Palladium-Catalysed Vinylic Substitution of Aryl/Vinyl Iodides and Triflates with α-Methylene-γ-butyrolactone − An Application to the Synthesis of 3-Alkyl-γ-Butyrolactones through Combined Palladium-Catalysed Coupling/Hydrogenation Reactions

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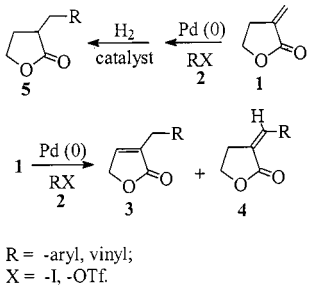
The palladium-catalysed arylation/vinylation of α-methylene-γ-butyrolactone (**1**) proceeds in good yield, mainly to give stereodefined aryl/vinyl-substituted α-alkylidene-γ-butyrolactones **4**. In addition, the palladium-catalysed arylation of α-methylene-γ-butyrolactone (**1**) may be directed towards the synthesis of 3-benzylfuran-2(5*H*)-ones **3** when the starting aryl iodides contain groups with electron-withdrawing conjugative properties. The combined palladium-catalysed coupling/hydrogenation reactions represent a new, simple route to functionalised 3-alkyl-γ-butyrolactones **5**, giving prominence to the possibility of stereocontrol in the formation of the new stereocentres.

Introduction

The palladium-catalysed arylation and vinylation of alkenes (Heck reaction) has become one of the most important and powerful transition metal catalysed transformations in organic synthesis for the generation of new carbon−carbon bonds.[1] The lack of selectivity once represented a serious drawback. The Heck reaction is increasing in importance for the synthesis of polyfunctional compounds because of the high levels of control over regioselectivity and stereoselectivity recently achieved and the flexibility of the methodology.[2]

In connection with our interest in developing new synthetic strategies for the construction of heterocycles involving palladium catalysis,[3] we thought that α-methylene-γ-butyrolactone (**1**) might represent a suitable building block for the synthesis of furan-2(5*H*)-ones **3** and stereodefined α-alkylidene-γ-butyrolactones **4**. Furthermore, combined palladium-catalysed coupling/hydrogenation reactions may represent an expeditious approach to 3-substituted-γ-butyrolactones **5** (Scheme 1).

In recent years, great interest has been focused on the synthesis of molecules containing the butenolide ring.[4] Some of these derivatives exhibit interesting biological properties and are useful synthetic intermediates.[5] The α-methylene-γ-butyrolactone moiety is a structural feature of many natural products exhibiting antitumour and cytotoxic activities.[6] The alkylation and arylation of the exocyclic double bond represent the main pathway for modulation of their biological activities as well as for modification of chemical and physical activities.[7] γ-Butyrolactones with a wide range of substituents are often observed in nature and are also of biological significance. Because of their importance as building blocks in natural products synthesis, in addition to their interesting pharmacological activities, a remarkable amount of effort has been devoted to the synthesis of this type of compounds.[8]



Scheme 1

Initially, we reported that the palladium-catalysed arylation[9] of α-methylene-γ-butyrolactone (**1**) could proceed in good yield, and might be directed towards the synthesis of 3-benzylfuran-2(5*H*)-one when the starting aryl iodides contained strongly electron-withdrawing groups. Moreover, combined palladium-catalysed arylation/hydrogenation treatment of α-methylene-γ-butyrolactone (**1**) produced 3-benzyl-γ-butyrolactones. With the aim of extending the procedure to vinyl iodides and triflates, we wish to report the full details of the results we have obtained, together with the scope and limitations of this synthetic methodology.

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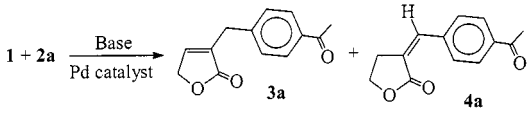
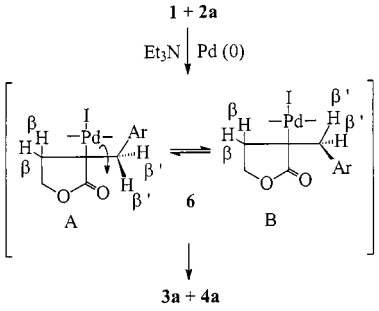
Results and Discussion

As part of our ongoing interest in the preparation of butenolides/methylene-γ-butyrolactones/γ-butyrolactones,[10] and on the basis of results of vinylic substitution of unsaturated halides/triflates with α-acetamidoacrylic acid derivatives and α-methylacrylic acid derivatives,[11] we decided to investigate the palladium-catalysed arylation of **1** using aryl/vinyl iodides/triflates **2** as σ-donors. The aim was to achieve the regioselective synthesis of furan-2(5*H*)-one derivatives **3** and the stereodefined synthesis of substituted α-alkylidene-γ-butyrolactones **4**. 4-Iodoacetophenone (**2a**) was selected as the model aryl iodide and the preparation of the corresponding coupling derivative with the aid of palladium catalysis was tried under a variety of conditions to evaluate the influence of the catalytic system, bases and **1**/**2** ratio on the reaction outcome (Scheme 2 and Table 1).



Scheme 2

When Et_3N was used as the base in the presence of catalytic amounts of $Pd(OAc)_2[Pd(o\text{-tolyl})_3]_2$ in DMF at 80 °C, the corresponding compounds **3a** and **4a** were isolated after 8 h, in 42% and 21% yields, respectively (Table 1, Entry 1; Scheme 3). Under these conditions, the primary reduction of Pd^{II} to Pd^0 is most probably accomplished by phosphane.[12] Surprisingly, the reaction showed a very low selectivity in the elimination step. *syn*-β′-Elimination of hydridopalladium species from the addition intermediate **6** could compete with *syn*-β-elimination. Very probably, rotation around the $C_\alpha-C_{\beta'}$ bond occurs faster than *syn*-elimination of hydridopalladium, and it can be assumed that **4a** originates from the favourable conformation[13] **6B**.



Scheme 3

No Michael arylation [by addition of aryl iodides onto α,β-unsaturated lactones[14] in the presence of catalytic amount of palladium(0) and triethylamine] was observed even in the presence of an excess of formic acid[15] (Table 1, Entry 2). Surprisingly, under these latter conditions, a change in the **3a**/**4a** ratio from 2:1 to 1:1 was observed, highlighting the influence that the reaction conditions have on the outcome of the reaction. To the best of our knowledge, this is the first example of butenolide derivative formation starting from **1**. Palladium-catalysed treatment of an arenediazonium salt with **1** has been reported[16] to give α-benzylidene-γ-butyrolactones in excellent yields as (*E*) + (*Z*) stereoisomeric mixtures. In contrast, our derivative **4a** was isolated as single (*Z*) stereoisomer. The olefin geometry was unambiguously assigned by T-ROESY NMR experiments. The cross-peak obtained for the olefinic proton at

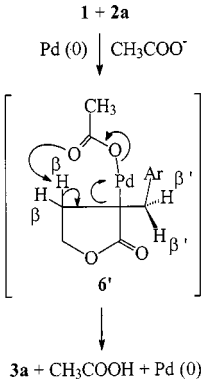
Table 1. Experimental conditions for the synthesis of **3a** and **4a** from **1** and 4-iodoacetophenone (**2a**)

Entry[a,b]	Base	Solvent	Catalyst	*t* [h]	Yield (%) of **3a** + **4a**	Ratio **3a**/**4a**
1	Et_3N	DMF	$Pd(OAc)_2/P(o\text{-tol})_3$	8	63	2
2	nBu_3N/HCOOH[c]	DMF	$Pd(OAc)_2/(PPh_3)$	2	75	1
3	Et_3N	DMF	$Pd(OAc)_2$	20	60	1.3
4	AcOK	DMF	$Pd(OAc)_2$	9	54	24
5	AcOK[d]	DMF	$Pd(OAc)_2$	48	53	5.6
6	AcOK[e]	DMF	$Pd(OAc)_2$	4	54	25
7	AcOK	NMP	$Pd(OAc)_2$	21	45	28
8	AcOK	DMA	$Pd(OAc)_2$	23	32	30
9	AcOK + Et_3N[f]	DMF	$Pd(OAc)_2$	9	66	11
10	AcOK + K_2CO_3 [g]	DMF	$Pd(OAc)_2$	5	–	–
11	AcOTl	DMF	$Pd(OAc)_2(PPh_3)_2$	24	33	8.5
12	AcOTl	DMF	$Pd(OAc)_2$	8	55	7.1

