

Radical Cation Cycloaddition Reactions of 2-Vinylbenzofurans and 2-Vinylfurans by Photoinduced Electron Transfer

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Dedicated to Professor Lennart Ebersson on the occasion of his 65th birthday

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2-Vinylbenzofuran (**2a**) and 2-isopropenylbenzofuran (**2b**) can be successfully employed in cycloaddition reactions involving photoinduced electron transfer with 1,3-cyclohexadienes **4**, styrenes **5** and acyclic 1,3-dienes **6**, yielding [4+2]- and/or [2+2]-cycloadducts. 2,4,6-Tri(4-methoxyphenyl)pyrylium tetrafluoroborate (**1a**) acts as an efficient sensitizer. Products are benzofuryl substituted cyclobutanes, 1,2,3,4-tetrahydrodibenzofurans, 2-benzofuryl bicyclo[2.2.2]-octenes, and benzofuryl substituted cyclohexenes. Of 2-vinylfurans, only the 5-bromo substituted derivative **3** reacted with 1,3-cyclohexadiene. The 2-vinylbenzofurans behave like styrenes in these photoinduced cycloaddition reactions mostly generating intermediate cyclobutyl radical cations. 1,3-sigmatropic C- and H-shifts taking place at the radical cation stage are likely in these reactions. The mechanisms are discussed in detail, supported by quantum chemical calculations.

The application of chemically, photochemically or electrochemically initiated electron transfer activation as the most simple means for redox umpolung has shown to be useful for a variety of reactions. Examples are substitution reactions,^{1–4} among them the well known S_{RN}1 reactions,⁵ addition and cycloaddition reactions,^{6,7} cycloreversions,⁸ eliminations,^{9,10} rearrangements,¹¹ isomerisations,^{2,12,13} and fragmentations.¹⁴ Electron-transfer induced radical cation cycloaddition reactions have been studied intensively over the last 15 years.¹⁵ They can be initiated by three types of electron transfer reaction: 1, thermally by use of one-electron transfer agents such as stable radical cation salts of thianthrene or triaryl amines,^{15b,16} transition-metal salts or complexes such as FeCl₃, Fe^{III} or Ru^{III} phenanthroline¹⁷ with the disadvantage that often high concentrations of the electron transfer agents have to be used; 2, electrochemically¹⁸ with the advantage that solvent-separated radical cations are generated; 3, photochemically using excited electron

acceptors such as cyanoarenes¹⁹ or triarylpyrylium salts²⁰ for singlet sensitization, or triplet sensitizers²¹ like fluorone or chloranil. Until recently, radical cation initiated cycloaddition reactions have been limited to simple hydrocarbon compounds like the well known dimerization of cyclohexadienes,^{20b,22} dimerization and cycloaddition of substituted 1,3-pentadienes,²³ or reactions of cyclohexadienes and styrenes.^{18a} More recently, heterosubstituted compounds have been studied more intensively: among them are vinylamines,²⁴ vinyl sulfides,²⁵ allenes and ketenes.²⁶ We have demonstrated the advantage of radical cation cycloadditions using indole as the dienophile together with endo- and exo-cyclic 1,3-dienes as dienes leading to 1,4-ethanotetrahydrocarbazoles or [b]annelated tetrahydrocarbazoles.^{20d–g} More recently, we successfully employed 2-vinylindoles acting as dienes together with 1,3-cyclohexadienes, styrenes,^{20h} or with β-acceptor substituted enamines yielding pyrido[1,2-a]-indoles^{18b,c,27} using either photoinduced electron transfer with triarylpyrylium salts as sensitizers, or electrochemical initiation. Similarly, 2-vinylpyrroles²⁸ and 3-vinylindoles²⁹ could be used.

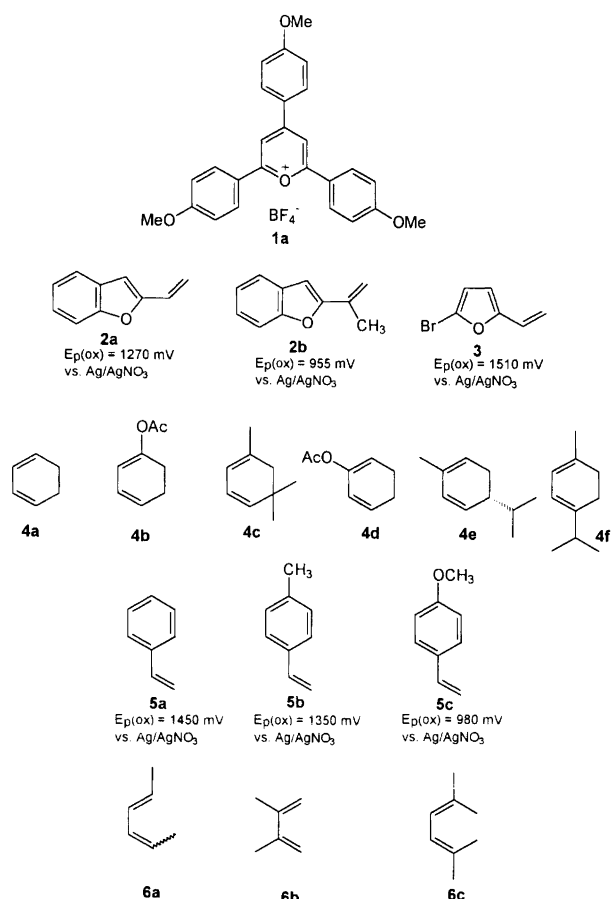
We therefore wanted to compare the results we

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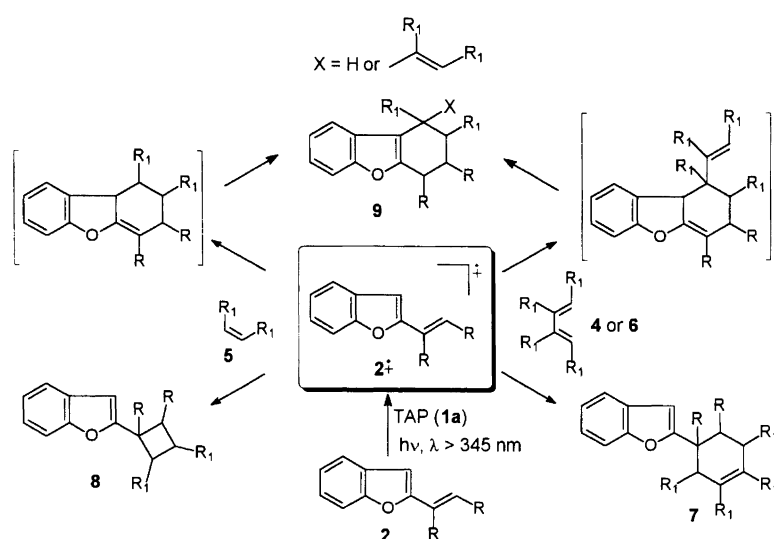
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obtained with 2-vinylindoles and 2-vinylpyrroles with the respective oxygen heterocycles 2-vinylbenzofurans and 2-vinylfurans. 2-Vinylbenzofurans are electron-rich compounds which thermally can undergo only [4+2]-cycloaddition reactions with very electron-poor partners such as tetracyanoethylene, maleic anhydride or 1,4-benzoquinone.³⁰ The reaction products are always tetrahydrodibenzofurans, so the 2-vinylbenzofuran acts solely as the diene. As reaction partners for the radical cation cycloaddition (redox umpolung) we selected, as electron-rich compounds, 1,3-cyclohexadienes, styrenes and acyclic 1,3-dienes which under normal conditions are not able to react. For electron transfer initiation we applied our well established photochemical method using small amounts of excited triarylpyrylium tetrafluoroborates as electron acceptors.²⁰ In this way we were able to study the influence of the heteroatom, electron density and steric factors on the course of the electron transfer induced cycloaddition.

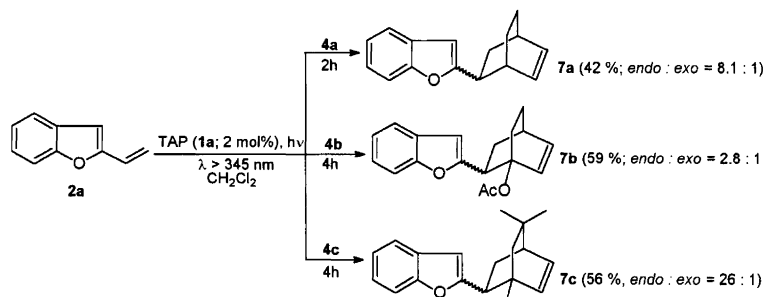
Selection of starting materials and sensitizers. As sensitizer we employed 2,4,6-tris(4-methoxyphenyl)pyrylium tetrafluoroborate (TAP, **1a**). The standard potential of the excited state is +1.98 V vs. NHE (**1a**).^{20b} As the heterocyclic starting materials we employed 2-vinylbenzofuran (**2a**), 2-isopropenylbenzofuran (**2b**) and 5-bromo-2-vinylfuran (**3**). As olefinic components we used 1,3-cyclohexadiene (**4a**), 1-acetoxy-1,3-cyclohexadiene (**4b**), 1,5,5-trimethyl-1,3-cyclohexadiene (**4c**), 2-acetoxy-1,3-cyclohexadiene (**4d**), (5*R*)-5-isopropenyl-2-methyl-1,3-cyclohexadiene [**4e**, (*R*)-(-)-phellandrene], α -terpinene (**4f**), styrene (**5a**), 4-methylstyrene (**5b**), 4-methoxystyrene (**5c**), 2,4-hexadiene (**6a**), 2,3-dimethyl-1,3-butadiene (**6b**), and 2,4-dimethyl-2,4-hexadiene (**6c**).



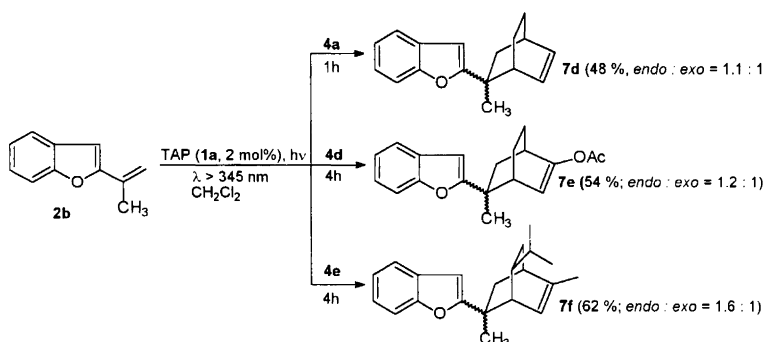
The radical cation cycloadditions can follow different reaction pathways. Besides cyclobutane formation via [2+2]-cycloaddition³¹ the 2-vinylfurans can act either as dienes or dienophiles in [4+2]cycloadditions. Usually, electron transfer induced cycloadditions are periselective, which means that only one of several possible products is formed. The possible products are given in Scheme 1.



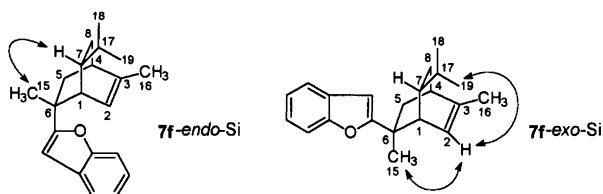
Scheme 1. Possible reaction pathways in the cycloaddition between 2-vinylfurans and olefins by photoinduced electron transfer.



Scheme 2. Results of the electron transfer induced cycloaddition between 2-vinylbenzofuran (**2a**) and 1,3-cyclohexadienes **4**.



Scheme 3. Results of the electron transfer induced cycloaddition between 2-isopropenylbenzofuran (**2b**) and 1,3-cyclohexadienes **4**.



Scheme 4. Determination of the configuration of the diastereomers by NOE.

Results

All reactions were performed using 1–2 mol% of **1a** in dichloromethane together with 2 mmol of the 2-vinylbenzofuran **2** and 4 mmol of the olefin component **4**, **5** or **6**. Irradiation was by means of a 450 W xenon arc lamp with filtering of the wavelengths to values above 345 nm.

Cycloadditions between 2-vinylbenzofurans 2 and 1,3-cyclohexadienes 4 by photoinduced electron transfer. The conditions of the experiments and the results are represented in Schemes 2 and 3. In addition to the cross-coupling products indicated, small amounts of cyclohexadiene and 2-vinylbenzofuran dimers are formed. When two equivalents of the cyclohexadiene were employed, the dimerization of the 2-vinylbenzofurans could be suppressed.

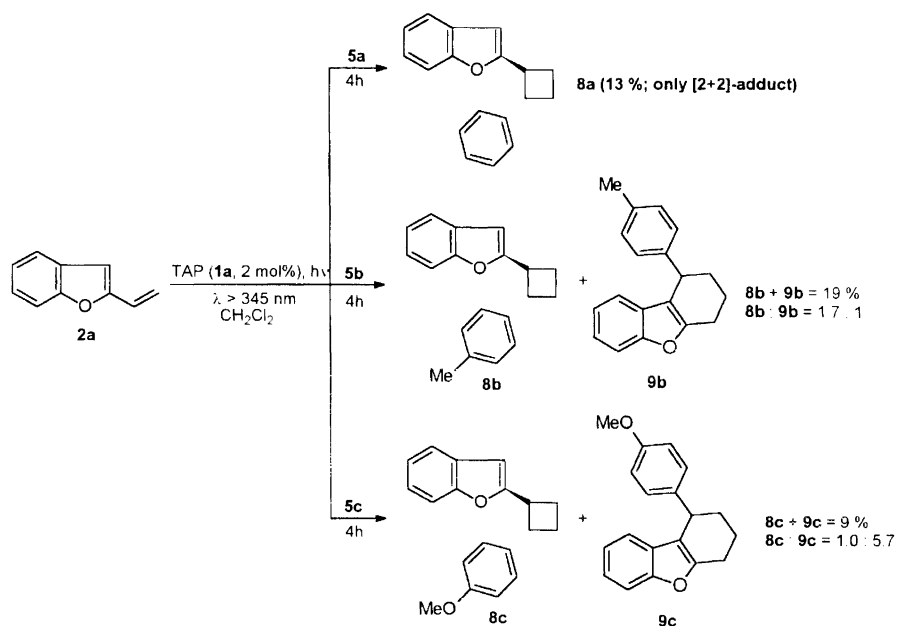
The benzofuryl-substituted bicyclo[2.2.2]octenes **7** were formed as the only products. The reaction between **2b** and the optically active enantiomerically pure **4e** is diastereofacially selective, resulting in the formation of

only two of the four possible diastereomers. These are formed by attack of the cyclohexadiene at the sterically less hindered *Si*-side of **2b** giving only **7f-endo-Si** and **7f-exo-Si** (Scheme 4). The relative configuration was determined by means of ^1H NMR NOE experiments. The increases of the signal intensities by saturation of the corresponding NMR frequencies are indicated by double arrows in Scheme 5.

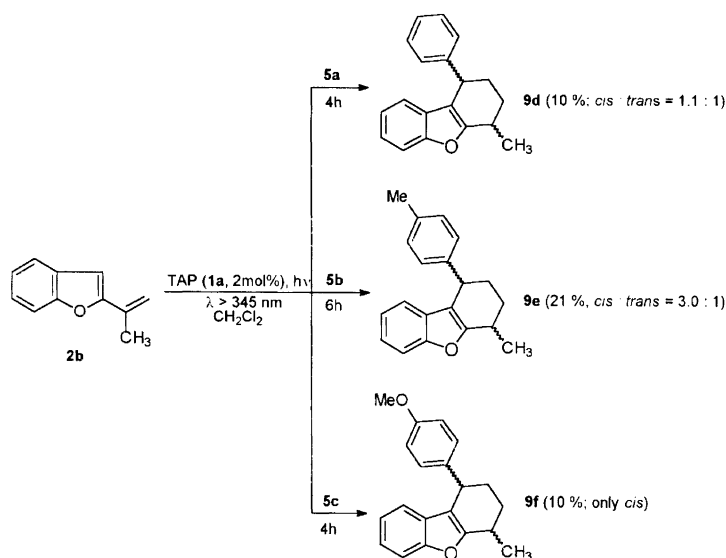
The reaction between **2a** and α -terpinene (**4f**) under the same conditions was also successful resulting in a mixture of two cross-coupling products in a yield of 47% and a ratio of 9.2:1. However, these products could not be separated. The reaction of **2b** with the same cyclohexadiene gave no product. The reason for this might be that the formation of the second bond is prevented because of a high degree of steric hindrance.

