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Transition-metal catalyzed synthesis of δ-hydroxy-γ-lactones from bis(trimethylsilyl) ketene acetals and allylic acetates via γ-unsaturated carboxylic acids. Comments on the formation of α-cyclopropyl carboxylic acids

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Abstract

Bis(trimethylsilyl)ketene acetals react with allylic acetates in the presence of Pd(0) complexes to give γ-unsaturated carboxylic acids together with α-cyclopropyl carboxylic acids. The unsaturated acids can be converted catalytically to δ-hydroxy-γ-lactones by the H_2O_2/MTO system (methyltrioxorhenium) and to butenolides by Pd(II) catalyzed intramolecular cyclization reactions. The structure of two of these lactones has been established by X-ray analysis. The mechanism of the formation of the cyclopropanic acids will be discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: bis(Trimethylsilyl)ketene acetals; Allylic acetates; Palladium; γ-Unsaturated carboxylic acids; α-Cyclopropyl carboxylic acids; Methyltrioxorhenium; Lactones

1. Introduction

Functionalized γ-lactones have important biological properties and are also known as starting material for the preparation of pharmacologically active compounds [1–4]. Their synthesis by means of catalytic reactions thus constitutes a worthwhile goal. As part of our interest in the synthesis of saturated and unsaturated lactones, we focused on δ-hydroxy-γ-lactones [5]. From a formal point of view they can be considered as arising from a double nucleophilic addition of the dianion of carboxylic acids to a suitably activated carbon–carbon double bond, via a series of two nucleophilic additions. In order to be able to perform the second nucleophilic addition, the first intermediate must again be activated, for example by an oxidation step. Such a scheme has been applied with moderate success to the direct transformation of arylethers into bicyclic lactones, in a one pot reaction, upon their interaction with enolates originating from bis(trimethylsilyl) ketene acetals [6–8].

According to Scheme 1, which describes this transformation, activation towards the first nucleophilic addition is achieved classically via a chromium(0)tricarbonyl complex. The intermediate potassium chromate is then oxidized with iodine in order to promote the rearomatization of the cyclohexadienyl group and release of the metal. Since during this transformation the metal is likely to be oxidized to Cr(II) [9], activation of the second carbon of the double bond towards a second nucleophile is again achieved: an intramolecular nucleophilic addition of the trimethylsilyl ester via an iodide assisted oxygen–silicon bond cleavage could then take place.

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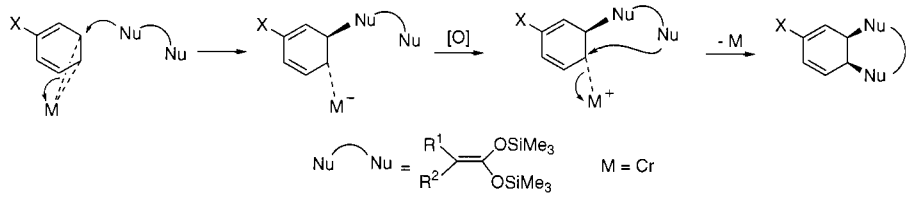
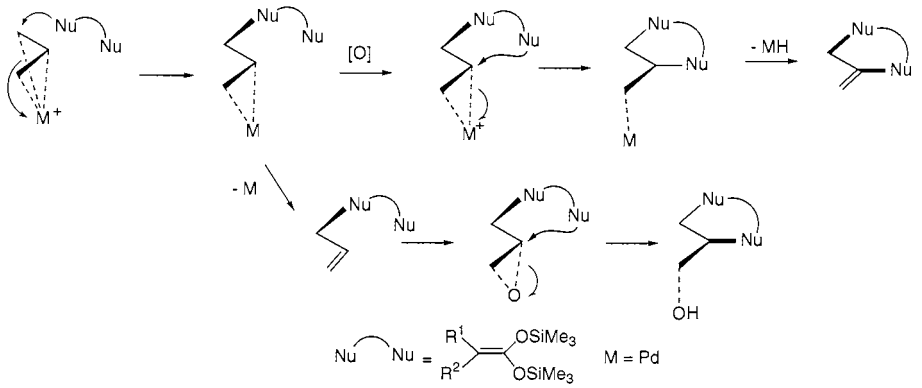


Scheme 1.



Scheme 2.

Such a process might also be possible starting from a suitably activated aliphatic carbon–carbon double bond: for example an allylic acetate can be activated catalytically towards nucleophiles via a π-allyl complex [10,11] (Scheme 2).

The interaction of a ketene acetal (or the enolate therefrom) and this complex might then give a Pd(0) π-complex. At this point, two possibilities exist: either release of the metal to give the γ-unsaturated carboxylic acid (or its TMS ester) or reoxidation of the catalyst to Pd(II) by the system Cu(II)/O_2 followed by a Wacker-type intramolecular nucleophilic addition [12]. This might then lead directly to an unsaturated γ-lactone. In the first case, the γ-unsaturated carboxylic acid might also be transformed, by known routes, to δ-hydroxy-γ-lactones, e.g. peroxy acid oxidation of the double bond, followed by an intramolecular oxirane opening reaction [13].

