Tetrahedron 67 (2011) 3216–3225

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Facile preparation of bicyclo[2.2.2]octenone derivatives via Diels–Alder cycloadditions of in situ-generated masked *o*-benzoquinones

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ARTICLE INFO

Article history:
Received 26 October 2010
Received in revised form 21 February 2011
Accepted 7 March 2011
Available online 12 March 2011

Keywords:
2,2-Dimethoxycyclohexa-3,5-dienone
retro-Diels–Alder/Diels–Alder cycloaddition
Masked *o*-benzoquinone
Phenol oxidation

ABSTRACT

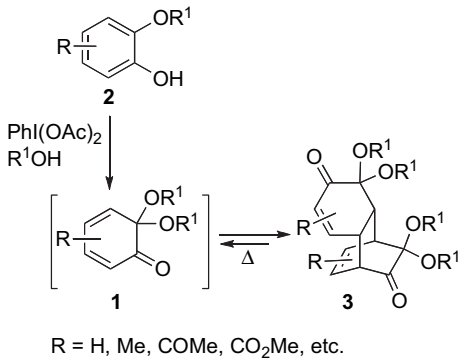
Diels–Alder cycloadditions of in situ-generated, substituted 2,2-dimethoxycyclohexa-3,5-dienones with olefinic dienophiles resulted in the development of an efficient method for the preparation of highly functionalized bicyclo[2.2.2]oct-5-en-2-ones with good to excellent yields.

1. Introduction

The Diels–Alder cycloaddition,[1] both inter- and intra-molecular reaction, constitutes a powerful tool for the construction of complex organic molecules, due to its versatility and its ability of forming two C–C bonds in a cyclohexene system in a highly regioselective and stereoselective manner.[2] A large variety of dienes and dienophiles, bearing different functional groups, can be used, and many different types of ring structures built up. It is frequently found, that although the reaction could conceivably give rise to a number of structurally or stereoisomeric products, one isomer is formed exclusively or at least as a major product.

2,2-Dialkoxycyclohexa-3,5-dienones[3] [masked *o*-benzoquinones (MOBs)], i.e., **1**, a synthetically useful class of *o*-benzoquinones, can be generated by in situ oxidation[4] of the readily available *o*-alkoxy phenols **2** using hypervalent iodine reagents in the presence of an alcohol (Scheme 1). Alternatively, when the substituted 2,2-dialkoxycyclohexa-3,5-dienones **1** are difficult to handle, due to their high propensity toward dimerization via self-cycloaddition reactions, thermolysis[5] of dimer **3** might be a convenient source of **1**.

Substituted 2,2-dialkoxycyclohexa-3,5-dienones have been shown[3] to be excellent components, either as a diene or a dienophile, in Diels–Alder reactions, undergoing regio- and stereoselective cycloadditions. Quite often, these Diels–Alder cycloadditions have been employed as a key-step in various elegant approaches[6] to a variety of structurally diverse natural products.



Scheme 1. Generation of 2,2-dialkoxycyclohexa-3,5-dienones.

We report herein our results of utilizing substituted cyclohexa-3,5-dienones **1** as 4π components in intermolecular Diels–Alder reactions, to synthesize various bicyclo[2.2.2]octenone derivatives, important starting materials of different target molecules such as polysubstituted cyclohexenes,[7] *cis*-decalins,[8] and triquinanes.[9]

2. Results and discussion

6-Allyl-2-methoxyphenol (**2a**), an easily prepared[10] *o*-methoxy phenol, undergoes a facile aromatic oxidation with (diacetoxy)-

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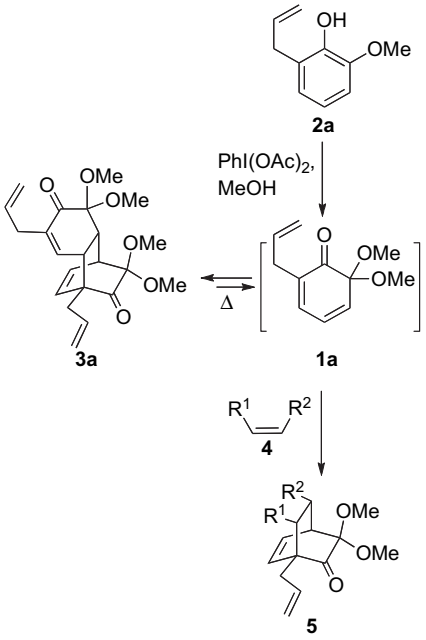
doi:10.1016/j.tet.2011.03.018

iodobenzene to furnish 6-allyl-2,2-dimethoxycyclohexa-3,5-dienone (**1a**), which dimerizes at room temperature to produce dimer **3a** (Scheme 2). Performing this oxidation in the presence of an excess of a suitable dienophile **4** afforded the desired cycloadduct **5** in low yields together with increased amounts of dimer **3a**. Presumably, the in situ-generated dienone **1a** is highly reactive and dimerized more rapidly than cycloadding with the added dienophile. To circumvent this problem, the alternative retro-Diels–Alder/Diels–Alder sequence was applied for the synthesis of the desired cycloadducts.



Scheme 2. Diels–Alder reactions of dienone **1a**.

All the retro-Diels–Alder/Diels–Alder reactions of dimer **3a** with the dienophiles **4** were carried out by heating at 230 °C for 6–43 h a solution of dimer **3a** and excess dienophile **4** in *o*-xylene in a sealed test-tube until the complete disappearance of the starting dimer (TLC monitoring). The bicyclo[2.2.2]octenones **5** (Table 1) were isolated by flash chromatography on silica gel in good to excellent yields (68–97%).

Table 1
retro-Diels–Alder/Diels–Alder reactions[a] of dimer **3a** with olefinic dienophiles **4** via Scheme 2

Entry	Substituents		Time[b] (h)	Product	Yield[c] (%)
	R^1	R^2			
1	$COCH_3$	H	30	**5aa**	74
2	CO_2CH_3	H	20	**5ab**	82
3	C_6H_5	H	43	**5ac**	95
4	C_6H_5S	H	25	**5ad**	77
5	$C_6H_4CH_2$		6	**5ae**	97
6	1,8-$C_{10}H_6$		18	**5af**	68

[a] All reactions were carried out by heating at 230 °C for 6–43 h, a solution of dimer **3a** (1.0 mmol), dienophiles **4** (7.35–10.6 mmol) in *o*-xylene (3 mL) in a sealed test-tube until the complete disappearance (TLC) of the starting dimer **3a**.
[b] Time required for the complete consumption of dimer **3a**.
[c] Yield of isolated product after flash chromatography.

Cycloadduct **5aa**, was obtained as a single isomer, in 74% yield, when 1-buten-3-one (**4a**) was allowed (at 230 °C for 30 h) to undergo reaction with dienone **1a**, generated by the thermolysis of dimer **3a**, in *o*-xylene (Table 1, entry 1). The reaction with methyl acrylate **4b** was also considered. Dienone **1a**, generated by thermolysis of dimer **3a**, reacts with methyl acrylate **4b** to give the corresponding cycloadduct **5ab**, as a single diastereomer, in 82% yield (Table 1, entry 2). Styrene **4c**, is also compatible for this reaction. Bicyclo[2.2.2]octenone **5ac** was isolated in 95% yield, as a single diastereomer, when dienone **1a** was generated, by thermolysis of dimer **3a**, in the presence of excess styrene **4c** (Table 1, entry 3). Phenylthioethylene (**4d**), an electron-rich dienophile, also underwent highly regioselective cycloaddition with dienone **1a** at 230 °C, affording bicyclo[2.2.2]octenone **5ad** as the sole product in 77% yield (Table 1, entry 4). Even if indene **4e** was expected to be less reactive as a dienophile, bicyclo[2.2.2]octenone **5ae** was isolated in 97% yield when dienone **1a**, generated by thermolysis of dimer **3a**, reacted at 230 °C with excess indene **4e** (Table 1, entry 5). Similarly, acenaphthylene **4f** was reacted with in situ-generated dienone **1a** to afford cycloadduct **5af**, as a single diastereomer, in 68% yield (Table 1, entry 6).

The Diels–Alder cycloadditions of dienone **1a** with dienophiles **4** had excellent regio- and stereo-selectivity. Structures of all adducts were unambiguously identified with IR, ^{1}H NMR, ^{13}C NMR spectroscopy, and elemental analyses. All the cycloadducts exhibited IR absorptions at 1730–1738 cm^{-1} due to the characteristic features of the carbonyl functional group adjacent to a *gem*-dimethoxy group in a functionalized bicyclo[2.2.2]octenone skeleton. All the cycloadducts **5** showed ^{13}C resonance at about δ 200.5–203.7 ppm revealing the presence of a carbonyl group. Furthermore, the peak corresponding to the quaternary carbon bearing two methoxy groups was found to be present at δ 93.7–94 ppm.

The observed selectivities have literature precedents.[11] The stereo- and regio-selectivities of the bicyclo[2.2.2]oct-5-en-2-ones **5**, determined by 2-D NMR studies, is exemplified for cycloadduct **5ac** (Fig. 1). The ^{1}H NMR chemical shift of the bridgehead proton H_a was observed at δ 3.19–3.21. The olefinic protons H_b and H_c were observed at δ 6.62 and δ 6.00, respectively. The methinic proton H_d was observed at δ 3.04. The methylenic proton H_f was observed at δ 1.65, whereas, as a result of the deshielding effect by the methoxy group, methylenic proton H_e appeared at δ 2.61, thus providing the assigned regiochemistry.[11] The coupling constants J (H_d–H_e)=9.6 Hz and J (H_d–H_f)=6.7 Hz showing the cis and trans relation, respectively, confirm the assigned stereoselectivity. The existence of a ROESY signal between the aromatic protons of the phenyl group and the olefinic proton H_c further confirms the assigned stereochemistry.

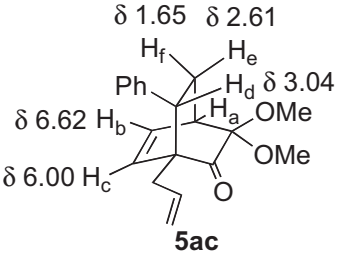
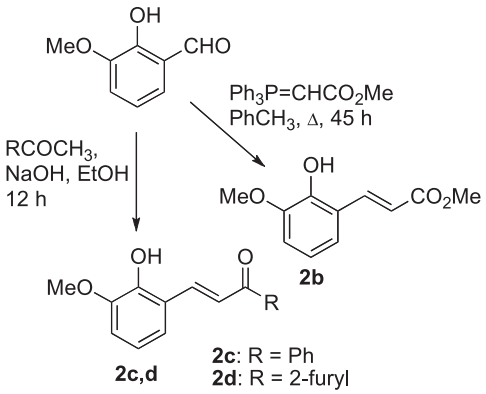


Fig. 1. Selected ^{1}H NMR signals of cycloadduct 5ac.

Encouraged by the results obtained from the Diels–Alder reactions of dienone **1a** with olefinic dienophiles **4**, we became interested in introducing other appendages and functional groups in the C6 position of an *o*-methoxy phenol in order to generate highly functionalized bicyclo[2.2.2]oct-5-en-2-ones. We first attempted the (diacetoxy)iodobenzene oxidation of *o*-vanillin in the presence of a dienophile, which provided a complex mixture of products. Consequently, the aldehyde function was chemically modified by condensation of *o*-vanillin with a phosphorus ylide[12] or a methyl ketone[13] to give the 2-(3-oxo-1-alkenyl)-6-methoxyphenols **2b–d** (Scheme 3).