Cycloadditions between 2-vinylbenzofurans 2 and styrenes 5 by photoinduced electron transfer. In this case, two types of product are formed: 1-substituted tetrahydrodibenzofurans **9** and *trans*-1,2-substituted cyclobutanes **8**, the [2+2]-cycloadducts (Schemes 5 and 6). The *trans* configuration in **8** was determined by NOE experiments.

In contrast with the reactions of 2-vinylbenzofuran (**2a**), in the reaction between 2-isopropenylbenzofuran (**2b**) and styrenes, only the 1,4-disubstituted tetrahydrodibenzofurans **9** are formed. The relative configuration of *cis*-1-(4-methoxyphenyl)-4-methyl-1,2,3,4-tetrahydrodibenzofuran (**9f**) was determined by X-ray crystallography. In the other cases, the configuration was



Scheme 5. Results of the electron transfer induced cycloaddition between 2-vinylbenzofuran (**2a**) and styrenes **5**.



Scheme 6. Results of the electron transfer induced cycloaddition between 2-isopropenylbenzofuran (**2b**) and styrenes **5**.

determined by comparison of the ^1H NMR coupling constants of the protons on C^1 and C^4 with those of **9f** (see Table 1).

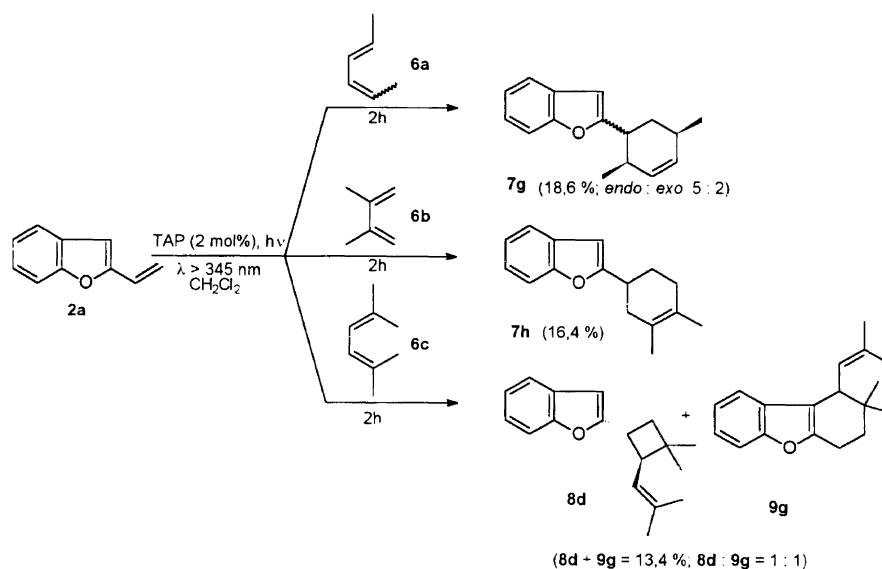
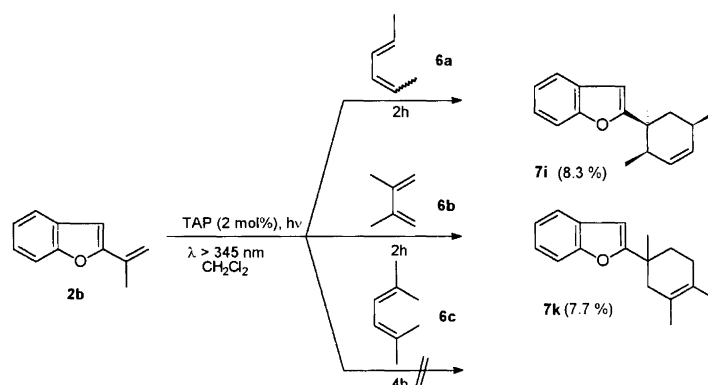
Cycloadditions between 2-vinylbenzofurans 2 and acyclic 1,3-dienes 6 by photoinduced electron transfer. While in the case of **2a** three different types of product are formed (2-cyclohexenylbenzofurans **7**, 1,2-*trans* disubstituted cyclobutanes **8**, and 1-substituted tetrahydrodibenzofurans **9**), in the case of **2b** only products of type **7** are found (Schemes 7 and 8). The relative configuration of products **7** was determined by NOE experiments as indicated in Scheme 9.

Dimerization of 2-vinylbenzofurans 2a and 2b by photoinduced electron transfer. The dimeric products had in both cases the structure of 1-mono- or 1,2-di-substituted tetrahydrodibenzofurans **9**. In the case of **2a**, a trimer **10** was also isolated. Its unexpected structure consisted of a bis-benzofurylcyclobutane with one benzofuryl system additionally substituted in the 3-position by a third 2-vinylbenzofuran (Scheme 10).

Cycloadditions between 5-bromo-2-vinylfuran (3) and 1,3-cyclohexadiene (4a) by photoinduced electron transfer. While we did not find any cycloaddition products in the photochemically induced electron transfer initiated reac-

Table 1. Coupling constants for the protons on C-1 and C-4 of compounds **9d–9f**.

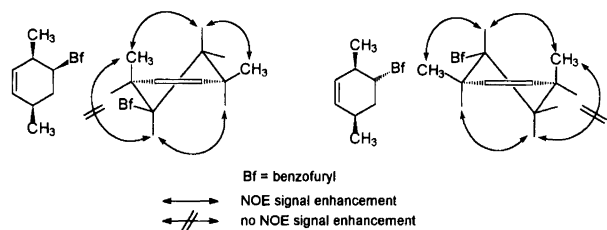
Compound	9f	9e	9d
<i>cis</i>	C-1: d, 5.8 Hz ($^3J_{\text{HH}}$) d, 5.8 Hz ($^3J_{\text{HH}}$) d, 1.5 Hz ($^5J_{\text{HH}}$)	C-1: d, 5.7 Hz ($^3J_{\text{HH}}$) d, 5.7 Hz ($^3J_{\text{HH}}$) d, 1.6 Hz ($^5J_{\text{HH}}$)	C-1: d, 5.8 Hz ($^3J_{\text{HH}}$) d, 5.8 Hz ($^3J_{\text{HH}}$) d, 1.6 Hz ($^5J_{\text{HH}}$)
	C-4: d, 8.5 Hz ($^3J_{\text{HH}}$) q, 6.7 Hz ($^3J_{\text{HH}}$) d, 1.5 Hz ($^5J_{\text{HH}}$)	C-4: d, 12.5 Hz ($^3J_{\text{HH}}$) q, 6.9 Hz ($^3J_{\text{HH}}$) d, 1.6 Hz ($^5J_{\text{HH}}$)	C-4: d, 12.5 Hz ($^3J_{\text{HH}}$) q, 7.0 Hz ($^3J_{\text{HH}}$) d, 1.6 Hz ($^5J_{\text{HH}}$)
<i>trans</i>		C-1: d, 8.8 Hz ($^3J_{\text{HH}}$) d, 5.5 Hz ($^3J_{\text{HH}}$) d, 2.6 Hz ($^3J_{\text{HH}}$)	C-1: d, 8.9 Hz ($^3J_{\text{HH}}$) d, 5.6 Hz ($^3J_{\text{HH}}$) d, 2.6 Hz ($^3J_{\text{HH}}$)
		C-4: d, 8.8 Hz ($^3J_{\text{HH}}$) q, 6.9 Hz ($^3J_{\text{HH}}$) d, 5.5 Hz ($^3J_{\text{HH}}$) d, 2.6 Hz ($^3J_{\text{HH}}$)	C-4: d, 8.7 Hz ($^3J_{\text{HH}}$) q, 6.9 Hz ($^3J_{\text{HH}}$) d, 6.2 Hz ($^3J_{\text{HH}}$) d, 2.6 Hz ($^3J_{\text{HH}}$)

Scheme 7. Results of the electron transfer induced cycloaddition between 2-vinylbenzofuran (**2a**) and acyclic 1,3-dienes **6**.Scheme 8. Results of the electron transfer induced cycloaddition between 2-isopropenylbenzofuran (**2b**) and acyclic 1,3-dienes **6**.

tions between 2-vinylfuran, 2-(1-dimethylaminovinyl)furan, 2-furylacrylonitrile or 5-cyano-2-vinylfuran and 1,3-cyclohexadienes or styrenes, the reaction between 5-bromo-2-vinylfuran (**3**) and 1,3-cyclohexadiene (**4a**)

was successful. The 5-bromo-2-furylbicyclo{2.2.2}octene **7l** was identified as only product (Scheme 11).

In the reaction of **3** with 4-methylstyrene (**5b**) two products were identified by GC-MS. The fragmentation

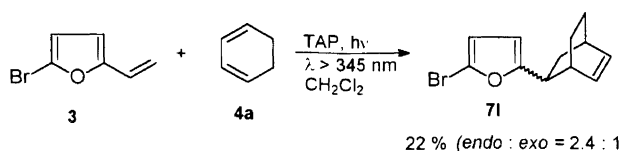


Scheme 9. NOE effects in the ^1H NMR spectra of compounds **7**.

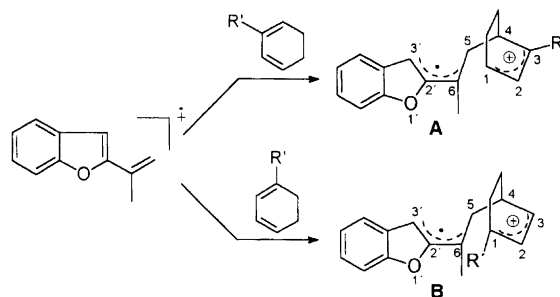
pattern indicated the presence of a [2+2]- and a [4+2]-cycloadduct. The amounts were low due to the destruction of the sensitizer within 5 min.

Discussion

Cycloadditions between 2-vinylbenzofurans **2** and 1,3-cyclohexadienes **4** by photoinduced electron transfer. The results of our experiments show that in the photochemically induced electron transfer initiated reaction between 2-vinyl benzofurans and 1,3-cyclohexadienes, the 2-vinylbenzofurans always act as dienophiles. All examples show total regioselectivity so that a substituent in the 1-position of the cyclohexadiene is always present in the 1-position of the bicyclo[2.2.2]octene product, while a substituent in the 2-position of the cyclohexadiene is found in the 3-position of the product. The same regioselectivity has been found in the reaction between cyclohexadienes and indoles.^{20d-f} In the case of indoles and 2-vinylindoles, the positive charge is stabilized at the nitrogen in the form of an iminium ion, and radical attack occurs at the cyclohexadiene with formation of a stabilized allyl radical. In contrast, for the 2-vinylbenzofuran radical cations, semiempirical calculations (at the UHF/AM1 level carried out using Hyperchem 5.0) point to an electrophilic attack by the



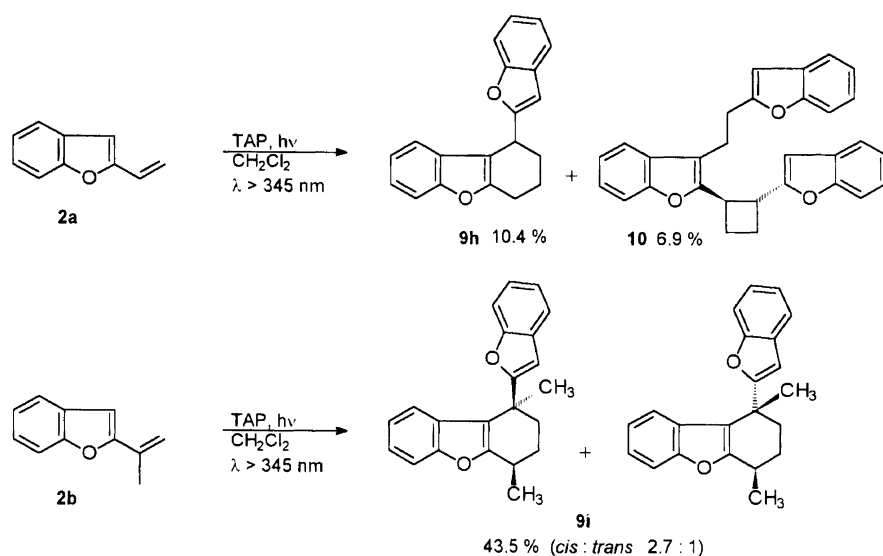
Scheme 11. Result of the cycloaddition between 5-bromo-2-vinylfuran (**3**) and 1,3-cyclohexadiene (**4a**) by photoinduced electron transfer.



Scheme 12. Formation of the intermediate distonic radical cations in the reaction of 2-vinylbenzofuran radical cations with 2-acetoxy-1,3-cyclohexadiene (**A**) and 1-acetoxy-1,3-cyclohexadiene (**B**) as calculated by quantum chemical methods ($\text{R}' = \text{OAc}$).

Table 2. Charges and spin densities of selected atoms in intermediate **A**.

Atom	Charge	Spin density
C-1	0.110	0.000
C-2	-0.291	0.000
C-3	0.374	0.001
C-4	-0.156	0.001
C-5	-0.105	0.004
C-6	-0.151	0.575
O-1'	-0.125	0.000
C-2'	0.020	0.258
C-3'	-0.143	0.521



Scheme 10. Results of the dimerization and trimerization of 2-vinylbenzofuran (**2a**) and isopropenylbenzofuran (**2b**) by photoinduced electron transfer.

Table 3. Charges and spin densities of selected atoms in intermediate **B**.

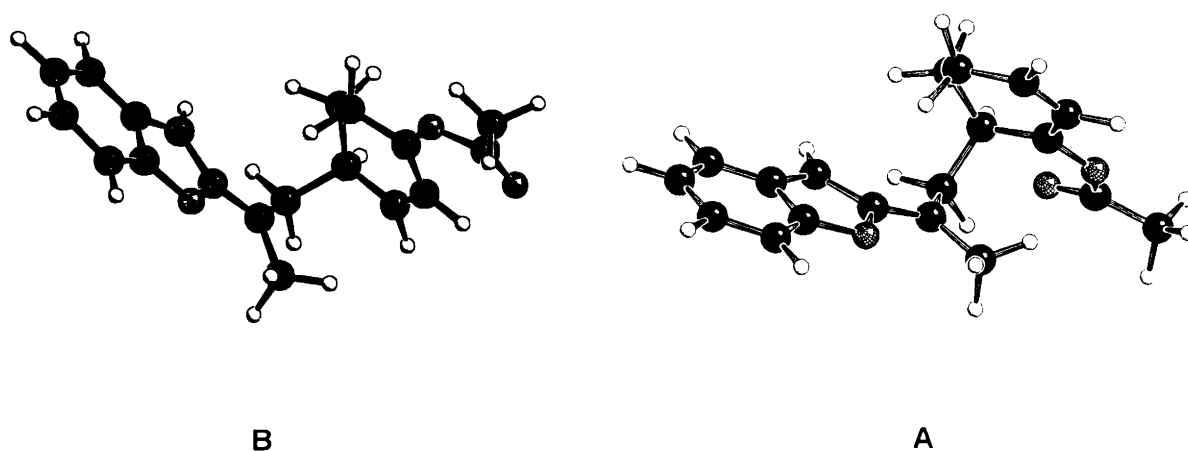
Atom	Charge	Spin density
C-1	0.366	0.000
C-2	-0.318	0.000
C-3	0.118	0.000
C-4	-0.138	0.001
C-5	-0.108	0.004
C-6	-0.145	0.588
O-1'	-0.129	0.000
C-2'	0.013	0.265
C-3'	-0.145	0.522

positively charged vinyl carbon on the cyclohexadiene forming the distonic radical cations **A** or **B** as shown in Scheme 12, with stabilization of the substituents in 1- or 3-position in the form of allylic cations.³² The highest spin densities as calculated are located at the benzofuryl allylic system as indicated in Scheme 12. The charges and spin densities of selected atoms are given in Tables 2 and 3. These results are also confirmed by single-point *ab initio* calculations at the UHF/STO-3G level. The UHF/AM1 optimized structures of the distonic radical cations formed in the reaction between **2b** and **4d** (leading to radical cation **A**) or between **2b** and **4b** (leading to radical cation **B**) are given in Scheme 13.