The purpose of this paper is twofold: first to demonstrate that both of the coupled reactions, which rely on known transformations, can be carried out catalytically, the first one involving only palladium, the second one involving successively palladium and the system H_2O_2/MTO.

Second, that during the first step, which leads to γ-unsaturated carboxylic acids, cyclopropyl carboxylic acids are also formed as secondary products. The ratio of the two products is essentially dependent on the structure of the ketene acetals, and to a smaller extend, on the reaction conditions.

2. Results and discussion

The reaction between alkyl(trimethylsilyl) ketene acetals and allylic carbonates in the presence of catalytic amounts of Pd(0) complexes leading to γ-unsaturated carboxylic acid esters was initially disclosed by Tsuji [14]. Subsequently, Musco found that allylic acetates could be used for the same purpose [15] and that the unsaturated esters were surprisingly found together with α-cyclopropyl carboxylic acid esters in moderate yields.

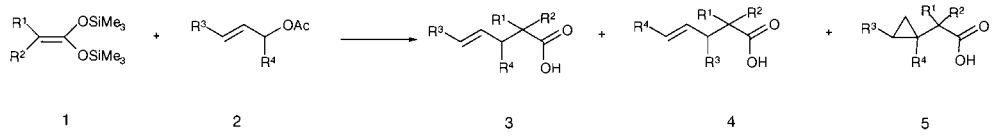
We have now established that for the direct synthesis of γ-unsaturated acids, bis(trimethylsilyl) ketene acetals in conjunction with allylic acetates and $Pd(PPh_3)_4$ are the suitable starting materials.

2.1. Formation of γ-unsaturated carboxylic acids from allylic acetates and bis(trimethylsilyl) ketene acetals

In a preliminary communication [16], we already described the preparation in moderate to good yields of a series of γ-unsaturated carboxylic acids by simple heating THF solutions of the ketene acetals and the allylic esters in the presence of 5% of the catalyst. We also obtained α-cyclopropyl carboxylic acids, in variable amounts, specific for some ketene acetals.

We have now observed that much better results can be obtained by carrying out the reaction at lower temperature, in refluxing dichloromethane. As can be seen in Table 1 (entries 3 and 4), whereas for example an overall 29% yield of the acids was observed for the

Table 1
γ-Hydroxy acids from allylic acetates and bis(trimethylsilyl)ketene acetals



1 2 3 4 5

Entry	R^1		R^2	R^3	R^4	Time (h)	Total yield (%)	Solvent	3	4	5
1	Me		H	Ph	H	16	61	THF	55	45	0
2	Et		H	Ph	H	47	34	THF	53	47	0
3	^{t}Bu		H	Ph	H	20	29	THF	79	21	0
4	^{t}Bu		H	Ph	H	16	52	CH_2Cl_2	89	11	0
5	Ph		H	Ph	H	16	49	THF	78	22	0
6	Me		Me	Ph	H	16	70	THF	49	27	24
7		$(CH)_5$		Ph	H	20	24	THF	69	27	14
8		$(CH)_5$		Ph	H	22	98	CH_2Cl_2	73	17	10
9	Ph		Ph	Ph	H	72	98	THF	100	0	0
10	OMe		H	Ph	H	50	42	THF	70	30	0
11	OMe		H	Ph	H	15	76	Tol	92	8	0
12	OPh		H	Ph	H	72	40	THF	100	0	0
13	OPh		H	Ph	H	16	100	CH_2Cl_2	77	23	0
14	Et		H	H	H	20	0	THF			
15	Et		H	H	H	19	79	CH_2Cl_2	88	0	12
16	Ph		H	H	H	16	65	THF	100	0	0
17	Me		Me	H	H	69	27	THF	76	0	24
18	Me		Me	H	H	22	81	CH_2Cl_2	67	0	33
19		$(CH)_5$		H	H	20	66	THF	76	0	24
20	Ph		Ph	H	H	20	95	THF	100	0	0
21	OMe		H	H	H	96	40	THF	100	0	0
22	OPh		H	H	H	120	70	THF	94	0	6
23	OPh		Me	H	H	72	91	THF	85	0	15
24	Me		H	^{n}Pr	H	19	95	CH_2Cl_2	70:23	7	0
25	Ph		H	^{n}Pr	H	25	93	THF	60:12	28	0
26	Ph		H	^{n}Pr	H	4	80	CH_2Cl_2	90:0	10	0
27	Me		Me	^{n}Pr	H	18	18	THF	60:15	25	0
28	Me		Me	^{n}Pr	H	24	77	CH_2Cl_2	79.5:20	0.5	0
29	Ph		Ph	^{n}Pr	H	2	96	THF	100	0	0
30	OMe		H	^{n}Pr	H	15	35	THF	53:15	25	0
31	OMe		H	^{n}Pr	H	144	68	CH_2Cl_2	66:20	14	0
32	OPh		Me	^{n}Pr	H	15	91	THF	95	S	0
33	OPh		Me	^{n}Pr	H	18	86	CH_2Cl_2	100	0	0
34	OPh		H	^{n}Pr	H	17	60	CH_2Cl_2	82:10	8	0
35	Me		H	Ph	Ph	16	67	CH_2Cl_2	30:70	0	0
36	Me		Me	Ph	Ph	18	70	CH_2Cl_2	100	0	0
37	CH_2=C(Me)		H	Ph	H	5	80	THF	100	0	0
38	$SiMe_3$		H	Ph	H	17	60	THF	70:30	0	0

transformation of **1** and **2** into the regioisomers **3** and **4**, the yield increased to 52% in dichloromethane in a shorter reaction time.

