H), 4.12 (dd, J = 8.0, 3.3 Hz, 1H), 3.81 (d, J = 8.0 Hz, 1H), 3.54 (s, 3H), 3.16 (dd, J = 4.4, 2.8 Hz, 1H), 2.37−2.34 (m, 1H), 2.19 (s, 3H), 1.80 (apparent m, ddq, J = 7.0, 1.3, 0.8 Hz, 1H), 1.28 (s, 3H), 1.04 (d, J = 7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.1, 168.7, 148.4, 114.0, 99.6, 73.5, 51.7, 50.2, 46.6, 46.4, 43.2, 20.7, 16.3, 15.4; MS (EI, 70 eV) *m*/*z* (relative intensity) 238 (M^+ − CO, 58), 196 (39), 195 (79), 181 (29), 179 (22), 141 (19), 99 (100), 96 (20), 71 (18), 43 (84); HRMS (EI) calcd for $C_{13}H_{18}O_4$ (M^+ − CO) 238.1205, found 238.1214.

(1*R,3*R**,6*R**,7*S**,10*R**)-3-Methoxy-1-methyl-2-oxo-10-phenyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-8-yl acetate (11c):** colorless solid (10% yield); mp 122−124 °C (from MeOH); IR (film) 2975, 1746 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.23 (m, 5H), 5.26 (d, J = 2.6 Hz, 1H), 4.19 (dd, J = 8.2, 3.1 Hz, 1H), 3.94 (d, J = 8.2 Hz, 1H), 3.59 (s, 3H), 3.42 (dd, J = 4.2, 2.6 Hz, 1H), 3.15 (apparent m, ddd, J = 4.2, 3.1, 1.7 Hz, 1H), 2.86 (d, J = 1.70 Hz, 1H), 2.27 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 169.2, 149.7, 140.8, 129.4, 128.1, 127.2, 113.9, 99.7, 74.1, 53.6, 51.8, 51.0, 48.4, 47.0, 20.9, 16.0; MS (EI, 70 eV) *m*/*z* (relative intensity) 300 (M^+ − CO, 4), 257 (7), 167 (13), 158 (22), 141 (15), 115 (33), 99 (100), 91 (26), 77 (14), 69 (16); HRMS (EI) calcd for $C_{19}H_{20}O_5$ (M^+) 328.1311, found 328.1315. Anal. Calcd for $C_{19}H_{20}O_5$: C, 69.48, H, 6.14. Found: C, 69.52, H, 6.19.

(1*S,3*R**,7*S**,8*S**)-3-Methoxy-1-methyl-2-oxo-4-oxatricyclo[5.3.1.0^{3,8}]undec-9-en-9-yl acetate (11d):** colorless solid (39% yield); mp 122−123 °C (from EtOAc−hexanes); IR (film) 2976, 1757, 1730 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.49 (d, J = 2.6 Hz, 1H), 3.94−3.89 (m, J = 12.8, 5.7, 1.5, 1.2 Hz, 1H), 3.55 (ddd, J = 13.1, 12.8, 2.8 Hz, 1H), 3.47 (s, 3H), 2.81−2.75 (m, 1H), 2.63 (dd, J = 3.6, 2.6 Hz, 1H), 2.19 (s, 3H), 1.99 (dd, J = 13.6, 11.6 Hz, 1H), 1.96−1.81 (m, 1H), 1.51−1.55 (m, 1H), 1.42 (dd, J = 13.6, 3.6 Hz, 1H), 1.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.4, 168.8, 153.2, 114.9, 93.3, 60.7, 51.3, 48.4, 47.4, 32.9, 29.8, 29.1, 20.8, 17.3; MS (EI, 70 eV) *m*/*z* (relative intensity) 238 (M^+ − CO, 6), 195 (27), 179 (45), 135 (14), 113 (80), 91 (12), 81 (22), 65 (5), 53 (23), 43 (100); HRMS (EI) calcd for $C_{13}H_{18}O_4$ (M^+ − CO) 238.1205, found 238.1207. Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.13, H, 6.82. Found: C, 63.10, H, 6.78.

