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TETRAHEDRON

Synthesis of Polysubstituted Bicyclo[3.3.1]nonane-3,7-diones from Cyclohexa-2,5-dienones and Dimethyl 1,3-Acetonedicarboxylate

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[b]*Departament de Cristal.lografia, Mineralogia i Dipòsits Minerals, Facultat de Geologia, Universitat de Barcelona, Av. Martí Franquès s/n; E-08028, Barcelona, Spain*

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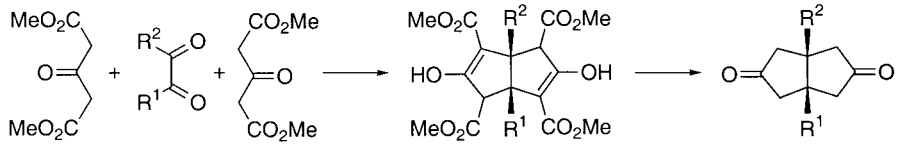
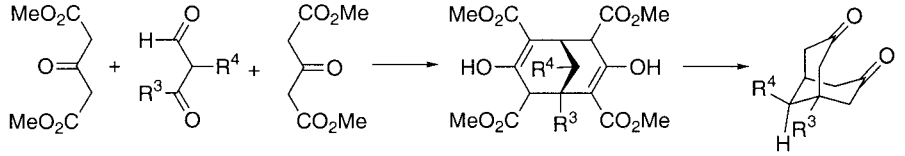
Abstract—Oxidation of polysubstituted phenols with phenyliodonium diacetate gives cyclohexa-2,5-dienones, which on reaction with dimethyl 1,3-acetonedicarboxylate afford double-Michael-addition derivatives, whose hydrolysis and decarboxylation provides polysubstituted bicyclo[3.3.1]nonane-3,7-diones. For steric and/or electronic reasons, the Michael reaction only works with 3,5-unsubstituted or 3-substituted cyclohexa-2,5-dienones, if the substituent is not an electron-releasing or a good electron-withdrawing group. Hydrolysis and decarboxylation of the double-Michael adducts from 2,4,4- or 2,4,4,6-substituted cyclohexa-2,5-dienones gives only products of partial hydrolysis and decarboxylation, which exist exclusively in the enol form.

The two-fold condensation of dimethyl 1,3-acetonedicarboxylate with 1,2-dicarbonyl compounds, the Weiss–Cook reaction, has been shown to be a versatile method for the formation of *cis*-bicyclo[3.3.0]octane-3,7-dione derivatives (Scheme 1).[1,2] A large number of *cis*-bicyclo[3.3.0]octane-3,7-diones, mono- or di-substituted at positions 1 and/or 5, are easily available by this procedure. These diketones have been widely used as precursors for the synthesis of many polyquinane natural products and non-natural polyquinanes of theoretical interest.[2,3] Bertz extended the above reaction to a 1,3-dicarbonyl compound (malondialdehyde), making bicyclo[3.3.1]nonane-3,7-dione readily available from inexpensive starting materials (Scheme 1).[4,5] Only a few examples of this kind of reaction are known starting from other 1,3-dicarbonyl compounds to give 1- or 9-monosubstituted bicyclo[3.3.1]nonane-3,7-diones.[4,6] In most cases, under similar reaction conditions, phenols were the only isolated products.[7]





Scheme 1. Synthesis of *cis*-bicyclo[3.3.0]octane-3,7-diones and bicyclo[3.3.1]nonane-3,7-diones from 1,2- and 1,3-dicarbonyl compounds.

Keywords: phenols, cyclohexenones; bicyclic aliphatic compounds; X-ray crystal structures.

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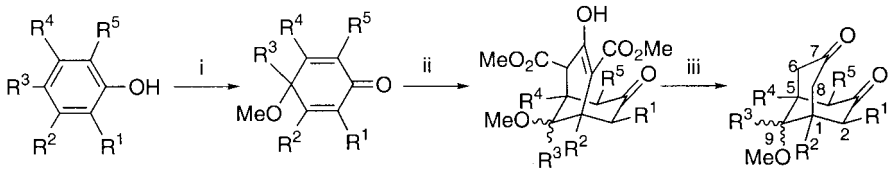
PII: S0040-4020(00)00680-3



R^1 = H or Me; R^2 = H, COOMe, Me, NHCOMe, COMe; R^3 = H, Me, Et, *i*-Pr, MeO; R^4 = H, Me, COOMe; R^5 = H, Me. For specific compounds, see Tables 1 and 2.

Scheme 2. Synthesis of polysubstituted bicyclo[3.3.1]nonane-3,7-diones from phenols. (i) Phenyliodonium diacetate, MeOH, room temp., 4 h; (ii) dimethyl 1,3-acetonedicarboxylate, NaOMe, MeOH, reflux, 48 h; (iii) (a) NaOH, H_2O, MeOH, reflux, 12 h; (b) 2N HCl, room temp., 1 h.

Several bicyclo[3.3.1]nonane-3,7-diones have been prepared through an alternative approach, which involves a double Michael condensation of dimethyl 1,3-acetonedicarboxylate with *p*-benzoquinone monoacetals[8,9] or 4,4-dialkylcyclohexa-2,5-dienones,[10,11] followed by hydrolysis and decarboxylation of the resulting diesters to give 9,9-dialkoxy- or 9,9-dialkyl-bicyclo[3.3.1]nonane-3,7-diones. We published the synthesis of 9-methoxy-9-methylbicyclo[3.3.1]nonane-3,7-dione, **28**, through a similar procedure.[12]

It is known that oxidation of phenols with phenyliodonium diacetate (PIDA) to *p*-benzoquinone monoacetals and 4-alkoxy-4-alkylcyclohexa-2,5-dienones proceeds in good yields under mild conditions.[13] This prompted us to study the scope of the sequence phenol oxidation-double Michael addition of dimethyl 1,3-acetonedicarboxylate-hydrolysis-decarboxylation for the synthesis of diversely substituted bicyclo[3.3.1]nonane-3,7-diones, which is herein described (Scheme 2).

Results and Discussion

Table 1 summarizes the results obtained in the oxidation of the commercially available phenols **1**–**3**, **5**, and **7**–**11**, and of the known phenols **4**[14] and **6**,[15] with PIDA. Oxidation of the 4-substituted phenols, **1**–**6** and **8**, and the 4-unsubstituted phenols, **7** and **9**–**11**, with one or 2 equiv. of PIDA, respectively, in MeOH at room temperature led to the expected, and in many cases known, 4-alkyl-4-methoxy- or 4,4-dimethoxy-cyclohexa-2,5-dienones in good to moderate yields. Only the oxidation of phenol **9** failed, giving a complex mixture of products which did not contain any cyclohexadienone.

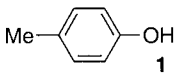
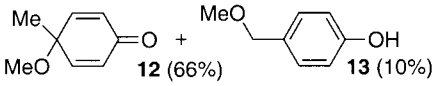
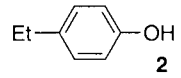
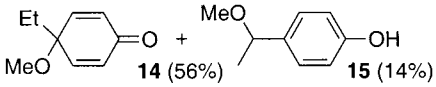
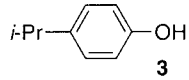
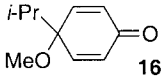
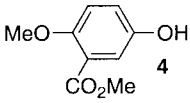
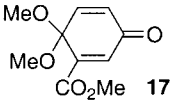
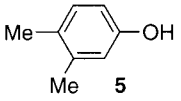
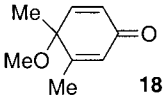
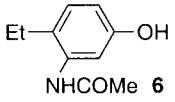
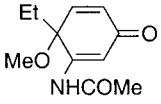
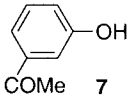
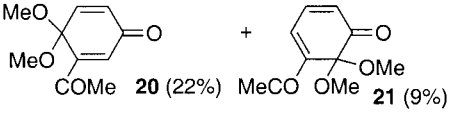
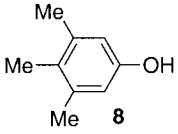
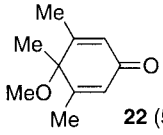
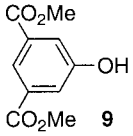
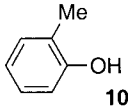
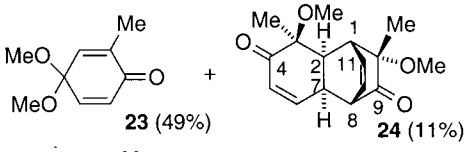
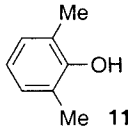
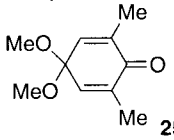
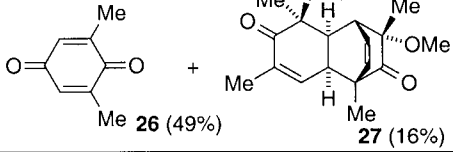
It is worth noting the byproducts isolated in several of these reactions:

(1) From the oxidation of phenols **1** and **2**, products **13** and **15**, derived from the methoxylation of the benzylic position, were isolated in 10 and 14% yield, respectively, after column chromatography. The formation of these byproducts suggests the intermediacy of a quinone methide intermediate,[16] which on nucleophilic addition of MeOH would lead to the 4-(α-methoxyalkyl)phenols **13** and **15**. Although similar byproducts were not observed in other oxidations of the phenols shown in Table 1, their possible formation cannot be ruled out.