This is a general trend except for the more elaborate ketene acetals such as those derived from alkoxy and aryloxy acids. Thus, no reaction at all was observed in dichloromethane, whereas in THF a 42% and in toluene a 76% yield was obtained (entries 10 and 11). Moreover, the reaction times were longer for these substrates. A more striking example is found in entries 7 and 8, and 12 and 13, the yields varying respectively from 24 to 98%, and from 40 to 100%.

For the γ-unsaturated acids, two classes of isomers are formed (Scheme 3 and Table 1):

- regioisomers **3** and **4** arising from the fixation of the enolate derived from the ketene acetals at the two termini of the π-allyl ligand derived from the allylic acetates. These were separated either by fractional

crystallization or silica gel chromatography, or better, were directly converted into lactones upon oxidation (vide infra).

- *E* and *Z* stereoisomers **3a** and **3b** resulting from double bond isomerisation.

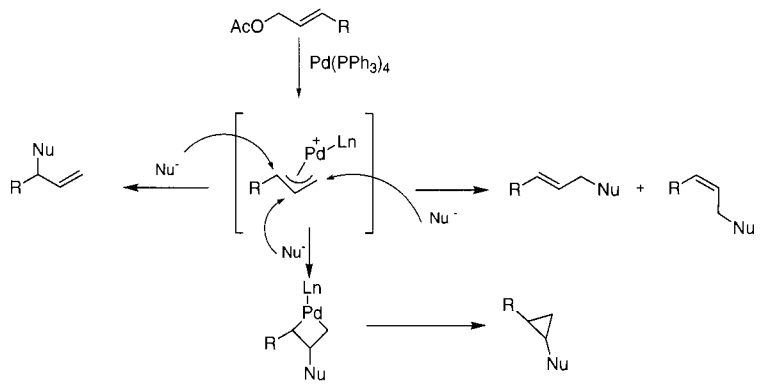
As far as the regioisomers are concerned, their ratio is highly dependent, as expected, on the size of the substituents on the starting ketene acetals, the amount of isomers arising from a S_N2' reaction increasing when the size of these substituents decrease. This appears clearly for example in the entries 1 and 12, the ratios being respectively, for $R^1 = Me$ and $R^2 = H$, 55:45, and for $R^1 = OPh$ and $R^2 = H$, 100:0, for the same substrate, cinnamyl acetate.

A second observation should be put to the fore: side reactions are also observed, e.g. formation of α,β-unsaturated acids derived from the ketene acetals. Thus for $R^1 = Et$ and $R^2 = H$ (entry 14), significant amounts of crotonic acid were formed as the result of an oxidation reaction. This transformation takes place when the reaction is carried out in THF, no secondary products being observed in dichloromethane (entry 15). Such a transformation can be related to the formation of α,β-unsaturated carbonyl compounds from silyl enol ethers derived from ketones, as described by Tsuji [17].

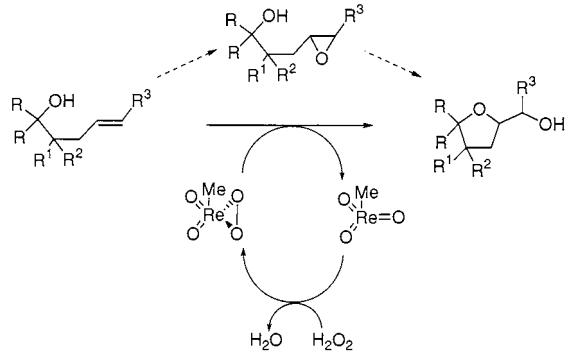
2.2. Formation of α-cyclopropylcarboxylic acids

According to Tsuji [14] and subsequently reported by Morimoto [18], the interaction of alkyl(trimethylsilyl) ketene acetals with allylic carbonates led exclusively to unsaturated carboxylic acid esters. In contrast however, Musco and coworkers first found that cyclohexenyl acetates and methyl(trimethylsilyl) ketene acetals reacted in THF to give bicyclo [3.1.0] hexane derivatives in significant amounts, in addition to the expected unsaturated esters [15]. However, this transformation took place only in the presence of bidentate phosphorus-containing ligands, no reaction being observed in the presence of the monodentate ligand triphenylphosphine. Later on, these authors observed the same behaviour of a series of linear allylic esters [19] which gave cyclopropanes even in the presence of monodentate phosphines. Several other examples involving π-allyl complexes of palladium and either ketene acetals or enolates of esters and ketones, and leading to cyclopropanes either in stoichiometric or in catalytic reactions can be found and have been discussed in the literature [20–29]. The beneficial role of σ-donor ligands such as amines (Et_3N, TMEDA) has been observed. Moreover, a palladacyclobutane could be isolated by Hoffmann upon interaction of a preformed π-allyl complex bearing the TMEDA ligand with a ketone enolate. Its transformation in the presence of CO led to the expected, substituted cyclopropane [22].

