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Inverse-electron-demand Diels–Alder reactions of masked *o*-benzoquinones with enol ethers and styrene

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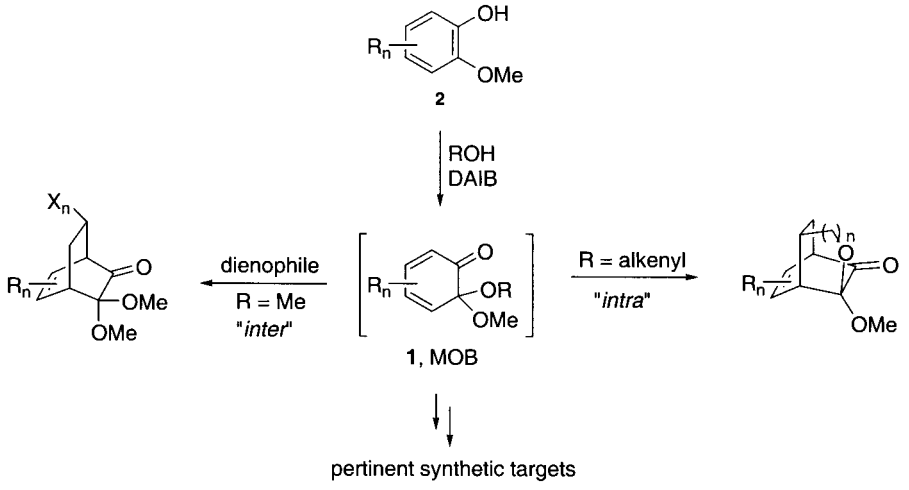
Abstract—Regio- and stereoslective inverse-electron-demand Diels–Alder reactions of masked *o*-benzoquinones (MOBs) **1a**–**1h** derived from the corresponding 2-methoxyphenols **2a**–**2h** with benzyl vinyl ether, dihydrofuran and styrene to afford the highly functionalized bicyclo[2.2.2]octenone derivatives are described. The MOBs having electron-deficient substituents were found to undergo more facile Diels–Alder cycloadditions with these dienophiles. The electron-rich dienophile dihydropyran is not a suitable 2π-partner for MOBs. Attempts are made to explain the observed regiochemistry of these Diels–Alder cycloadditions in terms of frontier molecular orbital theory.

1. Introduction

Masked *o*-benzoquinones (MOBs, **1**), a type of cyclohexa-2,4-dienones, are a relatively under-utilized class of compounds,[1,2] in contrast to their counterparts derived from *p*-benzoquinones.[3] Prior to our studies, there have been only sparodic reports on their chemistry.[1,4] This paucity of examples may be due to the fact that their high propensity towards dimerization[5] makes their isolation difficult. Our laboratory has succeeded in developing efficient procedures for their generation and in identifying their immense synthetic potential, especially as dienes in Diels–Alder reactions, during the past decade. They can be easily generated in situ by the oxidation of the corresponding 2-methoxyphenols **2** with hypervalent iodine reagents such as (diacetoxy)iodobenzene (DAIB) or phenyliodonium(III) bis(trifluoroacetate) (PIFA) in the presence of an alcohol. In situ generated MOBs undergo rather facile intermolecular Diels–Alder reactions in a regio- and stereocontrolled manner with electron-deficient dienophiles,[6,7] acyclic dienes[8] and cyclopentadiene[9] to produce the corresponding bicyclo[2.2.2]octenone derivatives derived *via endo*-addition. Very recently, we have demonstrated the dienophilic behaviour of heteroaromatics namely, furans[10]



Scheme 1.

Keywords: orthoquinone monoketal; 2-methoxyphenols; diacetoxyiodobenzene; bicyclo[2.2.2]octenones; inverse-electron-demand Diels–Alder reaction.
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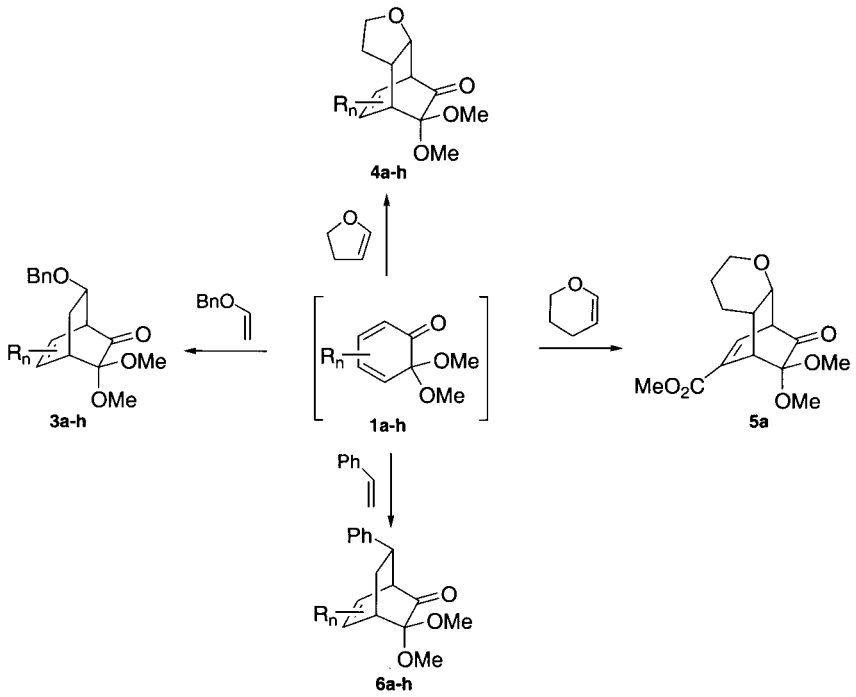


Scheme 2.

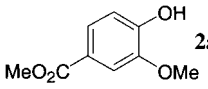
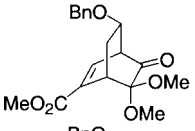
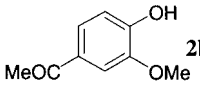
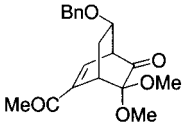
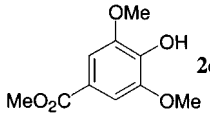
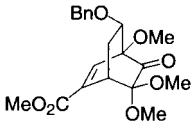
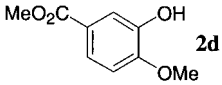
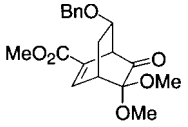
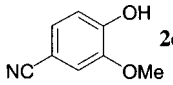
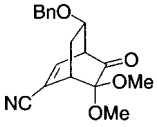
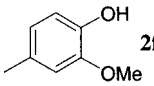
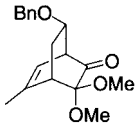
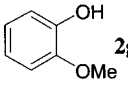
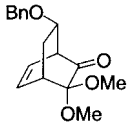
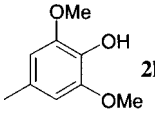
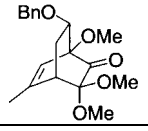
and indoles[11] in the Diels–Alder cycloadditions with MOBs. When the oxidation of 2-methoxyphenols was carried out in the presence of an alkenol, MOBs undergo facile intramolecular cycloaddition reactions via a tandem oxidative acetalization process[6,12] (Scheme 1). The inter- and intramolecular Diels–Alder reactions of MOBs have already utilized as a key step in the stereoselective syntheses of various compounds, including polysubstituted cyclohexene derivatives,[13] *cis*-decalins,[14] bicyclo[4.2.2]decenones,[14] tricyclo[3.3.0.0^{2,8}]octenones,[13,15] and bicyclo[4.2.0]-octenones.[15] In addition, these reactions were employed as the key step in the total syntheses of cleradone diterpenic acids,[16] forsythide aglucone dimethyl ester[17] and pallescensin B[18] and in a formal synthesis of reserpine.[19]

Inverse-electron-demand Diels–Alder reactions are employed predominantly by systems incorporating heteroatoms in either or both the diene and dienophile.[20] Among the purely carbon-containing diene systems, 2-pyrones[21] appear to be the most widely used electron-deficient dienes. The Diels–Alder reactions of cycloalkane-annulated dienes with electron-rich dienophiles were reported recently.[22] In contrast to the case of electron-deficient dienophiles, the Diels–Alder reactions of MOBs or related cyclohexa-2,4-dienones with electron-rich dienophiles were not studied in detail before, presumably due to the lack of convenient procedures for the preparation of the more reactive MOBs particularly with electron-deficient substituents, and also due to their high propensity towards dimerization. Nevertheless, some examples of the Diels–Alder reactions of MOBs do exist with electron-rich dienophiles.[23–26] Ethyl vinyl ether and styrene were employed as dienophiles in the reactions of MOBs having bulky substituents in our laboratory.[23] Vinyl acetate underwent inefficient and non-selective Diels–Alder reactions with various cyclohexa-2,4-dienones including some MOBs.[6,25] However, benzyl vinyl ether and ethyl vinyl sulfide were successfully employed in Diels–Alder reactions with two stable polycyclic MOBs in the total syntheses of aconite alkaloids, napelline and diacetyloxodenudatine, respectively.[26] Herein, we report the regio- and stereoselective Diels–Alder reactions of MOBs with benzyl vinyl ether (BVE), dihydrofuran (DHF), dihydropyran (DHP) and styrene leading to highly functionalized bicyclo[2.2.2]octenone derivatives **3**–**6**.[27]

