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1,3-Bis(diarylmethylidene)-2-methylidenecyclohexanes in cycloaddition and cyclodimerization reactions. The role of stereoelectronic factors

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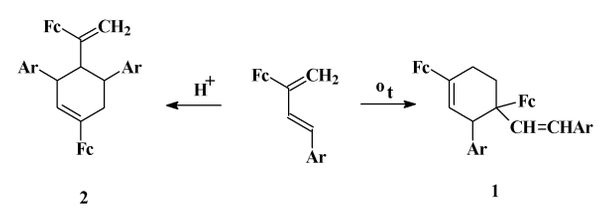
Cycloaddition and cyclodimerization reactions of 1,3-dibenzylidene- and 1,3-bis(*p*-methoxybenzylidene)-2-methylidenecyclohexanes, *i.e.*, the diaryltrienes with fixed *S-cis*-configurations of exocyclic double bonds are studied. These compounds undergo *in situ* cyclodimerization of the [4+2]-type upon dehydration of the precursor tertiary alcohols and form *endo*-adducts in the Diels–Alder reaction with *N*-phenylmaleimide. In the presence of CF_3COOH, acid-catalyzed cyclodimerization takes place leading to methylidene-substituted spirocyclodimers, which undergo intramolecular cyclization upon prolonged contact with CF_3COOH to form a fused carbocyclic system containing a central, 'three-petal' fragment of six-membered rings.

Introduction

Previously, we have discussed the role of stereoelectronic factors in the cycloaddition and cyclodimerization reactions of ferrocenyl-substituted dienes and trienes.[1–5] The high regio- and diastereoselectivities of these processes have been established, which resulted in exclusive or predominant formation of one of diastereomers of compounds **1** or **2** (Scheme 1) depending on the reaction conditions.



2 **1**

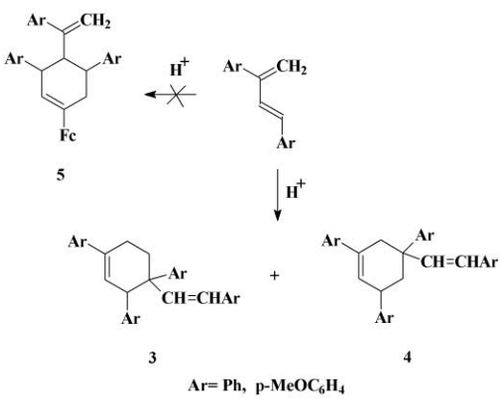
Ar= Ph, p-MeOC$_6$H$_4$
Fc= C$_5$H$_5$FeC$_5$H$_4$

Scheme 1

Unlike ferrocenyl-1,3-dienes, 1,3-diarylbuta-1,3-dienes[6,7] undergo smooth cyclodimerization upon acid-catalyzed dehydration of 1,3-diarylbut-1-en-3-ols resulting in a *ca.* 1 : 1 mixture of cyclodimers **3** and **4** (Scheme 2).

The lack of regioselectivity in this reaction and the absence of the cationic cycloaddition products of the type **5** makes 1,3-diarylbutadienes essentially different from their ferrocenyl-containing analogues.

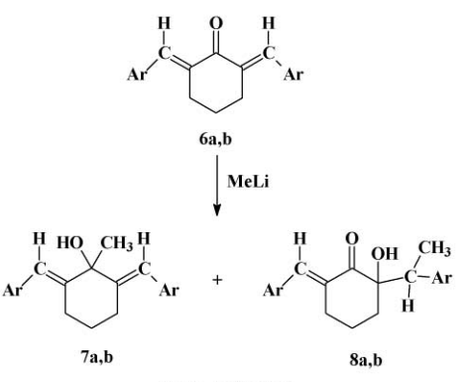
Information on the synthesis and properties of *exo*-cyclic cross-conjugated trienes with aryl substituents at the multiple bonds is almost completely absent. Studies of chemical properties of this type of compounds, in particular, their behavior in cycloaddition and cyclodimerization reactions, deserve special attention, since the peculiarities of their spatial and electronic structures allow one to expect unusual results which might be of interest for both their synthetic and theoretical aspects.



Scheme 2

Results and discussion

In the present paper, we describe our approaches to the synthesis of *S-cis*-diaryltrienes starting from bis(arylmethylidene)cyclohexanones **6a**,**b**[8] (Scheme 3).



Scheme 3

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The *E,E*-dienones **6a**,**b** were prepared by the condensation of cyclohexanone with benzaldehyde and *p*-anisaldehyde, respectively, in aqueous ethanol in the presence of an alkali.[9]

The reactions with MeLi[1–3] gave *ca*. 70% of the corresponding alcohols **7a**,**b**. These compounds were isolated as the single *E,E*-isomers, which was established by X-ray diffraction analysis.[8] In the presence of traces of oxygen, a side process takes place, *viz.*, the addition of MeLi in positions 3,4 of the conjugated heterodiene systems of the dienones giving rise to substituted 2-hydroxycyclohexanones **8a**,**b** (9–12%). The latter were isolated in a crystalline state from the mother liquors following crystallization of the alcohols **7a**,**b** from ethanol. ^{1}H NMR spectrosopic data of compounds **8a**,**b** suggest that they were formed in single diastereomeric forms.

The structure of the hydroxyketone **8b** was established based on the X-ray diffraction data of single crystals prepared by crystallization from methanol. The general view of the molecule of 2-hydroxy-6-(4-methoxyphenylmethylene)-2-[1-(4-methoxyphenyl)ethyl]cyclohexanone **8b** is shown in Fig. 1; the main geometrical parameters are given in the caption and require no further comment. X-ray structural data show that the arylmethylene fragment has the *E* configuration for the double bond as in the alcohols **7a**,**b**.[8] The monoclinic crystals of the racemic form of compound **8b** contain two asymmetrical molecules of the hydroxy ketone corresponding to the *R* and *S* enantiomers in a unit cell. The keto and hydroxy groups of the enantiomers are bound through hydrogen bonds (Fig. 2).