We have now found in several instances the formation of up to 33% of cyclopropyl carboxylic acids together with the expected γ-unsaturated acids in the absence of any added base. Increasing amounts of cyclopropane derivatives were formed upon increasing the number and the size of the substituents on the β-carbon of the ketene acetals. As can be seen for example in the entries 6, 17, 18 and 19, the ketene acetals **1** ($R^1 = R^2 = Me$ and $R^1R^2 = (CH_2)_5$) gave about the same yield (24%) of α-cyclopropyl carboxylic acid **5**, a yield which increased to 33% when dichloromethane was used instead of THF. The *trans* stereochemistry of **5** (R^1, $R^2 = Me$, $R^3 = Ph$) has been established by DEPT, $^1H-^{13}C$-NMR correlation and DNOES experiments. Since separation of the unsaturated carboxylic acids from cyclopropanic acids is exceedingly difficult using silica gel chromatography, it was desirable to increase the yield of the latter compounds. Since the use of nitrogen-containing bidentate ligands has been found to favour the formation of cyclopropanes, we reacted allyl acetate and dimethylbis(trimethylsilyl)ketene acetal **1** ($R^1 = R^2 = Me$) in refluxing dichloromethane in the presence of 3% $Pd_2(dba)_3$ and 15% TMEDA. Gratifyingly, the cyclopropane was formed as almost the sole product (90%) although the overall yield was only moderate (44%). It is clear that TMEDA has a positive effect in the



Scheme 3.



Scheme 4.

formation of cyclopropanes although the structure of the ketene acetals appears according to this report as well as in the results of Musco [15,19] as fundamental.

Even a monosubstituted ketene acetal ($R^1 = Et$, entry 15) also gave **5** in a low 12% yield. Whereas in the case of the methoxy substituted ketene acetal **1** ($R^1 = OMe$, entry 21) no cyclopropyl carboxylic acid **5** could be detected, a 15% yield of **5** was again observed for the phenoxy-substituted ketene acetal **1** ($R^1 = OPh$, $R^2 =$ Me, entry 23).

Compounds **5** could be easily separated from the unsaturated acids upon transformation of these latter into lactones (vide infra).

In summary, all these experimental results confirm

- that no added base is necessary for the interaction of ketene acetals with allylic acetates [25].
- that no nitrogen-containing ligand is essential for the observation of the cyclopropanes but that TMEDA has a positive effect in their formation.
- but conversely, that the nature of the substituents on the ketene acetals and the allylic acetates is crucial for the outcome of the reaction: sterically demanding groups in one or the other reacting substrates favour the formation of the cyclopropyl carboxylic acids.

2.3. Catalytic synthesis of δ-hydroxy-γ-lactones from γ-unsaturated carboxylic acids

2.3.1. A two-step procedure involving palladium and methyltrioxorhenium

The formation of lactones from unsaturated carboxylic acids is a well recognized and very useful bond construction process in organic synthesis.

Several methods exist for this transformation. The most popular is the halolactonization reaction which leads either to halolactones or to saturated lactones [30,31].

Other methods involve the intramolecular opening of transient epoxides which are formed upon reaction of the carbon–carbon double bond with peroxyacids [12] and lead to δ-hydroxy-γ-lactones.

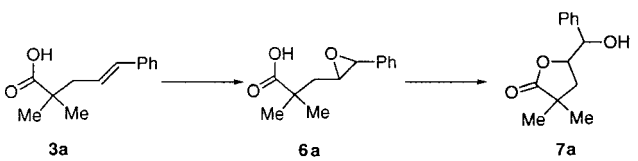
During our investigations directed towards the use of H_2O_2 and methyltrioxorhenium (MTO) [32,33] as catalyst for the synthesis of acid sensitive epoxides [34], we found that such species could be prepared in the presence of pyridines, in a biphasic medium (H_2O_2/CH_2Cl_2). Especially rewarding was the synthesis of epoxides derived from γ-unsaturated alcohols. Indeed, in the absence of these additives, intramolecular ring-opening of the oxiranes, leading to β-hydroxy tetrahydrofuranes were observed. We could establish that this reaction was catalyzed by MTO, which acts as a Lewis acid (Scheme 4).

Such an intramolecular reaction could also be applied successfully to the synthesis of δ-hydroxy-γ-lactones from γ-unsaturated carboxylic acids by using the following general procedure. Thus, MTO (0.36 mmol) was added to a mixture of unsaturated and cyclopropanic acids (7.3 mmol, 85/15) in chloroform (20 ml). Aqueous H_2O_2 (30%, 1.1 equivalents) was then added at room temperature and the solution stirred vigorously until the disappearance of the olefinic protons in the ^{1}H-NMR spectrum. Any remaining H_2O_2 was then decomposed either with dilute thiosulphite or with MnO_2. The organic layer was removed and the aqueous layer was treated with aqueous base then extracted with dichloromethane. The organic layers were dried and the products purified by column chromatography. The δ-hydroxy-γ-lactones were obtained almost quantitatively (80–95% yield), and depending on the substituents, either as single isomers, as positional isomers or as diastereoisomers (see Section 4). Similar results have recently been disclosed by Espenson [35].