Only one of the two possible geometric isomers was isolated from each condensation reaction. The *E*-configuration can be assigned to the condensation products on the basis of their ^{1}H NMR



Scheme 3. Preparation of phenols **2b**–**d**.

spectra. The trans-arrangement of the vinyl protons in the disubstituted olefinic phenols **2b**–**d** is indicated by the magnitude of the coupling constant [16.2 Hz (**2b**), 15.9 Hz (**2c**), 15.9 Hz (**2d**)].

Dimers **3b**–**d** were synthesized in good yields by the (diacetoxy)-iodobenzene oxidation of phenols **2b**–**d** in methanol, presumably via self-dimerization reaction of the unstable 2,2-dimethoxycyclohexa-3,5-dienones **1b**–**d**. It is quite remarkable, that these self-dimerization reactions proceed with absolute regio- and stereo-selectivity, furnishing a single dimer in all cases although four different products are possible. There are two different diene moieties when the dienone **3b**–**d** behaved as a 4π component (Fig. 2) and three double bonds, electronically differentiated, when the dienone **3b**–**d** behaved as a 2π component.

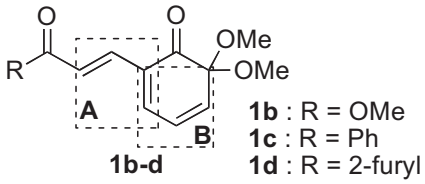


Fig. 2. Possible diene moieties of dienones **1b**–**d**.

The structures of dimers **3b**–**d** were established by ^{1}H and ^{13}C NMR spectral analyses, and are exemplified for the **3b** derivative. The existence of four doublet signals in the ^{1}H NMR spectrum at δ 5.96 (J=16.3 Hz), 6.55 (J=16 Hz), 7.07 (J=16 Hz), and 7.21 (J=16.3 Hz) corresponding to *trans*-olefinic protons confirms that dienone **1b** which behaved as a 4π component in the self-dimerization reaction reacts via diene subunit B (Fig. 1). The ^{13}C resonance signals at δ 193.3 ppm corresponding to an unsaturated carbonyl group and δ 199.5 ppm corresponding to a ring carbonyl group confirms that dienone **1b** which behaved as a 2π component in the self-dimerization reaction reacts as a dienophile exclusively at the C3 double bond. These results are in analogy with all the previously established structures of related dimers.[14] This cyclodimerization reaction is independent of the nature of the substituents on the dimethoxycyclohexa-3,5-dienone core of the system, as long as these substituents do not block the dimerization process. Apparently, the dimethoxy acetal plays some role in increasing the reactivity as well as the propensity to dimerize. There are four possible transition states for this dimerization reaction (Fig. 3). Reduced steric effects and increased secondary orbital interactions between the diene and unshared pair of electrons of the oxygen atom of the methoxy group of dienone acting as a dienophile favored the *endo*-mode of the dimerization process (structures **A**, **C** in Fig. 3). Proposed transition state **A** leading to dimer **3** display a C_2-axis of symmetry, while transition state **C** is not C_2-symmetric. The loss of the C_2-symmetry results in significant changes in bond length alternation between the reactive centers of the monomers. The stabilization[14a] of the C_2-symmetric transition state **A** likely originates from a better overlap of the π electronic clouds of the two partners, hence maximizing secondary overlap interactions.

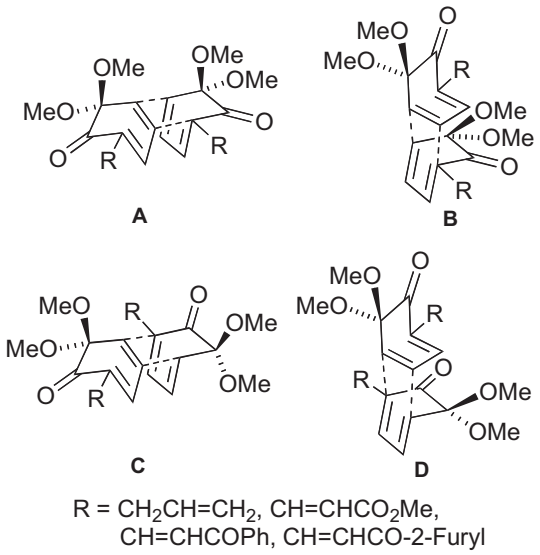
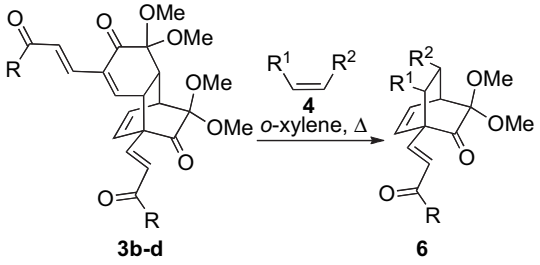


Fig. 3. The four possible transition states for the dimerization of dimethoxycyclohexa-3,5-dienones **4**.

Attempts to perform these oxidation reactions in the presence of various dienophiles failed, and only dimers **3b**–**d** were isolated. But, when the 2,2-dimethoxycyclohexa-3,5-dienones **1b**–**d** were generated in situ by thermolysis of dimers **3b**–**d** in a sealed test-tube at 230 °C, reaction with dienophiles **4** yielded the expected cycloadducts **6** (Scheme 4) in good to excellent yields (Table 2).



Scheme 4. Diels–Alder cycloadditions of dimers **3b**–**d**.

Under similar conditions as for the dimer **3a**, dienones **1b**–**d**, generated in situ by the thermolysis of dimers **3b**–**d** in the presence of 1-buten-4-one (**4a**) in a sealed test-tube at 230 °C, furnished cycloadducts **6ba**–**6da** in 74–87% yields (entries 1–3 of Table 2). Similarly, when methyl acrylate **4b** was employed as a dienophile, cycloadducts **6bb**–**6db** were isolated in 58–84% yields (entries 4–6 of Table 2). Styrene **4c** afforded cycloadducts **6bc**–**6dc** in 41–91% yields (entries 7–9 of Table 2). Phenylthioethylene (**4d**) also afforded cycloadducts **6bd**–**6dd** in 79—ca. 100% yields (entries 10–12 of Table 2). Cycloadducts **6be**–**6de** were isolated in 85–92% yields when the cycloaddition was extended to indene **4e** as the dienophile (entries 13–15 of Table 2). Under similar conditions as for the dimer **3a**, dimers **3b**–**d** reacted with acenaphthylene **4f** yielding cycloadducts **6bf**–**6df** in 61–85% yields (entries 16–18 of Table 2).

Again, all the Diels–Alder cycloadditions of dienones **1b**–**d** with dienophiles **4** showed excellent regio- and stereo-selectivity. Structures of all adducts were unambiguously identified with IR, ^{1}H NMR, ^{13}C NMR spectroscopy, and elemental analyses. Extensive decoupling experiments and comparing the δ and J coupling constants with those of similar reported compounds[11] ascertained

Table 2
retro-Diels–Alder/Diels–Alder reactions[a] of dimers **3b–d** with olefinic dienophiles **4** via Scheme 4

Entry	Substituents			Time[b] (h)	Product	Yield[c] (%)
	R	R^1	R^2			
1	CH_3O	CH_3CO	H	15	**6ba**	74
2	C_6H_5	CH_3CO	H	16	**6ca**	83
3	2-Furyl	CH_3CO	H	18	**6da**	83
4	CH_3O	CH_3CO_2	H	18	**6bb**	71
5	C_6H_5	CH_3CO_2	H	16	**6cb**	58
6	2-Furyl	CH_3CO_2	H	18	**6db**	91
7	CH_3O	C_6H_5	H	16	**6bc**	91
8	C_6H_5	C_6H_5	H	17	**6cc**	90
9	2-Furyl	C_6H_5	H	18	**6dc**	41
10	CH_3O	C_6H_5S	H	15	**6bd**	95
11	C_6H_5	C_6H_5S	H	16	**6cd**	ca.100
12	2-Furyl	C_6H_5S	H	16	**6dd**	79
13	CH_3O	$C_6H_4CH_2$		5.5	**6be**	92
14	C_6H_5	$C_6H_4CH_2$		5	**6ce**	98
15	2-Furyl	$C_6H_4CH_2$		17	**6de**	85
16	CH_3O	1,8-$C_{10}H_6$		15.5	**6bf**	85
17	C_6H_5	1,8-$C_{10}H_6$		16	**6cf**	61
18	2-Furyl	1,8-$C_{10}H_6$		17	**6df**	84

[a] All reactions were carried out by heating at 230 °C a solution of dimer **3b–d** (0.21–0.58 mmol), dienophile **4** (2.33–6.05 mmol) in *o*-xylene (3 mL) in a sealed test-tube until the complete disappearance (TLC) of the starting dimer.
[b] Time required for the complete consumption of dimer **3b–d**.
[c] Yield of isolated product after flash chromatography.

stereo- and regio-selectivities. As a result of the deshielding effect by the methoxy group, methylenic proton H_e appeared at δ 2.28–2.67, whereas methylenic proton H_f appeared at δ 1.43–1.76, thus providing the assigned regiochemistry (structure of cycloadducts **6ba**, **6bc** depicted in Fig. 3). The coupling constants J (H_d–H_e)=9.2–10.1 Hz and J (H_d–H_e)=5.2–6.7 Hz showing the cis and trans relation, respectively, could confirm the assigned stereochemistry. The existence of ROESY signals between the acetyl group (cycloadduct **6ba**) or the phenyl group (cycloadduct **6bc**) with the olefinic proton Hc further confirms the assigned stereochemistry (Fig. 4).

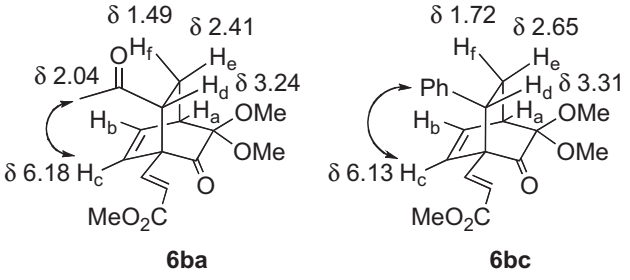


Fig. 4. Key signals of ROESY experiments of **6ba**, **6bc**.

The Diels–Alder reaction exhibits extremely high regioselectivity and stereoselectivity. There are four possible cycloadducts, as well as corresponding transition states (Fig. 5), but only one isomer is formed.[16] This extraordinary selectivity may be explained by invoking secondary orbital interactions. Additional and probably competitive, steric interactions developed at the *exo* TS between the substituent of the dienophile and the dimethoxy acetal group on the ethano bridge of the dienone can destabilize such an approach, favoring the *ortho-endo* TS.

At this stage, we turned our attention to eugenol **2e**, a naturally occurring phenol that has been used extensively as a flavoring agent and fragrance although pulmonary toxicity has been associated[15] with eugenol exposure. Eugenol can be activated, via a quinone methide, to form both DNA adducts and oxidative base damage, a fact that may contribute[17] to the observed toxic properties.