2. Results and discussion

Eight 2-methoxyphenols *viz* methyl vanillate (**2a**), acetovanillone (**2b**), methyl siringate (**2c**), methyl isovanillate (**2d**), vanillonitrile (**2e**), creosol (**2f**), guaiacol (**2g**) and 2,6-dimethoxy-4-methylphenol (**2h**) were selected for the present study. The Diels–Alder reactions were performed essentially by three procedures, A, B and C, based on the propensity of the particular MOB towards dimerization, its Diels–Alder reactivity towards added dienophile and the stability of the dienophiles towards the oxidant DAIB. In procedure A, MOB was generated by adding DAIB to a solution of 2-methoxyphenol in MeOH at 0°C followed by the addition of dienophile and the reaction was continued at the same temperature. In procedure B, a methanolic solution of DAIB was added slowly to a mixture of 2-methoxyphenol and dienophile in MeOH at 50°C. On the other hand, in procedure C, a methanolic solution of 2-methoxyphenol was added slowly to a mixture of dienophile and DAIB in MeOH at 50°C. The yields were optimized by performing the reactions at various concentrations of dienophiles in the above procedures and the results are summarized in Scheme 2 and Tables 1–3. All the reaction were carried out until the complete consumption of the MOB was reached (monitored by TLC analysis and the disappearance of the yellow colour of the reaction mixture). In most cases, the cycloadducts

Table 1. Diels–Alder reactions of MOBs **1a–h** with benzyl vinyl ether (BVE)

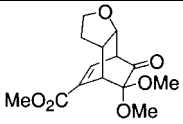
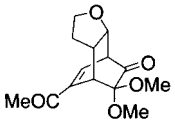
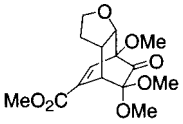
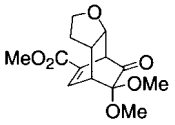
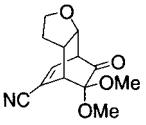
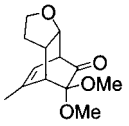
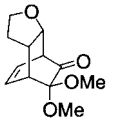
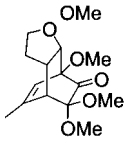
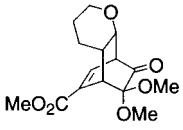
Entry	Phenol	MOB	BVE eq.	Method[a]	Time[b]/h	Product	Yield[c](%)
1	 **2a**	**1a**	5	A	0.5	 **3a**	78
2		**1a**	5	B	1		98
3	 **2b**	**1b**	5	A	0.5	 **3b**	70
4		**1b**	5	B	1		86
5	 **2c**	**1c**	5	A	0.5	 **3c**	6
6		**1c**	5	B	1		50
7		**1c**	5	B	2		59
8		**1c**	10	B	2		78
9	 **2d**	**1d**	5	A	0.5	 **3d**	18
10		**1d**	5	B	1		40
11		**1d**	5	B	2		43
12		**1d**	10	B	1		66
13		**1d**	20	B	0.5		83
14	 **2e**	**1e**	5	A	0.5	 **3e**	40
15		**1e**	10	A	1		45
16		**1e**	5	B	1		16
17		**1e**	5	B	2		30
18	 **2f**	**1f**	25	A[d]	8	 **3f**	48
19		**1f**	25	A[e]	96		65
20		**1f**	25	B[e]	12		78
21		**1f**	25	C[e]	8		68
22	 **2g**	**1g**	25	A[e]	4	 **3g**	22
23		**1g**	25	B[e]	8		61
24	 **2h**	**1h**	25	A[e]	8	 **3h**	–[f]
25		**1h**	25	B[e]	8		Trace[g]

[a] See Experimental. Method A: After the generation of MOB at 0°C, dienophile was added and the reaction was continued at 0°C. Method B: DAIB was added to a solution of methoxyphenol and dienophile at 50°C. Method C: Methoxyphenol was added to a solution of dienophile and DAIB at 50°C.
[b] Represents the reaction time in method A, in method B it represents the time during which DAIB was added, and in method C it represents the time during which phenol was added.
[c] Yields are of isolated products.
[d] Reaction was carried out at room temperature.
[e] Reaction was carried out at reflux temperature.
[f] A complex mixture was obtained.
[g] Observed in the ^{1}H NMR spectrum of the crude reaction mixture.

were obtained in very good-to-excellent yields. The products obtained in low yields were accompanied by the dimerization of MOBs, except in the case of phenol **2e**. The low yields of the adducts **3e** and **4e** are due to the oxidation of **1e–4e** by DAIB leading to unknown side products. The Diels–Alder cycloadditions of MOBs **1a–1c** and **1e** having electron-withdrawing groups proceeded smoothly with 5–10 equiv. of vinyl ethers BVE and DHF to furnish the cycloadducts. The reactions of phenols **2f** and **2g** were carried out with 25 equiv. of the dienophiles in order to get the optimum yields. BVE showed better performance in the cycloadditions with MOBs **1f** and **1g** in comparison of DHF. The cycloaddition between MOB **1h** and dienophiles BVE and DHF did not occur. Unlike vinyl ethers, styrene underwent smooth cycloaddition with the MOBs having electron-releasing groups to produce the corresponding bicyclo[2.2.2]octenone derivatives.

The structures of all the products were established by IR, ^{1}H and ^{13}C NMR, DEPT, and low- and high-resolution mass spectral analyses. The formation of a single adduct was revealed by the ^{1}H NMR (400 MHz) spectra. The regiochemistry of the reaction was clearly established by using ^{1}H–^{1}H decoupling experiments. The assigned

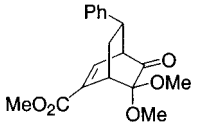
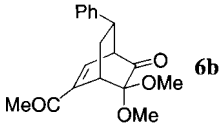
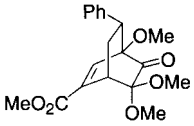
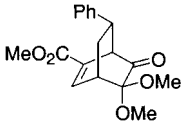
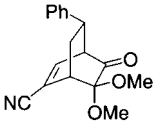
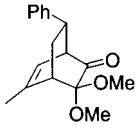
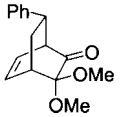
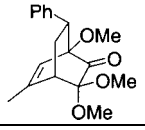
Table 2. Diels–Alder reactions of MOBs **1a–h** with dihydrofuran (DHF) and MOB **1a** with dihydropyran (DHP)

Entry	Phenol	MOB	Dienophile[a]	Method[b]	Time[c]/h	Product	Yield[d](%)
1	**2a**	**1a**	DHF(5)	A	0.5	 **4a**	76
2	**2a**	**1a**	DHF(5)	B	1		98
3	**2b**	**1b**	DHF(5)	A	0.5	 **4b**	69
4	**2b**	**1b**	DHF(5)	B	1		61
5	**2b**	**1b**	DHF(5)	B	2		65
6	**2b**	**1b**	DHF(10)	B	0.5		80
7	**2c**	**1c**	DHF(5)	A	0.5	 **4c**	5
8	**2c**	**1c**	DHF(5)	B	1		32
9	**2c**	**1c**	DHF(5)	B	2		40
10	**2c**	**1c**	DHF(10)	B	2		71
11	**2d**	**1d**	DHF(20)	A	0.5	 **4d**	11
12	**2d**	**1d**	DHF(20)	B	1		26
13	**2d**	**1d**	DHF(20)	B	1		25
14	**2d**	**1d**	DHF(20)	B	2		36
15	**2e**	**1e**	DHF(5)	A	1	 **4e**	45
16	**2e**	**1e**	DHF(5)	B	1		20
17	**2e**	**1e**	DHF(10)	B	2		52
18	**2e**	**1e**	DHF(10)	A	1		56
19	**2f**	**1f**	DHF(25)	A	96	 **4f**	9
20	**2f**	**1f**	DHF(25)	B	8		3
21	**2f**	**1f**	DHF(50)	A	96		25
22	**2g**	**1g**	DHF(25)	A	120	 **4g**	9
23	**2g**	**1g**	DHF(25)	B	8		12
24	**2g**	**1g**	DHF(50)	A	120		15
25	**2h**	**1h**	DHF(25)	A	8	 **4h**	–[e]
26	**2h**	**1h**	DHF(25)	B	8		Trace[f]
27	**2a**	**1a**	DHP(5)	A	20	 **5a**	20
28	**2a**	**1a**	DHP(5)	B	1		17
29	**2a**	**1a**	DHP(10)	A	16		34

[a] The values in parentheses indicate the number of equivalents used.
[b] See footnote a in Table 1.
[c] See footnote b in Table 1.
[d] Yields are of isolated products.
[e] A complex mixture was obtained.
[f] Observed in the ^{1}H NMR spectrum of the crude reaction mixture.