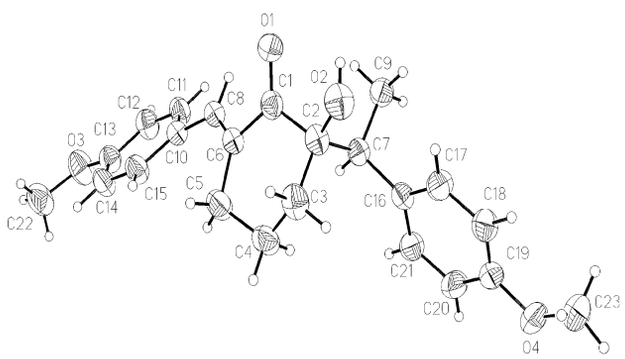


Fig. 1 Crystal structure of **8b**. Selected bond lengths/Å: O(1)–C(1) = 1.220(3); O(2)–C(2) = 1.417(3); C(1)–C(2) = 1.537(3); C(2)–C(7) = 1.562(3); C(6)–C(8) = 1.341(3).

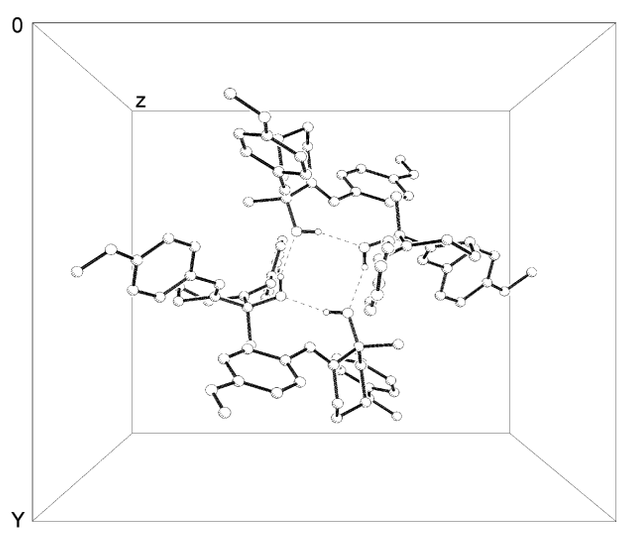
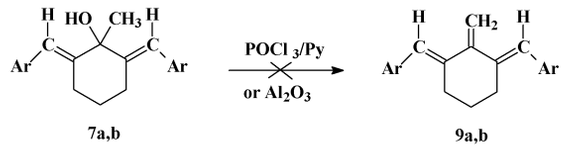


Fig. 2 Crystal packing of **8b**.

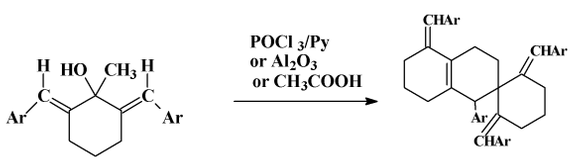
The target compounds, *viz.*, 1,3-bis(arylmethylene)-2-methylenecyclohexanes (**9a**,**b**) could not be isolated individually upon dehydration of the alcohols **7a** and **7b** under the action of $POCl_3$ in pyridine[1] or by treatment with Al_2O_3 (Brockmann activity I or II)[3] (Scheme 4).



7a,b **9a,b**

Scheme 4

In both cases, the Diels–Alder-type cyclodimerization products, *viz.*, spiro[2,6-bis(arylmethylene)cyclohexane-1,2′-(1-aryl-5-arylmethylene-1,2,3,4,5,6,7,8-octahydronaphthalenes)] **10a**,**b** were isolated (yields *ca*. 70–73%) (Scheme 5).



7a,b **10a,b**

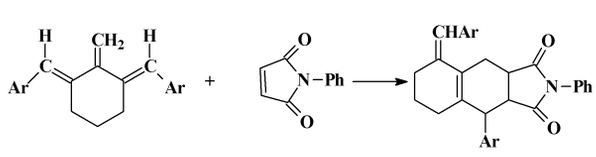
Scheme 5

These compounds were also obtained under the conditions of the classical acid-catalyzed cyclodimerization of buta-1,3-dienes,[2,10,11] *viz.*, upon boiling of alcohols **7a**,**b** in acetic acid.

The structures of the cyclodimers **10a**,**b** were established based on the following data. The ^{1}H NMR spectrum of compounds **10a**,**b** contains (*i*) multiplets of the protons of four aryl groups, (*ii*) three singlets of the olefinic protons of three arylmethylidene fragments, (*iii*) one singlet of the proton of the ArC(1)H group (δ 3.72 and 3.65, respectively), multiplets of the protons of eight methylene groups, and (*v*) four singlets of the methoxy groups for compound **10b** (δ 3.77, 3.80, 3.81, and 3.83). Additional information inferred from the ^{13}C NMR spectra. These contained, *inter alia*, four signals for the C(aromatic)$_{ipso}$ atoms, five signals for the olefinic C= atoms bearing no protons, eight signals for the CH_2 groups, one signal for the C(sp^3)H atom, and one signal for the C(spiro) atom. These data altogether point unequivocally to the dimeric structure of the type **10**.

Obviously, the cyclodimers **10a**,**b** originate from the trienes **9a**,**b**, which are formed upon dehydration of the alcohols **7a**,**b** and underwent the Diels–Alder-type [4+2]-cycloaddition. The reactions are regioselective and give one diastereomeric cyclodimer.

The results obtained are evidence, in our opinion, of the high proneness of the trienes **9a**,**b** to enter into the Diels–Alder cycloaddition reactions. This suggestion was confirmed by performing dehydration of the alcohols **7a**,**b** with $POCl_3$ in pyridine at ambient temperature in the presence of *N*-phenylmaleimide. The trienes **9a**,**b** formed *in situ* give the corresponding Diels–Alder adducts **11a**,**b** (Scheme 6).



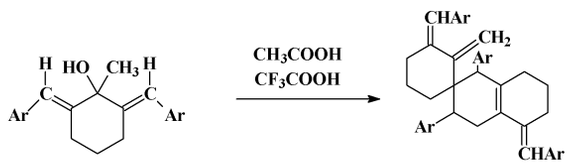
9a,b **11a,b**

Scheme 6

Compounds **11a**,**b** are formed stereospecifically and are isolated as single isomers exclusively, presumably *endo* isomers. This assignment is made based on the known[3] NMR criteria for the attribution of the Diels–Alder adducts to *exo* and *endo* isomers. The characteristic feature of the ^{1}H NMR spectra of these adducts is that the multiplets of the two protons of the

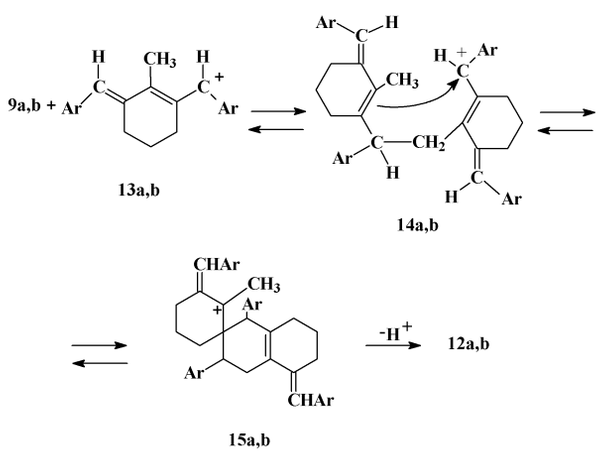
N-phenyl-substituted fragment resonate in higher field (δ 6.43 and 6.52) than the singlets of the olefinic protons of the ArCH= groups (δ 6.69 and 6.62, respectively) and the multiplets of other protons of the aromatic substituents, which is typical of the *endo* isomers.