[a,b] Unless otherwise stated, the reactions were carried out at 80 °C under nitrogen with the following molar ratios: **1**/**2**/catalyst/base = 1:1.5:0.05:3. – [b]Yields refer to single runs and are given for pure isolated products. – [c] The reaction was carried out at 80 °C under nitrogen with the following molar ratios: **1**/**2**/catalyst/HCOOH/nBu_3N = 1:2.4:0.02:3.4:2.64. – [d] Temperature 40 °C. – [e] The reaction was carried out at 80 °C under nitrogen with the following molar ratios: **1**/**2**/catalyst/TBACl/base = 1:1.5:0.05:1:3. – [f] The reaction was carried out at 80 °C under nitrogen with the following molar ratios: **1**/**2**/catalyst/CH_3COOK/Et_3N = 1:1.5:0.05:1:2. – [g] The reaction was carried out at 80 °C under nitrogen with the following molar ratios: **1**/**2**/catalyst/CH_3COOK/K_2CO_3 = 1:1.5:0.05:3:4.

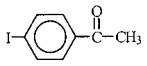
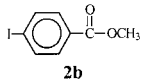
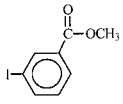
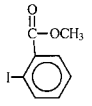
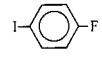
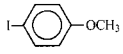
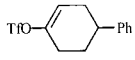
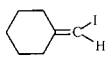
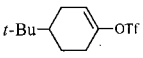
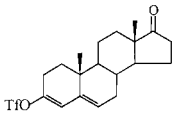
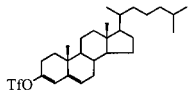
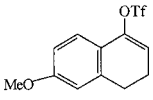
δ = 7.55 and for the methylene protons (OCH_2CH_2) at δ = 3.25 clearly indicates the (*Z*) geometry.

Stereodefined α-benzylidene-γ-lactones are useful intermediates for the synthesis of podophyllotoxin[17] and optically active α-spirocyclopropyllactones.[18] Recently, cross-coupling reactions of tosylates of (*E*)- and (*Z*)-α-hydroxymethylene-γ-butyrolactones with aryl, heteroaryl, alkyl and alkynylzinc chlorides under $Pd(PPh_3)_4$ catalysis conditions have been found to represent a suitable synthetic method for stereoselective preparation of α-alkylidene-γ-lactones.[19] With the aim of controlling the selectivity of the palladium-catalysed arylation reaction, we tried the following modification of the reaction conditions. Omission of the ligand (Table 1, Entry 3) produced only minor modifications of the reactivity and/or selectivity, at least from a synthetic point of view. Switching to AcOK, in the presence of catalytic amounts of $Pd(OAc)_2$ in DMF at 80 °C, chemoselectively produced **3a** in 54% yield (Table 1, Entry 4). In phosphane-free systems, the reduction of Pd^{II} to Pd^0 can be effected by amines, if these are used as base, or by olefins.[20] The addition of nBu_4NCl increased the reaction rate without modification of the selectivity (Table 1, Entry 6).[21] When *N*-methyl-2-pyrrolidone or *N*,*N*-dimethylacetamide were used as solvents the selectivity was higher than in DMF, but lower conversions were then observed (Table 1, Entries 7, 8). The role of the base for directing the β-elimination step of palladium hydride is also demonstrated by the lower selectivity obtained when using a mixed system AcOK/Et_3N (Table 1, Entry 9). Utilization of the KOAc/K_2CO_3 combination[22](Table 1, Entry 10) or Cs_2CO_3 [23] resulted in complete failure. Finally, we used AcOTl instead of AcOK, to make sure that the formation of **3a** was not a consequence of the migration of the double bond of the initially formed compound **4a**. Tl^I [24] salts are reported to block the isomerization of the double bond caused by a β-elimination of palladium hydride/readdition/elimination sequence. The isolation of **3a** as the main product also in the presence of AcOTl (Table 1, Entries 11,12) clearly rules out isomerization. An explanation based on the formation of a σ-alkylpalladium acetate intermediate **6′** has been considered. Its decomposition through basic intramolecular attack of the acetate moiety on the β-hydrogen atom might account for the regioselective β-elimination observed in the



Scheme 4

Table 2. Synthesis[a] of 3-alkylfuran-2(5*H*)-ones **3**, α-alkylidene-γ-butyrolactones **4** and 3-substituted γ-butyrolactones **5**

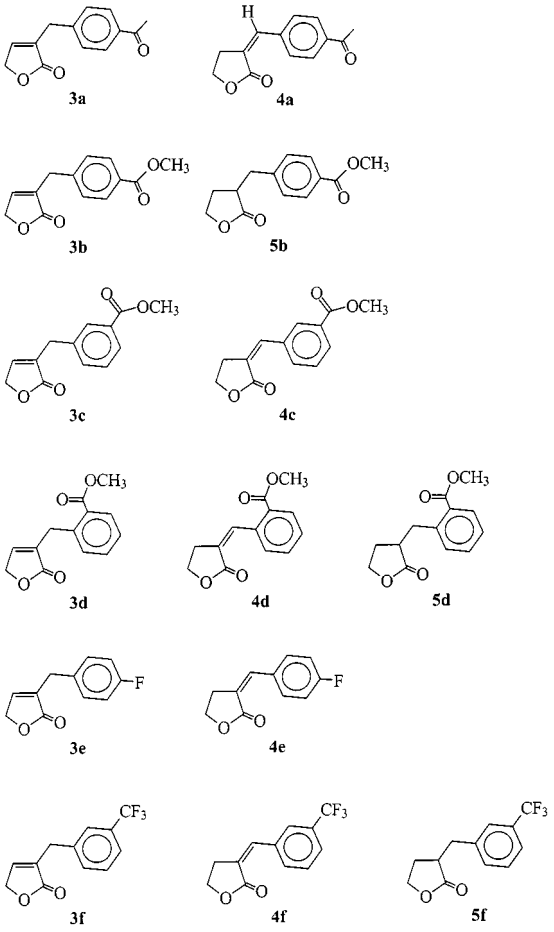
Entry	Procedure	2	Time (h)	3 (% yield)	4 (% yield)	5 (% yield)
1	A	 **2a**	2	**3a** (64)		
2	A	 **2b**	10	**3b** (60)		
3	B	**2b**	10+2			**5b** (57)
4	A	 **2c**	6	**3c** (26)	**4c** (48)	
5	A	 **2d**	4	**3d** (45)	**4d** (36)	
6	B	**2d**	4+2			**5d** (78)
7	A	 **2e**	5	**3e** (26)	**4e** (62)	
8	A	 **2f**	3	**3f** (34)	**4f** (47)	
9	B	**2f**	3+2			**5f** (78)
10	A	 **2g**	8	**3g** (30)	**4g** (52)	
11	B	**2g**	8+2			**5g** (70)
12	A	 **2h**	8	**3h** (20)	**4h** (42)	
13	B	**2h**	8+2			**5h** (59)
14	A	 **2i**	6	**3i** (25)	**4i** (47)	
15	A	 **2j**			**4j** (55)	
16	A	 **2k**		**3k** (7)	**4k** (65)	
17	B	 **2l**	8+3			**5l** (80)
18	B	 **2m**	18+3			**5m** (82)
19	B	 **2n**	6+3			**5n** (76)

[a] Yields refer to single runs, are given for pure isolated products, and are based on **2**.

