Efficient and Stereoselective Synthesis of Bicyclo[3.2.1]octan-8-ones: Synthesis and Palladium-Catalyzed Isomerization of Functionalized 2-Vinyl-2,3,3a,4,5,6-hexahydro-2,3-benzofurans

Peter Langer,* Edith Holtz, and Nehad N. R. Saleh[a]

Dedicated to Professor Dr. Lutz F. Tietze on the occasion of his 60th birthday

Abstract: A new C,O-cyclodialkylation of dilithiated cyclic β-keto esters and β-keto sulfones with 1,4-dibromo-2-butene is reported which results in regio- and diastereoselective formation of 2-vinyl-2,3,3a,4,5,6-hexahydro-2,3-benzofurans. The products could be efficiently transformed into functionalized bicyclo[3.2.1]octan-8-ones by a palladium-catalyzed rearrangement reaction. In case of sulfone derivatives, this rearrangement proceeds with high stereospecifity to give exclusively the *endo*-configured diastereomers. The bicyclo[3.2.1]octane skeleton is present in a large number of pharmacologically important natural products.

Keywords: dianions · cyclization · diastereoselectivity · palladium · regioselectivity

Introduction

Functionalized bicyclo[3.2.1]octanes are present in a variety of pharmacologically important natural products[1] including prominent examples such as aphidicolan,[2] kaurane,[3] and stemodane diterpenes,[4] hydroazulene,[5] himachalene,[5] α-cedrane,[5] gymnomitrol, guianin, and grayanotoxin sesquiterpenes,[5] bridged steroids,[6a] and aconitine-type alkaloids.[6b] Altough a number of strategies for the synthesis of the bicyclo[3.2.1]octane skeleton already exist,[7] conceptually new methods for the construction of functionalized systems need to be developed.

In the course of our studies related to the development of domino reactions of dianions and electroneutral dianion equivalents,[8–10] we have recently reported[11] the cyclization of 1,3-dicarbonyl dianions[12] with 1,4-dibromo-2-butene.[13] These reactions allowed a regio- and diastereoselective synthesis of a variety of 2-vinyl-2,3,3a,4,5,6-hexahydro-2,3-benzofurans which were efficiently transformed into functionalized bicyclo[3.2.1]octan-8-ones by palladium-catalyzed isomerizations. Unfortunately, these isomerizations proceeded with low *endo*/*exo*-selectivities. Herein, we wish to report, in full detail, the scope and the limitations of our methodology. In addition, the improvement of the stereoselectivity by extension of our strategy to sulfone derivatives is reported.

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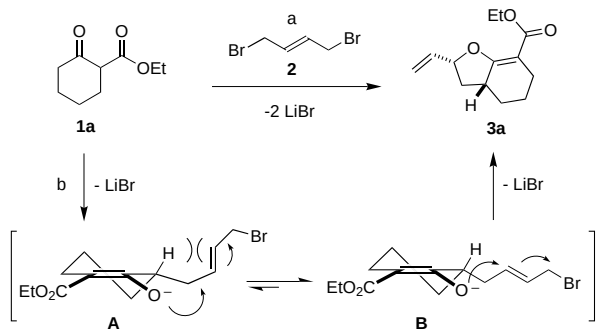
Results and Discussion

Synthesis of ester-derived 2-vinyl-hexahydro-2,3-benzofurans: The reaction of the dianion of ethyl cyclohexanone-2-carboxylate (**1a**) with dibromide **2** afforded the 2-vinyl-2,3,3a,4,5,6-hexahydro-2,3-benzofuran **3a** in good yield and with very good regio- and 1,3-diastereoselectivity.[11] The formation of **3a** can be explained by regioselective attack of the terminal carbon of the dianion onto **2** and subsequent cyclization via the neighbouring oxygen atom of the dianion (domino S_N/S_N' reaction).[14] The employment of a dianion rather than a monoanion is crucial to induce the desired regioselectivity. The 1,3-diastereoselectivity can be explained following a theory of Zhao:[13a] Transition state **A** is destabilized relative to **B**, due to a steric interaction between the tertiary hydrogen atom and the allyl group (Scheme 1). The use of 1,4-dibromo-2-butene proved mandatory as the reac-



Scheme 1. Cyclization of the dianion of **1a** with 1,4-dibromo-2-butene (**2**): a) 1) 2 equiv LDA, 2) **2**, $-78\,^{\circ}C$, THF; b) 2 equiv LDA, **2**.

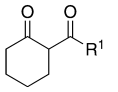
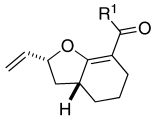
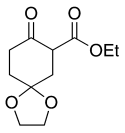
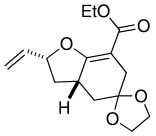
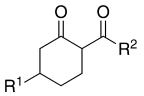
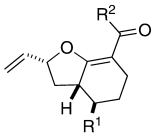
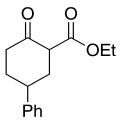
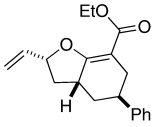
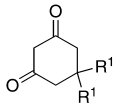
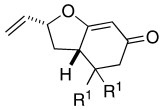
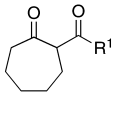
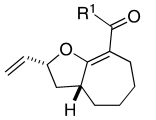
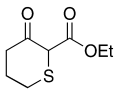
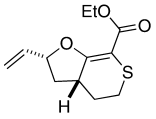
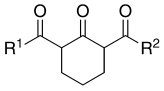
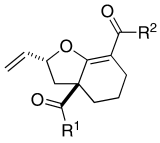
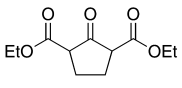
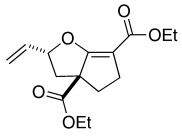
  0947-6539/02/0804-0917 $ 17.50+.50/0

tion of 1,3-dicarbonyl dianions with 1,4-dichloro-2-butene was reported to result in formation of mixtures of open-chain products in low yields.[15]

The reactions of the dianions of methyl, isopropyl and methoxyethyl cyclohexanone-2-carboxylate afforded the 2-vinylhexahydro-2,3-benzofurans **3b–d** in good yields and with very good diastereoselectivities (Table 1). Starting with cyclohexanone-2-carbaldehyde (**1e**) and amides **1f–g** the corresponding products **3e–g** were obtained. The reaction of **2** with the dianion of spiroketal **1h** afforded the 2-vinylhexahydro-2,3-benzofuran **3h**. Treatment of 1,4-dibromo-2-butene (**2**) with the dianions of ethyl 5-methylcyclohexanone-2-carboxylate (**1i**), methyl 5-ethylcyclohexanone-2-carboxylate (**1j**) and ethyl 5-butylcyclohexanone-2-carboxylate (**1k**) afforded the 2-vinylhexahydro-2,3-benzofurans **3i–k** in good yields. These reactions again proceeded with excellent diastereoselectivity. The initial attack of the dianion onto the dielectrophile proceeded with very good 1,2-diastereocontrol. The cyclization step proceeded with very good 1,3-diastereoselectivity. The stereochemical effect of a substituent at the 4-position of the cyclohexane moiety was studied next: Reaction of dibromide **2** with dilithiated ethyl 4-phenylcyclohexanone-2-carboxylate (**1l**) afforded **3l** with very good regio- and 1,3-diastereoselectivity. Starting with the dilithiated cyclohexane-1,3-dione derivatives **1m–n**, the hexahydro-2,3-benzofurans **3m–n** were prepared.

Then, the effect of the ring size on the stereoselectivity was investigated. No cyclization could be induced starting with the dianion of ethyl cyclopentanone-2-carboxylate. Reaction of 1,4-dibromo-2-butene (**2**) with the dianions of cycloheptanones **1o–p** afforded the respective 5,7-bicyclic products **3o–p** in good yields, but with only moderate stereoselectivities. Reaction of 1,4-dibromo-2-butene (**2**) with the dianion of **1q**, which represents a thio analogue of **1a**, afforded heterocycle **3q** with a diastereoselectivity of 5:1. For entropic reasons, the destabilization of intermediate **A** is less important in more flexible fused seven-membered rings or S-heterocycles than in more rigid six-membered carbacycles. Therefore, the best 1,3-diastereoselectivities were obtained for the formation of the 5,6-bicyclic products **3a–n**.

Table 1. Synthesis of 2-vinyl-hexahydro-2,3-benzofurans **3a–v**.

	1	3	R^1	R^2	Yield [%][a]	*ds*[b]
a			OEt	–	73	> 98:2
b			OMe	–	65	> 98:2
c			O(*i*Pr)	–	71	> 98:2
d			$O(CH_2)_2OMe$	–	74	> 98:2
e			H	–	33	> 98:2
f			$N(CH_2)_4$	–	23	> 98:2
g			$N(CH_2)_4O$	–	20	> 98:2
h			–	–	34	> 98:2
i			Me	OEt	71	> 98:2
j			Et	OMe	67	> 98:2
k			Bu	OMe	35	> 98:2
l			–	–	58	> 98:2
m			H	–	38	> 98:2
n			Me	–	37	> 98:2
o			OEt	–	63	70:30
p			*t*Bu	–	44	90:10
q			–	–	20	5:1
r			OEt	OEt	82[13b]	> 98:2
s			Me	OEt	27	> 98:2
t			Et	OEt	35	> 98:2
u			OEt	Ph	49 + 10[c]	> 98:2
v			–	–	78[13b]	5:1

[a] Isolated yields. [b] Diastereoselectivity in favour of the drawn isomers. [c] Separated regioisomers.

Abstract in German: *Die Cyclisierung von 1,4-Dibrom-2-buten mit dilithiierten cyclischen β-Ketoestern und β-Ketosulfonen erlaubt einen regio- und diastereoselektiven Zugang zu einer großen Vielfalt von 2-Vinyl-2,3,3a,4,5,6-hexahydro-2,3-benzofuranen. Diese Verbindungen können durch eine neuartige Palladium-katalysierte Umlagerung in Bicyclo[3.2.1]octan-8-one überführt werden. Im Falle von Sulfon-abgeleiteten Benzofuranen velaufen diese Isomerisierungen mit sehr guter Stereospezifität unter Bildung der endo-konfigurierten Diastereomere. Das Bicyclo[3.2.1]octan-Gerüst tritt in einer Reihe biologisch relevanter Naturstoffe auf.*

Our dianion methodology allows the transformation of unsymmetrical 1,3-dicarbonyl compounds into a variety of hexahydro-2,3-benzofurans containing a bridgehead hydrogen atom. Recently, the K_2CO_3-mediated cyclization of highly reactive, symmetrical 1,3,5-tricarbonyl compounds with 1,4-dibromo-2-butene (**2**) has been reported by Rodriguez and co-workers:[13b] For example, the reaction of **2** with diethyl cyclohexanone-2,6-dicarboxylate (**1r**) afforded the bicycle **3r**. Cyclizations of unsymmetrical 1,3,5-tricarbonyl compounds have to our knowledge not yet been studied. The reaction of dibromide **2** with ethyl 5-acetyl-cyclohexanone-2-carboxylate (**1s**) and ethyl 5-propionyl-cyclohexanone-2-carboxylate (**1t**)

0947-6539/02/0804-0918 $ 17.50+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 4

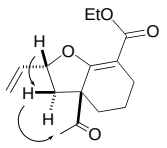
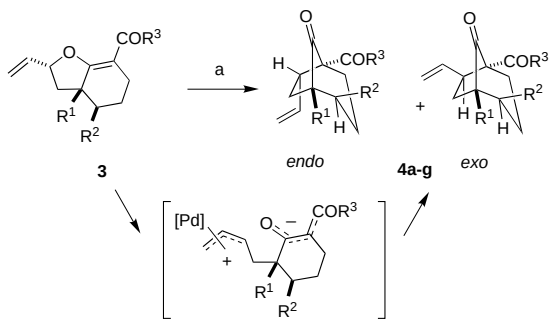


Figure 1. NOE interactions observed for the acetyl group.

diastereoselectively afforded the hexahydro-2,3-benzofurans **3s** and **3t**. The configuration of **3s** was proven by NOESY experiments. A strong NOE interaction was observed between the acetyl group and the CH- and CH_2 hydrogen atoms of the tetrahydrofuran moiety indicating that the acetyl group was located at the bridgehead position (Figure 1). The cyclization of **2** with ethyl 5-benzoyl-cyclohexanone-2-carboxylate afforded **3u**. The regioisomer containing the ester group at the bridgehead position was predominantly formed. The reaction of **2** with diethyl cyclopentanone-2,6-dicarboxylate **1v** has been reported to give the 5,5-bicyclic product **3v**.[13b]

Synthesis of ester-derived bicyclo[3.2.1]octan-8-ones: The unique functionality of 2-vinyl-hexahydro-2,3-benzofurans has been previously used for the synthesis of medium-sized rings and bicyclo[4.3.1]decan-10-ones by fragmentations[16] and thermal Claisen rearrangements,[17] respectively. Based on work by Trost[18] and others[19] related to tetrahydrofuran-derived π-allyl palladium complexes, we have developed a palladium-catalyzed rearrangement of 2-vinylhexahydro-2,3-benzofurans **3** into functionalized bicyclo[3.2.1]octan-8-ones **4**. Initial attempts to induce the desired transformation using $Pd(OAc)_2/PPh_3$ or $[Pd(PPh_3)_4]$ as the catalysts proved unsuccessful. A clean rearrangement was eventually observed when a solution of **3a** in DMSO was stirred in the presence of $[Pd(dppe)_2]$ for 6 h at 60–90 °C. The product, bicyclo[3.2.1]octan-8-one **4a**, was isolated in excellent yield as a separable *endo*/*exo* 1.2:1 mixture. The product was formed by initial ring-opening, formation of a π-allyl palladium complex[18, 19] and subsequent cyclization by nucleophilic attack of the carbon atom of the enolate onto the π-allyl palladium complex (Scheme 2, Table 2). The reaction proceeded with high regioselectivity; formation of a seven-membered ring was not observed. The low stereoselectivity can be explained by a π–σ–π isomerization of the π-allyl palladium complex.

Rearrangement of the esters **3b–d** afforded the bicyclo[3.2.1]octan-8-ones **4b–d** in high yields with very good regio-, but poor *endo*/*exo*-selectivities. The Pd-catalyzed



Scheme 2. Palladium-catalyzed rearrangement of 2-vinylhexahydro-2,3-benzofurans **3**, 5 mol% $[Pd(dppe)_2]$, DMSO, 60–90 °C, 6–24 h. dppe = 1,2-bis(diphenylphosphino)ethane.

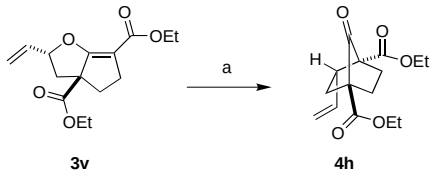
Table 2. Synthesis of bicyclo[3.2.1]octan-8-ones **4**.

4	R^1	R^2	R^3	Yield [%][a]
a	H	H	OEt	33+35
b	H	H	OMe	47+31
c	H	H	O(*i*Pr)	92
d	H	H	$O(CH_2)_2OMe$	91
e	CO_2Et	H	OEt	95
f	COMe	H	OEt	35+33
g	H	Me	OEt	34+17

[a] Isolated yields (diastereomeric mixture or separated diastereomers). The *endo*/*exo*-selectivities are in the range of 1.2:1 to 1.1:1.

rearrangement of **3r** and **3s**, with an ethoxycarbonyl and acetyl group at the bridgehead position, gave the bicyclo[3.2.1]octan-8-ones **4e** and **4f** in good yields, respectively. The hexahydro-2,3-benzofuran **3i**, containing a methyl group at the 5-position of the cyclohexane moiety, was transformed into bicyclo[3.2.1]octan-8-one **4g**. Surprisingly, no rearrangement could be induced for the ethyl and butyl substituted derivatives **3j** and **3k**, even under extended reaction times and higher temperatures.

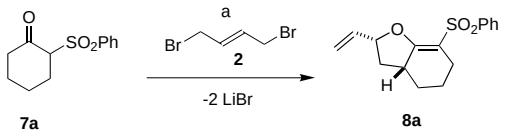
The palladium-catalyzed isomerization of 5,5-bicyclic tetrahydrofuran **3v** afforded the bicyclo[2.2.1]heptan-7-one **4h** (Scheme 3). Despite the formation of a relatively pure crude product (by ^1H NMR), the isolated yield of **4h** was relatively low (36%), presumably due to decomposition during silica gel chromatography.