It was also found that the dehydration of the alcohols **7a**,**b** in a 9 : 1 mixture of acetic and trifluoroacetic acids resulted in the formation of methylidene-substituted spirocyclodimers **12a**,**b** (Scheme 7).



Scheme 7

We believe that the cyclodimers **12a**,**b** are the cationic cyclodimerization products of the trienes **9a**,**b** formed upon dehydration of the alcohols **7a**,**b** (Scheme 8). This reaction pathway presumes the presence of both the trienes **9a**,**b** and the respective dienylcarbenium cations **13a**,**b**.



Scheme 8

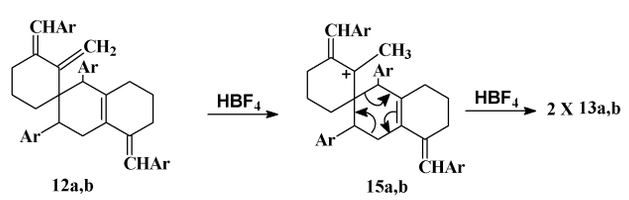
The cations **13a**,**b** add to the methylidene groups of the trienes **9a**,**b** to form dimeric bisdienyl cations **14a**,**b**, which undergo intramolecular cyclization into the cyclodimeric allylic cations **15a**,**b**. Subsequent spontaneous deprotonation of the latter affords the cyclodimers **12a**,**b**.

The structures of compounds **12a**,**b** were established based on the analysis of the analysis of the ^{1}H and ^{13}C NMR spectra. The characteristic features of the ^{1}H NMR spectra of the dimers **12a**,**b** are as follows: each contained one singlet of the ArCH group (δ 3.58 and 3.52) and one triplet of the ArCH group (δ 3.63 and 3.61), two singlets of the $=CH_2$ fragment (δ 6.40, 6.50 and 6.25, 6.37), two singlets of the ArCH= substituents (δ 6.61, 6.64 and 6.58, 6.65), and multiplets of the protons of seven methylene groups. The ^{13}C NMR spectroscopic data corroborate the cyclodimeric structures of compounds **12a**,**b**. The spectra contain, *inter alia*, four signals for the $C(aromatic)_{ipso}$ atoms, five signals for the C= atoms bearing no protons, one signal for the C(spiro) atom, seven signals for the methylene groups, one signal for the methylidene group $=CH_2$, and two signals for the olefinic carbon atoms of the ArCH= fragments.

Acid-catalyzed cyclodimerization of the trienes **9a**,**b** occurs in the presence of trifluoroacetic acid, which suggests, in our opinion, lower ability of these compounds, compared with the ferrocenyl analogs,[12,13] to undergo cationic cyclodimerization due apparently to easy deprotonation of the intermediate dienyl cations **13a**,**b**. Presumably, the presence of trifluoroacetic acid is required to suppress this deprotonation.

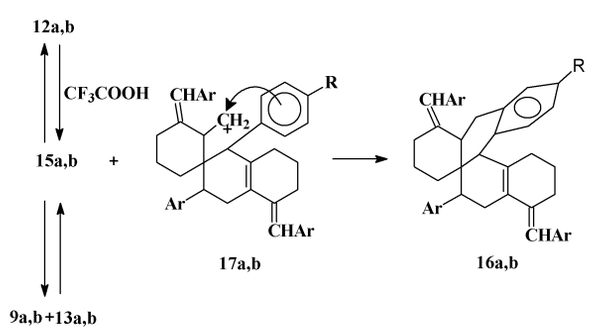
Spirocyclodimers **12a**,**b** are formed stereospecifically. Compounds **12a** and **12b** were isolated as single diastereomers, which is probably the consequence of favorable effects of both electronic and steric factors. Thus it is known that the electronic factor, which manifests itself in a fairly high ability of an aryl substituent at the carbenium center to stabilize it,[14,15] directs the addition of the cations **13a**,**b** exclusively at the exocyclic $=CH_2$ group of the trienes **9a**,**b**, resulting in stabilized dimeric α-aryldienyl cations **14a**,**b**. The *E* configurations of the double bonds of arylmethylidene fragments in the trienes **9a**,**b** do not prevent this direction of the addition (the steric factor). It is also known that the absence of substantial steric hindrances of the configurational nature in the intermediate linear dimeric allylic cations[16–18] is prerequisite for the intramolecular alkylation and formation of cyclodimeric cations of the type **15**. The configurational features of the cyclohexane moieties in **14a**,**b** seem to meet these demands and do not create considerable steric hindrances in the establishment of the conformation most favorable for the intramolecular cyclization of the cyclic cations **14a**,**b** into the cyclic carbocations **15a**,**b**. In turn, the latter represent arylallylic cations and seem to be no less stable than the linear cations **14a**,**b** (electronic factor). These factors altogether create prerequisites for the cationic cyclodimerization resulting in the cyclodimers **12a**,**b**.

We have investigated the behavior of the spirocyclodimers **12a**,**b** in reactions promoted by CF_3COOH and HBF_4 etherate. Treatment of compounds **12a**,**b** with an excess of HBF_4 etherate brings about their fragmentation resulting in the formation of insoluble tetrafluoroborates of the cations **13a**,**b** in quantitative yield (Scheme 9).



Scheme 9

The action of trifluoroacetic acid does not bring about complete fragmentation of the dimers **12a**,**b**. Their storage in CF_3COOH at ~20 °C results in slow accumulation of "three-petal" fused carbocyclic compounds **16a**,**b** representing intramolecular *ortho*-alkylation products of the Ar fragment (Scheme 10).



Scheme 10

Presumably, two competing protonation processes of the $=CH_2$ group occur in the reaction with CF_3COOH, *viz.*, the reversible fast protonation leading to the cations **15a**,**b** and non-standard (anti-Markovnikov) slow protonation leading to the cations **17a**,**b**, which alkylate immediately the *ortho*-position of the aryl substituent thus shifting the equilibrium towards compounds **16a**,**b**.