The reaction of eugenol **2e** with (diacetoxy)iodobenzene in methanol (Scheme 5) affords 2,2-dimethoxycyclohexa-3,5-dienone

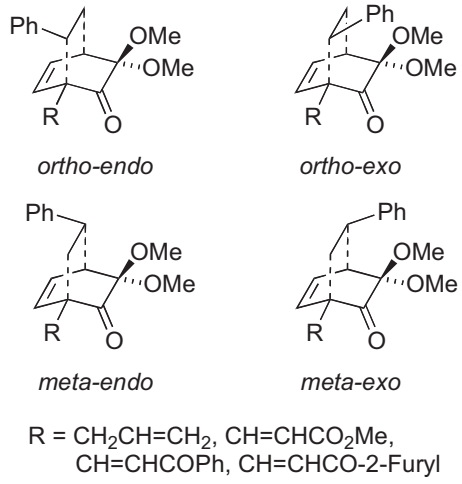
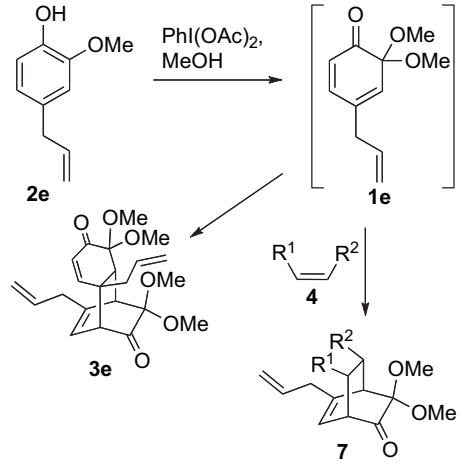


Fig. 5. The four possible transition states for the cycloaddition of dienone **4** and dienophile **4c**.



Scheme 5. Diels–Alder cycloadditions of dienone **1e**.

1e,[18] which dimerizes at room temperature to produce dimer **3e**,[19] a natural product with interesting biological properties. However, performing this oxidation reaction in the presence of an excess of dienophiles **4** yielded the expected cycloadducts **7** in good yields (Table 3). In all cases, the self-dimerization reaction of 2,2-dimethoxycyclohexa-3,5-dienone **1e** and the cycloaddition with the added dienophile is in competition to a varying degree. It is interesting to note that the oxidation of eugenol with (diacetoxy) iodobenzene in methanol, in the presence of styrene **4c**, phenylthioethylene (**4d**), takes place very smoothly at room temperature, to give a single product, as evidenced by TLC monitoring. These

Table 3
Diels–Alder reactions[a] of in situ-generated **1e** with olefinic dienophiles **4** via Scheme 5

Entry	Substituents		Time[b] (h)	Product	Yield[c] (%)
	R^1	R^2			
1	CH_3CO	H	65	**7ea**	79
2	CH_3CO_2	H	23	**7eb**	64
3	$C_6H_4CH_2$		9	**7ee**	18
4	1,8-$C_{10}H_6$		22	**7ef**	ca.100

[a] All reactions were carried out by stirring a solution of eugenol **2a** (2.3–2.6 mmol), (diacetoxy)iodobenzene (0.8 g, 2.5 mmol), appropriate dienophile **4** (0.74–10.1 mmol), and sodium hydrogen carbonate (0.25 g, 3.0 mmol) in methanol (25 mL) until complete disappearance (TLC) of the starting phenol.
[b] Time required for the complete consumption of phenol **1e**.
[c] Yield of isolated product after flash chromatography.

products could not be isolated, as even under mild conditions, they transformed into dimer **3e**. All attempts to use dimer **3e** as a source of dienone **1e** failed; instead it was found that dimer **3e** is stable under the reaction conditions (230 °C, *o*-xylene, sealed test-tube).

3. Conclusions

The Diels–Alder reactions of substituted 2,2-dimethoxycyclohexa-3,5-dienones with various electron-poor and electron-rich dienophiles have been studied. These cycloadditions provide easy access to highly substituted bicyclo[2.2.2]oct-5-en-2-ones. It should be pointed out that this Diels–Alder cycloaddition occurs with total regio- and stero-selectivity. Further transformations of these products will bring diversity to highly substituted compounds of chemical and biological interest.

In the absence of dienophiles, 2,2-dimethoxycyclohexa-3,5-dienones readily undergo self dimerization in a highly regio- and stereo-selective manner, one molecule acting as a diene the other as a dienophile. It may be concluded that the presence of electron-donating substituents at the C6 position of the dienone increased the propensity of the dienone to dimerize, making its intermolecular Diels–Alder reaction with dienophiles inefficient, while the same substituent at the C4 position of the dienone exerts an opposite effect. The thermolysis of the corresponding dimers constitutes an attractive alternative approach to the in situ-generated 2,2-dimethoxycyclohexa-3,5-dienones.

4. Experimental section

4.1. General

Melting points (uncorrected) were determined on a Buchi B-545 apparatus. For the IR spectra, a Perkin Elmer Spectrum GX FT-IR System spectrophotometer was used. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV-250, AV-400 and AV-500 instruments at the NMR center of the University of Ioannina. Elemental analyses were carried out by the Microanalytical Division of the Institute of Inorganic Chemistry, University of Wuerzburg. TLC analysis was conducted on precoated silica gel glass plates from Merck, Darmstadt, Germany. The spots were visualized either by UV irradiation (254 nm) or with a $KMnO_4$ solution. Silica gel (0.040–0.063 μm) from Merck, Darmstadt, Germany, was used for flash chromatography. All commercial reagents were used without further purification. Solvents were dried by standard methods and purified by distillation before use.

*4.1.1. Methyl (2E)-3-(2-hydroxy-3-methoxyphenyl)acrylate (**2b**).* A solution of *o*-vanillin (3.0 g, 19.7 mmol) and methyl (triphenylphosphoranylidene)acetate (6.7 g, 20.0 mmol) in toluene (50 mL) was heated to reflux and maintained for 45 h. The solvent was evaporated under reduced pressure, and the residue was recrystallized from EtOAc/pet. ether to afford phenol **2b** (2.46 g, 60%) as a white solid; mp 107–108 °C (EtOAc/pet. ether) [lit.[12] mp=106 °C]; R_f (CH_2Cl_2) 0.22; ν_{max} (KBr) 3312, 1707, 1624, 1475, 1317, 1266, 1222, 1179, 1083, 964, 908, 783 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.95 (d, *J*=16.2 Hz, 1H), 7.09 (dd, *J*=3.1, 6.4 Hz, 1H), 6.84–6.87 (m, 2H), 6.61 (d, *J*=16.2 Hz, 1H), 6.16 (br s, 1H), 3.91 (s, 3H), 3.80 (s, 3H); δ_C (62.5 MHz, $CDCl_3$) 168.4, 147.3, 145.8, 140.3, 121.4, 120.2, 119.3, 112.2, 56.7, 52.1.

*4.1.2. (2E)-1-Phenyl-3-(2-hydroxy-3-methoxyphenyl)prop-2-en-1-one (**2c**).* A 30% aqueous sodium hydroxide solution (10 mL) was added dropwise (~0.5 h) to a solution of *o*-vanillin (3.0 g, 19.7 mmol) and acetophenone (2.4 g, 20.0 mmol) in ethanol (20 mL). The resulting mixture was stirred overnight, acidified (pH 3) with dilute (5%) hydrochloric acid, and extracted with diethyl ether (2×100 mL). The combined organic layers were washed successively with water (2×100 mL), saturated $NaHSO_3$ solution (2×100 mL), water (2×100 mL), and dried (Na_2SO_4). The solvent was removed under reduced pressure, and the residue was recrystallized from ethanol to afford phenol **2c** (2.55 g, 51%) as a slight yellow solid; mp 109–111 °C (EtOH) [lit.[13] mp=110–111 °C]; R_f (CH_2Cl_2) 0.21; ν_{max} (KBr) 3288, 1650, 1586, 1475, 1447, 1230, 1076, 1005, 928, 862, 763 cm^{-1}; δ_H[13a] (250 MHz, $CDCl_3$) 8.02–8.08 (m, 3H), 7.75 (d, *J*=15.9 Hz, 1H), 7.47–7.58 (m, 3H), 7.20 (dd, *J*=3.7, 5.6 Hz, 1H), 6.88–6.90 (m, 2H), 6.32 (br s, 1H), 3.92 (s, 3H); δ_C (62.5 MHz, $CDCl_3$) 191.7, 147.4, 146.3, 140.6, 139.0, 133.1, 129.0, 124.0, 122.2, 121.8, 120.2, 112.4, 56.7.

*4.1.3. (2E)-1-(2-Furyl)-3-(2-hydroxy-3-methoxyphenyl)prop-2-en-1-one (**2d**).* A 30% aqueous sodium hydroxide solution (10 mL) was added dropwise (~0.5 h) to a solution of *o*-vanillin (3.0 g, 19.7 mmol) and 2-furyl methyl ketone (2.2 g, 20.0 mmol) in ethanol (60 mL). The resulting mixture was stirred overnight, acidified (pH 3) with dilute (5%) hydrochloric acid and extracted with diethyl ether (2×100 mL). The combined organic layers were washed successively with water (2×100 mL), saturated $NaHSO_3$ solution (2×100 mL), water (2×100 mL), and dried (Na_2SO_4). The solvent was removed under reduced pressure, and the residue was recrystallized from ethanol to afford phenol **2d** (3.36 g, 70%) as a slight yellow solid; mp 120–122 °C (EtOH); [found: C, 68.91; H, 5.02. $C_{14}H_{14}O_4$ requires C, 68.85; H, 4.95%]; R_f (CH_2Cl_2) 0.07; ν_{max} (KBr) 3381, 1655, 1592, 1468, 1365, 1331, 1254, 1075, 997, 922, 830, 768 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 8.08 (d, *J*=15.9 Hz, 1H), 7.61–7.62 (m, 1H), 7.61 (d, *J*=15.9 Hz, 1H), 7.29 (dd, *J*=0.6, 3.6 Hz, 1H), 7.16 (dd, *J*=3.2, 6.3 Hz, 1H), 6.84–6.86 (m, 2H), 6.55 (dd, *J*=1.7, 3.6 Hz, 1H), 6.28 (br s, 1H), 3.89 (s, 3H); δ_C (62.5 MHz, $CDCl_3$) 178.6, 153.9, 146.8, 146.4, 145.9, 139.2, 122.6, 121.8, 121.1, 119.7, 117.3, 112.3, 112.0, 56.2.

4.2. General experimental procedure for the preparation of dimers 3a–d

A solution of the appropriate phenol **2** (9.55–20.00 mmol) in methanol (30–80 mL) was slowly added to a stirring solution of (diacetoxy)iodobenzene (10.22–20.1 mmol) in methanol (30–60 mL). The resulting solution was stirred at room temperature for 1–17 h. The solvent was evaporated under reduced pressure and the residue was recrystallized from ethanol to afford dimer **3** as a white solid.

