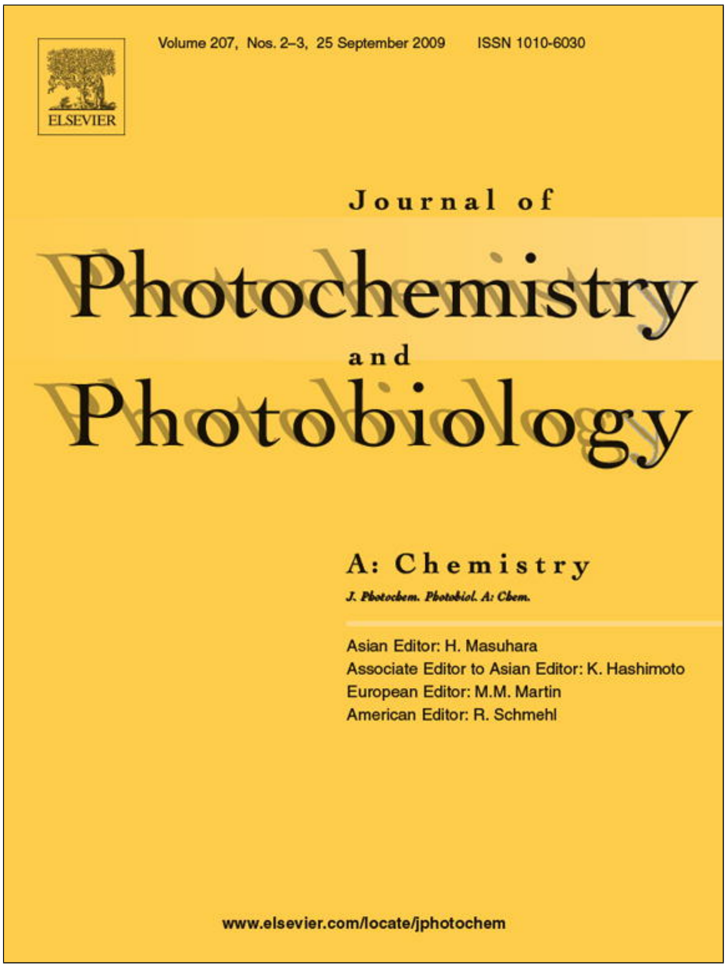

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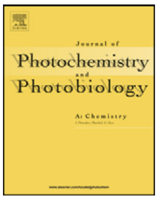

Photochemistry of ω-(*o*-vinylphenyl)-ω′-(phenyl/2-furyl) butadienes: New approach to 4-substituted benzobicyclo[3.2.1]octadienes

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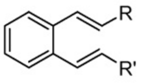
ABSTRACT

Novel 1-(*o*-vinylphenyl)-4-(phenyl/2-furyl) butadienes (**4a**,**b**), synthesized in one step, undergo intramolecular photocycloaddition reaction to benzobicyclo[3.2.1]octadiene derivatives (**6a**,**b**) in very good yield (70–90%). In the case of phenyl derivative (**4a**) only *endo*-phenyl-benzobicyclo[3.2.1]octadiene isomer (*endo*-**6a**) was isolated whereas the furan (**4b**) derivative resulted in a mixture of *endo*- and *exo*-bicyclic isomer (**6b**). Phenyl benzobicyclo[3.2.1]octadiene derivative (*endo*-**6a**) underwent further di-π-methane rearrangement leading to tricyclic structure (*endo*-**7a**). The isolated compound **6a** and the product of the rearrangement *endo*-**7a** were characterised by X-ray structure analysis.

1. Introduction

Synthetic organic photochemistry accasionally provides an easy access to complicated structures, difficult to obtain by a classical synthetic approach [1]. Among the most studied and used reactions are the intra- and intermolecular photocycloadditions [2]. In order to prepare new hetero-polycyclic compounds this methodology was used by us studying the photochemical behavior of β- or β,β′-substituted *o*-divinylbenzenes, i.e. heteroaryl substituted hexatrienes **1** with the central double bond incorporated into the benzene ring. Since our first report [3] on the intramolecular photocycloaddition reaction of *o*-vinyl substituted furostilbene **2a** and formation of benzo-furo fused bicyclo[3.2.1]octadiene structure **3a**, many results about the photochemical behaviour of *o*-vinyl substituted heteroaryl stilbene analogues **1** (heteroarene moiety = furan [4–15], pyrrole [16–23], thiophene [4,5], sydnone [24,25]) have been obtained.



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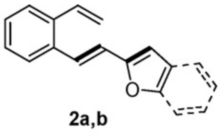
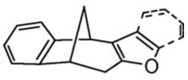
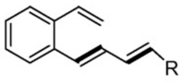
R = H; R' = furan, pyrrole, thiophene, sydnone
R = R' = furan, pyrrole, thiophene



2a,b



3a,b



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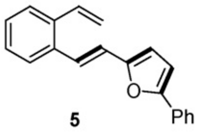

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The formation of benzobicyclo[3.2.1]octadiene structure **3a** includes initial five membered ring closure of **2a** followed by 1,6-closure through the participation of the furan double bond [3]. In the case of benzofuran derivative **2b** this process is even cleaner and more pronounced leading to the benzofuran-fused [3.2.1] bicyclic structure **3b** [13]. We imply that the substituted butadiene **4**, the vinylogue of divinylbenzene, could react similarly as **2a** and/or **2b** and give intramolecular cycloadduct. It should be mentioned that phenyl substituted furan derivative **5** gave upon irradiation [15] mainly high-molecular-weight products, besides only traces of substituted bicyclic structure **3a**.

As a part of our continuing interest in the photochemistry of conjugated systems we extended our research to new *o*-vinylphenyl

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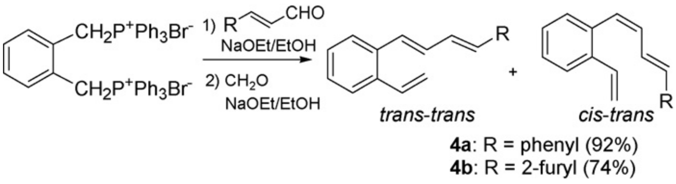


Scheme 1.

substituted butadienes **4** as substrates for photochemical transformations to benzobicyclo[3.2.1]octadiene skeleton [26–29], easily derivatised to saturated structures with various functionalities. The photoisomerization reactions [30–39] as well as some electrocyclisation reactions [40,41] of 1,4-diphenyl butadienes are studied but to the best of our knowledge no intramolecular photocycloadditions of their vinylogues are known. In this paper, we describe for the first time, one-step photochemical transformations of novel *o*-butadienylstyrenes **4**, octatetraenes with one double bond incorporated into the benzene ring.