(1*S,3*R**,6*R**,7*R**)-3-Methoxy-9-methyl-4-oxatricyclo-[4.3.1.0^{3,7}]dec-8-en-2-one (12a).** Following the general procedure (method A), MOB **7a** generated in situ from phenol **4** and allyl alcohol (**1a**) was reacted and the crude residue was subjected to column chromatography (EtOAc/hexanes = 1:4) to furnish **12a** (26% yield) as a colorless solid: mp 107−108 °C (from EtOAc−hexanes); IR (film) 2959, 1742 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (ddq, J = 6.5, 1.7, 1.6 Hz, 1H), 4.11 (dd, J = 8.0, 3.2 Hz, 1H), 3.79 (d, J = 8.0 Hz, 1H), 3.51 (s, 3H), 3.24 (dd, J = 6.5, 4.6 Hz, 1H), 2.97 (ddd, J = 3.1, 1.8, 1.7 Hz, 1H), 2.50−2.46 (m, 1H), 1.86 (d, J = 1.6 Hz, 3H), 1.85 (dd, J = 6.0, 1.8 Hz, 1H), 1.84 (dd, J = 6.0, 3.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.4, 140.4, 121.7, 100.7, 73.9, 51.2, 51.1, 42.4, 36.3, 30.7, 19.9; MS (EI, 70 eV) *m*/*z* (relative intensity) 166 (M^+ − CO, 59), 125 (81), 107 (73), 91 (100), 79 (70), 77 (32), 65 (22), 59 (11), 51 (16), 39 (34); HRMS (EI) calcd for $C_{10}H_{14}O_2$ (M^+ − CO) 166.0994, found 166.0997.

(1*S,3*R**,6*R**,7*R**,10*R**)-3-Methoxy-9,10-dimethyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (12b).** Following the general procedure (method A), MOB **7b** generated in situ from phenol **4** and *trans*-crotyl alcohol (**1b**) was reacted and the crude residue was subjected to column chromatography (EtOAc/hexanes = 2:7) to furnish **12b** (26% yield) as a colorless liquid: IR (film) 2966, 1741 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 (ddq, J = 6.7, 1.6, 1.4 Hz, 1H), 4.09 (dd, J = 8.0, 3.2 Hz, 1H), 3.80 (d, J = 8.0 Hz, 1H), 3.49 (s, 3H), 3.19 (dd, J = 6.7, 4.4 Hz, 1H), 2.85 (dd, J = 3.6, 1.4 Hz, 1H), 2.24−2.17 (m, 1H), 1.95−1.93 (apparent m, ddd, J = 4.4, 3.2, 1.2 Hz, 1H), 1.86 (d, J = 1.6, 3H), 0.97 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.4, 137.4, 120.7, 100.0, 73.8, 58.3, 51.2, 44.2, 42.3, 36.7, 21.7, 18.4; MS (EI, 70 eV) *m*/*z* (relative intensity) 180 (M^+ − CO, 45), 165 (5), 125 (47), 121 (100), 105 (63), 91 (58), 77 (38), 65 (19), 55 (19), 43 (74); HRMS (EI) calcd for $C_{11}H_{16}O_2$ (M^+ − CO) 180.1150, found 180.1152.

(1*S,3*R**,6*R**,7*R**,10*R**)-3-Methoxy-9-methyl-10-phenyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (12c).** Following the general procedure (method A), MOB **7c** generated in situ from phenol **4** and cinnamyl alcohol (**1c**) was reacted and the crude residue was subjected to column chromatography (EtOAc/hexanes = 1:4) to afford **12c** (15% yield) as a colorless solid: mp 118−119 °C (from EtOAc−hexanes); IR (film) 2961, 1744 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.11 (m, 5H), 6.00 (ddq, J = 6.7, 1.8, 1.6 Hz, 1H), 4.21 (dd, J = 8.1, 3.4 Hz, 1H), 3.94 (d, J = 8.1 Hz, 1H), 3.56 (s, 3H), 3.42 (dd, J = 6.7, 4.4 Hz, 1H), 3.38 (dd, J = 2.4, 2.3 Hz, 1H), 3.06−3.05 (m, 1H), 2.82−2.80 (m, 1H), 1.44 (d, J = 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 141.6, 137.3, 128.4, 127.8, 126.9, 121.9, 100.3, 74.2, 59.7, 51.4, 47.0, 44.0, 42.8, 21.4; MS (EI, 70 eV) *m*/*z* (relative intensity) 242 (M^+ − CO, 88), 183 (100), 167 (42), 141 (30), 125 (52), 115 (31), 105 (21), 91 (78), 77 (28), 59 (20); HRMS (EI) calcd for $C_{16}H_{18}O_2$ (M^+ − CO) 242.1307, found 242.1368. Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.52, H, 6.72. Found: C, 75.59, H, 6.76.