The cyclopropyl carboxylic acids were recovered quantitatively by acidification of the aqueous layer followed by extraction with dichloromethane.

2.3.2. Intermediate formation and detection of an epoxide

According to the above procedure, the unsaturated acid **3a** led, after 24 h, to the hydroxy lactone **7a** as a solid, m.p. 52°C. Its ^{1}H-NMR spectrum confirmed the presence of a secondary benzylic alcohol with a doublet at δ 5.13, and of an ether linkage, with a signal as a multiplet at δ 4.60 Eq. (1).



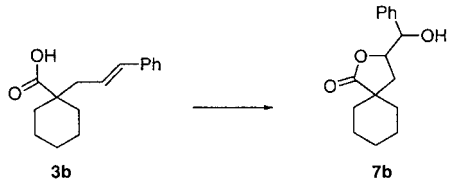
3a **6a** **7a**

(1)

When the course of the reaction was carefully monitored by ^{1}H-NMR spectroscopy, an intermediate epoxide **6a**, which disappeared progressively in favour of the

hydroxy lactone **7a**, could be detected: signals at δ 4.93 (d) and at 3.95 (m) confirmed such a structure.

The structure and the stereochemical outcome of these intramolecular reactions was confirmed by two X-ray analyses carried out on the lactones **7b** and **7c**. Their molecular structures appear respectively in the Figs. 1 and 2 and the crystallographic data are reported in Tables 2 and 3 Eq. (2)Eq. (3).



(2)

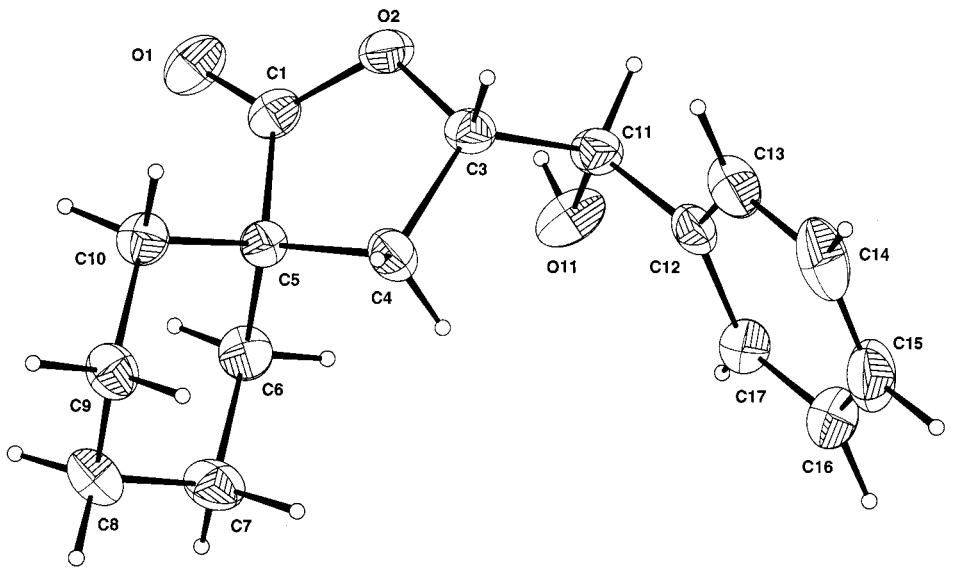


Fig. 1. Molecular structure of the hydroxy lactone **7b**.

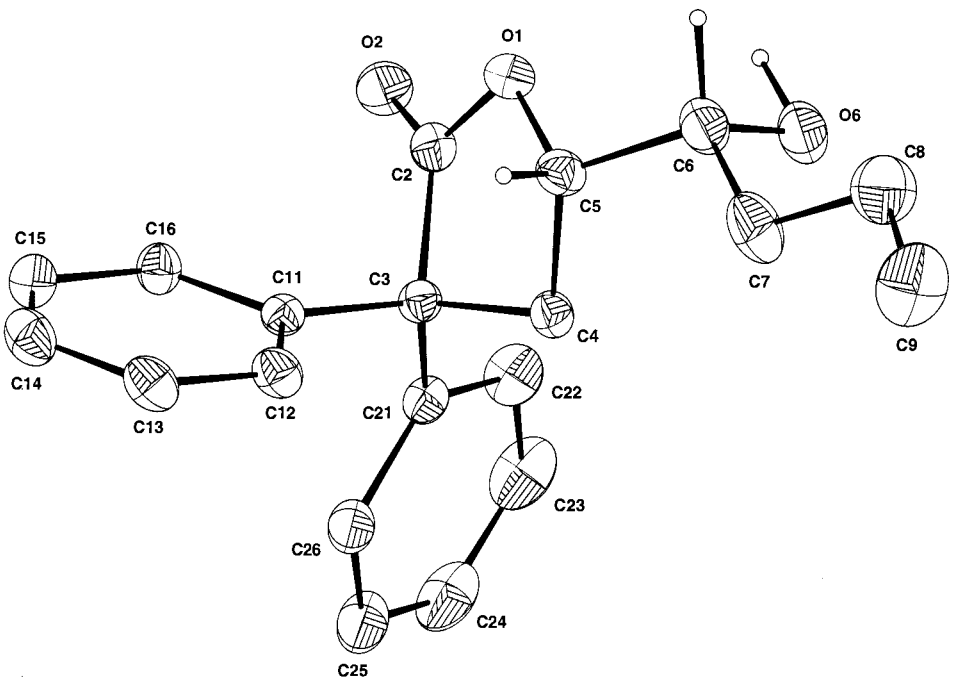
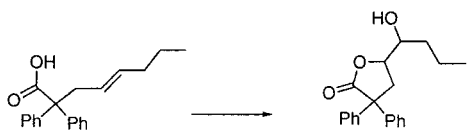