The dimers **12a**,**b** gave no fragmentation products upon treatment with CF_3COOH in contrast to the treatment with HBF_4. This may be due to slower cleavage of the spirocarbocations **15a**,**b** into the triene **9a**,**b** and cationic **13a**,**b** components (Scheme 10). This retardation of the cleavage process may be accounted for by the nearly identical stabilities of the allylic **15a**,**b** and dienyl **13a**,**b** cations.[4,5,14,15]

As a consequence, conditions are provided for the minor, unstable primary carbocations **17a**,**b** to alkylate the spatially proximal phenyl substituent, resulting in compounds **16a**,**b**, thereby shifting the reaction equilibrium (Scheme 10).

The structures of these compounds **12a**,**b** and **16a**,**b** were established based on the ^1H and ^{13}C NMR spectroscopic data. Thus the signals for the $=CH_2$ protons in the ^1H NMR spectra are absent contrary to the spectra of the dimers **12a**,**b**. The spectra of compounds **16a**,**b** contained each, *inter alia*, two doublets of two methylene groups (δ 2.75, 2.87 and 2.64, 2.75), two triplets and one singlet of three methine protons, and two singlets of the olefinic protons of the ArCH= fragments.

The ^{13}C NMR spectra contained five signals for the $C(aromatic)_{ipso}$ atoms, four signals for the C= atoms bearing no protons, one signal for the C(spiro) atom, two signals for the olefinic C atoms of the ArCH= groups, eight signals for the methylene carbon atoms, and three signals for the methine groups. These data altogether, as well as the presence of resonances of four aryl substituents, confirm unambiguously the fused structures of compounds **16a**,**b** (Fig. 3).

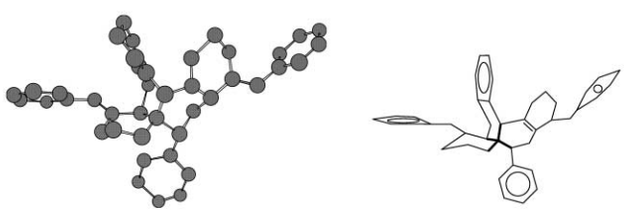


Fig. 3 General view of the compound **16a**, obtained from MM2 calculations, the hydrogens are omitted for clarity.

Thus, exocyclic diaryltrienes undergo cyclodimerization according to the [4+2]-cycloaddition and cationic cycloaddition pathways to yield cyclodimers **10a**,**b** and spirocyclodimers **12a**,**b**, respectively. The intramolecular, acid-catalyzed alkylation in compounds **12a**,**b** was accomplished for the first time, this resulted in "three-petal" fused carbocyclic compounds. Information on this type of processes is lacking in the chemical literature. Elucidation of the effects of various factors on the peculiarities of cationic cyclodimerization of exocyclic cross-conjugated trienes and intramolecular cyclization in the respective cyclodimers deserve, in our opinion, further studies.

Experimental

UV spectra were recorded on a Specord UV-VIS spectrophotometer. IR spectra were obtained for KBr pellets on a Specord 75-IR instrument. All ^1H and ^{13}C NMR spectra were recorded on a Unity Inova Varian spectrometer (300 and 75 MHz) for solutions in $CDCl_3$ with Me_4Si as the internal standard. Mass spectra (EI, 70 eV) were obtained on a Varian-MAT CH-6 mass spectrometer. Column chromatography was carried out on Al_2O_3 (Brockmann activity III). 2,6-Diarylmethylenecyclohexanones **6a**,**b** were synthesized by a standard procedure[9] from cyclohexanone and benzaldehyde or *p*-anisaldehyde in aqueous ethanolic alkali. Purification and isolation of the dienones **6a** and **6b** were carried out by column chromatography in a 3 : 1 hexane-chloroform solvent system. Compound 6a, yield 70%, mp 120–121 °C (Lit.[9]:mp 120 °C). Compound 6b, yield 67%, mp 153–154 °C (Lit.[9]:mp 153–154 °C).

2,6-Bis(arylmethylene)-1-methylcyclohexanols 7a,b. General procedure

A solution of the dienone **6a**,**b** (50 mmol) in dry benzene (50 ml) was added with stirring under dry nitrogen to an ethereal solution of MeLi (70 mmol). After 30 min the reaction mixture was quenched with 5% aqueous NaOH, the organic layer was separated, dried with $MgSO_4$, and the solvent was evaporated *in vacuo*. The residue was recrystallized from ethanol (30 ml). The crystals were filtered off, washed with ethanol on a filter, and dried *in vacuo* to give 2,6-dibenzylidene-1-methylcyclohexanol **7a**, yield 1.02 g (70%) and 2,6-bis(4-methoxybenzylidene)-1-methylcyclohexanol **7b**, yield 1.26 g (72%).

The ethanolic mother liquors were concentrated *in vacuo* and the residues were chromatographed on alumina (benzene–ethyl acetate, 2 : 1) to give 0.15 g (10%) of compound **8a**, mp 121–122 °C and 0.17 g (9%) of compound **8b**, mp 124–125 °C.

Compound **7a**, colorless crystals, mp 135–136 °C. [Found: C, 86.73; H, 7.78%. Calc. for $C_{21}H_{22}O$: C, 86.85; H, 7.63%]; ν_{max}(KBr)/cm^{-1}: 1140, 1357, 1444, 1491, 1600, 1640, 2932, 3309; λ_{max}($CHCl_3$)/nm: 249.5, 205.5; δ_H (300 MHz, $CDCl_3$): 1.46 (1 H, m, CH_2), 1.66 (3 H, s, CH_3), 1.86 (1 H, m, CH_2), 1.96 (1 H, s, OH), 2.28 (2 H, td, J = 4.6, 12.8 Hz, CH_2), 2.96 (2 H, td, J = 4.6, 12.8 Hz, CH_2), 6.83 (2 H, s, CH=), 7.19–7.40 (10 H, m, C_6H_5); δ_C (75 MHz, $CDCl_3$): 27.1 (2 CH_2), 27.5 (1 CH_2), 28.9 (CH_3), 76.50 (C–O), 119.95 (2 CH=), 126.2, 128.0, 129.0 (2 C_6H_5), 138.1 (2 C), 147.7 (2 C_{ipso}).