Scheme 3. Synthesis of bicyclo[2.2.1]heptan-7-one (**4h**), 5 mol% $[Pd(dppe)_2]$, DMSO, 60 °C, 6 h, *endo*/*exo* = 5:1, 36%.

To improve the stereospecifity of the new palladium-catalyzed rearrangement, we envisaged that 2-vinyl-hexahydro-2,3-benzofurans containing a better leaving group should more readily form the π-allyl palladium complex. It was hoped that, if the reaction proceeds at sufficiently low temperatures, no π–σ–π isomerization would occur. Therefore, we studied the cyclization of β-ketosulfones with 1,4-dibromo-2-butene (**2**). The starting materials were prepared according to a literature procedure by reaction of lithiated cyclohexanone derivatives with diphenyldisulfide to give the corresponding thioethers **6**.[20] Oxidation of the latter with *m*CPBA afforded the corresponding sulfones **7a–h** in generally good yields.

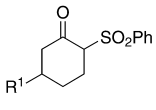
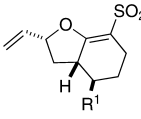
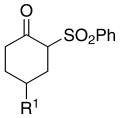
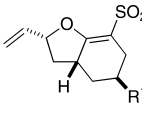
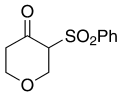
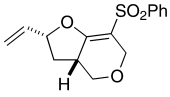
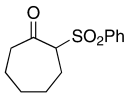
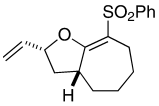
The dianion of β-ketosulfone **7a** was generated by means of two equivalents of LDA and subsequently treated with 1,4-dibromo-2-butene (**2**) to give the sulfone substituted 2-vinyl-hexahydro-2,3-benzofuran **8a** with very good regio- and 1,3-diastereoselectivity (Scheme 4). The moderate yield can be explained by the competing formation of the corresponding open-chain 2:1 product. Starting with β-ketosulfones **7b,c**, containing a methyl and a butyl group at carbon C5, the hexahydro-2,3-benzofurans **8b,c**, containing three



Scheme 4. Cyclization of dilithiated β-ketosulfone **7a** with 1,4-dibromo-2-butene (**2**), a) 1) 2 equiv LDA, 2) **2**, $-78\,^{\circ}C$, THF.

stereogenic centers, were obtained with very good regio-, 1,2- and 1,3-diastereoselectivities. Reaction of dibromide **2** with sulfones **7d**,**e**, containing a phenyl and a *tert*-butyl group at carbon C4, afforded the corresponding products **8d**,**e** with very good 1,3-diastereoselectivities (Table 3).

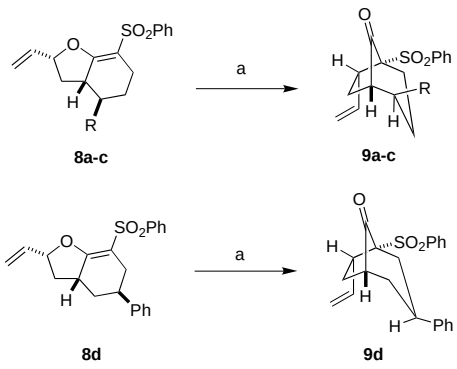
Table 3. Synthesis of 2-vinylhexahydro-2,3-benzofurans **8**.

	7	**8**	R^1	Yield [%][a]	*ds*[b]
a			H	45	> 98:2
b			Me	46	> 98:2
c			Bu	40	> 98:2
d			Ph	40	> 98:2
e			*t*Bu	32	> 98:2
f			Me	33	1:1
g			–	0	–
h			–	48	3:1

[a] Isolated yield. [b] Diastereoselectivity in favour of the isomer given.

Starting with the dianion of **7f**, hexahydro-2,3-benzofuran **8f** was obtained. In contrast to **8d**–**e**, **8f** was formed as a 1:1 diastereomeric mixture, presumably due to the low steric demand of the methyl group. The heterocyclic sulfone **7g** was prepared in two steps from pyran-4-one. Unfortunately, only starting materials could be recovered when **7g** was reacted with LDA and **2**, presumably due to the β-oxygen effect operating in the pyran system. Reaction of dibromide **2** with the dianion of sulfone **7h** resulted in formation of the 5,7-bicyclic tetrahydrofuran **8h** with very good regioselectivity. Similar to the formation of **3o**, this compound was formed with only moderate 1,3-diastereoselectivity.

Much to our satisfaction, the palladium-catalyzed rearrangement of **8a** proceeded with very good stereospecifity to give exclusively the *endo*-configured bicyclo[3.2.1]octan-8-one **9a** in very good yield (Scheme 5). The rearrangement of 2-vinyl-hexahydro-2,3-benzofurans **8b**,**c** afforded the bicyclo[3.2.1]octan-8-ones **9b**,**c** with again very good *endo*-selectivity. The isomerization of the phenyl-substituted derivative **8d** was equally successful and gave the *endo*-configured bicyclo[3.2.1]octan-8-one **9d**. Interestingly, isomerizations could be successfully induced for substrates containing relatively large substituents (**8c**, **d**, R^1 = Bu, Ph). In contrast, only starting materials were recovered in case of the corresponding ester-derived hexahydro-2,3-benzofurans **3j-l**.



Scheme 5. Palladium-catalyzed isomerizations of 2-vinylhexahydro-2,3-benzofurans **8a**–**d**, 5 mol% [Pd(dppe)$_2$], DMSO, $60\,^{\circ}C$, 24 h, *endo*/*exo* > 98:2, **9a** (R = H): 81%, **9b** (R = Me): 77%, **9c** (R = Bu): 35%, **9d** (R = Ph): 63%.

The *endo*-configuration of **9a** and **9b** was unambigiously proven by NOESY experiments. NOE interactions were observed between the vinyl group and the CH_2 groups of the cyclohexanone moiety (Figure 2).

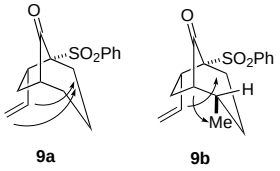


Figure 2. NOE interactions observed for the vinyl group.

In summary, the combination of our new domino S_N/S_N' reaction and the new palladium-catalyzed rearrangement constitutes a significant expansion of the methods known today for the synthesis of functionalized bicyclo[3.2.1]octanes which are of pharmacological relevance and of importance for natural product syntheses. Further studies related to the preparative scope and to applications of our methodology are in progress.

Experimental Section

General comments: All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere using oven-dried ($150\,^{\circ}C$) glassware. THF was freshly distilled from Na, CH_2Cl_2 from CaH_2. Ether refers to diethyl ether. For the ^1H and ^{13}C NMR spectra (^1H NMR: 200 or 300 MHz, ^{13}C NMR: 50 or 75 MHz) the deuterated solvents were used as indicated. The multiplicity of the ^{13}C NMR signals were determined with the DEPT 135 technique and quoted as: CH_3, CH_2, CH and C for primary, secondary, tertiary and quaternary carbon atoms. Isomer ratios were derived from suitable ^1H NMR integrals. Mass spectral data (MS) were obtained using the electron ionization (70 eV) or the chemical ionization technique (CI, H_2O). For preparative scale chromatography, silica gel (Merck, 60–200 mesh) was used. Elemental analyses were performed at the Microanalytical Laboratory of the University of Göttingen. All products were obtained as racemic materials.

Synthesis of methyl 5-ethylcyclohexanone-2-carboxylate (1i): 3-Ethylcyclohexanone (4.23 g, 33.5 mmol, 1.0 equiv) in dimethylcarbonate (25 mL) was added at $0\,^{\circ}C$ during 25 min to a suspension of sodium hydride (2.25 g, 94 mmol, 2.8 equiv) in dimethylcarbonate (50 mL). The suspension was stirred for 70 h at $20\,^{\circ}C$ and an aqueous solution of acetic acid (10%, 50 mL) was subsequently added. Ether (40 mL) was added, the organic

0947-6539/02/0804-0920 $ 17.50+.50/0 *Chem. Eur. J.* **2002**, *8*, No. 4

layer was separated and the aqueous layer was extracted with ether (2 × 40 mL). The combined organic layers were extracted with saturated solutions of brine (30 mL) and $NaHCO_3$ (60 mL), dried ($MgSO_4$), filtered, and the solvent of the filtrate was removed in vacuo. The residue was purified by chromatography (silica gel, petroleum ether/ether 50:1) to give **1i** (4.37 g, 71%) as a colourless liquid. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta =$ 0.72–0.85 (m, 1H, CH_2), 0.83 (t, $^3J = 7$ Hz, 3H; CH_2CH_3), 0.97–1.14 (m, 1H; CH, CH_2), 1.16–1.33 (m, 2H; CH_2), 1.35–1.53 (m, 1H; CH_2), 1.63–1.75 (m, 1H; CH_2), 1.74–1.89 (m, 1H; CH_2), 1.93–2.12 (m, 1H; CH_2), 2.18–2.32 (m, 1H; CH_2), 3.66 (s, 3H; O-CH_3), 12.02 (s, 1H; OH); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 10.98$ (CH_3), 21.82, 28.03, 28.43, 34.93 (CH_2), 34.79 (CH), 50.91 (OCH_3), 96.95 (C-2), 171.57, 172.65 (C-1, CO_2Me); MS (EI, 70 eV): *m*/*z* (%): 184 (1) $[M]^+$, 155 (50), 152 (100), 124 (47), 95 (45), 67 (41).

Synthesis of ethyl cyclohexanone-2-carboxylate (1h): Cyclohexane-1,4-dione-monoethyleneketal (1.90 g, 12.2 mmol) was dissolved in diethylcarbonate (10 mL) and added during 15 min at 0 °C to a suspension of sodium hydride (900 mg, 37.5 mmol, 3.08 equiv) in diethylcarbonat (18 mL). The suspension was stirred for 90 h, an aqueous solution of acetic acid (10%, 28 mL) was added and the organic layer was separated. The aqueous layer was extracted with ether (3 × 20 mL), and the combined organic layers were extracted with saturated aqueous solutions of brine (7 mL) and $NaHCO_3$ (22 mL), dried ($MgSO_4$), filtered, and the solvent of the filtrate was removed in vacuo. The residue was purified by chromatography (petroleum ether/ether 10:1) to give **1h** (1.49 g, 54%, keto–enol tautomers) as a colourless liquid. ^{1}H NMR (250 MHz, $CDCl_3$, enol): $\delta = 1.25$ (t, $^3J = 7$ Hz, 3H; CH_3), 1.80 (t, $^3J = 7$ Hz, 2H; CH_2), 2.43 (s, 2H; CH_2), partly overlapped by 2.45 (t, $^3J = 7$ Hz, 2H; CH_2), 3.90–4.00 (m, 4H; O-CH_2, acetal), 4.16 (q, $^3J = 7$ Hz, 2H; O-CH_2, ester), 12.20 (s, 1H; OH); ^{13}C NMR (62.9 MHz, $CDCl_3$, enol): $\delta = 14.13$ (CH_3), 27.77, 30.15, 32.60 (CH_2), 60.27 (O-CH_2, ester), 64.45 (O-CH_2, acetal, 2C), 95.17 (C, O-C=*C*), 107.11 (C, O-C-O), 170.90, 172.01 (C, CO, O-*C*=C); MS (EI, 70 eV): *m*/*z* (%): 228 (35) $[M]^+$, 140 (25), 99 (37), 86 (100); HR-MS (EI, 70 eV): calcd for $C_{11}H_{16}O_5$; found: 228.0997 ± 2 mD $[M]^+$; elemental analysis calcd (%) for $C_{11}H_{16}O_5$: C 57.89, H 7.07; found: C 58.13, H 6.83.

Synthesis of 2-methoxyethyl cyclohexanone-2-carboxylate (1d): $Ti(OiPr)_4$ (3.0 mL, 10.1 mmol) was added to a solution of ethyl cyclohexanone-2-carboxylate (2.016 g, 11.8 mmol) in 2-methoxyethanol (86 mL) and the solution was heated under reflux for 14 h. After cooling to ambient a dilute aqueous solution of HCl (50 mL, 1M) was added and the layers were separated. The aqueous layer was extracted with petroleum ether (2 × 150 mL) and the combined organic layers were extracted with a saturated aqueous solution of $NaHCO_3$ (30 mL), dried ($MgSO_4$) and filtered. The solvent and 2-methoxyethanol were removed in vacuo at 60 °C. The residue was purified by chromatography to give a yellowish liquid (1.19 g, 50%). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.54–1.76$ (m, 4H; CH_2), 2.09–2.20 (m, 1H; CH_2), 2.21–2.33 (m, 2H; CH_2), 2.33–2.43 (m, 1H; CH_2), 2.44–2.57 (m, 1H; CH), 3.40 (s, 3H; OCH_3), 3.64, 4.30 (2 × dd, $^3J = 6$, $^3J = 5$ Hz, 2 × 2H; CH_2O); ^{13}C NMR (50.3 MHz, $CDCl_3$, keto-enol-tautomers): $\delta = 21.72$, 22.18, 22.21, 23.18, 26.97, 28.94, 29.81 (CH_2), 41.40 (O=CCH_2), 56.95 (CH), 58.73, 58.85 (OCH_3), 63.08, 63.74, 70.15, 70.32 (CH_2O), 87.43 (C-2), 169.83, 172.21, 172.34 (CO_2, C-1, enol), 205.86 (C-1, ketone); MS (EI, 70 eV): *m*/*z* (%): 200 (11) $[M]^+$, 125 (51), 124 (54), 68 (100), 59 (74), 55 (56), 45 (54), 43 (44), 41 (80).

Synthesis of isopropyl cyclohexanone-2-carboxylate (1c): The synthesis was effected following the preceding procedure. Starting with ethyl cyclohexanone-2-carboxylate (2.02 g, 11.8 mmol), 2-propanol (86 mL) and $Ti(OiPr)_4$ (3.0 mL), **1c** was isolated as an orange oil (877 mg, 40%). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.19–1.37$ (m, 6H; CH_3), 1.54–1.77 (m, 4H; CH_2), 2.15–2.34 (m, 4H; CH_2), 4.13–4.28 (m, 1H; O-CH), 5.00–5.16 (m, 1H; CH); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 21.63$, 21.84 (CH_3), 21.87, 22.33, 23.14, 27.03, 29.00, 29.85 (CH_2), 41.43 (O=CCH_2), 57.19 (CH), 67.35, 68.44 (O-CH), 97.90 (C-2), 169.43, 171.68, 172.27 (CO_2, C-1, enol), 206.26 (C-1, ketone); MS (EI, 70 eV): *m*/*z* (%): 184 (22) $[M]^+$, 142 (38), 125 (32), 124 (100).

Synthesis of cyclohexanone-2-carboxylic amides: The amides **1f,g** were prepared according to a literature procedure in 34–48% yields.[21]

Cyclohexanone-2-carboxylic pyrrolidide (1f): ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.54–1.76$ (m, 2H; CH_2), 1.76–2.15 (m, 7H; CH_2), 2.15–2.42 (m, 2H; CH_2), 2.52–2.69 (m, 1H; CH_2), 3.28–3.64 (m, 5H; CH, NCH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 22.66$, 23.46, 25.21, 26.29, 29.12 (CH_2), 41.16, 44.99, 45.56 (O=C-CH_2, NCH_2), 55.33 (CH), 167.18 (C=O, amide), 206.60 (C=O, ketone); MS (EI, 70 eV): *m*/*z* (%): 195 (54) $[M]^+$, 126 (44), 122 (87), 121 (100), 70 (88).

Cyclohexanone-2-carboxylic morpholide (1g): ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.58–1.93$ (m, 2H; CH_2), 1.93–2.41 (m, 5H; CH_2), 2.54 (dt, $J = 15$, $J = 6$ Hz, 1H; CH_2), 3.31 (t, $J = 6$ Hz, 2H; NCH_2), 3.42–3.60 (m, 2H; NCH_2), 3.60–3.76 (m, 4H; OCH_2), 3.76–3.10 (m, 1H; CH); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 23.55$, 27.01, 30.11 (CH_2), 41.90 (CH_2, O=C-*C*H_2), 42.24, 46.21 (NCH_2), 54.05 (CH), 66.54, 66.76 (OCH_2), 167.96 (C=O, amide), 207.22 (C=O, ketone); MS (EI, 70 eV): *m*/*z* (%): 211 (100) $[M]^+$, 86 (85).

