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Fused dihydrofurans from the one-pot, three-component reaction of 1,3-cyclohexanedione, iodobenzene diacetate and alkenes

Dimitra Kalpogiannaki, Catherine-Irene Martini[†], Aggeliki Nikopoulou[†], John A. Nyxas, Vassiliki Pantazi[†], Lazaros P. Hadjiarapoglou^{*}

Department of Chemistry, University of Ioannina, GR-45110 Ioannina, Greece

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ABSTRACT

The one-pot, three-component reactions of substituted 1,3-cyclohexanediones, iodobenzene diacetate and alkenes, under photochemical activation, yields fused dihydrofuran derivatives in good yield via the in situ formation of iodonium ylides.

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1. Introduction

The dihydrofuran moiety is a common structural feature of numerous natural products with great biological and pharmaceutical interest.^{1,2} Hence, many synthetic approaches have been reported, such as decomposition³ of diazo ketones or α -elimination⁴ of dibromo ketones in the presence of olefinic trapping agents. However, the search for new methodologies proceeding that are efficient and involve readily available starting materials still remains an active area of research.

The employment of iodonium ylides in this chemistry has shown interesting complementary reactivity to that of diazo compounds without the common major drawbacks. Because of the hyper-leaving group ability of aryl- λ^3 -iodanyl groups, the reactivity of iodonium ylides is higher than the corresponding diazo compounds. This fact has allowed various cycloadditions⁵ to be performed under milder conditions, with better yields, even leading to the development of more enantioselective methods.

In the course of our studies focused on the development of new synthetic applications of iodonium ylides,⁶ we recently disclosed^{6a} a straightforward approach to fused dihydrofurans from inexpensive alkenes and iodonium ylides. By following this synthetic route, a large variety of fused dihydrofurans could be prepared

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starting from terminal alkenes. It should be realized that the fused cyclohexenone ring might be aromatized⁷ or appropriately modified⁸ through established enolate methodology.

In order to extend the scope of this synthetic methodology, we decided to explore the one-pot, three-component reaction, using six-membered cyclic 1,3-diketones, iodobenzene diacetate and al-kenes (Scheme 1). Since a catalyst is necessary for PhI(OAc)₂ vicinal oxygenation⁹ of alkenes, we anticipated that 1,3-cyclohexanedione as a nucleophile could react with PhI(OAc)₂ in a ligand exchange



Scheme 1. One-pot synthesis of dihydrofuran 3aa.





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^{*} Corresponding author. Tel.: +30 26510 08380; fax: +30 26510 08799; e-mail address: lxatziar@uoi.gr (L.P. Hadjiarapoglou).

[†] Undergraduate Research Participants.

reaction yielding the corresponding iodonium salt **5a**,¹⁰ which subsequently might lose a molecule of acetic acid to give the stable iodonium ylide **4a**. Under photochemical activation the in situ generated iodonium ylide should react with alkenes furnishing fused dihydrofurans.

In this work, we report an efficient process for the synthesis of fused dihydrofurans via a one-pot, three-component reaction of 1,3-cyclohexanedione derivatives, iodobenzene diacetate and alkenes.

2. Results and discussion

In our initial study to test our hypothesis, the three-component reaction of 1,3-cyclohexanedione (1a), iodobenzene diacetate and styrene 2a was employed to develop appropriate reaction conditions (Scheme 1). The best yield (66%) of dihydrofuran 3aa was obtained when a CH₂Cl₂-solution of 1a, Phl(OAc)₂ and 2a(excess) was irradiated for 1 h at room temperature. Alternatively, stirring a dichloromethane solution of 1a, and Phl(OAc)₂ at room temperature for 1 h, followed by addition of styrene 2a (excess) and irradiation for 1 h at room temperature yields dihydrofuran 3aa in 62% yield. For comparison, a 67% yield of dihydrofuran 3aa was isolated when a solution of iodonium ylide 4a and styrene 2a was irradiated for 1 h at room temperature, while without irradiation, a 30% yield of dihydrofuran 3aa was isolated after stirring at room temperature for 30 d.

To gain more information about dihydrofuran formation the reaction mixture of 1,3-cyclohexanedione and iodobenzene diacetate was analyzed by ¹H NMR spectroscopy at 0 °C and room temperature (Fig. 1). The proton spectra of iodonium ylide **4a** as well as iodobenzene diacetate and 1,3-cyclohexanedione were compared to determine their content in the reaction medium. It is evident that iodonium ylide **4a** was quickly generated at the beginning of the reaction, presumably the initially-formed iodonium salt **5** is rather unstable at ambient temperature. Evaporation of the solvent under reduced pressure and trituration of the residue with hexane, yields iodonium ylide **4a** quantitatively.

To further demonstrate the potential application of this one-pot, three-component reaction, additional reactions of other substituted 1,3-cyclohexanediones 1 with styrene 2a were next investigated. The reactions proceed at room temperature under photochemical activation within 60 min in moderate to good yields (Table 1). For example, a CH₂Cl₂-solution of 5-methyl-1,3-cyclohexanedione **1b**, iodobenzene diacetate and styrene 2a was irradiated for 1 h at room temperature. The solvent was subsequently evaporated and the residue was flash chromatographed on silica gel to afford dihydrofuran **3ba**¹¹ in 45% yield (entry 1, Table 1). Under similar conditions, 5-phenyl-1,3-cyclohexanedione (1c), 5-(p-methoxyphenyl)-1,3-cyclohexanedione (1d) and 5,5-dimethyl-1,3-cyclohexanedione (1e), were converted to the corresponding dihydrofuran derivatives **3ba**–**fa**¹¹(entries 2–5, Table 1). There is a comparison of the in situ procedure (method A) with the results obtained from the reaction of styrene 2a with the corresponding iodonium ylides 4 under photochemical activation (method B). In general, the yields of dihydrofuran derivatives are similar in both methods.

It had been reported,¹² that dihydrofuran **3ea** was isolated in 71% yield by stirring a mixture of dimedone **1e**, PhI(OAc)₂ and styrene **2a** at 0 °C for 1.5 h. When this procedure was repeated for 1,3-cyclohexadione **1a** and dimedone **1e**, dihydrofurans **3aa** or **3ea** were not detected in the crude reaction mixture; instead the corresponding iodonium ylides **4** were isolated quantitatively.

Several other acyclic dicarbonyl compounds were investigated; however, the results indicated that methyl acetoacetate and dimethyl malonate were not suitable for this reaction. On the other hand, when a dichloromethane solution of 2,2-dimethyl-1,3-dioxa-4,6-cyclohexanedione (**1f**), iodobenzene diacetate and styrene **2a**



Fig. 1. (a) ¹H NMR spectrum of 1,3-cyclohexanedione **1a**; (b) ¹H NMR spectrum of iodobenzene diacetate; (c) ¹H NMR spectrum of the reaction mixture of 1,3-cyclohexanedione **1a** and iodobenzene diacetate at 0 °C; (d) ¹H NMR spectrum of the reaction mixture of 1,3-cyclohexanedione **1a** and iodobenzene diacetate at 20 °C; (e) ¹H NMR spectrum of iodonium ylide **4a**.

Table 1

One-pot, three-component reactions^a of 1,3-cyclohexanediones 1 with styrene 2a



Entry	Cyclohexanedione	R ¹	\mathbb{R}^2	Method	Product	Yield ^b (%)
1	1a	Н	Н	А	3aa	66
				В		67
				С		62
				D		30
2	1b	CH ₃	Н	А	3ba	55
				В		59
3	1c	C ₆ H ₅	Н	А	3ca	55
				В		56
4	1d	p-CH ₃ C ₆ H ₄	Н	А	3da	57
				В		60
5	1e	CH ₃	CH_3	А	3ea	83
				В		85

^a Reaction conditions: **1** (0.96–1.96 mmol), PhI(OAc)₂ (0.99–1.99 mmol), **2a** (4.81–9.62 mmol), CH₂Cl₂ (10 mL), $h\nu$ (method A); **4** (0.99–4.14 mmol), **2a** (4.81–14.42 mmol), CH₂Cl₂ or CH₃CN(10 mL), $h\nu$ (method B); **1** (1 mmol), PhI(OAc)₂ (1 mmol), CH₂Cl₂ (10 mL), rt, 45 min, than **2a** (4.81 mmol), $h\nu$, 45 min (method C); **4** (2.0 mmol), **2a** (9.62 mmol), CH₃CN(10 mL), rt, 30 d (method D). ^b Isolated yield. was irradiated for 2 h at room temperature, cyclopropane **6**¹³ was isolated in 48% yield (Scheme 2). Cyclopropane **6** is the typical product of the metal- or photochemically catalyzed cycloaddition of the corresponding iodonium ylide with styrene **2a**. It is well known that the acidity of cyclic six-membered β -diketones is around pK_a 5, putting it close to acetic acid, while their acyclic analogues are less acidic. This acidity of the 1,3-diketone seems to play an important role in this tandem reaction, especially for the in situ formation of the iodonium ylide. The acetoxylation of acyclic 1,3-diketones under the influence of iodobenzene diacetate is a well-known procedure.¹⁴



Table 2

Cycloadditions^a of 1,3-cyclohexanedione **1a** with alkenes **2**

To explore the generality and scope of this tandem reaction, a range of alkenes **2** and 1,3-cyclohexanedione **1a** were surveyed (Table 2). A wide range of acyclic as well as cyclic alkenes can effectively participate in the reaction with good yields. There is a comparison of the in situ procedure (method A) with the results obtained from the reaction of alkenes 2 with iodonium ylides **4a** under photochemical activation (method B). The yields are rather similar in both examined methods.