(2) From the oxidation of phenol **7**, 6,6-dimethoxycyclohexa-2,4-dienone **21** was isolated after column chromatrography in 9% yield, which was stable enough to be fully characterized through its spectroscopic data and elemental analysis. However, from the oxidation of *o*-cresol, **10**, compound **24**, a Diels–Alder dimer of 6-methoxy-6-methylcyclohexa-2,4-dienone, was isolated in 11% yield. Similarly, from the oxidation of 2,6-dimethylphenol, **11**, compound **27**, a Diels–Alder dimer of 6-methoxy-2,6-dimethylcyclohexa-2,4-dienone having the same structure and stereochemistry as **24**, was isolated in 16% yield. The structure of both dimers **24** and **27** was fully established by X-ray diffraction analysis of monocrystals obtained by recrystallizaton from AcOEt (Figs. 1 and 2).

It is known that oxidation of substituted phenols with PIDA can yield either 4,4-disubstituted cyclohexa-2,5-dienones or 6,6-disubstituted cyclohexa-2,4-dienones, depending on the structure of the starting phenol.[17] The major or sole oxidation product in this kind of reactions is usually the 4,4-disubstituted cyclohexa-2,5-dienone but, in some cases, especially in the oxidation of 2-substituted phenols, competitive or preferential formation of 6,6-disubstituted cyclohexa-2,4-dienones has been observed.[17] Although several 6,6-disubstituted cyclohexa-2,4-dienones are stable at room temperature,[18] these kind of compounds usually undergo rapid Diels–Alder dimerization to give 1,4-ethanonaphthalene derivatives.[16,18–22] In fact, dimer **27** is a known compound, which was obtained by Adler et al. on oxidation of **11** with anhydrous periodic acid in MeOH.[16] Its structure was assigned by analogy with that of related dimers, whose structure had been established by X-ray diffraction analysis.[23,24] Thus, the Diels–Alder dimerization of 6-methoxy-6-methylcyclohexa-2,4-dienone and 6-methoxy-2,6-dimethylcyclohexa-2,4-dienone to give compounds **24** and **27**, respectively, takes place with the usual regio- and diastereo-selectivities, i.e., the dienophile reacts by the C4–C5 double bond (site selectivity); the diene and dienophile approach each other in a defined relative orientation (C2 diene/C4 dienophile and C5 diene/C5 dienophile: regioselectivity) from their less hindered faces (those where the less sterically demanding methoxy group is placed: face selectivity) in an *endo* arrangement (diastereoselectivity).[16,20,21] Moreover, it must be emphasized that dimers **24** and **27** derive from the cycloaddition of two units of the corresponding intermediate cyclohexadienones of the same chirality, in spite of their racemic nature. Cycloaddition of two cyclohexadienone units of opposed chirality with the same site-, regio-, and *endo*-diastereoselectivity must take place by the less hindered methoxy-face of one

Table 1. Synthesis of cyclohexa-2,5-dienones from substituted phenols

Starting material	Product (% yield)
 **1**	 **12** (66%) + **13** (10%)
 **2**	 **14** (56%) + **15** (14%)
 **3**	 **16** (38%)
 **4**	 **17** (82%)
 **5**	 **18** (59%)
 **6**	 **19** (34%)
 **7**	 **20** (22%) + **21** (9%)
 **8**	 **22** (56%)
 **9**	Complex mixture
 **10**	 **23** (49%) + **24** (11%)
 **11**	 **25** (48%)
11	 **26** (49%) + **27** (16%)

component and the more hindered methyl-face of its enantiomer, that would be less favorable.

(3) 2,6-Dimethylbenzoquinone, **26**, was obtained in 49% yield, instead of the desired 4,4-dimethoxy-2,6-dimethyl-cyclohexa-2,5-dienone, **25**, from the oxidation of **11** with PIDA, under the standard conditions. Since acetal hydrolysis of **25** could take place during the silica-gel column chromatography purification of the crude reaction product, in another assay, Et_3N was added to the eluent during the

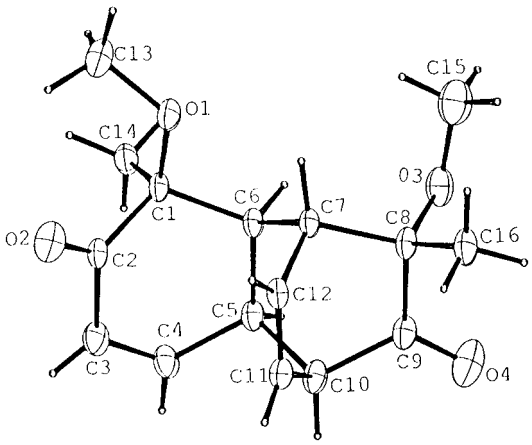


Figure 1. Crystal structure (ORTEP) of dimer **24**.

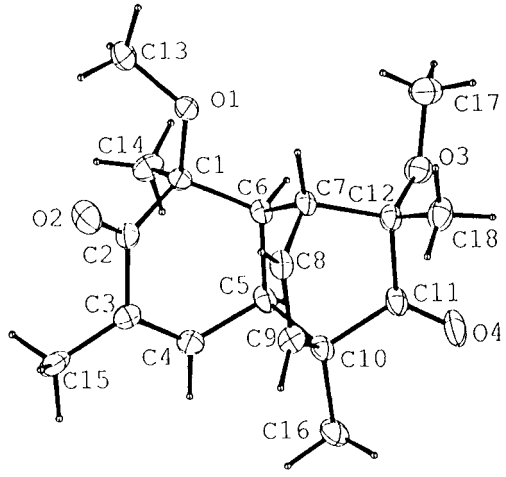
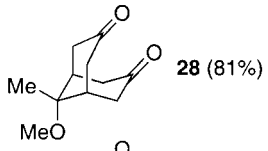
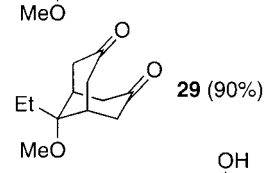
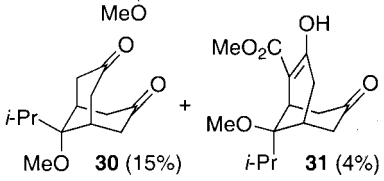
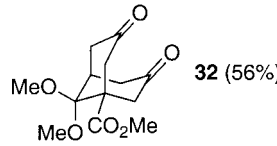
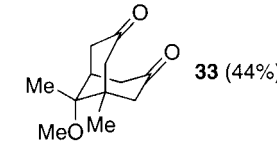
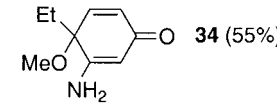
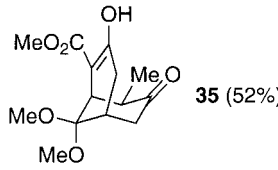
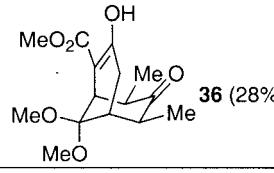


Figure 2. Crystal structure (ORTEP) of dimer **27**.

chromatography, isolating the desired dienone **25** in 48% yield. In this case no dimer **27** was isolated. In another attempt in which 4 equiv. of Na_2CO_3 were added to the reaction mixture to prevent the hydrolysis of the acetal group, compounds **25** and **27** were isolated in only 15 and 8% yield, respectively.

The synthesis of differently substituted bicyclo[3.3.1]nonane-3,7-diones from the obtained cyclohexa-2,5-dienones (Table 2) was carried out as described previously for the preparation of diketone **28**, i.e. by double Michael addition of dimethyl 1,3-acetonedicarboxylate to the cyclohexa-2,5-dienones under NaOMe catalysis in refluxing MeOH for 48 h, followed by hydrolysis and decarboxylation of the resulting diketo diester by successive treatment with NaOH/water under reflux for 12 h and with 2N HCl at room temperature for 1 h.[12] Products were isolated either by column chromatography, sublimation or recrystallization. Starting from 4,4-dimethoxycyclohexa-2,5-dienones, the faces of the C3 and C5 sp^2 carbon atoms are enantiotopic and thus non-distinguishable by the anion derived from dimethyl 1,3-acetonedicarboxylate. However, in the case of 4-alkyl-4-methoxycyclohexa-2,5-dienones, these faces are diastereotopic and thus the Michael addition would take place preferentially by the less hindered face. In the last case, after complete hydrolysis and decarboxylation, the obtained bicyclo[3.3.1]nonane-3,7-dione would be the same, no matter which face Michael addition had taken place.