Fig. 2. Molecular structure of the hydroxy lactone **7c**.

Table 2
Crystallographic data for compound $C_{16}H_{20}O_3$ (**7b**)

F_w	260.3
T (K)	295
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	6.162(5)
b (Å)	10.749(4)
c (Å)	11.146(4)
α (°)	74.44(3)
β (°)	74.65(6)
γ (°)	88.73(7)
V (Å^3)	684.8(7)
Z	2
Linear absorption coefficient μ (cm^{-1})	0.80
Density ρ (g cm^{-3})	1.26
Diffractometer	CAD4 Enraf-Nonius
Radiation (Mo–K$_\alpha$), λ (Å)	0.71069
Scan type	$\omega/2\theta$
Scan range (°)	$0.8+0.345$ tgθ
θ limits (°)	1–28
Octants collected	0, 8; −13, 14; −14, 14
No. of data collected	3601
No. of unique data collected	3296 ($R_{int}=0.01$)
No. of unique data used for refinement	1814 $(F_o)^2>3\sigma(F_o)^2$
$R=\Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$	0.0517
Rw [a] $=[\Sigma\, w(\|F_o\|-\|F_c\|)^2/\Sigma wF_o^2]^{1/2}$	0.0686
S	1.10
Extinction parameter	None
No. of variables	233
$\Delta\rho_{min}$ (e A^{-3})	−0.22
$\Delta\rho_{max}$ (e A^{-3})	0.41

[a] $w=w'[1\text{-}((\|F_o\|-\|F_c\|)/6\sigma(F_o))^2]^2$ with $w'=1/\Sigma_r\, A_rT_r(X)$ with three coefficients 8.51, 2.62 and 7.08 for a Chebyshev Series, for which X is F_c/F_c(max).



3c **7c** (3)

As can be seen in both structures, the lactones arising from the two *trans* olefins led to hydroxylactones in which the hydroxyl group is anti with respect to the carbon–oxygen bonds of the bridging ether linkage confirming the *anti*-5-*exo* tet cyclization mode [36].

A series of other lactones bearing various substituents was obtained according to the above procedure confirming the general scope of the transformation. Their physical data can be found in Section 4.

2.3.3. A two-step procedure involving only palladium

Since the first step of the transformation of γ-unsaturated carboxylic acids involves palladium, it would be highly advantageous to use the same metal to carry out the second step of the transformation, the intramolecular cyclization.

This might be possible since Wacker-type cyclizations, induced by palladium(II) are known for both unsaturated phenols and carboxylic acids [37,38]. They lead, respectively, to unsaturated furanes and unsaturated lactones.

We found on a few preliminary examples that such a transformation could also be carried out on the unsaturated carboxylic acids synthesized herein.

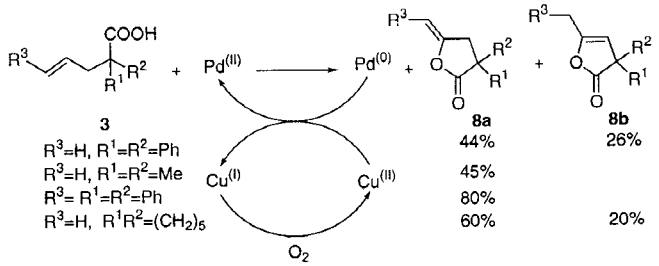
Two approaches have thus been made:

- first, the isolated carboxylic acids were heated to 60°C in DMF, in the presence of a catalytic amount of Pd(II) complexes (Na_2PdCl_4, $PdCl_2(PPh_3)_2$), together with $Cu(OAc)_2$ and oxygen. This gave the expected unsaturated lactones **8a** and **8b** in fairly good yields. The presence of DMF appeared to be critical since almost no lactones were formed in solvents such as THF. Whereas in the presence of Na_2PdCl_4 a 55:45 mixture of two lactones was obtained, in 81% yield, in the case of $PdCl_2(PPh_3)_2$ the *exo*-methylene butenolide **8a** was almost the sole product of the reaction (Scheme 5).
- second, attempts were made to use the palladium already present in the crude reaction mixture from

Table 3
Crystallographic data for compound $C_{20}H_{22}O_3$ (**7c**)