2. Results and discussion

The starting materials, 1-(*o*-vinylphenyl)-4-(phenyl/2-furyl substituted) butadienes (**4a**,**b**) were prepared by the Wittig reaction from β,β′-*o*-xylyl(ditriphenylphosphonium)dibromide and corresponding aldehydes (Scheme 1) in good yields (74–92%) as mixtures of *cis*,*trans*- and *trans*,*trans*-isomers, according to the procedure described in previous papers for the heteroarylstilbene analogues [42].

According to ^{1}H NMR spectra of the crude reaction mixtures the ratio of *trans*,*trans*- to *cis*,*trans*-isomers was very similar in both derivatives (~3:2). The isomers of **4a**,**b** were separated combining column chromatography and thin layer chromatography on silica gel and identified spectroscopically.

The UV spectra (Fig. 1) of separated *cis*,*trans*- and *trans*,*trans*-**4a** and **4b**, respectively, clearly show the substituent and configurational influence on absorption characteristics. The *trans*,*trans*-**4a**,**b** isomers show a bathochromic shift and an increase of the molar absorption coefficients in comparison to their *cis*,*trans*-isomers, as expected, because of increased molecular planarity of *trans*,*trans* configurations and the possibility of better delocalisation of π-electrons.

The phenyl derivatives, *trans*,*trans*-**4a** (Fig. 2) and *cis*,*trans*-**4a** (Fig. 3) were irradiated and the reaction course followed by taking the UV spectra at indicated times. It is evident from the absorption spectra that photoisomerization is the primary process followed by competitive photochemical reaction. It is difficult to discuss about the composition of the photostationary mixture because of unsymmetrical structure of **4a** and possibility of existence and interconversion of four isomers: *trans*,*trans*-, *trans*,*cis*-, *cis*,*trans*- and *cis*,*cis*-**4a**.

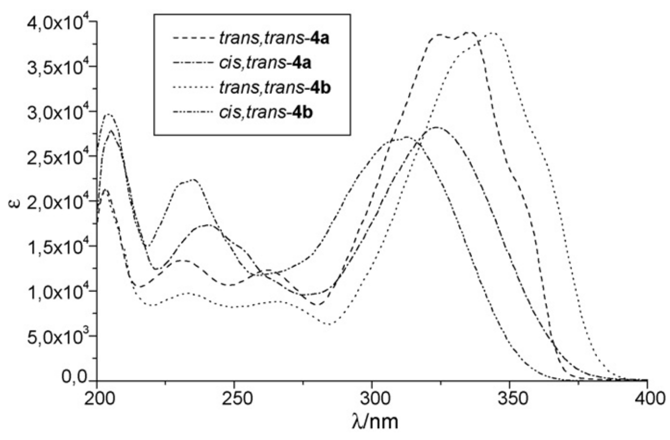


Fig. 1. UV spectra of *trans*,*trans*- and *cis*,*trans*-**4a**,**b** in EtOH.

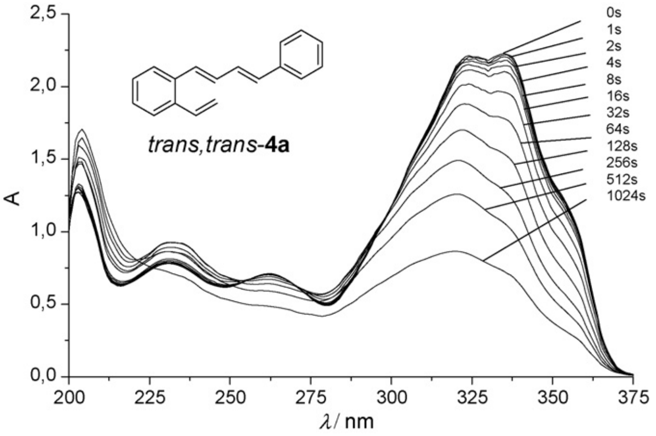


Fig. 2. The irradiation of *trans*,*trans*-**4a** followed by taking the UV spectra at indicated times.

The irradiation experiments of **4a**,**b** were performed in petroleum ether solutions under anaerobic conditions at 300 and 350 nm, giving in all cases *endo*-4-substituted benzobicyclo[3.2.1]octadienes **6a** or **6b**, respectively, as the main product (Scheme 2).

It is interesting to note that in the case of phenyl derivative **4a** only *endo*-isomer **6a** was isolated while the furyl derivative **4b** gave a mixture of *endo*- and *exo*-isomers **6b** in the ratio 3:1. On irradiation of phenyl derivative **4a** at 300 nm to full conversion of the starting material, besides *endo*-**6a** new compound *endo*-**7a** was isolated. In the case of furyl derivative **4b**, irradiated under the same conditions, no structure corresponding to *endo*-**7a** was observed, besides some tarry material. The photoproducts (*endo*-**6a**, *endo*-**6b**, *exo*-**6b**, *endo*-**7a**) were separated by column chromatography on silica gel and the structures deduced unequivocally from spectral studies.