Table 2. Synthesis of bicyclo[3.3.1]nonane-3,7-diones from substituted cyclohexa-2,5-dienones

Starting material	Product (% yield)
12	 **28** (81%)
14	 **29** (90%)
16	 **30** (15%) + **31** (4%)
17	 **32** (56%)
18	 **33** (44%)
19	 **34** (55%)
20	Complex mixture
22	No reaction
23	 **35** (52%)
25	 **36** (28%)

By this procedure, from dienone **14**, diketone **29** was obtained in 90% yield. However, starting from dienone **16**, the yield of the obtained diketone **30** was only 15%, taking into account the recovered unchanged starting dienone (32%). Also, a small amount of the partially hydrolyzed and decarboxylated product **31** (4%) was isolated. The configuration of compound **31** was assigned on the basis of its ^1H NMR data by comparison with related

diketones. The chemical shift of the 6-H*exo* and 8-H*exo* protons of **31** compared with the chemical shifts of the 2-H*exo*/4-H*exo* and the 6-H*exo*/8-H*exo* protons of **28**,[12] suggests them to be far from the methoxy group. This result is concordant with the expected preferential Michael addition of the anion of dimethyl 1,3-acetonedicarboxylate by the less hindered methoxy-face of dienone **16**. The low yield of the last reaction may be explained on the basis of the higher steric hindrance of the isopropyl group as compared with a methyl or ethyl group. Addition of the anion of dimethyl 1,3-acetonedicarboxylate to dienone **16** by the less hindered methoxy-face would give a cyclohexenone derivative, which should adopt a conformation with the isopropyl group and the substituent derived from dimethyl 1,3-acetonedicarboxylate in a *pseudoaxial* arrangement to be able to give the second intramolecular Michael addition. In this way, the isopropyl group would be an *axial* substituent for the cyclohexanone ring derived from the starting cyclohexa-2,5-dienone. Steric hindrance may also explain the isolation in this case of product **31**, corresponding to the partial hydrolysis and decarboxylation. This kind of partially hydrolyzed and decarboxylated product had already been observed in the preparation of a related 9,9-disubstituted bicyclo[3.3.1]nonane-3,7-dione.[8]

Reactions of the 3,4,4-trisubstituted cyclohexa-2,5-dienones **17**–**20** with dimethyl 1,3-acetonedicarboxylate were carried out to prepare 1,9,9-trisubstituted bicyclo[3.3.1]nonane-3,7-diones. Cyclohexadienone **17** was reacted with dimethyl 1,3-acetonedicarboxylate in the presence of NaOMe in MeOH at room temperature to give a crude product in which the corresponding diketo diester was a minor product. Curiously, under similar conditions, using NaOEt in EtOH, a crude product containing mainly the desired condensation product was obtained. Hydrolysis and decarboxylation of this product was carried out by using the method of Krapcho et al. for the decarbalkoxylation of β-keto esters (NaCl in wet DMSO at 140–190°C)[25,26] to prevent hydrolysis of the bridgehead ester. Under these conditions, compound **32** was obtained in 56% yield. The reactions starting from cyclohexadienones **18**–**20** were carried out under the standard conditions. From dienone **18**, diketone **33** was obtained in 44% yield, after hydrolysis and decarboxylation of the intermediate condensation product. However, treatment of dienone **19** under the same reaction conditions led to compound **34**, in 55% yield. Probably, **19** did not react with dimethyl 1,3-acetonedicarboxylate due to the electron releasing character of the acetamido group which reduces the reactivity of the C2–C3 double bond of **19** towards nucleophiles. Then, basic hydrolyis of **19** would give aminocyclohexadienone **34**.

Starting from the 3-acetylcyclohexadienone **20**, a complex mixture of products not containing the desired diketone was obtained. In this case, the Michael addition of a nucleophile at C2 could be more favorable than addition at C3. The resulting intermediate could lose methoxide to give a phenol derivative.

Dienone **22** failed to react with dimethyl 1,3-acetonedicarboxylate, probably due to steric hindrance. The starting product was mainly recovered after the hydrolysis and decarboxylation step.

Finally, reaction of dienones **23** and **25** with dimethyl 1,3-acetonedicarboxylate followed by hydrolysis and decarboxylation of the intermediate diketo diesters, under the standard conditions, gave the partially hydrolyzed and decarboxylated compounds **35** and **36** as the only isolated products in 52 and 28% yield, respectively. It is worth noting that in the case of **36**, similar results were obtained using a higher excess of NaOH and longer reaction times during the hydrolysis step. Moreover, several attempts to hydrolyze and decarboxylate compound **36** by reaction either with NaCl in wet DMSO at 170–190°C or with a mixture of HOAc/conc. HCl/water in the ratio of 2:1:1 under reflux resulted in decomposition of the product.

The value of the coupling constant 8-H/1-H (J=4.5 Hz) in the ^{1}H NMR spectrum of **35** and 6-H/5-H (J=4.5 Hz) and 8-H/1-H (J=4.0 Hz) in the ^{1}H NMR spectrum of **36**, are indicative of the *exo-axial* arrangement of 6-H and 8-H in **36** and of 8-H in **35**,[27] and consequently of the *endo-equatorial* arrangement of the methyl groups in both compounds. This fact was confirmed in the case of **36** by X-ray diffraction analysis (Fig. 3). The relative position of the methoxycarbonyl and methyl groups in compound **35** was established on the basis of the multiplicity of the signal of 1-H in its ^{1}H NMR spectrum. This proton appears as a doublet of doublets due to its *vicinal* coupling with 8-H (J=4.5 Hz) and its *W*-coupling with 5-H (J=3.0 Hz), showing the absence of protons at position 2. The formation of compounds **35** and **36** instead of the corresponding fully hydrolyzed and decarboxylated diketones could be explained on steric grounds. Steric hindrance either with the *endo*-8-methyl or *syn*-9-methoxy groups may prevent compounds **35** and **36** existing in the keto ester form, in which hydrolysis of the more electrophilic ester groups should be more favorable.

In conclusion, the oxidation of differently substituted phenols with PIDA, followed by double Michael addition of dimethyl 1,3-acetonedicarboxylate to the resulting cyclohexa-2,5-dienones, has allowed the synthesis of a series of differently substituted bicyclo[3.3.1]nonane-3,7-diones,

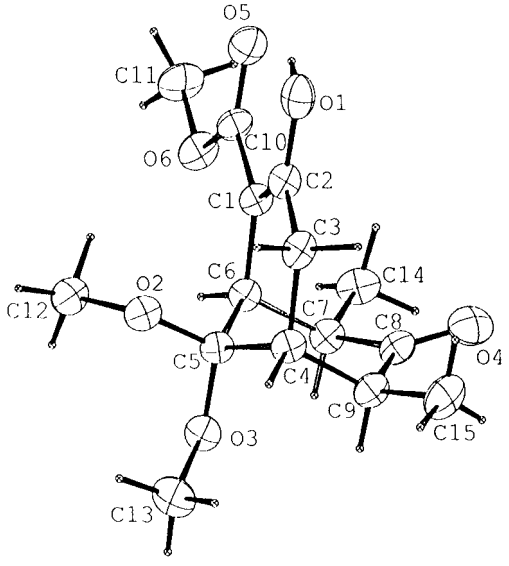


Figure 3. Crystal structure (ORTEP) of compound **36**.

such as **29**, **30**, **32** and **33**, and related derivatives, such as compounds **35** and **36**, not previously described and not easily available by other procedures. The steric and electronic effects of the substituents attached to the reaction centers of the intermediate cyclohexa-2,5-dienones play an important role in the success of the Michael addition step, while steric effects due to substituents at positions 6 and/or 8 of the adducts (from 2- and/or 6-substituted cyclohexa-2,5-dienones) may prevent, at least partly, the hydrolysis and decarboxylation of these bicyclic intermediates.

Experimental

General

Melting points were determined with a MFB 595010 M Gallenkamp melting point apparatus. 500 MHz ^{1}H NMR spectra were performed on a Varian VXR 500 spectrometer, 300 MHz ^{1}H and 75.4 MHz ^{13}C NMR spectra on a Varian Gemini 300, and 50.3 MHz ^{13}C NMR spectra on a Varian Gemini 200. Chemical shifts (δ) are reported in ppm related to internal tetramethylsilane (TMS). Assignments given for the NMR spectra of the polycyclic compounds are based on DEPT, ^{1}H/^{1}H and ^{1}H/^{13}C COSY experiments (HMQC sequence) and it was much facilitated by the observation in many cases of *W*-couplings between all or part of the following pairs of protons: 1-H/5-H, 2-H*exo*/8-H*exo*,4-H*exo*/6-H*exo*, 2-H*endo*/4-H*endo* and 6-H*endo*/8-H*endo* protons. Differentiation of the 2(4)-H*exo* and 8(6)-H*exo* protons in **29** and **30** was carried out by comparison with the data of **28**[12] for which NOESY experiments were performed. IR spectra were recorded on a FT/IR Perkin–Elmer spectrometer, model 1600. Unless otherwise stated, silica gel SDS 60 (60–200 μm) was utilized for the column chromatography. Elemental analyses were carried out at the Microanalysis Service of the *Centro de Investigación y Desarrollo* (C.I.D.), C.S.I.C., Barcelona, Spain.