stereochemistry of the epimeric [BnO or $(CH_2)_nO$ or Ph attached] carbon in all these adducts is based on the long-range coupling between the vinylic hydrogen and the hydrogen of the epimeric carbon observed in the ^{1}H NMR spectra for all the cycloadducts derived from the MOBs **1a–e** and **1g**,**h** except in the case of **6c**. The vinylic proton in compound **6c** resonates in the same region as the aromatic protons. The *anti* configuration of the benzyloxy group to the carbonyl function in **3e** was further confirmed from single-crystal X-ray diffraction method (Fig. 1). The regio- and stereochemistries of the cycloadducts were further confimed by comparing the chemical shifts of the vinylic and bridgehead protons of each set of the adducts derived from the same MOB wherever possible. For most of the adducts, either in the low-resolution mass spectra or in the high-resolution mass spectra recorded in electron impact mode (70 eV), the peak corresponding to molecular ion (M^+) could not be seen; instead the peak corresponding to M^+-28 was observed, indicating the extrusion of CO resulted from facile fragmentation. For the majority of the

Table 3. Diels–Alder reactions of MOBs **1a**–**h** with styrene

Entry	Phenol	MOB	Styrene eq.	Method[a]	Time[b]/h	Product	Yield[c](%)
1	**2a**	**1a**	25	C	4	 **6a**	86
2	**2b**	**1b**	25	C	4	 **6b**	90
3	**2c**	**1c**	25	C	4	 **6c**	92
4	**2d**	**1d**	25	C	4	 **6d**	93
5	**2e**	**1e**	25	C	4	 **6e**	91
6	**2f**	**1f**	25	C	8	 **6f**	77
7	**2f**	**1f**	25	A	24		73
8	**2f**	**1f**	25	B	8		66
9	**2g**	**1g**	25	A	4	 **6g**	18
10	**2g**	**1g**	25	C	8		25
11	**2g**	**1g**	50	C	8		45
12	**2h**	**1h**	25	A	2	 **6h**	15
13	**2h**	**1h**	25	C	8		84

[a] See footnote a in Table 1.
[b] See footnote b in Table 1.
[c] Yields are of isolated products.

cycloadducts, satisfactory elemental analyses were obtained.

The MOBs **1a**–**1d** exhibited excellent reactivities in general with the three dienophiles studied. It is quite clear from the Tables 1–3, by comparing the reaction time and yields, that the Diels–Alder reactivity of MOBs **1a**–**1e** bearing

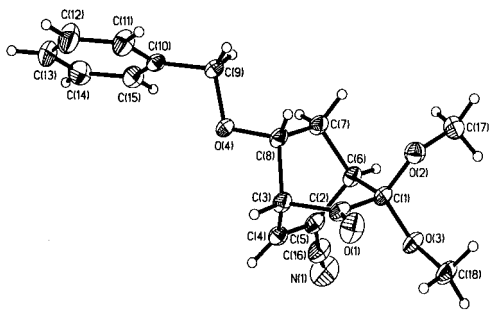


Figure 1. ORTEP diagram of **3e** (numbering is arbitrary).

Table 4. Energies of FMOs of MOBs **1a**, **1b** and **1d**–**g**, BVE, DHF and styrene obtained by semiempirical PM3 and ab initio RHF/3-21G level calculations

Compound	FMO	PM3	3-21G
1a	HOMO	−10.253	−9.586
	LUMO	−1.279	1.265
1b	HOMO	−10.187	−9.545
	LUMO	−1.184	1.181
1d	HOMO	−10.242	−9.641
	LUMO	−1.336	1.116
1e	HOMO	−10.370	−9.937
	LUMO	−1.507	0.860
1f	HOMO	−9.828	−9.211
	LUMO	−0.909	1.728
1g	HOMO	−10.043	−9.333
	LUMO	−0.950	1.725
BVE	HOMO	−9.600	−9.007
	LUMO	0.182	4.000
DHF	HOMO	−9.189	−8.860
	LUMO	1.086	5.560
Styrene	HOMO	−9.129	−8.381
	LUMO	−0.122	3.037

Table 5. Energy gaps (eV): FMO interactions of MOBs **1a**, **1b** and **1d–g** with BVE, DHF and styrene

MOB	Method	Energy gaps to BVE		Energy gaps to DHF		Energy gaps to styrene	
		$HOMO_{MOB}$–$LUMO_{BVE}$	$HOMO_{BVE}$–$LUMO_{MOB}$	$HOMO_{MOB}$–$LUMO_{DHF}$	$HOMO_{DHF}$–$LUMO_{MOB}$	$HOMO_{Styr.}$–$LUMO_{MOB}$	$HOMO_{Styr.}$–$LUMO_{MOB}$
1a	PM3	10.435	8.320	11.338	7.910	10.375	7.850
	3-21G	13.586	10.272	15.146	10.125	12.623	9.646
1b	PM3	10.369	8.415	11.272	8.005	10.309	7.945
	3-21G	13.545	10.188	15.105	10.041	12.576	9.562
1d	PM3	10.424	8.264	11.327	7.853	10.119	7.793
	3-21G	13.545	9.932	15.105	9.785	12.582	9.306
1e	PM3	10.552	8.093	11.455	7.682	10.247	7.622
	3-21G	13.937	9.867	15.497	9.720	12.974	9.241
1f	PM3	10.010	8.691	10.913	8.280	9.705	8.220
	3-21G	13.211	10.735	14.771	10.588	12.248	10.109
1g	PM3	10.225	8.650	11.289	8.239	9.921	8.179
	3-21G	13.333	10.732	14.893	10.585	12.370	10.106

Table 6. Coefficients (C_i) of HOMOs and LUMOs of MOBs **1a**, **1b** and **1d–g**, BVE, DHF and styrene (obtained from RHF/3-21G calculations; numbering scheme employed is shown in Fig. 2)

Compound	HOMO						LUMO					
	C_1	C_2	C_3	C_4	C_5	ΔC_i[a]	C_1	C_2	C_3	C_4	C_5	ΔC_i[a]
1a		0.269	0.194	−0.199	−0.230	−0.039		0.148	−0.191	−0.134	0.238	0.090
1b		0.257	0.179	−0.212	−0.242	−0.015		0.154	−0.193	−0.125	0.233	0.079
1d		0.244	0.183	−0.214	−0.261	−0.017		0.206	−0.208	−0.085	0.152	−0.054
1e		0.249	0.180	−0.207	−0.246	−0.003		0.161	−0.196	−0.140	0.231	0.070
1f		0.245	0.167	−0.215	−0.271	0.026		0.172	−0.229	−0.124	0.179	0.007
1g		0.260	0.197	−0.196	−0.252	−0.008		0.177	−0.210	−0.140	0.192	0.015
BVE	0.246	0.317				0.071	0.052	−0.007				−0.046
DHF		0.248	0.309			0.061		0.345	−0.280			−0.065
Styrene	0.156	0.224				0.068	0.152	−0.211				0.059

[a] $\Delta C_i = |C_5| - |C_2|$ for MOBs **1a**, **1b**, **1d–g** and $\Delta C_i = |C_2| - |C_i|$ for BVE and styrene and $\Delta C_i = |C_3| - |C_2|$ for DHF.

electron-deficient substituents (CO_2Me, COMe, CN) is greater than that of MOBs **1f–1h** having either electron releasing (Me, OMe) or no substituents with a particular dienophile. Guaiacol (**2g**) reacted with BVE and styrene to furnish the desired cycloadducts **3g** and **6g**, respectively in acceptable yields. The MOB **1h** having two electron-releasing substituents (Me and OMe) only participated with difficulty in the [4+2] cycloaddition with BVE and DHF. It is quite interesting to note that the Diels–Alder reactions of furan[10a] and DHF are comparable with MOBs **1a–1d**, in general, and **1d** in particular, in terms of yields. However, the regiochemistry procured from the reactions of DHP is opposite to that obtained from the reactions of furans.[10,11] Furthermore, the Diels–Alder reactivity of MOB **1a** is much lower towards DHP in comparison with DHF. It is worth mentioning that 4-methyl-1,2-benzoquinone produced from *p*-cresol via tyrosinase-catalyzed hydroxylation followed by oxidation reacted with DHF to afford the corresponding [4+2] cycloadduct; DHP did not work in a similar manner.[28] Styrene showed excellent reactivity in almost all cases studied.