F_w	310.4
T (K)	295
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	8.739(2)
b (Å)	19.612(6)
c (Å)	9.961(2)
α (°)	90
β (°)	98.18(2)
γ (°)	90
V (Å^3)	1689.7(7)
Z	4
Linear absorption coefficient μ (cm^{-1})	0.75
Density ρ (g cm^{-3})	1.22
Diffractometer	CAD4 Enraf-Nonius
Radiation (Mo–K$_\alpha$), λ (Å)	0.71069
Scan type	$\omega/2\theta$
Scan range (°)	$0.8+0.345$ tgθ
θ limits (°)	1–26
Octants collected	0, 10; 0, 24; −12, 12
No. of data collected	3655
No. of unique data collected	3311 ($R_{int}=0.01$)
No. of unique data used for refinement	1582 $(F_o)^2>3\sigma(F_o)^2$
$R=\Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$	0.0651
Rw [a] $=[\Sigma\, w(\|F_o\|-\|F_c\|)^2/\Sigma wF_o^2]^{1/2}$	0.0810
S	1.10
Extinction parameter	512
No. of variables	210
$\Delta\rho_{min}$ (e A^{-3})	−0.27
$\Delta\rho_{max}$ (e A^{-3})	0.34

[a] $w=w'[1\text{-}((\|F_o\|-\|F_c\|)/6\sigma(F_o))^2]^2$ with $w'=1/\Sigma_r\, A_rT_r(X)$ with three coefficients 5.68, 0.250 and 4.01 for a Chebyshev Series, for which X is F_c/F_c(max).



Scheme 5.

the first transformation: no reaction was observed in THF, in the presence of Cu(II) and oxygen. However, when THF was exchanged for DMF, and the reaction conducted under the same conditions as above, conversion into the lactone was again observed. Thus, the solution resulting from the interaction of the ketene acetal **1** ($R_1 = R_2 = Me$) and allyl acetate was freed from THF. DMF was then added together with $Cu(OAc)_2$ and the solution heated to 80°C in the presence of oxygen for 5 h. Workup led to a single lactone **8a** (80%).

3. Conclusion

Direct access to a series of unsaturated carboxylic acids and δ-hydroxy-γ-lactones from allylic acetates and bis(trimethylsilyl)ketene acetals has been achieved by the use of two coupled catalytic reactions involving palladium(0) and oxorhenium catalysts. In addition to the unsaturated carboxylic acids, cyclopropane carboxylic acids were obtained. The yield of this latter compounds was highly dependent on the structure of the starting ketene acetals. A mechanism for their formation involving intermediate palladacyclobutanes has been tentatively suggested.

3.1. Structure solution and refinement

For products **7b** and **7c**, accurate cell dimensions and orientation matrices were obtained by least-squares refinements of 25 accurately centered reflections. No significant variations were observed in the intensities of two checked reflections during data collection. Complete data and collection parameters are listed in Tables 2 and 3. The data collected for Lorentz and polarization effects. Computations were performed by using the PC version of CRYSTALS. [52] Scattering factors and corrections for anomalous absorption were taken from [53] . The structures were solved by Fo–Patterson technique or direct method (SHELXS) [54]. Refinements were carried out by full-matrix least-squares. All non-hydrogen atoms were anisotropically refined, hydrogen atoms were introduced in calculated positions. The drawing of the molecules was carried out with the CAMERON program [55].

4. Experimental

General: all reactions were performed under a dry argon atmosphere. Solvents were distilled from sodium/benzophenone ketyl (diethyl ether, tetrahydrofurane), phosphorus pentoxide (dichloromethane) and saturated with argon. Silica gel (Merck, type 60, 0.063–0.200 mm) was used for column chromatography. ^{1}H-NMR: Bruker ARX-400 (400 MHz), DPX 250 (250 MHz), AC-200 (200 MHz). ^{13}C-NMR: Bruker ARX-400 (100 MHz), DPX-250 (60 MHz), AC-200 (50 MHz). All NMR spectra were recorded in $CDCl_3$ unless stated otherwise with $CHCl_3$ as internal standard. MS and HRMS were recorded on a JEOL MS 700. Melting points were performed on a Reichert apparatus and are uncorrected. TLC: 0.25 mm Merck silica gel plates 60 F_{254}.

The bis (trimethylsilyl) ketene acetals were prepared according to the literature [39].

4.1. Typical experimental procedure for the Pd catalyzed reactions

To an oven-dried 50 ml flask was added under an argon atmosphere the acetate (3 mmol), the acetal (3.30 mmol), $Pd(PPh_3)_4$ (5 mol%) and a solvent (20 ml). A reflux condenser was fitted and the solution was stirred and refluxed until complete consumption of the starting acetate as judged by ^{1}H-NMR. The solution was cooled to room temperature, the solvent removed and the residue filtered through a short pad of silica gel (70/30 ether/petroleum ether) to remove palladium complex and triphenyl phosphine. The products were then purified by either column chromatography (ether/petroleum ether) or acidbase workup.