(1*S,3*R**,7*S**,8*R**)-3-Methoxy-10-methyl-4-oxatricyclo-[5.3.1.0^{3,8}]undec-9-en-2-one (12d).** Following the general procedure (method A), MOB **7d** generated in situ from phenol **4** and homoallyl alcohol (**1d**) was reacted and the crude residue was subjected to column chromatography (EtOAc/hexanes = 1:4) to provide **12d** (3% yield) as a colorless liquid; IR (film) 2948, 1732 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 (ddq, J = 6.7, 2.1, 1.6 Hz, 1H), 3.94−3.89 (m, 1H), 3.63 (ddd, J = 13.2, 12.7, 2.9 Hz, 1H), 3.43 (s, 3H), 2.94 (apparent q, ddd, J = 2.8, 2.4, 2.1 Hz, 1H), 2.64 (dd, J = 6.7, 3.8 Hz, 1H), 2.24−2.30 (m, 1H), 1.99−1.93 (m, 2H), 1.84 (d, J = 1.6 Hz, 3H), 1.65 (ddd, J = 13.6, 3.1, 2.8 Hz, 1H), 1.54−1.52 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 137.7, 126.6, 93.8, 60.8, 54.1, 51.1, 43.2, 30.6, 28.9, 28.8, 19.8; MS (EI, 70 eV) *m*/*z* (relative intensity) 180 (M^+ − CO, 36), 152 (16), 137 (7), 121 (14), 105 (18), 93 (100), 77 (38), 65 (16), 59 (20), 43 (36); HRMS (EI) calcd for $C_{11}H_{16}O_2$ (M^+ − CO) 180.1150, found 180.1145.

(1*S,3*R**,6*R**,7*S**)-3-Methoxy-9-methyl-2-oxo-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-8-yl acetate (13a):** colorless solid (17% yield); mp 107−108 °C (from EtOAc−hexanes); IR (film) 2951, 1743 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.11 (dd, J = 8.0, 3.2 Hz, 1H), 3.78 (d, J = 8.0 Hz, 1H), 3.52 (s, 3H), 3.19 (d, J = 4.4 Hz, 1H), 2.99 (dd, J = 3.3, 2.0 Hz, 1H), 2.86−2.81 (m, 1H), 2.21 (s, 3H), 1.97 (ddd, J = 13.3, 9.9, 2.1 Hz, 1H), 1.85 (ddd, J = 13.3, 3.3, 1.5 Hz, 1H), 1.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.2, 169.0, 142.2, 122.0, 100.3, 73.6, 51.5, 50.1, 46.6, 36.6, 31.2, 20.4, 13.5; MS (EI, 70 eV) *m*/*z* (relative intensity) 224 (M^+ − CO, 16), 181 (45), 165 (26), 122 (17), 99 (90), 93 (16), 82 (13), 71 (13), 53 (13), 43 (100); HRMS (EI) calcd for $C_{12}H_{16}O_4$ (M^+ − CO) 224.1048, found 224.1043. Anal. Calcd for $C_{13}H_{16}O_5$: C, 61.90; H, 6.39. Found: C, 61.85; H, 6.37.

(1*S,3*R**,6*R**,7*S**,10*R**)-3-Methoxy-9,10-dimethyl-2-oxo-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-8-yl acetate (13b):** colorless solid (10% yield); IR (film) 2963, 1746, 1731 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.09 (dd, J = 8.0, 3.2 Hz, 1H), 3.81 (d, J = 8.0 Hz, 1H), 3.52 (s, 3H), 3.13 (d, J = 4.4 Hz, 1H), 2.85 (d, J = 2.8 Hz, 1H), 2.33−2.30 (m, 2H), 2.21 (s, 3H), 1.73 (s, 3H), 1.06 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.3, 170.0, 141.2, 119.1, 99.6, 73.5, 57.1, 51.4, 46.4, 44.4, 37.4, 20.4, 18.1, 15.2; MS (EI, 70 eV) *m*/*z* (relative intensity) 238 (M^+ − CO, 21), 195 (56), 179 (45), 163 (17), 136 (24), 121 (18), 107 (28), 99 (94), 67 (15), 43 (100); HRMS (EI) calcd for $C_{13}H_{18}O_4$

(M^+ − CO) 238.1205, found 238.1192. Anal. Calcd for $C_{13}H_{16}O_5$: C, 61.90; H, 6.39. Found: C, 61.85; H, 6.37.

(1*S,3*R**,6*R**,7*S**,10*R**)-3-Methoxy-9-methyl-2-oxo-10-phenyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-8-yl acetate (13c):** colorless solid (10% yield); IR (film) 2978, 1746 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.20 (m, 5H), 4.21 (dd, J = 8.1, 3.0 Hz, 1H), 3.93 (d, J = 8.1 Hz, 1H), 3.58 (s, 3H), 3.40 (d, J = 4.4 Hz, 1H), 3.37 (dd, J = 2.8, 1.0 Hz, 1H), 3.19−3.21 (m, 1H), 3.03 (d, J = 2.8 Hz, 1H), 2.28 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 169.5, 142.6, 141.1, 128.5, 128.0, 126.9, 118.7, 99.7, 74.1, 58.9, 51.8, 48.0, 47.2, 49.6, 20.6, 14.8; MS (EI, 70 eV) *m*/*z* (relative intensity) 300 (M^+ − CO, 72), 257 (100), 241 (77), 225 (47), 197 (53), 158 (94), 128 (56), 115 (69), 99 (100), 91 (55); HRMS (EI) calcd for $C_{18}H_{20}O_4$ (M^+ − CO) 300.1362, found 300.1350.