The reactions lead mainly to *endo* products. However, this is more pronounced for the 2-vinylbenzofuran (**2a**) than for the 2-isopropenyl derivative **2b**. This can also be explained by the proposed mechanism. As we have demonstrated for the reactions of exocyclic 1,3-dienes with indoles, calculation of the potential hypersurface indicate that electron transfer induced cycloaddition is a non-synchronous two-step process.^{20f,32} The first bond, resulting in the distonic radical cations given in Scheme 12, is usually formed with a minimal activation barrier, while the orbital interactions for the formation

of the second bond are small. Therefore the lifetime of this long-bond intermediate may be long enough to allow isomerization. This is especially the case if the bond formation is sterically more hindered, as in the case of **2b**.

Cycloadditions between 2-vinylbenzofurans 2 and styrenes 5 by photoinduced electron transfer: 2-vinylbenzofuran (2a) as substrate. Two types of product are formed in the electron transfer induced cycloaddition between **2a** and styrenes, namely [2+2]- (**8**) and formal [4+2]-cycloadducts (**9**). The cyclobutanes always have the *trans* configuration and the amounts in which they are formed increase with increased electron density of the styrene component. The [4+2]-adducts are always 1,2,3,4-tetrahydrodibenzofurans, while for the normal Diels–Alder reaction sequence 1,2,3,9b-tetrahydrodibenzofurans would be expected. This can be explained by the reformation of the heteroaromatic system via a [1,3]-hydrogen shift at the radical cation stage after the cycloaddition step but before back electron transfer has occurred. It has been shown before by Wiest^{10h,33} using quantum chemical calculations that in the case of the cycloaddition between a 2-vinylindole [3-methyl-2-(2-indolyl)acrylonitrile] radical cation and styrene the [1,3_s]-hydrogen shift is very much favoured at the product radical cation stage as compared with the symmetry-forbidden reaction of the neutral compound. In the present case, quantum chemical calculations for the radical cation cycloaddition between the 2-vinylbenzofuran **2b** and styrene leading to the cycloadduct *cis*-**9d** show that the [1,3_s]-hydrogen shift on the stage of the product radical cation has an activation barrier of 27.9 kcal mol⁻¹, which is much lower than for the neutral compound (68.7 kcal mol⁻¹). This value is slightly smaller than the *ab initio* results that Clark obtained for the propenyl radical cation (29.6 kcal mol⁻¹).³⁴ Our calculation was performed by the UHF/AM1 method. For the localization of the transition state, we used the



Scheme 13. UHF/AM1 optimized structures of the distonic long-bond radical cation intermediates in the radical cation induced reaction between 2-isopropenylbenzofuran (**2b**) and 1-acetoxy-1,3-cyclohexadiene (**4b**, **B**) or 2-acetoxy-1,3-cyclohexadiene (**4d**, **A**).

quadratic synchronous transit method (QST),³⁵ followed by a quasi-Newton method to find the saddle point on the energy hypersurface. Because electron correlation is not considered in these calculations, the activation barrier should be overestimated. In contrast with Clark's calculation, in our system the hydrogen shift leads to the re-aromatization of the benzofuran system. Our results are also strongly supported by the fact that, in the case of a thermal Diels–Alder reaction of 2-(α -phenylvinyl)benzofuran, no [1,3]-hydrogen shift is observed and the 1,2,3,9b-tetrahydro compound is formed.^{30b} The tetrahydrodibenzofurans **9** always carry the phenyl substituent in the 1-position while in the reaction between 2-vinylindoles and styrenes they are found in the 2-position.^{20h} This could be explained by the attack of an initially formed styrene radical cation on the vinyl group of the vinyl benzofuran.

All these observations support the assumption that 2-vinylbenzofurans, in contrast with 2-vinylindoles, behave more like a styrene by acting as a dienophile not only towards dienes but also towards other dienophiles. Thus the reaction behavior can be rationalized in a similar way as has been done in intensive studies of the radical cation induced dimerization of styrenes, especially by Farid.³⁶ The mechanism was later refined by Bauld³⁷ and Lewis³⁸ on the basis of their studies of the electron transfer induced dimerization of *cis*- and *trans*-anethole, and by Schepp and Johnston³⁹ in their investigation of the cycloaddition of *p*-methoxystyrene by laser-flash photolysis. To explain the total *trans*-selectivity of the

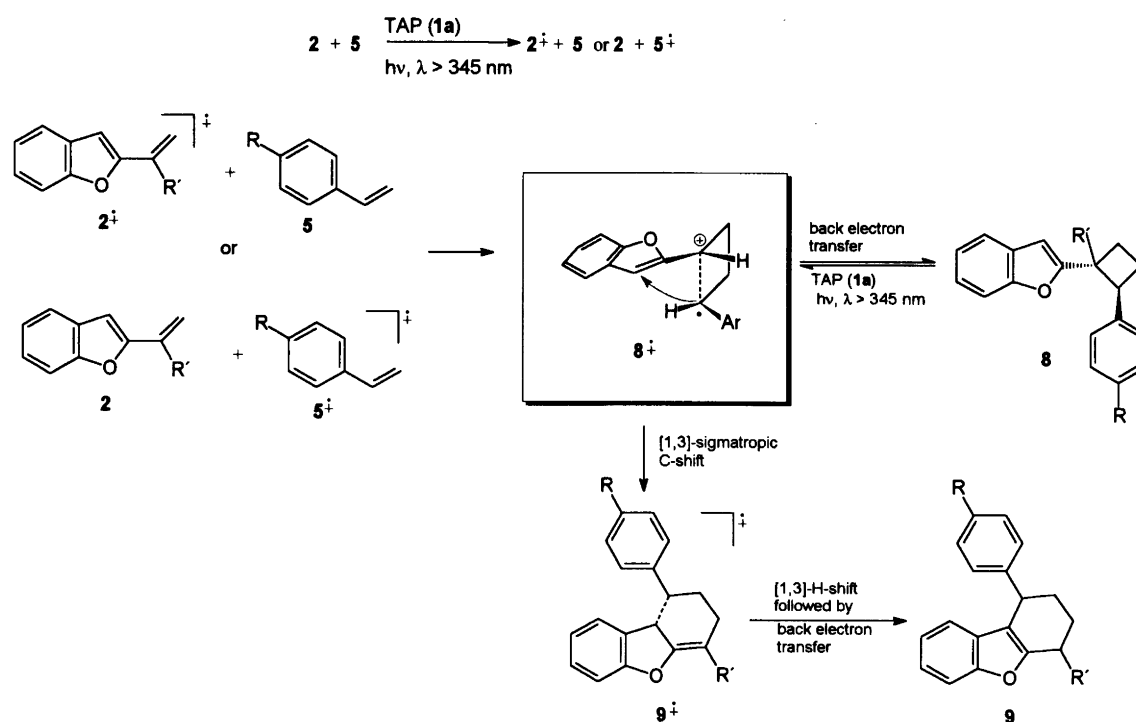
Table 4. Results of the rearrangement of 2-(2-arylcyclobutyl)benzofurans **8** by photoinduced electron transfer.

Cyclobutane	Conversion (%)	Tetrahydrodibenzofuran (%)
8a	68.4	—
8b	96.5	9b (45.7)
8c	98.1	9c (67.2)

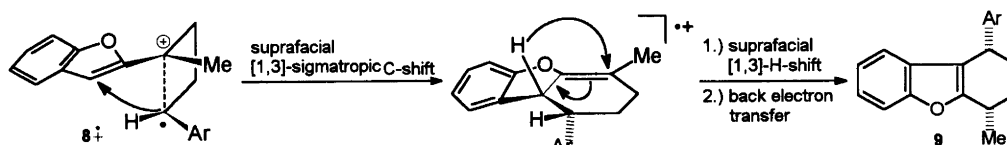
disubstituted cyclobutane products they assumed a concerted non-synchronous [$\pi 2_s + \pi 1_s$]-cycloaddition to give a cyclobutane radical cation with a one-electron two-center bond, a so-called *long-bond intermediate*, as shown in Scheme 14 for **8**⁺. In contrast with the radical cation induced reaction between 2-vinylbenzofurans **2** and 1,3-cyclohexadienes **4**, the highest spin densities within the distonic radical cations **8**⁺ are located in the benzyl system as calculated by UHF/AM1. In this intermediate the *trans*-configuration of the aryl substituents is practically conserved so that back electron transfer yields only *trans*-**8**. The formation of formal [4+2]-cycloadducts like **9** can be explained by a [1,3]-sigmatropic C-shift at the stage of **8**⁺ giving **9**⁺. This is followed by the [1,3]-H shift discussed before. Back electron transfer then leads to **9**.

The cyclobutane **8** forms an electron transfer equilibrium with **8**⁺. This was proved by irradiation of the isolated cyclobutanes **8** under the standard conditions, which gave the tetrahydrodibenzofurans **9** (Table 4).

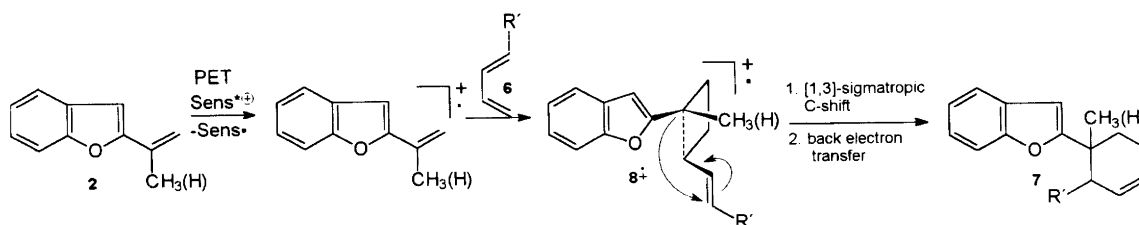
The cross-coupling reactions between two styrene-like



Scheme 14. Mechanistic interpretation of the photoinduced electron transfer initiated cycloaddition between 2-vinylbenzofurans **2** and styrenes **5**.



Scheme 15. Formation of the *cis*-1-aryl-4-methyltetrahydrodibenzofurans **9**.



Scheme 16. Formation of products **7** in the cycloaddition between 2-vinylbenzofurans **2** and acyclic 1,3-dienes **6** by photoinduced electron transfer.

compounds described here is different from the results described in the literature because in our case [2+2] and [4+2] cross-coupling products are formed at the same time.

2-Isopropenylbenzofuran (2b) as substrate. The selective formation of only the tetrahydrodibenzofurans **9** may be due to steric crowding of the cyclobutane structures **8**, which would be 1,1,2-trisubstituted, since radical cation initiated cycloaddition reactions have been shown to be very sensitive to steric effects. The predominant formation of *cis*-**9** can be explained by the reaction path given in Scheme 15.

As in the case of **2a** (Scheme 14), we assume the intermediate formation of a cyclobutane radical cation, which, because of the steric hindrance mentioned above, now undergoes a faster [1,3]-sigmatropic C-shift. Also because of steric reasons, this sigmatropic shift follows a suprafacial pathway with retention. At the radical cation stage of the vinyl cyclobutane, this is an energetically favourable reaction with a low activation barrier.⁴⁰ Finally, a suprafacial [1,3]-H shift again at the radical cation stage leads to the predominantly formed *cis*-product after back electron transfer.

Cycloadditions between 2-vinylbenzofurans 2 and acyclic 1,3-dienes by photoinduced electron transfer. The reactions of 2-vinylbenzofurans with acyclic dienes **6** led to the formation of substituted cyclohexene derivatives **7**, a cyclobutane **8d** and a tetrahydrodibenzofuran **9g**. The formation of **8d** and **9g** can be explained as in the reactions of **2a,b** with styrenes **5** via the formation of a cyclobutane radical cation as shown in Scheme 14. Products **7** are formed by [1,3]-sigmatropic C-shift to the vinylic double-bond of the cyclobutane radical cation (**8⁺**), instead of to the furan double-bond leading to **9** (Scheme 16).

The formation of **9g** in the reaction between **2a** and **6c** can be explained by the steric hindrance of the [1,3]-sigmatropic C-shift to the vinylic double bond, while the [1,3]-sigmatropic C-shift to the furan double bond lowers

the steric interactions of the four methyl groups. In the case of **2b**, because of the steric hindrance **6c** does not react at all.

Dimerization of 2-vinylbenzofurans 2 by photoinduced electron transfer. If no other dienes or dienophiles are present, 2-vinylbenzofurans **2** form the formal [4+2]-cycloadducts of type **9** presumably in the same way as in the reaction between 2-vinylbenzofurans and styrenes. The intermediate formation of a 1,2-disubstituted cyclobutane is supported by the formation of the trimer **10a** with an unexpected additional 3-substitution of a benzofuran unit by a 2-vinylbenzofuran.

Conclusions

2-Vinylbenzofuran (**2a**) and 2-isopropenylbenzofuran (**2b**) were successfully employed in photochemically induced electron transfer initiated cycloaddition reactions with 1,3-cyclohexadienes **4**, styrenes **5** and acyclic 1,3-dienes **6**, yielding [4+2]- and/or [2+2]-cycloadducts. 2,4,6-Tri(4-methoxyphenyl)pyrylium tetrafluoroborate (**1a**) acts as an efficient sensitizer. In contrast with 2-vinylindoles, 2-vinylbenzofurans **2** prefer to react as dienophiles very similarly to styrenes. In the reaction with 1,3-cyclohexadienes, [4+2]-cycloadducts **7** are formed with **2** reacting as a dienophile. The predominant *endo*-selectivity is determined by the lifetime of the long-bond intermediate. In the reaction with styrenes, [2+2]-adducts **8** and [4+2]-adducts **9** are formed. Both products are formed via an intermediate cyclobutyl radical cation, while in the case of 2-vinylindoles, we found only [4+2]-adducts, with the vinylindole acting as a diene.^{18c,20h,41} Compounds **9** are formed from this intermediate by a 1,3-sigmatropic C-shift which has a low activation barrier at the radical cation stage. This reaction path is a formal styrene cross-coupling dimerization and is paralleled by the dimerization of **2a** and **2b** also mainly leading to products of type **9**. Also, the photoinduced reaction of **2** with acyclic 1,3-dienes proceeds

via intermediate cyclobutyl radical cations mostly followed by a 1,3-sigmatropic C-shift to the vinylic double bond yielding formal [4+2]-adducts **7**. Of 2-vinylfurans, only the 5-bromo derivative **3** was successfully reacted with 1,3-cyclohexadiene, the former behaving very similarly to the 2-vinylbenzofuran.