*4.2.1. 1,4,4a,8a-Tetrahydro-5,5,9,9-tetramethoxy-1,7-bis(2-propenyl)-1,4-ethanonaphthalene-6,10(4H)-dione (**3a**).* By following the above mentioned procedure, in which *o*-eugenol **2a** (3.28 g, 20.0 mmol) and (diacetoxy)iodobenzene (6.47 g, 20.1 mmol) were stirred at room temperature for 3 h, dimer **3a** (2.41 g, 62%) was isolated as a white solid; mp 122–124 °C (EtOH); [found: C, 68.11; H, 7.19. $C_{22}H_{28}O_6$ requires C, 68.02; H, 7.27%]; R_f (CH_2Cl_2) 0.02; ν_{max} (KBr) 2946, 2918, 1731, 1697, 1643, 1446, 1369, 1228, 1158, 1045, 995, 930, 887 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 6.15–6.25 (m, 2H), 5.66–5.98 (m, 2H), 5.54 (d, *J*=8.1 Hz, 1H), 5.05–5.17 (m, 4H), 3.43 (s, 3H), 3.36 (s, 3H), 3.19 (s, 3H), 3.14–3.26 (m, 1H), 3.04–3.12 (m, 3H), 3.00 (s, 3H), 2.86–2.97 (m, 1H), 2.64 (dd, *J*=5.8, 14.3 Hz, 1H), 2.35 (dd, *J*=8.3, 14.3 Hz, 1H); δ_C (62.5 MHz, $CDCl_3$) 203.4, 194.2, 139.5, 139.0, 134.5, 133.8, 132.6, 131.5, 118.4, 117.5, 94.8, 94.7, 57.2, 50.4, 50.2, 49.6, 48.9, 40.5, 39.7, 39.3, 34.1, 33.8.

*4.2.2. Dimethyl (2E,2E′)-3,3′-(5,5,9,9-tetramethoxy-6,10-dioxo-4a,5,6,8a-tetrahydro-1,4-ethanonaphthalene-1,7-diyl)bisacrylate (**3b**).* By following the above mentioned procedure, in which phenol **2b** (2.41 g, 11.46 mmol) and (diacetoxy)iodobenzene (3.87 g, 12.0 mmol) were stirred at room temperature for 1 h, dimer **3b** (1.42 g, 52%) was isolated as a white solid; mp

177–179 °C (EtOH); [found: C, 60.65; H, 5.98. $C_{24}H_{28}O_{10}$ requires C, 60.50; H, 5.92%]; R_f (20% EtOAc/CH_2Cl_2) 0.52; ν_{max} (KBr) 2952, 2839, 1723, 1633, 1440, 1290, 1175, 1122, 1052, 994, 854 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.21 (d, J=16.3 Hz, 1H), 7.07 (d, J=16.0 Hz, 1H), 6.55 (d, J=16.0 Hz, 1H), 6.44 (d, J=3.8 Hz, 1H), 6.26–6.32 (m, 1H), 5.96 (d, J=16.3 Hz, 1H), 5.90 (d, J=8.3 Hz, 1H), 3.80 (s, 3H), 3.74 (s, 3H), 3.45 (s, 3H), 3.40 (s, 3H), 3.33–3.37 (m, 2H), 3.19 (s, 3H), 3.15–3.19 (m, 1H), 3.02 (s, 3H); δ_C (62.5 MHz, $CDCl_3$) 199.5, 193.3, 167.0, 165.5, 146.7, 141.9, 137.8, 135.9, 132.6, 128.6, 124.7, 121.4, 98.9, 94.7, 58.5, 51.8, 51.6, 50.4, 50.3, 49.7, 48.9, 43.6, 39.7, 39.4.

*4.2.3. 5,5,9,9-Tetramethoxy-1,7-bis[(1E)-3-oxo-3-phenylprop-1-enyl]-1,4a,5,8a-tetrahydro-1,4-ethanonaphthalene-6,10(4H)-dione (**3c**).* By following the above mentioned procedure, in which phenol **2c** (4.77 g, 18.8 mmol) and (diacetoxy)iodobenzene (6.20 g, 19.3 mmol) were stirred at room temperature for 1 h, dimer **3c** (2.24 g, 42%) was isolated as a white solid; mp 187–189 °C (EtOH); [found: C, 71.61; H, 5.61. $C_{34}H_{32}O_8$ requires C, 71.82; H, 5.67%]; R_f (20% EtOAc/CH_2Cl_2) 0.36; ν_{max} (KBr) 3063, 2949, 2836, 1710, 1668, 1606, 1450, 1298, 1218, 1162, 1048, 776 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.92–7.98 (m, 4H), 7.77 (d, J=15.6 Hz, 1H), 7.42–7.62 (m, 6H), 7.16–7.28 (m 2H), 7.03 (d, J=16.1 Hz, 1H), 6.63 (d, J=4.3 Hz, 1H), 6.35–6.41 (m, 1H), 6.07 (d, J=7.9 Hz, 1H), 3.52–3.55 (m, 1H), 3.50 (s, 3H), 3.45 (s, 3H), 3.41–3.43 (m, 1H), 3.25 (s, 3H), 3.23–3.24 (m, 1H), 3.08 (s, 3H); δ_C (62.5 MHz, $CDCl_3$) 200.3, 194.6, 190.7, 190.1, 148.9, 142.1, 138.1, 137.9, 137.8, 137.1, 133.8, 133.6, 133.4, 129.9, 129.4, 129.3, 129.2, 129.1, 129.0, 125.5, 99.8, 95.5, 59.8, 51.2, 51.1, 50.4, 49.7, 44.8, 40.5, 40.1.

*4.2.4. 1,7-Bis[(1E)-3-(furan-2-yl)-3-oxoprop-1-en-1-yl]-5,5,9,9-tetramethoxy-1,4a,5,8a-tetrahydro-1,4-ethanonaphthalene-6,10(4H)-dione (**3d**).* By following the above mentioned procedure, in which phenol **2d** (2.33 g, 9.55 mmol) and (diacetoxy)iodobenzene (3.29 g, 10.22 mmol) were stirred at room temperature for 17 h, dimer **3d** (1.26 g, 48%) was isolated as a white solid; mp 162–164 °C (EtOH); [found: C, 65.80; H, 5.24. $C_{30}H_{28}O_{10}$ requires C, 65.69; H, 5.15%]; R_f (20% EtOAc/CH_2Cl_2) 0.15; ν_{max} (KBr) 3088, 2947, 2839, 1730, 1663, 1605, 1464, 1393, 1310, 1220, 1164, 1052, 917, 881, 768 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.53–7.63 (m, 3H), 7.17–7.38 (m, 4H), 6.94 (d, J=16.1 Hz, 1H), 6.52–6.61 (m, 3H), 6.31–6.36 (m, 1H), 6.03 (d, J=7.9 Hz, 1H), 3.46 (s, 3H), 3.42 (s, 3H), 3.32–3.56 (m, 2H), 3.21 (s, 3H), 3.14–3.27 (m, 1H), 3.05 (s, 3H); δ_C (62.5 MHz, $CDCl_3$) 199.6, 194.0, 177.8, 176.6, 153.3, 153.0, 148.7, 147.1, 147.0, 140.8, 136.7, 136.3, 132.8, 129.2, 128.2, 124.4, 118.5, 118.2, 112.8, 112.5, 99.2, 94.9, 59.1, 50.6, 50.5, 49.9, 49.1, 44.1, 39.9, 39.6.

4.3. General experimental procedure for the Diels–Alder cycloadditions of 6-allyl-2,2-dimethoxycyclohexa-3,5-dienone (1a) with olefinic dienophiles 4

A mixture of dimer **3a** (0.39 g, 1.0 mmol), an excess of the appropriate dienophile **4** (7.35–10.60 mmol) in *o*-xylene (3 mL) was heated at 230 °C in a sealed test-tube for 6–43 h. The solvent was evaporated under reduced pressure and the residue was flash chromatographed on silica gel (CH_2Cl_2) to afford cycloadducts **5**.

*4.3.1. 7-Acetyl-1-allyl-3,3-dimethoxybicyclo[2.2.2]oct-5-en-2-one (**5aa**).* By following the above mentioned procedure, in which dimer **3a** (0.39 g, 1.0 mmol) and 1-buten-3-one (**4a**) (0.71 g, 10.1 mmol) were heated at 230 °C for 29 h, cycloadduct **5aa** (0.39 g, 74%) was isolated as a colorless oil; [found: C, 68.04; H, 7.70. $C_{15}H_{20}O_4$ requires C, 68.16; H, 7.63%]; R_f (CH_2Cl_2) 0.18; ν_{max} (liquid film) 2945, 2835, 1735, 1710, 1640, 1440, 1360, 1220, 1150, 1010, 880 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 6.32 (dd, J=7.0, 8.0 Hz, 1H), 5.93–5.98 (m, 1H), 5.74–5.89 (m, 1H), 4.95–5.02 (m, 2H), 3.32 (s, 3H), 3.30 (s, 3H), 3.08–3.14 (m, 1H), 2.96 (dd, J=7.0, 10.2 Hz, 1H), 2.31–2.65 (m, 3H), 2.06 (s, 3H), 1.31 (ddd, J=2.8, 7.0, 12.4 Hz, 1H); δ_C (62.5 MHz, $CDCl_3$) 206.6, 200.7, 134.1, 132.1130.9, 118.0, 93.9, 53.8, 49.9, 49.8, 48.0, 38.0, 33.3, 30.4, 27.6.

*4.3.2. Methyl 1-allyl-8,8-dimethoxy-7-oxobicyclo[2.2.2]oct-5-en-2-carboxylate (**5ab**).* By following the above mentioned procedure, in which dimer **3a** (0.39 g, 1.0 mmol) and methyl acrylate **4b** (0.91 g, 10.6 mmol) were heated at 230 °C for 19 h, cycloadduct **5ab** (0.46 g, 82%) was isolated as a colorless oil; [found: C, 64.41; H, 7.31. $C_{15}H_{20}O_5$ requires C, 64.27; H, 7.19%]; R_f (CH_2Cl_2) 0.08; ν_{max} (liquid film) 2920, 2849, 1738, 1640, 1440, 1357, 1199, 1149, 1056, 999, 921, 888 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 6.39 (dd, J=7.2, 8.0 Hz, 1H), 5.69–5.99 (m, 2H), 4.97–5.10 (m, 2H), 3.58 (s, 3H), 3.27 (s, 3H), 3.26 (s, 3H), 3.07–3.11 (m, 1H), 2.77 (dd, J=6.5, 9.9 Hz, 1H), 2.27–2.55 (m, 3H), 1.51 (ddd, J=2.8, 6.5, 12.7 Hz, 1H); δ_C (100 MHz, $CDCl_3$) 200.5, 173.4, 133.8, 133.5, 129.4, 118.1, 93.7, 53.4, 51.5, 49.9, 41.9, 38.1, 33.8, 28.2.

*4.3.3. 1-Allyl-3,3-dimethoxy-7-phenylbicyclo[2.2.2]oct-5-en-2-one (**5ac**).* By following the above mentioned procedure, in which dimer **3a** (0.39 g, 1.0 mmol) and styrene **4c** (1.0 g, 9.6 mmol) were heated at 230 °C for 43 h, cycloadduct **5ac** (0.57 g, 95%) was isolated as a colorless oil; [found: C, 76.55; H, 7.50. $C_{19}H_{22}O_3$ requires C, 76.48; H, 7.43%]; R_f (CH_2Cl_2) 0.31; ν_{max} (liquid film) 3060, 2940, 1735, 1493, 1453, 1149, 1056, 766, 734 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.08–7.19 (m, 5H), 6.62 (dd, J=7.2, 8.1 Hz, 1H), 6.00 (d, J=8.1 Hz, 1H), 5.66–5.78 (m, 1H), 4.91–4.94 (m, 1H), 4.78–4.82 (m, 1H), 3.42 (s, 3H), 3.37 (s, 3H), 3.19–3.21 (m, 1H), 3.04 (dd, J=6.7, 9.6 Hz, 1H), 2.61 (ddd, J=2.8, 9.6, 10.1 Hz, 1H), 2.35 (dd, J=6.1, 14.3 Hz, 1H), 1.81 (dd, J=8.0, 14.2 Hz, 1H), 1.65 (ddd, J=2.8, 6.6, 13.2 Hz, 1H); δ_C (100 MHz, $CDCl_3$) 202.4, 143.1, 134.6, 134.5, 128.9, 128.3, 126.9, 117.8, 94.0, 56.0, 50.3, 49.7, 44.7, 38.9, 34.4, 33.4.