(1*S,3*R**,7*S**,8*S**)-3-Methoxy-10-methyl-2-oxo-4-oxatricyclo[5.3.1.0^{3,8}]undec-9-en-9-yl acetate (13d):** colorless solid (10% yield); mp 91−92 °C (from EtOAc−hexanes); IR (film) 2949, 1749 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.93−3.88 (m, 1H), 3.58 (ddd, J = 13.2, 12.8, 2.8 Hz, 1H), 3.46 (s, 3H), 2.94 (dd, J = 3.0, 2.8 Hz, 1H), 2.82−2.76 (m, 1H), 2.58 (d, J = 3.6 Hz, 1H), 2.21 (s, 3H), 2.10 (ddd, J = 13.7, 11.3, 2.8 Hz, 1H), 1.96−1.87 (m, 1H), 1.71 (s, 3H), 1.65 (dd, J = 13.7, 3.3 Hz, 1H), 1.58−1.52 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.8, 169.0, 146.6, 119.5, 93.6, 60.7, 53.1, 51.3, 47.4, 30.1, 29.6, 28.7, 20.4, 13.3; MS (EI, 70 eV) *m*/*z* (relative intensity) 238 (M^+ − CO, 14), 195 (51), 179 (74), 163 (12), 135 (17), 113 (75), 107 (25), 81 (25), 53 (3), 43 (100); HRMS (EI) calcd for $C_{13}H_{18}O_4$ (M^+ − CO) 238.1205, found 238.1200. Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.13; H, 6.82. Found: C, 63.12; H, 6.78.

(1*S,3*R**,6*R**,7*R**)-8-Bromo-3-methoxy-4-oxatricyclo-[4.3.1.0^{3,7}]dec-8-en-2-one (20a).** Following the general procedure (method B), MOB **17a** generated in situ from phenol **14** and allyl alcohol (**1a**) was reacted and the crude residue was subjected to column chromatography (EtOAc/hexanes = 1:3) to furnish **20a** (58% yield) as a light brown color granules: mp 108−109 °C (from EtOAc−hexanes); IR (film) 2944, 1747 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.12 (dd, J = 8.0, 3.2 Hz, 1H), 3.77 (d, J = 8.0 Hz, 1H), 3.53 (s, 3H), 3.52 (m, 1H), 3.20 (ddd, J = 7.2, 2.8, 2.8 Hz, 1H), 2.72 (m, 1H), 1.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 129.3, 119.9, 100.1, 73.1, 52.4, 51.6, 47.4, 35.7, 30.7; MS (EI, 70 eV) *m*/*z* (relative intensity) 232 (47), 230 (M^+ − CO, 48), 191 (74), 189 (78), 171 (11), 151 (14), 119 (19), 92 (48), 91 (100); HRMS (EI) calcd for $C_{10}H_{11}O_3{}^{79}Br$ (M^+) 257.9892, found 257.9940.

(1*S,3*R**,6*R**,7*S**,10*R**)-8-Bromo-3-methoxy-10-methyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (20b).** Following the general procedure (method B), MOB **17b** generated in situ from phenol **14** and *trans*-crotyl alcohol (**1b**) was reacted and the crude residue was subjected to column chromatography (EtOAc/hexanes = 1:3) to furnish **20b** (70% yield) as a colorless crystals: mp 119−122 °C (from EtOAc−hexanes); IR (film) 2967, 1747 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.34 (dd, J = 7.2, 2.4 Hz, 1H), 4.09 (dd, J = 8.0, 3.2 Hz, 1H), 3.79 (d, J = 8.0 Hz, 1H), 3.51 (s, 3H), 3.48 (dd, J = 4.4, 2.2 Hz, 1H), 3.06 (dd, J = 7.2, 2.8 Hz, 1H), 2.20−2.18 (m, 2H), 1.00 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 126.7, 119.1, 99.3, 73.1, 54.4, 52.4, 51.6, 44.5, 36.9, 18.8; MS (EI, 70 eV) *m*/*z* (relative intensity) 246 (69), 244 (M^+ − CO, 71), 191 (57), 189 (57), 187 (21), 184 (24), 165 (24), 133 (20), 106 (83), 105 (100); HRMS (EI) calcd for $C_{10}H_{13}O_2{}^{79}Br$ (M^+ − CO) 244.0099, found 244.0087.