General procedure for the synthesis of 2-alkylidene-5-vinyltetrahydrofurans (3): A solution of LDA (4.7 mmol) in THF was prepared by addition of *n*BuLi (2 mL, 2.35M, in *n*-hexane) to a solution of diisopropylamine (0.65 mL) in THF (40 mL). The solution was stirred for 20 min at 0 °C and subsequently ethyl cyclohexanone-2-carboxylate (340 mg, 2 mmol) was added at 0 °C. The solution was stirred for 60 min and subsequently a solution of 1,4-dibromo-2-butene (**2**; 471 mg, 2.2 mmol) in THF (5 mL) was added at −78 °C. The application of an inverse addition protocol was possible. The temperature was allowed to increase during 4 h to 20 °C and the solution was stirred at 20 °C for 2 h. The solution was poured into an aqueous solution of HCl (0.1M) and the aqueous layer was extracted with ether. The combined organic layers were dried ($MgSO_4$), filtered and the solvent of the filtrate was removed in vacuo. The residue was purified by chromatography (silica gel, ether/petroleum ether 1:10 → 1:3) to give **3a** as a colourless oil.

7-Ethyloxycarbonyl-2-vinyl-2,3,3a,4,5,6-hexahydro-2,3-benzofuran (3a): Starting with ethyl cyclohexanone-2-carboxylate (340 mg, 2 mmol), diisopropylamine (0.65 mL, 4.6 mmol), *n*BuLi (2.0 mL, 4.6 mmol, in *n*-hexane) and 1,4-dibromo-2-butene (**2**; 471 mg, 2.2 mmol), **3a** was isolated as a colourless oil (325 mg, 73%, *ds* > 98:2). The purification was effected by chromatography (silica gel, petroleum ether/ether 4:1). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.14–1.28$ (m, 1H; CH_2), partly overlapped by 1.22 (t, $^3J = 6$ Hz, 3H; CH_3), 1.28–1.49 (m, 2H; CH_2), 1.73–1.85 (m, 1H; CH_2), 1.86–2.10 (m, 1H; CH_2), 2.12–2.32 (m, 3H; CH_2), 2.52–2.69 (m, 1H; 3a-H), 4.14 (q, $^3J = 6$ Hz, 2H; CH_2), 4.68 (ddd, $^3J = {}^3J = {}^3J = 5$ Hz, 1H; 2-H), 5.17 [d, $^3J(Z) = 10$ Hz, 1H; HC=CH_2], 5.34 [d, $^3J(E) = 15$ Hz, 1H; HC=CH_2], 5.78 [ddd, $^3J = 5$, $^3J(Z) = 10$, $^3J(E) = 15$ Hz, 1H; *H*C=CH_2]; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 13.92$ (CH_3), 21.73, 23.49, 26.98, 36.78 (CH_2), 41.25 (C-3a), 58.80 (O-CH_2), 82.93 (C-2), 96.25 (C, O-C=*C*), 116.60 (CH=*C*H_2), 135.80 (*C*H=CH_2), 166.37, 166.99 (C, CO, O-*C*=C); MS (EI, 70 eV): *m*/*z* (%): 222 (36) $[M]^+$, 177 (35), 168 (100), 122 (71), 55 (40), 46 (46), 41 (38); HR-MS (EI, 70 eV): calcd for $C_{13}H_{18}O_3$; found: 222.1256 ± 2 mD $[M]^+$.

7-Methyloxycarbonyl-2-vinyl-2,3,3a,4,5,6-hexahydro-2,3-benzofuran (3b): Starting with methyl cyclohexanone-2-carboxylate (938 mg, 6.0 mmol), diisopropylamine (2.0 mL, 13.8 mmol), *n*BuLi (6.0 mL, 13.8 mmol, in *n*-hexane) and 1,4-dibromo-2-butene (**2**; 1.41 g, 6.6 mmol), **3b** was isolated as yellow crystals (811 mg, 65%, *ds* > 98:2). The purification was effected by chromatography (silica gel, petroleum ether/ether 5:1). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.05–1.20$ (m, 1H; CH_2), 1.23–1.37 (m, 2H; CH_2), 1.75–2.00 (m, 2H; CH_2), 2.05–2.29 (m, 3H; CH_2), 2.50–2.65 (m, 1H; CH), 3.55 (O-CH_3), 4.65 (ddd, $^3J = {}^3J = 5$, $^3J = 7$ Hz, 1H; O-CH), 5.07 (d, $^3J(Z) = 10$ Hz, 1H; H-*H*C=CH), 5.26 (d, $^3J(E) = 17$ Hz, 1H; *H*-HC=CH), 5.77 (ddd, $^3J = 7$, $^3J(Z) = 10$, $^3J(E) = 17$ Hz, 1H; C*H*=CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 21.80$, 23.63, 27.07, 36.84 (CH_2), 41.35 (CH), 50.47 (O-CH_3), 83.28 (O-CH), 96.12 (C, O-C=*C*), 117.18 (CH=*C*H_2), 135.84 (*C*H=CH_2), 166.95, 167.21 (C, CO, O-*C*=C); MS (EI, 70 eV): *m*/*z* (%): 208 (37) $[M]^+$, 177 (27), 154 (100), 122 (59); HR-MS (EI, 70 eV): calcd for $C_{12}H_{16}O_3$; found: 208.1099 ± 2 mD $[M]^+$.

7-Isopropyloxycarbonyl-2-vinyl-2,3,3a,4,5,6-hexahydro-2,3-benzofuran (3c): Starting with isopropyl cyclohexanone-2-carboxylate (533 mg, 2.89 mmol), diisopropylamine (0.97 mL, 6.9 mmol), *n*BuLi (4.48 mL, 6.9 mmol, in *n*-hexane) and 1,4-dibromo-2-butene (**2**; 708 mg, 3.3 mmol), **3c** was isolated as a colourless oil (486 mg, 71%, *ds* > 98:2). The purification was effected by chromatography (silica gel, petroleum ether/ether 5:1). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.25$ (d, $^3J = 6$ Hz, 6H, CH_3), partly overlapped by 1.26–1.56 (m, 3H; CH_2), 1.84–2.14 (m, 2H; CH_2), 2.16–2.45 (m, 3H; CH_2), 2.60–2.81 (m, 1H; 3a-H), 4.74–4.86 (m, 1H; 2-H), 5.07 [sept, $^3J = 6$ Hz, 1H; OC*H*(CH_3)$_2$], 5.21 [d, $^3J(Z) = 11$ Hz, 1H;

HC=CH_2], 5.40 [d, $^3J(E) = 17$ Hz, 1H; HC=CH_2], 5.92 [ddd, $^3J = 6$, $^3J(Z) = 11$, $^3J(E) = 17$ Hz, 1H; *H*C=CH$_2$]; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 21.30$ (CH_3), 21.53, 23.26, 26.75, 36.59 (CH_2), 40.99 (C-3a), 65.44 [OC*H*(CH_3)$_2$], 82.49 (C-2), 96.24 (C-7), 116.27 (C=*C*H$_2$), 135.66 (C=*C*H-C), 165.57 (C=O), 166.62 (O-*C*=C); MS (EI, 70 eV): *m*/*z* (%): 236 (44) $[M]^+$, 182 (46), 177 (54), 150 (30), 140 (100), 122 (39); HR-MS (EI, 70 eV): calcd for $C_{14}H_{20}O_3$; found: 236.1412 ± 2 mD $[M]^+$.

7-(2-Methoxyethyloxycarbonyl)-2-vinyl-2,3,3a,4,5,6-hexahydro-2,3-benzofuran (3d): Starting with 2-methoxyethyl cyclohexanone-2-carboxylate (802 mg, 4 mmol), diisopropylamine (1.3 mL, 9.2 mmol), *n*BuLi (6.0 mL, 9.2 mmol, in *n*-hexane) and 1,4-dibromo-2-butene (**2**; 940 mg, 4.4 mmol), **3d** was isolated as a yellow oil (745 mg, 74%, *ds* > 98:2). The purification was effected by chromatography (silica gel, petroleum ether/ether 2:1). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.96 - 1.61$ (m, 3H; CH_2), 1.69 – 2.01 (m, 2H; CH_2), 2.01 – 2.38 (m, 3H; CH_2), 2.44 – 2.68 (m, 1H; 3a-H), 3.22 (s, 3H; CH_3), 3.46 (t, $^3J = 5$ Hz, 2H; CH_3OCH_2), 4.02 (dt, $^3J = 5$, $^2J = 13$ Hz, 1H; CH_2OC=O), 4.15 (dt, $^3J = 5$, $^2J = 13$ Hz, 1H; CH_2OC=O), 4.57 – 4.70 (m, 1H; 2-H), 5.05 [d, $^3J(Z) = 11$ Hz, 1H; HC=CH_2], 5.26 (d, $^3J(E) = 17$ Hz, 1H; HC=CH_2], 5.75 (ddd, $^3J = 6$, $^3J(Z) = 11$, $^3J(E) = 17$ Hz, 1H; *H*C=CH$_2$); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 22.07$, 23.80, 27.29, 37.11 (CH_2), 41.69 (CH, C-3a), 58.78 (CH_3), 62.62 (CH_2, CH_3OCH_2), 70.53 (CH_2, CH_2OC=O), 83.41 (C-2), 96.27 (C-7), 117.10 (C=*C*H$_2$), 136.12 (C=*C*H-C), 166.58 (C=O), 167.90 (O-*C*=C); MS (EI, 70 eV): *m*/*z* (%): 252 (48) $[M]^+$, 198 (69), 194 (45), 177 (100), 140 (62), 122 (56), 59 (49); HR-MS (EI, 70 eV): calcd for $C_{14}H_{20}O_4$; found: 252.1362 ± 2 mD $[M]^+$.

7-Formyl-2-vinyl-2,3,3a,4,5,6-hexahydro-2,3-benzofuran (3e): Starting with 2-hydroxymethylidene-cyclohexanone (374 mg, 2.96 mmol), diisopropylamine (0.91 mL, 6.4 mmol), *n*BuLi (6.4 mmol, in *n*-hexane) and 1,4-dibromo-2-butene (**2**; 700 mg, 3.27 mmol), **3e** was isolated as a colourless oil (175 mg, 33%, *ds* > 98:2). The purification was effected by chromatography (silica gel, petroleum ether/ether 10:1). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.06 - 1.30$ (m, 1H; CH_2), 1.30 – 1.58 (m, 2H; CH_2), 1.80 – 2.18 (m, 3H; CH_2), 2.18 – 2.55 (m, 2H; CH_2), 2.64 – 2.87 (m, 1H; CH), 4.78 (dt, $^2J = {}^2J = 6$ Hz, 1H; O-CH), 5.23 [d, $^3J(Z) = 11$ Hz, 1H; HC=CH_2], 5.35 [d, $^3J(E) = 18$ Hz, 1H; HC=CH_2], 5.88 [ddd, $^3J = 6$, $^3J(Z) = 11$, $^3J(E) = 18$ Hz, 1H; *H*C=CH$_2$], 10.00 (s, 1H; O=CH); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 19.76$, 21.19, 27.19, 37.01 (CH_2), 41.39 (C-3a), 84.55 (C-2), 108.80 (C, C-7), 118.28 (CH=*C*H$_2$), 135.66 (*C*H=CH$_2$), 174.95 (C, O-*C*=C), 188.50 (O=CH); MS (EI, 70 eV): *m*/*z* (%): 178 (10) $[M]^+$, 151 (82), 126 (78); HR-MS (EI, 70 eV): calcd for $C_{11}H_{14}O_2$; found: 178.0994 ± 2 mD $[M]^+$.

2-Vinyl-2,3,3a,4,5,6-hexahydro-2,3-benzofuran-7-carboxylic *N*-pyrrolidide (3f): Starting with cyclohexanone-2-carboxylic pyrrolidide (398 mg, 2.04 mmol), diisopropylamine (0.64 mL, 4.5 mmol), *n*BuLi (4.6 mmol, in *n*-hexane) and 1,4-dibromo-2-butene (**2**; 476 mg, 2.2 mmol), **3f** was isolated as a yellow oil (117 mg, 23%, *ds* > 98:2). The purification was effected by chromatography (silica gel, acetone/ether 1:11). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.94 - 1.45$ (m, 4H; CH_2), 1.45 – 1.98 (m, 5H; CH_2), 1.98 – 2.28 (m, 3H; CH_2), 2.31 – 2.54 (m, 1H; 3a-H), 3.06 – 3.46 (m, 4H; NCH_2), 4.32 – 4.52 (m, 1H; 2-H), 4.99 [d, $^3J(Z) = 11$ Hz, 1H; HC=CH_2], 5.12 [d, $^3J(E) = 19$ Hz, 1H; HC=CH_2], 5.63 [ddd, $^3J = 7$, $^3J(Z) = 11$, $^3J(E) = 19$ Hz, 1H; *H*C=CH$_2$]; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 22.05$, 24.30, 24.60, 25.68, 27.80, 38.07 (CH_2), 39.12 (C-3a), 45.16, 46.85 (NCH_2), 82.08 (CH, C=C-O-*C*H), 101.01 (C, C=*C*-C=O), 117.00 (C=*C*H$_2$), 137.08 (C=*C*H-C), 154.97, 168.80 (C, C=O, O-*C*=C); MS (EI, 70 eV): *m*/*z* (%): 247 (30) $[M]^+$, 193 (94), 177 (100), 70 (21); HR-MS (EI, 70 eV): calcd for $C_{15}H_{21}O_2N$; found: 247.1572 ± 2 mD $[M]^+$.

2-Vinyl-2,3,3a,4,5,6-hexahydro-2,3-benzofuran-7-carboxylic *N*-morpholide (3g): Starting with cyclohexanone-2-carboxylic *N*-morpholide (1.26 g, 6.0 mmol), diisopropylamine (1.93 mL, 13.6 mmol), *n*BuLi (8.97 mL, 13.8 mmol, in *n*-hexane) and 1,4-dibromo-2-butene (**2**; 1.41g, 6.6 mmol), **3g** (314 mg, 20%) was isolated as a slightly yellow oil. The purification was effected by chromatography (silica gel, ether). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.97 - 1.52$ (m, 3H; CH_2), 1.73 – 2.60 (m, 6H; CH_2, CH), 3.23 – 3.83 (m, 8H; NCH_2, OCH_2), 4.29 – 4.56 (m, 1H; 2-H), 5.06 [d, $^3J(Z) = 10$ Hz, 1H; HC=CH_2], 5.19 [d, $^3J(E) = 16$ Hz, 1H; HC=CH_2], 5.57 – 5.77 (m, 1H; H_2C=C*H*); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 21.84$, 24.56, 27.48, 37.77 (CH_2), 39.00 (C-3a), 41.85, 47.41 (NCH_2), 66.66, 67.41 (OCH_2), 82.05 (C-2), 98.23 (C-7), 117.14 (CH=*C*H$_2$), 136.55 (*C*H=CH$_2$), 155.15, 168.72 (C, O-*C*=C, C=O); MS (EI, 70 eV): *m*/*z* (%): 263 (21) $[M]^+$, 209 (47), 177 (75), 58 (40), 43 (100); HR-MS (EI, 70 eV): calcd for $C_{15}H_{21}O_3N$; found: 263.1521 ± 2 mD $[M]^+$.

7-Ethoxycarbonyl-2-vinyl-2,3,3a,4,5,6-hexahydro-2,3-benzofuran (3h): Starting with **1h** (1.16 g, 5.1 mmol), diisopropylamine (2.0 mL, 13.8 mmol), *n*BuLi (13.8 mmol, 6.0 mL, in *n*-hexane) and 1,4-dibromo-2-butene (**2**; 1.19 mg, 5.5 mmol), **3h** (487 mg, 34%) was isolated as slightly yellow needles. The purification was effected by chromatography (silica gel, petroleum ether/ether 1:2). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.26$ (t, $^3J = 7$ Hz, 3H; CH_3), 1.40 – 1.70 (m, 2H; CH_2), 2.04 (dd, $^3J_1 = 12$, $^3J_2 = 5$ Hz, 1H; CH_2), 2.34 (ddd, $^3J_1 = 12$, $^3J_2 = 7$, $^3J_3 = 5$ Hz, 1H; CH_2), 2.55 (s, 2H, O-C=C-CH_2), 3.05 – 3.20 (m, 1H; CH), 3.85 – 4.05 (m, 4H; O-CH_2, acetal), partly overlapped by 4.00 – 4.25 (m, 1H; O-CH_2, ester), 4.87 (ddd, $^3J_1 = 11$, $^3J_2 = 6$, $^3J_3 = 5$ Hz, 1H; O-CH), 5.23 (d, $^3J(Z) = 10$ Hz, 1H; H-*H*C=CH), 5.41 (d, $^3J(E) = 17$ Hz, 1H; *H*-HC=CH), 5.93 (ddd, $^3J = 6$, $^3J(Z) = 10$, $^3J(E) = 17$ Hz, 1H; C*H*=CH$_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 14.39$ (CH_3), 34.75, 36.36, 36.92 (CH_2), 40.31 (CH), 59.65 (O-CH_2, ester), 64.34, 64.64 (O-CH_2, acetal), 84.74 (O-CH), 94.43 (C, O-C=*C*), 107.95 (C, O-C-O), 117.68 (CH=*C*H$_2$), 135.84 (*C*H=CH$_2$), 166.12, 166.88 (C, CO, O-*C*=C); MS (EI, 70 eV): *m*/*z* (%): 280 (100) $[M]^+$, 235 (46), 194 (63), 148 (60), 127 (50), 120 (46), 99 (45), 87 (79), 86 (57); HR-MS (EI, 70 eV): calcd for $C_{15}H_{20}O_5$; found: 280.1310 ± 2 mD $[M]^+$.