General procedure for the preparation of cyclohexa-2,5-dienones from phenols

A solution of PIDA (1.0–1.6 mmol for the oxidation of 4-substituted phenols, 2.0–2.2 mmol for the oxidation of 4-unsubstituted phenols) in anhydrous MeOH (6–10 mL) was added dropwise over 40 min to a stirred solution of the phenol (1 mmol) in anhydrous MeOH (2 mL). The reaction mixture was stirred at room temperature for 4 h and evaporated at reduced pressure. The resulting yellow oily residue was submitted to column chromatography through silica gel (hexane/AcOEt mixtures, gradient elution), affording the corresponding cyclohexa-2,5-dienones.

4-Methoxy-4-methylcyclohexa-2,5-dienone (12)[17] and 4-(methoxymethyl)phenol (13). This reaction was carried out according to the procedure described above, from a solution of PIDA (16.4 g, 50.9 mmol) in anhydrous MeOH (400 mL) and a solution of phenol **1** (5.00 g, 46.3 mmol) in anhydrous MeOH (100 mL). On elution with hexane/AcOEt 95:5, cyclohexadienone **12** (4.20 g, 66% yield) was isolated as a yellowish oil. On elution with hexane/AcOEt 80:20, phenol **13** (0.67 g, 10% yield) was isolated as a white solid, mp 78–80°C (CH_2Cl_2) [lit.[28] mp 79–80°C (hexane)].

Spectroscopic data of **12**. IR (NaCl): ν 1689, 1634 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.44 (s, 3H, 4-CH_3), 3.21 (s, 3H, OCH_3), 6.31 [d, J=10.2 Hz, 2H, 2(6)-H], 6.77 [d, J=10.2 Hz, 2H, 3(5)-H]. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 26.1 (CH_3, 4-CH_3), 53.1 (CH_3, OCH_3), 72.4 (C, C4), 130.3 [CH, C2(6)], 151.6 [CH, C3(5)], 184.9 (C, C1).

Spectroscopic data of **13**: IR (KBr): ν 3286 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.38 (s, 3H, OCH_3), 4.40 (s, 2H, 4-CH_2), 5.49 (s, 1H, OH), 6.77 [d, J=8.5 Hz, 2H, 2(6)-H], 7.21 [d, J=8.5 Hz, 2H, 3(5)-H]. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 57.6 (CH_3, OCH_3), 74.5 (CH_2, 4-CH_2), 115.3 [CH, C2(6)], 129.2 (C, C4), 129.8 [CH, C3(5)], 155.7 (C, C1).

4-Ethyl-4-methoxycyclohexa-2,5-dienone (14)[29] and 4-(1-methoxyethyl)phenol (15).[30] This reaction was carried out according to the procedure described above, from a solution of PIDA (13.1 g, 40.7 mmol) in anhydrous MeOH (250 mL) and a solution of phenol **2** (5.00 g, 41.0 mmol) in anhydrous MeOH (60 mL). On elution with hexane/AcOEt 80:20, cyclohexadienone **14** (3.48 g, 56% yield) was isolated as a yellowish oil. On elution with hexane/AcOEt 70:30, phenol **15** (0.86 g, 14% yield) was isolated as a white solid, mp 97–99°C (CH_2Cl_2) [lit.[30] mp 98–100.5°C (Et_2O/hexane)].

Spectroscopic data of **14**. IR (NaCl): ν 1669, 1632 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.83 (t, J=7.5 Hz, 3H, CH_2CH_3), 1.77 (q, J=7.5 Hz, 2H, CH_2CH_3), 3.23 (s, 3H, OCH_3), 6.38 [d, J=10.3 Hz, 2H, 2(6)-H], 6.72 [d, J=10.3 Hz, 2H, 3(5)-H]. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 7.7 (CH_3, CH_2CH_3), 32.1 (CH_2, CH_2CH_3), 53.1 (CH_3, OCH_3), 76.3 (C, C4), 131.6 [CH, C2(6)], 150.9 [CH, C3(5)], 185.4 (C, C1).

Spectroscopic and analytical data of **15**: IR (KBr): ν 3214 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.44 (d, J=6.5 Hz, 3H, $CHCH_3$), 3.22 (s, 3H, OCH_3), 4.28 (q, J=6.5 Hz, 1H, $CHOCH_3$), 5.83 (br. s, 1H, OH), 6.82 [d, J=8.5 Hz, 2H, 2(6)-H], 7.18 [d, J=8.5 Hz, 2H, 3(5)-H]. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 23.6 (CH_3, $CHCH_3$), 56.1 (CH_3, OCH_3), 79.3 (CH, $CHCH_3$), 115.3 [CH, C2(6)], 127.7 [CH, C3(5)], 135.1 (C, C4), 155.3 (C, C1).

4-Isopropyl-4-methoxycyclohexa-2,5-dienone (16).[29] This compound was prepared according to the procedure described above, from a solution of PIDA (14.2 g, 44.1 mmol) in anhydrous MeOH (100 mL) and a solution of phenol **3** (5.00 g, 36.8 mmol) in anhydrous MeOH (30 mL). On elution with hexane/AcOEt 80:20, cyclohexadienone **16** (2.90 g), slightly contaminated with starting **3**, was separated. This product was taken up in CH_2Cl_2 (100 mL) and the resulting solution was washed with 1N NaOH (50 mL) and water (50 mL), dried with anhydrous Na_2SO_4 and evaporated at reduced pressure, to give pure cyclohexadienone **16** (2.34 g, 38% yield) as a colorless oil. IR (NaCl): ν 1668, 1632 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.93 [d, J=6.9 Hz, 6H, $CH(CH_3)_2$], 1.99 [heptet, J=6.9 Hz, 1H, $CH(CH_3)_2$], 3.21 (s, 3H, OCH_3), 6.41 [d,

J=10.2 Hz, 2H, 2(6)-H], 6.73 [d, J=10.2 Hz, 2H, 3(5)-H]. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 17.0 [CH_3, $CH(CH_3)_2$], 36.5 [CH, $CH(CH_3)_2$], 53.0 (CH_3, OCH_3), 78.3 (C, C4), 132.2 [CH, C2(6)], 150.1 [CH, C3(5)], 183.0 (C, C1).

4,4-Dimethoxy-3-(methoxycarbonyl)cyclohexa-2,5-dienone (17). This compound was prepared according to the procedure described above, from a solution of PIDA (5.14 g, 16.0 mmol) in anhydrous MeOH (100 mL) and a solution of phenol **4** (2.00 g, 11.0 mmol) in anhydrous MeOH (50 mL). On elution with hexane/AcOEt 80:20, cyclohexadienone **17** (1.92 g, 82% yield) was isolated as a yellowish oil, which decomposed after few days at room temperature or on heating. IR (NaCl): ν 1736, 1678, 1639 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.35 (s, 6H, OCH_3), 3.89 (s, 3H, $COOCH_3$), 6.47 (dd, J=10.4 Hz, J'=2.2 Hz, 1H, 6-H), 6.85 (d, J=10.4 Hz, 1H, 5-H), 6.89 (d, J=2.2 Hz, 1H, 2-H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 51.3 (CH_3, OCH_3), 52.2 (CH_3, $COOCH_3$), 94.6 (C, C4), 130.6 (CH, C6), 134.6 (CH, C2), 144.2 (C, C3), 144.4 (CH, C5), 163.9 (C, $COOCH_3$), 184.6 (C, C1). Anal. Calcd for $C_{10}H_{12}O_5$: C, 56.60; H, 5.70. Found: C, 56.52; H, 5.64.

4-Methoxy-3,4-dimethylcyclohexa-2,5-dienone (18).[31] This compound was prepared according to the procedure described above, from a solution of PIDA (8.22 g, 25.5 mmol) in anhydrous MeOH (100 mL) and a solution of phenol **5** (2.00 g, 16.4 mmol) in anhydrous MeOH (30 mL). On elution with hexane/AcOEt 90:10, cyclohexadienone **18** (1.46 g, 59% yield) was isolated as a yellowish solid, mp 35–36°C (acetonitrile) (Lit.[31] oil). IR (KBr): ν 1671, 1636 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.41 (s, 3H, 4-CH_3), 1.99 (d, J=1.4 Hz, 3H, 3-CH_3), 3.08 (s, 3H, OCH_3), 6.19 (dq, J=1.9 Hz, J'=1.4 Hz, 1H, 2-H), 6.30 (dd, J=10.0 Hz, J'=1.9 Hz, 1H, 6-H), 6.76 (d, J=10.0 Hz, 1H, 5-H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 17.7 (CH_3, 3-CH_3), 25.4 (CH_3, 4-CH_3), 52.6 (CH_3, OCH_3), 74.4 (C, C4), 129.0 (CH) and 130.0 (CH) (C2 and C6), 152.0 (CH, C5), 160.5 (C, C3), 185.5 (C, C1).