Experimental

General. Solvents were purified and dried by literature procedures. Reagents were employed as purchased. Thin-layer chromatography (TLC) was carried out on aluminium sheets, precoated with silica gel 60 F₂₅₄ (Merck) or neutral aluminium oxide 60 F₂₅₄ (Merck), or on glass plates precoated with RP-18 F_{254S} (Merck). The plates were inspected by UV light prior to development with iodine vapour, ninhydrin solution, or by treatment with ceric ammonium molybdate reagent and subsequent heating. Analytical HPLC was performed on a Merck–Hitachi instrument equipped with an L-3000 diode array detector in combination with an L-6200 pump and Rheodyne (20 µl) injector system or on Waters LC spectrometer model 481 in combination with a Waters pump model 510 and injector system UK 6 using an analytical or a semi-preparative flow-through cell. For preparative separations an HPLC system consisting of a Knauer UV detector, a Waters model 590 pump and a Waters UK 6 injector system was used. The following analytical columns were used: Lichrosphere 100 RP-18, 5 µm, 250 × 4 mm (Merck) and 250 × 8 mm (CS, Langerwehe) and Lichrosphere Si-60, 5 µm, 250 × 4 mm (CS, Langerwehe). For preparative purposes the following columns were employed: Lichrosorb 100 RP-18, 5 µm, 250 × 20 mm (CS, Langerwehe), Lichrosorb Si-60, 7 µm, 250 × 32 mm (Knauer, Berlin), Lichrosorb Si-60, 5 µm, 250 × 20 mm (CS, Langerwehe). For liquid chromatography flash silica gel 30–60 µm (Baker), silica gel 65–200 µm (Woelm) and neutral aluminium oxide 63–200 µm (Merck) were used. Melting points were recorded on a Reichert (Wien) melting point apparatus and are uncorrected. Mass spectra were taken with an AEI (Manchester) MS 50 instrument by EI (70 eV). Infrared spectra were obtained with a Perkin Elmer (Überlingen) FT-IR 1600 instrument. GC–MS spectra were obtained using a Hewlett Packard HP 5690 gas chromatograph coupled to a mass selective detector MSD 5970 (EI, 70 eV) and an HP 9133/HP 300 data system using an FS HP1 capillary column (12 m, 0.2 mm diameter, 0.33 µm film thickness, helium carrier gas). ¹H NMR and ¹³C NMR spectra were recorded on Bruker AC 200 and AC 400 instruments. Chemical shifts (δ) are reported in ppm relative to tetramethylsilane (TMS) using TMS or CDCl₃ as references. Potentials were measured by cyclic voltammetry using a computer-controlled electroanalytical system CYSY 1-H (Cypress Systems, Lawrence) in combination with a cell stand C1 A/B (Bioanalytical Systems, West Lafayette) containing a glassy carbon anode with a diameter of 3 mm, platinum wire cathode, and a Ag/AgNO₃ (570 mV vs. NHE) reference electrode in acetonitrile (0.1 M LiClO₄) as

electrolyte. Irradiation was performed using a 450 W xenon-arc lamp (Osram XBO-450 OFR) incorporated into a lamp housing LAX 1450 (Müller Elektronik, Moosinning) equipped with a long-pass filter 5146 (λ > 345 nm, Oriel, Stanford).

Materials. The following chemicals were prepared according to literature procedures: 2,4,6-trianisylpyrylium tetrafluoroborate (**1a**)^{20b} 1-acetoxy-1,3-cyclohexadiene (**4b**), 2-acetoxy-1,3-cyclohexadiene (**4d**), and 1,5,5-trimethyl-1,3-cyclohexadiene (**4c**).^{20d,e} 2-Vinylbenzofuran (**2a**) was synthesized by a Wittig reaction between benzofuran-2-carbaldehyde and methyl triphenylphosphonium bromide according to the literature.^{30d} Benzofuran-2-carbaldehyde was prepared by a known procedure from 2-(2,2-dimethoxyethoxy)benzaldehyde in acetic acid.⁴² 2-Isopropenylbenzofuran (**2b**) was synthesized by a Wittig reaction between 2-acetoxybenzofuran⁴³ and methyl triphenylphosphonium bromide according to the literature.^{30a}

5-Bromo-2-vinylfuran (3) was synthesized from 5-bromofuran-2-carbaldehyde⁴⁴ via Wittig reaction. Thus, to a suspension of methyl triphenylphosphonium bromide (9 g, 25 mmol) in dry THF was added sodium hydride (750 mg, 31 mmol). The mixture was stirred until all of the phosphonium salt had reacted (approx. 2 h) after which 5-bromofuran-2-carbaldehyde (4.38 g, 25 mmol) was added and the reaction was warmed to 70–75 °C for 1 h. From the brown suspension the solvent was evaporated off and, the residue was treated with 100 ml of water and extracted three times with diethyl ether. The organic phases were collected and dried, and the solvent was evaporated off *in vacuo*. The remaining residue was chromatographed on silica gel with *n*-pentane as the eluent to give 970 mg (5.6 mmol, 23%) of **3**. ¹H NMR (400 MHz, CDCl₃): δ 6.32 (dd, *J* = 17.7, 11.3 Hz, 1 H, H-1'), 6.20 (d, *J* = 3.3 Hz, 1 H, H-4), 6.12 (dd, *J* = 3.3, 0.5 Hz, 1 H, H-3), 5.57 (ddd, *J* = 17.7, 1.2, 0.5 Hz, 1 H, H-2'), 5.08 (dd, *J* = 11.3, 1.2 Hz, 1 H, H-2''). ¹³C NMR (100.5 MHz, CDCl₃): δ 155.1 (C-5), 124.1 (C-3,4), 121.7 (C-2), 112.9 (C-3,4), 112.9 (C-2), 110, 25 (C'-1). MS: *m/z* (rel. int.) 174 (*M*⁺, 13), 172 (13), 158 (3), 156 (3), 88 (10), 86 (64), 84 (100), 65 (18). HRMS: Found 171.9532, calc. for C₆H₅BrO: 171.9524.

Standard conditions for the photoinduced electron transfer initiated cycloadditions. The 2-vinylfuran **2a,b** or **3** (2 mmol), the coupling components **4, 5** or **6** (4 mmol), and the sensitizer **1a** (20 mg, 2 mol%) were placed in a Schlenk tube and 120 ml of dry dichloromethane were added. The mixture was then irradiated for the indicated times with water cooling (10–15 °C) at a wavelength of λ > 345 nm. If the fluorescence of the sensitizer faded during the reaction another 1 mol% of **1a** was added. After the irradiation, the pyrylium salt was separated from the products on a short filtration column using

dichloromethane as the eluent. Separation and isolation was carried out as indicated for the different products.

2-(Bicyclo[2.2.2]oct-5-en-2-yl)benzofuran (7a). According to the standard conditions the irradiation of **2a** and **4a** was performed for 2 h. Work-up by flash chromatography (*n*-heptane as the eluent) gave 189 mg (42%) of **7a** (*endo:exo* = 8.1 : 1).

endo-7a: M.p. 32 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.45 (m, 1 H, H-7), 7.39 (m, 1 H, H-4), 7.18 (ddd, *J* = 7.3, 7.3, 1.7 Hz, 1 H, H-5), 7.16 (ddd, *J* = 7.3, 7.3, 1.3 Hz, 1 H, H-6), 6.36 (ddd, *J* = 8.0, 6.6, 1.4 Hz, 1 H, H-5'), 6.24 (dd, *J* = 1.0, 1.0 Hz, 1 H, H-3), 6.13 (ddd, *J* = 8.0, 6.4, 1.4 Hz, 1 H, H-6'), 3.15 (m, 1 H, H-2'), 2.97 (m, 1 H, H-1'), 2.66 (m, 1 H, H-4'), 2.06 (ddd, *J* = 12.6, 10.0, 2.7 Hz, 1 H, H-3'), 1.72 (m, 1 H, H-7'), 1.60 (m, 1 H, H-8'), 1.53 (m, 1 H, H-3''), 1.39 (m, 1 H, H-7''), 1.32 (m, 1 H, H-8''). ¹³C NMR (100.5 MHz, CDCl₃): δ 164.1 (C-2), 154.5 (C-7a), 134.8 (C-5'), 132.07 (C-6'), 128.9 (C-3a), 123.1 (C-5), 122.4 (C-6), 120.3 (C-7), 110.0 (C-4), 100.9 (C-3), 37.3 (C-2'), 34.3 (C-1'), 32.7 (C-3'), 29.7 (C-4'), 26.1 (C-7'), 24.3 (C-8). MS: *m/z* (rel. int.) 224 (*M*⁺, 20), 194 (21), 165 (25), 145 (23), 144 (100), 115 (34), 89 (29), 79 (32), 77 (36). HRMS: Found 224.1198, calc. for C₁₆H₁₆O: 224.1201.

exo-7a: M.p. 40 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.51 (m, 1 H, H-7), 7.43 (m, 1 H, H-4), 7.23 (ddd, *J* = 7.3, 7.3, 1.4 Hz, 1 H, H-5), 7.20 (ddd, *J* = 7.3, 7.3, 1.6 Hz, 1 H, H-6), 6.52 (dd, *J* = 2.0, 2.0 Hz, 1 H, H-3), 6.45 (ddd, *J* = 8.0, 6.6, 1.3 Hz, 1 H, H-6'), 6.36 (ddd, *J* = 8.0, 6.5, 1.2 Hz, 1 H, H-5'), 2.93 (m, 1 H, H-2'), 2.91 (m, 1 H, H-1'), 2.65 (m, 1 H, H-4'), 1.73–1.88 (m, 2 H, H-3') 1.62 (m, 1 H, H-7'), 1.60 (m, 1 H, H-8'), 1.30 (m, 1 H, H-8''), 1.11 (m, 1 H, H-7''). ¹³C NMR (100.5 MHz, CDCl₃): δ 162.5 (C-2), 154.8 (C-7a), 134.7 (C-5',6'), 134.6 (C-5',6'), 128.9 (C-3a), 123.2 (C-5), 122.4 (C-6), 120.3 (C-7), 111.8 (C-4), 102.1 (C-3), 37.1 (C-2'), 33.90 (C-1'), 30.1 (C-3'), 29.8 (C-4'), 26.1 (C-7'), 20.1 (C-8'). MS: *m/z* (rel. int.) 224 (*M*⁺, 7), 145 (20), 144 (100), 115 (38), 89 (13), 79 (18), 77 (17). HRMS: Found 224.1198, calc. for C₁₆H₁₆O: 224.1201.

The relative configuration was determined by NOE (Scheme 4).

2-(1-Acetoxybicyclo[2.2.2]oct-5-en-2-yl)benzofuran (7b). According to the standard conditions the irradiation of **2a** and **4b** was performed for 4 h. Work-up by flash chromatography (cyclohexane–chloroform 3:2 as the eluent) gave 335 mg (59%) of **7b** (*endo:exo* = 2.8 : 1). For separation of the diastereomers HPLC using a LiChrosphere RP-18 column (250 × 20 mm, 5 μm; methanol–water 77:23; flow 20 ml min⁻¹) was performed.

endo-7b: ¹H NMR (400 MHz, CDCl₃): δ 7.51 (m, 1 H, H-7), 7.42 (m, 1 H, H-4), 7.16–7.25 (m, 2 H, H-5,6), 6.56 (dt, *J* = 8.7, 1.1 Hz, 1 H, H-6'), 6.54 (t, *J* = 0.9 Hz, 1 H, H-3), 6.26 (dd, *J* = 8.7, 6.4 Hz, 1 H, H-5'), 3.92 (ddd, *J* = 9.7, 7.5, 2.2 Hz, 1 H, H-2'), 2.68 (m, 1 H, H-4'), 2.06 (m, 1 H, H-7'), 2.04 (s, 3 H, CH₃), 1.98 (m, 1 H, H-3'), 1.95 (m, 1 H, H-3''), 1.87 (m, 1 H, H-7''), 1.38–1.52

(m, 2 H, H-8). ¹³C NMR (100.5 MHz, CDCl₃): δ 170.7 (CO), 158.6 (C-2), 155.0 (C-7a), 135.9 (C-5'), 131.8 (C-6'), 128.7 (C-3a), 123.5 (C-5), 122.5 (C-6), 120.5 (C-7), 110.9 (C-4), 104.3 (C-3), 82.1 (C-1'), 38.7 (C-2'), 32.1 (C-3'), 29.7 (C-4'), 26.2 (C-7', 8'), 25.43 (C-7', 8'), 22.1 (CH₃). MS: *m/z* (rel. int.) 282 (*M*⁺, 9), 145 (6), 144 (48), 138 (42), 115 (5), 96 (100), 77 (5). HRMS: Found 282.1257, calc. for C₁₈H₁₈O₃: 282.1256.

exo-7b: ¹H NMR (400 MHz, CDCl₃): δ 7.47 (m, 1 H, H-7), 7.40 (m, 1 H, H-4), 7.14–7.22 (m, 2 H, H-5,6), 6.36 (dd, *J* = 8.7, 6.5 Hz, 1 H, H-5), 6.34 (t, *J* = 0.8 Hz, 1 H, H-3), 6.18 (dd, *J* = 8.7, 1.1 Hz, 1 H, H-6'), 4.01 (dd, *J* = 10.2, 5.2 Hz, 1 H, H-2'), 2.68 (m, 1 H, H-4'), 2.45 (m, 1 H, H-7') 2.17 (ddd, *J* = 12.8, 10.2, 2.6 Hz, 1 H, H-3'), 1.95 (s, 3 H, CH₃), 1.73–1.80 (m, 2 H, H-7'', 8'), 1.70 (ddt, *J* = 12.8, 5.2, 30 Hz, 1 H, H-3''), 1.52 (m, 1 H, H-8''). ¹³C NMR (100.5 MHz, CDCl₃): δ 170.6 (CO), 160.5 (C-2), 154.63 (C-7a), 133.3 (C-5'), 132.4 (C-6'), 128.7 (C-3a), 123.3 (C-5), 122.4 (C-6), 120.4 (C-7), 110.8 (C-4), 103.3 (C-3), 83.5 (C-1'), 39.7 (C-2'), 34.1 (C-3'), 29.7 (C-4'), 29.2 (C-7', 8'), 25.6 (C-7'', 8''), 22.2 (CH₃). MS: *m/z* (rel. int.) 282 (*M*⁺, 9), 145 (5), 144 (60), 138 (52), 115 (7), 96 (100), 77 (5). HRMS: Found 282.1249, calc. for C₁₈H₁₈O₃: 282.1256.

The relative configuration was determined by NOE (Scheme 4).

2-(1,8,8-Trimethylbicyclo[2.2.2]oct-5-en-2-yl)benzofuran (7c). According to the standard conditions the irradiation of **2a** and **4c** was performed for 4 h. Work-up by flash chromatography (cyclohexane as the eluent) gave 295 mg (56%) of **7c** (*endo:exo* = 26 : 1).

endo-7c: M.p. 39 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.60 (m, 1 H, H-7), 7.56 (m, 1 H, H-4), 7.28–7.34 (m, 2 H, H-5,6), 6.64 (dd, *J* = 8.0, 6.6 Hz, 1 H, H-5'), 6.42 (d, *J* = 1.0 Hz, 1 H, H-3), 6.00 (dd, *J* = 8.0, 1.0 Hz, 1 H, H-6'), 2.97 (dd, *J* = 9.7, 6.6 Hz, 1 H, H-2'), 2.56 (ddd, *J* = 13.0, 9.7, 3.0 Hz, 1 H, H-3'), 2.29 (dddd, *J* = 6.6, 3.0, 2.5, 1.1 Hz, 1 H, H-4'), 1.60 (ddd, *J* = 13.0, 6.6, 2.5 Hz, 1 H, H-3''), 1.40 (d, *J* = 12.5 Hz, 1 H, H-7') 1.26 (s, 3 H, CH₃), 1.25 (d, *J* = 12.5 Hz, 1 H, H-7''), 1.11 (s, 3 H, CH₃), 1.05 (s, 3 H, CH₃). ¹³C NMR (100.5 MHz, CDCl₃): δ 163.4 (C-2), 154.4 (C-7a), 136.0 (C-5', 6'), 134.6 (C-5', 6'), 129.0 (C-3a), 122.9 (C-5,6), 122.3 (C-5,6), 120.2 (C-7), 110.9 (C-4), 102.2 (C-3), 51.7 (C-7'), 42.5 (C-4'), 41.7 (C-2'), 39.8 (C-1'), 34.4 (C-8'), 32.6 (C-3'), 32.0 (CH₃), 30.1 (CH₃)₇, 23.6 (CH₃). MS: *m/z* (rel. int.) 266 (*M*⁺, 12), 210 (5), 145 (12), 144 (94), 123 (9), 122 (100), 115 (8), 108 (7), 107 (83), 91 (11). HRMS: Found 266.1668, calc. for C₁₉H₂₂O: 266.1671.

exo-7c: M.P. 45 °C ¹H NMR (400 MHz, CDCl₃): δ 7.49 (m, 1 H, H-7), 7.41 (m, 1 H, H-4), 7.20 (ddd, *J* = 7.3, 7.3, 1.7 Hz, 1 H, H-5), 7.17 (ddd, *J* = 7.3, 7.3, 1.4 Hz, 1 H, H-6), 6.48 (dd, *J* = 0.9 Hz, 1 H, H-3), 6.34 (dd, *J* = 8.3, 6.5 Hz, 1 H, H-5'), 6.02 (ddd, *J* = 8.3, 0.9, 0.9 Hz, 1 H, H-6'), 2.65 (ddd, *J* = 11.8, 6.0, 2.2 Hz, 1 H, H-2'), 2.20 (ddd, *J* = 13.5, 6.0, 2.0 Hz, 1 H, H-3'), 2.11 (m, 1 H, H-4'), 1.70 (d, *J* = 13.4 Hz, 1 H, H-7'), 1.68 (ddd, *J* = 13.5, 11.8, 3.6 Hz, 1 H, H-3''), 1.31 (s, 3 H, CH₃), 0.96

(s, 3 H, CH₃), 0.90 (s, 3 H, CH₃), 0.88 (dd, $J=13.4$, 2.2 Hz, 1 H, H-7''). ¹³C NMR (100.5 MHz, CDCl₃): δ 160.7 (C-2), 154.6 (C-7a), 138.3 (C-5', 6'), 135.2 (C-5' 6'), 128.8 (C-3a), 123.1 (C-5, 6), 122.4 (C-5,6), 120.2 (C-7), 110.9 (C-4), 104.1 (C-3), 43.1 (C-3'), 42.7 (C-4'), 42.4 (C-2'), 38.8 (C-1',8'), 35.5 (C-1',8'), 32.2 (CH₃), 28.1 (CH₃), 27.4 (C-7'), 23.9 (CH₃). MS: m/z (rel. int.) 266 (M^+ , 10), 210 (5), 145 (11), 144 (92), 123 (10), 122 (100), 115 (11), 107 (89), 91 (14). HRMS: Found 266.1673, calc. for C₁₉H₂₂O: 266.1671.