7-Ethoxycarbonyl-4-methyl-2-vinyl-2,3,3a,4,5,6-hexahydro-2,3-benzofuran (3i): Starting with ethyl 5-methylcyclohexanone-2-carboxylate (368 mg, 2.0 mmol), diisopropylamine (0.65 mL, 4.6 mmol), *n*BuLi (4.6 mmol, in *n*-hexane) and 1,4-dibromo-2-butene (**2**; 471 mg, 2.2 mmol), **3i** (338 mg, 71%) was isolated as slightly yellow needles. The purification was effected by chromatography (silica gel, petroleum ether/ether 5:1). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.03$ (d, $^3J = 6$ Hz, 3H; CH_3), 1.18 (d, $^3J = 13$ Hz, 1H; CH), 1.21 – 1.48 (m, 2H; CH_2), partly overlapped by 1.28 (t, $^3J = 7$ Hz, 3H; CH_3), 1.82 (ddt, $^3J = 6$, $^3J = 13$, $^3J = 2$ Hz, 1H; CH), 2.21 – 2.48 (m, 4H; 3a-H, CH_2), 4.06 – 4.31 (m, 2H; OCH_2), 4.80 (ddd, $^3J = {}^3J = {}^3J = 6$ Hz, 1H; 2-H), 5.22 [d, $^3J(Z) = 11$ Hz, 1H; HC=CH_2], 5.40 [d, $^3J(E) = 18$ Hz, 1H; HC=CH_2], 5.92 [ddd, $^3J = 6$, $^3J(Z) = 11$, $^3J(E) = 18$ Hz, 1H; *H*C=CH$_2$]; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 14.16$, 20.00 (CH_3), 24.03, 30.80, 35.79 (CH_2), 33.84, 48.44 (CH), 59.17 (OCH_2), 83.44 (C-2), 96.33 (C-7), 116.96 (CH=*C*H$_2$), 136.02 (*C*H=CH$_2$), 166.60, 166.71 (C, CO, O-*C*=C); MS (EI, 70 eV): *m*/*z* (%): 236 (60) $[M]^+$, 191 (54), 182 (100), 167 (81), 136 (66); HR-MS (EI, 70 eV): calcd for $C_{14}H_{20}O_3$; found: 236.1412 ± 2 mD $[M]^+$.

4-Ethyl-7-methoxycarbonyl-2-vinyl-2,3,3a,4,5,6-hexahydro-2,3-benzofuran (3j): Starting with methyl 5-ethylcyclohexanone-2-carboxylate (745 mg, 4.0 mmol), diisopropylamine (1.30 mL, 9.2 mmol), *n*BuLi (9.2 mmol, in *n*-hexane) and 1,4-dibromo-2-butene (**2**; 945 mg, 4.4 mmol), **3j** (642 mg, 67%) was isolated as a slight yellow viscous oil. The purification was effected by chromatography (silica gel, petroleum ether/ether 5:1). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.94$ (t, $^3J = 7$ Hz, 3H; CH_3), 1.04 – 1.49 (m, 4H; CH_2), 1.49 – 1.69 (m, 2H; CH_2), 1.95 (dd, $^3J = 6$, $^3J = 13$ Hz, 1H; CH_2), 2.18 – 2.53 (m, 3H; CH, CH_2), 3.71 (s, 3H; OCH_3), 4.73 – 4.86 (m, 1H; 2-H), 5.23 [d, $^3J(Z) = 11$ Hz, 1H; HC=CH_2], 5.40 [d, $^3J(E) = 17$ Hz, 1H; HC=CH_2], 5.92 [ddd, $^3J = 6$, $^3J(Z) = 11$, $^3J(E) = 17$ Hz, 1H; *H*C=CH$_2$]; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 10.40$ (CH_3), 23.93, 26.69, 26.92, 35.72 (CH_2), 40.02, 46.68 (CH), 50.40 (OCH_3), 83.47 (CH, C=C-O-*C*H), 95.88 (C, C=*C*-C=O), 117.03 (C=*C*H$_2$), 135.85 (C=*C*H-C), 166.77, 166.86 (C, CO, O-*C*=C); MS (EI, 70 eV): *m*/*z* (%): 236 (19) $[M]^+$, 153 (100); HR-MS (EI, 70 eV): calcd for $C_{14}H_{20}O_3$; found: 236.1412 ± 2 mD $[M]^+$.

4-Butyl-7-methoxycarbonyl-2-vinyl-2,3,3a,4,5,6-hexahydro-2,3-benzofuran (3k): Starting with ethyl 5-butylcyclohexanone-2-carboxylate (849 mg, 4.0 mmol), diisopropylamine (1.30 mL, 9.2 mmol), *n*BuLi (9.2 mmol, in *n*-hexane) and 1,4-dibromo-2-butene (**2**; 945 mg, 4.4 mmol), **3k** (370 mg, 35%) was isolated as a slightly yellow viscous oil. The purification was effected by chromatography (silica gel, petroleum ether/ether 5:1). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.89$ (t, $^3J = 6$ Hz, 3H; CH_3), 1.04 – 1.51 (m, 5H; CH, CH_2), 1.95 (dd, $J = 6$, $J = 12$ Hz, 2H; CH_2), 2.15 – 2.48 (m, 7H, CH; CH_2), 3.72 (s, 3H, OCH_3), 4.79 (m, 1H; 2-H), 5.23 [dd, $^2J = 1$, $^3J(Z) = 10$ Hz, 1H; HC=CH_2], 5.34 (dd, 1H; $^2J = 1$, $^3J(E) = 17$ Hz, HC=CH_2), 5.92 (ddd, $^3J = 6$, $^3J(Z) = 10$, $^3J(E) = 17$ Hz, 1H; H_2C=C*H*]; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 13.82$ (CH_3), 22.76, 24.21, 27.79, 28.46, 34.13, 36.04 (CH_2), 38.79, 47.30 (CH), 50.73 (OCH_3), 83.73 (C-2), 96.26 (C, C-7), 117.41 (H_2C=CH), 136.08 (H_2C=*C*H), 166.94, 167.20 (C=O, O-*C*=C); MS (EI, 70 eV): *m*/*z* (%): 264 (27) $[M]^+$, 210 (17), 154 (23), 153 (100); HR-MS (EI, 70 eV): calcd for $C_{16}H_{24}O_3$; found: 264.1725 ± 2 mD $[M]^+$.

7-Ethyloxycarbonyl-5-phenyl-2-vinyl-2,3,3a,4,5,6-hexahydrobenzo[*b*]furan (3l): Starting with ethyl 4-phenylcyclohexanone-2-carboxylate (550 mg, 2.0 mmol), diisopropylamine (0.65 mL, 4.6 mmol), *n*BuLi (4.6 mmol,

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2.0 mL, in *n*-hexane) and 1,4-dibromo-2-butene (**2**; 473 mg, 2.2 mmol), **3l** (358 mg, 58%) was isolated by chromatography (petroleum ether/ether 2:1) as a colourless solid. ^{1}H NMR (250 MHz, CD_3OD): $\delta = 1.23$ (t, $^3J = 7$ Hz, 3H; CH_3), 1.35–1.51 (m, 2H; CH_2), 1.76–1.92 (m, 1H; CH_2), 1.97–2.36 (m, 2H; CH_2), 2.45 (ddd, $J = 5$, $J = 6$, $J = 11$ Hz, 1H; CH_2), 2.52–2.68 (m, 1H; CH), 2.81–2.95 (m, 1H; CH), 4.13 (t, $^3J = 7$ Hz, 2H; O-CH_2), 4.79–4.99 (m, 1H; CH), 5.23 (d, $^3J(Z) = 11$ Hz, 1H; HC=C*H*-H), 5.44 (d, $^3J(E) = 18$ Hz, 1H; HC=CH-*H*), 5.97 (ddd, $^3J = 6$, $^3J(Z) = 11$, $^3J(E) = 18$ Hz, 1H; *H*C=CH_2); ^{13}C NMR (62.9 MHz, CD_3OD): $\delta = 14.74$ (CH_3), 34.49, 35.22, 38.29 (CH_2), 41.95, 44.10 (CH), 60.70 (O-CH_2), 85.91 (O-CH), 97.19 (O-C=*C*), 117.74 (CH=CH_2), 127.42 (CH, Ph, *para*), 127.86, 129.56 (CH, Ph, *ortho*, *meta*), 137.86 (*C*H=CH_2), 147.06 (C, Ph), 168.75, 170.26 (C, CO, O-*C*=C); MS (EI, 70 eV): *m*/*z* (%): 298 (1) $[M]^+$, 158 (100), 143 (56), 130 (37), 104 (35); HR-MS (EI, 70 eV): calcd for $C_{19}H_{22}O_3$; found: 298.1569 ± 2 mD $[M]^+$.

6-Oxo-2-vinyl-2,3,3a,4,5,6-hexahydro-2,3-benzofuran (3m): Starting with 1,3-cyclohexanedione (448 mg, 4.0 mmol), hexamethylphosphorous triamide (HMPT) (2.4 mL), diisopropylamine (1.24 mL, 8.8 mmol), *n*BuLi (8.8 mmol, in *n*-hexane) and 1,4-dibromo-2-butene (**2**; 940 mg, 4.4 mmol) were treated according to the general procedure. The reaction mixture was warmed during 5 h to 20 °C and was stirred overnight. Water (2 mL) and ether (40 mL) were added, the organic layer was extracted with an aqueous solution of HCl (10%, 3 × 20 mL) and water (20 mL). The combined aqueous layers were extracted with ether (5 × 30 mL) and the combined organic layers were washed with a saturated aqueous solution of brine (20 mL), dried ($MgSO_4$), filtered and the filtrate was concentrated in vacuo. The purification was effected by chromatography (silica gel, petroleum ether/ether 5:1) to give **3m** as a yellow solid (250 mg, 38%). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.57$ (ddd, $^2J = {}^3J = {}^3J = 12$ Hz, 1H; 3-H), partly overlapped by 1.62–1.84 (m, 1H; 3-H), 2.01–2.54 (m, 4H; CH_2), 2.96–3.13 (m, 1H; 3a-H), 4.94 (ddd, $^3J = 5$, $^3J = 6$, $^3J = 12$ Hz, 1H; 2-H), 5.32 [d, $^3J(Z) = 11$ Hz, 1H; HC=CH_2], 5,42 (d, $^3J(E) = 18$ Hz, 1H; HC=CH_2), partly overlapped by 5.45 (s, 1H; 7-H), 5.90 [ddd, $^3J = 6$, $^3J(Z) = 11$ Hz, $^3J(E) = 18$ Hz, 1H; *H*C=CH_2]; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 27.60$, 36.28, 36.97 (CH_2), 40.82 (C-3a), 86.31 (C-2), 100.50 (C-7), 119.28 (CH=*C*H_2), 135.03 (*C*H=CH_2), 182.41 (C, O-*C*=CH), 199.49 (C, CO); MS (EI, 70 eV): *m*/*z* (%): 164 (100) $[M]^+$, 136 (84), 69 (71), 67 (71); HR-MS (EI, 70 eV): HR-MS (EI, 70 eV): calcd for $C_{10}H_{12}O_2$; found: 164.0837 ± 2 mD $[M]^+$.

4,4-Dimethyl-6-oxo-2-vinyl-2,3,3a,4,5,6-hexahydro-2,3-benzofuran (3n): Starting with 5,5-dimethyl-1,3-cyclohexanedione (825 mg, 5.9 mmol), HMPT (3.6 mL in 25 mL THF), diisopropylamine (2.05 mL, 14.0 mmol), *n*BuLi (9.0 mL, 14.0 mmol, in *n*-hexane) and 1,4-dibromo-2-butene (**2**; 1.424 g, 6.66 mmol, in 25 mL THF) in THF (100 mL), **3n** (425 mg, 37%) was isolated as a yellow solid. The purification was effected by chromatography (silica gel, petroleum ether/ether 1:2). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.93$ (s, 3H; CH_3), 1.07 (s, 3H; CH_3), 1.62 (ddd, $^3J = {}^3J = {}^3J = 12$ Hz, 1H; CH_2), 2.18–2.34 (m, 3H; CH_2), 2.99 (dd, $^3J = 12$, $^3J = 7$ Hz, 1H; 3a-H), 4.88 (ddd, $^3J = {}^3J = 7$, $^3J = 12$ Hz, 1H; 2-H), 5.30 [d, $^3J(Z) = 10$ Hz, 1H; HC=CH_2], 5.39 [d, $^3J(E) = 17$ Hz, 1H; HC=CH_2], partly overlapped by 5.42 (s, 1H; 7-H), 5.88 [ddd, $^3J = 7$, $^3J(Z) = 10$, $^3J(E) = 17$ Hz, 1H; C*H*=CH_2]; ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 19.92$, 29.38 (CH_3), 30.87 (CH_2), 35.01 [*C*(CH_3)$_2$], 51.07 (CH), 52.07 (CH_2, O=C-*C*H_2), 85.60 (O-CH), 99.60 (CH, C=*C*H-C=O), 119.15 (C=CH_2), 135.03 (*C*H=CH_2), 180.07 (C, O-*C*=C), 198.78 (C, CO); MS (EI, 70 eV): *m*/*z* (%): 192 (86) $[M]^+$, 136 (100), 69 (40), 67 (60); HR-MS (EI, 70 eV): calcd for $C_{12}H_{16}O_2$; found: 192.1150 ± 2 mD $[M]^+$.

6-Ethoxycarbonyl-9-vinyl-8-oxabicyclo[5.3.0]-6-decene (3o): Starting with ethyl cycloheptanone-2-carboxylate (545 mg, 2.96 mmol), diisopropylamine (0.91 mL, 6.4 mmol), *n*BuLi (6.4 mmol, in *n*-hexane) and 1,4-dibromo-2-butene (**2**; 698 mg, 3.26 mmol), **3o** (438 mg, 63%, *ds* 7:3) was isolated as a colourless oil. The purification was effected by chromatography (silica gel, petroleum ether/ether 5:1). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.29$ (t, $^3J = 8$ Hz, 3H; CH_3, both isomers), 1.44–1.63 (m, 3H; CH_2, both isomers), 1.68–1.99 (m, 4H; CH_2, both isomers), 1.99–2.19 (m, 3H; CH_2, both isomers), 2.78–2.94 (m, 1H; CH_2, both isomers), 2.99–3.18 (m, 1H; 3a-H, both isomers), 4.18 (q, $^3J = 8$ Hz, 2H; OCH_2, both isomers), 4.75 (ddd, $^3J = {}^3J = {}^3J = 8$ Hz, 1H; 2-H), 5.02 (ddd, $^3J = {}^3J = {}^3J = 6$ Hz, 1H; 2-H), 5.15 [d, $^3J(Z) = 11$ Hz, 1H; HC=CH_2], 5.20 [d, $^3J(Z) = 11$ Hz, 1H, HC=CH_2], 5.29 [d, $^3J(E) = 16$ Hz, 1H; HC=CH_2], 5.38 [d, $^3J(E) = 16$ Hz, 1H; HC=CH_2], 5.86 [ddd, $^3J = 6$, $^3J(Z) = 11$, $^3J(E) = 16$ Hz, 1H; *H*C=CH_2], 5.94 [ddd, $^3J = 6$, $^3J(Z) = 11$, $^3J(E) = 16$ Hz, 1H; *H*C=CH_2]; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 13.94$ (CH_3), 26.32, 26.66, 29.99, 30.74, 31.63, 32.62, 37.00, 37.65 (CH_2), 43.69, 44.23 (CH), 59.16 (O-CH_2), 82.94, 82.96 (O-CH), 102.05 (C, O-C=*C*), 115.80, 116.09 (CH=*C*H_2), 136.23, 136.50 (*C*H=CH_2), 167.13, 167.35, 171.78, 172.25 (C, CO, O-*C*=C); MS (EI, 70 eV): *m*/*z* (%): 236 (35) $[M]^+$, 191 (32), 182 (83), 136 (100); HR-MS (EI, 70 eV): calcd for $C_{14}H_{20}O_3$; found: 236.1412 ± 2 mD $[M]^+$.