3-Acetamido-4-ethyl-4-methoxycyclohexa-2,5-dienone (19). This compound was prepared according to the procedure described above, from a solution of PIDA (1.78 g, 5.53 mmol) in anhydrous MeOH (30 mL) and a solution of phenol **6** (770 mg, 4.30 mmol) in anhydrous MeOH (10 mL). On elution with hexane/AcOEt 60:40, cyclohexadienone **19** (310 mg, 34% yield) was isolated as a white solid, mp 134–135°C (CH_2Cl_2). IR (KBr): ν 3274, 1717, 1665, 1607 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.78 (t, J=7.5 Hz, 3H, CH_2CH_3), 1.90 (m, 2H, CH_2CH_3), 2.24 (s, 3H, $NHCOCH_3$), 3.22 (s, 3H, OCH_3), 6.41 (dd, J=10.2 Hz, J'=1.9 Hz, 1H, 6-H), 6.56 (d, J=10.2 Hz, 1H, 5-H), 7.38 (broad s, 1H, $NHCOCH_3$), 7.41 (d, J=1.9 Hz, 1H, 2-H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 7.7 (CH_3, CH_2CH_3), 25.0 (CH_3, $NHCOCH_3$), 32.5 (CH_2, CH_2CH_3), 53.2 (CH_3, OCH_3), 77.5 (C, C4), 114.7 (CH, C2), 132.2 (CH, C6), 145.0 (CH, C2), 150.9 (C, C3), 169.2 (C, $NHCOCH_3$), 186.8 (C, C1). Anal. Calcd for $C_{11}H_{15}NO_3$: C, 63.14; H, 7.23; N, 6.69. Found: C, 62.89; H, 7.04; N, 6.56.

3-Acetyl-4,4-dimethoxycyclohexa-2,5-dienone (20) and 5-acetyl-6,6-dimethoxycyclohexa-2,4-dienone (21). This reaction was carried out according to the procedure described above, from a solution of PIDA (15.0 g, 46.6 mmol) in anhydrous MeOH (240 mL) and a solution of phenol **7** (3.00 g, 22.1 mmol) in anhydrous MeOH (135 mL), and using silica gel (40–60 μm) for the column chromatography. On elution with hexane/AcOEt 80:20, dienone **21** (0.39 g, 9% yield) and dienone **20** (0.96 g, 22% yield) were consecutively isolated as yellowish oils.

Spectroscopic and analytical data of **20**. IR (NaCl): ν 1685, 1662, 1634 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.53 (s, 3H, $COCH_3$), 3.40 (s, 6H, OCH_3), 6.45 (dd, J=10.1 Hz, J'=2.3 Hz, 1H, 6-H), 6.76 (d, J=2.3 Hz, 1H, 2-H), 6.82 (d, J=10.5 Hz, 1H, 5-H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 29.7 (CH_3, $COCH_3$), 51.1 (CH_3, OCH_3), 95.2 (C, C4), 131.2 (CH) and 131.8 (CH) (C2 and C6), 143.2 (CH, C5), 150.1 (C, C3), 185.3 (C, C1), 197.9 (C, $COCH_3$). Anal. Calcd for $C_{10}H_{12}O_4$: C, 61.21; H, 6.17. Found: C, 61.17; H, 6.15.

Spectroscopic and analytical data of **21**. IR (NaCl): ν 1731, 1672, 1625 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.46 (s, 3H, $COCH_3$), 3.24 (s, 6H, OCH_3), 6.25 (dd, J=9.7 Hz, J'=1.2 Hz, 1H, 2-H), 7.03 (dd, J=9.7 Hz, J'=6.3 Hz, 1H, 3-H), 7.17 (dd, J=6.3 Hz, J'=1.2 Hz, 1H, 4-H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 29.2 (CH_3, $COCH_3$), 50.9 (CH_3, OCH_3), 94.0 (C, C6), 129.6 (CH, C2), 131.5 (CH) and 138.5 (CH) (C3 and C4), 145.4 (C, C5), 194.6 (C, C1), 196.8 (C, $COCH_3$). Anal. Calcd for $C_{10}H_{12}O_4$. 1/5H_2O: C, 60.11; H, 6.26. Found: C, 60.10; H, 6.16.

4-Methoxy-3,4,5-trimethylcyclohexa-2,5-dienone (22).[32] This compound was prepared according to the procedure described above, from a solution of PIDA (7.80 g, 24.2 mmol) in anhydrous MeOH (120 mL) and a solution of phenol **8** (3.00 g, 22.1 mmol) in anhydrous MeOH (45 mL), with a reaction time of 1 h, and using silica gel (40–60 μm) for the column chromatography. On elution with hexane/AcOEt 90:10, cyclohexadienone **22** (2.05 g, 56% yield) was isolated as colorless crystals, mp 70–71°C [Lit.[32] mp 50–52°C (sublimed)]. IR (KBr): ν 1674, 1621 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.35 (s, 3H, 4-CH_3), 1.97 [s, 6H, 3(5)-CH_3], 2.92 (s, 3H, OCH_3), 6.13 [s, 2H, 2(6)-H]. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 17.7 (CH_3, 4-CH_3), 24.8 [CH_3, 3(5)-CH_3], 52.2 (CH_3, OCH_3), 76.8 (C, C4), 129.0 [C, C2(6)], 160.7 [C, C3(5)], 185.2 (C, C1).

4,4-Dimethoxy-2-methylcyclohexa-2,5-dienone (23)[22] **and (1*RS*,2*RS*,3*SR*,7*SR*,8*SR*,10*SR*)-3,10-dimethoxy-3,10-dimethyltricyclo[6.2.2.0^{2,7}]dodeca-5,11-diene-4,9-dione (24).** This reaction was carried out according to the procedure described above, from a solution of PIDA (12.5 g, 38.8 mmol) in anhydrous MeOH (190 mL) and a solution of phenol **10** (2.00 g, 18.5 mmol) in anhydrous MeOH (35 mL), with a reaction time of 1 h. On elution with hexane/AcOEt 90:10, dienone **23** (1.51 g, 49% yield) was isolated as a colorless oil. On elution with hexane/AcOEt 80:20, compound **24** (290 mg, 11% yield) was isolated as colorless crystals, mp 191–192°C (AcOEt).

Spectroscopic data of **23**: IR (NaCl): ν 1679, 1650 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.92 (d, J=1.5 Hz, 3H, 2-CH_3), 3.37 (s, 6H, OCH_3), 6.27 (d, J=10.5 Hz, 1H, 6-H), 6.62 (dq, J=3.3 Hz, J'=1.5 Hz, 1H, 3-H), 6.81 (dd, J=10.5 Hz, J'=3.3 Hz, 1H, 5-H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ

15.6 (CH_3, 2-CH_3), 50.2 (CH_3, OCH_3), 92.8 (C, C4), 129.8 (CH, C6), 136.7 (C, C2), 138.3 (CH, C3), 142.8 (C, C5), 185.6 (C, C1).

Spectroscopic and analytical data of **24**: IR (KBr): ν 1736, 1695 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 1.23 (s, 3H, 3-CH_3), 1.44 (s, 3H, 10-CH_3), 3.13–3.17 (complex signal, 2H, 2-H and 8-H), 3.29 (ddd, J=8.0 Hz, J'=4.0 Hz, J''=2.0 Hz, 1H, 7-H), 3.33 (ddd, J=7.0 Hz, J'=J''=1.5 Hz, 1H, 1-H), 3.34 (s, 3H) and 3.45 (s, 3H) (3-OCH_3 and 10-OCH_3), 5.84 (ddd, J=8.0 Hz, J'=6.5 Hz, J''=1.5 Hz, 1H, 12-H), 5.95 (dd, J=10.0 Hz, J'=2.0 Hz, 1H, 5-H), 6.27 (dd, J=10.0 Hz, J'=4.0 Hz, 1H, 6-H), 6.31 (ddd, $J\approx J'\approx$7.5 Hz, J''=1.0 Hz, 1H, 11-H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 19.9 (CH_3, 3-CH_3), 25.0 (CH_3, 10-CH_3), 38.9 (CH, C7), 41.8 (CH, C2), 42.9 (CH, C1), 51.0 (CH_3) and 51.7 (CH_3) (3-OCH_3 and 10-OCH_3), 52.7 (CH, C8), 76.0 (C) and 77.9 (C) (C3 and C10), 128.4 (CH, C12), 129.8 (CH, C5), 135.8 (CH, C11), 144.0 (CH, C6), 200.6 (C, C4), 208.8 (C, C9). Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30. Found: C, 69.60; H, 7.40.

4,4-Dimethoxy-2,6-dimethylcyclohexa-2,5-dienone (25)[33] and (1*RS*,2*RS*,3*SR*,7*SR*,8*SR*,10*SR*)-3,10-dimethoxy-3,5,8,10-tetramethyltricyclo[6.2.2.0^{2,7}]dodeca-5,11-diene-4,9-dione (27).[16] This reaction was carried out according to the procedure described above, from a solution of PIDA (10.6 g, 32.9 mmol) in anhydrous MeOH (160 mL) and a solution of phenol **11** (1.96 g, 16.1 mmol) in anhydrous MeOH (30 mL), with a reaction time of 1 h. On elution with a mixture of hexane/AcOEt/Et_3N 90:10:1, dienone **25** (1.42 g, 48% yield), slightly contaminated with 2,6-dimethyl-1,4-benzoquinone, was isolated as a colorless oil.