The relative configuration was determined by NOE (Scheme 4).

2-(2-Methylbicyclo[2.2.2]oct-5-en-2-yl)benzofuran (7d). According to the standard conditions the irradiation of **2b** and **4a** was performed for 1 h. Work-up by flash chromatography (*n*-heptane as the eluent) gave 228 mg (48%) of **7d** (*endo:exo* = 1.1:1).

endo-7d: M.p. 32 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.51 (m, 1 H, H-7), 7.45 (m, 1 H, H-4), 7.18–7.26 (m, 2 H, H-5,6), 6.28 (d, $J=1.0$ Hz, 1 H, H-3), 6.27 (ddd, $J=8.0$, 6.4, 1.3 Hz, 1 H, H-6'), 6.22 (ddd, $J=8.0$, 6.4, 1.5 Hz, 1 H, H-5'), 2.87 (m, 1 H, H-1'), 2.67 (m, 1 H, H-4'), 2.02–2.11 (m, 2 H, H-7', 3'), 1.63 (dddd, $J=12.2$, 10.0, 5.0, 2.3 Hz, 1 H, H-8'), 1.58 (dd, $J=12.8$, 2.3 Hz, 1 H, H-3''), 1.53 (s, 3 H, CH₃), 1.39 (tdd, $J=12.2$, 3.0, 3.0 Hz, 1 H, H-8''), 1.30 (tdd, $J=12.2$, 5.0, 3.0 Hz, 1 H, H-7''). ¹³C NMR (100.5 MHz, CDCl₃): δ 167.8 (C-2), 154.4 (C-7a), 135.4 (C-6'), 132.4 (C-5'), 128.9 (C-3a), 122.9 (C-5), 122.3 (C-6), 120.3 (C-7), 110.7 (C-4), 100.4 (C-3), 40.2 (C-3'), 39.4 (C-2'), 38.7 (C-1'), 30.7 (C-4'), 28.3 (CH₃), 25.0 (C-8'), 21.1 (C-7'). MS: m/z (rel. int.) 238 (M^+ , 12), 159 (27), 158 (100), 143 (23), 115 (22), 79 (17), 77 (17), HRMS: Found 238.1353, calc. for C₁₇H₁₈O: 238.1358.

exo-7d: M.p. 45 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.50 (m, 1 H, H-7), 7.43 (m, 1 H, H-4), 7.16–7.24 (m, 2 H, H-5,6), 6.52 (d, $J=1.0$ Hz, 1 H, H-3), 6.36 (ddd, $J=8.0$, 6.6, 1.4 Hz, 1 H, H-6'), 6.30 (ddd, $J=8.0$, 6.6, 1.4 Hz, 1 H, H-5'), 2.85 (m, 1 H, H-1'), 2.64 (m, 1 H, H-4'), 2.21 (dd, $J=13.0/2.7$ Hz, 1 H, H-3'), 1.48 (dddd, $J=11.6$, 9.4, 4.2, 2.2 Hz, 1 H, H-7'), 1.40 (dddd, $J=12.0$, 9.4, 3.0/2.6 Hz, 1 H, H-8') 1.35 (ddd, $J=13.0$, 3.0, 3.0 Hz, 1 H, H-3''), 1.25 (s, 3 H, CH₃), 1.20 (dddd, $J=11.6$, 3.1, 3.1, 3.1 Hz, 1 H, H-7''), 1.07 (tdd, $J=12.0$, 4.2, 3.1 Hz, 1 H, H-8''). ¹³C NMR (100.5 MHz, CDCl₃): δ 167.1 (C-2), 154.8 (C-7a), 133.5 (C-5', 6'), 133.5 (C-5', 6'), 128.9 (C-3a), 123.1 (C-5), 122.4 (C-6), 120.3 (C-7), 110.9 (C-4), 101.0 (C-3), 40.4 (C-2'), 39.7 (C-1'), 39.1 (C-3'), 30.7 (C-4'), 30.2 (CH₃), 23.7 (C-7'), 22.4 (C-8'). MS: m/z (rel. int.) 238 (M^+ , 18), 165 (12), 159 (28), 158 (100), 143 (27), 115 (31), 79 (22), 77 (22). HRMS: Found 238.1353, calc. for C₁₇H₁₈O: 238.1358.

The relative configuration was determined by NOE (Scheme 4).

2-(5-Acetoxy-2-methylbicyclo[2.2.2]oct-5-en-2-yl)benzofuran (7e). According to the standard conditions the

irradiation of **2b** and **4d** was performed for 4 h. Work-up by flash chromatography (cyclohexane–chloroform 20:1 as the eluent) gave 320 mg (54%) of **7e** (*endo:exo* = 1.2:1). Separation of the diastereomers was performed by HPLC on a LiChrosphere Si-60 column (250 × 20 mm; 5 μm; *n*-heptane–chloroform 20:1; flow 18 ml min⁻¹).

endo-7e: ¹H NMR (400 MHz, CDCl₃): δ 7.48 (m, 1 H, H-7), 7.40 (m, 1 H, H-4), 7.20 (dd, $J=7.3$, 7.3, 1.6 Hz, 1 H, H-5,6), 7.16 (dd, $J=7.3$, 7.3, 1.4 Hz, 1 H, H-5,6), 6.35 (d, $J=1.0$ Hz, 1 H, H-3), 5.62 (dd, $J=7.3$, 2.4 Hz, 1 H, H-6'), 2.92 (ddd, $J=7.3$, 2.8, 2.8 Hz, 1 H, H-1'), 2.60 (m, 1 H, H-4'), 2.39 (ddd, $J=13.3$, 3.2, 3.2 Hz, 1 H, H-3'), 2.12 (s, 3 H, CH₃), 2.06 (dddd, $J=13.2$, 9.5, 3.7, 2.8 Hz, 1 H, H-7'), 1.71 (tdd, $J=12.2$, 3.7, 3.2 Hz, 1 H, H-8'), 1.61 (dddd, $J=12.2$, 9.5, 5.3, 2.4 Hz, 1 H, H-8''), 1.55 (dd, $J=13.3$, 2.4 Hz, 1 H, H-3''), 1.52 (s, 3 H, CH₃), 1.37 (dddd, $J=13.2$, 12.2, 5.3, 2.8 Hz, 1 H, H-7''). ¹³C NMR (100.5 MHz, CDCl₃): δ 169.4 (CO), 166.9 (C-2), 154.5 (C-7a), 152.5 (C-5'), 128.9 (C-3a), 123.0 (C-5), 122.2 (C-6), 120.5 (C-7), 116.6 (C-6'), 110.7 (C-4), 101.2 (C-3), 40.3 (C-2'), 40.2 (C-3'), 39.5 (C-1'), 35.1 (C-4'), 27.7 (CH₃), 24.6 (C-8'), 21.7 (C-7'), 20.9 (CH₃). MS: m/z (rel. int.) 296 (M^+ , 8), 254 (10), 236 (20), 159 (30), 158 (100), 115 (26), 96 (40). HRMS: Found 296.1417, calc. for C₁₉H₂₀O₃: 296.1412.

exo-7e: M.p. 45 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.50 (m, 1 H, H-7), 7.43 (m, 1 H, H-4), 7.23 (dd, $J=7.3$, 7.3, 1.6 Hz, 1 H, H-5,6), 7.19 (dd, $J=7.3$, 7.3, 1.4 Hz, 1 H, H-5,6), 6.52 (d, $J=1.0$ Hz, 1 H, H-3), 5.85 (dd, $J=7.4$, 2.9 Hz, 1 H, H-6'), 2.97 (ddd, $J=7.4$, 2.9, 2.9 Hz, 1 H, H-1'), 2.59 (septet, $J=2.9$ Hz, 1 H, H-4'), 2.23 (dd, $J=12.9$, 2.9 Hz, 1 H, H-3'), 2.18 (s, 3 H, CH₃), 1.72 (ddd, $J=12.9$, 2.9, 2.9 Hz, 1 H, H-3''), 1.56 (m, 1 H, H-8'), 1.50 (ddd, $J=12.2$, 5.1, 2.9 Hz, 1 H, H-8''), 1.42 (m, 1 H, H-7'), 1.31 (s, 3 H, CH₃), 1.19 (dddd, $J=12.8$, 11.3, 5.1, 2.9 Hz, 1 H, H-7''), ¹³C NMR (100.5 MHz, CDCl₃): δ 169.4 (CO), 166.3 (C-2), 154.7 (C-7a), 152.76 (C-5'), 128.8 (C-3a), 123.2 (C-5), 122.4 (C-6), 120.4 (C-7), 114.8 (C-6'), 110.9 (C-4), 101.2 (C-3), 41.3 (C-2'), 40.3 (C-1'), 38.9 (C-3'), 35.0 (C-4'), 29.9 (CH₃), 24.0 (C-8'), 23.0 (C-7'), 21.0 (CH₃). MS: m/z (rel. int.) 296 (M^+ , 7), 254 (12), 236 (14), 159 (32), 158 (100), 115 (20), 96 (38). HRMS: Found 296.1417, calc. for C₁₉H₂₀O₃: 296.1412.

The relative configuration was determined by NOE (Scheme 4).

(7R)-2-(7-Isopropyl-2,5-dimethylbicyclo[2.2.2]oct-5-en-2-yl)benzofuran (7f). According to the standard conditions the irradiation of **2b** and **4e** was performed for 4 h. Work-up by flash chromatography (cyclohexane as the eluent) gave 362 mg (62%) of **7d** (*endo:exo* = 1.6:1). Separation of the diastereomers was performed by HPLC on a LiChrosphere RP-18 column (250 × 8 mm; 5 μm; acetonitrile–water 84:16; flow 4 ml min⁻¹).

endo-7f: ¹H NMR (400 MHz, CDCl₃): δ 7.47 (mn, 1 H, H-7), 7.42 (m, 1 H, H-4), 7.20 (ddd, $J=7.5$, 7.5, 1.8 Hz, 1 H, H-5), 7.15 (ddd, $J=7.5$, 7.5, 1.5 Hz, 1 H, H-6), 6.21

(d, $J=1.0$ Hz, 1 H, H-3), 5.62 (dq, $J=6.5$, 1.6 Hz, 1 H, H-6'), 2.82 (dd, $J=6.5$, 2.0 Hz, 1 H, H-1'), 2.37 (m, 1 H, H-4'), 1.95 (ddd, $J=13.0$, 3.5, 3.0 Hz, 1 H, H-3'), 1.74 (m, 1 H, 11.5, 9.3, 2.5 Hz, H-8'), 1.72 (d, $J=1.6$ Hz, 3 H, CH₃), 1.68 (m, 1 H, H-7'), 1.47 (s, 3 H, CH₃), 1.45 (dd, $J=13.0$, 3.2 Hz, 1 H, H-3''), 1.15 (septetd, $J=6.5$, 2.5 Hz, 1 H, CH isopropyl), 1.03 (dq, $J=11.5$, 3.0 Hz, 1 H, H-8''), 0.95 (d, $J=6.5$ Hz, 3 H, CH₃), 0.85 (d, $J=6.5$ Hz, 3 H, CH₃). ¹³C NMR (100.5 MHz, CDCl₃): δ 168.3 (C-2), 154.43 (C-7a), 140.9 (C-5'), 129.02 (C-3a), 124.8 (C-6'), 122.7 (C-5), 122.2 (C-6), 120.2 (C-7), 110.7 (C-4), 100.3 (C-3), 42.2 (C-1'), 40.8 (C-2'), 40.5 (C-7'), 38.7 (C-3'), 37.0 (C-4'), 33.4 (C isopropyl), 31.9 (C-8'), 27.9 (CH₃), 21.4 (CH₃), 20.7 (CH₃), 19.9 (CH₃). MS: m/z (rel. int.) 294 (M^+ , 17), 251 (5), 159 (22), 158 (100), 136 (23), 115 (21), 93 (69), 77 (42). HRMS: Found 294.1989, calc. for C₂₁H₂₆O: 294.1984.

exo-7f: M.p. 83 °C ¹H NMR (400 MHz, CDCl₃): δ 7.50 (m, 1 H, H-7), 7.43 (m, 1 H, H-4), 7.21 (ddd, $J=7.2$, 7.2, 1.8 Hz, 1 H, H-5), 7.18 (ddd, $J=7.2$, 7.2, 1.5 Hz, 1 H, H-6), 6.46 (d, $J=1.0$ Hz, 1 H, H-3), 5.80 (dt, $J=6.5$, 1.5 Hz, 1 H, H-6'), 2.90 (dd, $J=6.5$, 1.6 Hz, 1 H, H-1'), 2.38 (m, 1 H, H-4'), 2.10 (dd, $J=13.0$, 2.6 Hz, 1 H, H-3'), 1.82 (d, $J=1.8$ Hz, 3 H, CH₃), 1.58 (ddd, $J=11.3$, 8.5, 2.8 Hz, 1 H, H-8'), 1.31 (dt, $J=13.0$, 3.0 Hz, 1 H, H-3''), 1.20 (s, 3 H, CH₃), 1.7 (m, 1 H, H-7'), 1.03 (m, 1 H, CH-isopropyl), 0.86 (m, 1 H, H-8''), 0.80 (d, $J=6.3$ Hz, 3 H, CH₃), 0.64 (d, $J=6.3$ Hz, 3 H, CH₃). ¹³C NMR (100.5 MHz, CDCl₃): δ 167.4 (C-2), 154.7 (C-7a), 141.7 (C-5'), 128.9 (C-3a), 122.9 (C-6', 5), 122.9 (C-6', 5), 122.2 (C-6), 120.2 (C-7), 110.7 (C-4), 101.0 (C-3), 42.7 (C-1'), 42.2 (C-7'), 41.6 (C-2'), 37.6 (C-3'), 37.03 (C-4'), 33.2 (CH isopropyl), 31.1 (C-8'), 30.1 (CH₃), 21.0 (CH₃), 20.4 (CH₃), 19.8 (CH₃). MS: m/z (rel. int.) 294 (M^+ , 30), 159 (38), 158 (100), 136 (38), 115 (40), 93 (97), 77 (42). HRMS: Found 294.1988, calc. for C₂₁H₂₆O: 294.1984.

The relative configuration was determined by NOE (Scheme 4).