It is worth mentioning that the reaction exhibits high regioselectivity. The carbonyl oxygen of the 1,3-cyclohexanedione **1a** added exclusively onto the more substituted carbon of the double bond, i.e., terminal alkenes afforded 2-substituted dihydrofuran exclusively, the other possible regioisomer was not detected at all. For example, ethyl vinyl acetate **2b** and vinyl acetate **2c** afforded 2ethoxy- and 2-acetoxy-2,3-dihydrofuran derivatives **3ab,ac**,^{8c} respectively (entries 1,2 of Table 2). The lower yields of the one-pot, three-component reaction (method A) when compared to the corresponding cycloaddition of iodonium ylide **4a** (method B) should arise from the small excess of alkenes **2b,c** employed (13.9 or 11.6 mmol vs 10 mL). Phenylthioethylene **2d** reacts also via the

	1a	2 R ¹ Ch ₂ Ol ₂ ,	3	
Entry	Alkene	Method	Product	Yield ^b (%)
1	EtO	А		60
	2b	В	OEt O 3ab	86
2	AcO	А	° L	45
	2c	В		81
3	PhS	А	° , , , , , , , , , , , , , , , , , , ,	67
	2d	В	│	71
4	Ph 2e	А	O Ph	51
	Me 20	В	O 3ae	64
5	Ph	А	O Ph	66
	Ph 21	В	O Saf	61
6	MeO 2g	А	O O O 3ag	68
		В		56
7	PhS 2h	А		83 ^c
		В	SPh O 3ah	77 ^c

hv, PhI(OAc)

Table 2 (continued)



^a Reaction conditions: 1 (1.00–2.00 mmol), PhI(OAc)₂ (1.00–2.00 mmol), 2 (4.05–14.71 mmol), CH₂Cl₂ (10 mL), *hν* (method A); 4 (1.00–6.37 mmol), 2 (4.00–130 mmol), CH₂Cl₂ or CH₃CN(10 mL), *hν* (method A).

^b Isolated yield.

^c *E*/*Z* ratio=60:40.

one-pot, three-component reaction with 1,3-cyclohexanedione **1a** yielding dihydrofuran **3ad**¹⁵ in 67% yield (entry 3, Table 2). Under similar reaction conditions, α -methylstyrene **2e** and 1,1-diphenylethylene **2f** yielded 2-methyl-2-phenyl- and 2,2-diphenyl-2,3-dihydrofuran derivatives **3ae,af**, respectively (entries 4,5 of Table 2).

Reactions of (*E*)- and (*Z*)-anethole **2g** with 1,3-cyclohexanedione **1a** were carried out to examine the stereochemistry of this tandem reaction. From both alkenes, (*E*)-2-(*p*-methoxyphenyl)-3-methyl-4oxo-2,3,4,5,6,7-hexahydrobenzo[*b*]furan (**3ag**) was obtained, indicating that the reaction proceeded in a non-stereospecific way (entry 6, Table 2). Such a *trans* stereochemistry is a common structural moiety present in many neolignan natural products.¹⁶ In a similar fashion, the reaction of 1,3-cyclohexanedione **1a** with 1-(phenylthio)-1-propene **2h** (ratio *E*/*Z*=50:50) yields 2-(phenylthio)-3-methyl-4-oxo-2,3,4,5,6,7-hexahydrobenzo[*b*]furan **3ah**^{11,17} in 83% yield (entry 7, Table 2). The reaction was regioselective, but a mixture of stereoisomers was formed in a ratio of *E*/*Z*=60:40. It is known that both isomers can be converted into furanoterpenoids by oxidation followed by elimination.¹⁸

Cyclic alkenes can effectively participate in this tandem cycloaddition. cis-2,3-Dihydrofuran 3ai was obtained, as a single isomer, in 34% yield, when cyclopentane 2i was allowed to undergo reaction with 1,3-cyclohexanedione 1a and iodobenzene diacetate under photochemical activation (entry 8, Table 2). The reaction with 2,3-dihydrofuran 2j was also considered. The one-pot, threecomponent cycloaddition of 1,3-cyclohexanedione 1a, iodobenzene diacetate and dihydrofuran 2j gives the fused dihydrofuran cycloadduct **3aj**,^{3c,19} as a single diastereomer in 71% yield (entry 9, Table 2). Indene 2k, is also compatible for this reaction. Fused dihydrofuran **3ak** was isolated in 55% yield, as a single diastereomer, when a dichloromethane solution of 1,3-cyclohexanedione 1a, iodobenzene diacetate and indene 2k was irradiated at room temperature (entry 10, Table 2). Similarly, acenaphthylene 21 was reacted with 1,3-cyclohexanedione 1a and iodobenzene diacetate under photochemical activation to afford cycloadduct 3al, as a single diastereomer, in 59% yield (entry 11, Table 2).Structures of all cycloadducts were unambiguously identified with IR, ¹H and ¹³C NMR spectroscopy and HRMS spectra. All the cycloadducts **3** exhibited IR absorptions at 1628–1694 cm⁻¹ due to the characteristic feature of α , β -unsaturated six-membered carbonyl functional group. All the cycloadducts **3** showed ¹³C resonance at about δ 194–196 ppm revealing the presence of a six-membered α , β -unsaturated carbonyl group. Furthermore, the β -carbon atom of the enone moiety was found to be present at δ 175–178 ppm.

The observed selectivities have literature precedent. The stereoand regio-selectivities of the dihydrofurans **3** determined by 2-D NMR studies, is exemplified for cycloadducts **3ad**, **3ag**, **3ak**. The ¹H NMR spectrum of **3ad** displays signals at δ 7.54–7.52 (m, 2H), 7.35–7.32 (m, 3H), 6.09 (dd, *J*=9.9, 6.0 Hz, 1H), 3.28 (dd, *J*=15.7, 9.9 Hz, 1H), 2.83 (dd, *J*=15.7, 6.0 Hz, 1H), 2.46–2.43 (m, 2H), 2.33–2.30 (m, 2H), 2.06–2.09 (m, 2H) attributable only to dihydrofuran structure **3ad**. The H-2 and 3-CH₂ hydrogens, related by H,H-COSY correlation, appeared as double doublets at 6.09 (*J*=9.9, 6.0 Hz), 3.28 (*J*=15.7, 9.9 Hz) and 2.83 ppm (*J*=15.7, 6.0 Hz), respectively. The double doublet signal at δ 6.09 showed a C,H-COSY correlation with the carbon signal at δ 91.0 ppm and HMBCs (Fig. 2)



Fig. 2. Chemical shifts and selected HMBCs in 3ad.

with C-7a at 175.8, C-3a at 113.2 ppm. Both double doublet signals at δ 3.28 and 2.83 ppm showed C,H-COSY correlation with the same carbon signal at δ 32.9 ppm, thus the large *gem*-coupling constant (J=15.7 Hz). The other coupling constants J=9.9 and J=6.0 Hz shows the *cis* and *trans* relation, respectively.¹⁷ These signals showed HMBCs with C-7a at 175.8 and C-3a at 113.2 ppm. The 6-CH₂ hydrogens appearing as a multiplet at δ 2.06–2.09 ppm are related by H.H-COSY correlation with the multiplet signals at δ 2.46–2.43 and 2.33-2.30 ppm enabling its assignment to the C-6 position. This multiplet is related by C,H-COSY correlation with the carbon signal at δ 21.4 ppm and showed HMBCs with C-7 at 23.8, C-5 at 36.2, C-7a at 175.8 and C-4 at 194.8 ppm. The 7-CH₂ hydrogens appeared as a multiplet at δ 2.46–2.43 ppm, and is related by C,H-COSY correlation with the carbon signal at δ 23.8 ppm and showed HMBCs with C-6 at 21.4, C-5 at 36.2, C-3a at 113.2 and C-7a at 175.8 ppm. The 5-CH₂ hydrogens appeared as a multiplet at δ 2.33–2.30 ppm, is related by C,H-COSY correlation with the carbon signal at δ 36.2 ppm and showed HMBCs with C-6 at 21.4, C-7 at 23.8, C-3a at 113.2 and C-4 at 194.8 ppm.