Note 1: When the reaction was carried out in the presence of Na_2CO_3 (4 equiv.), dienone **25** (15% yield) and compound **27** (8% yield) were isolated after column chromatography.

Note 2: When no base was used during the reaction and no Et_3N was added to the mixture of eluents for the chromatographic purification, 2,6-dimethyl-1,4-benzoquinone, **26**, (49% yield) and dimer **27** (16% yield) as a white solid were isolated after column chromatography.

Spectroscopic data of **25**. IR (NaCl): ν 1682, 1652, 1619 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.83 [s, 6H, 2(6)-CH_3], 3.27 (s, 6H, OCH_3), 6.51 [s, 2H, 3(5)-H]. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 15.9 [CH_3, 2(6)-CH_3], 50.2 (CH_3, OCH_3), 92.7 (C, C4), 136.6 [CH, C3(5)], 138.3 [C, C2(6)], 186.2 (C, C1).

Spectroscopic and analytical data of **27**: mp 143–144°C (AcOEt) [described: mp 134–135°C (*i*-Pr_2O)[16]]. IR (KBr): ν 1727, 1697 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 1.21 (s, 3H, 3-CH_3), 1.29 (s, 3H, 8-CH_3), 1.39 (s, 3H, 10-CH_3), 1.77 (dd, J=J'=1.5 Hz, 3H, 5-CH_3), 2.83 (ddm, J=8.0 Hz, J'=3.5 Hz, 1H, 7-H), 3.11 (dd, J=8.0 Hz, J'=1.5 Hz, 1H, 2-H), superimposes in part 3.32 (dm, J=7.5 Hz, 1H, 1-H), 3.33 (s, 3H) and 3.44 (s, 3H) (3-OCH_3 and 10-OCH_3), 5.46 (dd, $J\approx$8.0 Hz, J'=1.0 Hz, 1H, 12-H), 6.11 (br. d, $J\approx$3.5 Hz, 1H, 6-H), 6.24 (dd, J=J'=7.5 Hz, 1H, 11-H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 15.7 (CH_3, 8-CH_3), 16.4 (CH_3, 5-CH_3), 20.1 (CH_3, 3-CH_3), 24.7 (CH_3, 10-CH_3), 41.5 (CH, C1), 42.7 (CH, C2), 43.0 (CH, C7), 50.7 (CH_3) and 51.7 (CH_3) (3-OCH_3 and 10-OCH_3), 53.8 (C, C8), 76.1 (C) and 77.9 (C) (C3 and C10), 133.7 (CH, C12), 135.1 (CH, C11), 136.5 (CH, C6), 137.6 (C, C5), 201.6 (C, C4), 210.6 (C, C9).

General procedure for the preparation of bicyclo-[3.3.1]nonane-3,7-diones from cyclohexa-2,5-dienones

To a stirred mixture of sodium (0.1–0.2 mmol) in anhydrous MeOH (3 mL), a solution of cyclohexadienone (1 mmol) in anhydrous MeOH (4 mL) and a solution of dimethyl 1,3-acetonedicarboxylate (2.1 mmol) in anhydrous MeOH (4 mL) were successively added dropwise, and the reaction mixture was heated under reflux for 48 h. The resulting solution was cooled to room temperature and treated with water (6 mL) and NaOH pellets (4 mmol). The mixture was heated under reflux overnight. The organic solvent was evaporated *in vacuo*, and the resulting aqueous mixture was made acidic with 2N HCl (4 mL), stirred at room temperature for 1 h, and extracted with CH_2Cl_2 (3×10 mL). The combined organic extracts were dried with anhydrous Na_2SO_4 and evaporated at reduced pressure to give a residue, which was purified by column chromatography through silica gel, recrystallization or sublimation.

9-Ethyl-9-methoxybicyclo[3.3.1]nonane-3,7-dione (29). This compound was prepared according to the procedure described above, from sodium (30 mg, 1.30 mmol) in anhydrous MeOH (20 mL), a solution of **14** (2.00 g, 13.2 mmol) in anhydrous MeOH (40 mL) and a solution of dimethyl 1,3-acetonedicarboxylate (4.57 g, 26.3 mmol) in anhydrous MeOH (40 mL). The obtained solid residue consisted of pure diketone **29** (2.50 g, 90% yield). The analytical sample of **29** was obtained by recrystallization: white solid, mp 141–142°C (Et_2O). IR (KBr): ν 1710, 1697 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 0.99 (t, J=7.5 Hz, 3H, CH_2CH_3), 1.95 (q, J=7.4 Hz, 2H, CH_2CH_3), 2.13 [br. d, J=15.5 Hz, 2H, 2(4)-H*endo*], 2.33 [br. d, J=16.5 Hz, 2H, 6(8)-H*endo*], 2.60 [dm, J=16.5 Hz, 2H, 6(8)-H*exo*], 2.64 [m, 2H, 1(5)-H], 2.90 [dm, J=15.5 Hz, 2H, 2(4)-H*exo*], 3.31 (s, 3H, OCH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 6.5 (CH_3, CH_2CH_3), 22.3 (CH_2, CH_2CH_3), 36.5 [CH, C1(5)], 43.8 [CH_2, C2(4)], 44.7 [CH_2, C6(8)], 48.4 (CH_3, OCH_3), 74.7 (C, C9), 207.8 (C, C7), 209.5 (C, C3). Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.70; H, 8.73.

9-Isopropyl-9-methoxybicyclo[3.3.1]nonane-3,7-dione (30) and methyl 3-hydroxy-*anti*-9-isopropyl-*syn*-9-methoxy-7-oxobicyclo[3.3.1]non-2-ene-2-carboxylate (31). This compound was prepared according to the procedure described above, from sodium (50 mg, 2.17 mmol) in anhydrous MeOH (10 mL), a solution of **16** (2.00 g, 12.0 mmol) in anhydrous MeOH (30 mL) and a solution of dimethyl 1,3-acetonedicarboxylate (4.63 g, 26.6 mmol) in anhydrous MeOH (30 mL). The resulting residue was submitted to column chromatography through silica gel (hexane/AcOEt mixtures, gradient elution), isolating consecutively starting **16** (640 mg), compound **31** (100 mg, 3% yield, 4% yield based on recovered **16**), and diketone **30** (270 mg, 10% yield, 15% yield based on recovered **16**). The analytical samples of **30** and **31** were obtained by recrystallization.

Spectroscopic and analytical data of **30**: white solid, mp 145–146°C (Et_2O). IR (KBr): ν 1716, 1703 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 1.22 [d, J=7.0 Hz, 6H, $CH(CH_3)_2$], 2.16 [br. d, J=13.5 Hz, 2H, 2(4)-H*endo*], 2.35 [br. d, J=17.0 Hz, 2H, 6(8)-H*endo*], 2.37 [heptet, J=7.0 Hz, 1H, $CH(CH_3)_2$], 2.61 [dm, J=17.0 Hz, 2H, 6(8)-H*exo*], 2.86–2.93 [complex signal, 4H, 1(5)-H and 2(4)-H*exo*], 3.48 (s, 3H, OCH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 17.3 [CH_3, $CH(CH_3)_2$], 30.2 [CH, $CH(CH_3)_2$], 35.8 [CH, C1(5)], 44.3 [CH_2, C2(4)], 44.6 [CH_2, C6(8)], 52.5 (CH_3, OCH_3), 76.0 (C, C9), 208.0 (C, C7), 209.5 (C, C3). Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.60; H, 9.00.

Spectroscopic and analytical data of **31**: white solid, mp 145–148°C (Et_2O). IR (KBr): ν 1713, 1652, 1613 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 1.15 (d, J=6.5 Hz, 3H) and 1.24 (d, J=7.0 Hz, 3H) [$CH(CH_3)_2$], 2.07 (dd, J=18.5 Hz, J'=1.0 Hz, 1H, 4-H*endo*), 2.26 (ddd, J=16.5 Hz, J'=2.5 Hz, J''=1.5 Hz, 1H, 6-H*endo*), 2.37 [heptet, J=6.5 Hz, 1H, $[CH(CH_3)_2]$, 2.43 (ddd, J=16.0 Hz, J'=J''=3.0 Hz, 1H, 8-H*endo*), 2.53–2.60 (complex signal, 2H, 6-H*exo* and 8-H*exo*), 2.62 (m, 1H, 5-H), 2.89 (ddd, J=18.5 Hz, J'=7.0 Hz, J''=1.5 Hz, 1H, 4-H*exo*), 3.30 (s, 3H, OCH_3), 3.42 (m, 1H, 1-H), 3.78 (s, 3H, $COOCH_3$), 12.1 (s, 1H, OH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 16.4 (CH_3) and 17.8 (CH_3) [$CH(CH_3)_2$], 30.8 [CH, $CH(CH_3)_2$], 32.3 (CH, C1), 34.8 (CH_2, C4), 34.9 (CH, C5), 43.1 (CH_2, C8), 45.8 (CH_2, C6), 51.7 (CH_3, $COOCH_3$), 53.3 (CH_3, OCH_3), 76.2 (C, C9), 98.3 (C, C2), 171.6 (C) and 172.3 (C) (C3 and $COOCH_3$), 210.0 (C, C7). Anal. Calcd for $C_{15}H_{22}O_5$: C, 63.81; H, 7.86. Found: C, 63.67; H, 7.95.