2-(2,5-Dimethylcyclohex-3-enyl)benzofuran (7g). According to the standard conditions the irradiation of **2a** and **6a** was performed for 2 h. Work-up by flash chromatography (*n*-heptane as the eluent) gave 84 mg (18.6%) of **7g** (*endo*:*exo*=5:2). Separation of the diastereomers was performed by HPLC on a LiChrosphere RP-18 column (250 × 20 mm; 5 μ m; methanol–water 88:12; flow 20 ml min⁻¹).

2-(c-2,c-5-Dimethylcyclohex-3-ene-r-1-yl)benzofuran. ¹H NMR (400 MHz, CDCl₃): δ 7.51 (m, 1 H, H-7), 7.43 (m, 1 H, H-4), 7.22 (ddd, $J=7.3$, 7.3, 0.8 Hz, 1 H, H-6), 7.19 (ddd, $J=7.3$, 7.3, 1.4 Hz, 1 H, H-5), 6.40 (t, $J=1.1$ Hz, 1 H, H-3), 5.75 (ddd, $J=9.8$, 5.0, 2.5 Hz, 1 H, H-1'), 5.55 (ddd, $J=9.8$, 3.3, 1.5 Hz, 1 H, H-6'), 3.25 (dddd, $J=12.8$, 5.6, 2.5, 1.2 Hz, 1 H, H-3'), 2.74 (m, 1 H, H-2'), 2.39 (m, 1 H, H-5'), 2.02 (ddquintet, $J=12.8$, 5.6, 1.5 Hz, 1 H, H-4'), 1.55 (td, $J=12.8$, 10.9 Hz, 1 H, H-4'), 1.10 (d, $J=7.1$ Hz, 3 H, CH₃), 0.72 (d, $J=7.1$ Hz, 3 H,

CH₃). ¹³C NMR (100.5 MHz, CDCl₃): δ 162.3 (C-2), 154.7 (C-7a), 132.3 (C-1', 6'), 131.8 (C1', 6'), 128.8 (C-3a), 123.2 (C-5), 122.4 (C-6), 120.4 (C-7), 110.8 (C-4), 101.6 (C-3), 37.9 (C-3'), 32.3 (C-2'), 31.6 (C-4'), 29.5 (C-5'), 21.8 (CH₃), 16.3 (CH₃). MS: m/z (rel. int.) 226 (M^+ , 28), 158 (8), 145 (24), 144 (100), 131 (4), 115 (7). HRMS: Found 226.1357, calc. for C₁₆H₁₈O: 226.1358.

2-(t-2,t-5-Dimethylcyclohex-3-en-r-1-yl)benzofuran. ¹H NMR (400 MHz, CDCl₃): δ 7.48 (m, 1 H, H-7), 7.41 (m, 1 H, H-4), 7.20 (ddd, $J=7.4$, 7.4, 1.6 Hz, 1 H, H-6), 7.17 (ddd, $J=7.4$, 7.4, 1.4 Hz, 1 H, H-5), 6.41 (t, $J=0.8$ Hz, 1 H, H-3), 5.63 (dddd, $J=10.0$, 4.0, 2.2, 1.0 Hz, 1 H, H-1', 6'), 5.56 (ddd, $J=10.0$, 2.5, 1.7 Hz, 1 H, H-1', 6'), 2.73 (ddd, $J=8.4$, 8.0, 3.0 Hz, 1 H, H-3'), 2.50 (m, 1 H, H-2', 5'), 2.29 (m, 1 H, H-2', 5'), 2.08 (ddd, $J=13.2$, 8.4, 5.8 Hz, 1 H, H-4'), 1.71 (dddd, $J=13.2$, 3.7, 3.0, 1.1 Hz, 1 H, H-4'), 1.05 (t, $J=7.2$ Hz, 6 H, CH₃). ¹³C NMR (100.5 MHz, CDCl₃): δ 162.9 (C-2), 154.5 (C-7a), 132.0 (C-1', 6'), 131.4 (C-1', 6'), 129.0 (C-3a), 123.1 (C-5), 122.4 (C-6), 120.3 (C-7), 110.9 (C-4), 101.5 (C-3), 38.0 (C-3'), 34.4 (C-2'), 34.1 (C-4'), 29.7 (C-5'), 21.3 (CH₃), 20.7 (CH₃). MS: m/z (rel. int.) 226 (M^+ , 29), 145 (19), 144 (100), 131 (5), 115 (9). HRMS: Found 226.1357, calc. for C₁₆H₁₈O: 226.1358.

The relative configuration of the diastereomers was determined by NOE experiments (see Scheme 9).

2-(3,4-Dimethylcyclohex-3-enyl)benzofuran (7h). According to the standard conditions the irradiation of **2a** and **6b** was performed for 2 h. Work-up by flash chromatography (*n*-heptane as the eluent) gave 74 mg (16.4%) of **7h**.

7h: ¹H NMR (400 MHz, CDCl₃): δ 7.39 (m, 1 H, H-7), 7.32 (m, 1 H, H-4), 7.12 (ddd, $J=7.5$, 7.5, 0.9 Hz, 1 H, H-6), 7.08 (ddd, $J=7.5$, 7.5, 1.6 Hz, 1 H, H-5), 6.28 (t, $J=0.8$ Hz, 1 H, H-3), 2.91 (m, 1 H, H-3'), 1.10–2.30 (m, 6 H, H-2', 4', 5'), 1.16–1.59 (m, 6 H, CH₃). ¹³C NMR (100.5 MHz, CDCl₃): δ 163.5 (C-2), 154.5 (C-7a), 128.9 (C-3a), 125.6 (C1', 6'), 124.2 (C-1', 6'), 123.1 (C-5), 122.4 (C-6), 120.3 (C-7), 110.8 (C-4), 100.2 (C-3), 36.2 (C-2'), 34.5 (C-3'), 31.4 (C-4'), 27.9 (C-5'), 19.1 (CH₃), 19.0 (CH₃). MS: m/z (rel. int.) 226 (M^+ , 24, 145 (10), 144 (100), 131 (4), 115 (6) HRMS: Found 226.1350, calc. for C₁₆H₁₈O: 226.1358.

2-(1,c-2,c-5-Trimethylcyclohex-3-en-r-1-yl)benzofuran (7i). According to the standard conditions the irradiation of **2b** and **6a** was performed for 2 h. Work-up by flash chromatography (*n*-heptane as the eluent) gave 40 mg (8.3%) of **7i**.

7i: ¹H NMR (400 MHz, CDCl₃): δ 7.41 (m, 1 H, H-7), 7.35 (m, 1 H, H-4), 7.12 (ddd, $J=7.4$, 7.4, 1.7 Hz, 1 H, H-6), 7.09 (ddd, $J=7.4$, 7.4, 1.5 Hz, 1 H, H-5), 6.40 (d, $J=0.7$ Hz, 1 H, H-3), 5.57 (ddd, $J=9.8$, 5.0, 2.5 Hz, 1 H, H-1', 6'), 5.40 (ddt, $J=9.8$, 1.5, 1.5 Hz, 1 H, H-1', 6'), 2.20–2.34 (m, 2 H, H-2', 5'), 1.68 (ddt, $J=12.8$, 5.7, 1.5 Hz, 1 H, H-4'), 1.55 (dd, $J=12.8$, 11.0 Hz, 1 H, H-4'), 1.31 (s, 3 H, CH₃), 1.01 (d, $J=6.9$ Hz, 3 H, CH₃), 0.55 (d, $J=7.1$ Hz, 3 H, CH₃). ¹³C NMR (100.5 MHz,

CDCl₃): δ 166.3 (C-2), 154.5 (C-7a), 130.8 (C-1', 6'), 130.6 (C-1',6'), 128.7 (C-3a), 123.1 (C-5), 122.3 (C-6), 120.4 (C-7), 110.9 (C-4), 100.7 (C-3), 38.7 (C-2'), 38.5 (C-3'), 34.9 (C-4'), 27.6 (C-5'), 24.3 (CH₃), 21.5 (CH₃), 18.6 (CH₃). MS: m/z (rel. int.) 240 (M^+ , 16), 159 (27), 158 (100), 143 (9), 131 (5), 115 (7). HRMS: Found 240.1511, calc. for C₁₇H₂₀O: 240.1514.

The relative configuration was determined by NOE (see Scheme 9).

2-(1,3,4-Trimethylcyclohex-3-enyl)benzofuran (**7k**). According to the standard conditions the irradiation of **2b** and **6b** was performed for 2 h. Work-up by flash chromatography (*n*-heptane as the eluent) gave 37 mg (7.7%) of **7k**.

7k: ¹H NMR (400 MHz, CDCl₃): δ 7.47 (m, 1 H, H-7), 7.41 (m, 1 H, H-4), 7.20 (ddd, $J=7.3, 7.3, 1.6$ Hz, 1 H, H-6), 7.16 (ddd, $J=7.3, 7.3, 1.3$ Hz, 1 H, H-5), 6.28 (d, $J=1.0$ Hz, 1 H, H-3), 2.44 (m, 1 H), 2.02–2.08 (m, 2 H), 1.94–2.01 (m, 1 H), 1.82–1.90 (m, 1 H), 1.71 (m, 1 H), 1.67 (m, 3 H, CH₃), 1.59 (m, 3 H, CH₃), 1.32 (s, 3 H, CH₃). ¹³C NMR (100.5 MHz, CDCl₃): δ 166.4 (C-2), 154.6 (C-7a), 129.0 (C-3a), 124.6 (C-1', 6'), 123.2 (C-1',6'), 123.01 (C-5), 122.3 (C-6), 120.4 (C-7), 110.8 (C-4), 99.9 (C-3), 42.6 (C-2'), 35.6 (C-3'), 33.2 (C-5'), 29.2 (C-4'), 25.6 (CH₃), 19.3 (CH₃), 18.8 (CH₃). MS: m/z (rel. int.) 240 (M^+ , 23), 158 (100), 143 (6), 131 (4), 115 (6). HRMS: Found 240.1516, calc. for C₁₇H₂₀O: 240.1514.

2-(Bicyclo[2.2.2]oct-5-en-2-yl)-5-bromofuran (**7l**). According to the standard conditions the irradiation of **3** and **4a** was performed for 1 h. Work-up by flash chromatography (*n*-hexane as the eluent) gave 112 mg (22%) of **7l** (*endo:exo*=2.4:1).

endo-**7l**: ¹H NMR (400 MHz, CDCl₃): δ 6.31 (ddd, $J=8.0, 6.6, 1.4$ Hz, 1 H, H-5'), 6.12 (dd, $J=3.2, 0.4$ Hz, 1 H, H-4), 6.07 (ddd, $J=8.0, 6.4, 1.3$ Hz, 1 H, H-6'), 5.80 (dd, $J=3.2, 1.2$ Hz, 1 H, H-3), 2.98 (m, 1 H, H-2'), 2.82 (dddd, $J=7.9, 4.7, 2.4, 1.3$ Hz, 1 H, H-1'), 2.59 (m, 1 H, H-4'), 1.94 (ddd, $J=12.6, 10.0, 2.7$ Hz, 1 H, H-3'), 1.63 (m, 1 H, H-7') 1.52 (m, 1 H, H-8'), 1.35 (ddd, $J=12.6, 5.8, 2.7$ Hz, 1 H, H-3''), 1.22–1.33 (m, 2 H, H-7'',8''). ¹³C NMR (100.5 MHz, CDCl₃): δ 163.1 (C-2), 134.8 (C-5'), 131.9 (C-6'), 118.8 (C-5), 111.5 (C-4), 106.63 (C-3), 37.0 (C-2'), 34.30 (C-1'), 32.5 (C-3'), 29.7 (C-4'), 25.9 (C-7'), 24.2 (C-8'). MS: m/z (rel. int.) 254 (M^+ , 12), 152 (12), 174 (100), 172 (100), 80 (38), 79 (25), 65 (13). HRMS: Found 252.0150, calc. for C₁₂H₁₃BrO: 252.0156.

exo-**7l**: ¹H NMR (400 MHz, CDCl₃): δ 6.36 (ddd, $J=8.0, 6.5, 1.4$ Hz, 1 H, H-3'), 6.29 (ddd, $J=8.0, 6.5, 1.3$ Hz, 1 H, H-5'), 6.20 (d, $J=3.2$ Hz, 1 H, H-4), 6.07 (dd, $J=3.2, 1.2$ Hz, 1 H, H-3), 2.75 (m, 1 H, H-2'), 2.72 (m, 1 H, H-1'), 2.57 (m, 1 H, H-4'), 1.59 (ddt, $J=12.8, 11.3, 3.4$ Hz, 1 H, H-3'), 1.55 (ddd, $J=12.8, 6.9, 2.3$ Hz, 1 H, H-3''), 1.52 (m, 1 H, H-7'), 1.49 (ddd, $J=9.9, 3.4, 2.4$ Hz, 1 H, H-8'), 1.23 (m, 1 H, H-8'), 1.05 (m, 1 H, H-7'). ¹³C NMR (100.5 MHz, CDCl₃): δ 161.4 (C-2), 134.5 (C-5',6'), 134.4 (C-5',6'), 119.3 (C-5), 111.5 (C-4), 107.8 (C-3), 36.8 (C-2'), 34.0 (C-1'), 29.8 (C-3'), 29.7 (C-4'), 26.1 (C-7'), 19.8 (C-8'). MS: m/z (rel. int.) 254 (M^+ , 11),

152 (11), 174 (100), 172 (100), 80 (32), 79 (17), 65 (9). HRMS: Found 252.0139, calc. for C₁₂H₁₃BrO: 252.0156.

The relative configuration of the diastereomers was determined by NOE experiments.

trans-2-(2-Phenylcyclobutyl)benzofuran (**8a**). According to the standard conditions the irradiation of **2a** and **5a** was performed for 4 h. Work-up by flash chromatography (petroleum ether–dichloromethane 25:1 as the eluent) gave 51 mg (13%) of **8a**.

trans-**8a**: ¹H NMR (400 MHz, CDCl₃): δ 7.61 (m, 1 H, H-7), 7.58 (m, 1 H, H-4), 7.58–7.45 (m, 7 H, H-5,6,CH-phenyl), 6.56 (t, $J=0.7$ Hz, 1 H, H-3), 3.97 (m, 1 H, CH-cyclobutyl), 3.75 (m, 1 H, CH-cyclobutyl), 2.27–2.57 (m, 4 H, CH₂-cyclobutyl). ¹³C NMR (100.5 MHz, CDCl₃): δ 160.6 (C-2), 154.8 (C-7a), 144.0 (C-1-phenyl), 128.9 (C-3a), 128.4 (C-3,5,-phenyl), 126.4 (C-2,6-phenyl), 126.2 (C-4-phenyl), 123.4 (C-5), 122.5 (C-6), 120.5 (C-7), 111.0 (C-4), 101.6 (C-3), 45.8 (CH-cyclobutyl), 41.6 (C-cyclobutyl), 25.4 (CH₂-cyclobutyl), 24.4 (CH₂-cyclobutyl). MS: m/z (rel. int.) 248 (M^+ , 7%), 219 (9), 201 (7), 189 (9), 164 (7), 145 (31), 144 (100), 115 (47), 89 (22), 77 (18). HRMS: Found 248.1204, calc. for C₁₈H₁₆O: 248.1201.

The *trans* configuration was determined by NOE.

trans-2-[2-(4-Methylphenyl)cyclobutyl]benzofuran (**8b**) and 1-(4-Methylphenyl)-1,2,3,4-tetrahydribenzofuran (**9b**). According to the standard conditions the irradiation of **2a** and **5b** was performed for 4 h. Work-up by flash chromatography (petroleum ether–dichloromethane 20:1 as the eluent), followed by separation of the two products by HPLC on a LiChrosphere Si-60 column (250 × 32 mm; 5 μ m; *n*-hexane–dichloromethane 25:1; flow 19 ml min⁻¹), gave 64 mg (12%) of **8b** and 37 mg (7%) of **9b**.

trans-**8b**: M.p. 28 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.58 (m, 1 H, H-7), 7.55 (m, 1 H, H-4), 7.19–7.34 (m, 6 H, H-5,6 and 2,3,5,6-phenyl), 6.5 (t, $J=0.8$ Hz, 1 H, H-3), 3.91 (m, 1 H, CH-cyclobutyl), 3.70 (m, 1 H, CH-cyclobutyl), 2.42 (s, 3 H, CH₃), 2.24–2.50 (m, 4 H, CH₂-cyclobutyl). ¹³C NMR (100.5 MHz, CDCl₃): δ 160.7 (C-2), 154.8 (C-7a), 141.0 (C-1-phenyl), 135.8 (C-4-phenyl), 129.1 (C-3,5-phenyl), 129.0 (C-3a), 126.3 (C-2,6-phenyl), 123.4 (C-5), 122.5 (C-6), 120.5 (C-7), 111.0 (C-4), 101.5 (C-3), 45.7 (CH-cyclobutyl), 41.8 (CH-cyclobutyl), 25.6 (CH₂-cyclobutyl), 24.3 (CH₂-cyclobutyl), 21.1 (CH₃). MS: m/z (rel. int.) 262 (M^+ , 7), 219 (9), 201 (7), 189 (9), 164 (7), 145 (31), 144 (100), 115 (47), 89 (22), 77 (18). HRMS: Found 262.1354, calc. for C₁₉H₁₈O: 262.1358. The *trans* configuration was determined by NOE.