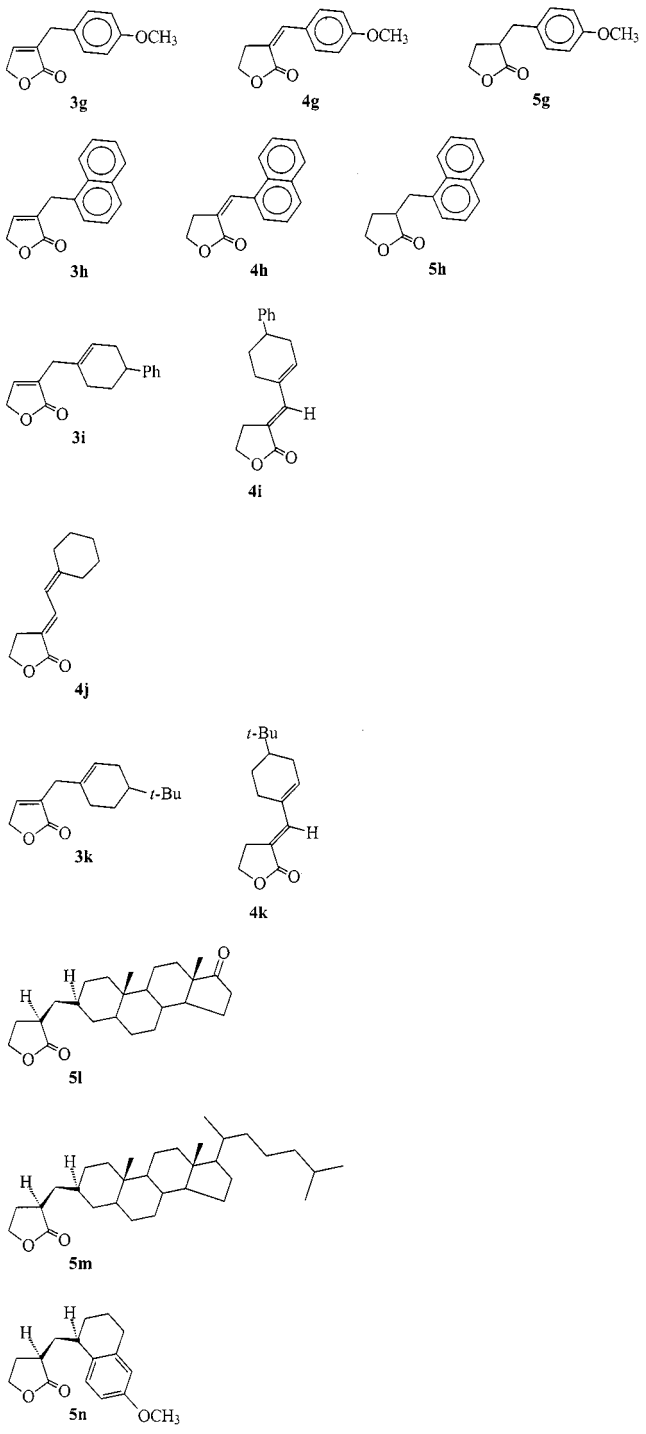
presence of favourable electronic effects. The presence of the electron-withdrawing acyl group on the aromatic ring makes the β′-elimination of hydridopalladium more difficult (Scheme 4). Related mechanisms involving a seven-membered cyclic transition state containing palladium have been suggested.[25]

Similarly, when the system was extended to other aryl iodides, the chemoselective formation of the butenolide derivatives **3** (Table 2) was accomplished only in the presence of conjugating electron-withdrawing *para* substituents on the aromatic moiety. This suggests the importance of conjugative effects for the determination of the selectivity.

Otherwise (*Z*)-benzylidene derivatives **4c**−**h** were isolated as the prevalent reaction product (Table 2 and Scheme 5). (*Z*)-Olefin geometry of the benzylidene derivatives **4a** and **4c**−**h** was established in all cases by means of the NOEs between the olefinic protons and the 4-CH_2 protons. Saturation of the signal of the olefinic proton resulted in an increase of 13−16% in the methylene protons, depending only slightly on the aryl substituent. It must be emphasized that variable amounts of biaryl derivatives were observed in all the reactions, and better results were usually obtained when using 1.5 mol equivalents of α-methylene-γ-butyrolactone (**1**) over the halide. Surprisingly, switching to the vinyl triflate **2i** (Table 2, Entry 14; Scheme 6) as σ-donor allowed



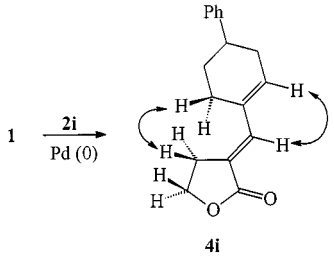
Scheme 5. Structures of compounds **3**−**5**



Scheme 5 *(Continued)*

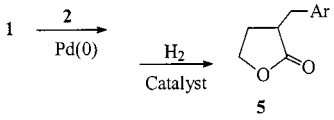
the (*E*)-vinyl-substituted α-alkylidene-γ-lactone **4i** to be synthesised. The stereochemistry of **4i** was investigated by NMR. T-ROESY NMR experiments clearly showed that the cyclohexenyl and butyrolactone moieties were in (*E*) orientation [no interaction between the olefinic proton of the methylene-γ-butyrolactone fragment (δ = 7.13) and the OCH_2CH_2 protons was observed; this interaction might reflect (*Z*) geometry]. Additionally, the NOE between the olefinic proton of the cyclohexenyl ring (δ = 6.24) and the

olefinic proton of the methylene-γ-butyrolactone fragment (δ = 7.13) showed the *s-trans* configuration of the diene fragment. Saturation at δ = 6.24 resulted in an increase of 16% in the olefinic proton at δ = 7.13.



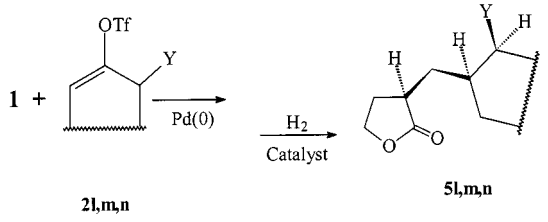
Scheme 6

Analogously, the regioselective and stereoselective synthesis of the (*E*)-vinyl-substituted α-alkylidene-γ-lactones **4j** and **4k** was achieved by using the vinyl iodide **2j** and the vinyl triflate **2k** as σ-donors (Table 2, Entries 15, 16). Very probably, the (*E*) stereoselectivity was due to the formation of intermediate π-allylpalladium complexes,[26] which isomerize to give the thermodynamically favoured stereoisomer[27] [ab initio molecular orbital calculations at the HF/6−31G(d) level show that the energy difference between the more stable compound (*E*)-**4** and the corresponding (*Z*)-**4** stereoisomer is > 20 kJ·mol^{-1}]. Combined arylation/hydrogenation to give **5** has also been accomplished (Scheme 7).



Scheme 7

Interestingly, the application of this synthetic methodology (Scheme 8), using vinyl triflates as σ-donors in the palladium-catalysed Heck-type step, gives particular prominence to the possibility of stereocontrol in the formation of the new stereocentres.



Scheme 8

Steroidal substrates possessing 3,5-diene functionality, obtained in coupling reactions with **2l** and **2m**, were reduced from the α-face as expected, in the absence of any β-directing group. Since hydrogen addition takes place in *cis* manner, the newly formed stereogenic centres possess 3α-H and 5α-H. Consequently, the butyrolactone moiety is attached at the 3β-position, resulting in the thermodynamically more stable epimers **5l** and **5m**. [The almost exclusive formation of the 5α-epimer is supported by the δ(19-CH_3) value, which is characteristic of A/B *trans* anullation.[28]] No attempts were made to determine the configuration of the newly formed stereogenic centre of the butyrolactone ring. Similarly, the prevalent formation of one diastereomer has been observed in the case of **5n**, as a hydrogenated product with two stereogenic centres.

Conclusion

In conclusion, the results reported here show that the palladium-catalysed arylation/vinylation of α-methylene-γ-butyrolactone (**1**) proceeds in good yield to give mixtures of 3-benzylfuran-2(5*H*)-ones and stereodefined aryl/vinyl-substituted α-alkylidene-γ-butyrolactones. Moreover, the palladium-catalysed arylation of α-methylene-γ-butyrolactone (**1**) may be directed towards the synthesis of 3-benzylfuran-2(5*H*)-ones when the starting aryl iodides contain groups with electron-withdrawing conjugative properties. Combined palladium-catalysed coupling/hydrogenation reactions of α-methylene-γ-butyrolactone (**1**) represent a new, simple route to functionalised 3-alkyl-γ-butyrolactones, emphasizing the possibilities for stereocontrol in the formation of the new stereocentres.