6-(2,2-Dimethyl-1-oxopropyl)-9-vinyl-8-oxabicyclo[5.3.0]-6-decene (3p): Starting with 2-(2,2-dimethyl-1-oxopropyl)cycloheptanone (785 mg, 4.0 mmol), diisopropylamine (1.30 mL, 9.2 mmol), *n*BuLi (9.2 mmol, in *n*-hexane) and 1,4-dibromo-2-butene (**2**; 948 mg, 4.4 mmol), **3p** was isolated as a colourless oil (430 mg, 44%, *ds* 9:1). The purification was effected by chromatography (silica gel, petroleum ether/ether 5:1). ^{1}H NMR (250 MHz, $CDCl_3$, major isomer): $\delta = 1.18$ (s, 9H; CH_3), 1.38–1.64 (m, 4H; CH_2), 1.71–1.91 (m, 3H; CH_2), 1.91–2.13 (m, 2H; CH_2), 2.20 (m, 1H; CH_2), 2.86–3.03 (m, 1H; 3a-H), 4.77 (ddd, $^3J = {}^3J = {}^3J = 6$ Hz, 1H; 2-H), 5.12 [d, $^3J(Z) = 11$ Hz, 1H; HC=CH_2], 5.23 [d, $^3J(E) = 17$ Hz, 1H; HC=CH_2], 5.81 [ddd, $^3J = 6$, $^3J(Z) = 11$, $^3J(E) = 17$ Hz, 1H; *H*C=CH_2]; ^{13}C NMR (62.9 MHz, $CDCl_3$, major isomer): $\delta = 27.05$ (CH_3), 27.54, 29.43, 30.69, 32.08, 38.00 (CH_2), 41.68 (C-3a), 43.99 [*C*(CH_3)$_3$], 81.25 (C-2), 111.16 (C-8), 115.68 (CH=*C*H_2), 137.10 (*C*H=CH_2), 159.75 (C, O-C=C), 214.75 (C, CO); MS (EI, 70 eV): *m*/*z* (%): 248 (2) $[M]^+$, 191 (100); HR-MS (EI, 70 eV): calcd for $C_{16}H_{24}O_2$; found: 248.1776 ± 2 mD $[M]^+$.

7-Ethoxycarbonyl-2-vinyl-6-thia-2,3,3a,4,5,6-hexahydro-2,3-benzofuran (3q): Starting with ethyl 3-oxothian-2-carboxylate (379 mg, 2.0 mmol), diisopropylamine (0.65 mL, 4.6 mmol), *n*BuLi (3.0 mL, 4.6 mmol, in *n*-hexane) and 1,4-dibromo-2-butene (**2**; 468 mg, 2.2 mmol), **3q** was isolated as a yellowish oil (100 mg, 20%, *ds* 5:1). The purification was effected by chromatography (silica gel, petroleum ether/ether 1:5). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.24$ (t, $^3J = 6$ Hz, 3H; CH_3), 1.38–1.47 (m, 2H; CH_2), 2.33–2.47 (m, 2H; CH_2), 2.65–2.94 (m, 3H, CH_2; CH), 4.04–4.27 (m, 2H; OCH_2), 4.74 (m, 1H; 2-H), 5.18 [d, $^3J(Z) = 11$ Hz, 1H; HC=CH_2], 5.35 [d, $^3J(E) = 17$ Hz, 1H; HC=CH_2], 5.84 [ddd, $^3J = 6$, $^3J(Z) = 11$, $^3J(E) = 17$ Hz, 1H; *H*C=CH_2]; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 13.89$, 14.07 (CH_3), 26.55, 26.69, 28.03, 34.72, 36.84 (CH_2), 38.03, 40.74 (C-3a), 60.33 (OCH_2), 81.64, 93.92 (C-7), 82.92 (C-2), 116.05, 117.76 (H_2C=C), 135.45, 135.64 (C=*C*H), 161.62, 162.30, 163.68 (CO, C-7a); MS (EI, 70 eV): *m*/*z* (%): 240 (6) $[M]^+$, 155 (100), 95 (36); HR-MS (EI, 70 eV): calcd for $C_{12}H_{16}O_3S$; found: 240.0820 ± 2 mD $[M]^+$.

General procedure for the reaction of 1,3,5-tricarbonyl compounds with 1,4-dibromo-2-butene (2): A suspension of K_2CO_3 (3.0 equiv) and tricarbonyl compound (1.0 equiv) in THF (30 mL) was stirred for 15 min at 20 °C. Subsequently 1,4-dibromo-2-butene (**2**; 1.1 equiv, dissolved in 10 mL THF) was added. The mixture was refluxed until no starting material could be detected by tlc (ca. 24 h).

3a,7-Bis(ethoxycarbonyl)-2-vinyl-2,3,3a,4,5,6-hexahydro-2,3-benzofuran (3r): This compound has been previously reported in the literature.[13b]

3a-Acetyl-7-ethoxycarbonyl-2-vinyl-2,3,3a,4,5,6-hexahydro-2,3-benzofuran (3s): Starting with ethyl 6-acetylcyclohexanone-2-carboxylate (636 mg, 3.0 mmol) and 1,4-dibromo-2-butene (**2**), **3s** was isolated by chromatography (214 mg, 27%, *ds* > 98:2, one regioisomer). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.17–1.49$ (m, 2H, CH_2), partly overlapped by 1.29 (t, $^3J = 6$ Hz, 3H; CH_2CH_3), 1.64 (dd, $^3J = 11$, $^3J = 13$ Hz, 1H; CH_2), 1.75–1.90 (m, 1H; CH_2), 2.27 (s, 3H; O=CCH_3), 2.34–2.49 (m, 2H; CH_2), 2.55 (dd, $^3J = 6$, $^3J = 13$ Hz, 2H; CH_2), 4.08–4.36 (m, 2H; OCH_2), 4.61–4.77 (m, 1H; 2-H), 5.23 [d, $^3J(Z) = 11$ Hz, 1H; HC=CH_2], 5.41 [d, $^3J(E) = 18$ Hz, 1H; HC=CH_2], 5.86 [ddd, $^3J = 6$, $^3J(Z) = 11$, $^3J(E) = 18$ Hz, 1H; *H*C=CH_2]; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 14.19$ (CH_2CH_3), 19.31, 23.34, 31.56, 41.30 (CH_2), 27.82 (O=CCH_3), 59.56 (OCH_2), 60.83 (C-3a), 81.41 (C-2), 99.67 (C-7), 117.57 (C=*C*H_2), 135.42 (C=*C*HC), 164.39, 166.41 (CO_2, C-7a), 208.78 (CH_3CO); MS (EI, 70 eV): *m*/*z* (%): 264 (27) $[M]^+$, 222 (80), 219 (46), 210 (38), 176 (100), 164 (40), 91 (21), 85 (53), 43 (34); HR-MS (EI, 70 eV): calcd for $C_{15}H_{20}O_4$; found: 264.1362 ± 2 mD $[M]^+$.

7-Ethyloxycarbonyl-3a-propanoyl-2-vinyl-2,3,3a,4,5,6-hexahydrobenzo[*b*]-furan (3t): The reaction of 2-ethoxycarbonyl-5-propanoylcyclohexanone (**1t**) (230 mg, 1.01 mmol) with K_2CO_3 (410 mg, 2.96 mmol) and 1,4-dibromo-2-butene (**2**; 242 mg, 1.13 mmol) afforded after chromatography (silica gel, petroleum ether/ether 3.5:1) **3t** (97 mg, 35%) as a yellow oil.

Isomer **3t**: ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.01$ (t, $^3J = 7$ Hz, 3H; CH_3), 1.27 (t, $^3J = 7$ Hz, 3H; CH_3), partly overlapped by 1.20–1.40 (m, 2H; CH_2),

1.60 (dd, $^3J = {}^3J = 12$ Hz, 1H; CH_2), 1.70 – 1.90 (m, 1H; CH_2), 2.20 – 2.50 (m, 3H; CH_2), partly overlapped by 2.40 – 2.70 (m, 3H; CH_2), 4.10 – 4.30 (m, 2H; O-CH_2), 4.62 (ddd, $^3J = {}^3J = 6$, $^3J = 11$ Hz, 1H; O-CH), 5.20 (d, $^3J(Z) = 10$ Hz, 1H; H-*H*C=CH), 5.38 (d, $^3J(E) = 17$ Hz, 1H; *H*-HC=CH), 5.83 (ddd, $^3J = 6$, $^3J(Z) = 10$, $^3J(E) = 17$ Hz, 1H; C*H*=CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 7.57$, 14.36 (CH_3), 19.47, 23.56, 32.16, 34.50, 42.04 (CH_2), 59.75 (O-CH_2), 60.72 (O=C-*C*H_2), 81.64 (O-CH), 100.04 (C, O-C=*C*), 117.69 (CH=CH_2), 135.64 (*C*H=CH_2), 164.68, 166.57 (C, CO, ester, O-*C*=C), 212.01 (C, CO, ketone); MS (EI, 70 eV): *m*/*z* (%): 278 (10) $[M]^+$, 222 (75), 176 (100); HR-MS (EI, 70 eV): calcd for $C_{16}H_{22}O_4$; found: 278.1518 ± 2 mD $[M]^+$.

7-Benzoyl-3a-ethoxycarbonyl-2-vinyl-2,3,3a,4,5,6-hexahydro-2,3-benzofuran and **7-ethoxycarbonyl-3a-benzoyl-2-vinyl-2,3,3a,4,5,6-hexahydro-2,3-benzofuran (3u)**: Starting with ethyl 6-benzoylcyclohexanone-2-carboxylate (**1u**; 1.083 g, 4.13 mmol), K_2CO_3 (1.624 g, 11.8 mmol) and 1,4-dibromo-2-butene (**2**; 0.912 g, 4.26 mmol), two isomers of **3u**, **3u-1** (675 mg, 49%) as a colourless viscous oil and **3u-2** (142 mg, 10%) as a yellowish solid, were isolated by chromatography (silica gel, petroleum ether/ether 5:1).

Isomer **3u-1**: ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.12$ (t, $^3J = 7$ Hz, 3H; CH_3), 1.18 – 1.52 (m, 2H; CH_2), partly overlapped by 1.43 (dd, $^3J = {}^3J = 13$ Hz, 1H; CH_2), 1.61 – 1.77 (m, 1H; CH_2), 2.13 (dd, $^3J = 6$, $^2J = 17$ Hz, 1H; CH_2), 2.28 – 2.55 (m, 3H; CH_2), 4.05 (q, $^3J = 7$ Hz, 2H; CH_2), 4.32 – 4.46 (m, 1H; 2-H), 4.74 [d, $^3J(Z) = 10$ Hz, 1H; HC=CH_2], partly overlapped by 4.77 [d, $^3J(E) = 17$ Hz, 1H; HC=CH_2], 5.37 [ddd, $^3J = 6$, $^3J(Z) = 11$, $^3J(E) = 17$ Hz, 1H; *H*C=CH_2], 7.08 – 7.23 (m, 3H; *m*,*p*-Ph-H), 7.65 (d, $^3J = 8$ Hz, 2H; *o*-Ph-H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 13.53$ (CH_3), 19.01, 24.02, 31.25, 41.48 (CH_2), 53.75 (C-3a), 61.02 (OCH_2), 80.42 (C-2), 106.25 (C-7), 116.48 (H_2C=C), 126.97, 128.30 (*o*,*m*-Ph-C), 130.78, 134.76 (*p*-Ph-C, *C*H=CH_2), 139.32 (Ph-C), 160.48, 172.26 (CO_2, C-7a), 195.84 (C, PhC=O); MS (EI, 70 eV): *m*/*z* (%): 326 (22) $[M]^+$, 272 (81), 226 (54), 198 (57), 105 (100), 77 (47); elemental analysis calcd (%) for $C_{20}H_{22}O_4$: C 73.60, H 6.79; found: C 73.89, H 6.88.

Isomer **3u-2**: ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.10 – 1.42$ (m, 1H; CH_2), partly overlapped by 1.25 (t, $^3J = 7$ Hz, 3H; CH_3), 1.50 – 1.80 (m, 2H; CH_2), 1.90 (dd, $^3J = {}^3J = 13$ Hz, 1H; CH_2), 2.22 – 2.42 (m, 2H; CH_2), 2.67 – 2.82 (m, 1H; CH_2), 2.92 (dd, $^3J = 4$, $^3J = 13$ Hz, 1H; CH_2), 4.05 – 4.35 (m, 2H; OCH_2), 4.56 – 4.72 (m, 1H; 2-H), 5.18 [d, $^3J(Z) = 10$ Hz, 1H; HC=CH_2], 5.35 [d, $^3J(E) = 17$ Hz, 1H; HC=CH_2], 5.85 [ddd, $^3J = 6$, $^3J(Z) = 11$, $^3J(E) = 17$ Hz, 1H; *H*C=CH_2], 7.28 – 7.57 (m, 3H; *m*,*p*-Ph-H), 7.88 (d, $^3J = 8$ Hz, 2H; *o*-PhH); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 14.26$ (CH_3), 19.10, 23.07, 32.86, 42.10 (CH_2), 59.52 (OCH_2), 60.40 (C-3a), 81.27 (C-2), 99.85 (C-7), 117.67 (H_2C=C), 128.38, 128.90 (*o*,*m*-Ph-C), 132.69, 135.30 (*p*-Ph-C, *C*H=CH_2), 135.07 (Ph-C), 164.74, 166.66 (CO_2, C-7a), 200.43 (PhC=O); MS (EI, 70 eV): *m*/*z* (%): 326 (10) $[M]^+$, 176 (42), 105 (100), 77 (27); elemental analysis calcd (%) for $C_{20}H_{22}O_4$: C 73.60, H 6.79; found: C 73.85, H 6.94.

4,7-Bis(ethoxycarbonyl)-2-vinyl-1-oxabicyclo[3.3.0]oct-7-ene (3v): The synthesis of this compound has been previously reported in the literature.[13b]

General procedure for the synthesis of bicyclo[3.2.1]octan-8-ones (4): A solution of **3a** (200 mg, 0.90 mmol) in DMSO (2.5 mL) was thoroughly degassed and subsequently treated with $[Pd(dppe)_2]$ (40 mg, 5.0 mol%). The red solution was stirred for 6 – 24 h at 60 °C. To the mixture was added ether (20 mL) and the suspension formed was filtered through a pad of celite which was subsequently washed with ether (200 mL). The filtrate was concentrated in vacuo and the catalyst was removed by filtration (silica gel, ether). The product **4a** was isolated as a mixture of two diastereomers (180 mg, 90%, *endo*/*exo* = 1.2:1). The purification was effected by chromatography (silica gel, petroleum ether/ether 5:1). The diastereomers could be separated by chromatography (silica gel, ether/petroleum ether 1:20 → 1:3) to give *endo*-**4a** (66 mg, 33%) and *exo*-**4a** (70 mg, 35%) as colourless oils.