(1*R,3*R**,6*R**,7*R**,10*R**)-8-Bromo-3-methoxy-10-phenyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (20c).** Following the general procedure (method B), MOB **17c** generated in situ from phenol **14** and cinnamyl alcohol (**1c**) was reacted and the crude residue was subjected to column chromatography (EtOAc/hexanes = 1:4) to give **20c** (78% yield) as colorless needles: mp 139−141 °C (from EtOAc−hexanes); IR (film) 2973, 1749 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.00 (m, 1H), 3.31 (dd, J = 3.2, 7.2 Hz, 1H), 3.36 (dd, J = 2.0, 2.0 Hz, 1H), 3.58 (s, 3H), 3.69 (dd, J = 2.4, 4.4 Hz, 1H), 3.94 (d, J = 8.2 Hz, 1H), 4.21 (dd, J = 3.2, 8.2 Hz, 1H), 6.16 (dd, J = 2.4, 7.2 Hz, 1H), 7.32−7.24 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 141.1, 128.7, 128.0, 127.3, 126.7, 120.4, 99.8, 73.5, 55.6, 53.3, 51.9, 47.4, 45.0; MS (EI, 70 eV) *m*/*z* (relative intensity) 308 (65), 306 (M^+ − CO, 62), 249 (11), 247 (11), 191 (19), 189 (19), 168 (93), 167 (100), 153 (21), 152 (26); HRMS (EI) calcd for $C_{16}H_{15}O_3{}^{79}Br$ (M^+) 334.0205, found 334.0223.

(1*S,3*R**,7*S**,8*R**)-9-Bromo-3-methoxy-4-oxatricyclo-[5.3.1.0^{3,8}]undec-9-en-2-one (20d).** Following the general procedure (method B), MOB **17d** generated in situ from phenol **14** and homoallyl alcohol (**1d**) was reacted and the crude residue was subjected to column chromatography (EtOAc/hexanes = 1:4) to provide **20d** (38% yield) as a noncrystallizable brown color solid: IR (film) 2945, 1737 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.35 (dd, J = 6.8, 2.4 Hz, 1H), 3.92−3.88 (m, 1H), 3.58 (ddd, J = 12.8, 12.8, 2.8 Hz, 1H), 3.46 (s, 3H), 3.16 (ddd, J = 6.8, 3.2, 3.2 Hz, 1H), 2.98 (dd, J = 3.2, 2.4 Hz, 1H), 2.53 (dt, J = 11.6, 3.2 Hz, 1H), 2.02 (ddd, J = 14.0, 11.6, 2.8 Hz, 1H), 1.88−1.97 (m, 1H), 1.66 (ddd, J = 13.6, 3.2, 3.2 Hz, 1H), 1.56 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.4, 127.3, 123.8, 93.3, 60.7, 53.0, 51.5, 50.1, 29.8, 29.1, 28.5; MS (EI, 70 eV) *m*/*z* (relative intensity) 246 (96), 244 (M^+ − CO, 100), 165 (20), 159 (22), 157 (22), 133 (15), 105 (36); HRMS (EI) calcd for $C_{10}H_{13}O_2{}^{79}Br$ (M^+ − CO) 244.0028, found 244.0087.

(1*S,3*R**,6*R**,7*S**)-8-Bromo-3-methoxy-1-methyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one** (**21a**). Following the general procedure (method B), MOB **18a** generated in situ from phenol **15** and allyl alcohol (**1a**) was reacted and the crude residue was subjected to column chromatography (EtOAc/hexanes = 2:7) to furnish **21a** (73% yield) as a colorless solid: mp 99−100 °C (from EtOAc−hexanes); IR (film) 2973, 1749 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.11 (d, J = 2.0 Hz, 1H), 4.12 (dd, J = 8.0, 3.6 Hz, 1H), 3.78 (d, J = 8.0 Hz, 1H), 3.51 (s, 3H), 3.50 (dd, J = 4.4, 2.0 Hz, 1H), 2.77 (ddd, J = 10.4, 4.4, 3.6 Hz, 1H), 1.88 (dd, J = 13.2, 10.4 Hz, 1H), 1.64 (d, J = 4.4, 2.0 Hz, 1H), 1.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 134.4, 100.5, 119.3, 73.5, 51.9, 51.6, 49.5, 38.5, 37.2, 16.8; MS (EI, 70 eV) *m*/*z* (relative intensity) 272 (M^+, 2), 246 (59), 244 (59), 203 (100), 165 (30), 133 (27), 105 (80), 91 (64), 77 (64), 39 (20); HRMS (EI) calcd for $C_{10}H_{13}{}^{79}BrO_2$ (M^+ − CO) 244.0098, found 244.0099; $C_{10}H_{13}{}^{81}BrO_2$ 246.0079, found 246.0078. Anal. Calcd for $C_{11}H_{13}BrO_3$: C, 48.37, H, 4.80. Found: C, 48.68, H, 4.96.