From the ^{1}H and ^{13}C NMR spectra, using different techniques (COSY, NOESY and HSQC), all protons were completely assigned (Fig. 4; see Section 3). The very well resolved seven-proton-pattern in the ^{1}H NMR spectra of the photoproducts **6a**,**b** between 2 and 6.5 ppm unmistakably pointed to the same benzobicyclo[3.2.1]octadiene structure. The multiplets in the lower field between 5 and 6.5 ppm are assigned to the **A** and **B** protons on the double bond whereas the **F** and **G** protons on methano bridge

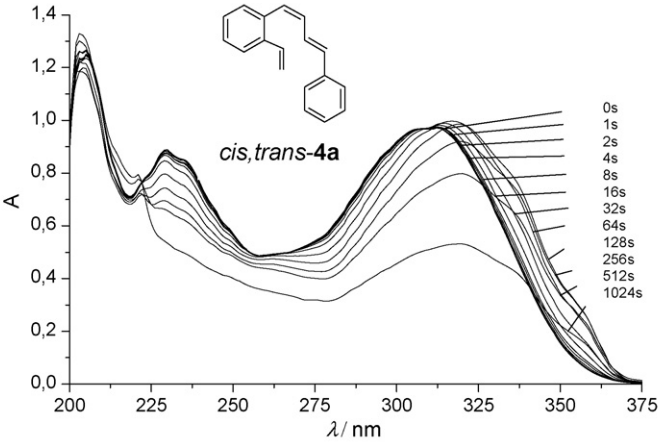
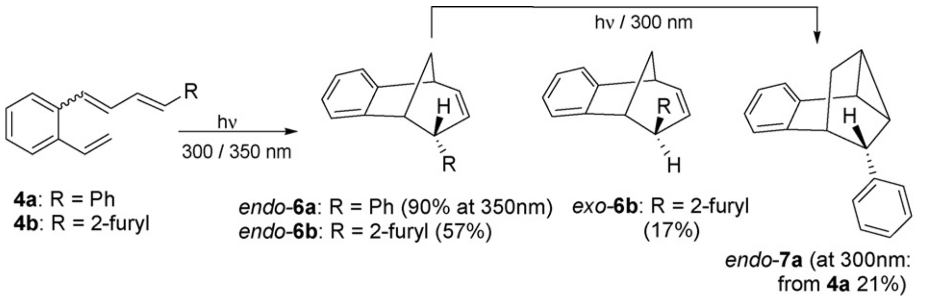
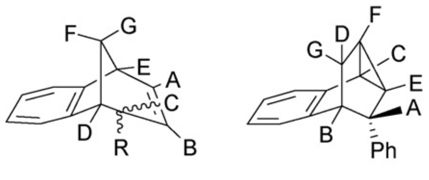


Fig. 3. The irradiation of *cis*,*trans*-**4a** followed by taking the UV spectra at indicated times.



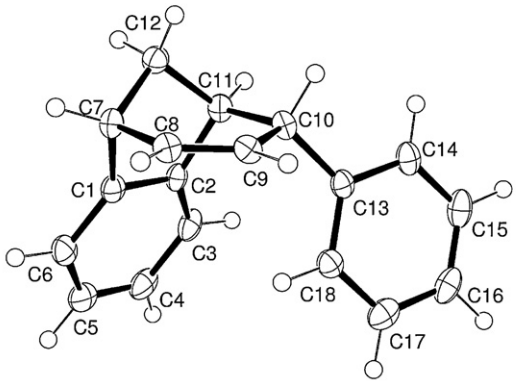
Scheme 2.



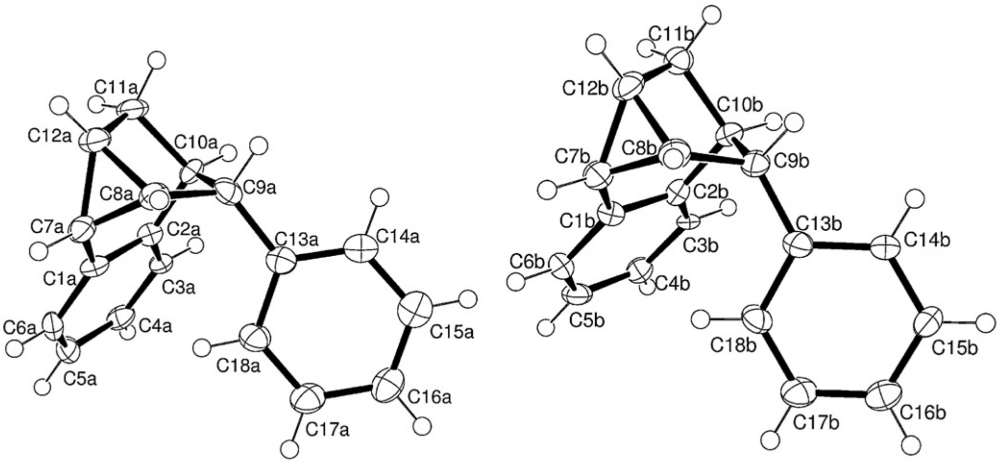
6 *endo*-**7a**

Fig. 4. Structures of photoproducts **6** and *endo*-**7a** with proton assignments (A–G).

carbon are in the higher field between 2 and 2.6 ppm. Proton **E** is not affected by the different substituents (Ph, 2-furyl) and appears in all photoproducts in a narrow range between 3.2 and 3.4 ppm. Protons **C** and **D** appear in the *endo*-**6a** and *endo*-**6b** between 3.4 and 4.1 ppm while the same protons overlap in the *exo*-**6b** isomer and appear at 3.4–3.5 ppm as a narrow multiplet. One of the aromatic protons, H_{ar} of the benzo-moieties is shifted to the higher field due to the anisotropic effect of *endo*-substituent, being more pronounced by phenyl than furyl group. This effect is absent in the case of *exo*-**6b**, as expected. The ^{13}C NMR spectra of *endo*-**6b** and *exo*-**6b** are very similar and indicate to the same skeleton, benzobicyclo[3.2.1]octadiene structure. The benzotricyclic structure *endo*-**7a** has a completely different pattern in the ^{1}H NMR spectrum. All seven protons appear between 1 and 3.5 ppm with the corresponding multiplicity (see Section 3). Its ^{13}C NMR spectrum shows six sp^3 carbons in the region between 16 and 45 ppm in comparison to four carbons between 40 and 49 ppm of *endo*-**6a**.



endo-**6a**



endo-**7a**

Fig. 5. Molecular structures (in the crystal) of *endo*-**6a** (top) and the product *endo*-**7a** with two molecules in an asymmetric unit (bottom). Thermal ellipsoids are drawn for the 50% probability level; hydrogen atoms are depicted as spheres of arbitrary radii.