1-Ethoxycarbonyl-7-vinylbicyclo[3.2.1]octan-8-one (4a): *endo*-**4a**: ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.21$ (t, $^3J = 7$ Hz, 3H; CH_3), 1.94 – 2.14 (m, 7H; CH_2), 2.35 – 2.53 (m, 2H; CH_2, 5-H), 2.90 (dt, $^3J = 6$, $^3J = 10$ Hz, 1H; 7-H), 4.10 (q, $^3J = 7$ Hz, 2H; OCH_2), 4.84 [d, $^3J(Z) = 10$ Hz, CH=CH_2], 4.92 [d, $^3J(E) = 16$ Hz, CH=CH_2], 5.55 [ddd, $^3J = {}^3J(Z) = 10$, $^3J(E) = 16$ Hz, 1H; C*H*=CH_2]; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 14.02$ (CH_3), 17.42, 30.44, 36.85, 39.99 (CH_2), 46.17, 46.57 (C-5, C-7), 60.41 (OCH_2), 60.63 (C-1), 114.24 (CH=*C*H_2), 139.98 (*C*H=CH_2), 169.69 (CO_2), 215.01 (C-8); MS (EI, 70 eV): *m*/*z* (%): 222 (100) $[M]^+$, 121 (37); elemental analysis calcd (%) for $C_{13}H_{18}O_3$: C 70.24, H 8.16; found: C 70.36, H 8.10. *exo*-**4a**: ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.22$ (t, $^3J = 7$ Hz, 3H; CH_3), 1.48 – 2.09 (m, 5H; CH_2), 2.09 – 2.39 (m, 3H; CH_2), 2.39 – 2.61 (m, 1H; 5-H), 3.39 – 3.55 (m, 1H; 7-H), 4.06 – 4.27 (m, 2H; O-CH_2), 5.06 – 5.24 (m, 2H; CH=CH_2), 5.94 (ddd, $^3J = 7$, $^3J(Z) = 11$, $^3J(E) = 18$ Hz, 1H; C*H*=CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 14.11$ (CH_3), 17.15, 27.34, 33.82, 36.60 (CH_2), 41.47, 46.01 (C-5, C-7), 60.99 (OCH_2), 61.61 (C-1), 117.53 (CH=*C*H_2), 135.40 (*C*H=CH_2), 170.63 (CO_2), 214.90 (C-8); MS (EI, 70 eV): *m*/*z* (%): 222 (100) $[M]^+$, 193 (99), 177 (67), 176 (94), 147 (46), 79 (53); elemental analysis calcd (%) for $C_{13}H_{18}O_3$: C 70.24, H 8.16; found: C 70.40, H 8.02.

1-Methoxycarbonyl-7-vinylbicyclo[3.2.1]octan-8-one (4b): Following the general procedure, **3b** (206 mg, 0.987 mmol) was treated with the catalyst (50 mg, 57 μmol) in DMSO (2.5 mL) at 60 – 70 °C. The isomers were separated by chromatography (silica gel, petroleum ether/ether 5:1).

Diastereomer **4b-1** (64 mg, 31%) as a colourless oil. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.55 – 1.85$ (m, 3H; CH_2), 1.95 – 2.05 (m, 2H; CH_2), 2.18 – 2.39 (m, 3H; CH_2), 2.47 – 2.55 (m, 1H; CH), 3.50 (ddd, $^3J = 6$, $^3J = 7$, $^3J = 12$ Hz, 1H; CH), 3.73 (s, 3H; CH_3), 5.19 (dd, $^3J = 1$, $^3J(Z) = 10$ Hz, 1H; HC=C*H*-H), partly overlapped by 5.20 (dd, $^3J = 1$, $^3J(E) = 17$ Hz, 1H; HC=CH-*H*), 5.96 (ddd, $^3J = 7$, $^3J(Z) = 10$, $^3J(E) = 17$ Hz, 1H; *H*C=CH_2); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 17.23$, 27.42, 33.95, 36.67 (CH_2), 41.59, 46.05 (CH), 52.25 (O-CH_3), 61.88 (C, O=C-*C*-C=O), 117.72 (CH=*C*H_2), 135.35 (*C*H=CH_2), 171.22 (C, CO, ester), 214.99 (C, CO, ketone); MS (EI, 70 eV): *m*/*z* (%): 208 (100) $[M]^+$, 179 (72), 177 (53), 176 (73), 79 (42); HR-MS (EI, 70 eV): calcd for $C_{12}H_{16}O_3$; found: 208.1099 ± 2 mD $[M]^+$.

Diastereomer **4b-2** (96 mg, 47%) as a colourless oil. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.56 – 1.85$ (m, 3H; CH_2), partly overlapped by 1.82 – 2.21 (m, 4H; CH_2), 2.36 – 2.2.54 (m, 2H; CH, CH_2), 2.90 (ddd, $^3J_1 = {}^3J_2 = 10$, $^3J_3 = 6$ Hz, 1H; CH), 3.63 (s, 3H; CH_3), 4.87 (d, $^3J(Z) = 10$ Hz, 1H; HC=C*H*-H), partly overlapped by 4.93 (d, $^3J(E) = 17$ Hz, 1H; HC=CH-*H*), 5.96 (ddd, $^3J = {}^3J(Z) = 10$, $^3J(E) = 17$ Hz, 1H; *H*C=CH_2); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 17.51$, 30.52, 36.93, 40.05 (CH_2), 46.28, 46.70 (CH), 51.53 (O-CH_3), 61.20 (C, O=C-*C*-C=O), 114.45 (CH=*C*H_2), 139.95 (*C*H=CH_2), 170.33 (C, CO, ester), 215.08 (C, CO, ketone); MS (EI, 70 eV): *m*/*z* (%): 208 (100) $[M]^+$, 121 (46), 120 (34), 79 (46); HR-MS (EI, 70 eV): calcd for $C_{12}H_{16}O_3$; found: 208.1099 ± 2 mD $[M]^+$.

1-Isopropoxycarbonyl-7-vinylbicyclo[3.2.1]octan-8-one (4c): A solution of **3c** (133 mg, 0.56 mmol) in DMSO (2 mL) was treated with the catalyst (32 mg, 35 μmol) at 70 – 80 °C. The product was isolated by chromatography as a colourless oil (122 mg, 92%, *ds* 1.1:1). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.08 – 1.26$ (m, 12H; CH_3, both isomers), 1.46 – 1.79 (m, 4H; CH_2, both isomers), 1.79 – 2.11 (m, 6H; CH_2, both isomers), 2.11 – 2.53 (m, 8H; CH_2, 5-H, both isomers), 2.68 (dt, $^3J = 5$, $^3J = 10$ Hz, 1H; 7-H), 3.45 (dt, $^3J = 13$, $^3J = 6$ Hz, 1H; 7-H), 4.77 – 5.19 [m, 6H; CH=CH_2, O*C*H(CH_3)$_2$, both isomers], 5.66 [ddd, $^3J = {}^3J(Z) = 10$, $^3J(E) = 16$ Hz, 1H; C*H*=CH_2], 5.91 [ddd, $^3J = 6$, $^3J(Z) = 11$, $^3J(E) = 17$ Hz, 1H; C*H*=CH_2]; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 17.18$, 17.54 (CH_2), 21.68, 21.70, 21.72, 21.78 (CH_3), 27.39, 30.59, 33.78, 36.63, 36.97, 40.11 (CH_2), 41.53, 46.06, 46.28, 46.66 (CH), 60.37, 61.49 (C-1), 68.07, 68.73 [OCH(CH_3)$_2$], 114.22, 117.45 (CH=*C*H_2), 135.50, 140.22 (*C*H=CH_2), 169.21, 170.13 (CO_2), 214.88, 215.08 (C-8); MS (EI, 70 eV): *m*/*z* (%): 236 (31) $[M]^+$, 194 (100), 177 (78), 176 (69); HR-MS (EI, 70 eV): calcd for $C_{14}H_{20}O_3$; found: 236.1412 ± 2 mD $[M]^+$.

1-Methoxyethoxycarbonyl-7-vinylbicyclo[3.2.1]octan-8-one (4d): Starting with **3d** (378 mg, 1.50 mmol), **4d** (344 mg, 91%, *ds* 1.1:1) was isolated as a colourless oil. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.51 – 1.86$ (m, 6H; CH_2, both isomers), 1.86 – 2.17 (m, 6H; CH_2, both isomers), 2.17 – 2.39 (m, 4H; CH_2, both isomers), 2.39 – 2.57 (m, 3H; 5-H, both isomers, 7-H, one isomer), 2.93 (dt, $^3J = 6$, $^3J = 10$ Hz, 1H; 7-H), 3.34 (s, 3H; OCH_3), 3.35 (s, 3H; OCH_3), 3.58 – 3.65 (m, 4H; CH_3OCH_2, both isomers), 4.17 – 4.39 (m, 4H; O=COCH_2, both isomers), 4.87 [d, $^3J(Z) = 11$ Hz, 1H; CH=CH_2], 4.95 [d, $^3J(E) = 17$ Hz, 1H; CH=CH_2], 5.14 – 5.27 (m, 2H; CH=CH_2), 5.71 [ddd, $^3J = {}^3J(Z) = 11$, $^3J(E) = 17$ Hz, 1H; C*H*=CH_2], 5.95 [ddd, $^3J = 7$, $^3J(Z) = 11$, $^3J(E) = 17$ Hz, 1H; C*H*=CH_2]; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 17.00$, 17.36, 27.23, 30.39, 33.66, 36.44, 36.74, 39.84 (CH_2), 40.56, 41.38, 46.07, 46.50 (C-5, C-7), 58.55, 58.61 (OCH_3), 60.71, 61.61 (C-1), 63.28, 63.77 (CH_2, CH_3OCH_2), 70.00, 70.14 (O=CO*C*H_2), 114.31, 117.56 (CH=*C*H_2), 135.17, 139.89 (*C*H=CH_2), 169.53, 170.51 (CO_2), 214.50, 214.62 (C-8); MS (EI, 70 eV): *m*/*z* (%): 252 (56) $[M]^+$, 194 (47), 177 (46), 176 (45), 59 (100), 58 (46); HR-MS (EI, 70 eV); calcd for $C_{14}H_{20}O_4$; found: 252.1362 ± 2 mD $[M]^+$.

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1,5-Bis(ethoxycarbonyl)-6-vinylbicyclo[3.2.1]octan-8-one (4e): Following the general procedure, **3q** (240 mg, 0.82 mmol) was treated with the catalyst (51 mg, 56 μmol) in DMSO (2.0 mL) at 70–80 °C. The product was purified by filtration through a pad of silica gel to give **4e** as a colourless oil (228 mg, 95 %, *ds* 1.1:1). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.04-1.31$ (m, 12H; CH_3, both isomers), 1.49–2.45 (m, 16H; CH_2, both isomers), 2.64–2.87 (m, 1H; 6-H, both isomers), 3.52 [dt, $^3J = 14$, $^3J = 7$ Hz, 1H; 6-H], 3.90–4.21 [m, 8H; OCH_2, both isomers], 4.75–4.96 (m, 2H; CH=CH_2), 5.04–5.19 (m, 2H; CH=CH_2), 5.54–5.91 (m, 2H; CH=CH_2, both isomers); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 13.79$, 13.80, 13.85, 13.86 (CH_3), 17.92, 17.93, 31.08, 33.25, 33.87, 38.17, 38.51, 39.53 (CH_2), 40.01, 44.56 (C-6), 58.68, 59.27, 61.32, 62.30 (C-1, C-5), 60.44, 60.45, 60.95, 60.96 (OCH_2), 114.59, 117.95 (CH=*C*H_2), 134.34, 139.15 (*C*H=CH_2), 168.70, 169.42, 169.85, 169.88 (CO_2), 208.23, 208.38 (CO); MS (EI, 70 eV): *m*/*z* (%): 294 (100) $[M]^+$, 249 (41), 175 (51); HR-MS (EI, 70 eV); calcd for $C_{16}H_{22}O_5$; found: 294.1467 ± 2 mD $[M]^+$.

5-Acetyl-1-ethoxycarbonyl-6-vinylbicyclo[3.2.1]octan-8-one (4f): Following the general procedure, **3r** (60 mg, 0.23 mmol) was treated with the catalyst (15 mg, 17 μmol) in DMSO (0.6 mL). The diastereomers were separated by chromatography (petroleum ether/ether 4:1).

Isomer **4f-1** (21 mg, 35 %). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.15-1.37$ (m, 2H; CH_2), partly overlapped by 1.21 (t, $^3J = 7$ Hz, 3H; CH_2-CH_3), 1.71–1.99 (m, 2H; CH_2), 1.99–2.43 (m, 3H; CH_2), partly overlapped by 2.30 (s, 3H; O=CCH_3), 2.45–2.58 (m, 1H; CH_2), 2.92 (dt, $^3J = 6$, $^3J = 9$ Hz, 1H; 7-H), 4.15 (q, $^3J = 7$ Hz, 2H; OCH_2), 4.90–5.07 (m, 2H; CH=CH_2), 5.73 [ddd, $^3J = {}^3J(Z) = 10$, $^3J(E) = 17$ Hz, 1H; CH=CH_2]; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 14.20$ (CH_2CH_3), 27.56 (O=C*C*H_3), 17.78, 30.12, 33.96, 39.00 (CH_2), 40.40 (C-7), 61.46 (OCH_2), 63.07, 64.47 (C-1, C-5), 118.46 (CH=*C*H_2), 134.45 (*C*H=CH_2), 169.84 (CO_2), 205.21, 210.96 (CO); MS (EI, 70 eV): *m*/*z* (%): 264 (16) $[M]^+$, 222 (77), 176 (100), 43 (86). Isomer **4f-2** (20 mg, 33 %). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.17-1.38$ (m, 1H; CH_2), partly overlapped by 1.28 (t, $^3J = 7$ Hz, 3H; CH_2CH$_3$), 1.66–1.93 (m, 3H; CH_2), 2.08–2.36 (m, 3H; CH_2), partly overlapped by 2.29 (s, 3H; O=CCH_3), 2.78 (t, $^3J = 13$ Hz, 1H; CH_2), 3.58 (dt, $^3J = 13$, $^3J = 7$ Hz, 1H; 7-H), 4.10–4.34 (m, 2H; OCH_2), 5.19–5.32 (m, 2H; CH=CH_2), 5.96 [ddd, $^3J = 7$, $^3J(Z) = 10$, $^3J(E) = 17$ Hz, 1H; CH=CH_2]; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 14.18$ (CH_2CH_3), 27.61 (O=C*C*H_3), 17.76, 33.10, 39.48, 40.30 (CH_2), 44.81 (C-7), 60.95 (OCH_2), 62.23, 65.01 (C-1, C-5), 115.23 (CH=*C*H_2), 139.24 (*C*H=CH_2), 169.06 (CO_2), 205.36, 211.06 (CO); MS (EI, 70 eV): *m*/*z* (%): 264 (100) $[M]^+$, 84 (35), 43 (60); HR-MS (EI, 70 eV): calcd for $C_{15}H_{20}O$; found: 264.1362 ± 2 mD $[M]^+$.

1-Ethoxycarbonyl-4-methyl-7-vinylbicyclo[3.2.1]octan-8-one (4g): Following the general procedure, **3h** (171 mg, 0.72 mmol) was treated with the catalyst (49 mg, 54 μmol) in DMSO (2.0 mL) at 60–70 °C. The isomers of **4g** were separated by chromatography (silica gel, petroleum ether/ether 5:1).

Isomer **4g-1** (30 mg, 17 %) as a colourless solid. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.01$ (d, $^3J = 7$ Hz, 3H; CH_3), 1.19–1.38 (m, 1H; CH_2), partly overlapped by 1.25 (t, $^3J = 7$ Hz, 3H; CH_3), 1.64–1.79 (m, 1H; CH_2), 1.91–2.18 (m, 2H; CH_2), 2.22–2.51 (m, 4H; 5-H, CH_2), 3.40–3.57 (m, 1H; 7-H), 4.19 (q, $^3J = 7$ Hz, 2H; OCH_2), 5.13–5.29 (m, 2H; CH=CH_2), 5.96 [ddd, $^3J = 7$, $^3J(Z) = 10$, $^3J(E) = 17$ Hz, 1H; CH=CH_2]; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 13.92$, 17.63 (CH_3), 23.20, 28.24, 29.32 (CH_2), 40.14, 41.43, 51.59 (CH), 61.00 (C-1), 60.71 (OCH_2), 117.27 (CH=*C*H_2), 135.61 (*C*H=CH_2), 170.43 (CO_2), 212.26 (CO).

Isomer **4g-2** (59 mg, 34 %) as a colourless solid. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.96$ (d, $^3J = 7$ Hz, 3H; CH_3), 1.20 (t, $^3J = 7$ Hz, 3H; CH_3), 1.27–1.43 (m, 1H; CH_2), 1.67–1.81 (m, 1H; CH_2), 2.00–2.16 (m, 3H; CH_2), 2.16–2.36 (m, 3H; 5-H, CH_2), 2.89 (dt, $^3J = 6$, $^3J = 10$ Hz, 1H; 7-H), 4.10 (q, $^3J = 7$ Hz, 2H; OCH_2), 4.84 [d, $^3J(Z) = 10$ Hz, 1H; CH=CH_2], 4.92 [d, $^3J(E) = 17$ Hz, 1H; CH=CH_2], 5.67 [ddd, $^3J = {}^3J(Z) = 10$, $^3J(E) = 17$ Hz, 1H; CH=CH_2]; ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 13.92$, 17.48 (CH_3), 23.51, 31.08, 35.48 (CH_2), 41.36, 44.94, 52.07 (CH), 59.89 (C-1), 60.21 (OCH_2), 114.04 (CH=*C*H_2), 139.94 (*C*H=CH_2), 169.55 (CO_2), 212.03 (CO); MS (EI, 70 eV): *m*/*z* (%): 236 (25) $[M]^+$, 207 (100), 191 (21), 161 (29), 134 (39); HR-MS (EI, 70 eV): calcd for $C_{14}H_{20}O_3$; found: 236.1412 ± 2 mD $[M]^+$.