The stereochemistry of cycloadduct **3ag** was clearly assigned as *trans* since the coupling constant (J=7.0 Hz) between C-2 and C-3 hydrogens compared more favourably with the *trans* coupling constant of 6.0 Hz than *cis* coupling constant of 9.9 Hz. The existence of NOESY signals between the C-3 hydrogen with the *ortho*-hydrogens of the aryl group at C-2 position clearly indicates the *trans* configuration in the dihydrofuran ring.

The stereochemistry between C-2 and C-3 hydrogens of cycloadduct **3ak** was clearly assigned as *cis* since the coupling constant (*J*=8.9 Hz) compared more favourably with the *cis* coupling constant of 9.9 Hz than *trans* coupling constant of 6.0 Hz. The C-2 hydrogen appeared as doublet (*J*=8.9 Hz) showed C,H-COSY correlation with the carbon signal at δ 93.2 ppm, and is related by H,H-COSY correlation only with the C-3 hydrogen (Fig. 3). The C-3 hydrogen appeared as a multiplet at δ 4.01–3.94 and showed C,H-COSY correlation with the carbon signal at δ 41.7 ppm and is related by H,H-COSY correlation with the C-2 hydrogen and the fivemembered methylene hydrogens. The latter appeared as double doublets at δ 3.31 (*J*=17.1, 8.3 Hz) and 3.13 (*J*=17.1, 2.3 Hz) showed C,H-COSY correlation with the carbon signal at d 37.3 ppm and is related by H,H-COSY correlation only with the C-3 hydrogen.



Fig. 3. Key H,H-COSY correlation in 3ak.

The speculative but plausible reaction mechanism in Scheme 3 is proposed to rationalize this one-pot multicomponent reaction. It is reasonable to assume²⁰ that the first step of this one-pot, threecomponent reaction occurs via the initial nucleophilic substitution on the tricoordinate iodine of iodobenzene diacetate by 1,3cyclohexanedione 1a to give iodonium salt 5a as the first intermediate. Since the reaction takes place at room temperature, the unstable iodonium salt **5a** subsequently loses a molecule of acetic acid under the influence of heat to give the stable iodonium ylide 4a, which is the actual reaction intermediate of the dihydrofuranforming reaction. The cycloaddition reaction between the iodonium ylide 4a with the various alkenes, i.e., styrene 2a, might proceeds via the zwitterionic intermediate 7, generated directly by electrophilic attack of the iodonium ylide 4a on styrene 2a. The ring closure and subsequent iodobenzene extrusion affords the observed dihydrofuran **3aa** (path A). Under photochemical activation, iodonium ylide 4a might lose iodobenzene serving as a source of carbene **8**. Direct 1,3-dipolar cycloaddition of dipole **9** yields dihydrofuran **3aa** (path B). The third possible route (path C) involves the initial formation of cyclopropane **10**. This stable cyclopropane was completely rearranged²¹ into dihydrofuran **3aa** under the same reaction conditions.



Scheme 3. A speculative but plausible mechanism.

3. Conclusion

In summary, we have developed a simple efficient protocol for the synthesis of substituted fused dihydrofurans. This reaction is performed using inexpensive starting materials in a safe reaction medium. The regioselectivity is extremely high, only one regiosiomer is obtained. This tandem cycloaddition exhibited wide generality: a series of substituted alkenes reacted with 1,3cyclohexanedione to generate fused dihydrofurans with good yields.

4. Experimental section

4.1. General experimental details

All commercial reagents and solvents were used without further purification. TLC analysis was performed on Merck silica gel 60 F₂₅₄ plates. The spots were visualized either by UV irradiation (254 nm) or KMnO₄. Silica gel (0.040–0.063 μ m) from Merck was used for flash column chromatography. ¹H and ¹³C NMR, as well as DEPT-135 experiments, were recorded on Bruker Avance AV250 and AV500 instruments. The residual solvent protons (¹H) or the solvent carbon atoms (¹³C) were used as internal standards. The ¹H NMR spectroscopic data are presented as follows: chemical shift in parts per million relative to tetramethylsilane (multiplicity, coupling constant, integration). The following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; ddd, doublet of doublet of doublets; m, multiplet. High resolution mass spectra were determined using ES ionization techniques on a Thermo LTQ Orbitrap XL instrument. IR spectra were recorded with a Perkin–Elmer Spectrum BX spectrophotometer. Melting points (uncorrected) were determined on a Buchi B-510 apparatus. The photochemical reactions were performed by using solutions in heavy-duty wall test tubes immersed in water at room temperature (external cooling) in a reactor cage fitted with a naked 250W Philips HPL-N250WE40 HG lamp from a 10 cm distance. 1,3-Cyclohexanedione **2b**,²² **2c**,²³ **2d**,²³ phenylthioethylene **2d**²⁴ and 1-(phenylthio)-1-propene (**2g**)²⁵ were synthesized following the literature procedures.

4.2. General procedure for the one-pot, three-component synthesis of dihydrofurans **3**

A solution of 1,3-cyclohexanedione **1** (1.00–2.00 mmol), iodobenzene diacetate (1.00–2.00 mmol) and alkene **2** (4.05–14.71 mmol) in dichloromethane (10 mL) was irradiated (250 W) at room temperature for 40–360 min. The solvent was evaporated under reduced pressure, and the residue was purified by flash chromatography to afford fused dihydrofuran **3**.

4.2.1. 2-Phenyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (**3aa**). From 1,3-cyclohexanedione (**1a**) (0.22 g, 1.96 mmol), iodobenzene diacetate (0.64 g, 1.99 mmol) and styrene **2a** (1.0 g, 9.62 mmol) in dichloromethane (10 mL), irradiated for 60 min. Purification by flash chromatography (dichloromethane/ethyl acetate 4:1) gave 2-phenyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (**3aa**) (0.28 g, 66% yield) as a colourless oil; R_f (CH₂Cl₂) 0.05; ν_{max} (liquid film) 3052, 2947, 1632, 1400, 1230, 1180, 1061, 760, 702 cm⁻¹. δ_H (250 MHz, CDCl₃) 7.39–7.26 (m, 5H), 5.72 (dd, *J*=10.5, 8.0 Hz, 1H), 3.31–3.20 (m, 1H), 2.89–2.79 (m, 1H), 2.50–2.44 (m, 2H), 2.38–2.33 (m, 2H), 2.05 (dd, *J*=12.7, 6.4 Hz, 2H). δ_C (62.5 MHz, CDCl₃) 194.4, 176.4, 140.0, 127.9, 127.6, 125.0, 112.0, 85.3, 35.7, 33.3, 23.0, 20.9. HRMS (ESI-TOF): MNa⁺, found 237.0884. C₁₄H₁₄O₂Na requires 237.0887.