Compound **7b**, colorless crystals, mp 160–161 °C. [Found: C, 78.67; H, 7.64. Calc. for $C_{23}H_{26}O_3$: C, 78.82; H, 7.48%]; ν_{max}(KBr)/cm^{-1}: 1143, 1250, 1290, 1458, 1509, 1607, 1640, 2930, 3295; λ_{max}($CHCl_3$)/nm: 260.0, 208.0; δ_H (300 MHz, $CDCl_3$): 1.39 (1 H, m, CH_2), 1.62 (3 H, s, CH_3), 1.81 (1 H, m, CH_2), 1.90 (1 H, s, OH), 2.23 (2 H, td, J = 4.5, 12.2 Hz, CH_2), 2.96 (2 H, td, J = 4.5, 12.2 Hz, CH_2), 3.80 (6 H, s, 2 OCH_3), 6.74 (2 H, s, CH=), 6.86 (4 H, d, J = 8.6 Hz, C_6H_4), 7.13 (4 H, d, J = 8.6 Hz, C_6H_4); m/z 350 $[M]^+$.

Compound **8a**, colorless crystals, mp 121–122 °C. [Found: C, 82.49; H, 7.12. Calc. for $C_{21}H_{22}O_2$.: C, 82.32; H, 7.24%]; ν_{max}(KBr)/cm^{-1}: 1133, 1412, 1590, 1606, 1631, 1720, 2930, 3319; δ_H (300 MHz, $CDCl_3$): 1.15 (3 H, d, J = 5.7 Hz, CH_3), 1.94 (4 H, m, 2 CH_2), 2.30 (1 H, s, OH), 2.70 (1 H, m, CH_2), 3.15 (1 H, q, J = 5.7 Hz, CH), 3.28 (1 H, m, CH_2), 6.96–7.65 (10 H, m, 2 C_6H_5); m/z 306 $[M]^+$.

Compound **8b**, colorless crystals, mp 124–125 °C. [Found: C, 75.17; H, 7.24. Calc. for $C_{23}H_{26}O_4$: C, 75.38; H, 7.15%]; ν_{max}(KBr)/cm^{-1}: 1139, 1240, 1271, 1450, 1501, 1603, 1635, 1715, 2929, 3318; δ_H (300 MHz, $CDCl_3$): 1.10 (3 H, d, J = 6.0, CH_3), 1.86 (4 H, m, 2 CH_2), 2.19 (1 H, s, OH), 2.61 (1 H, m, CH_2), 3.08 (1 H, q, J = 6.0 Hz, CH), 3.23 (1 H, m, CH_2), 3.77 (3 H, s, OCH_3), 3.82 (3 H, s, OCH_3), 6.82–7.46 (8 H, m, 2 C_6H_4)); m/z 366 $[M]^+$.

Dehydration of the alcohols 7a,b with $POCl_3$ in pyridine. General procedure

$POCl_3$ (2 ml, 2.2 mmol) was added dropwise at 5–10 °C to a stirred solution of the alcohol **7a** (2.9 g) or the alcohol **7b** (3.5 g) in dry pyridine (120 ml). Stirring was continued for 4 h at ~20 °C and then water (200 ml) was added. The reaction products were extracted with benzene (3 × 50 ml), the combined extracts were washed with water (2 × 20 ml) and dried with $CaCl_2$. The solvent was evaporated and the residue was chromatographed on Al_2O_3 (hexane–benzene, 4:1) to give 1.82 g (67%) of spiro[2,6-dibenzylidenecyclohexane-1,2′-(5-benzylidene-1-phenyl-1,2,3,4,5,6,7,8-octahydronaphthalene)] **10a** and 2.3 g (72%) of spiro[2,6-bis(4-methoxybenzylidene)cyclohexane-1,2′-(5-(4-methoxybenzylidene)-1-(4-methoxyphenyl)-1,2,3,4,5,6,7,8-octahydronaphthalene)] **10b**.

Compound **10a**, colorless powder, mp 235–236 °C. [Found: C, 92.43; H, 7.58. Calc. for $C_{42}H_{40}$: C, 92.60; H, 7.40%.];

ν_{max}(KBr)/cm^{-1}: 1141, 1447, 1492, 1598, 1632, 2855, 2917, 2938; λ_{max}($CHCl_3$)/nm: 204.5; δ_H (300 MHz, $CDCl_3$): 1.50–1.88 (4 H, m, 2 CH_2), 2.0–2.4 (6 H, m, 3 CH_2), 2.45–2.78 (6 H, m, 3 CH_2), 3.72 (1 H, s, CH), 5.50 (1 H, s, CH=), 6.59 (1 H, s, CH=), 6.66 (1 H, s, CH=), 6.68 (2 H, m, Ph), 7.1–7.38 (18 H, m, Ph); δ_C (75 MHz, $CDCl_3$): 18.5, 18.9, 19.1, 19.7, 20.5, 22.1, 22.9, 27.0 (8CH_2); 46.8 (C_{spiro}); 50.1 (CH); 116.3, 118.9, 120.4 (3 CH=); 120.6, 120.8, 120.9, 121.2, 122.6 (3 C), 122.9 (2 C), 123.1 (2 C), 123.3 (2 C), 123.7 (2 C), 124.3 (2 C), 124.7 (3 C) (4 Ph); 132.6, 133.7, 133.8 (2 C), 134.2 (5 C); 137.8, 141.0 (2 C), 141.4 (4 C_{ipso}); *m*/*z* 544, 546 $[M]^+$

Compound **10b**, colorless powder, mp 268–269 °C. [Found: C, 82.95; H, 7.31. Calc. for $C_{46}H_{48}O_4$: C, 83.10; H, 7.28%]; ν_{max}(KBr)/cm^{-1}: 1036, 1177, 1250, 1460, 1510, 1607, 1635, 2835, 2933; λ_{max}($CHCl_3$)/nm: 204.5; δ_H (300 MHz, $CDCl_3$): 1.52–1.92 (4 H, m, 2CH_2), 2.02–2.30 (6 H, m, 3 CH_2), 2.52–2.73 (6 H, m, 3 CH_2), 3.65 (1H, s, CH), 3.77 (H, s, OCH_3), 3.81 (H, s, OCH_3), 3.83 (3 H, s, OCH_3), 3.85 (3 H, s, OCH_3), 5.43 (1 H, s, CH=), 6.51 (1 H, s, CH=), 6.57 (1 H, s, CH=), 6.63–6.91 (10 H, m, Ar), 7.02–7.29 (6 H, m, Ar); δ_C (75 MHz, $CDCl_3$): 23.6, 23.9, 24.2, 24.6, 25.5, 27.2, 28.0, 27.0 (8 CH_2); 39.6 (C_{spiro}); 51.8 (CH); 54.1 (OCH_3), 55.2 (3 OCH_3); 113.0, 113.1, 113.4 (3 CH=); 113.6, 113.8, 120.6, 123.0, 124.6, 129.4 (2 C), 123.8 (2 C), 130.4 (3 C), 130.5 (3 C), 131.4 (4 Ar); 131.7, 131.8, 134.9, 137.2, 137,3 (5 C); 141.9, 144.6 (2 C), 145.7 (4 C_{ipso}); 157.5, 157.7, 158.0, 158.1 (4 Ar–O); *m*/*z* 664 $[M]^+$.