Methyl 9,9-dimethoxy-3,7-dioxobicyclo[3.3.1]nonane-1-carboxylate (32). To a stirred mixture of sodium (25 mg, 1.09 mmol) in absolute EtOH (10 mL), a solution of **17** (1.12 g, 5.28 mmol) in absolute EtOH (10 mL) and a solution of dimethyl 1,3-acetonedicarboxylate (1.01 g, 5.80 mmol) in absolute EtOH (10 mL) were successively added dropwise, and the reaction mixture was heated at room temperature for 48 h. The resulting solution was evaporated in vacuo and the resulting residue was taken up in $CHCl_3$ (30 mL), and washed with 5N HCl (20 mL) and water (20 mL). The organic solution was dried with anhydrous Na_2SO_4 and evaporated at reduced pressure to give a crude product (2.05 g), which consisted mainly of the corresponding bicyclic diester (^1H NMR). A thoroughly stirred solution of an aliquot of this crude product (1.00 g) in a mixture of DMSO (6 mL) and water (1 mL) was heated at 170°C for 30 min. NaCl (420 mg) was added and the reaction mixture was heated at 170°C for an additional 1-h-period and at 190°C for 30 min, and was cooled to room temperature. To the cold mixture, $CHCl_3$ (7 mL) was added and the resulting precipitate was filtered off in vacuo. The filtrate was concentrated by distillation of the organic solvents at reduced pressure. The resulting residue was taken up in CH_2Cl_2 (30 mL), and the organic solution was washed with water (3×25 mL), dried with anhydrous Na_2SO_4, and evaporated at reduced pressure. Sublimation of the resulting residue (460 mg) at 140°C/0.5 Torr afforded pure diketone **32** (390 mg, 56% yield). The analytical sample of **32** was obtained by recrystallization, mp 138–140°C (Et_2O). IR (KBr): ν 1737, 1712 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 2.24 [m, 2H, 4(6)-H*endo*], 2.27 [m, 2H, 2(8)-H*endo*], 2.83 (s, 1H, 5-H), 2.84 [m, 2H, 4(6)-H*exo*], 3.37 [d, J=15.5 Hz, 2H, 2(8)-H*exo*], 3.37 (s, 6H, 9-OCH_3), 3.73 (s, 3H, $COOCH_3$). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 37.7 (CH, C5), 43.8 [CH_2, C4(6)], 47.7 [CH_2, C2(8)], 49.5 (CH_3, 9-OCH_3), 52.3 (C, C1), 52.9 (CH_3, $COOCH_3$), 100.3 (C, C9), 171.8 (C, $COOCH_3$), 206.3 [C, C3(7)]. Anal. Calcd for $C_{13}H_{18}O_6$: C, 57.77; H, 6.72. Found: C, 57.82; H, 6.86.

9-Methoxy-1,9-dimethylbicyclo[3.3.1]nonane-3,7-dione (33). This compound was prepared according to the general procedure described above, from a mixture of sodium (12 mg, 0.52 mmol) in anhydrous MeOH (10 mL), a solution of **18** (700 mg, 4.60 mmol) in anhydrous MeOH (20 mL) and a solution of dimethyl 1,3-acetonedicarboxylate (2.00 g, 11.5 mmol) in anhydrous MeOH (20 mL). Sublimation of the resulting residue (800 mg) at 110°C/1 Torr afforded pure diketone **33** (430 mg, 44% yield) as a white solid. The analytical sample of **33** was obtained by recrystallization: mp 186–188°C (isopropanol). IR (KBr): ν 1710 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 1.02 (s, 3H, 1-CH_3), 1.53 (s, 3H, 9-CH_3), 1.96 (dd, J=15.5 Hz, J'=2.5 Hz, 1H, 2-H*endo*), 2.15 (dd, J=13.5 Hz, J'=2.5 Hz, 1H, 4-H*endo*), 2.20 (dd, J=16.5 Hz, J'=2.5 Hz, 1H, 8-H*endo*), 2.38 (ddd, J=16.5 Hz, J'=J''=2.5 Hz, 1H, 6-H*endo*), 2.46 (dd, J=16.5 Hz, J'=2.5 Hz, 1H, 8-H*exo*), 2.58 (dm, J=16.5 Hz, 1H, 6-H*exo*), 2.70–2.78 (complex signal, 2H, 4-H*exo* and 5-H), 2.91 (dd, J=15.5 Hz, J'=2.5 Hz, 1H, 2-H*exo*), 3.34 (s, 3H, 9-OCH_3). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 16.6 (CH_3, 9-CH_3), 23.3 (CH_3, 1-CH_3), 37.6 (CH, C5), 43.3 (C, C1), 43.9 (CH_2, C4), 45.1 (CH_2, C6), 48.9 (CH_3, 9-OCH_3), 50.8 (CH_2, C2), 52.4 (CH_2, C8), 75.0 (C, C9), 207.4 (C, C3), 209.3 (C, C7). Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.51; H, 8.62.

Attempted synthesis of 1-acetamido-9-ethyl-9-methoxybicyclo[3.3.1]nonane-3,7-dione from 19: obtention of 3-amino-4-ethyl-4-methoxycyclohexa-2,5-dienone (34). From sodium (6 mg, 0.26 mmol) in anhydrous MeOH (10 mL), a solution of **19** (430 mg, 2.06 mmol) in anhydrous MeOH (15 mL) and a solution of dimethyl 1,3-acetonedicarboxylate (1.00 g, 5.74 mmol) in anhydrous MeOH (15 mL), slightly impure cyclohexadienone **34** (190 mg, 55% yield) was obtained. An analytical sample of **34** was obtained by recrystallization: white solid, mp 165–166°C ($CHCl_3$). IR (KBr): ν 3363, 3175, 1677, 1652, 1556 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.76 (t, J=7.5 Hz, 3H, CH_2CH_3), 1.78 (q, J=7.5 Hz, 2H, CH_2CH_3), 3.16 (s, 3H, OCH_3), 5.30 (br. signal, 2H, NH_2), 5.61 (d, J=1.7 Hz, 1H, 2-H), 6.30 (dd, J=10.0 Hz, J'=1.7 Hz, 1H, 6-H), 6.39 (d, J=10.0 Hz, 1H, 5-H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 7.5 (CH_3, CH_2CH_3), 33.4 (CH_2, CH_2CH_3), 53.0 (CH_3, OCH_3), 78.0 (C, C4), 101.8 (CH, C2), 132.4 (CH, C6), 143.4 (CH, C5), 164.0 (C, C3), 185.6 (C, C1). No correct elemental analysis was obtained for this compound.

Attempted synthesis of 9,9-dimethoxy-2-methylbicyclo[3.3.1]nonane-3,7-dione from 23: obtention of methyl 3-hydroxy-9,9-dimethoxy-*endo*-8-methyl-7-oxobicyclo-[3.3.1]non-2-ene-2-carboxylate (35). Ester **35** was obtained when **23** was submitted to the reaction conditions of the general procedure described above. From sodium (120 mg, 5.22 mmol) in anhydrous MeOH (60 mL), a

solution of **23** (1.16 g, 6.90 mmol) in anhydrous MeOH (25 mL) and a solution of dimethyl 1,3-acetonedicarboxylate (2.61 g, 15.0 mmol) in anhydrous MeOH (25 mL), a brown oily residue (1.23 g), was obtained. An aliquot of this crude product (1.13 g) was recrystallized from $CHCl_3$ (1 mL), affording pure ester **35** (450 mg) as a white solid. The mother liquors were evaporated at reduced pressure and the resulting residue was submitted to column chromatograhy through silica gel (25 g, 40–60 μm) (hexane/AcOEt mixtures, gradient elution). On elution with hexane/AcOEt 85:15, pure ester **35** (480 mg) (52% total yield) was isolated, mp 139–140°C ($CHCl_3$). IR (KBr): ν 3397, 1708, 1654, 1618 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 0.88 (d, J=7.0 Hz, 3H, 8-CH_3), 2.16 (dd, J=16.5 Hz, J'=3.5 Hz, 1H, 6-H*endo*), 2.21 (d, J=18.0 Hz, 1H, 4-H*endo*), 2.67–2.74 (complex signal, 3H, 4-H*exo*, 5-H, 6-H*exo*), 2.97 (dq, J=4.5 Hz, J'=7.0 Hz, 1H, 8-H), 3.19 (s, 3H) and 3.35 (s, 3H) [9-$(OCH_3)_2$], 3.31 (dd, J=4.5 Hz, J'=3.0 Hz, 1H, 1-H), 3.71 (s, 3H, $COOCH_3$), 12.28 (br. s, 1H, OH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 12.1 (CH_3, 8-CH_3), 34.5 (CH, C5), 35.0 (CH_2, C4), 40.5 (CH, C1), 45.1 (CH_2, C6), 45.2 (CH, C8), 48.0 (CH_3) and 48.5 (CH_3) [9-$(OCH_3)_2$], 51.4 (CH_3, $COOCH_3$), 95.9 (C, C2), 99.7 (C, C9), 171.9 (C) and 172.2 (C) (C3 and $COOCH_3$), 211.3 (C, C7). Anal. Calcd for $C_{14}H_{20}O_6$: C, 59.14; H, 7.10. Found: C, 58.86; H, 7.09.