Experimental Section

General Remarks: Melting points are uncorrected and were measured with a Büchi apparatus. − ^{1}H NMR and ^{13}C NMR spectra were recorded with a Varian Inova 400 or with a Bruker AC 200 E spectrometer. − EI (70 eV) mass spectra were recorded with a TSQ 700 Finnigan/Mat instrument. − IR spectra were recorded with a Perkin−Elmer 683 spectrometer. − CHN analyses were recorded with an Eager 200 analyser. − All starting materials, α-methylene-γ-butyrolactone (**1**), aryl iodides, catalysts, ligands, bases and solvents (anhydrous solvents included) are commercially available unless otherwise stated, and were used as purchased, without further purification.− Triflates[29] and vinyl iodides[30] were prepared as reported. The products, after conventional workup, were purified by flash chromatography on silica gel, eluting with *n*-hexane/ethyl acetate mixtures.

Procedure A: Aryl iodide or vinyl iodide/triflate (2 mmol), α-methylene-γ-butyrolactone (**1**) (3 mmol), AcOK (6 mmol) and $Pd(OAc)_2$ (0.1 mmol) were dissolved in DMF (3 mL), and the mixture was stirred under nitrogen at 80 °C. After it had cooled, the reaction mixture was washed with a mixture ethyl acetate and saturated aqueous $NaHCO_3$. The phases were separated and the combined organic phases dried with Na_2SO_4. After removal of the solvent, the crude product was purified by flash chromatography.

3-(4-Acetylbenzyl)-2(5*H*)-furanone (3a): 0.276 g; 64%; m.p. 126−127 °C. − IR (KBr): $\tilde{\nu}$ = 1745, 1670, 1260 cm^{-1}. − ^{1}H NMR (400 MHz $CDCl_3$): δ = 7.85 (d, *J* = 8.5 Hz, 2 H, Ar-H), 7.30 (d, *J* = 8.5 Hz, 2 H, Ar-H), 6.97 (m, 1 H, HC=), 4.75 (m, 2 H, OCH_2), 3.63 (d, *J* = 2.0 Hz, 2 H, $ArCH_2$), 2.55 (s, 3 H, $COCH_3$). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 197.5 (CO), 173.5 (*C*O-O), 146.2 (=*C*H), 135.6 (C_{Ar}), 132.8 (C_{Ar}), 130.7 (=*C*CO), 128.9 [C_{Ar}(H)], 128.6 [C_{Ar}(H)], 70.2 (OCH_2), 31.5 ($ArCH_2$), 26.4 (CH_3). − MS: *m*/*z* (%) = 216 (33) [M$^+$], 201 (100), 173 (35), 143 (26), 128 (40), 115 (79). − $C_{13}H_{12}O_3$: calcd. C 72.21, H 5.29; found C 71.32, H 6.41.

3-(4-Methoxycarbonylbenzyl)-2(5*H*)-furanone (3b): 0.278 g; 60%; m.p. 97−98 °C. − IR (KBr): $\tilde{\nu}$ = 1750, 1710, 1280 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 8.3 Hz, 2 H, Ar-H), 7.33 (d, *J* = 8.3 Hz, 2 H, Ar-H), 7.01 (m, 1 H, HC=), 4.80 (m, 2 H, OCH_2), 3.92 (s, 3 H, OCH_3), 3.66 (d, *J* = 1.8 Hz, 2 H, $ArCH_2$). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 174.3 (CO-O), 167.4 (Ar*C*O-O), 146.6 (=*C*H), 143.2 (C_{Ar}), 133.8 (C_{Ar}), 130.6 (=*C*CO), 128.5 [C_{Ar}(H)], 128.0 [C_{Ar}(H)], 70.9 (O*C*H$_2$), 52.7 (OCH_3), 32.3 (Ar*C*H$_2$). − MS: *m*/*z* (%) = 232 (7) [M^+], 201 (15), 187 (10), 173 (36), 129 (100), 115 (32). − $C_{13}H_{12}O_4$: calcd. C 67.23, H 5.24; found C 66.57, H 5.62.

3-(3-Methoxycarbonylbenzyl)-2(5*H*)-furanone (3c): 0.120 g; 26%; oil. − IR (neat): $\tilde{\nu}$ = 1750, 1715, 1275 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 7.90 (m, 2 H, Ar-H), 7.40 (m, 2 H, Ar-H), 6.95 (m, 1 H, HC=), 4.74 (m, 2 H, OCH_2), 3.83 (s, 3 H, OCH_3), 3.63 (d, *J* = 2.0 Hz, 2 H, $ArCH_2$). − ^{13}C NMR (100.58 MHz, $CDCl_3$): δ = 173.6 (*C*O-O), 166.8 (*C*OOCH$_3$), 145.8 (=*C*H), 137.7 (C_{Ar}), 133.7 (C_{Ar}), 133.5 [C_{Ar}(H)], 130.6 (=*C*CO), 129.9 [C_{Ar}(H)], 128.8 [C_{Ar}(H)], 128.1 [C_{Ar}(H)], 70.2 (O*C*H$_2$), 52.1 (O*C*H$_3$), 31.6 (Ar*C*H$_2$). − MS: *m*/*z* (%) = 232 (6) [M^+], 200 (100), 172 (12), 155 (11), 129 (30). − $C_{13}H_{12}O_4$: calcd. C 67.23, H 5.24; found C 66.19, H 5.48.

(*Z*)-3-(3-Methoxycarbonylbenzylidene)dihydro-2(3*H*)-furanone (4c): 0.223 g; 48%; m.p.103−105 °C. − IR (KBr): $\tilde{\nu}$ = 1745, 1710, 1260 cm^{-1}. −^1H NMR (400 MHz, $CDCl_3$): δ = 8.10 (1 H, br. s, HC=), 7.97 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.60 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.45 (m, 2 H, Ar-H), 4.41 (t, *J* = 7.2 Hz, 2 H, OCH_2), 3.87 (s, 3 H, OCH_3), 3.2 (dt, *J* = 7.2, 3.2 Hz, 2 H, CH_2). − ^{13}C NMR (100.58 MHz, $CDCl_3$): δ = 171.9 (*C*O-O), 166.2 (*C*OOCH$_3$), 145.9 (=*C*H), 135.0 [C_{Ar}(H)], 134.7 (C_{Ar}), 134.0 [C_{Ar}(H)], 130.7 (C_{Ar}), 130.4 [C_{Ar}(H)], 128.9 [C_{Ar}(H)], 125.0 (=*C*CO), 65.3 (O*C*H$_2$), 52.2 (O*C*H$_3$), 27.2 (*C*H$_2$). − MS: *m*/*z* (%) = 232 (42) [M^+], 217 (100), 201 (60), 174 (19), 143 (19), 115 (56). − $C_{13}H_{12}O_4$: calcd. C 67.21, H 5.25; found C 67.80; H 5.72.

3-(2-Methoxycarbonylbenzyl)-2(5*H*)-furanone (3d): 0.209 g; 45%; m.p. 58−59 °C. − IR (KBr): $\tilde{\nu}$ = 1760, 1715, 1290 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 7.90 (dd, *J* = 7.6, 1.2 Hz, 1 H, Ar-H), 7.52 (dt, *J* = 7.2, 0.8 Hz, 1 H, Ar-H), 7.3 (m, 2 H, Ar-H), 6.85 (m, 1 H, HC=), 4.67 (m, 2 H, OCH_2), 3.92 (m, 2 H, $ArCH_2$), 3.81 (s, 3 H,OCH_3). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 173.7 (*C*O-O), 167.2 (*C*OOCH$_3$), 145.5 (=*C*H), 138.8 (C_{Ar}), 133.7 (=*C*CO), 133.3 [C_{Ar}(H)], 132.2 (C_{Ar}), 131.5 [C_{Ar}(H)], 130.8 [C_{Ar}(H)], 126.7 [C_{Ar}(H)], 70.0 (O*C*H$_2$), 52.7 (O*C*H$_3$), 30.0 (Ar*C*H$_2$). − MS: *m*/*z* (%) = 232 (1) [M^+], 200 (100), 156 (28), 128 (47), 115 (67), 86 (66). − $C_{13}H_{12}O_4$: calcd. C 67.21, H 5.25; found C 69.37; H 6.60.