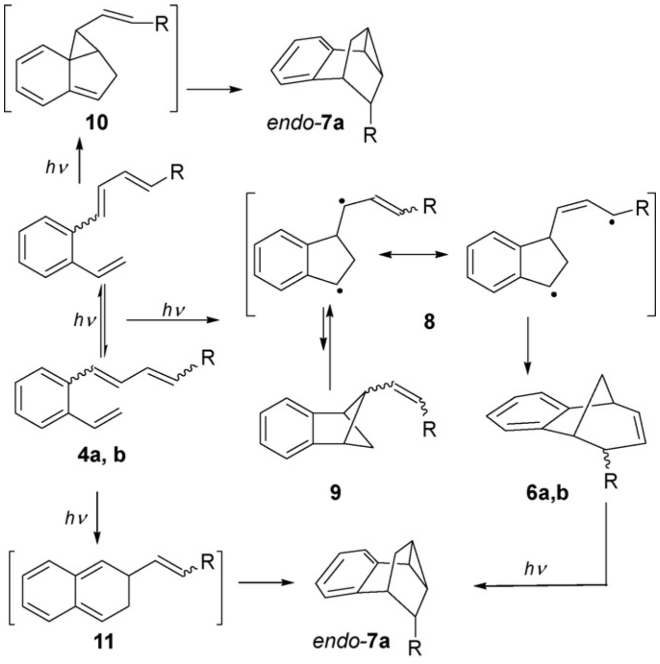
Table 1
Crystallographic data and structure refinement details for compounds *endo*-**6a** and *endo*-**7a**.

Compound	*endo*-**6a**	*endo*-**7a**
Empirical formula	$C_{18}H_{16}$	$C_{18}H_{16}$
Formula wt./g mol^{-1}	232.32	232.32
Crystal dimensions/mm	0.32 × 0.28 × 0.14	0.36 × 0.10 × 0.05
Space group	*Fdd*2	$P2_1/c$
a/Å	5.6905 (9)	28.23 (6)
b/Å	14.135 (1)	7.223 (1)
c/Å	63.366 (6)	12.059 (5)
α/°	90	90
β/°	90	100.4 (1)
γ/°	90	90
Z	16	8
V/Å^3	5097 (1)	2419 (5)
D_{calc}/g cm^{-3}	1.211	1.276
μ/mm^{-1}	0.511	0.539
Θ range/°	2.79–75.85	3.18–76.45
Range of h, k, l	$-7 > h > 7$; $-17 > k > 0$; $0 > l > 78$	$0 > h > 35$; $-9 > k > 0$; $-14 > l > 15$
Reflections collected	2643	5112
Independent reflections	1461	5009
Observed reflections ($I \geq 2\sigma$)	1323	3185
R_{int}	0.0889	0.1069
$R(F)$	0.0368	0.1648
$R_w(F^2)$	0.1021	0.4455
Goodness of fit	1.015	1.555
$\Delta\rho_{max}$, $\Delta\rho_{min}$/eÅ^{-3}	0.239; −0.255	0.903; −0.573

The structure of benzobicyclic *endo*-**6a** and benzotricyclic compound *endo*-**7a** were also confirmed by X-ray analyses (Fig. 5). The overall molecular conformations in both compounds are folded and can be described by torsion angles around C2–C11–C10–C13 of −59.75(3)° for *endo*-**6a** and C2–C10–C9–C13 of 58(1)° for both molecules of *endo*-**7a**; ±syn-clinal conformation appears to be energetically optimal. In the folded conformation dihedral angles between aromatic rings are: 38.0(1)° for *endo*-**6a**, 67.9(4)° and 69.8(4)° for molecules a and b of *endo*-**7a**. In the crystal of *endo*-**7a** two conformers occurred but no significant differences were encountered (Fig. 5). According to the space groups symmetries (Table 1) racemates 1:1 of *endo*-**6a** and *endo*-**7a** are present in the crystals.

Regarding the mechanistic considerations, the formation of benzobicyclic structures **6a**,**b** could be explained by initial intramolecular cycloaddition and formation of resonance-stabilized intermediate **8** followed by 1,6-ring closure (Scheme 3), as seen in the photochemical reactions of β-heteroaryl substituted *o*-divinylbenzenes [3,4,8,11,13,15]. It might be assumed that even if the 1,4-ring closure [4,10] to benzobicyclo[2.1.1]hexene derivative **9** is operating the formed derivative **9** could thermally be reversed to **8** and subsequently give the more stable product **6**.

The formation of benzotricyclic compound *endo*-**7a** from the starting compound **4a** could be explained [43] either by initial five-membered-ring-closure *via* **10**, followed by re-aromatisation and intramolecular trapping of the formed biradical, or by sixmembered-ring-closure *via* **11**. The compound *endo*-**7a** may also arise from primarily formed the benzobicyclic structure **6a**. To establish whether the compound *endo*-**7a** is formed directly from **4a** or from the primary formed **6a** the *endo*-**6a** is isolated and irradiated at 300 nm. Complete conversion to *endo*-**7a** resulted and the experiment confirmed that formation of *endo*-**7a** follows from *endo*-**6a** by di-π-methane rearrangement (Scheme 4) [26,27,44]. Irradiation of a mixture of *endo*- and *exo*-furyl isomers **6b** at 300 nm and monitoring the reaction course by GC/MS did not show the presence of new photoproducts.



Scheme 3.

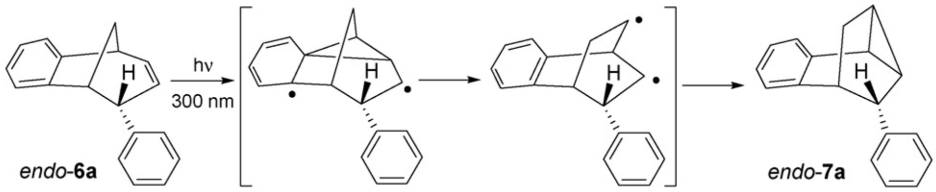
The ring closure predominantly gives *endo*-isomers (**6a**,**b**). The stereoselectivity of the reaction and preferable ring closure to *endo*-isomer can be ascribed to the stabilization of the transition state in *endo*-orientation by the strong and medium attractive intramolecular π–π interactions of the benzo-phenyl and benzo-furyl groups, respectively [45–47].

In conclusion, ω-(*o*-vinylphenyl)-ω′-(phenyl/2-furyl) butadienes are easy accessable substrates suitable for intramolecular cycloadditions and formation of polycyclic structures in one step.