4.2.2. 6-*Methyl-2-phenyl-2*,3,6,7-*tetrahydrobenzofuran-4*(*5H*)-*one* (**3ba**). From 5-methyl-1,3-cyclohexanedione (**1b**) (0.12 g, 1.07 mmol), iodobenzene diacetate (0.32 g, 0.99 mmol) and styrene **2a** (0.5 g, 4.81 mmol) in dichloromethane (10 mL), irradiated for 60 min. Purification by flash chromatography (dichloromethane/ethyl acetate 9:1) gave 6-methyl-2-phenyl-2,3,6,7-tetrahydrobenzofuran-4(5*H*)- one (**3ba**)¹¹ (0.10 g, 45% yield) as a colourless oil (racemic mixture); *R*_f (20% EtOAc/CH₂Cl₂) 0.45; *v*_{max} (liquid film) 2958, 1634, 1402, 1212, 1052, 736, 700 cm⁻¹. $\delta_{\rm H}$ (250 MHz, CDCl₃) 7.39–7.26 (m, 5H), 5.78–5.70 (m, 1H), 3.29–3.19 (m, 1H), 2.89–2.79 (m, 1H), 2.59–2.52 (m, 1H), 2.47–2.27 (m, 2H), 2.22–2.09 (m, 2H), 1.12 (d, *J*=6.2 Hz, 3H). $\delta_{\rm C}$ (62.5 MHz, CDCl₃) 195.09, 195.05, 176.93, 140.54, 140.44, 128.64, 128.36, 128.34, 125.74, 125.63, 112.52, 112.35, 86.58, 86.34, 44.83, 33.76, 31.80, 29.81, 29.64, 20.90, 20.86. HRMS (ESI-TOF): MH⁺, found 229.1223. C₁₅H₁₇O₂ requires 229.1223.

4.2.3. 2,6-Diphenyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (**3ca**). From 5-phenyl-1,3-cyclohexanedione (**1c**) (0.18 g, 0.96 mmol), iodobenzene diacetate (0.32 g, 0.99 mmol) and styrene **2a** (0.5 g, 4.81 mmol) in dichloromethane (10 mL), irradiated for 60 min. Purification by flash chromatography (dichloromethane/ethyl acetate 9:1) gave 2,6-diphenyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (**3ca**) (0.15 g, 55% yield), as white crystals (racemic mixture); R_f (20% Et₂OAc/CH₂Cl₂) 0.50; mp 134–136 °C (EtOH). ν_{max} (KBr) 3030, 1634, 1404, 1208, 910, 734, 700 cm⁻¹. $\delta_{\rm H}$ (250 MHz, CDCl₃) 7.45–7.34 (m,

5H), 7.31–7.25 (m, 5H), 5.86–5.78 (m, 1H), 3.57–3.44 (m, 1H), 3.41–3.27 (m, 1H), 3.00–2.88 (m, 1H), 2.79–2.72 (m, 2H), 2.69–2.65 (m, 2H). δ_{C} (62.5 MHz, CDCl₃) 194.17, 194.12, 176.64, 176.61, 142.45, 142.42, 140.39, 140.27, 128.77, 128.58, 128.53, 127.08, 126.71, 126.69, 125.92, 125.76, 113.00, 112.79, 87.01, 86.74, 43.77, 43.68, 40.36, 40.25, 33.79, 33.76, 31.46, 31.43. HRMS (ESI-TOF): MH⁺, found 291.1381; C₂₀H₁₉O₂ requires 291.1380.

4.2.4. 6-(4-Methoxyphenyl)-2-phenyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (3da). From 5-(4-methoxyphenyl)-1,3-cyclohexanedione (1d) (0.22 g, 1.01 mmol), iodobenzene diacetate (0.32 g, 0.99 mmol) and styrene 2a (0.5 g, 4.81 mmol) in dichloromethane (10 mL), irradiated for 60 min. Purification by flash chromatography (dichloromethane/ethyl acetate 9:1) gave 6-(4-methoxyphenyl)-2phenyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (3da) (0.19 g, 59% vield) as white crystals (racemic mixture); R_f (CH₂Cl₂) 0.067; mp 165–167 °C (MeOH). v_{max} (KBr) 3032, 2949, 1632, 1512, 1400, 1248, 1034, 831, 702 cm $^{-1}$. $\delta_{\rm H}$ (250 MHz, CDCl_3) 7.41 –7.31 (m, 5H), 7.20 and 6.90 (AA'BB' system, 4H), 5.85-5.76 (m, 1H), 3.80 (s, 3H), 3.51-3.27 (m, 2H), 2.98–2.87 (m, 1H), 2.83–2.54 (m, 4H). δ_{C} (62.5 MHz, CDCl₃) 194.13, 194.08, 176.52, 176.48, 158.50, 140.47, 140.34, 134.62, 134.59, 128.75, 128.53, 128.49, 127.66, 127.63, 125.89, 125.73, 114.09, 112.96, 112.76, 86.92, 86.65, 55.21, 44.09, 44.02, 39.62, 39.50, 33.81, 31.73, 31.71. HRMS (ESI-TOF): MH⁺, found 321.1473. C₂₁H₂₁O₃ requires 321.1485.

4.2.5. 6.6-Dimethyl-2-phenyl-2.3.6.7-tetrahydrobenzofuran-4(5H)one (**3ea**). From 5.5-dimethyl-1.3-cyclohexanedione (**1e**) (0.14 g. 1.00 mmol), iodobenzene diacetate (0.32 g, 0.99 mmol) and styrene 2a (0.5 g, 4.81 mmol) in dichloromethane (10 mL), irradiated for 60 min. Purification by flash chromatography (dichloromethane/ 6,6-dimethyl-2-phenyl-2,3,6,7ethyl acetate 9:1) gave tetrahydrobenzofuran-4(5H)-one (3ea) (0.20 g, 83% yield) as a colourless oil; R_f (20% EtOAc/CH₂Cl₂) 0.40; ν_{max} (liquid film) 3030, 2961, 1635, 1404, 1216, 1041, 762, 703 cm⁻¹. $\delta_{\rm H}$ (250 MHz, CDCl₃) 7.39–7.27 (m, 5H), 5.75 (dd, J=10.5, 7.8 Hz, 1H), 3.32–3.22 (m, 1H), 2.90–2.80 (m, 1H), 2.35 (s, 2H), 2.25 (s, 2H), 1.12 (s, 6H). $\delta_{\rm C}$ (62.5 MHz, CDCl₃) 194.7, 176.1, 140.6, 128.6, 128.3, 125.6, 111.2, 86.4, 50.8, 37.6, 34.0, 33.7, 28.7, 28.4. HRMS (ESI-TOF): MH⁺, found 243.1380. C₁₆H₁₉O₂ requires 243.1380.

4.2.6. 2-*Ethoxy*-2,3,6,7-*tetrahydrobenzofuran*-4(5*H*)-*one* (**3ab**). From 1,3-cyclohexanedione (**1a**) (0.22 g, 1.96 mmol), iodobenzene diacetate (0.64 g, 1.99 mmol) and ethyl vinyl ether **2b** (1.0 g, 13.90 mmol) in dichloromethane (10 mL), irradiated for 60 min. Purification by flash chromatography (dichloromethane/ethyl acetate 4:1) gave 2-ethoxy-2,3,6,7-tetrahydrobenzofuran-4(5*H*)-one (**3ab**) (0.21 g, 60% yield) as a colourless oil; R_f (Et₂O) 0.28; v_{max} (liquid film) 3056, 2976, 1634, 1406, 1376, 1178, 1112, 900, 736 cm⁻¹. δ_H (250 MHz, CDCl₃) 5.52 (dd, *J*=7.3, 3.4 Hz, 1H), 3.68 (ddd, *J*=14.2, 9.5, 7.1 Hz, 1H), 3.43 (ddd, *J*=14.2, 9.5, 7.1 Hz, 1H), 2.74–2.64 (m, 1H), 2.47–2.38 (m, 1H), 2.29–2.24 (m, 2H), 2.15–2.10 (m, 2H), 1.95–1.73 (m, 2H), 1.03 (t, *J*=7.1 Hz, 3H). δ_C (62.5 MHz, CDCl₃) 194.6, 175.2, 111.8, 108.0, 64.5, 35.9, 32.3, 23.4, 21.1, 14.5. HRMS (ESI-TOF): MH⁺, found 183.1009. C₁₀H₁₅O₃ requires 183.1016.