(*Z*)-3-(2-Methoxycarbonylbenzylidene)dihydro-2(3*H*)-furanone (4d): 0.213 g; 36%; oil. − IR (neat): nu(tilde = 1750, 1710, 1260 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 8.10 (m, 1 H, HC=), 7.95 (dd, 1 H, *J* = 8, 1.2 Hz, Ar-H), 7.42 (m, 3 H, Ar-H), 4.36 (t, *J* = 7.2 Hz, 2 H, OCH_2), 3.1 (dt, *J* = 7.2, 2.8 Hz, 2 H, CH_2), 3.86 (s, 3 H, OCH_3). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 171.6 (*C*O-O), 166.8 (*C*OOCH$_3$), 135.7 (=*C*H), 131.9 [C_{Ar}(H)], 130.7 (C_{Ar}), 130.1 [C_{Ar}(H)], 128.8 (C_{Ar}), 128.7 [C_{Ar}(H)], 125.4 (=*C*CO), 65.4 (O*C*H$_2$), 52.2 (O*C*H$_3$), 26.7 (*C*H$_2$). − MS: *m*/*z* (%) = 232 (13) [M^+], 217 (13), 188 (100), 173 (75), 128 (10**0**), **1**14 (52), 103 (50). − $C_{13}H_{12}O_4$: calcd. C 67.21, H 5.25; found C 65.72; H 5.90.

3-(4-Fluorobenzyl)-2(5*H*)-furanone (3e): 0.100 g; 26%; m.p.92−94. − IR (KBr): $\tilde{\nu}$ = 1760cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 7.18 [dd, *J* = 8.8 Hz, 2 H, $^3J(^1H,^{19}F)$ = 5.2 Hz, Ar-H], 7.0 [t, *J* = 8.8 Hz, 2 H, $^4J(^1H,^{19}F)$ = 8.8 Hz, Ar-H], 6.92 (m, 1 H, HC=), 4.75 (m, 2 H, OCH_2), 3.56 (d, *J* = 1.6 Hz, 2 H, $ArCH_2$). −^{13}C NMR (100.58 MHz, $CDCl_3$): δ = 173.0 (*C*O-O), 161.8 [$^1J(^{19}F,^{13}C)$ = 245 Hz, C_{Ar}−F], 145.4 (*C*H=), 134.2 (C_{Ar}−CH_2), 133.0 (CO*C*=), 130.4 [d, $^3J(^{13}C,^{19}F)$=8 Hz, C_{Ar}(H)], 115.6 [d, $^2J(^{13}C,^{19}F)$ = 21 Hz, C_{Ar}(H)], 70.2 (O*C*H$_2$), 31.1 (Ar*C*H$_2$). − MS: *m*/*z* (%) = 192 (29) [M^+], 173 (4), 147 (100), 133 (21). − $C_{11}H_9FO_2$: calcd. C 68.74, H 4.72; found C 68.80; H 4.85.

(*Z*)-3-(4-Fluorobenzylidene)dihydro-2(3*H*)-furanone (4e): 0.238 g; 62%; oil. − IR (neat): $\tilde{\nu}$ = 1750, 1660 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 7.46 (m, 3 H, Ar-H + HC=), 7.10 [t, *J* = 8.8 Hz, 2 H, $^4J(^1H,^{19}F)$ = 8.8 Hz, Ar-H], 4.44 (t, 2 H, *J* = 7.2 Hz, OCH_2), 3.19 (dt, *J* = 7.2, 2.8 Hz, 2 H, CH_2). − ^{13}C NMR (100.58 MHz, $CDCl_3$): δ = 172.3 (*C*O-O), 163.2 [d, $^1J(^{19}F,^{13}C)$ = 251 Hz, C_{Ar}−F], 135.3 (=*C*H), 131.8 [d, $^3J(^{13}C,^{19}F)$ = 8.4 Hz, C_{Ar}(H)], 130.9 (C_{Ar}−CH=), 123.1 (CO*C*=), 116.1 [d, $^2J(^{13}C,^{19}F)$ = 22 Hz, C_{Ar}(H)], 65.3 (O*C*H$_2$), 27.2 (*C*H$_2$). − MS: *m*/*z* (%) = 192 (100) [M^+], 164 (13), 147 (35), 133 (70). − $C_{11}H_9FO_2$: calcd. C 68.74, H 4.72; found C 69.56; H 4.43.

3-(3-Trifluoromethylbenzyl)-2(5*H*)-furanone (3f): 0.165 g; 34%; oil. − IR (neat): $\tilde{\nu}$ = 1760 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 7.40 (m, 4 H, Ar-H), 6.97 (m, 1 H, =CH), 4.67 (m, 2 H, OCH_2), 3.55 (m, 2 H, Ar-CH_2). −^{13}C NMR (100.58 MHz, $CDCl_3$): δ = 172.6 (CO-O), 145.0 (=CH), 133.7 (C_{Ar}), 132.2 (C_{Ar}), 131.4 (C_{Ar}), 128.5 (C_{Ar}), 128.2 (=*C*CO), 124.4 (C_{Ar}), 123.9 (CF_3, q, *J* = 276.6 Hz), 122.8 (C_{Ar}), 69.3 (O*C*H$_2$), 30.6 (Ar-*C*H$_2$). − MS: *m*/*z* (%) = 242 (73) [M^+], 223 (11), 197 (14), 184 (32), 129 (39), 115 (100). − $C_{12}H_9F_3O_2$: calcd. C 59.51, H 3.75; found C 59.35; H 3.83.

(*Z*)-3-(3-Trifluoromethylbenzylidene)dihydro-2(3*H*)-furanone (4f): 0.227 g; 47%; m.p. 91−92 °C. − IR (KBr): $\tilde{\nu}$ = 1750, 1655 cm^{-1}. − ^1H NMR (400 MHz $CDCl_3$): δ = 7.60 (1 H, br s, =CH), 7.50 (m, 4 H, Ar-H), 4.42 (t, *J* = 10.5 Hz, 2 H, OCH_2), 3.20 (dt, *J* = 10.5, 4.4 Hz, 2 H, CH_2). − ^{13}C NMR (100.58 MHz, $CDCl_3$): δ = 170.4 (*C*O-O), 137.2 (=*C*H), 137.1 (C_{Ar}), 133.2 (C_{Ar}), 132.0 (C_{Ar}), 131.3 (C_{Ar}), 130.7 (C_{Ar}), 128.5 (C_{Ar}), 126.2 (CF_3, q, *J* = 251.5 Hz), 125.1 (=*C*CO), 64.4 (O*C*H$_2$), 26.3 (*C*H$_2$). − MS: *m*/*z* (%) = 242 (14) [M^+], 223 (10), 197 (30), 129 (39), 177 (64), 129 (53), 84 (83). − $C_{12}H_9F_3O_2$: calcd. C 59.51, H 3.75; found C 59.80; H 3.72.

3-(4-Methoxybenzyl)-2(5*H*)-furanone (3g): 0.122 g; 30%; oil. − IR (neat): $\tilde{\nu}$ = 1760 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 7.06 (d, *J* = 8.5 Hz, 2 H, Ar-H), 6.82 (m, 1 H, HC=), 6.76 (d, *J* = 8.5 Hz, 2 H, Ar-H), 4.63 (m, 2 H, OCH_2), 3.68 (s, 3 H, OCH_3), 3.43 (m, 2 H, $ArCH_2$). − ^{13}C NMR (100.58 MHz, $CDCl_3$): δ = 173.7 (*C*O-O), 158.1 (C_{Ar}−OCH_3), 145.4 (=*C*H), 129.5 [C_{Ar}(H)], 129.1 (C_{Ar}−CH_2), 127.0 (=*C*CO), 113.7 [C_{Ar}(H)], 70.0 (O*C*H$_2$), 54.9 (O*C*H$_3$), 30.6 (Ar*C*H$_2$). − MS: *m*/*z* (%) = 204 (15) [M^+], 159 (28), 144 (26), 115 (14). − $C_{12}H_{12}O_3$: calcd. C 70.57, H 5.92; found C 69.81, H 6.14.