The cycloaddition reactions appear to be under frontier orbital control; the frontier molecular orbital (FMO) model seems capable of explaining the observed regio- and stereoselectivities. Therefore, attempts were made to correlate the energies and coefficients of the FMOs.[29] Semi-empirical and ab initio HF/3-21G methods[30,31] were used to calculate the energy levels (HOMOs and LUMOs) of MOBs **1a**, **1b**, and **1d–g** and BVE, DHF and styrene. The geometries were fully optimized by PM3 semiempirical methods and used as the basis for optimization at the Hartree–Fock level using the 3-21G basis set; the energy levels thus obtained are summarized in Table 4. The calculations suggest that the main HOMO–LUMO interaction occurs between the LUMO of the diene ($LUMO_{MOB}$) and the HOMO of the dienophile ($HOMO_{dienophile}$) indicating that these cycloadditions are inverse-electron-demand Diels–Alder reactions.[33] In all the cases studied, the difference in energy gaps for the possible interactions varies from 2.1 to 5.8 eV (Table 5). For an inverse-electron-demand Diels–Alder cycloaddition, the presence of an electron-withdrawing group in the diene and an electron-releasing substituent on the dienophile contracts the $HOMO_{dienophile}$–$LUMO_{diene}$ energy separation through raising the energy of the $HOMO_{dienophile}$ and lowering the energy of the $LUMO_{diene}$, respectively, and hence increases the reactivity. This trend is noticed in the present study too. For instance, the cycloaddition of MOB **1a** having an electron-withdrawing substituent (4-CO_2Me) is faster than that of MOB **1f** having an electron-releasing substituent (4-Me) with all three dienophiles ($\Delta\Delta E$ for **1a** and **1f** (eV): 3.3, 2.5 (BVE); 5.0, 4.2 (DHF); 3.0, 2.1 (styrene)) (Table 5).

Table 6 illustrates the relative magnitudes of HOMO and LUMO coefficients of MOBs **1a**, **1b**, and **1d–g** and dienophiles BVE, DHF and styrene obtained from ab initio calculations performed at the RHF/3-21G level. The regiochemistry observed and predicted by calculations are the same in all cases studied except for the adducts derived from the MOB **1d** (Fig. 2). However, the small difference (ΔC_i=0.007) from the coefficients of C_5 and C_2 of LUMO in the case of MOB **1f** can not explain the high regioselectivity observed.

In summary, the Diels–Alder reactions of masked *o*-benzoquinones with electron-rich dienophiles such as benzyl vinyl ether, dihydrofuran and styrene proceeded in a highly regio- and stereocontrolled manner to produce highly functionalized bicyclo[2.2.2]octenone derivatives.[34] Whereas electron-deficient substituents on the MOB

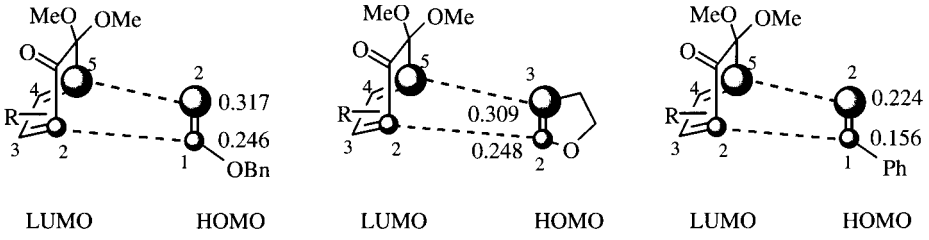


Figure 2. Preferred interaction between the FMOs of MOBs **1a**, **1b** and **1d–g**, BVE, DHF and styrene.

increased the reactivity, electron-releasing substituents on the MOB decreased the reactivity. Calculations based on frontier molecular orbital theory suggested that these cycloadditions are inverse- electron-demand Diels–Alder reactions. The observed regio- and stereoselectivities are in agreement with the prediction based on the calculations.

3. Experimental

BVE was prepared from ethyl vinyl ether and benzyl alcohol.[35] All the other reagents were obtained from commercial sources and used without further purification. 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 analysing 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 400 and 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 in electron-impact mode (70 eV) by NSC Instrumentation Center at Hsinchu, Taiwan. Elemental analyses were performed by NSC Instrumentation Center at Tainan, Taiwan.

3.1. General procedure for Diels–Alder reactions

3.1.1. Procedure A: To a solution of a 2-methoxyphenol **2** (1 mmol) in anhydrous MeOH (10 ml) was added DAIB (1.1 mmol) at 0°C. After 10 min stirring, a dienophile was added and stirring was continued at the same temperature for an appropriate period of time (as shown in the Tables 1–3) until the reaction was complete as indicated by TLC and disappearance of a yellow colour (MOB). Then, all the volatiles were removed under reduced pressure and the residue was subjected to purification by column chromatography on silica gel using a mixture of ethyl acetate and hexanes as eluent to obtain the desired cycloadducts.

3.1.2. Procedure B: To a mixture of a 2-methoxyphenol **2** (1 mmol) and a dienophile in MeOH (4 ml) was added DAIB (2 mmol) in MeOH (6 ml) during a period of time (as mentioned in the tables) with the aid of a syringe pump at 50°C. The reaction mixture was stirred further for 1 h at that temperature and worked up as described in procedure A.

3.1.3. Procedure C: To a mixture of DAIB (2 mmol) and a dienophile in MeOH (6 ml) was added a 2-methoxyphenol **2** (1 mmol) in MeOH (4 ml) during a period of time (as mentioned in the tables) with the aid of a syringe pump at 50°C. The reaction mixture was stirred further for 1 h at that temperature and worked up as described in procedure A.

3.2. Methyl (1*S**,4*S**,7*S**)-7-(benzyloxy)-3,3-dimethoxy-2-oxobicyclo[2.2.2]oct-5-ene-5-carboxylate (3a)

IR (neat) 3045 (w), 1742 (m), 1716 (s), 1628 (w), 1255 (m), 1108 (m), 1078 (m), 1051 (s) cm^{-1}; ^{1}H NMR δ 1.44 (ddd, J=3.2, 3.6, 13.8 Hz, 1H), 2.48 (ddd, J=2.9, 8.3, 13.8 Hz, 1H), 3.26 (s, 3H), 3.29 (s, 3H), 3.72 (ddd, J=2.0, 2.9, 3.2 Hz, 1H), 3.75 (dd, J=2.8, 6.4 Hz, 1H), 3.78 (s, 3H), 4.12 (dddd, J=1.0, 2.8, 3.6, 8.3 Hz, 1H), 4.42 (ABq, J=12.0 Hz, 1H), 4.50 (ABq, J=12.0 Hz, 1H), 7.02 (ddd, J=1.0, 2.0, 6.4 Hz, 1H), 7.25–7.35 (m, 5H); ^{13}C NMR δ 29.9 (CH_2), 37.6 (CH), 49.8 (CH_3), 50.4 (CH_3), 52.0 (CH_3), 54.8 (CH), 70.9 (CH_2), 74.3 (CH), 93.0 (C), 127.5 (CH), 127.8 (CH), 128.4 (CH), 134.5 (CH), 137.3 (C), 137.4 (C), 164.3 (C), 200.0 (C); MS m/z(%) 318 (M^+-28, 45), 212 (54), 211 (100), 210 (16), 209 (73), 179 (11), 163 (9), 105 (9), 77 (12), 65 (9) HRMS (EI) Calcd for $C_{18}H_{22}O_5$ (M^+-28) 318.1467, Found 318.1471.

3.3. (1*S**,4*S**,7*S**)-5-Acetyl-7-(benzyloxy)-3,3-dimethoxybicyclo[2.2.2]oct-5-en-2-one (3b)

IR (neat) 3043 (w), 1741 (s), 1671 (s), 1616 (w), 1250 (m), 1102 (s), 1044 (s) cm^{-1}; ^{1}H NMR δ 1.34 (ddd, J=3.4, 3.8, 13.8 Hz, 1H), 2.36 (s, 3H), 2.48 (ddd, J=3.0, 8.1, 13.9 Hz, 1H), 3.21 (s, 3H), 3.29 (s, 3H), 3.76 (dd, J=2.9, 6.4 Hz, 1H), 3.88 (ddd, J=1.7, 3.0, 3.4 Hz, 1H), 4.14 (dddd, J=1.1, 2.9, 3.8, 8.1 Hz, 1H), 4.47 (ABq, J=12.6 Hz, 1H), 4.50 (ABq, J=12.0 Hz, 1H), 6.92 (ddd, J=1.1, 1.7, 6.4 Hz, 1H), 7.25–7.35 (m, 5H); ^{13}C NMR δ 24.7 (CH_3), 29.7 (CH_2), 35.4 (CH), 49.9 (CH_3), 50.3 (CH_3), 54.9 (CH), 70.9 (CH_2), 74.4 (CH), 93.0 (C), 127.5 (CH), 127.9 (CH), 128.5 (CH), 134.7 (CH), 137.4 (C), 145.8 (C), 194.3 (C), 200.0 (C); MS m/z(%) 302 (M^+-28, 21), 196 (52), 195 (59), 193 (20), 153 (10), 149 (11), 91 (100), 77 (10), 65 (10), 43 (29); HRMS (EI): Calcd for $C_{18}H_{22}O_4$ (M^+-28) 302.1518, Found 302.1512; Anal. Calcd for $C_{19}H_{22}O_5$: C, 69.07%; H, 6.71%. Found: C, 68.99%; H, 6.74%.