4.2.7. 2-Acetoxy-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (**3ac**). From 1,3-cyclohexanedione (**1a**) (0.22 g, 1.96 mmol), iodobenzene diacetate (0.64 g, 1.99 mmol) and vinyl acetate **2c** (1.0 g, 11.60 mmol) in dichloromethane (10 mL), irradiated for 60 min. Purification by flash chromatography (dichloromethane/ethyl acetate 9:1) gave 2-acetoxy-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (**3ac**)^{8c} (0.17 g, 45% yield) as a colourless oil; R_f (CH₂Cl₂) 0.03; ν_{max} (liquid film) 2952, 1760, 1636, 1428, 1406, 1380, 1266, 1240, 1216, 1166, 936, 736 cm⁻¹. δ_H (250 MHz, CDCl₃) 6.69 (dd, *J*=7.5, 2.6 Hz, 1H), 3.08–2.96 (m, 1H), 2.80–2.71 (m, 1H), 2.49–2.43 (m, 2H), 2.36–2.31 (m, 2H), 2.08 (s,

3H), 2.09–1.98 (m, 2H). δ_C (62.5 MHz, CDCl_3) 195.1, 175.3, 169.4, 112.2, 98.5, 36.3, 31.9, 23.4, 21.4, 20.8. HRMS (ESI-TOF): MH^+, found 197.0815. $C_{10}H_{13}O_4$ requires 197.0808.

4.2.8. 2-Phenylthio-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (**3ad**). From 1,3-cyclohexanedione (**1a**) (0.22 g, 1.96 mmol), iodobenzene diacetate (0.64 g, 1.99 mmol) and phenylthio-ethylene **2d** (1.0 g, 7.35 mmol) in dichloromethane (10 mL), irradiated for 60 min. Purification by flash chromatography (dichloromethane/ethyl acetate 9:1) gave 2-phenylthio-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (**3ad**)¹⁵ (0.32 g, 67% yield) as a colourless oil; R_f (20% EtOAc/CH₂Cl₂) 0.37; ν_{max} (liquid film) 3060, 2946, 1642, 1398, 1222, 1182, 900, 872, 740 cm⁻¹. $\delta_{\rm H}$ (250 MHz, CDCl₃) 7.54–7.52 (m, 2H), 7.35–7.32 (m, 3H), 6.09 (dd, *J*=9.9, 6.0 Hz, 1H), 3.28 (dd, *J*=15.7, 9.9 Hz, 1H), 2.83 (dd, *J*=15.7, 6.0 Hz, 1H), 2.46–2.43 (m, 2H), 2.33–2.30 (m, 2H), 2.06–2.09 (m, 2H). $\delta_{\rm C}$ (62.5 MHz, CDCl₃) 194.8, 175.8, 132.5, 132.1, 129.0, 128.1, 113.2, 91.0, 36.2, 32.9, 23.8, 21.4. HRMS (ESI-TOF): MH⁺, found 247.0786. C₁₄H₁₅O₂S requires 247.0787.

4.2.9. 2-Methyl-2-phenyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (**3ae**). From 1,3-cyclohexanedione (**1a**) (0.22 g, 1.96 mmol), iodobenzene diacetate (0.64 g, 1.99 mmol) and α -methylstyrene **2e** (1.0 g, 8.47 mmol) in dichloromethane (10 mL), irradiated for 40 min. Purification by flash chromatography (dichloromethane/ethyl acetate 9:1) gave 2-methyl-2-phenyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (**3ae**) (0.23 g, 51% yield) as a colourless oil; *R*_f (10% EtOAc/CH₂Cl₂) 0.36; ν_{max} (liquid film) 3058, 2946, 1636, 1402, 1372, 1252, 1184, 1000, 736 cm⁻¹. δ_{H} (250 MHz, CDCl₃) 7.35–7.22 (m, 5H), 3.10–2.95 (m, 2H), 2.51–2.43 (m, 2H), 2.35–2.30 (m, 2H), 2.07–1.96 (m, 2H), 1.69 (s, 3H). δ_{C} (62.5 MHz, CDCl₃) 195.0, 175.4, 145.1, 128.0, 127.0, 123.7, 112.01, 92.0, 40.2, 36.0, 29.2, 23.6, 21.2. HRMS (ESI-TOF): MH⁺, found 229.1213. C₁₅H₁₇O₂ requires 229.1223.

4.2.10. 2,2-Diphenyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (**3af**). From 1,3-cyclohexanedione (**1a**) (0.22 g, 1.96 mmol), iodobenzene diacetate (0.64 g, 1.99 mmol) and 1,1-diphenylethylene **2f** (1.0 g, 5.56 mmol) in dichloromethane (10 mL), irradiated for 90 min. Purification by flash chromatography (dichloromethane/ ethyl acetate 4:1) gave 2,2-diphenyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (**3af**) (0.38 g, 66% yield) as a colourless oil; *R*_f (20% EtOAc/ CH₂Cl₂) 0.30; *v*_{max} (liquid film) 3055, 2947, 1636, 1400, 1250, 737, 702 cm⁻¹. $\delta_{\rm C}$ (250 MHz, CDCl₃) 7.38–7.17 (m, 10H), 3.56 (s, 2H), 2.51–2.47 (m, 2H), 2.31–2.26 (m, 2H), 2.00–1.90 (m, 2H). $\delta_{\rm C}$ (62.5 MHz, CDCl₃) 194.8, 175.2, 144.1, 128.0, 127.3, 127.2, 112.2, 94.9, 40.2, 35.9, 23.4, 21.2. HRMS (ESI-TOF): MH⁺, found 291.1369. C₂₀H₁₉O₂ requires 291.1380.

4.2.11. (*E*)-2-(4-*Methoxyphenyl*)-3-*methyl*-2,3,6,7-*tetrahydrobenzofuran*-4(5*H*)-*one* (**3ag**). From 1,3-cyclohexanedione (**1a**) (0.11 g, 1.00 mmol), iodobenzene diacetate (0.32 g, 0.99 mmol) and *trans*-anethole **2g** (0.6 g, 4.05 mmol) in dichloromethane (10 mL), irradiated for 50 min. Purification by flash chromatography (dichloromethane/ethyl acetate 4:1) gave (*E*)-2-(4-methoxyphenyl)-3-methyl-2,3,6,7-tetrahydrobenzofuran-4(5*H*)-one (**3ag**) (0.17 g, 68% yield) as a colourless oil; *R*_f(20% EtOAc/CH₂Cl₂) 0.46; *v*_{max} (liquid film) 2958, 1628, 1516, 1400, 1250, 1176, 1034, 912, 734 cm⁻¹. $\delta_{\rm H}$ (250 MHz, CDCl₃) 7.19 and 6.85 (AA'BB' system, 4H), 5.05 (d, *J*=7.0 Hz, 1H), 3.74 (s, 3H), 3.25–3.19 (m, 1H), 2.53–2.35 (m, 2H), 2.33–2.28 (m, 2H), 2.06–1.96 (m, 2H), 1.30 (d, *J*=6.7 Hz, 3H). $\delta_{\rm C}$ (62.5 MHz, CDCl₃) 195.7, 176.8, 159.6, 131.8, 127.1, 117.0, 113.9, 93.7, 55.0, 42.3, 36.6, 23.8, 21.6, 18.9. HRMS (ESI-TOF): MH⁺, found 259.1322. C₁₆H₁₉O₃ requires 259.1329.

4.2.12. 2-(Phenylthio)-3-methyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (**3ah**). From 1,3-cyclohexanedione (**1a**) (0.23 g, 2.05 mmol), iodobenzene diacetate (0.64 g, 1.99 mmol) and 1(phenylthio)-1-propene (2h) (1.0 g, 6.67 mmol) in dichloromethane (10 mL), irradiated for 120 min. Purification by flash chromatography (eluant: dichloromethane/ethyl acetate 9:1) gave (E)-2-(phenylthio)-3-methyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one $(E-3ah)^{17}$ (0.26 g, 50% yield) as a colourless oil; R_f (20% EtOAc/ CH₂Cl₂) 0.56; *v*_{max} (liquid film) 3055, 2955, 1637, 1400, 1225, 1180, 900, 739 cm⁻¹. $\delta_{\rm H}$ (250 MHz, CDCl₃) 7.52–7.46 (m, 2H), 7.39–7.29 (m, 3H), 5.54 (d, J=5.4 Hz, 1H), 3.23-3.17 (m, 1H), 2.48-2.40 (m, 2H), 2.35-2.26 (m, 2H), 2.07-1.97 (m, 2H), 1.30 (d, J=6.8 Hz, 3H). δ_C (62.5 MHz, CDCl₃) 195.5, 175.9, 132.8, 131.9, 129.0, 128.0, 117.9, 98.1, 41.4, 36.4, 24.0, 21.5, 18.7. HRMS (ESI-TOF): MH⁺, found 261.0949. C₁₅H₁₇O₂S requires 261.0944 and (E)-2-(phenylthio)-3methyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one $(Z-3ah)^{17}$ (0.17 g, 33% yield) as a colourless oil; R_f (20% EtOAc/CH₂Cl₂) 0.53; ν_{max} (liquid film) 3057, 2949, 1634, 1396, 1379, 1223, 1180, 1136, 903, 739 cm⁻¹. $\delta_{\rm H}$ (250 MHz, CDCl₃) 7.51–7.49 (m, 2H), 7.39–7.29 (m, 3H), 6.09 (d, J=9.0 Hz, 1H), 3.64-3.52 (m, 1H), 2.51-2.42 (m, 2H), 2.38–2.29 (m, 2H), 2.09–1.99 (m, 2H), 1.37 (d, J=7.0 Hz, 3H). $\delta_{\rm C}$ (62.5 MHz, CDCl₃) 195.0, 175.7, 133.8, 131.3, 129.0, 127.6, 118.0, 97.2, 38.2, 36.7, 23.8, 21.5, 14.4. HRMS (ESI-TOF): MH⁺, found 261.0945. C₁₅H₁₇O₂S requires 261.0944.