1,4-Bis(ethoxycarbonyl)-2-vinylbicyclo[2.2.1]heptan-7-one (4h): Following the general procedure, **3v** (201 mg, 0.72 mmol) was treated with the catalyst (48 mg, 53 μmol) in DMSO (2.0 mL) at 80 °C. Owing to the instability of the product during chromatography (silica gel) the crude product was dissolved in ether (5 mL) and rapidly filtered through a 4 cm layer of silica gel. The silica gel was washed with ether (120 mL). The solvent was removed in vacuo to give **4h** as a colourless viscous oil (72 mg, 36 %) (*endo*/*exo* = 5:1). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.14-1.36$ (m, 6H; CH_3), 1.70–1.91 (m, 2H; CH_2), 1.91–2.17 (m, 1H; CH_2), 2.17–2.56 (m, 2H; CH_2), 2.56–2.74 (m, 1H; CH_2), 3.40 (dt, $^3J = 13$, $^3J = 6$ Hz, 1H; 2-H), 4.01–4.34 (m, 4H; OCH_2), 5.17–5.31 (m, 2H; CH=CH_2), 5.83 [ddd, $^3J = 6$, $^3J(Z) = 11$, $^3J(E) = 17$ Hz, 1H; CH=CH_2]; ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 14.09$, 14.14 (CH_3), 19.48, 26.93, 30.61 (CH_2), 38.55 (C-2), 57.77, 58.10 (C-1, C-4), 61.18, 61.21 (OCH_2), 118.48 (CH=*C*H_2), 135.18 (*C*H=CH_2), 168.72, 168.80 (CO_2), 201.43 (CO); MS (EI, 70 eV): *m*/*z* (%): 280 (20) $[M]^+$; HR-MS (EI, 70 eV): calcd for $C_{15}H_{20}O_5$; found: 280.1311 ± 2 mD $[M]^+$.

Synthesis of the 2-phenylthio-cycloalkanones (6a–h): 2-Phenylthio-cycloalkanones **6** were prepared according to a literature procedure from the respective cycloalkanones, LDA and diphenyl disulfide (38–66 % yield).[20]

2-Phenylthiocyclohexanone (6a):[20] Starting with cyclohexanone (5.88 g, 60.0 mmol), **6a** was prepared (5.93 g, 48 %). ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 1.65-2.40$ (m, 7H; CH_2), 2.94 (m, 1H; CH_2), 3.82 (t, $J = 6$ Hz, 1H; CH), 7.20–7.45 (m, 5H; Ph).

2-Phenylthio-5-methylcyclohexanone (6b): Starting with 3-methylcyclohexanone (6.72 g, 60.0 mmol), **6b** was prepared (5.94 g, 45 %). ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 1.00$ (m, 3H; CH_3), 1.60–2.30 (m, 6H; CH_2), 2.75 (m, 1H), 3.68 (m, 1H; CH), 7.15–7.40 (m, 5H; Ph); ^{13}C NMR ($CDCl_3$, 62.5 MHz, two diastereomers): $\delta = 21.56/22.06$, 29.28/32.82, 31.48/33.24, 32.82/34.61, 45.33/49.07, 54.25/62.98, 127.43/127.20, 129.04/128.92, 131.36/131.21, 132.19/133.81, 207.78/209.46; MS (EI, 70 eV): *m*/*z* (%): 220 (32) $[M]^+$, 236 (100).

2-Phenylthio-5-butylcyclohexanone (6c): Starting with 3-butylcyclohexanone (6.16 g, 40.0 mmol), **6c** was prepared (6.91 g, 66 %). ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.75$ (m, 3H; CH_3), 1.18 (m, 6H; CH_2), 1.50–2.30 (m, 6H; CH, CH_2), 2.50–2.70 (m, 1H), 3.60–3.85 (m, 1H; CH), 7.05–7.35 (m, 5H; Ph); ^{13}C NMR ($CDCl_3$, 62.5 MHz, two diastereomers): $\delta = 13.72$, 22.57/22.61, 25.20/26.81, 28.67/28.77, 31.18/31.40, 38.92/39.49, 41.33/43.48, 47.24/48.02, 54.50/57.30, 126.96/127.19, 128.78/128.90, 130.92/131.11, 133.90/134.03, 206.06/207.48.

2-Phenylthio-4-methylcyclohexanone (6f): Starting with 4-methylcyclohexanone (6.72 g, 60.0 mmol), **6f** was prepared (5.28 g, 40 %). ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.85$, 0.90 (2 × d, 3H; CH_3), 1.28 (m, 2H; CH_2), 1.70–2.30 (m, 4H; CH, CH_2), 3.00, 3.60, 3.90 (3 × m, 1H), 3.60–3.85 (m, 1H; CH), 7.10–7.30 (m, 5H; Ph); ^{13}C NMR ($CDCl_3$, 62.5 MHz, two diastereomers, 4:1): $\delta = 20.37/20.51$ (CH_3), 26.52/30.51 (CH), 34.20/34.47, 35.74/34.78, 40.15/40.21 (CH_2), 53.73/56.49 (CH), 126.50/126.79, 128.35/128.48, 130.53/131.57 (CH), 133.60, 207.23/205.80 (C); MS (EI, 70 eV): *m*/*z* (%): 220 (100) $[M]^+$, 110 (80).

2-Phenylthiopyran-4-one (6g): Starting with pyran-4-one (1.00 g, 10.0 mmol), **6g** was prepared (0.85 g, 41 %). ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 2.48$, 2.92 (2 × m, 2 × 1H; CH_2), 3.82–4.05 (m, 4H; CH, CH_2), 4.12 (q, $J = 10$ Hz, 1H; CH_2), 7.25 (m, 3H; Ph), 7.40 (m, 2H; Ph); ^{13}C NMR ($CDCl_3$, 62.5 MHz): $\delta = 40.74$ (CH_3), 56.22 (CH), 68.09, 72.23 (CH_2), 127.46, 128.77, 131.75 (CH), 132.48, 202.22 (C).

2-Phenylthiocycloheptanone (6h): Starting with cycloheptanone (6.72 g, 60.0 mmol), **6h** was prepared (6.34 g, 48 %). ^{1}H NMR ($CDCl_3$, 250 MHz, two diastereomers, 8:1): $\delta = 1.20-1.95$ (m, 6H; CH_2), 2.15, 2.35, 2.39, 2.68 (4 × m, 4 × 1H; CH, CH_2), 3.72, 3.94 (2 × m, 1H; CH, *cis*, *trans*), 7.10–7.25 (m, 3H; Ph), 7.32 (m, 2H; Ph); ^{13}C NMR ($CDCl_3$, 62.5 MHz, main isomer): $\delta = 23.93$, 25.08, 26.74, 29.53, 39.54 (CH_2), 56.83, 127.06, 128.57, 131.36 (CH), 133.51, 208.35 (C); MS (EI, 70 eV): *m*/*z* (%): 220 (100) $[M]^+$, 110 (90); a small amount of an unknown impurity could not be separated.

Synthesis of 2-phenylsulfonylcyclohexanones (7a–h): Sulfones **7** were prepared from sulfides **6** according to a literature procedure by oxidation with *m*-CPBA (75–88 %).[20]

2-Phenylsulfonyl-cyclohexanone (7a): Starting with **6a** (4.12 g, 20.0 mmol), **7a** was prepared (3.62 g, 88 %). ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 1.65-2.10$ (m, 3H; CH_2), 2.25 (m, 2H; CH_2), 2.35–2.60 (m, 2H; CH_2), 2.80 (m, 1H; CH_2), 3.83 (t, $J = 6$ Hz, 1H; CH), 7.50–7.70 (m, 3H; Ph), 7.90 (d, $J = 10$ Hz, 2H; Ph); MS (EI, 70 eV): *m*/*z* (%): 238 (24) $[M]^+$, 174 (68), 143 (100).

2-Phenylsulfonyl-5-methylcyclohexanone (7b): Starting with **6b** (4.40 g, 20.0 mmol), **7b** was prepared (4.03 g, 80 %). ^{1}H NMR ($CDCl_3$, 250 MHz):

$\delta = 0.90-1.10$ (m, 3H; CH_3), 1.75 (m, 1H), 1.80–2.10 (m, 3H; CH_2), 2.40–2.80 (m, 3H; CH_2), 3.76, 3.92 (2 × m, 1H; CH), 7.45–7.65 (m, 3H; Ph), 7.78, 7.95 (2 × d, $J = 10$ Hz, 2H; Ph); ^{13}C NMR ($CDCl_3$, 62.5 MHz, two diastereomers): $\delta = 21.15/21.72$ (CH_3), 25.62/25.95 (CH_2), 28.93/31.33 (CH_2), 33.62/33.71 (CH), 48.90/49.84 (CH_2), 71.49/71.81 (CH), 128.21/128.35, 128.70/129.11, 133.75/134.03 (CH), 137.84/138.08 (C), 201.09/202.22 (CO).

2-Phenylsulfonyl-5-butylcyclohexanone (7c): Starting with **6c** (5.24 g, 20.0 mmol), **7c** was prepared (4.59 g, 78%). ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.90$ (m, 3H; CH_3), 1.28 (m, 6H; CH_2), 1.70–2.25 (m, 4H; CH, CH_2), 2.45–2.90 (m, 3H), 3.70–4.30 (m, 1H; CH), 7.50–7.70 (m, 3H; Ph), 7.75–8.00 (m, 2H; Ph); MS (EI, 70 eV): *m*/*z* (%): 294 (10) $[M]^+$, 230 (22), 152 (100).

2-Phenylsulfonyl-4-phenylcyclohexanone (7d): Starting with **6d** (5.64 g, 20.0 mmol), **7d** was prepared (4.71 g, 75%, two diastereomers). ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 1.90-2.35$ (m, 3H; CH_2), 2.40–2.90 (m, 3H; CH_2), 3.05, 3.76 (m, 1H; CH), 3.95, 3.35 (m, 1H; CH), 7.05–7.35 (m, 6H; Ph), 7.45–7.65 (m, 2H; Ph), 7.82, 8.05 (2 × d, $J = 9$ Hz, 2H; Ph); ^{13}C NMR ($CDCl_3$, 62.5 MHz): $\delta = 29.83/32.44$ (CH_2), 33.19/33.38 (CH_2), 37.23/46.46 (CH), 48.90/49.84 (CH_2), 71.49/71.81 (CH), 126.27/126.35, 126.50/126.68, 128.09/128.34, 128.30/128.45, 128.96/129.17, 133.50/133.92 (CH), 137.41/137.58, 142.54, 143.13 (C), 200.17/201.18 (CO); MS (EI, 70 eV): *m*/*z* (%): 314 (16) $[M]^+$, 190 (22), 173 (100).

2-Phenylsulfonyl-4-*tert*-butylcyclohexanone (7e): Starting with **6e** (5.24 g, 20.0 mmol), **7e** was prepared (4.23 g, 72%, two diastereomers). ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.86$, 0.82 (2 × s, 2 × 9H; *t*Bu), 1.20–3.00 (m, 2 × 7H; CH, CH_2), 3.75, 3.90–4.30 (m, 2 × 1H; CH), 7.40–8.00 (m, 2 × 5H; Ph); MS (EI, 70 eV): *m*/*z* (%): 294 (12) $[M]^+$, 279 (18), 230 (20), 153 (100); a small amount of unknown impurities could not be separated.

2-Phenylsulfonyl-4-methylcyclohexanone (7f): Starting with **6f** (4.40 g, 20.0 mmol), **7f** was prepared (4.08 g, 81%, two diastereomers). ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.95-1.05$ (2 × d, 3H; CH_3), 1.38, 1.70, 1.95 (3 × m, 4H; CH_2), 2.25–2.75, 2.95 (m, 3H; CH, CH_2), 3.75, 4.05–4.25 (m, 1H; CH), 7.45–7.60 (m, 3H; Ph), 7.75, 7.90–8.05 (2 × m, 2 × 1H; Ph); ^{13}C NMR ($CDCl_3$, 62.5 MHz): $\delta = 20.98/21.04$, 26.86, 30.67/31.21, 34.70/34.43, 40.37/41.62, 71.06/72.41, 128.17/128.45, 128.74/129.22, 129.78/130.02, 133.39/133.83, 201.75/202.80 (CO); MS (EI, 70 eV): *m*/*z* (%): 252 (4) $[M]^+$, 156 (100), 139 (81).

2-Phenylsulfonylpyran-4-one (7g): Starting with **6g** (832 mg, 5.0 mmol), **7g** was prepared (912 mg, 76%). ^{1}H NMR ([D$_6$]acetone, 250 MHz): $\delta = 2.41$ (m, 1H; CH_2), 2.90 (m, 1H; CH_2), 3.75–4.05 (m, 2H; CH, CH_2), 4.15 (m, 2H; CH_2), 4.65 (m, 1H; CH_2), 7.55–7.90 (m, 5H; Ph); ^{13}C NMR ($CDCl_3$, 62.5 MHz): $\delta = 40.86$ (CH_2), 56.42 (CH), 68.26, 72.40 (CH_2), 127.63, 128.99, 131.96 (CH), 132.25, 202.36 (C); MS (EI, 70 eV): *m*/*z* (%): 240 (6) $[M]^+$, 125 (34), 99 (100).

Procedure for the synthesis of 7-phenylsulfonyl-2-vinyl-2,3,3a,4,5,6-hexahydro-2,3-benzofurans (8): Hexahydro-2,3-benzofurans **8** were prepared according to the procedure given for the preparation of hexahydro-2,3-benzofurans **3**.

7-Phenylsulfonyl-2-vinyl-2,3,3a,4,5,6-hexahydro-2,3-benzofuran (8a): Starting with sulfone **7a** (800 mg, 3.36 mmol), **8a** was isolated as a colourless oil (444 mg, 45%). ^{1}H NMR ([D$_6$]acetone, 250 MHz): $\delta = 1.05-1.30$ (m, 3H; CH_2), 1.55 (m, 1H; CH_2), 2.00 (m, 1H; CH_2), 2.20–2.60 (m, 3H; CH_2), 2.75 (m, 1H; CH_2), 4.80 (dt, $J = 6$ Hz, 1H; 2-H), 5.10–5.40 (m, 2H; =CH_2), 5.70 (m, 1H; C*H*=CH_2), 7.50–7.70 (m, 3H; Ph), 7.93 (d, $J = 10$ Hz, 2H; Ph); ^{13}C NMR ([D$_6$]acetone, 62.5 MHz): $\delta = 22.26$, 23.76, 26.82, 37.04, 41.52, 84.57, 105.83, 117.02, 127.08, 128.62, 132.36, 136.46, 143.70, 165.45; IR (KBr): $\tilde{\nu} = 3444$ (br), 3077 (w), 2933 (m), 2854 (m), 1652 (s), 1446 (m), 1334 (m), 1286 (m), 1210 (m), 1147 (s), 1134 (s), 1087 (s), 1022 (m) cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 290 (32) $[M]^+$, 236 (100); elemental analysis calcd (%) for $C_{16}H_{18}O_3S$ (290.4): C 66.18, H 6.25; found: C 65.85, H 6.19.

4-Methyl-7-phenylsulfonyl-2-vinyl-2,3,3a,4,5,6-hexahydro-2,3-benzofuran (8b): Starting with sulfone **7b** (562 mg, 2.23 mmol), **8b** was isolated as a colourless oil (312 mg, 46%). ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.82$ (m, 1H; CH_2), 0.95 (d, 3H; CH_3), 1.10–1.30 (m, 3H; CH, CH_2), 1.80 (m, 1H; CH_2), 2.22–2.38 (m, 2H; CH_2), 2.57 (m, 1H; CH), 4.75 (m, 1H; 2-H), 5.10–5.30 (m, 2H; =CH_2), 5.58 (m, 1H; C*H*=CH_2), 7.35–7.50 (m, 3H; Ph), 7.88 (d, $J = 9$ Hz, 2H; Ph); ^{13}C NMR ($CDCl_3$, 62.5 MHz): $\delta = 19.66$ (CH_3), 23.79, 30.78 (CH_2), 33.57 (CH), 35.71 (CH_2), 48.21 (CH), 84.75 (CH), 105.58 (C), 117.91 (CH_2), 127.05, 128.29, 132.26, 135.38 (CH), 142.40, 164.39 (C); IR (KBr): $\tilde{\nu} = 3444$ (br), 3077 (w), 2933 (m), 2854 (m), 1652 (s), 1446 (m), 1334 (m), 1286 (m), 1210 (m), 1147 (s), 1134 (s), 1087 (s), 1022 (m) cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 304 (68) $[M]^+$, 250 (100), 235 (60), 163 (62); HR-MS (EI, 70 eV): calcd for $C_{17}H_{20}O_3S$; found: 304.1133 ± 2 mD $[M]^+$.