Dehydration of the alcohols 7a,b with $POCl_3$ in pyridine in the presence of *N*-phenylmaleimide. General procedure

$POCl_3$ (0.2 ml) was added dropwise to a solution of the alcohol **7a** (or **7b**) (1 mmol) and *N*-phenylmaleimide (0.26 g, 1.5 mmol) in dry pyridine (30 ml) and the mixture was stirred for 20 h at ~20 °C. Then water (100 ml) was added and the reaction products were extracted with benzene. Subsequent processing and column chromatography (hexane–benzene, 2 : 1) as described above gave 0.32 g (73%) of *N*-phenyl-5-benzylidene-1-phenyl-1,2,3,4,5,6,7,8-octahydronaphthalene-2,3-dicarboximide **11a** and 0.36 g (70%) of *N*-phenyl-5-(4-methoxybenzylidene)-1-(4-methoxyphenyl)-1,2,3,4,5,6,7,8-octahydronaphthalene-2,3-dicarboximide **11b**.

Compound **11a**, white finely crystalline powder, mp 244–245 °C. [Found: C, 83.69; H, 6.28; N,2.92. Calc. for $C_{31}H_{27}NO_2$: C, 83.57; H, 6.11; N, 3.14%]; ν_{max}(KBr)/cm^{-1}: 1145, 1365, 1412, 1600, 1622, 1665, 1720, 2912; δ_H (300 MHz, $CDCl_3$): 1.74 (1 H, m, CH_2), 2.0 (1 H, m, CH_2), 2.23 (1 H, m, CH_2), 2.53 (2 H, m, CH_2), 2.86 (1 H, m, CH_2), 3.14 (2 H, m, CH_2), 3.47 (2 H, m, 2 CH), 3.54 (1 H, d, *J* = 6.9 Hz, CH), 6.69 (1 H, s, CH=), 6.43 (2 H, m, Ph), 7.14–7.39 (13 H, m, Ph); δ_C (75 MHz, $CDCl_3$):21.2, 23.2, 27.4, 31.2 (4 CH_2), 37.9, 44.1, 47.2 (3 CH); 123.0 (CH=); 126.3 (3 C), 127.8, 128.1 (2 C), 128.4, 128.8 (2 C), 128.9 (2 C), 129.3 (2 C), 129.5 (2 C) (3 Ph) 131.4, 136.7, 137.7 (3 C); 136.8, 136.9 (2 C_{ipso}); 169.8 (C–N) 178.5 (2 C=O); *m*/*z* 445 $[M]^+$.

Compound **11b**, white powder, mp 273–274 °C. [Found: C, 78.52; H, 6.04; N,2.58. Calc. for $C_{33}H_{31}NO_4$: C, 78.39; H, 6.18; N, 2.77%]; ν_{max}(KBr)/cm^{-1}: 1138, 1257, 1345, 1437, 1597, 1623, 1670, 1728, 2903; δ_H (300 MHz, $CDCl_3$): 1.51 (1 H, m, CH_2), 1.76 (1 H, m, CH_2), 2.03 (1 H, m, CH_2), 2.25 (1 H, m, CH_2), 2.47 (1 H, m, CH_2), 2.85 (1 H, m, CH_2), 3.10 (2 H, m, CH_2), 3.43 (2 H, dm, 2 CH), 3.75 (3 H, s, OCH_3), 3.83 (3 H, s, OCH_3), 3.88 (1 H, d, *J* = 6.2 Hz, CH), 6.62 (1 H, s, CH=), 6.52 (2 H, m, Ph), 6.80 (2 H, d, *J* = 9.0 Hz, An), 6.91 (2 H, d, *J* = 8.7 Hz, An), 7.06 (2 H, d, *J* = 8.7 Hz, An), 7.27 (2 H, d, *J* = 9.0 Hz, An), 7.29 (3 H, m, Ph); δ_C (75 MHz, $CDCl_3$): 21.1, 22.3, 27.5, 31.1 (4 CH_2); 37.9, 44.3, 46.4 (3 CH); 55.2, 55.3 (OCH_3), 113.5 (CH=) 114.1 (2 C), 122.4, 126.3 (2 C), 128.4, 128.8, 130.4 (2 C), 130.5 (2 C), 129.5 (2 C) (3 Ar); 127.9, 129.5, 130.6 (3 C); 136.3, 136.4 (2 C_{ipso}); 158.0, 159.3 (2 Ar–O) 177.1 (C–N); 179.0 (2 C=O); *m*/*z* 505 $[M]^+$.

Dehydration of the alcohols 7a,b on alumina (Brockmann activity II). General procedure

The alcohols **7a**,**b** (5 mmol) were severally dissolved in dry benzene (25 ml) and Al_2O_3 (Brockmann activity II) (50 g) was added. The suspensions were left at ~20 °C until the solvent evaporated, the sorbent was applied onto a top of a column with fresh alumina (30 g) and eluted with a 4 : 1 hexane–benzene mixture to give 1.02 g (75%) of the cyclodimer **10a**, mp 236 °C, and 1.16 g (71%) of the cyclodimer **10b**, mp 268–269 °C.

Dehydration of the alcohols 7a,b in acetic acid. General procedure

A solution of the alcohol **7a** (or **7b**) (10 mmol) in glacial acetic acid (100 ml) was refluxed for 30 min and cooled to the ambient temperature. The finely crystalline colorless precipitate that sedimented was filtered off, washed with ethanol, and dried *in vacuo*. The yields of the cyclodimers **10a** and **10b** were virtually quantitative. Following recrystallization from ethanol, **10a** had mp 235–236 °C, and **10b**, mp 268–269 °C.