4.2.13. 1,2,3,3a,5,6,7,8b-Octahydro-8H-cyclopenta[b]benzo-furan-8one (**3ai**). From 1,3-cyclohexanedione (**1a**) (0.22 g, 1.96 mmol), iodobenzene diacetate (0.64 g, 1.99 mmol) and cyclopentene **2i** (1.0 g, 14.71 mmol) in dichloromethane (10 mL), irradiated for 30 min. Purification by flash chromatography (dichloromethane/ ethyl acetate 4:1) gave 1,2,3,3a,5,6,7,8b-octahydro-8H-cyclopenta[b]benzofuran-4(5H)-one (**3ai**)(0.12 g, 34% yield) as a colourless oil; R_f (20% EtOAc/CH₂Cl₂) 0.43; ν_{max} (liquid film) 2950, 1634, 1404, 1240, 1180, 1138, 1000, 946, 922 cm⁻¹. $\delta_{\rm H}$ (250 MHz, CDCl₃) 5.13 (dd, *J*=7.5, 5.8 Hz, 1H), 3.52–3.47 (m, 1H), 2.35–2.29 (m, 2H), 2.25–2.20 (m, 2H), 1.97–1.89 (m, 3H), 1.79–1.72 (m, 1H), 1.66–1.55 (m, 3H), 1.41–1.28 (m, 1H). $\delta_{\rm C}$ (62.5 MHz, CDCl₃) 195.4, 178.1, 115.8, 91.6, 43.4, 36.4, 34.8, 31.6, 23.7, 22.9, 21.6. HRMS (ESI-TOF): MH⁺, found 179.1055. C₁₁H₁₅O₂ requires 179.1067.

4.2.14. 2,3,3*a*,6,7,8*a*-Hexahydro-furo[2,3-*b*]benzofuran-4(5H)-one (**3a***j*). From 1,3-cyclohexanedione (**1a**) (0.22 g, 1.96 mmol), iodobenzene diacetate (0.64 g, 1.99 mmol) and 2,3-dihydrofuran **2j** (1.0 g, 14.29 mmol) in dichloromethane (10 mL), irradiated for 60 min. Purification by flash chromatography (dichloromethane/ ethyl acetate 4:1) gave 2,3,3a,6,7,8a-hexahydrofuro[2,3-*b*]benzo-furan-4(5H)-one (**3a***j*)¹⁹ (0.25 g, 71% yield) as a colourless oil; *R*_f (20% EtOAc/CH₂Cl₂) 0.36; *v*_{max} (liquid film) 2952, 2882, 1634, 1406, 1244, 1086, 950, 898, 734 cm⁻¹. $\delta_{\rm H}$ (250 MHz, CDCl₃) 6.13 (d, *J*=5.9 Hz, 1H), 3.99–3.95 (m, 1H), 3.63–3.47 (m, 2H), 2.48–2.43 (m, 2H), 2.23 (t, *J*=6.5 Hz, 2H), 2.03–1.85 (m, 4H). $\delta_{\rm C}$ (62.5 MHz, CDCl₃) 194.9, 177.2, 113.3, 112.5, 67.6, 43.5, 36.3, 30.0, 23.4, 21.3. HRMS (ESI-TOF): MH⁺, found 181.0858. C₁₀H₁₃O₃ requires 181.0859.

4.2.15. 4b,6,7,8,9b,10-Hexahydro-9H-benz[b]indeno[2,1-d]-furan-9one (**3ak**). From 1,3-cyclohexanedione (**1a**) (0.22 g, 1.96 mmol), iodobenzene diacetate (0.64 g, 1.99 mmol) and indene **2k** (1.0 g, 8.62 mmol) in dichloromethane (10 mL), irradiated for 45 min. Purification by flash chromatography (dichloromethane/ethyl acetate 4:1) gave 4b,6,7,8,9b,10-hexahydro-9H-benz[b]indeno[2,1-d] furan-9-one (**3ak**) (0.24 g, 55% yield) as white crystals; mp=131–133 °C (EtOAc/hexanes). R_f (20% EtOAc/CH₂Cl₂) 0.48; ν_{max} (KBr) 3052, 2946, 1634, 1402, 1368, 1234, 1174, 1060, 988, 760 cm⁻¹. $\delta_{\rm H}$ (250 MHz, CDCl₃) 7.46–7.43 (m, 1H), 7.33–7.21 (m, 3H), 6.14 (d, *J*=8.9 Hz, 1H), 4.01–3.94 (m, 1H), 3.31 (dd, *J*=17.1, 8.3 Hz, 1H), 3.13 (dd, *J*=17.1, 2.3 Hz, 1H), 2.39–2.20 (m, 4H), 1.98–1.79 (m, 2H). $\delta_{\rm C}$ (62.5 MHz, CDCl₃) 195.5, 176.5, 143.3, 139.2, 129.7, 126.9, 125.7, 125.5, 116.6, 93.2, 41.7, 37.3, 36.5, 23.9, 21.5. HRMS (ESI-TOF): $\rm MH^+,$ found 227.1058. $\rm C_{15}H_{15}O_2$ requires 227.1067.

4.2.16. 8,9,10,11b-Tetrahydroacenaphtho[1,2-b]benzo[d]-furan-11(6bH)-one (**3a**]). From 1,3-cyclohexanedione (**1a**) (0.22 g, 1.96 mmol), iodobenzene diacetate (0.65 g, 2.02 mmol) and acenaphthylene **2l** (1.0 g, 6.58 mmol) in dichloromethane (10 mL), irradiated for 240 min. Purification by flash chromatography (dichloromethane/ethyl acetate 8:1) gave 8,9,10,11b-tetrahydroacenaphtho[1,2-b]benzo[d]furan-11(6bH)-one (**3a**]) (0.30 g, 59% yield) as brown crystals; mp=152–153 °C (EtOAc/hexanes). *R*_f (CH₂Cl₂) 0.081; ν_{max} (KBr) 3076, 2957, 2934, 1649, 1630, 1394, 1169, 1016, 791 cm⁻¹. $\delta_{\rm H}$ (250 MHz, CDCl₃) 7.83 (d, *J*=7.9 Hz, 1H), 7.77 (d, *J*=6.9 Hz, 1H), 7.70–7.49 (m, 4H), 6.57 (d, *J*=7.9 Hz, 1H), 5.17 (d, *J*=5.9 Hz, 1H), 2.51–2.22 (m, 4H), 2.10–1.88 (m, 2H). $\delta_{\rm C}$ (62.5 MHz, CDCl₃) 194.9, 177.2, 143.5, 139.9, 136.9, 131.1, 128.5, 127.6, 125.9, 123.0, 121.7, 121.5, 115.1, 90.6, 49.3, 36.4, 23.8, 21.2. HRMS (ESI-TOF): MH⁺, found 263.1075. C₁₈H₁₅O₂ requires 263.1067.

4.3. General procedure for the preparation of iodonium ylides 4

A solution of 1,3-cyclohexanedione **1** (10.00–30.00 mmol) and iodobenzene diacetate (10.00–30.00 mmol) in dichloromethane (200 mL) was stirred at room temperature for 120–180 min. The yellow solution was then washed with an aqueous 5% KOH solution (2×100 mL), water (2×50 mL) and dried (MgSO₄). The solvent was evaporated under reduced pressure (water bath below 30 °C), the solid residue triturated with hexanes (100 mL) and filtered to afford iodonium ylide **4**.