3. Experimental

3.1. General

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-600 Spectrometer at 300 or 600 MHz and 75 or 150 MHz, respectively. All NMR spectra were measured in $CDCl_3$ using tetramethylsilane as reference. The assignment of the signals is based on 2D-CH correlation and 2D-HH-COSY, LRCOSY and NOESY experiments. UV spectra were measured on a Varian Cary 50 UV/VIS Spectrophotometer. Mass spectra were obtained on a GC–MS (Varian CP-3800 Gas Chromatograph-Varian Saturn 2200) equipped with FactorFour Capillary Column VF-5ms. Irradiations were performed in a quartz or pyrex vessel in petroleum ether



Scheme 4.

solutions in a Rayonet reactor equipped with RPR 3000 Å and RPR 3500 Å lamps. All irradiation experiments were carried out in deoxygenated solutions by bubbling a stream of argon prior to irradiation. Melting points were obtained using an Original Kofler Mikroheitztisch apparatus (Reichert, Wien) and are uncorrected. Elemental analyses were carried out on Perkin-Elmer, Series II, CHNS Analyzer 2400. Silica gel (Merck 0.063–0.2 mm) was used for chromatographic purifications. Thin-layer chromatography (TLC) was performed on Merck precoated silica gel 60 F_{254} plates. Solvents were purified by distillation. Boiling range of petroleum ether, used for chromatographic separation, was 40–70 °C.

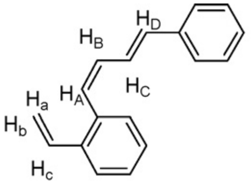
The starting compounds *trans*-cinnamaldehyde and *trans*-β-(2-furylacrolein) were obtained from a commercial source. β,β′-*o*-Xylyl(ditriphenylphosphonium)dibromide was synthesized from the corresponding dibromide and triphenylphosphine in benzene solution.

3.2. Preparation of **4a**,**b**

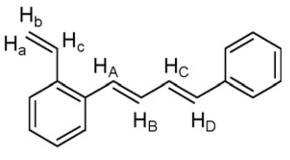
Starting compounds **4a**,**b** were prepared from the β,β′-*o*-xylyl-(ditriphenylphosphonium)dibromide and corresponding aldehydes, *trans*-cinnamaldehyde and *trans*-β-(2-furylacrolein), respectively. To a stirred solution of β,β′-*o*-xylyl-ditriphenylphosphonium)dibromide (3.94 g, 0.005 mol) and the corresponding aldehydes (0.0055 mol) in absolute ethanol (100 mL) a solution of sodium ethoxide (0.12 g, 0.0052 mol in 20 mL ethanol) was added dropwise. Stirring was continued under a stream of nitrogen for 1 h at RT. Under the stream of dry nitrogen, gaseous formaldehyde (obtained by decomposition of paraformaldehyde taken in excess, 1 g, 0.033 mol) was introduced and the next quantity of sodium ethoxide (0.12 g, 0.0052 mol in 20 mL ethanol) was added dropwise. The reaction was completed within 2 h (usually was left to stand overnight). After removal of the solvent, the residue was worked up with water and benzene. The benzene extracts were dried (anhydrous $MgSO_4$) and concentrated. The crude reaction mixture was purified and the isomers of products **4a**,**b** were separated by repeated column chromatography on silica gel using petroleum ether as eluent. The first fractions yielded *cis*,*trans*- and the last fractions *trans*,*trans*-isomer. Characterization data of the new compounds **4a**,**b** are given below.

3.2.1. 4-Phenyl-1-(2-vinylphenyl)-1,3-butadiene (**4a**)

Yield 92.0%; according to ^{1}H NMR spectroscopy, a mixture of 53% *cis*,*trans*- and 47% of *trans*,*trans*-isomer.



cis,trans-**4a**



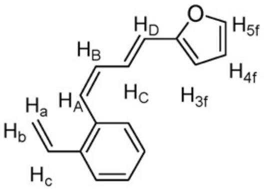
trans,trans-**4a**

cis,*trans*-**4a**: R_f 0.52 (petroleum ether); colourless oil; UV (EtOH) λ_{max} (log ε) 306 (4.46, sh), 236 (4.14, sh); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.57 (d, J = 7.3 Hz, 1H), 7.31–7.34 (m, 7H), 7.20 (t, J = 7.3 Hz, 1H), 7.03 (dd, J = 15.6; 11.3 Hz, 1H, H_C), 6.91 (dd, J = 17.5; 11.2 Hz, 1H, H_c), 6.69 (d, J = 15.6 Hz, 1H, H_D), 6.62 (d, J = 11.2 Hz, 1H, H_A), 6.50 (t, J = 11.2 Hz, 1H, H_B), 5.70 (dd, J = 17.5; 1.2 Hz, 1H, H_a), 5.29 (dd, J = 11.2; 1.2 Hz, 1H, H_b); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 137.33 (s), 136.53 (s), 135.74 (s), 135.18 (d), 134.49 (d), 131.23 (d), 130.26 (d), 129.34 (d), 128.60 (d), 127.68 (d), 127.53 (d), 127.40 (d), 126.59 (d), 125.76 (d), 125.54 (d), 115.63 (t); MS m/z (EI) 232 (M^+, 2%), 128 (100).

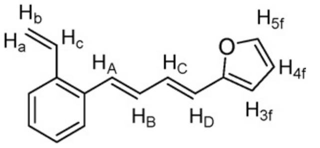
trans,*trans*-**4a**: R_f 0.48 (petroleum ether); colourless crystals; mp 91–92 °C; UV (EtOH) λ_{max} (log ε) 354 (4.33, sh), 336 (4.58), 262 (4.09) 234 (4.09); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.51 (d, J = 7.5 Hz, 1H), 7.41–7.45 (m, 3H), 7.31 (t, J = 7.5 Hz, 1H), 7.19–7.26 (m, 3H), 7.06 (dd, J = 17.4; 11.0 Hz, 1H, H_c), 6.97 (dd, J = 15.8; 10.5 Hz, 1H, H_C), 6.95 (d, J = 15.4 Hz, 1H, H_A), 6.83 (dd, J = 15.4; 10.5 Hz, 1H, H_B), 6.65 (d, J = 15.8 Hz, 1H, H_D), 5.62 (dd, J = 17.4; 1.2 Hz, 1H, H_a), 5.35 (dd, J = 11.0; 1.2 Hz, 1H, H_b); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 136.91 (s), 135.90 (s), 134.93 (s), 134.52 (d), 132.58 (d), 130.94 (d), 129.82 (d), 129.03 (d), 128.33 (d), 127.38 (d), 127.18 (d), 126.27 (d), 126.00 (d), 125.99 (d), 125.46 (d), 116.11 (t); MS m/z (EI) 232 (M^+, 100%); Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.96. Found: C, 93.41; H, 6.58.