9b: ¹H NMR (400 MHz, CDCl₃): 7.40 (m, 1 H, H-9), 7.12 (m, 1 H, H-8), 7.08–7.12 (m, 4 H, H-2,3,5,6-phenyl), 6.98 (m, 1 H, H-7), 6.79 (m, 1 H, H-6), 4.08 (ddt, $J=7.0, 5.0, 3.0$ Hz, 1 H, H-1), 2.85 (dddd, $J=16.0, 7.5, 6.0, 3.0$ Hz, 1 H, H-4), 2.81 (dddd, $J=16.0, 5.5, 5.5, 3.0$ Hz, 1 H, H-4), 2.32 (s, 3 H, CH₃), 2.20 (m, 1 H, H-2), 2.03 (m, 1 H, H-3), 1.87 (m, 1 H, H-3), 1.80 (m, 1 H, H-2).

^{13}C NMR (100.5 MHz, CDCl_3): δ 155.2 (C-4a,5a), 154.6 (C-4a,5a), 141.4 (C-1-phenyl), 135.9 (C-4-phenyl), 129.1 (C-3,5-phenyl), 128.2 (C-9a), 128.0 (C-2,6-phenyl), 122.9 (C-7,8), 122.1 (C-7,8), 119.8 (C-6), 115.0 (C-9b), 110.7 (C-9), 39.1 (C-1), 34.0 (C-2), 23.6 (C-4), 21.2 (C-3), 21.1 (CH_3). MS: m/z (Rel. int.) 262 (M^+ , 62), 258 (48), 234 (38), 219 (100), 202 (25), 189 (39), 144 (58), 115 (45). HRMS: Found 262.1354, calc. for $\text{C}_{19}\text{H}_{18}\text{O}$: 262.1358.

trans-2-[2-(4-Methoxyphenyl)cyclobutyl]benzofuran (**8c**) and 1-(4-methoxyphenyl)-1,2,3,4-tetrahydrodibenzofuran (**9c**). According to the standard conditions the irradiation of **2a** and **5c** was performed for 4 h. Work-up by flash chromatography (cyclohexane–dichloromethane 6:1 as the eluent), followed by separation of the two products by HPLC on a LiChrosphere RP-18 column (250 \times 8 mm; 5 μm ; methanol–water = 87:13; flow 3 ml min^{-1}), gave 8 mg (1.4%) of **8c** and 44 mg (7.8%) of **9c**.

trans-**8c**: ^1H NMR (400 MHz, CDCl_3): δ 7.49 (m, 1 H, H-7), 7.47 (m, 1 H, H-4), 7.45 (m, 1 H, H-5), 7.43 (m, 1 H, H-6), 7.16–7.24 (m, 2 H, H-2,6-phenyl), 6.81 (m, 2 H, H-3,5-phenyl), 6.44 (t, $J=0.8$ Hz, 1 H, H-3), 3.79 (s, 3 H, CH_3), 3.77 (m, 1 H, CH-cyclobutyl), 3.58 (m, 1 H, CH-cyclobutyl), 2.13–2.40 (m, 4 H, CH_2 -cyclobutyl). ^{13}C NMR (100.5 MHz, CDCl_3): δ 160.7 (C-2), 158.1 (C-4-phenyl), 154.8 (C-7a), 136.2 (C-1-phenyl), 128.9 (C-3a), 127.5 (C-2,6-phenyl), 123.4 (C-5), 122.5 (C-6), 120.5 (C-7), 113.8 (C-3,5-phenyl), 111.0 (C-4), 101.5 (C-3), 55.9 (CH_3), 45.4 (CH-cyclobutyl), 42.0 (CH-cyclobutyl), 25.7 (CH_2 -cyclobutyl), 24.2 (CH_2 -cyclobutyl). MS: m/z (rel. int.) 278 (M^+ , 2), 250 (2), 145 (12), 144 (95), 134 (100), 119 (15), 115 (12), 91 (8). HRMS: Found 278.1317, calc. for $\text{C}_{19}\text{H}_{18}\text{O}_2$: 278.1307. The *trans* configuration was determined by NOE.

9c: ^1H NMR (400 MHz, CDCl_3): 7.43 (ddd, $J=8.6$, 0.9, 0.9 Hz, 1 H, H-9), 7.17 (ddd, $J=8.6$, 7.3, 1.3 Hz, 1 H, H-8), 7.15 (m, 2 H, H-2,6-phenyl), 7.01 (ddd, $J=7.3$, 7.3, 0.9 Hz, 1 H, H-7), 6.85 (m, 2 H, H-3,5-phenyl), 6.81 (ddd, $J=7.3$, 1.3, 0.9 Hz, 1 H, H-6), 4.09 (ddt, $J=7.5$, 5.5, 2.0 Hz, 1 H, H-1), 3.70 (s, 3 H, CH_3), 2.87 (dddd, $J=16.9$, 8.0, 5.5, 2.0 Hz, 1 H, H-4), 2.82 (dddd, $J=16.9$, 5.5, 5.5, 2.0 Hz, 1 H, H-4'), 2.21 (dddd, $J=12.0$, 7.5, 5.5, 2.5 Hz, 1 H, H-2), 2.04 (dddd, $J=10.4$, 8.0, 5.5, 5.5, 2.5 Hz, 1 H, H-3) 1.89 (dddd, $J=10.5$, 10.4, 7.5, 5.5, 2.5 Hz, 1 H, H-3), 1.79 (dddd, $J=12.0$, 10.5, 7.5, 2.5 Hz, 1 H, H-2). ^{13}C NMR (100.5 MHz, CDCl_3): δ 158.1 (C-4-phenyl), 155.1 (C-4a,5a), 154.5 (C-4a,5a), 136.5 (C-1-phenyl), 129.0 (C-2,6-phenyl), 128.2 (C-9a), 122.9 (C-7,8), 122.1 (C-7,8), 119.8 (C-6), 115.1 (C-9b), 113.7 (C-3,5-phenyl), 110.7 (C-9), 55.23 (CH_3), 38.67 (C-1), 34.03 (C-2), 23.52 (C-4), 21.16 (C-3). MS: m/z (rel. int.) 278 (M^+ , 100), 250 (78), 234 (10), 219 (52), 207 (11), 171 (11), 145 (7), 115 (4). HRMS: Found 278.1300, calc. for $\text{C}_{19}\text{H}_{18}\text{O}_2$: 278.1307.

4-Methyl-1-phenyl-1,2,3,4-tetrahydrodibenzofuran (**9d**). According to the standard conditions the irradiation of **2b** and **5a** was performed for 4 h. Work-up by flash chromatography (cyclohexane–dichloromethane 8:1 as the eluent) gave 52 mg (10%) of **9d** (*cis:trans* = 1.1:1). Separation of the diastereomers was performed by HPLC on a LiChrosphere RP-18 column (250 \times 8 mm; 5 μm ; methanol–water 84:16; flow 3.2 ml min^{-1}).

cis-**9d**: M.p. 98 $^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 7.40 (ddd, $J=8.0$, 0.9, 0.9 Hz, 1 H, H-9), 7.12–7.29 (m, 6 H, H-8 and CH-phenyl), 6.99 (ddd, $J=7.8$, 7.8, 0.9 Hz, 1 H, H-7), 6.84 (ddd, $J=7.8$, 1.5, 0.9 Hz, 1 H, H-6), 4.11 (ddd, $J=5.8$, 5.8, 1.6 Hz, 1 H, H-1), 3.06 (dq, $J=12.5$, 7.0, 1.6 Hz, 1 H, H-4), 2.15 (m, 1 H, H-2), 1.96 (m, 1 H, H-3), 1.90 (m, 1 H, H-2'), 1.64 (m, H-3'), 1.41 (d, $J=7.0$ Hz, 3 H, CH_3). ^{13}C NMR (100.5 MHz, CDCl_3): δ 159.3 (C-4a), 154.6 (C-5a), 144.4 (C-1-phenyl), 128.4 (C-2,3,5,6-phenyl), 128.2 (C-9a), 128.2 (C-2,3,5,6-phenyl), 126.4 (C-4-phenyl), 123.1 (C-8), 122.1 (C-7), 119.8 (C-6), 113.9 (C-9b), 110.9 (C-9), 39.2 (C-1), 31.4 (C-2), 29.0 (C-4), 28.9 (C-3), 19.2 (CH_3). MS: m/z (rel. int.) 296 (M^+ , 8), 262 (100), 247 (47), 234 (18), 220 (55), 219 (56), 169 (33), 158 (48), 115 (12), 91 (13). HRMS: Found 262.1351, calc. for $\text{C}_{19}\text{H}_{18}\text{O}$: 262.1358.

trans-**9d**: M.p. 106 $^\circ\text{C}$ ^1H NMR (400 MHz, CDCl_3): δ 7.41 (ddd, $J=8.1$, 0.9, 0.9 Hz, 1 H, H-9), 7.19–7.30 (m, 5 H, CH-phenyl), 7.14 (ddd, $J=8.1$, 7.7, 1.4 Hz, 1 H, H-8), 6.95 (ddd, $J=7.7$, 7.7, 0.9 Hz, 1 H, H-7), 6.68 (ddd, $J=7.7$, 1.4, 0.9 Hz, 1 H, H-6), 4.08 (ddd, $J=8.9$, 5.6, 2.6 Hz, 1 H, H-1), 3.11 (dq, $J=8.7$, 6.9, 6.2, 2.6 Hz, 1 H, H-4), 2.27 (dddd, $J=13.5$, 6.6, 5.6, 2.5 Hz, 1 H, H-2), 2.15 (dddd, $J=13.2$, 6.6, 6.2, 2.5 Hz, 1 H, H-3), 1.77 (dddd, $J=13.5$, 11.4, 8.9, 2.5 Hz, 1 H, H-2), 1.57 (dddd, $J=13.2$, 11.4, 8.7, 2.5 Hz, 1 H, H-3), 1.38 (d, $J=6.9$ Hz, 3 H, CH_3). ^{13}C NMR (100.5 MHz, CDCl_3): δ 158.9 (C-4a), 154.6 (C-5a), 144.5 (C-1-phenyl), 128.4 (C-2,3,5,6-phenyl), 128.1 (C-9a), 128.1 (C11,15/12,14), 126.5 (C-4-phenyl), 122.9 (C-8), 122.0 (C-7), 120.1 (C-6), 114.4 (C-9b), 110.8 (C-9), 405. (C-1), 33.5 (C-2), 31.3 (C-3), 29.6 (C-4), 18.7 (CH_3). MS: m/z (rel. int.) 262 (M^+ , 100), 247 (40), 234 (13), 220 (34), 219 (35), 169 (31), 158 (61), 115 (14), 91 (16). HRMS: Found 262.1348, calc. for $\text{C}_{19}\text{H}_{18}\text{O}$: 262.1358.

The relative configuration of the diastereomers was determined by the ^1H NMR coupling constants taking the X-ray crystallographic structure of *cis*-**9f** as the basis (see Table 1).

1-(4-Methylphenyl)-4-methyl-1,2,3,4-tetrahydrodibenzofuran (**9e**). According to the standard conditions the irradiation of **2b** and **5b** was performed for 6 h. Work-up by flash chromatography (*n*-heptane–dichloromethane 20:1 as the eluent) gave 118 mg (21%) of **9e** (*cis:trans* = 3.0:1). Separation of the diastereomers was performed by HPLC on a LiChrosphere RP-18 column (250 \times 8 mm; 5 μm ; acetonitrile–water 79:21; flow 6 ml min^{-1}).

cis-**9e** ^1H NMR (400 MHz, CDCl_3): δ 7.44 (ddd, $J=$

8.4, 0.8, 0.8 Hz, 1 H, H-9), 7.17 (ddd, $J=8.4, 7.2, 1.4$ Hz, 1 H, H-8), 7.09–7.11 (m, 4 H, H-2,3,5,6-phenyl), 7.02 (ddd, $J=8.2, 7.2, 0.8$ Hz, 1 H, H-7), 6.99 (ddd, $J=8.2, 1.4, 0.8$ Hz, 1 H, H-6) 4.11 (ddd, $J=5.7, 5.7, 1.6$ Hz, 1 H, H-1), 3.06 (dq, $J=12.5, 6.9, 1.6$ Hz, 1 H, H-4), 2.15 (m, H-2), 2.33 (s, 3 H, CH₃), 1.96 (dddd, $J=12.5, 8.5, 5.8, 2.7$ Hz, 1 H, H-3), 1.90 (m, H-2), 1.64 (m, H-3), 1.43 (d, $J=6.9$ Hz, 3 H, CH₃). ¹³C NMR (100.5 MHz, CDCl₃): δ 158.8 (C-4a), 154.6 (C-5a), 141.4 (C-1-phenyl), 135.9 (C-4-phenyl), 129.1 (C-3,5-phenyl), 128.2 (C-9a), 128.0 (C-2,6-phenyl), 122.9 (C-7,8), 122.0 (C-7,8), 120.1 (C-6), 114.6 (C-9b), 110.8 (C-9), 40.0 (C-1), 33.5 (C-2), 31.3 (C-3), 29.6 (C-4), 21.2 (CH₃), 18.7 (CH₃). MS: m/z (rel. int.) 276 (M^+ , 100), 261 (42), 248 (36), 234 (51), 233 (68), 219 (34), 218 (32), 185 (18), 169 (50), 158 (53), 115 (18), 105 (17), 91 (20). HRMS: Found 276.1515, calc. for C₂₀H₂₀O: 276.1514.

trans-**9e**: ¹H NMR (400 MHz, CDCl₃): δ 7.41 (ddd, $J=8.3, 0.9, 0.9$ Hz, 1 H, H-9), 7.14 (ddd, $J=8.3, 7.2, 1.2$ Hz, 1 H, H-8), 7.09–7.10 (m, 4 H, H-2,3,5,6-phenyl), 6.96 (ddd, $J=8.2, 7.2, 0.9$ Hz, 1 H, H-7), 6.72 (ddd, $J=8.2, 1.2, 0.9$ Hz, 1 H, H-6), 4.05 (ddd, $J=8.8, 5.5, 2.6$ Hz, 1 H, H-1), 3.11 (dq, $J=8.8, 6.9, 5.5, 2.6$ Hz, 1 H, H-4), 2.33 (s, 3 H, CH₃), 2.25 (dddd, $J=13.3, 6.9, 5.5, 2.6$ Hz, 1 H, H-2), 2.14 (dddd, $J=13.0, 6.9, 5.5, 2.6$ Hz, 1 H, H-3), 1.75 (dddd, $J=13.3, 11.3, 8.8, 2.6$ Hz, 1 H, H-2), 1.55 (dddd, $J=13.0, 11.3, 8.8, 2.6$ Hz, 1 H, H-3), 1.43 (d, 3 H, $J=6.9$ Hz, CH₃). ¹³C NMR (100.5 MHz, CDCl₃): δ 159.3 (C-4a), 154.6 (C-5a), 141.4 (C-1-phenyl), 135.8 (C-4-phenyl), 129.1 (C-3,5-phenyl), 128.3 (C-9a), 128.0 (C-2,6-phenyl), 123.0 (C-7,8), 122.1 (C-7,8), 119.8 (C-6), 114.1 (C-9b), 110.8 (C-9), 38.8 (C-1), 31.5 (C-2), 31.3 (C-4), 29.1 (C-3), 21.1 (CH₃), 19.2 (CH₃). MS: m/z (rel. int.) 276 (M^+ , 100), 261 (31), 248 (23), 234 (35), 233 (43), 219 (15), 218 (14), 185 (12), 169 (34), 158 (43), 115 (10), 105 (17), 91 (8). HRMS: Found 276.1515, calc. for C₂₀H₂₀O: 276.1514.