Dehydration of the alcohols 7a,b in a mixture of acetic and trifluoroacetic acids. General procedure

A solution of the alcohol **7a** (or **7b**) (10 mmol) in a mixture of glacial acetic acid (90 ml) and anhydrous trifluoroacetic acid (10 ml) was refluxed for 1 h and cooled to ~20 °C. The reaction mixture was partitioned between benzene and water (100 ml each), the organic layer was separated, washed with water (2 × 20 ml), and dried with $CaCl_2$. The solvent was evaporated *in vacuo* and the residue was chromatographed on alumina (hexane-benzene, 3:1) to give 1.85 g (68%) of spiro[3-benzylidene-2-methylidenecyclohexane-1,2′-(5-benzylidene-1,3-diphenyl-1,2,3,4,5,6,7,8-octahydronaphthalene)] **12a** and 2.22 g (67%) of spiro[3-(4-methoxybenzylidene)-2-methylidenecyclohexane-1,2′-(5-(4-methoxybenzylidene)-1,3-bis(4-methoxyphenyl)-1,2,3,4,5,6,7,8-octahydronaphthalene)] **12b**.

Compound **12a**, white powder, mp 228–229 °C. [Found: C, 92.74; H, 7.25. Calc. for $C_{42}H_{40}$: C, 92.60; H, 7.40%]; ν_{max} (KBr)/cm^{-1}: 841, 898, 1441, 1497, 1597, 1661, 2855, 2919, 3020; δ_H (300 MHz, $CDCl_3$): 1.63–1.78 (2 H, m, CH_2), 1.88–2.0 (4 H, m, 2 CH_2), 2.05–2.18 (4 H, m, 2 CH_2), 2.60 (2 H, m, CH_2), 2.77 (2 H, d, *J* = 5.6 Hz, CH_2), 3.58 (1 H, s, CH), 3.63 (1 H, t, *J* = 5.6 Hz, CH), 6.40 (1 H, s, CH_2=), 6.51 (1 H, s, CH_2=), 6.61 (1 H, s, CH=), 6.64 (1 H, s, CH=), 7.1–7.43 (20 H, m, 4 Ph); δ_C (75 MHz, $CDCl_3$):18.4, 21.2, 23.3, 28.0, 28.1, 31.1, 32.9 (7 CH_2); 41.7 (C_{spiro}); 46.2, 58.2 (2 CH); 121.2 (CH_2=); 125.2, 125.3 (2 CH=); 125.9, 126.2, 126.5, 126.6, 126.7, 127.9 (3 C), 128.1 (3C), 128.1 (2 C), 128.4, 128.5, 129.3 (3 C), 129.7 (2 C) (4 Ph); 129.1, 129.5, 132.8, 135.9, 137.7 (5 C); 138.0, 138.5 (2 C), 141.4, 144.1 (4 C_{ipso}); *m*/*z* 544, 546 $[M]^+$.

Compound **12b**, white powder, mp 265–266 °C. [Found: C, 83.23; H, 7.09. Calc. for $C_{46}H_{48}O_4$: C, 83.10; H, 7.28%]; ν_{max} (KBr)/cm^{-1}: 838, 1021, 1165, 1220, 1441, 1500, 1601, 1670, 2848, 2924, 3033; δ_H (300 MHz, $CDCl_3$): 1.58–1.80 (2 H, m, CH_2), 1.90–2.05 (4 H, m, 2 CH_2), 2.11–2.18 (4 H, m, 2 CH_2), 2.68 (2 H, m, CH_2), 2.74 (2 H, d, *J* = 6.1, CH_2), 3.52 (1 H, s, CH), 3.61 (1 H, t, *J* = 6.1 Hz, CH), 3.75 (3 H, s, OCH_3), 3.82 (3 H, s, OCH_3), 3.85 (3 H, s, OCH_3), 3.87 (3 H, s, OCH_3), 6.25 (1H, s, CH_2=), 6.37 (1 H, s, CH_2=), 6.59 (1 H, s, CH=), 6.65 (1 H, s, CH=), 7.00–7.31 (16 H, m, 4 An); δ_C (75 MHz, $CDCl_3$): 23.4, 23.8, 24.3, 24.4, 25.6, 27.3, 31.5 (7 CH_2); 30.6 (C_{spiro}); 44.9, 52.9 (2 CH); 54.4, 54.5, 54.7, 55.0 (4 OCH_3); 118.1 (CH_2=); 121.1, 122.0 (2 CH=); 123.2, 123.6, 124.6, 124.8, 125.1, 126.1 (2 C), 126.5 (2 C), 126.8 (2 C), 127.0 (2 C), 127.8 (2 C), 128.0 (4 An); 127.9, 128.2, 128.9, 130.2, 131.34 (5 C); 134.9, 135.9, 137.2, 139.9 (4 C_{ipso}); 152.9, 153.8, 155.7, 156.1 (4 Ar–O); *m*/*z* 664 $[M]^+$.

The action of CF_3COOH on the cyclodimers 12a,b. General procedure

A solution of compound **12a** or **12b** (1 mmol) in anhydrous trifluoroacetic acid (50 ml) was kept for 7–10 d at ambient temperature. Then the mixture was partitioned between benzene and water (50 ml each) and the organic layer was processed as described above to give after column chromatography (hexane-benzene, 3:1) 0.07 g (12%) of the starting **12a**, mp. 235 °C, or 0.05 g (8%) of the starting **12b**, mp. 268 °C, and 0.33 g (60%) of 4,10-dibenzylidene-6-phenyl-1,2,3,4,5,6,6a,7,8,9,10,10a,11,15b-tetradecahydronaphtho[1,2-*f*]-anthracene **16a** and 0.44 g (65%) of 4,10-bis(4-methoxybenzylidene)-13-methoxy-6-(4-methoxyphenyl)-1,2,3,4,5,6,6a,7,8,9,10,10a, 11, 15b-tetradecahydronaphtho[1,2-*f*]-anthracene **16b**, respectively.