*4.3.4. 1-Allyl-3,3-dimethoxy-7-(phenylthio)bicyclo[2.2.2]oct-5-en-2-one (**5ad**).* By following the above mentioned procedure, in which dimer **3a** (0.39 g, 1.0 mmol) and phenylthioethylene (**4d**) (1.0 g, 7.35 mmol) were heated at 230 °C for 25 h, cycloadduct **5ad** (0.51 g, 77%) was isolated as a colorless oil; [found: C, 68.95; H, 6.82. $C_{19}H_{22}O_3S$ requires C, 69.06; H, 6.71%]; R_f (CH_2Cl_2) 0.31; ν_{max} (liquid film) 3062, 2967, 2941, 1735, 1475, 1437, 1149, 1059, 997, 921, 733 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.35–7.59 (m, 5H), 6.62–6.68 (m, 1H), 5.99–6.17 (m, 2H), 5.25–5.45 (m, 2H), 3.64–3.75 (m, 1H), 3.50 (s, 3H), 3.48 (s, 3H), 3.23–3.29 (m, 1H), 2.90–2.98 (m, 1H), 2.73–2.84 (m, 2H), 1.85–1.94 (m, 1H); δ_C (62.5 MHz, $CDCl_3$) 201.7, 135.5, 135.1, 133.8, 131.1, 129.3, 128.8, 126.7, 118.4, 93.8, 56.5, 50.2, 49.4, 47.8, 47.6, 37.7, 34.2.

*4.3.5. 4-Allyl-11,11-dimethoxy-4,4a,9,9a-tetrahydro-1H-1,4-ethanofluoren-10-one (**5ae**).* By following the above mentioned procedure, in which dimer **3a** (0.39 g, 1.0 mmol) and indene **4e** (1.16 g, 10.0 mmol) were heated at 230 °C for 6 h, cycloadduct **5ae** (0.60 g, 97%) was isolated as a colorless oil; [found: C, 77.31; H, 7.21. $C_{20}H_{22}O_3$ requires C, 77.39; H, 7.14%]; R_f (CH_2Cl_2) 0.19; ν_{max} (liquid film) 3069, 2948, 2837, 1734, 1638, 1439, 1228, 1149, 1057, 994, 916, 846, 733 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.32–7.35 (m, 1H), 7.12–7.22 (m, 3H), 6.27–6.34 (m, 1H), 5.92–6.09 (m, 1H), 5.76 (dd, J=1.0, 8.3 Hz, 1H), 5.12–5.23 (m, 2H), 3.55 (d, J=9.2 Hz, 1H), 3.47 (s, 3H), 3.38 (s, 3H), 3.13–3.36 (m, 4H), 2.71–2.84 (m, 2H); δ_C (62.5 MHz, $CDCl_3$) 203.7, 144.7, 141.4, 134.8, 131.9, 131.0, 127.3, 126.5, 125.9, 124.4, 117.9, 94.0, 56.2, 51.6, 50.3, 49.7, 43.1, 37.6, 36.9, 34.0.

*4.3.6. 10-Allyl-12,12-dimethoxy-6b,7,10,10a-tetrahydro-7,10-ethanofluornanthen-11-one (**5af**).* By following the above mentioned procedure, in which dimer **3a** (0.39 g, 1.0 mmol) and acenaphthylene **4f** (1.52 g, 10.0 mmol) were heated at 230 °C for 18 h, cycloadduct **5af** (0.48 g, 68%) was isolated as a colorless oil; [found: C, 79.64; H, 6.29. $C_{23}H_{22}O_3$ requires C, 79.44; H, 6.40%]; R_f (CH_2Cl_2) 0.20; ν_{max} (liquid film) 3050, 2960, 2832, 1730, 1597, 1459, 1421, 1367, 1234, 1143, 1054,

912, 835, 791 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.64–7.71 (m, 2H), 7.45–7.54 (m, 3H), 7.34 (d, *J*=7.0 Hz, 1H), 6.10–6.22 (m, 1H), 5.93–6.00 (m, 1H), 5.52 (d, *J*=8.2 Hz, 1H), 5.24–5.37 (m, 2H), 4.31 (dd, *J*=1.9, 7.3 Hz, 1H), 3.94 (d, *J*=7.3 Hz, 1H), 3.70–3.74 (m, 1H), 3.62 (s, 3H), 3.45 (s, 3H), 2.94 (d, *J*=6.7 Hz, 2H); δ_C (62.5 MHz, $CDCl_3$) 203.4, 145.7, 143.3, 141.0, 134.6, 131.6, 131.1, 129.7, 127.7, 127.6, 123.5, 122.8, 121.4, 118.2, 93.8, 55.9, 50.1, 49.8, 48.7, 44.6, 43.1, 33.5.

4.4. General experimental procedure for the Diels–Alder cycloadditions of dimers 3b–d with olefinic dienophiles 4

A mixture of dimers **3b**–**d** (0.21–0.58 mmol), an excess of the appropriate dienophile **4** (2.33–6.05 mmol) in *o*-xylene (3 mL) was heated at 230 °C in a sealed test-tube for 5.5–18 h. The solvent was evaporated under reduced pressure and the residue was flash chromatographed on silica gel (CH_2Cl_2, (4:1) CH_2Cl_2/EtOAc) to afford cycloadducts **6**.

*4.4.1. (E)-Methyl 3-(6-ethanoyl-3,3-dimethoxy-2-oxobicyclo-[2.2.2] oct-7-en-1-yl)prop-2-enoate (**6ba**).* By following the above mentioned procedure, in which dimer **3b** (0.24 g, 0.5 mmol) and 1-buten-3-one (**4a**) (0.35 g, 5.0 mmol) were heated at 230 °C for 15 h, cycloadduct **6ba** (0.23 g, 74%) was isolated as a white solid; mp 131–133 °C (EtOH); [found: C, 62.21; H, 6.37. $C_{16}H_{20}O_6$ requires C, 62.33; H, 6.54%]; R_f (20% EtOAc/CH_2Cl_2) 0.58; ν_{max} (KBr) 2970, 2946, 2841, 1714, 1661, 1436, 1367, 1330, 1297, 1204, 1152, 1049, 1017, 981 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.08 (d, *J*=16.3 Hz, 1H), 6.47 (dd, *J*=8.0, 8.1 Hz, 1H), 6.18 (d, *J*=8.1 Hz, 1H), 5.95 (d, *J*=16.3 Hz, 1H), 3.72 (s, 3H), 3.33 (s, 3H), 3.29 (s, 3H), 3.24 (dd, *J*=6.8, 10.1 Hz, 1H) 3.19–3.21 (m, 1H), 2.41 (ddd, *J*=3.0, 10.1, 12.7 Hz, 1H), 2.04 (s, 3H), 1.49 (ddd, *J*=2.8, 6.8, 12.7 Hz, 1H); δ_C (125 MHz, $CDCl_3$) 205.6, 197.8, 165.9, 143.0, 133.5, 127.2, 123.7, 93.8, 55.7, 51.6, 50.9, 50.2, 49.8, 38.1, 30.4, 26.6.

*4.4.2. (E)-6-Ethanoyl-3,3-dimethoxy-1-(3-oxo-3-phenylprop-1-enyl)-bicyclo[2.2.2]oct-7-en-2-one (**6ca**).* By following the above mentioned procedure, in which dimer **3c** (0.29 g, 0.51 mmol) and 1-buten-3-one (**4a**) (0.35 g, 5.0 mmol) were heated at 230 °C for 18 h, cycloadduct **6ca** (0.30 g, 83%) was isolated as a white solid; mp 141–142 °C (EtOH); [found: C, 71.50; H, 6.50. $C_{21}H_{22}O_5$ requires C, 71.17; H, 6.26%]; R_f (20% EtOAc/CH_2Cl_2) 0.47; ν_{max} (KBr) 3058, 2960, 1737, 1711, 1671, 1625, 1446, 1336, 1302, 1212, 1150, 1052, 1016, 983, 768 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.88–7.92 (m, 2H), 7.40–7.53 (m, 3H), 7.11 (d, *J*=16.1 Hz, 1H), 6.95 (d, *J*=16.1 Hz, 1H), 6.47–6.53 (m, 1H), 6.27 (d, *J*=8.3 Hz, 1H), 3.34 (s, 3H), 3.30 (s, 3H), 3.20–3.27 (m, 2H), 2.36–2.47 (m, 1H), 2.03 (s, 3H), 1.52 (ddd, *J*=2.8, 6.7, 12.7 Hz, 1H); δ_C (62.5 MHz, $CDCl_3$) 205.9, 198.0, 190.0, 142.8, 137.4, 133.6, 132.8, 128.6, 128.5, 128.3, 127.5, 93.9, 56.1, 51.1, 50.2, 49.9, 38.2, 30.6, 26.7.

*4.4.3. (E)-6-Ethanoyl-1-(3-(furan-2-yl)-3-oxoprop-1-enyl)-3,3-dimethoxybicyclo[2.2.2]oct-7-en-2-one (**6da**).* By following the above mentioned procedure, in which dimer **3d** (0.28 g, 0.51 mmol) and 1-buten-3-one (**4a**) (0.35 g, 5.0 mmol) were heated at 230 °C for 18 h, cycloadduct **6da** (0.29 g, 83%) was isolated as a white solid; mp 158–160 °C (EtOH); [found: C, 66.31; H, 5.94. $C_{19}H_{20}O_6$ requires C, 66.27; H, 5.85%]; R_f (20% EtOAc/CH_2Cl_2) 0.35; ν_{max} (KBr) 2978, 2947, 1737, 1709, 1667, 1624, 1462, 1397, 1339, 1304, 1216, 1153, 1057, 983, 785 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.52 (dd, *J*=0.7, 1.7 Hz, 1H), 7.17 (dd, *J*=0.7, 3.6 Hz, 1H), 7.10 (br s, 1H), 6.82 (d, *J*=16.1 Hz, 1H), 6.45 (dd, *J*=1.7, 3.6 Hz, 1H), 6.40 (d, *J*=7.2 Hz, 1H), 6.19 (d, *J*=8.3 Hz, 1H), 3.25 (s, 3H), 3.21 (s, 3H), 3.10–3.17 (m, 2H), 2.28–2.39 (m, 1H), 1.95 (s, 3H), 1.43 (ddd, *J*=2.8, 6.7, 12.7 Hz, 1H); δ_C (62.5 MHz, $CDCl_3$) 205.7, 197.8, 176.8, 152.8, 146.7, 142.1, 133.5, 127.3, 127.0, 118.1, 112.3, 93.8, 55.9, 51.0, 50.1, 49.7, 38.1, 30.4, 26.5.