4-Butyl-7-phenylsulfonyl-2-vinyl-2,3,3a,4,5,6-hexahydro-2,3-benzofuran (8c): Starting with sulfone **7c** (1.30 g, 4.42 mmol), **8c** was isolated as a colourless oil (610 mg, 40%). ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.78$ (m, 3H; CH_3), 1.05–1.30 (m, 8H; CH_2), 1.35, 1.90 (2 × m, 2 × 1H; CH_2), 2.20–2.40 (m, 3H; CH, CH_2), 2.58 (m, 1H; CH_2), 4.69 (m, 1H; 2-H), 5.05–5.25 (m, 2H; =CH_2), 5.55 (m, 1H; C*H*=CH_2), 7.30–7.50 (m, 3H; Ph), 7.85 (d, $J = 9$ Hz, 2H; Ph); ^{13}C NMR ($CDCl_3$, 62.5 MHz): $\delta = 13.62$ (CH_3), 22.47, 23.69, 27.68, 28.19, 33.52, 35.76 (CH_2), 38.23, 46.83, 84.55 (CH), 105.47 (C), 117.63 (CH_2), 126.85, 128.12, 132.08, 135.27 (CH), 142.31, 164.42 (C); IR (neat): $\tilde{\nu} = 3467$ (br), 3065 (w), 2955 (s), 2930 (s), 2860 (m), 1712 (m), 1656 (s), 1447 (s), 1306 (s), 1216 (m), 1147 (s), 1098 (m), 1083 (s) cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 346 (46) $[M]^+$, 235 (78), 205 (100), 195 (96); HR-MS (EI, 70 eV): calcd for $C_{20}H_{26}O_3S$; found: 346.1603 ± 2 mD $[M]^+$.

5-Phenyl-7-phenylsulfonyl-2-vinyl-2,3,3a,4,5,6-hexahydro-2,3-benzofuran (8d): Starting with sulfone **7d** (2.214 g, 7.04 mmol), **8d** was isolated as a colourless oil (1.026 g, 40%). ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 1.20-1.60$ (m, 2H; CH_2), 1.80–2.20 (m, 2H; CH_2), 2.40 (m, 2H; CH_2), 2.85–3.00 (m, 2H; CH, CH_2), 4.80 (m, 1H; 2-H), 5.15–5.40 (m, 2H; =CH_2), 5.70 (m, 1H; C*H*=CH_2), 7.10–7.35 (m, 5H; Ph), 7.35–7.60 (m, 3H; Ph), 7.95 (d, $J = 10$ Hz, 2H; Ph); ^{13}C NMR ($CDCl_3$, 62.5 MHz): $\delta = 27.44$, 33.32 (CH_2), 36.19 (CH), 36.25 (CH_2), 36.37, 84.53 (CH), 104.78 (C), 118.10 (CH_2), 126.09, 126.58, 127.04, 128.16, 128.42, 132.42, 135.17 (CH), 142.22, 143.75, 164.90 (C); IR (KBr): $\tilde{\nu} = 3442$ (br), 3025 (w), 2976 (w), 2922 (m), 1722 (m), 1652 (s), 1446 (s), 1304 (s), 1217 (m), 1146 (s), 1133 (s), 1087 (s) (s) cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 366 (100) $[M]^+$, 312 (26), 262 (52), 225 (71); HR-MS (EI, 70 eV): calcd for $C_{22}H_{22}O_3S$; found: 366.1290 ± 2 mD $[M]^+$.

5-*tert*-Butyl-7-phenylsulfonyl-2-vinyl-2,3,3a,4,5,6-hexahydro-2,3-benzofuran (8e): Starting with sulfone **7e** (1.235 g, 4.20 mmol), **8e** was isolated as a colourless oil (0.465 g, 32%). ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 0.91$ (s, 9H; *t*Bu), 1.15–1.55 (m, 3H; CH_2), 1.95–2.20 (m, 2H; CH_2), 2.30 (m, 1H; CH_2), 2.60–2.80 (m, 2H; CH, CH_2), 4.75 (m, 1H; 2-H), 5.10–5.30 (m, 2H; =CH_2), 5.55 (m, 1H; C*H*=CH_2), 7.40–7.60 (m, 3H; Ph), 7.96 (d, $J = 10$ Hz, 2H; Ph); ^{13}C NMR ($CDCl_3$, 62.5 MHz): $\delta = 25.38$ (CH_2), 27.19 (CH_3), 28.35 (CH_2), 32.50 (C), 37.16 (CH_2), 42.55, 44.60 (CH), 85.10 (CH), 118.04 (CH_2), 127.25, 128.41, 132.33, 135.50 (CH), 142.63, 165.01 (C); IR (KBr): $\tilde{\nu} = 3483$ (br), 3066 (w), 2962 (s), 2870 (m), 1719 (m), 1661 (m), 1478 (m), 1447 (m), 1397 (m), 1368 (m), 1306 (s), 1146 (s), 1084 (s) cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 346 (27) $[M]^+$, 292 (7), 236 (100); HR-MS (EI, 70 eV): calcd for $C_{20}H_{26}O_3S$; found: 346.1602 ± 2 mD $[M]^+$.

5-Methyl-7-phenylsulfonyl-2-vinyl-2,3,3a,4,5,6-hexahydro-2,3-benzofuran (8f): Starting with sulfone **7f** (1.360 g, 5.39 mmol), **8f** was isolated as a colourless oil (540 mg, 33%). ^{1}H NMR ($CDCl_3$, 250 MHz, two diastereomers, 1:1): $\delta = 0.85-1.00$ (m, 3H; CH_3), 1.15, 1.60–1.95, 2.10–2.30, 2.35–2.80 (4 × m, 4 × 2H; CH, CH_2), 4.72 (m, 1H; 2-H), 5.05–5.25 (m, 2H; =CH_2), 5.53 (m, 1H; C*H*=CH_2), 7.30–7.50 (m, 3H; Ph), 7.85 (m, 2H; Ph); ^{13}C NMR ($CDCl_3$, 62.5 MHz): $\delta = 19.02/21.11$ (CH_3), 25.98/29.28 (CH), 30.14/31.96, 32.25/34.88, 36.62/36.72 (CH_2), 36.14/41.92, 84.44/84.88 (CH), 104.53/105.20 (C), 117.77/117.87 (CH_2), 126.82/126.87, 128.09/128.20, 132.17/132.19, 135.24/135.27 (CH), 142.24/142.29, 164.09/164.99 (C); IR (KBr): $\tilde{\nu} = 3463$ (br), 2957 (m), 2928 (m), 1719 (m), 1654 (s), 1448 (m), 1323 (m), 1289 (s), 1212 (m), 1148 (s), 1138 (s), 1085 (s) cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 304 (50) $[M]^+$, 250 (100); HR-MS (EI, 70 eV): calcd for $C_{17}H_{20}O_3S$; found: 304.1133 ± 2 mD $[M]^+$.

8-Phenylsulfonyl-2-vinyl-2,3,3a,4,5,6,7-heptahydro-2,3-benzofuran (8h): Starting with sulfone **7h** (1.405 g, 5.57 mmol), **8h** was isolated as a colourless oil (805 mg, 48%). ^{1}H NMR ($CDCl_3$, 250 MHz, two diastereomers, 3:1): $\delta = 1.30-1.50$ (m, 2H; CH_2), 1.70–2.50 (m, 6H; CH, CH_2), 2.90–3.20 (m, 3H; CH, CH_2), 3.89, 4.61 (2 × m, 1H; 2-H), 4.85–5.15 (m, 2H; =CH_2), 5.40–5.70 (m, 1H; C*H*=CH_2), 7.35–7.55 (m, 3H; Ph), 7.90 (d, $J = 10$ Hz, 2H; Ph); ^{13}C NMR ($CDCl_3$, 62.5 MHz): $\delta = 26.00/26.17$, 26.38/26.60, 29.11/29.66, 30.90/31.44, 36.14/37.08 (CH_2), 43.24/44.20, 83.59/83.92 (CH), 110.59 (C), 115.43/116.17 (CH_2), 126.52/126.56, 127.66/127.73, 131.53/131.57, 135.14/135.48 (CH), 142.81/143.02, 169.46/169.79 (C); IR (KBr): $\tilde{\nu} = 3455$ (br), 3064 (w), 2928 (s), 2856 (m), 1709 (m), 1633 (m), 1447 (s), 1305 (s), 1209 (m), 1143 (s), 1083 (m) cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 304 (52)

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$[M]^+$, 250 (100), 163 (82); HR-MS (EI, 70 eV): calcd for $C_{17}H_{20}O_3S$; found: 304.1133 ± 2 mD $[M]^+$.

Procedure for the synthesis of 1-phenylsulfonyl-7-vinylbicyclo [3.2.1]octan-8-ones (9): Compounds **9** were prepared according to the procedure given for the synthesis of bicyclo[3.2.1]octan-8-ones **4** ($T = 60\,^\circ C$, $t = 14$ h).

1-Phenylsulfonyl-7-vinylbicyclo[3.2.1]octan-8-one (9a): Starting with **8a** (168 mg, 0.58 mmol), **9a** was isolated as a colourless oil (136 mg, 81 %). ^1H NMR ($CDCl_3$, 250 MHz): $\delta = 1.65$ (m, 1H; 3-H), 1.75 (m, 1H; 6-H), 1.95 (m, 2H; 4-H), 2.18 (m, 1H; 3-H), 2.30 (m, 1H; 6-H), 2.45 (m, 1H; 5-H), 2.55 (m, 2H; 2-H), 3.49 (m, 1H; 7-H), 5.35 (dd, $J = 14$, $J = 3$ Hz, 2H; $=CH_2$), 6.32 (m, 1H; C*H*$=CH_2$), 7.50–7.70 (m, 3H; Ph), 8.02 (d, $J = 9$ Hz, 2H; Ph); ^{13}C NMR ([D$_6$]acetone, 62.5 MHz): $\delta = 17.13$, 26.91, 32.63, 36.09 (CH_2), 37.60, 45.32 (CH), 74.06 (C), 117.70 (CH_2), 128.44, 130.92, 133.87, 134.67 (CH), 136.43, 210.21 (C); IR (KBr): $\tilde{\nu} = 3447$ (br), 2957 (w), 2928 (w), 1752 (s), 1446 (m), 1306 (s), 1142 (s), 1084 (m) cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 290 (32) $[M]^+$, 236 (100); elemental analysis calcd (%) for $C_{16}H_{18}O_3S$ (290.4): C 66.18, H 6.25; found: C 65.85, H 6.19.

4-Methyl-1-phenylsulfonyl-7-vinylbicyclo[3.2.1]octan-8-one (9b): Starting with **8b** (236 mg, 0.78 mmol), **9b** was isolated as a colourless oil (182 mg, 77 %). ^1H NMR ($CDCl_3$, 250 MHz): $\delta = 0.85$ (d, $J = 9$ Hz, 3H; CH_3), 1.28 (dd, $J = 6$, $J = 14$ Hz, 1H; CH_2), 1.75 (dd, $J = 7$, $J = 14$ Hz, 1H; CH_2), 2.00–2.50 (m, 6H; CH_2), 3.35 (m, 1H; CH), 5.25 (m, 2H; $=CH_2$), 6.26 (m, 1H; C*H*$=CH_2$), 7.45–7.65 (m, 3H; Ph), 7.98 (d, $J = 9$ Hz, 2H; Ph); ^{13}C NMR ($CDCl_3$, 62.5 MHz): $\delta = 17.59$ (CH_3), 23.25, 27.92, 28.25 (CH_2), 36.57, 41.13, 51.00 (CH), 73.57 (C), 117.59 (CH_2), 128.37, 130.73, 133.80, 134.89 (CH), 136.24, 208.03 (C); IR (KBr): $\tilde{\nu} = 3475$ (br), 3072 (m), 2959 (m), 2936 (m), 2875 (m), 1750 (s), 1448 (m), 1327 (m), 1304 (s), 1290 (s), 1152 (s), 1088 (s) cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 304 (51) $[M]^+$, 275 (100); elemental analysis calcd (%) for $C_{17}H_{20}O_3S$ (304.4): C 67.07, H 6.62; found: C 66.85, H 6.51.

4-Butyl-1-phenylsulfonyl-7-vinylbicyclo[3.2.1]octan-8-one (9c): Starting with **8c** (207 mg, 0.60 mmol), **9c** was isolated as a colourless oil (72 mg, 35 %). ^1H NMR ($CDCl_3$, 250 MHz): $\delta = 0.80$ (m, 3H; CH_3), 1.10–1.30 (m, 6H; CH_2), 1.42, 1.78 (2 × m, 2 × 1H; CH_2), 2.04 (m, 2H; CH, CH_2), 2.20–2.50 (m, 4H; CH, CH_2), 3.35 (m, 1H; CH), 5.30 (m, 2H; $=CH_2$), 6.35 (m, 1H; C*H*$=CH_2$), 7.50–7.70 (m, 3H; Ph), 8.05 (d, $J = 9$ Hz, 2H; Ph); ^{13}C NMR ($CDCl_3$, 62.5 MHz): $\delta = 13.93$ (CH_3), 21.66, 22.42, 27.98, 28.60, 29.58, 31.24 (CH_2), 36.88, 46.83, 49.23 (CH), 73.92 (C), 117.73 (CH_2), 128.53, 130.95, 133.90, 135.04 (CH), 136.80, 208.35 (C); IR (KBr): $\tilde{\nu} = 3474$ (br), 2961 (m), 2927 (m), 1749 (s), 1455 (m), 1300 (m), 1149 (s), 1088 (m) cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 346 (76) $[M]^+$, 317 (98), 289 (100); HR-MS (EI, 70 eV): calcd for $C_{20}H_{26}O_3S$; found: 346.1603 ± 2 mD $[M]^+$.

3-Phenyl-1-phenylsulfonyl-7-vinylbicyclo[3.2.1]octan-8-one (9d): Starting with **8d** (146 mg, 0.40 mmol), **9d** was isolated as a colourless oil (91 mg, 63 %). ^1H NMR ($CDCl_3$, 250 MHz, *endo*/*exo* = 3.5:1): $\delta = 1.90–2.20$ (m, 3H; CH_2), 2.25–2.45 (m, 2H; CH_2), 2.58, 2.68 (2 × m, 2 × 1H; CH, CH_2), 3.45, 3.58 (2 × m, 2 × 1H; CH, CH_2), 5.20, 5.46 (2 × m, 2H; $=CH_2$, *exo*, *endo*), 6.15, 6.45 (2 × m, 1H; C*H*$=CH_2$, *exo*, *endo*), 7.08–7.35 (m, 5H; Ph), 7.50–7.70 (m, 3H; Ph), 8.05 (d, $J = 9$ Hz, 2H; Ph); ^{13}C NMR ($CDCl_3$, 62.5 MHz, *endo*-isomer): $\delta = 26.80$ (CH_3), 34.95, 37.24 (CH), 39.06, 42.31 (CH_2), 44.82 (CH), 72.96 (C), 117.72 (CH_2), 126.63, 126.75, 128.31, 128.36, 130.51, 133.78, 134.24 (CH), 136.27, 141.46, 209.45 (C); IR (KBr): $\tilde{\nu} = 3477$ (br), 3061 (w), 3028 (w), 2951 (m), 2924 (m), 1750 (s), 1637 (m), 1601 (m), 1495 (m), 1446 (s), 1307 (s), 1286 (s), 1145 (s), 1978 (m) cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 366 (80) $[M]^+$, 261 (31), 225 (55), 91 (100); HR-MS (EI, 70 eV): calcd for $C_{22}H_{22}O_3S$; found: 366.1290 ± 2 mD $[M]^+$.

Acknowledgements

P.L. thanks Professor A. de Meijere for his support. Financial support from the Fonds der Chemischen Industrie e.V. (Liebig scholarship and funds for P.L.) and from the Deutsche Forschungsgemeinschaft (Heisenberg scholarship to P.L.) is gratefully acknowledged.

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Received: March 12, 2001 [F3124]
publication delayed at author's request

  0947-6539/02/0804-0928 $ 17.50+.50/0