3.4. Methyl (1*S**,4*R**,7*R**)-7-(benzyloxy)-1,3,3-trimethoxy-2-oxobicyclo[2.2.2]oct-5-ene-5-carboxylate (3c)

IR (neat) 3020 (w), 1758 (m), 1718 (s), 1257 (s), 1149 (m), 1074 (s), 1042 (m) cm^{-1}; ^{1}H NMR δ 1.52 (ddd, J=3.2, 3.5, 13.9 Hz, 1H), 2.45 (ddd, J=2.3, 8.5, 13.9 Hz, 1H), 3.25 (s, 3H), 3.31 (s, 3H), 3.58 (s, 3H), 3.66 (ddd, J=2.0, 2.3, 3.5 Hz, 1H), 3.79 (s, 3H), 4.00 (ddd, J=1.8, 3.2, 8.5 Hz, 1H), 4.53 (ABq, J=12.4 Hz, 1H), 4.76 (ABq, J=12.4 Hz, 1H), 7.17 (dd, J=1.8, 2.0 Hz, 1H), 7.25–7.30 (m, 5H); ^{13}C NMR δ 30.5 (CH_2), 36.5 (CH), 49.6 (CH_3), 50.5 (CH_3), 52.1 (CH_3), 54.5 (CH_3), 72.8 (CH_2), 76.2 (CH), 90.6 (C), 93.0 (C), 127.7 (CH), 127.7 (CH), 128.3 (CH), 135.3 (C), 135.6 (CH), 138.0 (C), 163.9 (C), 199.7 (C); MS m/z(%) 348 (M^+-28, 66), 333 (15), 268 (18), 241 (70), 239 (60), 197 (10), 193 (10), 134 (13), 92 (95), 79 (78); HRMS (EI) Calcd for $C_{19}H_{24}O_6$ (M^+-28) 348.1573, Found 348.1586.

3.5. Methyl (1*S**,4*S**,7*S**)-7-(benzyloxy)-3,3-dimethoxy-2-oxobicyclo[2.2.2]oct-5-ene-6-carboxylate (3d)

IR (neat) 3023 (w), 1741 (s), 1719 (s), 1630 (w), 1245 (m), 1104 (s), 1056 (m) cm^{-1}; ^{1}H NMR δ 1.37 (ddd, J=3.0, 3.0, 14.1 Hz, 1H), 2.41 (ddd, J=2.4, 8.3, 14.1 Hz, 1H),

3.24–3.29 (m, 1H), 3.25 (s, 3H), 3.29 (s, 3H), 3.76 (s, 3H), 4.12 (ddd, *J*=2.5, 3.0, 8.3 Hz, 1H), 4.29 (dd, *J*=2.0, 2.5 Hz, 1H), 4.36 (ABq, *J*=11.4 Hz, 1H), 4.61 (ABq, *J*=11.4 Hz, 1H), 7.24–7.30 (m, 5H), 7.44 (dd, *J*=2.0, 7.0 Hz, 1H); ^{13}C NMR δ 29.3 (CH_2), 38.6 (CH), 49.5 (CH_3), 50.6 (CH_3), 52.0 (CH_3), 52.1 (CH), 70.6 (CH_2), 73.5 (CH), 93.4 (C), 127.8 (CH), 127.8 (CH), 128.4 (CH), 128.6 (C), 137.5 (C), 142.7 (CH), 164.3 (C), 200.6 (C); MS *m*/*z*(%) 346 (M^+, 45), 318 (5), 211 (25), 210 (66), 209 (71), 105 (19), 91 (100), 77 (30), 65 (19), 59 (13); HRMS (EI) Calcd for $C_{18}H_{22}O_5$ (M^+-28) 318.1467, Found 318.1471.

3.6. (1*S**,4*S**,7*S**)-7-(Benzyloxy)-5-cyano-3,3-dimethoxybicyclo[2.2.2]oct-5-en-2-one (3e)

IR (neat) 3067 (w), 2219 (w), 1741 (s), 1096 (s), 1053 (m), 1026 (m) cm^{-1}; ^{1}H NMR δ 1.59 (ddd, *J*=3.2, 3.3, 14.2 Hz, 1H), 2.46 (ddd, *J*=2.6, 8.2, 14.2 Hz, 1H), 3.27–3.30 (m, 1H), 3.28 (s, 6H), 3.75 (dd, *J*=3.2, 6.4 Hz, 1H), 4.12 (dddd, *J*=1.1, 3.2, 3.2, 8.2 Hz, 1H), 4.46 (s, 2H), 6.83 (ddd, *J*=1.1, 1.6, 6.4 Hz, 1H), 7.24–7.32 (m, 5H); ^{13}C NMR δ 29.3 (CH_2), 41.2 (CH), 49.7 (CH_3), 50.6 (CH_3), 54.9 (CH), 71.0 (CH_2), 74.0 (CH), 92.4 (C), 116.4 (C), 118.0 (C), 127.5 (CH), 128.0 (CH), 128.5 (CH), 137.1 (C), 140.6 (CH), 198.3 (C); MS *m*/*z*(%): 285 (M^+, 48), 179 (23), 178 (71), 177 (86), 176 (100), 91 (97), 77 (36), 65 (34), 59 (21), 28 (22); HRMS (EI) Calcd for $C_{17}H_{19}NO_3$ (M^+-28) 285.1365, Found 285.1368; Anal. Calcd for $C_{18}H_{19}NO_4$: C, 68.99%; H, 6.11%. Found: C, 68.95%; H, 6.16%.

3.7. (1*S**,4*S**,7*S**)-7-(Benzyloxy)-3,3-dimethoxy-5-methylbicyclo[2.2.2]oct-5-en-2-one (3f)

IR (neat) 2952 (m), 1737 (s), 1164 (w), 1098 (s), 1052 (s) cm^{-1}; ^{1}H NMR δ 1.38 (apparent dt; ddd, *J*=13.7, 5.0, 3.4 Hz, 1H), 1.94 (d, *J*= 1.6, Hz, 3H), 2.38 (ddd, *J*=13.7, 8.3, 2.8 Hz, 1H), 2.85 (dd, *J*=2.8, 5.0 Hz, 1H), 3.25 (s, 3H), 3.32 (s, 3H), 3.35 (dd, *J*=2.5, 6.2 Hz, 1H), 4.03–4.06 (m, 1H), 4.46 (ABq, *J*=12.0 Hz, 1H), 4.49 (ABq, *J*=12.0 Hz, 1H), 5.67 (apparent d, *J*=6.2 Hz, 1H), 7.26–7.32 (m, 5H); ^{13}C NMR δ 21.1 (CH_3), 29.9 (CH_2), 43.0 (CH), 49.4 (CH_3), 50.5 (CH_3), 53.2 (CH), 70.6 (CH_2), 74.0 (CH), 93.9 (C), 116.5 (CH), 127.5 (CH), 127.6 (2CH), 128.3 (2CH), 137.9 (C), 144.8 (C), 201.2 (C); MS *m*/*z*(%) 274 (M^+-28, 10), 270 (1), 194 (6), 180 (3), 166 (25), 151 (20), 135 (6), 119 (6), 91 (100), 75 (32), 65 (27), 59 (12); HRMS (EI) Calcd for $C_{18}H_{22}O_4$: 302.1518; found 302.1509.

3.8. (1*S**,4*S**,7*S**)-7-(Benzyloxy)-3,3-dimethoxybicyclo-[2.2.2]oct-5-en-2-one (3g)

IR (neat): 3065 (w), 1738 (s), 1497 (w), 1142 (m), 1111 (s), 1093 (s), 1052 (s) cm^{-1}; ^{1}H NMR δ 1.41 (ddd, *J*=3.2, 3.5, 13.8 Hz, 1H), 2.40 (ddd, *J*=2.9, 8.3, 13.8 Hz, 1H), 3.07 (dddd, *J*=1.6, 2.9, 3.2, 7.5 Hz, 1H), 3.27 (s, 3H), 3.29 (s, 3H), 3.58 (ddd, *J*=1.3, 2.4, 6.6 Hz, 1H), 4.07 (dddd, *J*=1.2, 2.4, 3.5, 8.3 Hz, 1H), 4.47 (ABq, *J*=12.0 Hz, 1H), 4.50 (ABq, *J*=12.0 Hz, 1H), 6.07 (dddd, *J*=1.2, 1.6, 6.6, 7.0 Hz, 1H), 6.51 (ddd, *J*=1.3, 7.0, 7.5 Hz, 1H),7.26–7.34 (m, 5H); ^{13}C NMR δ 30.0 (CH_2), 37.9 (CH), 49.6 (CH_3), 50.2 (CH_3), 53.6 (CH), 70.7 (CH_2), 73.7 (CH), 93.7 (C), 124.7 (CH), 127.5 (CH), 127.7 (CH), 128.4 (CH), 134.4 (CH), 137.8 (C), 201.3 (C); MS *m*/*z*(%) 260 (M^+-28, 44), 153 (27), 152 (100), 150 (86), 137 (10), 92 (10), 91 (99), 76 (10), 74 (15), 59 (10); HRMS (EI) Calcd for $C_{16}H_{20}O_3$ (M^+-28) 260.1412, Found 260.1412.