*4.4.4. (E)-Methyl 5,5-dimethoxy-1-(3-methoxy-3-oxoprop-1-enyl)-6-oxobicyclo[2.2.2]oct-7-ene-2-carboxylate (**6bb**).* By following the above mentioned procedure, in which dimer **3b** (0.10 g, 0.21 mmol) and methyl acrylate **4b** (0.20 g, 2.33 mmol) were heated at 230 °C for 18 h, cycloadduct **6bb** (0.10 g, 71%) was isolated as a colorless oil; [found: C, 59.51; H, 6.50. $C_{16}H_{20}O_7$ requires C, 59.25; H, 6.22%]; R_f (20% EtOAc/CH_2Cl_2) 0.34; ν_{max} (liquid film) 2951, 1740, 1439, 1321, 1283, 1198, 1177, 1151, 1057, 984, 737 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.14 (d, *J*=16.3 Hz, 1H), 6.51–6.57 (m, 1H), 6.10 (d, *J*=8.3 Hz, 1H), 5.94 (d, *J*=16.3 Hz, 1H), 3.72 (s, 3H), 3.54 (s, 3H), 3.30 (s, 3H), 3.28 (s, 3H), 3.16–3.22 (m, 1H), 3.06 (dd, *J*=6.4, 9.9 Hz, 1H), 2.31–2.41 (m, 1H), 1.65 (ddd, *J*=2.8, 6.4, 12.9 Hz, 1H); δ_C (62.5 MHz, $CDCl_3$) 197.6, 172.5, 165.9, 142.8, 134.7, 126.3, 123.4, 93.8, 55.7, 51.8, 51.6, 50.2, 49.9, 44.0, 38.2, 27.1.

*4.4.5. (E)-Methyl 5,5-dimethoxy-6-oxo-1-(3-oxo-3-phenylprop-1-enyl)bicyclo[2.2.2]oct-7-ene-2-carboxylate (**6cb**).* By following the above mentioned procedure, in which dimer **3c** (0.33 g, 0.58 mmol) and methyl acrylate **4b** (0.52 g, 6.05 mmol) were heated at 230 °C for 16 h, cycloadduct **6cb** (0.25 g, 58%) was isolated as a colorless oil; [found: C, 68.39; H, 5.72. $C_{21}H_{22}O_6$ requires C, 68.10; H, 5.99%]; R_f (CH_2Cl_2) 0.10; ν_{max} (liquid film) 3059, 2949, 1732, 1674, 1626, 1448, 1335, 1300, 1213, 1148, 1058, 980, 770 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.87–7.93 (m, 2H), 7.41–7.57 (m, 3H), 7.15 (d, *J*=16.2 Hz, 1H), 6.93 (d, *J*=16.2 Hz, 1H), 6.56–6.62 (m, 1H), 6.23 (d, *J*=8.3 Hz, 1H), 3.53 (s, 3H), 3.33 (s, 3H), 3.31 (s, 3H), 3.20–3.24 (m, 1H), 3.14 (dd, *J*=6.4, 9.9 Hz, 1H), 2.35–2.45 (m, 1H), 1.70 (ddd, *J*=2.8, 6.4, 12.8 Hz, 1H); δ_C (62.5 MHz, $CDCl_3$) 197.7, 190.2, 172.6, 142.5, 137.3, 134.8, 132.8, 128.7, 128.5, 128.2, 126.6, 93.8, 56.1, 51.8, 50.2, 49.9, 44.2, 38.3, 27.2.

*4.4.6. (E)-Methyl 1-(3-(furan-2-yl)-3-oxoprop-1-enyl)-5,5-dimethoxy-6-oxobicyclo[2.2.2]oct-7-ene-2-carboxylate (**6db**).* By following the above mentioned procedure, in which dimer **3d** (0.28 g, 0.51 mmol) and methyl acrylate **4b** (0.43 g, 5.0 mmol) were heated at 230 °C for 18 h, cycloadduct **6db** (0.21 g, 91%) was isolated as a white solid; mp 56–58 °C ($CHCl_3$/pet. ether); [found: C, 63.21; H, 5.51. $C_{19}H_{20}O_7$ requires C, 63.33; H, 5.59%]; R_f (20% EtOAc/CH_2Cl_2) 0.37; ν_{max} (KBr) 2953, 2841, 1735, 1670, 1626, 1565, 1464, 1395, 1330, 1162, 1057, 885, 763 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.55 (dd, *J*=0.7, 1.7 Hz, 1H), 7.18–7.24 (m, 2H), 6.82 (d, *J*=16.2 Hz, 1H), 6.53 (d, *J*=7.9 Hz, 1H), 6.48 (dd, *J*=1.7, 3.6 Hz, 1H), 6.15 (d, *J*=8.3 Hz, 1H), 3.45 (s, 3H), 3.26 (s, 3H), 3.23 (s, 3H), 3.12–3.19 (m, 1H), 3.04–3.10 (m, 1H), 2.28–2.38 (m, 1H), 1.62 (ddd, *J*=2.8, 6.4, 12.9 Hz, 1H); δ_C (62.5 MHz, $CDCl_3$) 197.6, 177.0, 172.5, 152.8, 146.8, 141.8, 134.7, 126.9, 126.4, 118.2, 112.4, 93.7, 55.9, 51.7, 50.1, 49.8, 44.1, 38.2, 27.1.

*4.4.7. (E)-Methyl 3-(3,3-dimethoxy-2-oxo-6-phenylbicyclo-[2.2.2] oct-7-en-1-yl)prop-2-enoate (**6bc**).* By following the above mentioned procedure, in which dimer **3b** (0.16 g, 0.34 mmol) and styrene **4c** (0.35 g, 3.37 mmol) were heated at 230 °C for 16 h, cycloadduct **6bc** (0.21 g, 91%) was isolated as a colorless oil; [found: C, 70.41; H, 6.66. $C_{20}H_{22}O_5$ requires C, 70.16; H, 6.48%]; R_f (20% EtOAc/CH_2Cl_2) 0.58; ν_{max} (liquid film) 3059, 2947, 1730, 1439, 1317, 1279, 1198, 1177, 1150, 1057, 735, 704 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 7.15–7.22 (m, 3H), 7.05–7.07 (m, 2H), 7.00 (d, *J*=16.3 Hz, 1H), 6.72–6.74 (m, 1H), 6.13 (d, *J*=8.3 Hz, 1H), 5.49 (d, *J*=16.3 Hz, 1H), 3.62 (s, 3H), 3.41 (s, 3H), 3.36 (s, 3H), 3.31 (dd, *J*=6.7, 9.7 Hz, 1H), 3.27–3.29 (m, 1H), 2.65 (ddd, *J*=3.0, 9.7, 13.4 Hz, 1H), 1.72 (ddd, *J*=2.8, 6.7, 13.4 Hz, 1H); δ_C (125 MHz, $CDCl_3$) 199.2, 165.9, 143.5, 141.9, 135.5, 128.5, 128.2, 127.1, 126.6, 123.0, 93.9, 58.6, 51.4, 50.4, 49.8, 45.3, 38.8, 32.0.

*4.4.8. (E)-3,3-Dimethoxy-1-(3-oxo-3-phenylprop-1-enyl)-6-phenylbicyclo[2.2.2]oct-7-en-2-one (**6cc**).* By following the above mentioned procedure, in which dimer **3c** (0.29 g, 0.51 mmol) and styrene **4c** (0.52 g, 5.0 mmol) were heated at 230 °C for 17 h,

cycloadduct **6cc** (0.36 g, 90%) was isolated as a colorless oil; [found: C, 77.51; H, 6.06. $C_{25}H_{24}O_4$ requires C, 77.30; H, 6.23%]; R_f (20% EtOAc/CH_2Cl_2) 0.58; ν_{max} (liquid film) 3059, 2945, 1736, 1713, 1672, 1626, 1450, 1302, 1217, 1150, 1057, 982, 770 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.44–7.50 (m, 3H), 7.18–7.36 (m, 5H), 7.10–7.13 (m, 2H), 7.00 (d, *J*=16.3 Hz, 1H), 6.73–6.79 (m, 1H), 6.40 (d, *J*=16.3 Hz, 1H), 6.23 (d, *J*=8.2 Hz, 1H), 3.42 (s, 3H), 3.37 (s, 3H), 3.29–3.32 (m, 2H), 2.63–2.7 (m, 1H),1.76 (ddd, *J*=2.7, 6.7, 13.3 Hz, 1H); δ_C (62.5 MHz, $CDCl_3$) 199.1, 190.8, 143.3, 142.2, 137.3, 135.5, 132.4, 128.7, 128.6, 128.5, 128.3, 128.1, 127.1, 126.8, 93.9, 58.9, 50.3, 49.8, 45.5, 38.7, 32.1.

*4.4.9. (E)-1-(3-(Furan-2-yl)-3-oxoprop-1-enyl)-3,3-dimethoxy-6-phenylbicyclo[2.2.2]oct-7-en-2-one (**6dc**).* By following the above mentioned procedure, in which dimer **3d** (0.28 g, 0.51 mmol) and styrene **4c** (0.52 g, 5.0 mmol) were heated at 230 °C for 18 h, cycloadduct **6dc** (0.16 g, 41%) was isolated as a white solid; mp 61–63 °C (EtOAc/pet. ether); [found: C, 73.09; H, 5.81. $C_{23}H_{22}O_5$ requires C, 73.00; H, 5.86%]; R_f (20% EtOAc/CH_2Cl_2) 0.51; ν_{max} (KBr) 2950, 1735, 1669, 1623, 1567, 1464, 1394, 1317, 1152, 1054, 767, 706 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.51 (dd, *J*=0.8, 1.7 Hz, 1H), 7.05–7.20 (m, 6H), 6.91 (d, *J*=3.6 Hz, 1H), 6.70–6.76 (m, 1H), 6.44 (dd, *J*=1.7, 3.6 Hz, 1H), 6.33 (d, *J*=16.2 Hz, 1H), 6.19 (d, *J*=8.2 Hz, 1H), 3.40 (s, 3H), 3.35 (s, 3H), 3.26–3.37 (m, 2H), 2.60–2.70 (m, 1H), 1.73 (ddd, *J*=2.8, 6.6, 13.3 Hz, 1H); δ_C (62.5 MHz, $CDCl_3$) 199.2, 177.3, 152.8, 146.6, 142.7, 142.1, 135.5, 128.7, 128.3, 127.4, 127.3, 127.2, 118.0, 112.2, 94.1, 59.0, 50.5, 49.9, 45.7, 38.9, 32.0.

*4.4.10. (E)-Methyl 3-(3,3-dimethoxy-2-oxo-6-(phenylthio)bicyclo[2.2.2]oct-7-en-1-yl)prop-2-enoate (**6bd**).* By following the above mentioned procedure, in which dimer **3b** (0.24 g, 0.5 mmol) and phenylthioethylene (**4d**) (0.68 g, 5.0 mmol) were heated at 230 °C for 15 h, cycloadduct **6bd** (0.35 g, 95%) was isolated as a colorless oil; [found: C, 64.50; H, 6.11. $C_{20}H_{22}O_5S$ requires C, 64.15; H, 5.92%]; R_f (20% EtOAc/CH_2Cl_2) 0.61; ν_{max} (liquid film) 3061, 2949, 2839, 1724, 1655, 1634, 1583, 1475, 1439, 1315, 1274, 1192, 1152, 1059, 980 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.14–7.27 (m, 5H), 6.91 (d, *J*=16.2 Hz, 1H), 6.50–6.56 (m, 1H), 6.15 (d, *J*=8.2 Hz, 1H), 5.99 (d, *J*=16.2 Hz, 1H), 3.64–3.73 (m, 1H), 3.61 (s, 3H), 3.27 (s, 3H), 3.23 (s, 3H), 3.06–3.08 (m, 1H), 2.58–2.68 (m, 1H), 1.49–1.48 (m, 1H); δ_C (62.5 MHz, $CDCl_3$) 198.7, 165.6, 142.7, 134.9, 134.6, 131.7, 128.7, 126.9, 125.9, 123.6, 93.6, 59.1, 51.3, 50.2, 49.5, 47.9, 37.8, 31.4.