(*Z*)-3-(4-Methoxybenzylidene)dihydro-2(3*H*)-furanone (4g): 0.212 g; 52%; m.p. 104−105 °C. − IR (KBr): $\tilde{\nu}$ = 1740, 1650 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 7.38 (t, *J* = 2.8 Hz, 1 H, HC=), 7.35 (d, *J* = 8.8 Hz, 2 H, Ar-H), 6.87 (d, *J* = 8.8 Hz, 2 H, Ar-H), 4.32 (t, *J* = 7.3 Hz, 2 H, OCH_2), 3.75 (s, 3 H, OCH_3), 3.08 (dt, *J* = 7.3, 2.8 Hz, 2 H, CH_2). − ^{13}C NMR (100.58 MHz $CDCl_3$): δ = 172.5 (CO-O), 160.6 (C_{Ar}−OCH_3), 135.7 (Ar*C*H=), 133.9 (C_{Ar}−CH=), 131.5 [C_{Ar}(H)], 120.1 (=*C*CO), 114.1 [C_{Ar}(H)], 65.0 (O*C*H$_2$), 55.1 (O*C*H$_3$), 27.0 (*C*H$_2$). − MS: *m*/*z* (%) = 204 (100) [M^+], 176 (17), 159 (29), 146 (67), 103 (53), 77 (45). − $C_{12}H_{12}O_3$: calcd. C 70.57, H 5.92; found C 69.66, H 6.30.

3-(1-Naphthylmethyl)-2(5*H*)-furanone (3h): 0.090 g; 20%; m.p. 161−163 °C. − IR (KBr): $\tilde{\nu}$ = 1740 cm^{-1}. − ^1H NMR (400 MHz $CDCl_3$): δ = 7.85 (m, 1 H, Ar-H), 7.78 (d, *J* = 8.0 Hz, 1 H, Ar-

H), 7.4−7.56 (m, 5 H, Ar-H), 6.66 (m, 1 H, HC=), 4.65 (m, 2 H, $ArCH_2$), 4.02 (m, 2 H, OCH_2). − ^{13}C NMR (100.58 MHz $CDCl_3$): δ = 172.9 (*C*O-O), 69.2 (O*C*H_2), 29.8 (Ar*C*H_2). − MS: *m*/*z* (%) = 224 (33) [M^+], 179 (100), 165 (24), 152 (25), 115 (19), $C_{16}H_{12}O_2$: calcd. C 80.34, H 5.39; found C 79.66, H 5.60.

(*Z*)-3-(1-Naphthylmethylene)dihydro-2(3*H*)-furanone (4h): 0.188 g; 42%; m.p. 98−100 °C. − IR (KBr): $\tilde{\nu}$ = 1750, 1645 cm^{-1}. − ^1H NMR (400 MHz $CDCl_3$): δ = 8.30 (t, *J* = 3.0 Hz, 1 H, HC=), 8.1 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.85 (m, 2 H, Ar-H), 7.35−7.58 (m, 4 H, Ar-H), 4.42 (t, 2 H, *J* = 8 Hz, CH_2), 3.16 (dt, 2 H, *J* = 8, 3 Hz, OCH_2CH_2). − ^{13}C NMR (50.3 MHz $CDCl_3$): δ = 171.0 (*C*O-O), 64.6 (O*C*H_2), 26.3 (*C*H_2). − MS: *m*/*z* (%) = 224 (42) [M^+], 196 (26), 179 (83), 165 (100), 152 (37), 82 (57). − $C_{12}H_{12}O_3$: calcd. C 80.34, H 5.39; found C 79.48, H 5.65.

3-[(4-Phenylcyclohexen-1-yl)methyl]-2(5*H*)-furanone (3i): 0.127 g; 25%; m.p. 87−90 °C. − IR (KBr): $\tilde{\nu}$ = 1780 cm^{-1}. − ^1H NMR (200 MHz $CDCl_3$): δ = 7.32−7.18 (m, 5 H, ArH), 7.09 (1 H, br. s, HC=), 5.59 (1 H, br. s, HC=), 4.77 (m, 2 H, OCH_2), 2.97 [2 H, br. s, CH_2-(C=)$_2$], 2.55−2.45 (m, 4 H, CH_2CH_2), 2.90−2.75 (m, 1 H, CH), 2.14−2.00 (m, 2 H, CH_2). − ^{13}C NMR (50.3 MHz $CDCl_3$): δ = 174.2 (*C*O-O), 146.7 (=*C*H), 139.5 (C_{Ar}), 133.4 (=*C*H), 128.4 (C_{Ar}), 126.7 (C_{Ar}), 126.2 (C_{Ar}), 126.0 (=*C*), 119.9 (=*C*CO), 70.1 (O*C*H_2), 39.7, 34.3, 33.3, 29.8, 28.7, 27.2. − MS: *m*/*z* (%) = 254 (22) [M^+], 157 (8), 104 (100), 91 (27). − $C_{17}H_{18}O_2$: calcd. C 80.28, H 7.13; found C 79.50, H 7.60.

(3*E*)-3-[(4-Phenylcyclohex-1-en-1-yl)methylene]-2(3*H*)-furanone (4i): 0.229 g; 45%; m.p. 158 °C. − IR (KBr): $\tilde{\nu}$ = 1750, 1650 cm^{-1}. − ^1H NMR (200 MHz $CDCl_3$): δ = 7.66−7.20 (m, 5 H, Ar-H), 7.12 (t, *J* = 1.4 Hz, 1 H, HC=), 6.3 (1 H, br. s, HC=), 4.37 (dt, *J* = 7.4, 1.5 Hz, 2 H, OCH_2), 3.16 (2 H, bt, *J* = 7.4 Hz, CH_2), 2.90−2.75 (m, 1 H,), 2.55−2.45 (m, 4 H, CH_2CH_2), 1.80−2.10 (m, 2 H, CH_2). − ^{13}C NMR (50.3 MHz $CDCl_3$): δ = 173.0 (*C*O-O), 145.8 (C_{Ar}); 139.7 (=CH), 138.5 (=CH), 132.3 (=*C*), 128.3 (C_{Ar}), 126.7 (C_{Ar}), 126.0 (C_{Ar}),123.7 (=*C*CO), 65.2 (O*C*H_2), 38.9 (*C*Ph), 34.3 (CH*C*H_2), 29.5 (CH*C*H_2), 27.5 (CH_2), 26.8 (OCH_2CH_2). − MS: *m*/*z* (%) = 254 (22) [M^+], 150 (11), 117 (18), 104 (100), 91 (53). − $C_{17}H_{18}O_2$: calcd. C 80.28, H 7.13; found C 79.41, H 7.74.

(3*E*)-3-(2-Cyclohexylideneethylidene)dihydro-2(3*H*)-furanone (4j): 0.211 g; 55%; oil cm^{-1}. − ^1H NMR (400 MHz $CDCl_3$): δ = 7.37 (dt, 1 H, *J* = 12, 2 Hz, HC=), 5.83 (d, *J* = 12.0 Hz, 1 H, HC=), 4.35 (t, *J* = 7.6 Hz, 2 H, OCH_2), 2.9 (m, 2 H, CH_2), 2.4 (s, 4 H, 2 CH_2), 1.6 (6 H, br. s, 3 CH_2). − MS: *m*/*z* (%) = 192 (69), 164 (35), 149 (25), 119 (86), 106 (48), 91 (100), 79 (80).

3-[(4-*tert*-Butylcyclohex-1-en-1-yl)methyl]-2(5*H*)-furanone (3k): 0.033 g; 7%; oil. − IR (neat): $\tilde{\nu}$ = 1770 cm^{-1}. − ^1H NMR (200 MHz $CDCl_3$): δ = 7.15 (t, *J* = 1.5 Hz, 1 H, HC=), 5.53 (1 H, br. s, HC=), 4.79 (m, 2 H, OCH_2), 2.91 [2 H, br. s, $CH_2(C=)_2$], 2.50−1.80 (m, 5 H, 2 CH_2 + CH), 1.28−1.13 (m, 2 H, CH_2), 0.89 (s, 9 H, 3 CH_3). − ^{13}C NMR (50.3 MHz $CDCl_3$): δ = 174.2 (*C*O-O), 145.3 (=*C*H), 133.1 (=*C*H), 124.5 (=*C*), 119.2 (=*C*CO), 69.9 (O*C*H_2), 43.7, 31.9, 28.0, 26.9, 23.7. − MS: *m*/*z* (%) = 234 (11) [M^+], 178 (100), 131 (33), 105 (51), 98 (79), 91(61), 79 (76), 57 (66).