3.9. Methyl (1*R**,2*R**,6*R**,7*R**)-11,11-dimethoxy-3-oxa-10-oxotricyclo[5.2.2.0^{2,6}]undec-8-ene-8-carboxylate (4a)

IR (neat) 3065 (w), 1743 (s), 1715 (s), 1629 (w), 1293 (m), 1249 (s), 1144 (s), 1103 (s) cm^{-1}; ^{1}H NMR δ 1.42 (dddd, *J*=7.5, 7.8, 9.6, 12.7 Hz, 1H), 2.10 (dddd, *J*=3.1, 6.3, 9.1, 12.7 Hz, 1H), 2.98 (dddd, *J*=2.3, 7.5, 8.5, 9.1 Hz, 1H), 3.26 (s, 3H), 3.34 (s, 3H), 3.51 (ddd, *J*=6.3, 8.7, 9.6 Hz, 1H), 3.73 (dd, *J*=3.2, 6.5 Hz, 1H), 3.77–3.82 (m, 2H), 3.80 (s, 3H), 4.37 (apparent dd, *J*=3.2, 8.5 Hz, 1H), 7.05 (ddd, *J*=1.2, 2.0, 6.5 Hz, 1H); ^{13}C NMR δ 30.1 (CH_2), 38.0 (CH), 42.0 (CH), 49.7 (CH_3), 50.1 (CH_3), 51.9 (CH_3), 55.7 (CH), 68.8 (CH_2), 76.7 (CH), 92.6 (C), 135.3 (C), 136.2 (CH), 164.7 (C), 199.7 (C); MS *m*/*z*(%) 254 (M^+-28, 100), 223 (13), 210 (10), 209 (85), 207 (20), 179 (7), 169 (7), 165 (9), 163 (8), 91 (10); HRMS (EI) Calcd for $C_{13}H_{18}O_5$, (M^+-28) 254.1154, Found 254.1177.

3.10. (1*R**,2*R**,6*R**,7*R**)-11-Acetyl-8,8-dimethoxy-3-oxatricyclo[5.2.2.0^{2,6}]undec-10-en-9-one (4b)

IR (neat) 3064 (w), 1741 (s), 1671 (s), 1635 (w), 1237 (w), 1142 (w), 1093 (m), 1048 (s) cm^{-1}; ^{1}H NMR δ 1.25 (dddd, *J*=8.0, 8.3, 9.8, 12.4 Hz, 1H), 2.06 (dddd, *J*=3.1, 6.3, 9.0, 12.4 Hz, 1H), 2.37 (s, 3H), 2.98 (apparent dddd, *J*=2.5, 8.3, 8.7, 9.0 Hz, 1H), 3.20 (s, 3H), 3.34 (s, 3H), 3.49 (ddd, *J*=6.3, 8.8, 9.8 Hz, 1H), 3.74–3.79 (m, 2H), 3.95 (dd, *J*=2.0, 2.5 Hz, 1H), 4.38 (apparent dd, *J*=3.4, 8.6, Hz, 1H), 6.98 (ddd, *J*=0.9, 2.0, 5.7 Hz, 1H); ^{13}C NMR δ 24.7 (CH_3), 30.2 (CH_2), 37.9 (CH), 40.0 (CH), 49.9 (CH_3), 50.3 (CH_3), 55.8 (CH), 69.0 (CH_2), 79.1 (CH), 92.8 (C), 136.4 (CH), 143.9 (C), 195.3 (C), 200.1 (C); MS *m*/*z*(%) 266 (M^+, 1), 238 (M^+-28, 100), 223 (37), 207 (18), 193 (59), 181 (19), 165 (16), 163 (25), 91 (20), 43 (22); HRMS (EI) Calcd for $C_{13}H_{18}O_4$, (M^+-28) 238.1205, Found 238.1200; Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.15%; H, 6.81%. Found: C, 63.41%; H, 6.82%.

3.11. Methyl (1*S**,2*R**,6*R**,7*R**)-1,11,11-trimethoxy-3-oxa-10-oxotricyclo[5.2.2.0^{2,6}]undec-8-ene-8-carboxylate (4c)

IR (neat): 3063 (w), 1754 (m), 1717 (s), 1254 (s), 1142 (w), 1091 (m), 1061 (s) cm^{-1}; ^{1}H NMR δ 1.47 (dddd, *J*=7.2, 8.1, 9.0, 12.6 Hz, 1H), 2.14 (dddd, *J*=3.5, 6.7, 9.3, 12.6 Hz, 1H), 3.07 (dddd, *J*=2.5, 7.2, 8.7, 9.3 Hz, 1H), 3.26 (s, 3H), 3.36 (s, 3H), 3.58 (ddd, *J*=6.7, 8.9, 9.0 Hz, 1H), 3.75 (dd, *J*=2.0, 2.5 Hz, 1H), 3.80 (s, 3H), 3.80 (m, 1H), 4.33 (dd, *J*=1.6, 8.7 Hz, 1H), 7.09 (dd, *J*=1.6, 2.0 Hz, 1H); ^{13}C NMR δ 30.4 (CH_2), 38.8 (CH), 41.1 (CH), 49.7 (CH_3), 50.3 (CH_3), 52.2 (CH_3), 54.2 (CH_3), 69.1 (CH_2), 80.3 (CH), 89.0 (C), 92.8 (C), 133.8 (C), 137.1 (CH), 164.3 (C), 199.1 (C); MS *m*/*z*(%) 284 (M^+-28, 100), 280 (67), 269 (94), 239 (40), 237 (44), 221 (24), 209 (52), 193 (36), 177 (41), 171 (28); HRMS (EI) Calcd for $C_{14}H_{20}O_6$, (M^+-28) 284.1260, Found 284.1252; Anal. Calcd for $C_{15}H_{20}O_7$: C, 57.69%; H, 6.45%. Found: C, 57.49%; H, 6.49%.

3.12. Methyl (1*R**,2*R**,6*R**,7*R**)-11,11-dimethoxy-3-oxa-10-oxotricyclo[5.2.2.0^{2,6}]undec-8-ene-9-carboxylate (4d)

IR (neat) 3062 (w), 1742 (s), 1719 (s), 1631 (w), 1247 (s), 1138 (m), 1097 (s), 1056 (m) cm^{-1}; ^{1}H NMR δ 1.51 (dddd, *J*=7.7, 8.0, 9.6, 12.4 Hz, 1H), 2.09 (dddd, *J*=3.0, 6.3, 9.0, 12.4 Hz, 1H), 2.90 (dddd, *J*=2.8, 7.7, 8.5, 9.0 Hz, 1H), 3.26 (s, 3H), 3.34 (s, 3H), 3.38 (dd, *J*=2.8, 6.9, Hz 1H), 3.50 (ddd, *J*=6.3, 8.4, 9.6 Hz, 1H), 3.76 (s, 3H), 3.82 (ddd, *J*=3.0, 8.0, 8.4 Hz, 1H), 4.12 (dd, *J*=1.8, 3.5 Hz, 1H), 4.37 (dd, *J*=3.5, 8.5 Hz, 1H), 7.30 (dd, *J*=1.8, 6.9 Hz, 1H); ^{13}C NMR δ 30.7 (CH_2), 38.2 (CH), 43.2 (CH), 49.6 (CH_3), 50.4 (CH_3), 52.0 (CH_3), 53.9 (CH), 68.8 (CH_2), 78.7 (CH), 92.9 (C), 130.5 (C), 141.6 (CH), 164.0 (C), 200.2 (C); MS *m*/*z*(%) 254 (M^+-28, 75), 209 (100), 195 (23), 179 (21), 163 (24), 91 (45), 88 (49), 77 (23), 65 (20), 59 (39); HRMS (EI) Calcd for $C_{13}H_{18}O_5$, (M^+-28) 254.1154, Found 254.1159; Anal. Calcd for $C_{14}H_{18}O_6$: C, 59.57%; H, 6.43%, Found: C, 59.31%; H, 6.40%.

3.13. (1*R**,2*R**,6*R**,7*R**)-11,11-Dimethoxy-10-oxo-3-oxatricyclo[5.2.2.0^{2,6}]undec-8-en-8-yl cyanide (4e)

IR (neat) 3064 (w), 2218 (w), 1744 (s), 1100 (m), 1081 (s), 1031 (m) cm^{-1}; ^{1}H NMR δ 1.63 (dddd, *J*=7.3, 8.0, 9.8, 12.5 Hz, 1H), 2.19 (dddd, *J*=2.9, 6.4, 9.1, 12.5 Hz, 1H), 2.97 (dddd, *J*=2.7, 7.3, 8.6, 9.1 Hz, 1H), 3.31 (s, 3H), 3.34 (s, 3H), 3.37 (dd, *J*=2.2, 2.7 Hz, 1H), 3.54 (ddd, *J*=6.4, 8.5, 9.8 Hz, 1H) 3.76 (dd, *J*=3.4, 6.4 Hz, 1H), 3.90 (ddd, *J*=2.9, 8.0, 8.5 Hz, 1H), 4.36 (apparent dd, *J*=3.4, 8.6 Hz, 1H), 6.90 (ddd, *J*=1.2, 2.2, 6.4 Hz, 1H); ^{13}C NMR δ 30.3 (CH_2), 38.0 (CH), 45.9 (CH), 49.8 (CH_3), 50.6 (CH_3), 55.8 (CH), 68.9 (CH_2), 78.8 (CH), 92.1 (C), 116.4 (C), 116.9 (C), 142.6 (CH), 198.0 (C) MS *m*/*z*(%) 249 (M^+, 0.01), 221 (M^+-28, 86), 190 (19), 177 (14), 176 (100), 146 (17), 116 (15), 91 (19), 77 (11), 59 (21); HRMS (EI) Calcd for $C_{12}H_{15}NO_3$, (M^+-28) 221.1052, Found 221.1064 Anal. Calcd for $C_{13}H_{15}NO_4$: C, 62.64%; H, 6.07%. Found: C, 62.59%; H, 6.13%.