(1*R,3*R**,6*R**,7*R**,10*R**)-8-Bromo-3-methoxy-1,10-dimethyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (21b).** Following the general procedure (method B), MOB **18b** generated in situ from phenol **15** and *trans*-crotyl alcohol (**1b**) was reacted and the crude residue was subjected to column chromatography (EtOAc/hexanes = 1:4) to provide **21b** (74% yield) as a colorless solid: mp 100−101 °C (from EtOAc−hexanes); IR (film) 2968, 1744 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.97 (d, J = 2.8 Hz, 1H), 4.10 (dd, J = 8.0, 3.6 Hz, 1H), 3.78 (d, J = 8.0 Hz, 1H), 3.52 (s, 3H), 3.45 (dd, J = 4.8, 2.8 Hz, 1H), 2.25 (ddd, J = 4.8, 3.6, 1.6 Hz, 1H), 1.79 (q, J = 1.6, 7.4 Hz, 1H), 1.25 (s, 3H), 0.98 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.0, 131.6, 118.4, 99.8, 73.0, 53.6, 51.5, 51.2, 46.1, 42.3, 16.6, 15.0; MS (EI, 70 eV) *m*/*z* (relative intensity) 286 (M^+, 100), 258 (83), 203 (60), 200 (33), 170 (8), 146 (13), 119 (48), 105 (42), 63 (11), 53 (7); HRMS (EI) calcd for $C_{11}H_{15}{}^{79}BrO_2$ (M^+ − CO) 258.0255, found 258.0256. Anal. Calcd for $C_{12}H_{15}BrO_3$: C, 50.19, H, 5.26. Found: C, 50.15, H, 5.29.

(1*R,3*R**,6*R**,7*R**,10*R**)-8-Bromo-3-methoxy-1-methyl-10-phenyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one** (**21c**)**.** Following the general procedure (method B), MOB **18c** generated in situ from phenol **15** and cinnamyl alcohol (**1c**) was reacted and the crude residue was subjected to column chromatography (EtOAc/hexanes = 1:5) to afford **21c** (79% yield) as a colorless solid: mp 161−162 °C (from EtOAc−hexanes); IR (film) 2973, 1744 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29−7.01 (m, 5H), 5.86 (d, J = 2.8 Hz, 1H), 4.18 (dd, J = 8.0, 3.2 Hz, 1H), 3.93 (d, J = 8.0 Hz, 1H), 3.58 (s,

3H), 3.67 (dd, J = 4.6, 2.8 Hz, 1H), 3.00 (ddd, J = 4.6, 3.2, 2.0 Hz, 1H), 2.85 (d, J = 2.0 Hz, 1H), 1.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 140.5, 131.7, 128.9, 128.4, 128.3, 127.3, 119.9, 100.0, 73.6, 54.4, 53.1, 52.4, 51.7, 48.3, 15.7; MS (EI, 70 eV) *m*/*z* (relative intensity) 348 (M^+, 2), 322 (42), 320 (43), 241 (18), 205 (42), 181 (100), 165 (67), 152 (23), 115 (33), 91 (39); HRMS (EI) calcd for $C_{16}H_{17}{}^{79}BrO_2$, (M^+ − CO) 320.0411, found 320.0412; calcd for $C_{16}H_{17}{}^{81}BrO_2$, 322.0392, found 322.0392. Anal. Calcd for $C_{17}H_{17}BrO_3$: C, 58.47; H, 4.91. Found: C, 58.34; H, 4.91.

(1*S,3*R**,7*S**,8*R**)-9-Bromo-3-methoxy-1-methyl-4-oxatricyclo[5.3.1.0^{3,8}]undec-9-en-2-one (21d).** Following the general procedure (method B), MOB **18d** generated in situ from phenol **15** and homoallyl alcohol (**1d**) was reacted and the crude residue was subjected to column chromatography (EtOAc/hexanes = 1:6) to furnish **21d** (62% yield) as a colorless solid: mp 90−91 °C (from EtOAc−hexanes); IR (film) 2968, 1730 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.05 (d, J = 2.4 Hz, 1H), 3.91−3.89 (m, 1H), 3.54 (ddd, J = 12.8, 12.8, 3.2 Hz, 1H), 2.97 (dd, J = 3.6, 2.4 Hz, 1H), 3.46 (s, 3H), 2.58 (m, 1H), 1.56−1.51 (m, 2H), 1.51−1.56 (m, 1H), 1.42 (dd, J = 13.6, 3.2 Hz, 1H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.3, 132.5, 123.2, 93.7, 60.7, 52.7, 52.0, 51.3, 37.0, 29.9, 29.8, 17.0; MS (EI, 70 eV) *m*/*z* (relative intensity) 286 (M^+, 19), 258 (100), 243 (9), 227 (36), 207 (18), 179 (15), 147 (47), 119 (98), 105 (37), 89 (100); HRMS (EI) calcd for $C_{11}H_{15}{}^{79}BrO_2$ (M^+ − CO) 258.0255, found 258.0256. Anal. Calcd for $C_{12}H_{15}BrO_3$: C, 50.19; H, 5.26. Found: C, 49.98; H, 5.28.