(3*E*)-3-[(4-*tert*-Butylcyclohex-1-en-1-yl)methylene]-2(3*H*)-furanone (4k): 0.304 g; 65%; m.p. 92−95 °C. − IR (KBr): $\tilde{\nu}$ = 1730, 1640 cm^{-1}. − ^1H NMR (200 MHz $CDCl_3$): δ = 7.07 (s, 1 H, HC=), 6.23 (1 H, br. s, HC=), 4.40−4.30 (m, 2 H, OCH_2), 3.15 (2 H, br. s, CH_2), 2.55−1.90 (m, 5 H, 2 CH_2 + CH), 1.28−1.16 (m, 2 H, CH_2), 0.89 (s, 9 H, 3 CH_3). − ^{13}C NMR (50.3 MHz $CDCl_3$): δ = 173.0 (*C*O-O), 139.8 (=*C*H), 134.7 (=*C*), 132.5 (=*C*), 124.3 (=*C*CO), 65.1 (O*C*H_2), 43.0, 29.4, 27.0, 26.6, 24.0. − MS: *m*/*z* (%) = 234 (55) [M^+], 177 (100), 131 (47), 105 (61), 91 (68), 57 (79). − $C_{15}H_{22}O_2$: calcd. C 76.87, H 9.49; found C 78.42, H 9.36.

(3*Z*)-3-(4-Acetylbenzylidene)dihydro-2(3*H*)-furanone (4a): 4-Iodoacetophenone (**2a**) (**1.3**5 g, 5.47 mmol), α-methylene-γ-butyrolactone (**1**) (0.224 g, 2.28 mmol), Bu_3N (1.44 g, 7.75 mmol), Ph_3P (0.024 g, 0.091 mmol) and $Pd(OAc)_2$ (0.010 g, 0.045 mmol) were dissolved in DMF (3 mL). The mixture was gently purged with nitrogen, and formic acid (6 mmol) was added in one portion. The mixture was stirred under nitrogen at 80 °C for 2 h. After it had cooled, the reaction mixture was washed with a mixture of ethyl acetate and 0.1 N HCl. The phases were separated and the combined organic phases dried with Na_2SO_4. After removal of the solvent, the crude product was purified by flash chromatography on silica gel, eluting with an *n*-hexane/ethyl acetate (95:3) mixture, and affording **3a** (0.182 g, 37%) and **4a** (0.186 g, 38%); m.p. 150−152 °C. − IR (KBr): $\tilde{\nu}$ = 1730, 1660, 1255 cm^{-1}. − ^1H NMR (400 MHz $CDCl_3$): δ = 7.98 (d, *J* = 8.5 Hz, 2 H, Ar-H), 7.55 (d, *J* = 8.5 Hz, 2 H, Ar-H), 7.55 (s, 1 H, HC=), 4.46 (t, *J* = 7.2 Hz, 2 H, OCH_2), 3.25 (dt, *J* = 7.2, 3.2 Hz, 2 H, CH_2), 2.59 (s, 3 H, $COCH_3$). − ^{13}C NMR (50.3 MHz $CDCl_3$): δ = 197.2 (CO), 171.9 (CO-O), 146.1 (=*C*H), 138.6 [C_{Ar}(H)], 137.2 (C_{Ar}), 129.2 (C_{Ar}), 128.7 [C_{Ar}(H)], 126.2 (=*C*CO), 65.4 (O*C*H_2), 27.4 (*C*H_3), 26.6 (*C*H_2). − MS: *m*/*z* (%) = 216 (13) [M^+], 201 (50), 171 (44), 129 (52). − $C_{13}H_{12}O_3$: calcd. C 72.20, H 5.55; found C 71.76, H 6.04.

Procedure B: A mixture of aryl iodide or vinyl triflate (2 mmol), α-methylene-γ- butyrolactone (**1**) (3 mmol), AcOK (6 mmol) and $Pd(OAc)_2$ (0.1 mmol) in DMF (3 mL) was stirred under nitrogen at 80 °C for 3 h. After it had cooled, the reaction mixture was washed with a mixture of ethyl acetate and saturated aqueous $NaHCO_3$. The phases were separated and the combined organic phases were dried with Na_2SO_4. After removal of the solvent, the crude product was dissolved in ethyl acetate and was hydrogenated in the presence of Pd/C (5%) at atmospheric pressure. After completion of the hydrogenation, the catalyst was filtered off, the solvent was evaporated and the crude product was purified by chromatography (silica gel; $CHCl_3$/petroleum ether, 1:1).

α-(4-Methoxycarbonylbenzyl)-γ-butyrolactone (5b): 0.235 g; 57%; m.p. 72−73 °C. − IR (KBr): $\tilde{\nu}$ = 1755, 1720 cm^{-1}. − ^1H NMR (400 MHz $CDCl_3$): δ = 7.92 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.22 (d, *J* = 8.0 Hz, 2 H, Ar-H), 4.19 (dt, *J* = 2.8, 8.8 Hz, 1 H, O*C*H_aH$_b$), 4.09 (dt, *J* = 6.8, 9.2 Hz, 1 H, OCH$_a$*H$_b$*), 3.85 (s, 3 H, OCH_3), 3.23 (dt, *J* = 3.6, 13.2 Hz, 1 H, ArC*H$_a$*H$_b$), 2.81 (m, 1 H, $ArCH_2CH$), 2.77 (m, 1 H, ArCH$_a$*H$_b$*), 2.19 (m, 1 H, OCH_2CH_aH$_b$), 1.92 (m, 1 H, OCH_2CH_a*H$_b$*). − ^{13}C NMR (100.58 MHz $CDCl_3$): δ = 178.2 (*C*O-O), 166.8 (*C*OOCH_3), 143.7, 129.9, 128.9, 128.7, 66.4 (O*C*H_2), 52.0 (O*C*H_3), 40.7 (CO*C*H), 36.0 (Ar*C*H_2), 28.0 (OCH_2CH_2). − MS: *m*/*z* (%) = 234 (85) [M^+], 206 (73), 203 (50), 101 (33), 175 (100), 162 (34), 149 (64). − $C_{13}H_{14}O_4$: calcd. C 66.66, H 6.02; found C 65.48, H 6.06.

α-(2-Methoxycarbonylbenzyl)-γ-butyrolactone (5d): 0.315 g; 78%; oil. − IR (neat): $\tilde{\nu}$ = 1720, 1770 cm^{-1}. − ^1H NMR (400 MHz $CDCl_3$): δ = 7.85 (d, *J* = 7.2 Hz, 1 H, Ar-H), 7.37 (t, *J* = 7.2 Hz, 1 H, Ar-H), 7.23 (m, 2 H, Ar-H), 4.22 (dt, *J* = 2.4, 8.4 Hz, 1 H, O*C*H_aH$_b$), 4.04 (dt, *J* = 6.8, 9.2 Hz, 1 H, OCH$_a$*H$_b$*), 3.81 (s, 3 H, OCH_3), 2.92 (m, 2 H, $ArCH_2CH$ + ArC*H$_a$*H$_b$), 2.77 (m, 1 H, ArCH$_a$*H$_b$*), 2.19 (m, 1 H, OCH_2CH_aH$_b$), 1.94 (m, 1 H, OCH_2CH_a*H$_b$*). − ^{13}C NMR (100.58 MHz $CDCl_3$): δ = 178.7 (*C*O-O), 167.7 (*C*OOCH_3), 140.5, 132.2, 131.6, 131.0, 129.6, 126.8, 66.5 (O*C*H_2), 52.0 (O*C*H_3), 40.8 (CO*C*H), 34.2 (Ar*C*H_2), 28.3 (OCH_2CH_2). − MS: *m*/*z* (%) = 234 (22) [M^+], 202 (100), 174 (38), 158 (89), 145 (39), 130 (49), 115 (35), 91 (49). − $C_{13}H_{14}O_4$: calcd. C 66.66, H 6.02; found C 65.10, H 6.20.