3.14. (1*R**,2*R**,6*R**,7*R**)-8,8-Dimethoxy-11-methyl-3-oxatricyclo[5.2.2.0^{2,6}]undec-10-en-9-one (4f)

IR (neat) 3064 (w), 1737 (s), 1430 (w), 1140 (m), 1088 (s), 1052 (s) cm^{-1}; ^{1}H NMR δ 1.45 (dddd, *J*=7.9, 8.2, 9.6, 12.2 Hz, 1H), 1.91 (d, *J*=2.0 Hz, 3H), 2.03 (dddd, *J*=3.0, 6.2, 9.0, 12.2 Hz, 1H), 2.86 (dddd, *J*=3.0, 8.2, 8.5, 9.0 Hz, 1H), 2.94 (dd, *J*=2.0, 3.0 Hz, 1H), 3.28 (s, 3H), 3.31 (s, 3H), 3.39 (dd, *J*=2.9, 6.4 Hz, 1H), 3.53 (ddd, *J*=6.2, 8.4, 9.6 Hz, 1H), 3.87 (ddd, *J*=3.0, 7.9, 8.4 Hz, 1H), 4.29 (dd, *J*=2.9, 8.5 Hz, 1H), 5.66–5.69 (m, 1H); ^{13}C NMR δ 23.4 (CH_3), 30.3 (CH_2), 38.3 (CH), 47.1 (CH), 49.6 (CH_3), 50.6 (CH_3), 54.3 (CH), 69.1 (CH_2), 78.3 (CH), 93.7 (C), 118.1 (CH), 142.6 (C), 201.3 (C); MS *m*/*z*(%) 238 (M^+, 0.25), 210 (M^+-28, 66), 195 (17), 179 (20), 178 (52), 165 (43), 135 (100), 105 (28), 91 (62), 77 (30); HRMS (EI) Calcd for $C_{13}H_{18}O_4$, (M^+) 238.1205, Found 238.1208.

3.15. (1*R**,2*R**,6*R**,7*R**)-8,8-Dimethoxy-3-oxatricyclo-[5.2.2.0^{2,6}]dodec-10-en-9-one (4g)

IR (neat) 3060 (w), 1740 (s), 1451 (w), 1143 (m), 1091 (s), 1051 (m) cm^{-1}; ^{1}H NMR δ 1.60 (dddd, *J*=7.5, 8.0, 9.3, 12.3 Hz, 1H), 2.06 (dddd, *J*=2.7, 6.4, 9.3, 12.3 Hz, 1H), 2.89 (dddd, *J*=2.6, 7.5, 8.2, 9.3 Hz, 1H), 3.17 (ddd, *J*=1.6, 2.6, 6.4 Hz, 1H), 3.29 (s, 3H), 3.32 (s, 3H), 3.51–3.57 (m, 2H), 3.87 (ddd, *J*=2.7, 8.0, 8.2 Hz, 1H), 4.34 (ddd, *J*=1.2, 3.4, 8.2 Hz, 1H), 6.11 (dddd, *J*=1.2, 1.6, 6.4, 8.0 Hz, 1H), 6.33 (ddd, *J*=1.3, 6.4, 8.0 Hz, 1H); ^{13}C NMR δ 30.7 (CH_2), 38.4 (CH), 42.3 (CH), 49.7 (CH_3), 50.2 (CH_3), 55.0 (CH), 69.1 (CH_2), 79.0 (CH), 93.4 (C), 127.0 (CH), 132.6 (CH), 201.2 (C); MS *m*/*z*(%) 196 (M^+-28, 96), 165 (29), 151 (100), 139 (10), 121 (44), 111 (18), 91 (61), 79 (17), 77 (36), 65 (23); HRMS (EI) Calcd for $C_{11}H_{16}O_3$, (M^+-28) 196.1099, Found 196.1099.

3.16. Methyl (1*R**,2*R**,7*R**,8*R**)-12,12-dimethoxy-11-oxo-3-oxatricyclo[6.2.2.0^{2,7}]dodec-9-ene-9-carboxylate (5a)

IR (neat) 3059 (w), 1742 (s), 1716 (s), 1628 (w), 1247 (s), 1124 (m), 1085 (s), 1052 (s) cm^{-1}; ^{1}H NMR δ 1.04–1.15 (m, 1H), 1.47–1.61 (m, 2H), 1.76–1.86 (m, 1H), 2.33 (dddd, *J*=2.2, 5.5, 7.9, 13.1 Hz, 1H), 3.25 (s, 3H), 3.33 (s, 3H), 3.50 (ddd, *J*=4.4, 9.0, 10.9 Hz, 1H), 3.59–3.62 (m, 2H), 3.74 (ddd, *J*=6.5, 10.7, 10.9 Hz, 1H), 3.79 (s, 3H), 3.94 (ddd, *J*=1.2, 3.2, 7.9 Hz, 1H), 7.08 (ddd, *J*=1.2, 2.0, 6.4 Hz, 1H); ^{13}C NMR δ 20.0 (CH_2), 21.4 (CH_2), 34.5 (CH), 43.3 (CH), 49.8 (CH_3), 50.3 (CH_3), 51.9 (CH_3), 56.0 (CH), 62.8 (CH_2), 72.9 (CH), 93.8 (C), 135.3 (CH), 135.6 (C), 164.8 (C), 199.9 (C); MS *m*/*z*(%) 268 (M^+-28, 100), 265 (10), 221 (11), 210 (17), 209 (87), 163 (13), 105 (10), 73 (13), 59 (13), 18 (62); HRMS (EI) Calcd for $C_{14}H_{20}O_5$, (M^+-28) 268.1311, Found 268.1311; Anal. Calcd for $C_{15}H_{20}O_6$: C, 60.80%; H, 6.80%. Found: C, 60.53%; H, 6.81%.

3.17. (1*S**,4*R**,7*R**)-3,3-Dimethoxy-2-oxo-7-phenyl-bicyclo[2.2.2]-oct-5-ene-5-carboxylate (6a)

IR (neat) 3062 (w), 1741 (s), 1716 (s), 1624 (w), 1494 (w), 1285 (m), 1102 (s), 1044 (s) cm^{-1}; ^{1}H NMR δ 1.59 (m, 1H), 2.61 (ddd, *J*=3.2, 10.4, 20.4 Hz, 1H), 3.32 (s, 3H), 3.41 (s, 3H), 3.43–3.48 (m, 2H), 3.82 (s, 3H), 3.85 (apparent dd, *J*=2.0, 5.2 Hz, 1H), 7.10 (dd, *J*=2.0, 7.2 Hz, 1H), 7.06–7.27 (m, 5H); ^{13}C NMR δ 29.9 (CH_2), 39.0 (CH), 40.1 (CH), 50.0 (CH_3), 50.1 (CH_3), 51.9 (CH_3), 55.9 (CH), 93.0 (C), 126.8 (CH), 127.2 (CH), 128.6 (CH), 135.3 (CH), 138.2 (C), 143.2 (C), 164.2 (C), 200.1 (C); MS *m*/*z*(%) 288 (M^+-28, 100); HRMS (EI) Calcd for $C_{17}H_{20}O_4$, (M^+-28) 288.1362, Found 288.1511.

3.18. (1*S**,4*R**,7*R**)-5-Acetyl-3,3-dimethoxy-7-phenyl-bicyclo-[2.2.2]oct-5-en-2-one (6b)

IR (neat) 3034 (w), 1740 (s), 1671 (s), 1494 (w), 1251 (m), 1093 (s), 1059 (s), 1038 (s) cm^{-1}; ^{1}H NMR δ 1.52 (ddd, *J*=2.8, 6.4, 14.0 Hz, 1H), 2.39 (s, 3H), 2.58 (ddd, *J*=2.8, 9.6, 13.2 Hz, 1H), 3.27 (s, 3H), 3.40 (m, 4H), 3.44 (dd, *J*=1.6, 6.8 Hz, 1H), 3.50 (t, *J*= 8.0 Hz, 1H), 4.01 (apparent dd, *J*=3.2, 5.2 Hz, 1H), 7.00 (dd, *J*=2.0, 6.4 Hz, 1H), 7.04–7.26 (m, 5H); ^{13}C NMR δ 24.8 (CH_3), 29.3 (CH_2), 37.0 (CH), 40.3 (CH), 50.1 (CH_3), 56.1 (CH), 93.2 (C), 126.9 (CH), 127.1 (CH), 128.7 (CH), 135.4 (CH), 143.2 (C), 146.8 (C), 194.2 (C), 200.5 (C); MS *m*/*z*(%) 272 (M^+-28, 100), 225 (19), 197 (12), 155 (8), 153 (7), 115 (5), 91 (5), 43 (13); HRMS (EI) Calcd for $C_{17}H_{20}O_3$, (M^+-28) 272.1412, Found 272.1400.