4.3.1. (2,6-Dioxocyclohexyl)phenyliodonium inner salt (**4a**). From 1,3-cyclohexanedione **1a** (3.36 g, 30.00 mmol), and iodobenzene diacetate (9.66 g, 30.00 mmol) in dichloromethane (200 mL), stirred for 2 h. Usual work-up gave (2,6-dioxocyclohexyl)phenyliodonium inner salt (**4a**) (7.33 g, 78% yield) as a white solid; mp 126–128 °C; lit.²⁶ mp 109–110 °C; ν_{max} (KBr) 3055, 2939, 1535, 1362, 1288, 1188, 964, 741 cm⁻¹. $\delta_{\rm H}$ (250 MHz, CDCl₃) 7.82–7.79 (m, 2H), 7.52–7.46 (m, 1H), 7.36–7.26 (m, 2H), 2.60–2.56 (m, 4H), 1.93–1.88 (m, 2H). $\delta_{\rm C}$ (62.5 MHz, CDCl₃) 189.4, 133.9, 131.5, 131.3, 111.3, 96.6, 37.0, 20.8. HRMS (ESI-TOF): MH⁺, found 314.9876. C₁₂H₁₂IO₂ requires 318.9878.

4.3.2. (2,6-Dioxo-4-methylcyclohexyl)phenyliodonium inner salt (**4b**). From 5-methyl-1,3-cyclohexanedione **1b** (1.26 g, 10.00 mmol) and iodobenzene diacetate (3.24 g, 10.06 mmol) in dichloromethane (100 mL), stirred for 2 h. Usual work-up gave (2,6-dioxo-4-methylcyclohexyl)phenyliodonium inner salt (**4b**) (2.80 g, 85% yield) as a white solid; mp 104–105 °C; ν_{max} (KBr) 3050, 2951, 1605, 1558, 1528, 1443, 1346, 1254, 1134, 1007, 987, 872, 744 cm⁻¹. $\delta_{\rm H}$ (250 MHz, CDCl₃) 7.74–7.70 (m, 2H), 7.43–7.37 (m, 1H), 7.28–7.21 (m, 2H), 2.58–2.52 (m, 2H), 2.24–2.08 (m, 3H), 0.95 (d, *J*=5.9 Hz, 3H). $\delta_{\rm C}$ (62.5 MHz, CDCl₃) 188.7, 133.4, 131.2, 130.9, 111.8, 96.2, 44.7, 28.1, 20.3. HRMS (ESI-TOF): MH⁺, found 329.0013. C₁₃H₁₄IO₂ requires 329.0033.

4.3.3. (2,6-Dioxo-4-phenylcyclohexyl)phenyliodonium inner salt (**4c**). From 5-phenyl-1,3-cyclohexanedione **1c** (1.88 g, 10.00 mmol) and iodobenzene diacetate (3.22 g, 10.00 mmol) in dichloromethane (200 mL), stirred for 3 h. Usual work-up gave (2,6-dioxo-4-phenylcyclohexyl)phenyliodonium inner salt (**4c**) (3.36 g, 86% yield) as a white solid; mp 126–127 °C; ν_{max} (KBr) 3055, 2939, 1605, 1528, 1470, 1439, 1350, 1288, 991, 760, 721, 698 cm⁻¹. $\delta_{\rm H}$ (250 MHz, CDCl₃) 7.86–7.82 (m, 2H), 7.57–7.50 (m, 1H), 7.40–7.22 (m, 7H), 3.46–3.34 (m, 1H), 2.91–2.85 (m, 4H). $\delta_{\rm C}$ (62.5 MHz, CDCl₃) 188.1, 142.7, 134.1, 131.7, 131.6, 128.7, 126.8, 126.7, 111.5, 95.9, 43.9, 38.8.

HRMS (ESI-TOF): MH⁺, found 391.0159. $C_{18}H_{16}IO_2$ requires 391.0189.

4.3.4. [2,6-Dioxo-4-(4-methoxyphenyl)cyclohexyl]phenyliodonium inner salt (**4d**). From 5-(4-methoxyphenyl)-1,3-cyclohexanedione **1d** (2.18 g, 10.00 mmol) and iodobenzene diacetate (3.22 g, 10.00 mmol) in dichloromethane (100 mL), stirred for 2 h. Usual work-up gave [2,6-dioxo-4-(4-methoxyphenyl)cyclohexyl]phenyl-iodonium inner salt (**4d**) (3.20 g, 76% yield) as a white solid; mp 129–131 °C; ν_{max} (KBr) 3051, 2939, 1605, 1527, 1470, 1305, 1250, 1180, 1038, 991, 829, 721 cm⁻¹. $\delta_{\rm H}$ (250 MHz, CDCl₃) 7.83–7.79 (m, 2H), 7.55–7.48 (m, 1H), 7.38–7.31 (m, 2H), 7.13 and 6.82 (AA; BB; system, 4H), 3.77 (s, 3H), 3.39–3.27 (m, 1H), 2.92–2.72 (m, 4H). $\delta_{\rm C}$ (62.5 MHz, CDCl₃) 188.0, 158.3, 134.7, 133.9, 131.6, 131.4, 127.6, 114.0, 111.6, 96.0, 55.2, 44.1, 37.9. HRMS (ESI-TOF): MNa⁺, found 421.0265. C₁₉H₁₇IO₃Na requires 421.0295.

4.3.5. (2,6-Dioxo-4,4-dimethylcyclohexyl)phenyliodonium inner salt (**4e**). From 5,5-dimethyl-1,3-cyclohexanedione (**1e**) (2.80 g, 20.00 mmol) and iodobenzene diacetate (6.40 g, 19.88 mmol) in dichloromethane (100 mL), stirred for 2 h. Usual work-up gave (2,6-dioxo-4,4-dimethylcyclohexyl)phenyliodonium inner salt (**4e**) (6.27 g, 92% yield) as a white solid; mp 129–130 °C; lit.²⁷ mp 130 °C; ν_{max} (KBr) 3052, 2930, 1519, 1352, 998, 739 cm⁻¹. $\delta_{\rm H}$ (250 MHz, CDCl₃) 7.74–7.72 (m, 2H), 7.43–7.40 (m, 1H), 7.28–7.24 (m, 2H), 2.40 (s, 4H), 0.96 (s, 6H). $\delta_{\rm C}$ (62.5 MHz, CDCl₃) 188.4, 133.8, 131.5, 131.3, 111.9, 94.5, 50.6, 31.9, 28.0. HRMS (ESI-TOF): MH⁺, found 343.0186. C₁₄H₁₆lO₂ requires 343.0189.

4.4. General procedure for the cycloaddition of iodonium ylides with alkenes

A solution of iodonium ylide **4** (1.00-4.14 mmol), and alkene **2** (4.05-145 mmol) in dichloromethane (10 mL) or acetonitrile (10 mL) was irradiated (250 W) at room temperature for 40-360 min. The solvent was evaporated under reduced pressure, and the residue was purified by flash chromatography to afford fused dihydrofuran **3**.

4.4.1. 2-Phenyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (**3aa**). From iodonium ylide **4a** (1.30 g, 4.14 mmol) and styrene **2a** (1.5 g, 14.42 mmol) in acetonitrile (10 mL), irradiated for 75 min. Purification by flash chromatography (dichloromethane/ethyl acetate 4:1) gave 2-phenyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (**3aa**) (0.59 g, 67% yield) as a colourless oil.

4.4.2. 6-Methyl-2-phenyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (**3ba**). From iodonium ylide **4b** (0.66 g, 2.01 mmol), and styrene **2a** (1.0 g, 9.62 mmol) in acetonitrile (10 mL), irradiated for 1 h. Purification by flash chromatography (dichloromethane/ethyl acetate 9:1) gave 6-methyl-2-phenyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (**3ba**) (0.27 g, 59% yield) as a colourless oil (racemic mixture).

4.4.3. 2,6-Diphenyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (**3ca**). From iodonium ylide **4c** (0.78 g, 2.00 mmol), and styrene **2a** (1.0 g, 9.62 mmol) in acetonitrile (10 mL), irradiated for 1 h. Purification by flash chromatography (dichloromethane/ethyl acetate 4:1) gave 2,6-diphenyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (**3ca**) (0.20 g, 35% yield), as white crystals (racemic mixture).