3.2.2. 2-[4-(o-Vinylphenyl)buta-1,3-dienyl]furan (**4b**)

Yield 74.0%; according to ^{1}H NMR spectroscopy, a mixture of 41% *cis*,*trans*- and 59% of *trans*,*trans*-isomer.



cis,trans-**4b**



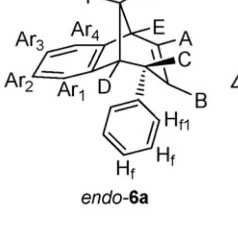
trans,trans-**4b**

cis,*trans*-**4b**: R_f 0.62 (petroleum ether); colourless oil; UV (EtOH) λ_{max} (log ε) 323 (4.45), 251 (4.18, sh), 241 (4.24); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.54 (dd, J = 7.4; 1.1 Hz, 1H), 7.23–7.35 (m, 4H), 6.95 (dd, J = 15.5; 11.4 Hz, 1H, H_C), 6.90 (dd, J = 17.5; 11.0 Hz, 1H, H_c), 6.60 (d, J = 11.2 Hz, 1H, H_A), 6.47 (d, J = 15.5 Hz, 1H, H_D), 6.42 (t, J = 11.4 Hz, 1H, H_B), 6.36 (m, 1H, H_{4f}), 6.26 (d, J = 2.9; 1.2 Hz, 1H, H_{3f}), 5.69 (d, J = 17.5 Hz, 1H, H_a), 5.28 (d, J = 11.0 Hz, 1H, H_b); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 152.71 (s), 141.81 (d, C_{5f}), 135.99 (s), 135.11 (s), 134.57 (d), 130.22 (d), 129.72 (d), 128.90 (d), 126.98 (d), 126.90 (d), 125.21 (d), 123.57 (d), 121.42 (d), 115.15 (t), 111.13 (d, $C_{3f/4f}$), 108.29 (d, $C_{3f/4f}$); MS m/z (EI) 222 (M^+, 3%), 128 (100).

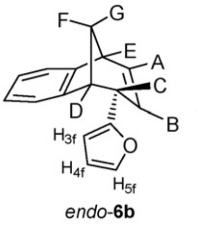
trans,*trans*-**4b**: R_f 0.60 (petroleum ether); pale-yellow crystals; mp 82–83 °C; UV (EtOH) λ_{max} (log ε) 360 (4.43, sh), 345 (4.59), 331 (4.56, sh), 265 (3.94); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.46 (dd, J = 7.6; 1.3 Hz, 1H), 7.39 (dd, J = 7.6; 1.3 Hz, 1H), 7.33 (d, J = 1.1 Hz, H_{5f}), 7.15–7.23 (m, 2H), 7.00 (dd, 1H, J = 17.4; 11.0 Hz, 1H, H_c), 6.90 (d, J = 15.3 Hz, 1H, H_A), 6.83 (dd, J = 15.4; 10.9 Hz, 1H, H_C), 6.73 (dd, J = 15.3; 10.9 Hz, 1H, H_B), 6.41 (d, J = 15.4 Hz, 1H, H_D), 6.35 (dd, J = 3.2; 1.1 Hz, 1H, H_{4f}), 6.25 (d, J = 3.2 Hz, 1H, H_{3f}), 5.62 (dd, J = 17.4; 1.2 Hz, 1H, H_a), 5.35 (dd, J = 11.0; 1.2 Hz, 1H, H_b); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 152.80 (s), 141.75 (d, C_{5f}), 135.84 (s), 134.83 (s), 134.42 (d), 130.36 (d), 129.82 (d), 127.62 (d), 127.28 (d), 127.07 (d), 126.22 (d), 125.32 (d), 119.88 (d), 116.04 (t), 111.2 (d, $C_{3f/4f}$), 108.07 (d, $C_{3f/4f}$); MS m/z (EI) 222 (M^+, 100%); Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.31; H, 6.46.

3.3. Photochemistry of **4a**,**b** (irradiation experiments)

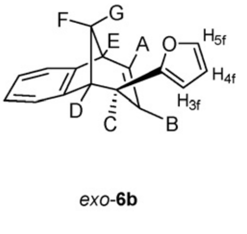
A mixture of *cis*,*trans*- and *trans*,*trans*-isomers of **4a**,**b**, respectively, in petroleum ether (**4a**: 4.3 × 10^{-3} M; **4b**: 4.0 × 10^{-3} M) was purged with argon for 20 min and irradiated at 350 nm in a Rayonet reactor in a pyrex tube for 2–4 h. Solvent was removed in vacuum and the oily residue chromatographed on silica gel column using petroleum ether as eluent.



endo-**6a**



endo-**6b**



exo-**6b**

*3.3.1. Irradiation of 4-phenyl-1-(2-vinylphenyl)-1,3-butadiene (**4a**)*

After column chromatography, 90% of the *endo*-6-phenyl-6,9-dihydro-5*H*-5,9-methano-benzocycloheptene (**6a**) was isolated. High-molecular-weight products remained on the column.