α-(3-Trifluoromethylbenzyl)-γ-butyrolactone (5f): 0.380 g; 78%; oil. − IR (neat): $\tilde{\nu}$ = 1770 cm^{-1}. − ^1H NMR (400 MHz $CDCl_3$): δ = 7.38−7.50 (m, 4 H, Ar-H), 4.24 (dt, *J* = 2.4, 8.8 Hz, 1 H, OCH_aH_b), 4.15 (dt, *J* = 6.4, 9.2 Hz, 1 H, OCH_aH_b), 3.28 (dd, *J* = 3.2, 12.8 Hz, 1 H, $ArCH_aH_b$), 2.82 (m, 2 H, $ArCH_2CH$ + $ArCH_aH_b$), 2.25 (m, 1 H, $OCH_2CH_aH_b$), 1.95 (m, 1 H, $OCH_2CH_aH_b$). − ^{13}C NMR (100.58 MHz $CDCl_3$): δ = 178.1 (*C*O-O), 139.4, 132.3, 131.0 (q, $^1J(^{13}C,^{19}F)$ = 32 Hz), 129.2, 125.5, 123.6, 122.7, 66.4 (OCH_2), 40.8 (CO*C*H), 35.8 ($ArCH_2$), 28.0 (OCH_2CH_2). − MS: *m*/*z* (%) = 244 (65) [M^+], 216 (95), 215 (78), 172 (30), 159 (100). − $C_{12}H_{11}F_3O_2$: calcd. C 59.02, H 4.54; found C 58.48, H 5.06.

α-(4-Methoxybenzyl)-γ-butyrolactone (5g): 0.288 g; 70%; m.p. 40−41 °C. − IR (KBr): $\tilde{\nu}$ = 1780, 1610, 800, 715 cm^{-1}. − ^1H NMR (400 MHz $CDCl_3$): δ = 7.12 (d, *J* = 8.4 Hz, 2 H, Ar-H), 6.82 (d, *J* = 8.4 Hz, 2 H, Ar-H), 4.15 (dt, *J* = 2.8, 8.8 Hz, 1 H, OCH_aH_b), 4.09 (dt, *J* = 6.8, 8.8 Hz, 1 H, OCH_aH_b), 3.74 (s, 3 H, OCH_3), 3.12 (dd, *J* = 4.0, 13.4 Hz, 1 H, $ArCH_aH_b$), 2.76 (m, 1 H, *J* = 3.6, 8.4 Hz, 18.0 Hz, $ArCH_2CH$), 2.68 (dd, *J* = 8.8, 13.4 Hz, 1 H, $ArCH_aH_b$), 2.20 (dddd, 1 H, $OCH_2CH_aH_b$), 1.94 (m, 1 H, $OCH_2CH_aH_b$). − ^{13}C NMR (100.58 MHz $CDCl_3$): δ = 178.9 (*C*O-O), 158.3, 130.3, 129.8, 113.9, 66.5 (OCH_2), 55.1 (OCH_3), 41.1 (CO*C*H), 35.0 ($ArCH_2$), 27.7 (OCH_2CH_2). − MS: *m*/*z* (%) = 206 (25) [M^+], 178 (7), 121 (100). − $C_{12}H_{14}O_3$: calcd. C 69.88, H 6.84; found C 69.57, H 6.89.

α-(1-Naphthylmethyl)-γ-butyrolactone (5h): 0.267 g; 59%; m.p. 75−77 °C. − IR (KBr): $\tilde{\nu}$ = 1770, 1595, 760 cm^{-1}. − ^1H NMR (400 MHz $CDCl_3$): δ = 8.04 (d, *J* = 8.4 Hz, 1 H, Ar-H), 7.86 (d, 1 H, *J* = 9.2 Hz. Ar-H), 7.76 (d, *J* = 8.4 Hz, 1 H, Ar-H), 7.50 (m, 2 H, Ar-H), 7.4 (t, *J* = 7.2 Hz, 1 H, Ar-H), 7.32 (d, *J* = 6.8 Hz, 1 H, Ar-H), 4.30 (dt, *J* = 2.8, 9.0 Hz, 1 H, OCH_aH_b), 4.10 (dt, *J* = 9.0, 6.4 Hz, 1 H, OCH_aH_b), 3.92 (dd, *J* = 2.8, 13.2 Hz, 1 H, $ArCH_aH_b$), 3.00 (m, 1 H, $ArCH_2CH$), 2.96 (dd, *J* = 13.2, 10.4 Hz, 1 H, $ArCH_aH_b$), 2.11 (m, 1 H, $OCH_2CH_aH_b$), 2.0 (m, 1 H, $OCH_2CH_aH_b$). − ^{13}C NMR (100.58 MHz $CDCl_3$): δ = 178.8 (*C*O-O), 134.7, 134.0, 131.5, 129.0, 127.6, 126.7, 126.4, 125.8, 125.4, 123.3, 66.6 (OCH_2), 40.4 (CO*C*H), 33.5 ($ArCH_2$), 28.8 (OCH_2CH_2). − MS: *m*/*z* (%) = 226 (15) [M^+], 181 (100). − $C_{15}H_{14}O_2$: calcd. C 79.62, H 6.24; found C 79.37; H 6.07.

α-(17-Oxo-5α-androstan-3β-ylmethyl)-γ-butyrolactone (5l): 0.595 g; 80%; m.p. 142−144 °C. − IR (KBr): $\tilde{\nu}$ = 1770, 1745 cm^{-1}. − ^1H NMR (400 MHz $CDCl_3$): δ = 4.26 (dt, 1 H, OCH_aH_b), 4.12 (dt, 1 H, OCH_aH_b), 2.6 (m, 1 H,), 2.35 (m, 2 H, 16-CH_2), 0.78 (s, 3 H, 18-CH_3), 0.72 (s, 3 H, 19-CH_3). − ^{13}C NMR (50.3 MHz $CDCl_3$): δ = 221.5 (CO), 180.1 (*C*O-O), 67.0 (OCH_2), 51.1, 47.7, 46.4, 46.3, 38.3, 37.2, 36.2, 35.8, 35.0, 34.4, 31.5, 30.8, 30.5, 29.2, 28.3, 27.7, 24.8, 20.7, 20.5, 13.7, 12.1. − MS: *m*/*z* (%) = 372 (22) [M^+], 357 (16), 354 (34), 328 (62), 301 (61), 269 (68), 86 (100). − $C_{24}H_{36}O_3$: calcd. C 77.38, H 9.74; found C 77.26, H 9.37.

α-(5α-Cholestan-3β-ylmethyl)-γ-butyrolactone (5m): 0.771 g; 82%; m.p. 143−144 °C. − IR (KBr): $\tilde{\nu}$ = 1775 cm^{-1}. − ^1H NMR (400 MHz $CDCl_3$): δ = 4.32 (dt, 1 H, OCH_aH_b), 4.16 (m, 1 H, OCH_aH_b), 2.6 (m, 1 H, CO*C*H), 2.36 (m, 1 H, 3-C*H*), 0.63 (s, 3 H, 18-CH_3), 0.74 (s, 3 H, 19-CH_3), 0.85 (d, 6 H, 26-CH_3 + 27-CH_3); 0.9 (d, 3 H, 21-CH_3). − ^{13}C NMR (50.3 MHz $CDCl_3$): δ = 180.0 (*C*O-O), 66.4 (OCH_2), 46.5 (CO*C*H), 46.4, 42.5, 40.5, 40.1, 38.4, 36.9, 35.9, 35.7, 35.4, 34.5, 32.1, 30.1, 29.2, 28.9, 28.2, 27.9, 24.1, 23.9, 23.8, 22.5, 21.3, 21.0, 18.0, 12.0. − MS: *m*/*z* (%) = 470 (13) [M^+], 455 (20), 330 (10), 315 (100), 301 (28), 247 (75). − $C_{32}H_{54}O_2$: calcd. C 81.64, H 11.56; found C 81.36, H 11.24.

α-[6-Methoxytetrahydronaphth-1-yl)methyl]-γ-butyrolactone (5n): 0.395 g; 76%; m.p. 90−92 °C. − IR (KBr): $\tilde{\nu}$ = 1767 cm^{-1}. − ^1H NMR (400 MHz $CDCl_3$): δ = 7.0 (d, *J* = 8.0 Hz, 1 H), 6.65 (dd, *J* = 8, 2 Hz, 1 H), 6.58 (d, *J* = 2.0 Hz, 1 H), 4.30 (m, 1 H, OCH_aH_b), 4.12 (m, 1 H, OCH_aH_b), 3.70 (s, 3 H, OCH_3), 1.6−2.9 (m, 12 H). − MS: *m*/*z* (%) = 260 (10) [M^+], 174(100), 161 (70). − $C_{16}H_{20}O_3$ calcd. C 73.82, H 7.74; found C 74.11, H 7.96.

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