Attempted synthesis of 9,9-dimethoxy-2,4-dimethylbicyclo[3.3.1]nonane-3,7-dione from 25: obtention of methyl 3-hydroxy-9,9-dimethoxy-*endo*-6,*endo*-8-dimethyl-7-oxobicyclo[3.3.1]non-2-ene-2-carboxylate (36). Ester **36** was obtained when **25** was submitted to the reaction conditions of the general procedure described above. From sodium (209 mg, 9.09 mmol) in anhydrous MeOH (12 mL), a solution of **25** (1.40 g, 7.69 mmol) in anhydrous MeOH (18 mL) and a solution of dimethyl 1,3-acetonedicarboxylate (2.77 g, 15.9 mmol) in anhydrous MeOH (18 mL), a brown oily residue (1.57 g) was obtained. An aliquot of this crude product (0.89 g) was submitted to column chromatograhy through silica gel (27 g, 40–60 μm) (hexane/AcOEt mixtures, gradient elution). On elution with hexane/AcOEt 80:20, pure ester **36** (367 mg) (28% yield) was isolated as a white solid. Note: In a reaction carried out by using a higher excess of NaOH (13 equiv.) with a hydrolysis time of 60 h, and a higher excess of 2N HCl (9 mL/mmol starting cyclohexadienone) with a reaction time of 3 h, ester **36** was obtained in the same yield. The analytical sample of **36** was obtained by recrystallization: mp 159–163°C (AcOEt). IR (KBr): ν 3401, 1710, 1650, 1617 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 0.86 (d, J=7.0 Hz, 3H, 8-CH_3), 0.99 (d, J=7.0 Hz, 3H, 6-CH_3), 2.31 (d, J=19.0 Hz, 1H, 4-H*endo*), 2.45 (dd, J=19.0 Hz, J'=7.0 Hz, 1H, 4-H*exo*), 2.50 (ddd, J=7.0 Hz, J'=4.5 Hz, J''=3.5 Hz, 1H, 5-H), 2.85 (dqm, J=4.5 Hz, J'=7.0 Hz, 1H, 6-H), 2.99 (ddq, J=1.0 Hz, J'=4.0 Hz, J''=7.0 Hz, 1H, 8-H), 3.18 (s, 3H) and 3.36 (s, 3H) [9-$(OCH_3)_2$], 3.30 (dd, J=4.0 Hz, J'=3.5 Hz, 1H, 1-H), 3.70 (s, 3H, $COOCH_3$), 12.2 (br. s, 1H, OH). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 11.6 (CH_3, 6-CH_3), 11.8 (CH_3, 8-CH_3), 28.7 (CH_2, C4), 41.1 (CH) and 41.2 (CH) (C1 and C5), 43.3 (CH, C6), 45.3 (CH, C8), 48.0 (CH_3) and 48.5 (CH_3) [9-$(OCH_3)_2$], 51.4 (CH_3, $COOCH_3$), 95.7 (C, C2), 100.1 (C, C9), 172.1 (C) and 172.3 (C) (C3 and $COOCH_3$), 212.4 (C, C7). Anal. Calcd for $C_{15}H_{22}O_6$: C, 60.39; H, 7.44 Found: C, 60.52; H, 7.49.

X-Ray crystal-structure determination of 24[34]

A prismatic crystal was selected and mounted on a Enraf-Nonius CAD4 four-circle diffractometer. Unit-cell parameters were determined by automatic centering of 25 reflections ($12 < \theta < 21°$) and refined by the least-squares method. Intensities were collected with graphite-monochromatized Mo-$K\alpha$ radiation, using $\omega/2\theta$ scan technique. 4039 reflections were measured in the range $2.41 \leq \theta \leq 30.12$, 4011 of which were non-equivalent by symmetry [R_{int} (on I)=0.021]. 2432 reflections were assumed as observed by applying the condition $I > 2\sigma(I)$. Three reflections were measured every two hours as orientation and intensity control; significant intensity decay was not observed. Lorentz polarization but no absorption corrections were made. The structure was solved by Direct methods, using the SHELXS computer program[35] and refined by the full-matrix least-squares method with the SHELX-93 computer program[36] using 3961 reflections (very negative intensities were not assumed). The function minimized was $\Sigma w(|F_o|^2 - |F_c|^2)^2$, where $w = [\sigma^2(I) + (0.1735P)^2]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$. f, f' and f'' were taken from International Tables of X-ray Crystallography.[37] 4H Atoms were located from a difference synthesis and refined with an overall isotropic temperature factor and 16H atoms were computed and refined with an overall isotropic temperature factor using a riding model. Goodness of fit on F^2=0.967 for all observed reflections. Mean shift/e.s.d.=0.0 (Table 3).

X-Ray crystal-structure determination of 27[34]

The same procedure described above was followed. 4523 reflections were measured in the range $2.27 \leq \theta \leq 29.96$, 4493 of which were non-equivalent by symmetry [R_{int} (on I)=0.003]. 3530 reflections were assumed as observed by applying the condition $I > 2\sigma(I)$. The structure was solved as before using 4493 reflections (very negative intensities were not assumed). The function minimized was $\Sigma w(|F_o|^2 - |F_c|^2)^2$, where $w = [\sigma^2(I) + (0.1056P)^2 + 0.0543P]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$. f, f' and f'' were taken from International Tables of X-ray Crystallography.[37] 45H Atoms were located from a difference synthesis and refined with an overall isotropic temperature factor and 3H atoms were computed and refined with an overall isotropic temperature factor using a riding model. Goodness of fit on F^2=1.038 for all observed reflections. Mean shift/e.s.d.=0.00 (Table 3).

X-Ray crystal-structure determination of 36[34]

The same procedure described above was followed. 4560 reflections were measured in the range $2.63 \leq \theta \leq 29.96$, 4390 of which were non-equivalent by symmetry [*R*int (on I)=0.031]. 2994 reflections were assumed as observed by applying the condition $I > 2\sigma(I)$. The structure was solved as before using 4390 reflections (very negative intensities were not assumed). The function minimized was $\Sigma w(|F_o|^2 - |F_c|^2)^2$, where $w = [\sigma^2(I) + (0.1426P)^2]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$. f, f' and f'' were taken from International Tables of X-ray Crystallography.[37] 15H Atoms were located from a difference synthesis and refined with

Table 3. Experimental data of the X-ray crystal structure determination of compounds **24**, **27** and **36**

	24	**27**	**36**
Molecular formula	$C_{16}H_{20}O_4$	$C_{18}H_{24}O_4$	$C_{15}H_{22}O_6$
Molecular mass	276.32	304.37	298.33
Temperature	293 (2)K	293(2) K	293(2)K
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P1	P1	$P2_1/c$
Cell parameters	[a]	[a]	[a]
a [Å]	6.941(8)	7.068(4)	12.109(6)
b [Å]	9.185(4)	9.647(2)	8.059(3)
c [Å]	11.978(3)	12.561(2)	15.63(3)
α [°]	100.64(3)	71.01	90
β [°]	101.70(5)	79.01	98.00(8)
γ [°]	107.41(3)	76.92	90
V [Å^3]	688.5(9)	782.5(5)	1510(3)
Z	2	2	4
$F(000)$	296	328	640
d (calcd) [Mg m^{-3}]	1.333	1.292	1.312
Size of crystal [mm]	0.1×0.1×0.2	0.1×0.1×0.2	0.1×0.1×0.2
Measured reflections	4039	4523	4560
Independent reflections	4011	4493	4390
Observed reflections	2432	3530	2994
μ(Mo-$K\alpha$) [mm^{-1}][b]	0.100	0.100	0.100
R	0.190	0.051	0.063
Rw	0.967	0.141	0.172
$\Delta\rho_{max}$[c] (eÅ^{-3})	0.601	0.335	0.368
$\Delta\rho_{min}$[d] (eÅ^{-3})	−0.559	−0.291	−0.301
Refined parameters	134	286	258
Max. shift/e.s.d	0.0	0.00	0.00

[a] Determined by automatic centering of 25 reflections ($12 \leq \theta \leq 21°$).
[b] μ(Mo-$K\alpha$), linear absorption coefficient. Radiation Mo-$K\alpha$ (λ=0.71069 Å).
[c] Maximum peaks in final difference synthesis.
[d] Minimum peaks in final difference synthesis.

an overall isotropic temperature factor and 7H atoms were computed and refined with an overall isotropic temperature factor using a riding model. Goodness of fit on F^2=0.970 for all observed reflections. Mean shift/e.s.d.=0.00. (Table 3)

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