endo-6-Phenyl-6,9-dihydro-5*H*-5,9-methano-benzocycloheptene (*endo*-**6a**): R_f 0.44 (petroleum ether); colourless crystals; mp 51 °C; UV (EtOH) λ_{max} ($\log\varepsilon$) 275 (2.88), 263 (2.90), 203 (4.46); ^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.17–7.18 (m, 3H, H_f), 7.12 (d, J = 7.3 Hz, 1H, H_{Ar4}), 7.03 (t, J = 7.4 Hz, 1H, H_{Ar3}), 6.81 (t, J = 7.4 Hz, 1H, H_{Ar2}), 6.73–6.76 (m, 2H, H_{f1}), 6.37 (ddd, J_{AB} = 9.5 Hz; J_{AE} = 6.0 Hz; J_{AC} = 2.5 Hz, 1H, H_A), 6.18 (d, J = 7.3 Hz, 1H, H_{Ar1}), 5.33 (dt, J_{AB} = 9.5 Hz; J_{BC} = 2.5 Hz, 1H, H_B), 3.98 (m, 1H, H_C), 3.38 (t, J_{CD} = J_{DF} = 4.7 Hz, 1H, H_D), 3.29 (dd, J_{AE} = 6.0 Hz; J_{EF} = 4.7 Hz, 1H, H_E), 2.52 (dt, J_{FG} = 9.9 Hz; J_{EF} = J_{DF} = 4.7 Hz, 1H, H_F), 2.38 (d, J_{FG} = 9.9 Hz, 1H, H_G); ^{13}C NMR (CDCl$_3$, 150 MHz) δ 152.27 (s), 142.44 (s), 141.93 (s), 132.71 (d), 128.21 (d), 127.60 (d), 126.34 (d), 126.10 (d), 126.05 (d), 125.97 (d), 124.89 (d), 120.03 (d), 48.59 (d), 46.29 (d), 44.13 (t, C_{FG}), 40.37 (d); MS m/z (EI) 232 (M$^+$, 100%), 117 (25), 115 (10); Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.76; H, 6.54.

*3.3.2. Irradiation of 2-[4-(o-vinylphenyl)buta-1,3-dienyl]furan (**4b**)*

After column chromatography, using petroleum ether as eluent, in the first fraction 57% of the *endo*-2-(6,9-dihydro-5*H*-5,9-methano-benzocyclohepten-6-yl)furan (*endo*-**6b**) and in the last fractions 17% of the *exo*-2-(6,9-dihydro-5*H*-5,9-methano-benzocyclohepten-6-yl)furan (*exo*-**6b**) were isolated. High-molecular-weight products remained on the column.

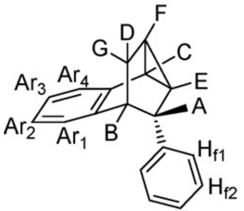
endo-2-(6,9-Dihydro-5*H*-5,9-methano-benzocyclohepten-6-yl)furan (*endo*-**6b**): R_f 0.33 (petroleum ether); colourless oil; UV (EtOH) λ_{max} ($\log\varepsilon$) 269 (2.85), 259 (2.83); ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.34 (dd, J = 1.5; 0.8 Hz; 1H, H_{5f}), 7.09 (d, J = 7.4 Hz, 1H, H_{Ar}), 7.01 (t, J = 7.4 Hz, 1H, H_{Ar}), 6.89 (t, J = 7.4 Hz, 1H, H_{Ar}), 6.56 (d, J = 7.4 Hz, 1H, H_{Ar}), 6.34 (m, 1H, H_A), 6.18 (dd, J = 3.2; 1.5 Hz; 1H, H_{4f}), 5.58 (dd, J = 3.2; 0.8 Hz; 1H, H_{3f}), 5.31 (dt, J_{AB} = 9.2 Hz; J_{BC} = 2.5 Hz, 1H, H_B), 4.01 (m, 1H, H_C), 3.68 (t, J_{CD} = J_{DF} = 4.8 Hz, 1H, H_D), 3.27 (dd, J_{AE} = 6.1 Hz; J_{EF} = 4.8 Hz, 1H, H_E), 2.48 (dt, J_{FG} = 9.8 Hz; J_{EF} = J_{DF} = 4.8 Hz, 1H, H_F), 2.28 (d, J_{FG} = 9.8 Hz, 1H, H_G); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 156.2 (s), 152.41 (d), 142.48 (s), 141.37 (d, C_{5f}), 135.72 (d), 126.15 (d), 125.55 (d), 125.33 (d), 123.33 (d), 120.23 (d), 109.90 (d, $C_{3f/4f}$), 105.37 (d, $C_{3f/4f}$), 45.78 (d), 42.62 (t), 40.39 (d), 40.15 (d); MS m/z (EI) 222 (M$^+$, 100%), 154 (25), 107 (15); Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.22; H, 6.69.

exo-2-(6,9-Dihydro-5*H*-5,9-methano-benzocyclohepten-6-yl)furan (*exo*-**6b**): R_f 0.37 (petroleum ether); colourless oil; UV (EtOH) λ_{max} ($\log\varepsilon$) 268 (2.84), 260 (2.83); ^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.39 (dd, J = 1.7; 0.7 Hz; 1H, H_{5f}), 7.07-7.16 (m, 4H, H_{ar}), 6.34 (m, 2H, H_A and H_{4f}), 6.11 (dd, J = 3.2; 0.7 Hz, 1H, H_{3f}), 5.33 (dt, J_{AB} = 9.6 Hz; J_{BC} = 3.3 Hz, 1H, H_B), 3.41–3.48 (m, 2H, H_C and H_D), 3.35 (dd, J = 6.7; 4.1 Hz, 1H, H_E), 2.13–2.18 (m, 2H, H_F and H_G); ^{13}C NMR (CDCl$_3$, 150 MHz) δ 156.88 (s), 151.51 (s), 144.93 (s), 140.81 (d, C_{5f}), 135.54 (d), 125.85 (d), 125.71 (d), 123.44 (d), 122.66 (d), 120.22 (d), 109.71 (d, $C_{3f/4f}$), 105.25 (d, $C_{3f/4f}$), 44.40 (d), 40.74 (d), 40.52 (d), 37.26 (t, C_{FG}); MS m/z (EI) 222 (M$^+$, 100%), 154 (15), 107 (10).

*3.3.3. Irradiation of **4a**,**b** at 300 nm*

A mixture of *cis*,*trans*- and *trans*,*trans*-isomers of **4a** and **b**, respectively, in petroleum ether (**4a**: 3.7 × 10^{-3} M; **4b**: 4.1 × 10^{-3} M) was purged with argon for 20 min and irradiated at 300 nm in a Rayonet reactor in a quartz tube for 1–4 h. Solvent was removed in vacuum and the oily residue chromatographed on silica gel column using petroleum ether as eluent.