4.4.4. 6-(4-Methoxyphenyl)-2-phenyl-2,3,6,7-tetrahydrobenzo-furan-4(5H)-one (**3da**). From iodonium ylide **4d** (0.80 g, 1.90 mmol), styrene **2a** (1.0 g, 9.62 mmol) in acetonitrile (10 mL), irradiated for 2 h. Purification by flash chromatography (dichloromethane/ ethyl acetate 4:1) gave 6-(4-methoxyphenyl)-2-phenyl-2,3,6,7tetrahydrobenzofuran-4(5H)-one (3da) (0.37 g, 61% yield) as white crystals (racemic mixture).

4.4.5. 6,6-Dimethyl-2-phenyl-2,3,6,7-tetrahydrobenzofuran-4(5H)one (**3ea**). From iodonium vlide **4e** (0.68 g, 1.99 mmol), and styrene 2a (0.5 g, 4.81 mmol) in acetonitrile (10 mL), irradiated for 1 h. Purification by flash chromatography (dichloromethane/ethyl acetate gave 6.6-dimethyl-2-phenyl-2.3.6.7-tetrahydrobenzofuran-9:1) 4(5H)-one (**3ea**) (0.41 g, 85% yield) as a colourless oil.

4.4.6. 2-Ethoxy-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (**3ab**). From iodonium ylide 4a (0.60 g, 1.91 mmol) and ethyl vinyl ether 2b (10 mL) in dichloromethane (10 mL), irradiated for 120 min. Purification by flash chromatography (dichloromethane/ethyl acetate 9:1) gave 2-ethoxy-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (**3ab**) (0.30 g, 86% yield) as a colourless oil.

4.4.7. 2-Acetoxy-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (3ac). From iodonium ylide 4a (0.60 g, 1.91 mmol), and ethyl vinyl ether 2c (10 mL) in dichloromethane (10 mL), irradiated for 2 h. Purification by flash chromatography (dichloromethane/ethyl acetate 9:1) gave 2acetoxy-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (**3ac**) (0.30 g, 81% vield) as a colourless oil.

4.4.8. 2-Phenylthio-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (3ad). From iodonium ylide 4a (1.20 g, 3.82 mmol), and phenylthioethylene 2d (2.0 g, 14.71 mmol) in acetonitrile (15 mL), irradiated for 1 h. Purification by flash chromatography (dichloromethane/ ethvl acetate 9:1) gave 2-phenvlthio-2.3.6.7tetrahydrobenzofuran-4(5H)-one (3ad) (0.65 g, 71% yield) as a colourless oil.

4.4.9. 2-Methyl-2-phenyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (3ae). From iodonium ylide 4a (0.61 g, 1.94 mmol), and α -methylstyrene 2e (1.0 g, 8.47 mmol) in acetonitrile (10 mL), irradiated for 50 min. Purification by flash chromatography (dichloromethane/ethyl acetate 9:1) gave 2-methyl-2-phenyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (**3ae**) (0.28 g, 64% yield) as a colourless oil.

4.4.10. 2,2-Diphenyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (3af). From iodonium ylide 4a (0.59 g, 1.88 mmol), and 1,1diphenylethylene 2f (1.0 g, 5.56 mmol) in acetonitrile (10 mL), irradiated for 50 min. Purification by flash chromatography (dichloromethane/ethyl acetate 4:1) gave 2,2-diphenyl-2,3,6,7tetrahydrobenzofuran-4(5H)-one (**3af**) (0.33 g, 61% yield) as a colourless oil.

4.4.11. (E)-2-(4-Methoxyphenyl)-3-methyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (3ag). From iodonium ylide 4a (0.63 g, 2.01 mmol), and 0.6 g trans-anethole 2g (0.81 g, 5.47 mmol) in acetonitrile (10 mL), irradiated for 120 min. Purification by flash chromatography (dichloromethane/ethyl acetate 4:1) gave (E)-2-(4-methoxyphenyl)-3-methyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (**3ag**) (0.29 g, 56% yield) as a colourless oil.

4.4.12. 2-(Phenylthio)-3-methyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (**3ah**). From iodonium ylide **4a** (0.63 g, 2.01 mmol), and 1-(phenylthio)-1-propene (2h) (1.0 g, 6.67 mmol) in acetonitrile (10 mL), irradiated for 1 h. Purification by flash chromatography (eluant: dichloromethane/ethyl acetate 4:1) gave 2-(phenylthio)-3methyl-2,3,6,7-tetrahydrobenzofuran-4(5H)-one (3ah)(0.40 g, 77% yield) as a colourless oil (E/Z ratio=60:40).

4.4.13. 1,2,3,3a,5,6,7,8b-Octahydro-8H-cyclopenta/b]benzofuran-8one (3ai). From iodonium ylide 4a (0.63 g, 2.01 mmol), and cyclopentene 2i (1.0 g, 14.71 mmol) in acetonitrile (10 mL), irradiated for 60 min. Purification by flash chromatography (dichloromethane/ethyl acetate 4:1) gave 1,2,3,3a,5,6,7,8b-octahydro-8H-cyclopenta[b]benzofuran-4(5H)-one (**3ai**) (0.14 g, 39% yield) as a colourless oil.

4.4.14. 2,3,3a,6,7,8a-Hexahydro-furo[2,3-b]benzofuran-4(5H)-one (3aj). From iodonium ylide 4a (0.60 g, 1.91 mmol) and 2,3dihvdrofuran 2i (1.0 mL, 13.24 mmol) in acetonitrile (10 mL), irradiated for 30 min. Purification by flash chromatography (dichloromethane/ethyl acetate 4:1) gave 2,3,3a,6,7,8a-hexahydrofuro[2,3-b]benzofuran-4(5H)-one (3aj) (0.23 g, 68% yield) as a colourless oil.

4.4.15. 4b,6,7,8,9b,10-Hexahydro-9H-benz[b]indeno[2,1-d]-furan-9one (**3ak**). From iodonium ylide **4a** (2.00 g, 6.37 mmol), and indene 2k (3.0 mL) in acetonitrile (20 mL), irradiated for 105 min. Purification by flash chromatography (dichloromethane/ethyl acetate 4:1) gave 4b,6,7,8,9b,10-hexahydro-9*H*-benz[*b*]indeno[2,1-*d*]furan-9-one (**3ak**) (0.72 g, 50% yield) as white crystals.

4.4.16. 8,9,10,11b-Tetrahydroacenaphtho[1,2-b]benzo[d]furan-11(6bH)-one (**3al**). From iodonium vlide **4a** (0.60 g, 1.91 mmol), and acenaphthylene 21 (1.0 g, 5.68 mmol) in acetonitrile (10 mL), irradiated for 300 min. Purification by flash chromatography (dichloromethane/ethyl acetate 4:1) gave 8,9,10,11b-tetrahydroacenaphtho[1,2-b]benzo[d]furan-11(6bH)-one (**3al**) (0.30 g, 55% yield) as brown crystals.

4.4.17. 6.6-Dimethyl-1-phenyl-5.7-dioxaspiro[2.5]octane-4.8-dione (6). A solution of 2,2-dimethyl-1,3-dioxa-4,6-cyclohexanedione (1f) (0.29 g, 2.01 mmol), iodobenzene diacetate (0.64 g, 1.99 mmol) and styrene 2a (1.0 g, 9.62 mmol) in dichloromethane (10 mL) was irradiated at room temperature for 120 min. The solvent was evaporated under reduced pressure. Purification by flash chromatography (hexanes/ethyl acetate 4:1) gave 6,6-dimethyl-1phenyl-5,7-dioxaspiro[2.5]octane-4,8-dione (6) (0.23 g, 48% yield) as white crystals; mp=131-133 °C (EtOAc/hexanes); lit.¹³ mp 133–134 °C; R_f (CH₂Cl₂) 0.56; δ_H (250 MHz, CDCl₃) 7.32 (s, 5H), 3.43 (t, J=9.4 Hz, 1H), 2.65 (dd, J=9.4, 4.8 Hz, 1H), 2.50 (dd, J=9.4, 4.8 Hz, 1H), 1.69 (s, 6H). δ_C (62.5 MHz, CDCl₃) 167.6, 163.3, 131.1, 129.4, 128.6, 128.3, 104.8, 44.4, 33.0, 27.8, 27.5, 22.8. HRMS (ESI-TOF): MNa⁺, found 269.0774. C₁₄H₁₄O₄Na requires 269.0784.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2012.12.006. These data include MOL files and InChiKeys of the most important compounds described in this article.

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