Compound **16a**, white powder, mp 248–249 °C.[Found: C, 92.74; H, 7.21. Calc. for $C_{42}H_{40}$: C, 92.60; H, 7.40%]; ν_{max} (KBr)/cm^{-1}: 1368, 1441, 1502, 1603, 2904, 2938; $\lambda_{max}(CHCl_3)$/nm: 206.5; δ_H (300 MHz, $CDCl_3$): 1.69 (4 H, m, 2 CH_2), 1.88 (4 H, m, 2 CH_2), 2.04 (2 H, m, CH_2), 2.28 (2 H, m, CH_2), 2.75 (2 H, d, J = 6.8 Hz, CH_2), 2.87 (2 H, d, J = 7.1 Hz, CH_2), 3.62 (1 H, t, J = 6.8 Hz, CH), 3.99 (1 H, t, J = 7.1 Hz, CH), 4.06 (1 H, s, CH), 5.75 (1 H, s, CH=), 6.27 (1 H, s, CH=), 6.93–7.74 (19 H, m, 3 C_6H_5, C_6H_4); δ_C (75 MHz, $CDCl_3$): 21.0, 21.95, 22.7, 23.25, 28.9, 30.35, 34.4, 40.7 (8 CH_2); 45.3 (CH); 55.6 (C_{spiro}); 65.1, 65.6 (2 ArCH); 119.2 (2 PhCH=), 121.0, 121.3, 121.7, 121.9, 122.2, 122.4, 122.65 (3 C), 122.9 (3 C), 123.1, 123.2, 123.5, 124.0 (3 C), 124.6 (3 Ph, 1C_6H_4); 125.0, 129.9, 135.2, 134.1 (4 C); 136.0, 138.1, 140.2, 141.0, 142.15 (5 C_{ipso}); *m*/*z* 546 $[M]^+$.

Compound **16b**, white powder, mp 276–277 °C. [Found: C, 82.88; H, 7.41. Calc. for $C_{46}H_{48}O_4$: C, 83.10; H, 7.28%]; ν_{max} (KBr)/cm^{-1}: 1050, 1180, 1247, 1453, 1508, 1603, 1620, 2830, 2954; $\lambda_{max}(CHCl_3)$/nm: 205.5; δ_H (300 MHz, $CDCl_3$): 1.69 (4 H, m, 2 CH_2), 1.93 (4 H, m, 2 CH_2), 2.01 (2 H, m, CH_2), 2.19 (2 H, m, CH_2), 2.64 (2 H, d, J = 6.4 Hz, CH_2), 2.75 (2 H, d, J = 6.8 Hz, CH_2), 3.59 (1 H, t, CH, J = 6.4 Hz), 3.75 (3 H, s, OCH_3), 3.78 (3 H, s, OCH_3), 3.83 (3 H, s, OCH_3), 3.87 (3 H, s, OCH_3), 3.96 (1 H, t, J = 6.8 Hz, CH), 4.07 (1 H, s, CH), 5.72 (1 H, s, CH=), 6.22 (1 H, s, CH=), 7.00–7.65 (15 H, m, 3 C_6H_4, C_6H_3) δ_C (75 MHz, $CDCl_3$): 21.4, 22.9, 23.6, 23.9, 28.1, 30.9, 36.0, 39.9 (8 CH_2); 44.1 (CH); 53.1 (C_{spiro}); 54.0, 54.1, 55.2, 55.4 (4 OCH_3); 63.9, 65.4 (2 ArCH); 117.95, 119.0 (2 ArCH=); 120.6, 122.9, 124.0, 124.2, 124.4 (3 C), 126.5 (3 C), 127.2, 127.5, 127.6, 127.9, 128.1 (3 C_6H_4, C_6H_3); 125.8, 127.9, 132.9, 134.0 (4 C); 135.9, 137.1, 138.3, 139.8, 141.1 (5 C_{ipso}); 156.7, 157.4, 157.95, 158.0 (4 Ar–O); *m*/*z* 664 $[M]^+$.

Fragmentation of the cyclodimers 12a,b. General procedure

Tetrafluoroboric acid etherate (3 ml) was added dropwise with stirring in an atmosphere of dry nitrogen to a solution of compound **12a** (or **12b**) (1.5 mmol) in dry ether (100 ml) and the mixture was stirred for 1 h at ~20 °C. A dark violet precipitate was filtered off, washed with several portions of dry ether and dry hexane, and dried *in vacuo*. The yield of the salt **13a** was 0.94 g (87%); the yield of the salt **13b** was 1.03 g (82%).

Compound **13a**, decomposes at ~300 °C. [Found: C,69.93; H, 6.01; F, 20.99. Calc. for $C_{21}H_{21}BF_4$: C, 70.02; H, 5.88; F, 21.10%]; δ_H (300 MHz, CD_2Cl_2): 2.16 (2 H, m, CH_2), 3.07 (3 H, s, CH_3), 3.13 (4 H, t, J= 5.7 Hz, 2 CH_2), 7.21–7.43 (6 H, m, C_6H_5), 7.64–8.10 (4 H, m, C_6H_5), 8.81 (2 H, s, 2 CH=).

Compound **13b**, decomposes at ~312 °C. [Found: C,65.49; H, 6.18; F, 17.87. Calc. for $C_{23}H_{25}BF_4O_2$: C, 65.73; H, 6.00; F, 18.08%]; δ_H (300 MHz, CD_2Cl_2): 2.06 (2 H, m, CH_2), 2.95 (3 H, s, CH_3), 3.08 (4 H, t, J = 6.0 Hz, 2 CH_2), 4.08 (6 H, s, 2 OCH_3), 7.21 (4 H, d, J = 8.8 Hz, C_6H_4), 8.02 (4 H, d, J = 8.8 Hz, C_6H_4), 8.55 (2 H, s, CH=).

Crystal structure determination

The unit cell parameters and the X-ray diffraction intensities were recorded on a Siemens P4/PC diffractometer. The structure of compound **8b** was solved by the direct method (SHELXS) and refined using full-matrix least-squares on F^2. Crystal data for $C_{23}H_{26}O_4$, M_r = 366.44 g mol^{-1}, colorless prism, size 0.40 × 0.24 × 0.08, monoclinic $P2(1)/c$, a = 12.915(2) Å, b = 5.694(2) Å, c = 27.080(3) Å, β = 98.69°, V = 1968.5(8) $Å^3$, T = 293°K, Z = 4, ρ = 1.26 g cm^{-3}, λ(Cu K_α) = 1.54178 Å, $F(000)$ = 784, index ranges $-1 \le h \le 13$, $-1 \le k \le 6$, $-28 \le l \le 28$,scan range $3.30 \le 2\theta \le 56.7°$, 2626 independent reflections, R_{int} = 0.0281, 2187 reflections with $F_o > 3.0\ \sigma(F)$, 248 parameters, Final R indices [$I > 2\sigma(I)$] R_1 = 0.0423, wR_2 =0.1037, R indices (all data) R_1 = 0.0533, wR_2 = 0.1124, Largest difference peak and hole 0.137/−0.149 e $Å^{-3}$. †

† CCDC reference number 169688. See http://www.rsc.org/suppdata/ob/b2/b210890a/ for crystallographic data in .cif or other electronic format.

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