*4.4.11. (E)-3,3-Dimethoxy-1-(3-oxo-3-phenylprop-1-enyl)-6-(phenylthio)bicyclo[2.2.2]oct-7-en-2-one (**6cd**).* By following the above mentioned procedure, in which dimer **3c** (0.29 g, 0.51 mmol) and phenylthioethylene (**4d**) (0.71 g, 5.22 mmol) were heated at 230 °C for 16 h, cycloadduct **6cd** (0.43 g, ca. 100%) was isolated as a colorless oil; [found: C, 71.12; H, 5.91. $C_{25}H_{24}O_4S$ requires C, 71.40; H, 5.75%]; R_f (20% EtOAc/CH_2Cl_2) 0.61; ν_{max} (liquid film) 3030, 2946, 2836, 1738, 1671, 1625, 1475, 1446, 1332, 1300, 1217, 1149, 1061, 977, 737 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.85 (dd, *J*=1.5, 7.0 Hz, 2H), 7.38–7.56 (m, 3H), 7.27–7.30 (m, 2H), 7.11–7.21 (m, 3H), 6.98 (s, 2H), 6.59–6.65 (m, 1H), 6.31 (d, *J*=8.3 Hz, 1H), 3.75 (dd, *J*=5.2, 9.2 Hz, 1H), 3.33 (s, 3H), 3.31 (s, 3H), 3.13–3.16 (m, 1H), 2.70 (ddd, *J*=2.7, 9.2, 13.8 Hz, 1H), 1.67 (ddd, *J*=3.3, 5.2, 13.8 Hz, 1H); δ_C (62.5 MHz, $CDCl_3$) 199.0, 190.6, 143.1, 137.5, 135.0, 134.7, 132.5, 131.8, 128.9, 128.8, 128.7, 128.3, 127.2, 126.5, 93.8, 59.6, 50.4, 49.7, 48.4, 38.0, 31.8.

*4.4.12. (E)-1-(3-(Furan-2-yl)-3-oxoprop-1-enyl)-3,3-dimethoxy-6-(phenylthio)bicyclo[2.2.2]oct-7-en-2-one (**6dd**).* By following the above mentioned procedure, in which dimer **3d** (0.28 g, 0.51 mmol) and phenylthioethylene (**4d**) (0.68 g, 5.0 mmol) were heated at 230 °C for 16 h, cycloadduct **6dd** (0.33 g, 79%) was isolated as a colorless oil; [found: C, 67.22; H, 5.35. $C_{23}H_{22}O_5S$ requires C, 67.30; H, 5.40%]; R_f (20% EtOAc/CH_2Cl_2) 0.43; ν_{max} (liquid film) 3060, 2945, 2837, 1737, 1669, 1624, 1568, 1467, 1393, 1311, 1267, 1152, 1055, 978,748 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.53 (dd, *J*=0.8, 1.7 Hz, 1H), 7.20–7.25 (m, 2H), 7.06–7.16 (m, 5H), 6.89 (d, *J*=16.1 Hz, 1H), 6.52–6.58 (m, 1H), 6.46 (dd, *J*=1.7, 3.6 Hz, 1H), 6.25 (d, *J*=8.3 Hz, 1H), 3.67–3.73 (m, 1H), 3.27 (s, 3H), 3.24 (s, 3H), 3.05–3.11 (m, 1H), 2.59–2.69 (m, 1H), 1.59 (ddd, *J*=3.3, 5.2, 13.9 Hz, 1H); δ_C (62.5 MHz, $CDCl_3$) 198.8, 176.8, 152.8, 146.5, 142.1, 134.9, 134.6, 131.8, 128.8, 127.4, 127.1, 126.5, 117.9, 112.2, 93.7, 59.4, 50.3, 49.6, 48.5, 37.9, 37.1.

*4.4.13. Methyl (2E)-3-(11,11-dimethoxy-10-oxo-1,4a,9,9a-tetrahydro-4H-1,4-ethanofluoren-4-yl)acrylate (**6be**).* By following the above mentioned procedure, in which dimer **3b** (0.25 g, 0.53 mmol) and indene **4e** (0.58 g, 5.0 mmol) were heated at 230 °C for 5.5 h, cycloadduct **6be** (0.35 g, 92%) was isolated as a colorless oil; [found: C, 70.95; H, 6.51. $C_{21}H_{22}O_5$ requires C, 71.17; H, 6.26%]; R_f (20% EtOAc/CH_2Cl_2) 0.50; ν_{max} (liquid film) 2952, 2841, 1728, 1659, 1441, 1313, 1177, 1060, 881, 839, 742 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.34 (d, *J*=16.3 Hz, 1H), 6.96–7.10 (m, 4H), 6.28–6.34 (m, 1H), 5.85 (d, *J*=16.3 Hz, 1H), 5.85 (br s, 1H), 3.75 (s, 3H), 3.66 (d, *J*=8.8 Hz, 1H), 3.38 (s, 3H), 3.26 (s, 3H), 3.22–3.31 (m, 2H), 3.10 (dd, *J*=10.2, 16.5 Hz, 1H), 2.69 (dd, *J*=4.8, 16.5 Hz, 1H); δ_C (62.5 MHz, $CDCl_3$) 200.5, 165.9, 144.1, 144.0, 140.3, 132.7, 127.4, 127.0, 125.7, 125.6, 124.0, 123.3, 93.9, 58.8, 53.0, 51.5, 50.1, 49.5, 43.3, 37.1, 36.2.

*4.4.14. 11,11-Dimethoxy-4-[(1E)-3-oxo-3-phenylprop-1-en-1-yl]-4,4a,9,9a-tetrahydro-1H-1,4-ethanofluoren-10-one (**6ce**).* By following the above mentioned procedure, in which dimer **3c** (0.29 g, 0.51 mmol) and indene **4e** (0.58 g, 5.0 mmol) were heated at 230 °C for 5 h, cycloadduct **6ce** (0.40 g, 98%) was isolated as a colorless oil; [found: C, 78.15; H, 6.21. $C_{26}H_{24}O_4$ (400.47): C, 77.98%]; H, 6.04; R_f (20% EtOAc/CH_2Cl_2) 0.54; ν_{max} (liquid film) 3062, 2949, 2837, 1735, 1673, 1624, 1448, 1303, 1221, 1148, 1058, 987, 763, 732 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.97 (d, *J*=7.1 Hz, 2H), 7.41–7.57 (m, 4H), 6.93–7.11 (m, 5H), 6.36–6.42 (m, 1H), 6.05 (d, *J*=8.4 Hz, 1H), 3.75 (d, *J*=8.8 Hz, 1H), 3.44 (s, 3H), 3.33 (s, 3H), 3.26–3.39 (m, 2H), 3.15 (dd, *J*=10.2, 16.6 Hz, 1H), 2.74 (dd, *J*=4.7, 16.6 Hz, 1H); δ_C (62.5 MHz, $CDCl_3$) 200.6, 189.5, 144.0, 143.8, 140.4, 137.3, 132.8, 132.7, 128.5, 128.3, 127.8, 127.5, 127.4, 125.9, 125.7, 124.0, 94.0, 59.2, 53.3, 50.2, 49.6, 43.3, 37.2, 36.2.

*4.4.15. 4-[(1E)-3-(Furan-2-yl)-3-oxoprop-1-en-1-yl]-11,11-dimethoxy-4,4a,9,9a-tetrahydro-1H-1,4-ethanofluoren-10-one (**6de**).* By following the above mentioned procedure, in which dimer **3d** (0.28 g, 0.51 mmol) and indene **4e** (0.58 g, 5.0 mmol) were heated at 230 °C for 17 h, cycloadduct **6de** (0.34 g, 85%) was isolated as a white solid; mp 78–80 °C (Et_2O/pet. ether); [found: C, 73.90; H, 5.74. $C_{24}H_{22}O_5$ requires C, 73.83; H, 5.68%]; R_f (20% EtOAc/CH_2Cl_2) 0.54; ν_{max} (KBr) 3139, 2954, 1737, 1668, 1626, 1565, 1465, 1395, 1324, 1247, 1150, 1050, 986, 798, 755 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.57–7.58 (m, 1H), 7.49 (d, *J*=16.2 Hz, 1H), 7.24 (d, *J*=3.6 Hz, 1H), 6.90–7.12 (m, 4H), 6.84 (d, *J*=16.2 Hz, 1H), 6.52 (ddd, *J*=0.3, 1.7, 3.6 Hz, 1H), 6.34–6.40 (m, 1H), 6.03 (d, *J*=8.5 Hz, 1H), 3.74–3.79 (m, 1H), 3.41 (s, 3H), 3.30 (s, 3H), 3.25–3.35 (m, 2H), 3.09–3.20 (m, 1H), 2.72 (dd, *J*=4.7, 16.6 Hz, 1H); δ_C (62.5 MHz, $CDCl_3$) 200.6, 177.0, 153.0, 146.7, 144.1, 143.5, 140.5, 132.8, 127.7, 127.5, 127.0, 126.0, 125.8, 124.1, 118.1, 112.4, 94.2, 59.3, 53.6, 50.3, 49.7, 43.5, 37.3, 36.3.

*4.4.16. Methyl (2E)-3-(11,11-dimethoxy-12-oxo-10,10a-dihydro-7,10-ethanofluornthen-7(6bH)-yl)acrylate (**6bf**).* By following the above mentioned procedure, in which dimer **3b** (0.24 g, 0.5 mmol) and acenaphthylene **4f** (0.76 g, 5.0 mmol) were heated at 230 °C for 15.5 h, cycloadduct **6bf** (0.33 g, 85%) was isolated as a white solid; mp 141–143 °C ($CHCl_3$ –pet. ether); [found: C, 73.51; H, 5.80. $C_{24}H_{22}O_5$ requires C, 73.83; H, 5.68%]; R_f (20% EtOAc/CH_2Cl_2) 0.72; ν_{max} (KBr) 3037, 2952, 2836, 1725, 1656, 1599, 1440, 1291, 1232,

1176, 1142, 1056, 987, 786 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.60 (dd, *J*=4.5, 8.3 Hz, 2H), 7.23–7.51 (m, 4H), 7.10–7.13 (m, 1H), 5.97 (dd, *J*=8.3, 15.7 Hz, 2H), 3.83 (s, 3H), 3.70 (ddd, *J*=1.5, 3.0, 6.8 Hz, 1H), 3.36 (s, 3H), 3.54 (s, 3H); δ_C (62.5 MHz, $CDCl_3$) 200.3, 166.1, 144.6, 143.5, 142.1, 140.7, 132.6, 130.9, 127.7, 127.6, 125.8, 124.1, 123.7, 122.9, 121.0, 118.3, 94.1, 58.5, 51.7, 50.4, 50.1, 49.9, 44.3, 43.3.