3.19. Methyl (1*S**,4*R**,7*R**)-1,3,3-trimethoxy-2-oxo-7-phenylbicyclo[2.2.2]oct-5-ene-5-carboxylate (6c)

IR (neat) 3061 (w), 1755 (s), 1718 (s), 1628 (w), 1460 (m), 1283 (s), 1055 (s), 1021 (s) cm^{-1}; ^1H NMR δ 1.63 (ddd, J=2.8, 6.4, 13.2 Hz, 1H), 2.65 (ddd, J=3.2, 9.6, 14.0 Hz, 1H), 3.33 (s, 3H), 3.40–3.42 (m, 4H), 3.79 (apparent dd, J=2.8, 4.4 Hz, 1H), 3.86 (s, 3H), 7.08–7.27 (m, 6H); ^{13}C NMR δ 32.1 (CH_2), 37.9 (CH), 44.2 (CH), 49.9 (CH_3), 50.2 (CH_3), 52.2 (CH_3), 54.1 (CH_3), 87.5 (C), 93.1 (C), 127.0 (CH), 128.2 (CH), 128.6 (CH), 136.1 (C), 136.9 (C), 141.0 (C), 163.8 (C), 199.5 (C). MS m/z(%) 318 (M^+-28, 100); HRMS (EI) Calcd for $C_{18}H_{22}O_5$, (M^+-28) 318.1447, Found 318.1465.

3.20. Methyl (1*S**,4*R**,7*R**)-3,3-dimethoxy-2-oxo-7-phenylbicyclo[2.2.2]oct-5-ene-6-carboxylate (6d)

IR (neat) 3061 (w), 1721 (s), 1628 (m), 1493 (m), 1280 (m), 1097 (m) cm^{-1}; ^1H NMR δ 1.58 (ddd, J=2.8, 6.3, 13.5 Hz, 1H), 2.55 (ddd, J=3.1, 10.9, 13.5 Hz, 1H), 3.32 (s, 3H), 3.38 (s, 3H), 3.39–3.41 (m, 1H), 3.46 (ddd, J=1.6, 6.5, 9.9 Hz, 1H), 3.63 (s, 3H), 3.84 (apparent dd, J=1.8, 1.8 Hz, 1H), 7.53 (dd, J=1.6, 7.2 Hz, 5H); ^{13}C NMR δ 28.6 (CH_2), 39.9 (CH), 39.2 (CH), 49.8 (CH_3), 50.4 (CH_3), 51.8 (CH_3), 53.6 (CH), 93.2 (C), 126.8 (CH), 127.0 (CH), 128.5 (CH), 129.6 (C), 142.8 (C), 144.1 (CH), 164.1 (C), 200.5 (C); MS m/z (%) 288 (M^+-28, 100), 241 (23), 229 (11), 213 (17), 197 (17), 181 (17), 169 (13), 155 (27), 153 (41), 128 (21), 91 (21); HRMS (EI) Calcd for $C_{17}H_{20}O_4$, (M^+-28) 288.1362, Found 288.1490.

3.21. (1*S**,4*R**,7*R**)-6,6-Dimethoxy-5-oxo-8-phenylbicyclo[2.2.2]oct-2-en-2-yl cyanide (6e)

IR (neat) 3063 (w), 2218 (m), 1742 (s), 1601 (w), 1457 (m), 1152 (m), 1127 (m), 1075 (s) cm^{-1}; ^1H NMR δ 1.78 (ddd, J=2.8, 6.4, 14.0 Hz, 1H), 2.60 (ddd, J=2.8, 9.6, 13.1 Hz, 1H), 3.36 (s, 3H), 3.41 (s, 3H), 3.43–3.51 (m, 3H), 6.92 (dd, J=1.6, 6.4 Hz, 1H), 7.07–7.31 (m, 5H); ^{13}C NMR δ 28.9 (CH_2), 40.2 (CH), 42.6 (CH), 50.0 (CH_3), 50.5 (CH_3), 56.1 (CH), 92.4 (C), 116.4 (C), 118.8 (C), 127.1 (CH), 127.3 (CH), 128.8 (CH), 141.5 (CH), 142.1 (C), 198.5 (C); MS m/z(%) 255 (M^+-28, 100), 224 (14), 180 (34), 153 (13), 127 (5), 115 (9), 104 (10), 77 (13), 59 (8); HRMS (EI) Calcd for $C_{16}H_{17}O_2N$, (M^+-28) 255.1259, Found 255.1259.

3.22. (1*S**,4*R**,7*R**)-3,3-Dimethoxy-5-methyl-7-phenylbicyclo[2.2.2]oct-5-en-2-one (6f)

IR (neat) 3029 (s), 1750 (s), 1228 (w), 1148 (m), 1070 (s), 1032 (s) cm^{-1}; ^1H NMR δ 1.55 (ddd, J=2.6, 6.8, 13.0 Hz, 1H), 2.00 (d, J=1.6 Hz, 3H), 2.48 (ddd, J=3.2, 9.9, 13.0 Hz, 1H), 3.01 (apparent dd, J=2.6, 5.0 Hz, 1H), 3.13 (dd, J=1.6, 6.8 Hz, 1H), 3.34–3.42 (m, 1H), 3.38 (s, 3H), 3.39 (s, 3H), 5.73 (apparent d, J=6.3 Hz, 1H), 7.14–7.27 (m, 5H); ^{13}C NMR δ 21.1 (CH_3), 29.9 (CH_2), 39.8 (CH), 44.5 (CH), 49.9 (CH_3), 50.5 (CH_3), 54.6 (CH), 94.1 (C), 117.7 (CH), 126.6 (2CH), 127.7 (CH), 128.5 (2CH), 144.5 (C), 145.5 (C), 201.8 (C); MS m/z(%) 244 (M^+-28, 43), 229 (9), 213 (10), 197 (5), 169 (52), 153 (13), 121 (3), 91 (16), 75 (100); HRMS (EI) Calcd for $C_{17}H_{20}O_3$, 272.1398, Found 272.1412.

3.23. (1*S**,4*R**,7*R**)-3,3-Dimethoxy-7-phenylbicyclo-[2.2.2]oct-5-en-2-one (6g)

IR (neat) 3058 (w), 1739 (s), 1144 (m), 1091 (s), 1057 (s) cm^{-1}; ^1H NMR δ 1.60 (m, 2H), 2.51 (ddd, J=2.8, 9.6, 19.6 Hz, 1H), 3.21–3.25 (m, 2H), 3.36 (s, 3H), 3.40 (s, 3H), 6.14 (t, J=6.4 Hz, 1H), 6.59 (ddd, J=1.2, 7.6, 8.8 Hz, 1H), 7.20–7.28 (m, 5H); ^{13}C NMR δ 29.8 (CH_2), 39.2 (CH), 39.2 (CH), 49.8 (CH_3), 50.1 (CH_3), 54.9 (CH), 93.7 (C), 125.6 (CH), 126.6 (CH), 127.6 (CH), 128.3 (CH), 135.3 (CH), 144.1 (C), 201.6 (C); MS m/z(%) 258 (0.08), 231 (31), 230 (92), 199 (44), 155 (100), 115 (35), 91 (44).

3.24. (1*S**,4*R**,7*R**)-1,3,3-Trimethoxy-5-methyl-7-phenylbicyclo[2.2.2]oct-5-en-2-one (6h)

IR (neat) 3029 (w), 1749 (s), 1601 (w), 1494 (m), 1228 (w) cm^{-1}; ^1H NMR δ 1.55 (ddd, J=2.8, 6.4, 13.2 Hz, 1H), 2.0 (s, 3H), 2.52 (ddd, J= 2.5, 10.0, 13.2 Hz, 1H), 2.92 (dd, J=2.8, 5.2 Hz, 1H), 3.31 (s, 3H), 3.37 (s, 3H), 3.38 (s, 3H), 3.33–3.36 (m, 1H), 5.81 (apparent dd, J=1.6, 3.2 Hz, 1H), 7.17–7.24 (m, 5H); ^{13}C NMR δ 21.0 (CH_3), 32.0 (CH_2), 43.3 (CH), 49.5 (CH_3), 50.5 (CH_3), 53.3 (CH_3), 85.8 (C), 94.1 (C), 119.8 (CH), 126.6 (CH), 128.0 (CH), 128.7 (CH), 142.1 (C), 143.5 (C), 200.6 (C); MS m/z(%) 302 (0.16), 274 (18), 259 (100), 243 (6), 227 (12), 199 (51), 167 (33), 155 (19), 141 (11), 109 (10), 91 (14), 77 (12), 59 (10); HRMS (EI) Calcd for $C_{17}H_{22}O_3$, (M^+-28) 274.1569, Found 274.1557.

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