(1*S,3*R**,6*R**,7*R**)-8-Bromo-3-methoxy-9-methyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (22a).** Following the general procedure (method B), MOB **19a** generated in situ from phenol **16** and allyl alcohol (**1a**) was reacted and the crude residue was subjected to column chromatography (EtOAc/hexanes = 1:3) to furnish **22a** (60% yield) as a colorless solid: mp 128−129 °C (from EtOAc−hexanes); IR (film) 2889, 1739 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.10 (dd, J = 8.0, 3.2 Hz, 1H), 3.76 (d, J = 8.0 Hz, 1H), 3.52 (d, J = 4.0 Hz, 1H), 3.50 (s, 3H), 3.12 (dd, J = 3.2, 2.4 Hz, 1H), 2.71 (m, 1H), 1.87 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 136.6, 113.8, 100.6, 73.3, 52.5, 52.1, 51.4, 36.3, 30.6, 19.4; MS (EI, 70 eV) *m*/*z* (relative intensity) 272 (M^+, 85), 246 (88), 244 (95), 229 (12), 205 (90), 203 (100), 133 (12), 105 (72), 91 (30), 63 (10); HRMS (EI) calcd for $C_{10}H_{13}{}^{79}BrO_2$ (M^+ − CO) 244.0098, found 244.0099; calcd for $C_{10}H_{13}{}^{81}BrO_2$ 246.0079, found 246.0078. Anal. Calcd for $C_{11}H_{13}BrO_3$: C, 48.37; H, 4.80. Found: C, 48.38; H, 4.84.

(1*S,3*R**,6*R**,7*R**,10*R**)-8-Bromo-3-methoxy-9,10-dimethyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (22b).** Following the general procedure (method B), MOB **19b** generated in situ from phenol **16** and *trans*-crotyl alcohol (**1b**) was reacted and the crude residue was subjected to column chromatography (EtOAc/hexanes = 1:4) to afford **22b** (73% yield) as a colorless solid: mp 88−89 °C (from EtOAc−hexanes); IR (film) 2962, 1749 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.07 (dd, J = 8.0, 2.8 Hz, 1H), 3.78 (d, J = 8.0 Hz, 1H), 3.50 (s, 3H), 3.47 (d, J = 4.4 Hz, 1H), 2.98 (d, J = 2.8 Hz, 1H), 2.19 (m, 2H), 1.88 (s, 3H), 0.96 (d, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 133.9, 112.6, 99.9, 73.2, 59.5, 51.8, 51.5, 44.2, 37.0, 21.1, 18.6; MS (EI, 70 eV) *m*/*z* (relative intensity) 286 (M^+, 100), 260 (87), 258 (95), 203 (75), 179 (5), 146 (10), 119 (62), 105 (51), 91 (12), 63 (10); HRMS (EI) calcd for $C_{11}H_{15}{}^{79}BrO_2$ (M^+ − CO) 258.0255, found 258.0255; calcd for $C_{11}H_{15}{}^{81}BrO_2$ 260.0236, found 260.0235. Anal. Calcd for $C_{12}H_{15}BrO_3$: C, 50.19; H, 5.26. Found: C, 50.01; H, 5.33.