The relative configuration of the diastereomers was determined by the ¹H NMR coupling constants taking the X-ray crystallographic structure of *cis*-**9f** as the basis (see Table 1).

1-(4-Methoxyphenyl)-4-methyl-1,2,3,4-tetrahydrodibenzofuran (9f). According to the standard conditions the irradiation of **2b** and **5c** was performed for 4 h. Work-up by flash chromatography (petroleum ether–dichloromethane 5:1 as the eluent) gave 60 mg (10%) of *cis*-**9f**.

cis-**9f**: M.p. 85 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.45 (ddd, $J=8.6, 0.9, 0.9$ Hz, 1 H, H-9), 7.17 (ddd, $J=8.6, 7.8, 1.3$ Hz, 1 H, H-8), 7.12 (m, 2 H, H-2,6-phenyl), 7.03 (ddd, $J=7.8, 7.8, 0.9$ Hz, 1 H, H-7), 6.85 (m, 2 H, H-3,5-phenyl), 6.90 (ddd, $J=7.8, 1.3, 0.9$ Hz, 1 H, H-6), 4.11 (ddd, $J=5.8, 5.8, 1.5$ Hz, 1 H, H-1), 3.80 (s, 3 H, CH₃), 3.05 (dq, $J=8.5, 6.7, 1.5$ Hz, 1 H, H-4), 2.15 (dddd, $J=13.2, 9.4, 5.7, 2.6$ Hz, 1 H, H-2), 1.97 (dddd, $J=13.2, 8.5, 5.8, 2.6$ Hz, 1 H, H-3), 1.90 (dddd, $J=13.2, 9.4, 5.8, 5.8, 2.6$ Hz, 1 H, H-2), 1.66 (ddd, $J=13.2, 9.4, 2.6$ Hz, 1 H, H-3), 1.43 (d, 3 H, $J=6.7$ Hz, CH₃). ¹³C

NMR (100.5 MHz, CDCl₃): 159.2 (C-4a), 155.2 (C-4-phenyl), 154.6 (C-5a), 136.5 (C-1-phenyl), 129.1 (C-2,6-phenyl), 128.3 (C-9a), 123.0 (C-7), 122.1 (C-8), 119.9 (C-6), 114.2 (C-9b), 113.8 (C-3,5-phenyl), 110.8 (C-9), 55.3 (CH₃), 38.4 (C-1), 31.6 (C-2), 29.1 (C-4), 28.9 (C-3), 19.7 (CH₃). MS: m/z (rel. int.) 292 (M^+ , 100), 277 (15), 264 (30), 250 (39), 234 (17), 219 (9), 169 (28), 158 (8), 115 (5). HRMS: Found 292.1459, calc. for C₂₀H₂₀O₂: 292.1463.

The relative configuration was proved by X-ray crystallography.

trans-2-[3,3-Dimethyl-2-(2-methylprop-1-enyl)cyclobutyl]benzofuran (**8d**) and 2,2-dimethyl-1-(2-methylprop-1-enyl)-1,2,3,4-tetrahydrodibenzofuran (**9g**). According to the standard conditions the irradiation of **2a** and **6c** was performed for 2 h. Work-up by flash chromatography (*n*-heptane as the eluent), followed by separation of the two products by HPLC on a LiChrosphere RP-18 column (250 × 20 mm; 5 μm; methanol–water = 88:12; flow 20 ml min⁻¹), gave 34 mg (6.7%) of **8d** and 34 mg (6.7%) of **9g**.

trans-**8d**: M.p. 55 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.48 (m, 1 H, H-7), 7.44 (m, 1 H, H-4), 7.20 (ddd, $J=7.2, 7.2, 1.6$ Hz, 1 H, H-6), 7.17 (ddd, $J=7.2, 7.2, 1.4$ Hz, 1 H, H-5), 6.38 (dd, $J=0.9, 0.9$ Hz, 1 H, H-3), 5.24 (d, $J=9.5, 1.4, 1.4$ Hz, 1 H, CH-isobutenyl), 3.29 (qd, $J=9.5, 0.9$ Hz, 1 H, CH-cyclobutyl), 3.07 (t, $J=9.5$ Hz, 1 H, CH-cyclobutyl), 2.23 (d, $J=9.5$ Hz, 2 H, CH₂-cyclobutyl), 1.72 (d, $J=1.4$ Hz, 3 H, CH₃), 1.57 (d, $J=1.4$ Hz, 3 H, CH₃), 1.17 (s, 3 H, CH₃), 1.12 (s, 3 H, CH₃). ¹³C NMR (100.5 MHz, CDCl₃): δ 161.7 (C-2), 154.8 (C-7a), 134.3 (C-isobutenyl), 129.1 (C-3a), 124.2 (CH-isobutenyl), 123.1 (C-5), 122.4 (C-6), 120.3 (C-7), 110.9 (C-4), 101.0 (C-3), 49.2 (CH-cyclobutyl), 38.3 (CH₂-cyclobutyl), 37.3 (C-cyclobutyl), 35.9 (CH-cyclobutyl), 30.6 (CH₃), 26.0 (CH₃), 23.1 (CH₃), 18.5 (CH₃). MS: m/z (rel. int.) 254 (M^+ , 6), 198 (3), 183 (6), 144 (22), 115 (7), 110 (100), 95 (38). HRMS: Found 254.1674, calc. for C₁₈H₂₂O: 254.1671.

The *trans* configuration was determined by X-ray crystallography.

9g: ¹H NMR (400 MHz, CDCl₃): 7.41 (m, 1 H, H-6), 7.35 (m, 1 H, H-9), 7.19 (ddd, $J=7.3, 7.3, 1.6$ Hz, 1 H, H-7), 7.15 (ddd, $J=7.3, 7.3, 1.2$ Hz, 1 H, H-8), 5.16 (d, $J=10.8, 1.5, 1.5$ Hz, 1 H, H-1-isobutenyl), 3.43 (dt, $J=10.8, 1.9$ Hz, 1 H, H-1), 2.80 (dddd, $J=17.2, 7.7, 6.0, 1.9$ Hz, 1 H, H-4), 2.74 (dtd, $J=17.2, 6.0, 1.9$ Hz, 1 H, H-4), 1.90 (d, $J=1.5$ Hz, 3 H, CH₃), 1.85 (d, $J=1.5$ Hz, 3 H, CH₃), 1.82 (dt, $J=13.3, 6.0$ Hz, 1 H, H-3), 1.68 (ddd, $J=13.3, 7.7, 6.0$ Hz, 1 H, H-3), 1.05 (s, 3 H, CH₃), 0.93 (s, 3 H, CH₃). ¹³C NMR (100.5 MHz, CDCl₃): δ 154.9 (C-4a,5a), 152.6 (C-4a,5a), 132.7 (C-2-isobutenyl), 129.2 (C-9a), 124.9 (CH-1-isobutenyl), 122.8 (C-7,8), 122.0 (C-7,8), 119.4 (C-6), 115.2 (C-9b), 110.8 (c-9), 42.2 (C-1), 35.3 (C-4), 34.4 (C-2), 27.9 (CH₃), 26.1 (CH₃), 23.3 (CH₃), 21.0 (C-3), 18.4 (CH₃). MS: m/z (rel. int.) 254 (M^+ , 21), 198 (61), 183 (100), 168 (8), 115

(6), 109 (9), 95 (38). HRMS: Found 254.1672, calc. for $C_{18}H_{22}O$: 254.1671.

1-Benzofuran-2-yl-1,2,3,4-tetrahydrodibenzofuran (**9h**) and *2-[trans-2-(benzofuran-2-ylcyclobutyl)-3-(2-benzofuran-2-ylethyl)]benzofuran* (**10**). According to the standard conditions the irradiation of **2a** (576 mg, 4 mmol) in the presence of 1 mol% of **1a** was performed for 4 h. Work-up by flash chromatography (*n*-heptane–dichloromethane 10:1 as the eluent) gave 60 mg (10.4% of **9h** and 40 mg (6.9%) of **10**.

9h: 1H NMR (400 MHz, $CDCl_3$): δ 7.42–7.50 (m, 3 H), 7.18–7.28 (m, 4 H), 7.12 (m, 1 H), 6.32 (d, $J=1.0$ Hz, 1 H, H-3'), 4.45 (m, 1 H, H-1), 2.85 (m, 2 H, H-4), 2.30 (dddd, $J=13.3, 7.0, 4.9, 3.0$ Hz, 1 H, H-2), 2.18 (dddd, $J=13.3, 9.9, 5.6, 3.3$ Hz, 1 H, H-2), 1.91–2.09 (m, 2 H, H-3). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 160.1 (C-4a,5a,2',7a'), 155.5 (C-4a,5a,2',7a'), 154.9 (C-4a,5a,2',7a'), 154.5 (C-4a,5a,2',7a'), 128.8 (C-9a,3a'), 128.0 (C-9a,3a'), 123.5 (C-8,5'), 123.3 (C-8,5'), 122.6 (C-7,6'), 122.4 (C-7,6'), 120.6 (C-6,7'), 119.3 (C-6,7'), 112.3 (C-9b), 111.0 (C-9,4'), 111.0 (C-9,4'), 103.6 (C-3'), 32.7 (C-1), 28.8 (C-2), 23.5 (C-4), 20.1 (C-3). MS: m/z (rel. int.) 288 (M^+ , 81), 260 (100), 231 (19), 202 (9), 144 (29), 115 (6). HRMS: Found 288.1158, calc. for $C_{20}H_{16}O_2$: 288.1150.

10: 1H NMR (400 MHz, $CDCl_3$): δ 7.49–7.58 and 7.15 (m, 6 H, H-4,5-benzofuryl), 7.22–7.31 (m, 6 H, H-5,6-benzofuryl), 6.54 (q, $J=1$ Hz, 1 H, H-3-benzofuryl), 6.38 (t, $J=0.9$ Hz, 1 H, H-3-benzofuryl), 4.42 (dddd, $J=6.2, 6.2, 1.8, 0.8$ Hz, 1 H, CH-cyclobutyl), 3.14 (m, CH-cyclobutyl), 3.10 (m, 2 H, CH_2CH_2), 2.47 (dddd, $J=13.2, 8.7, 7.3/5.9$ Hz, 1 H, CH_2-CHH), 2.37 (m, 2 H, CH_2 -cyclobutyl), 2.22 (m, 2 H, CH_2 -cyclobutyl), 2.07 (dtd, $J=13.6, 8.0, 6.8$ Hz, 1 H, CH_2-CHH), 1.78 (m, CH_2 -cyclobutyl). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 159.8, 158.9, 157.8, 154.9, 154.8, 154.5 (C-2,7a-benzofuryl), 129.0, 128.7, 127.7 (C-3a-benzofuryl), 123.6, 123.5, 123.3 (C-5-benzofuryl), 122.6, 122.5, 122.5 (C-6-benzofuryl), 120.6, 120.3, 119.6 (C-7-benzofuryl), 112.5 (C-3), 111.1, 111.0, 110.82 (C-4-benzofuryl), 103.5 (CH-3-benzofuryl), 102.3 (CH-3-benzofuryl), 33.4 (CH-cyclobutyl), 33.2 (CH-cyclobutyl), 31.4 (CH_2CH_2), 27.2 (CH_2 -cyclobutyl), 26.5 (CH_2 -cyclobutyl), 26.4 (CH_2CH_2). MS: m/z (rel. int.) 432 (M^+ , 15), 300 (60), 288 (24), 274 (37), 260 (38), 144 (100), 131 (20), 115 (21). HRMS: Found 432.1737, calc. for $C_{30}H_{24}O_3$: 432.1725.

1-Benzofuran-2-yl-1,4-dimethyl-1,2,3,4-tetrahydrodibenzofuran (**9i**). According to the standard conditions the irradiation of **2b** (632 mg, 4 mmol) in the presence of 1 mmol of **1a** was performed for 4 h. Work-up by flash chromatography (*n*-heptane–dichloromethane 18:1 as the eluent) gave 275 mg (43.5%) of **9i** (*cis:trans* = 2.7:1).

cis-9i: M.p. 125 °C. 1H NMR (400 MHz, $CDCl_3$): δ 7.41–7.53 (m, 4 H), 7.14–7.28 (m, 4 H), 6.23 (d, $J=1.0$ Hz, 1 H, H-3'), 3.05 (dq, $J=9.0, 6.6, 5.8$ Hz, 1 H, H-4), 2.50 (ddd, $J=13.5, 5.8, 2.6$ Hz, 1 H, H-2), 2.02 (dtd, $J=13.4, 5.8, 2.7$ Hz, 1 H, H-3), 1.90 (s, 3 H, CH_3),

1.87 (ddd, $J=13.5, 12.0, 2.7$ Hz, 1 H, H-2), 1.56 (dddd, $J=13.4, 12.0, 9.0, 2.6$ Hz, 1 H, H-3), 1.40 (d, $J=6.6$ Hz, 3 H, CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 163.4 (C-4a,5a,2',7a'), 158.5 (C-4a,5a,2',7a'), 154.9 (C-4a,5a,2',7a'), 154.6 (C-4a,5a,2',7a'), 128.7 (C-9a,3a'), 127.5 (C-9a,3a'), 123.4 (C-8,5'), 123.1 (C-8,5'), 122.5 (C-7,6'), 122.8 (C-7,6'), 120.7 (C-6,7'), 120.6 (C-6,7'), 116.3 (C-9b), 111.2 (C-9,4'), 111.0 (C-9,4'), 103.3 (C-3'), 37.9 (C-1), 36.6 (C-2,3), 29.9 (C-4), 28.9 (C-2,3) 26.1 (CH_3), 18.6 (CH_3). MS: m/z (rel. int.) 316 (M^+ , 36), 301 (100), 286 (10), 183 (8) 143 (12). HRMS: Found 316.1464, calc. for $C_{22}H_{20}O_2$: 316.1463.

trans-9i: M.p. 116 °C. 1H NMR (400 MHz, $CDCl_3$): δ 7.43–7.51 (m, 3 H), 7.37 (m, 1 H), 7.18–7.27 (m, 3 H), 7.12 (m, 1 H), 6.36 (d, $J=1.0$ Hz, 1 H, H-3'), 3.12 (m, 1 H, H-4), 2.38 (m, 1 H, H-2), 2.09 (m, 1 H, H-3), 2.02 (m, 1 H, H-2), 1.79 (s, 3 H, CH_3), 1.69 (m, 1 H, H-3), 1.43 (d, $J=7.0$ Hz, 3 H, CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 163.5 (C-4a,5a,2',7a'), 158.4 (C-4a,5a,2',7a'), 154.9 (C-4a,5a,2',7a'), 154.6 (C-4a,5a,2',7a'), 128.70 (C-9a,3a'), 127.4 (C-9a,3a'), 123.4 (C-8,5'), 123.4 (C-8,5'), 122.5 (C-7,6'), 122.3 (C-7,6'), 120.7 (C-6,7'), 120.6 (C-6,7'), 116.5 (C-9b), 111.1 (C-9,4'), 111.1 (C-9,4'), 102.7 (C-3'), 37.7 (C-1), 35.0 (C-2,3), 29.1 (C-4), 28.1 (C-2,3) 25.5 (CH_3), 18.75 (CH_3). MS: m/z (rel. int.) 316 (M^+ , 32), 302 (28), 301 (100), 286 (16), 271 (18), 255 (14), 202 (13), 183 (36), 158 (20), 143 (18), 115 (42). HRMS: Found 316.1473, calc. for $C_{22}H_{20}O_2$: 316.1463.

The relative configuration of the diastereomers was determined by NOE experiments.

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