*4.4.17. 12,12-Dimethoxy-10-[(1E)-3-oxo-3-phenylprop-1-en-1-yl]-6b,7,10,10a-tetrahydro-7,10-ethanofluoranthen-11-one (**6cf**).* By following the above mentioned procedure, in which dimer **3c** (0.29 g, 0.51 mmol) and acenaphthylene **4f** (0.79 g, 5.2 mmol) were heated at 230 °C for 16 h, cycloadduct **6cf** (0.27 g, 61%) was isolated as a white solid; mp 94–96 °C (EtOAc/pet. ether); [found: C, 79.69; H, 5.65. $C_{29}H_{24}O_4$ requires C, 79.80; H, 5.54%]; R_f (20% EtOAc/CH_2Cl_2) 0.54; ν_{max} (KBr) 3056, 2946, 2833, 1733, 1673, 1625, 1304, 1218, 1178, 1142, 1052, 983, 779 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 8.00–8.04 (m, 2H), 7.42–7.61 (m, 7H), 7.30–7.36 (m, 2H), 7.16 (d, *J*=7.1 Hz, 1H), 7.02 (d, *J*=16.1 Hz, 1H), 5.99–6.05 (m, 1H), 5.80 (d, *J*=8.4 Hz, 1H), 4.31 (dd, *J*=2.7, 7.4 Hz, 1H), 4.07 (d, *J*=7.4 Hz, 1H), 3.74 (ddd, *J*=1.5, 3.0, 6.7 Hz, 1H), 3.58 (s, 3H), 3.41 (s, 3H); δ_C (62.5 MHz, $CDCl_3$) 200.4, 189.8, 144.6, 143.2, 142.2, 140.7, 137.4, 132.9, 132.6, 130.9, 128.8, 128.7, 128.5, 127.8, 127.6, 126.3, 123.7, 122.9, 121.2, 118.3, 94.2, 58.9, 50.5, 50.4, 49.9, 44.3, 43.3.

*4.4.18. 10-[(1E)-3-(Furan-2-yl)-3-oxoprop-1-en-1-yl]-12,12-dimethoxy-6b,7,10,10a-tetrahydro-7,10-ethanofluoranthen-11-one (**6df**).* By following the above mentioned procedure, in which dimer **3d** (0.28 g, 0.51 mmol) and acenaphthylene **4f** (0.76 g, 5.0 mmol) were heated at 230 °C for 17 h, cycloadduct **6df** (0.36 g, 84%) was isolated as a white solid; mp 172–174 °C ($CHCl_3$/pet. ether); [found: C, 76.11; H, 5.25. $C_{27}H_{22}O_5$ requires C, 76.04; H, 5.20%]; R_f (20% EtOAc/CH_2Cl_2) 0.55; ν_{max} (KBr) 3049, 2948, 1734, 1667, 1621, 1563, 1464, 1395, 1326, 1237, 1144, 1052, 981, 780 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.58–7.65 (m, 4H), 7.42–7.48 (m, 1H), 7.28–7.34 (m, 3H), 7.14 (d, *J*=7.0 Hz, 1H), 6.93 (d, *J*=16.1 Hz, 1H), 6.57 (dd, *J*=1.7, 3.6 Hz, 1H), 6.00–6.06 (m, 1H), 5.83 (d, *J*=8.3 Hz, 1H), 4.33–4.36 (m, 1H), 4.14 (d, *J*=7.4 Hz, 1H), 3.73 (ddd, *J*=1.4, 3.0, 6.7 Hz, 1H), 3.56 (s, 3H), 3.38 (s, 3H); δ_C (62.5 MHz, $CDCl_3$) 200.4, 177.2, 153.2, 146.9, 144.7, 142.9, 142.3, 140.9, 132.7, 131.0, 127.8, 127.7, 126.4, 123.8, 123.0, 121.4, 118.4, 118.3, 112.6, 94.3, 58.9, 50.7, 50.5, 50.0, 44.4, 43.5.

4.5. General experimental procedure for the Diels–Alder reactions of 4-allyl-2,2-dimethoxycyclohexa-3,5-dienone (1e) with olefinic dienophiles 4

A solution of eugenol **2e** (0.38–0.42 g, 2.3–2.6 mmol) in methanol (10 mL) was added to a suspension of (diacetoxy)-iodobenzene (0.80 g, 2.5 mmol) and sodium hydrogen carbonate (0.25 g, 3.0 mmol) in methanol (10 mL), which was cooled at 0 °C. The resulting mixture was stirred for 10 min, and a solution of the appropriate dienophile **4** in methanol (5 mL) was added. The resulting yellow solution was stirred at room temperature for 22–65 h. The solvent was evaporated under reduced pressure, the residue was dissolved in dichloromethane (40 mL), and washed with water (3×20 mL) and brine (20 mL). The organic layer was dried ($MgSO_4$), the solvent was evaporated under reduced pressure and the residue was flash chromatographed on silica gel (CH_2Cl_2 (4:1) CH_2Cl_2/EtOAc) to afford cycloadducts **7**.

*4.5.1. 7-Acetyl-5-allyl-3,3-dimethoxybicyclo[2.2.2]oct-5-en-2-one (**7ea**).* By following the above mentioned procedure, in which eugenol **2e** (0.38 g, 2.30 mmol), (diacetoxy)iodobenzene (0.80 g, 2.5 mmol), sodium hydrogen carbonate (0.25 g, 3.0 mmol), and 1-buten-3-one (**4a**) (0.74 g, 10.60 mmol) were stirred at room temperature for 65 h, cycloadduct **7ea** (0.48 g, 79%) was isolated as a colorless oil; [found: C, 68.31; H, 7.70. $C_{15}H_{20}O_4$ requires C, 68.16; H, 7.63%]; R_f (CH_2Cl_2) 0.15; ν_{max} (liquid film) 2950, 2836, 1740, 1715, 1640, 1430, 1360, 1090, 1065, 1000, 920 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 5.55–5.72 (m, 2H), 4.96–5.04 (m, 2H), 3.27 (dd, *J*=1.7, 6.5 Hz, 1H), 3.20 (s, 3H), 3.19 (s, 3H), 2.78–2.96 (m, 4H), 2.03 (s, 3H), 1.95–2.07 (m, 1H), 1.55 (ddd, *J*=2.9, 6.3, 12.9 Hz, 1H); δ_C (62.5 MHz, $CDCl_3$) 205.4, 200.8, 147.0, 133.9, 117.2, 117.1, 93.9, 53.2, 50.1, 49.1, 46.8, 41.8, 39.2, 27.9, 22.8.

*4.5.2. Methyl 3-allyl-5,5-dimethoxy-6-oxobicyclo[2.2.2]oct-2-ene-7-carboxylate (**7eb**).* By following the above mentioned procedure, in which eugenol **2e** (0.41 g, 2.50 mmol), (diacetoxy)iodobenzene (0.80 g, 2.5 mmol), sodium hydrogen carbonate (0.25 g, 3.0 mmol), and methyl acrylate **4b** (0.87 g, 10.10 mmol) were stirred at room temperature for 23 h, cycloadduct **7eb** (0.45 g, 64%) was isolated as a colorless oil; [found: C, 64.18; H, 7.32. $C_{15}H_{20}O_5$ requires C, 64.27; H, 7.19%]; R_f (CH_2Cl_2) 0.13; ν_{max} (liquid film) 2960, 2836, 1733, 1634, 1448, 1351, 1324, 1204, 1153, 1068, 990, 826, 748 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 5.68–5.84 (m, 2H), 5.06–5.16 (m, 2H), 3.65 (s,3H), 3.42 (dd, *J*=2.0, 6.4 Hz, 1H), 3.31 (s, 3H), 3.28 (s, 3H), 2.84–3.02 (m, 4H), 2.14–2.24 (m, 1H), 1.69 (ddd, *J*=2.8, 6.0, 13.2 Hz, 1H); δ_C (62.5 MHz, $CDCl_3$) 201.0, 173.4, 147.8, 134.2, 117.7, 117.4, 94.0, 52.1, 50.4, 49.8, 49.7, 41.9, 39.6, 39.1, 24.3.

*4.5.3. 2-Allyl-11,11-dimethoxy-4,4a,9,9a-tetrahydro-1H-1,4-ethanofluoren-10-one (**7ee**).* By following the above mentioned procedure, in which eugenol **2e** (0.42 g, 2.60 mmol), (diacetoxy)iodobenzene (0.80 g, 2.5 mmol), sodium hydrogen carbonate (0.25 g, 3.0 mmol), and indene **4e** (1.16 g, 10.00 mmol) were stirred at room temperature for 9 h, cycloadduct **7ee** (0.13 g, 18%) was isolated as a white solid; mp 99–101 °C (EtOAc/pet. ether); [found: C, 77.41; H, 7.01. $C_{20}H_{22}O_3$ requires C, 77.39; H, 7.14%]; R_f (CH_2Cl_2) 0.13; δ_H (250 MHz, $CDCl_3$) 7.27 (d, *J*=1.9 Hz, 1H), 7.10–7.18 (m, 3H), 5.61–5.77 (m, 1H), 5.48 (d, *J*=5.8 Hz, 1H), 5.04–5.15 (m, 2H), 3.77–3.85 (m, 1H), 3.64 (d, *J*=7.5 Hz, 1H), 3.42 (s, 3H), 3.40 (s, 3H), 3.10–3.26 (m, 3H), 2.85–3.02 (m, 2H), 2.64–2.73 (m, 1H); δ_C (62.5 MHz, $CDCl_3$) 203.0, 144.4, 143.9, 134.5, 127.0, 126.6, 126.5, 124.1, 124.0, 119.0, 117.2, 95.9, 56.6, 53.4, 50.4, 49.6, 47.6, 41.4, 36.9, 34.8.

*4.5.4. 8-Allyl-12,12-dimethoxy-6b,7,10,10a-tetrahydro-7,10-ethanofluoranthen-11-one (**7ef**).* By following the above mentioned procedure, in which eugenol **2e** (0.41 g, 2.50 mmol), (diacetoxy) iodobenzene (0.80 g, 2.5 mmol), sodium hydrogen carbonate (0.25 g, 3.0 mmol), and acenaphthylene **4f** (1.54 g, 10.10 mmol) were stirred at room temperature for 22 h, cycloadduct **7ef** (0.38 g, ca. 100%) was isolated as a white solid; mp 106–108 °C (EtOH); [found: C, 79.50; H, 6.53. $C_{23}H_{22}O_3$ requires C, 79.44; H, 6.40%]; R_f (CH_2Cl_2) 0.14; ν_{max} (KBr) 3042, 2946, 2833, 1734, 1631, 1600, 1425, 1365, 1310, 1227, 1135, 1049, 1002, 930, 838, 784 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 7.60 (dd, *J*=2.0, 8.2 Hz, 2H), 7.42–7.50 (m, 2H), 7.27 (dd, *J*=7.0, 10.7 Hz, 2H), 5.21–5.28 (m, 1H), 4.97–5.13 (m, 1H), 4.71–4.83 (m, 2H), 4.22 (dd, *J*=3.0, 7.4 Hz, 1H), 4.09–4.11 (m, 1H), 3.53 (dd, *J*=2.7, 6.4 Hz, 1H), 3.52 (s, 3H), 3.50 (dd, *J*=2.2, 3.1 Hz, 1H), 3.43 (s, 3H), 2.54 (dd, *J*=6.8, 16.0 Hz, 1H), 2.34–2.43 (m, 1H); δ_C (62.5 MHz, $CDCl_3$) 202.6, 145.1, 144.6, 144.5, 140.8, 134.3, 130.9, 128.3, 127.9, 127.6, 123.1, 122.8, 118.9, 117.7, 116.8, 94.6, 53.4, 50.5, 49.8, 46.9, 45.3, 43.2, 40.4.

Supplementary data

Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2011.03.018.

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