(1*S,3*R**,6*R**,7*R**,10*R**)-8-Bromo-3-methoxy-9-methyl-10-phenyl-4-oxatricyclo[4.3.1.0^{3,7}]dec-8-en-2-one (22c**). Following the general procedure (method B), MOB **19c** generated in situ from phenol **16** and cinnamyl alcohol (**1c**) was reacted and the crude residue was subjected to column chromatography (EtOAc/hexanes = 1:5) to provide **22c** (75% yield) as a colorless solid: mp 127−128 °C (from EtOAc−hexanes); IR (film) 2963, 1747 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.03 (m, 5H), 4.20 (dd, J = 8.4, 3.2 Hz, 1H), 3.92 (d, J = 8.4 Hz, 1H), 3.69 (d, J = 4.4 Hz, 1H), 3.57 (s, 3H), 3.36 (dd, J = 2.0, 2.0 Hz, 1H), 3.18 (d, J = 2.0 Hz, 1H), 3.01 (m, 1H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 140.7, 133.8, 128.7, 127.5, 127.1, 114.0, 100.2, 73.4, 61.0, 52.6, 51.6, 47.5, 44.1, 20.7; MS (EI, 70 eV) *m*/*z* (relative intensity) 348 (M^+, 72), 322 (98), 320 (100), 261 (7), 203 (80), 181 (28), 165 (42), 141 (10), 115 (20), 63 (10); HRMS (EI) calcd for $C_{16}H_{17}{}^{79}BrO_2$ (M^+ − CO) 320.0411, found 320.0412; calcd for $C_{16}H_{17}{}^{81}BrO_2$ 322.0392, found 322.0392. Anal. Calcd for $C_{17}H_{17}BrO_3$: C, 58.47; H, 4.91. Found: C, 58.31; H, 4.99.

(1*S,3*R**,7*S**,8*R**)-9-Bromo-3-methoxy-10-methyl-4-oxatricyclo[5.3.1.0^{3,8}]undec-9-en-2-one (22d).** Following the general procedure (method B), MOB **19d** generated in situ from phenol **16** and homoallyl alcohol (**1d**) was reacted and the crude residue was subjected to column chromatography (EtOAc/hexanes = 1:6) to afford **22d** (46% yield) as a colorless solid: mp 90−91 °C (from EtOAc−hexanes); IR (film) 2945, 1733 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.92−3.87 (m, 1H), 3.59 (ddd, J = 13.8, 12.8, 2.8 Hz, 1H), 3.46 (s, 3H), 3.09 (dd, J = 3.0, 2.8 Hz, 1H), 2.97 (d, J = 3.6 Hz, 1H), 2.53 (m, 1H), 2.01 (ddd, J = 13.6, 11.4, 2.8 Hz, 1H), 1.98−1.87 (m, 1H), 1.86 (s, 3H), 1.65 (ddd, J = 13.6, 3.2, 3.0 Hz, 1H), 1.59−1.54 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.7, 134.2, 117.8, 93.8, 60.6, 55.2, 52.5, 51.4, 29.9, 29.1, 28.7, 19.1; MS (EI, 70 eV) *m*/*z* (relative intensity) 286 (M^+, 45), 260 (92), 258 (100), 229 (30), 227 (42), 174 (5), 147 (12), 119 (23), 105 (18), 63 (10); HRMS (EI) calcd for $C_{11}H_{15}{}^{79}BrO_2$ (M^+ − CO) 258.0255, found 258.0255. Anal. Calcd for $C_{11}H_{13}BrO_3$: C, 50.19; H, 5.26. Found: C, 50.14; H, 5.29.

2-Methoxy-6-methyl-1,4-benzoquinone (23):[20] colorless liquid; IR (film) 1678, 1651 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.54 (apparent m, dq, J = 2.4, 1.6 Hz, 1H), 5.88 (d, J = 2.4 Hz, 1H), 3.82 (s, 3H), 2.07 (d, J = 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.4, 182.4, 158.8, 143.6, 133.8, 107.3, 56.2, 15.5; MS (EI, 70 eV) *m*/*z* (relative intensity) 152 (M^+, 59), 137 (12), 124 (83), 109 (32), 96 (20), 81 (14), 69 (100), 66 (31), 53 (32), 43 (22); HRMS (EI) calcd for $C_8H_8O_3$ (M^+) 152.0473, found 152.0474. Anal. Calcd for $C_8H_8O_3$: C, 63.14, H, 5.30. Found: C, 63.09, H, 5.29.

4-Hydroxy-3-methoxy-5-methylphenyl acetate (24): colorless liquid; IR (film) 3466, 2946, 1755 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.48 (s, 2H), 5.58 (br, 1H), 3.85 (s, 3H), 2.27 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 146.1, 142.7, 141.4, 124.0, 115.4, 102.5, 56.0, 21.0, 15.4; MS (EI, 70 eV) *m*/*z* (relative intensity) 196 (M^+, 16), 154 (100), 139 (51), 111 (30); HRMS (EI) calcd for $C_8H_{10}O_2$ (M^+) 196.0735, found 196.0733.

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Supporting Information Available: Copies of ^{1}H and ^{13}C NMR and DEPT spectra for compounds **8d**, **10a**−**d**, **12a**−**d**, and **20**−**22**(**a**−**d**) and a table of selected coupling constant values for the cycloadducts. This material is available free of charge via the Internet at http://pubs.acs.org.

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