*3.3.3.1. Irradiation of 4-phenyl-1-(2-vinylphenyl)-1,3-butadiene (**4a**).* After repeated column chromatography using petroleum ether as eluent, the first fractions yielded *endo*-6-phenyl-6,9-dihydro-5*H*-5,9-methano-benzocycloheptene (*endo*-**6a**) and the last fractions *endo*-7-phenyl-2,3-benzotricyclo[3.2.1.0^{4,6}]oct-2-ene (*endo*-**7a**) (21%). High-molecular-weight products remained on the column. Characterization data of the new benzotricyclic compound *endo*-**7a** are given below.



endo-**7a**

endo-7-Phenyl-2,3-benzotricyclo[3.2.1.0^{4,6}]oct-2-ene (*endo*-**7a**): R_f 0.36 (petroleum ether); colourless crystals; mp 58 °C; UV (EtOH) λ_{max} ($\log\varepsilon$) 275 (2.65), 265 (2.70), 203 (4.43) nm; ^{1}H NMR (600 MHz, CDCl$_3$) δ_H 7.26 (d, J = 7.8 Hz, 1H, H_{Ar4}), 7.06 (t, J = 7.8 Hz, 1H, H_{Ar3}), 7.01 (t, J = 7.8 Hz, 2H, H_{f2}), 6.96 (t, J = 7.8 Hz, 1H, H_{f3}), 6.91 (d, J = 7.8 Hz, 2H, H_{f1}), 6.87 (t, J = 7.8 Hz, 1H, H_{Ar2}), 6.64 (d, J = 7.8 Hz, 1H, H_{Ar1}), 3.45 (dd, J_{AB} = 4.7 Hz; J_{AE} = 2.3 Hz, 1H, H_A), 3.22 (t, J_{AB} = J_{BD} = 4.7 Hz, 1H, H_B), 2.36 (t, J_{CE} = J_{CF} = 7.2 Hz, 1H, H_C), 2.15 (ddd, J_{BD} = 4.7 Hz; J_{DF} = 2.8 Hz; J_{DG} = 11.6 Hz, 1H, H_D), 1.91 (dt, J_{AE} = 2.3 Hz; J_{CE} = J_{CF} = 7.2 Hz, 1H, H_E), 1.79 (dt, J_{CF} = J_{EF} = 7.2 Hz; J_{DF} = 2.8 Hz, 1H, H_F), 1.20 (d, J_{DG} = 11.6 Hz, 1H, H_G); ^{13}C NMR (150 MHz, CDCl$_3$) δ_C 140.60 (s), 136.46 (s), 135.50 (s), 127.47 (d, C–H_{f1}), 127.35 (d, C–H_{f2}), 125.68 (d, C–Ar_3), 125.52 (d, C–H_{f3}), 125.37 (d, C–Ar_4), 124.77 (d, C–Ar_1), 124.15 (d, C–Ar_2), 43.95 (d, C–A), 42.77 (d, C–B), 29.95 (t, C–D/G), 20.17 (d, C–E), 18.35 (d, C–C), 16.30 (d, C–F); MS (EI) m/z 232 (M$^+$, 100%), 127 (15); Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.67; H, 7.27.

*3.3.3.2. Irradiation of 2-[4-(o-vinylphenyl)buta-1,3-dienyl]furan (**4b**).* After column chromatography using petroleum ether as eluent, a mixture of *endo*- and *exo*-6-phenyl-6,9-dihydro-5*H*-5,9-methano-benzocycloheptene (*endo*- and *exo*-**6b**) (in the ratio 3:1) was isolated. High-molecular-weight products remained on the column.

*3.3.4. Irradiation of **6a**,**b** at 300 nm*

Petroleum ether solutions (3.5 × 10^{-3} M) of *endo*-**6a** and the mixture of *endo*- and *exo*-**6b** (in the ratio 3:1), were purged with argon for 20 min and irradiated at 300 nm in a Rayonet reactor in a quartz tube for 16 h. Solvent was removed in vacuum and the oily residue chromatographed on silica gel column using petroleum ether as eluent.

*3.3.4.1. Irradiation of endo-**6a**.* After column chromatography using petroleum ether as eluent, a mixture of *endo*-**6a** and *endo*-**7a** (in the ratio 1:5, according to ^{1}H NMR and GC/MS) was isolated. High-molecular-weight products remained on the column.

*3.3.4.2. Irradiation of endo-**6b**.* After column chromatography using petroleum ether as eluent, in the first fractions *endo*-**6b** and in the last fractions *exo*-**6b** (in the ratio 1:1, according to ^{1}H NMR and GC/MS) was isolated. High-molecular-weight products remained on the column.

*3.4. Details on X-ray structure analysis of endo-**6a** and endo-**7a***

The crystals of *endo*-**6a** were grown from petroleum ether (40–60 °C). Poor crystals of *endo*-**7a** were obtained only by slow evaporation from petroleum ether (40–60 °C). Crystallization from series of solvents was tried (ethanol, methanol, 1:1 mixture of water and ethanol, propalol-2, benzene, chloroform, acetone, pentane, hexane, dichlormethane, butyl-acetate, toluene, ethyl-acetate, diethyl-ether, petroleum ether) at various temperatures (room temperature, 18 and 4 °C) but with no success.

Single crystals were measured on an Enraf-Nonius CAD-4 diffractometer using graphite monochromated Cu Kα (1.54179 Å) radiation. Due to sensitivity of the crystals to light and X-rays, single crystal diffraction measurements were done at 150 K. Three standard reflections were measured every 120 min as intensity control. The WinGX standard procedure was applied for data reduction [48]. No absorption correction was applied. The structure was solved with SHELXS97 [49] and refined with SHELXL97 [49]. The models were refined using the full matrix least squares refinement. Hydrogen atoms were refined as riding entities for *endo*-**7a** and as free entities for *endo*-**6a**. The atomic scattering factors were those included in SHELXL97 [49]. Despite extremely poor data (even when collected at low temperature), structure of *endo*-**7a** gave reasonable geometric parameters and no residual electron density peaks larger than 0.9 eÅ^{-3}. Therefore, the structure of tricyclic compound can be unambigously confirmed. Molecular geometry calculations were performed with PLATON [50], and the molecular graphics were prepared using ORTEP-3 [51] and CCDC-Mercury [52]. Crystallographic and structure refinement data for *endo*-**6a** and *endo*-**7a** are shown in Table 1.

Supplementary materials

Supplementary crystallographic data for this paper can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033 or deposit@ccdc.cam.ac.uk). CCDC-721618 (for *endo*-**6a**) and CCDC-721619 (for *endo*-**7a**) contain the supplementary crystallographic data for this paper

Acknowledgements

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