4.2. 2-Methyl-5-phenyl-pent-4-enoic acid [40]

^{1}H-NMR (200 MHz, $CDCl_3$) δ: 7.38–7.20 (m, 5H, Ph), 6.47 (d, 1H, $J = 16$ Hz, Ph–C<u>H</u>=), 6.19 (dt, 1H, $J = 16$ Hz, $J = 8$ Hz, Ph–CH=C<u>H</u>), 2.62 (m, 2H, $C\underline{H}_2$), 1.3 (m, 1H, C<u>H</u>), 1.24 (d, 3H, $J = 8$ Hz, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 182.3 (CO), 137.4 (CPh), 132.5 (Ph–<u>C</u>H=), 128.8–126.3 (C Ph + Ph–CH=<u>C</u>H), 39.6 (<u>C</u>–COOH), 36.8 (CH_2), 16.6 (CH_3).

4.3. 2-Methyl-3-phenyl-pent-4-enoic acid [40]

4.3.1. α Diastereoisomer

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.38–7.20 (m, 5H, Ph), 6.20–5.80 (m, 1H, CH_2=C<u>H</u>), 5.20–5.00 (m, 2H, $C\underline{H}_2$=CH), 3.6 (m, 1H, Ph–C<u>H</u>), 2.70–2.30 (m,1H,

CH–COOH), 1.3 (d, $J = 8$ Hz, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 182.0 (CO), 141.2 (CPh), 139.5 (CH_2=CH), 128.8–126.3 (CPh), 115.9 (CH_2=CH), 53.4 (Ph–CH), 44.8 (C–COOH), 15.6 (CH_3).

4.3.2. β Diastereoisomer

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.38–7.20 (m, 5H, Ph), 6.20–5.80 (m, 1H, CH_2=CH), 5.20–5.00 (m, 2H, CH_2=CH), 2.90 (m, 1H, Ph–CH), 2.70–2.30 (m, 1H, CH–COOH), 1.0 (d, $J = 8$ Hz, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 181.4 (CO), 141.0 (CPh), 138.4 (CH_2=CH), 128.8–126.3 (CPh), 117.1 (CH_2=CH), 53.3 (Ph–CH), 45.3 (C–COOH), 16.0 (CH_3).

4.4. 2-Ethyl-5-phenyl-pent-4-enoic acid [41]

^{1}H-NMR (200 MHz, $CDCl_3$) δ: 7.41–7.24 (m, 5H, Ph), 6.50 (d, 1H, $J = 16$ Hz, Ph–CH=), 6.23 (dt, 1H, $J = 16$ Hz, $J = 8$ Hz, Ph–CH=CH), 2.62 (m, 2H, CH_2), 1.3 (m, 3H, CH–COOH + =CH–CH_2), 1.71 (m, 2H, CH_2–CH_3), 1.02 (t, 3H, $J = 8$ Hz, CH_3).

4.5. 2-Terbutyl-5-phenyl-pent-4-enoic acid

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.29–7.21 (m, 5H, Ph), 6.47 (d, 1H, $J = 15.8$ Hz, Ph–CH), 6.15 (m, 1H, Ph–CH=CH), 2.52–2.45 (m, 2H, CH_2), 2.35 (dd, 1H, $J = 11.6$ Hz, $J = 4.1$ Hz, CH–COOH), 1.07 (s, 9H, CH_3). HMRS Calc. for $C_{15}H_{19}O_2$, 231.1385. Found, 231.1386.

4.6. 2-Terbutyl-3-phenyl-pent-4-enoic acid

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.29–7.21 (m, 5H, Ph), 6.05 (m, 1H, CH_2=CH) 5.20–4.95 (m, 2H, CH_2=CH), 3.80 (m, 1H, Ph–CH), 2.77 (dd, 1H, $J = 12$ Hz, $J = 5$ Hz, CH–*t*Bu), 1.04 (s, 9H, CH_3).

4.7. 2,5-Diphenyl-pent-4-enoic acid [39]

^{1}H-NMR (200 MHz, $CDCl_3$) δ: 7.36–7.03 (m, 10H, Ph), 6.35 (d, 1H, $J = 16$ Hz, Ph–CH), 6.03 (m, 1H, Ph–CH=CH), 3.63 (t, 1H, $J = 8$ Hz, CH), 2.89 (m, 1H, CH_2), 2.60 (m, 1H, CH_2), 1.3. ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 179.6 (CO), 138.5, 136.6 (CPh), 128.9–126.3 (CPh + Ph–CH=CH), 132.5 (Ph–CH), 51.8 (C–COOH), 36.6 (CH_2).

4.8. 2,3-Diphenyl-pent-4-enoic acid [40]

4.8.1. α Diastereoisomer

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.36–7.00 (m, 10H, Ph), 5.62 (ddd, 1H, $J = 17.2$ Hz, $J = 10.2$ Hz, $J = 7.2$ Hz, CH_2=CH), 4.77 (dd, 1H, $J = 10.2$ Hz, $J = 1.2$ Hz, CHH=CH), 4.67 (dd, 1H, $J = 17.2$ Hz, $J = 1.2$ Hz, CHH=CH), 3.91 (m, 2H, Ph–CH). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 178.5 (CO), 138.5, 136.6, 128.9–126.3, (CPh), 132.8 (CH_2=CH), 118.1 (CH_2=CH), 57.2, 52.7 (Ph–CH).

4.8.2. β Diastereoisomer

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.36–7.00 (m, 10H, Ph), 5.00 (ddd, 1H, $J = 17.2$ Hz, $J = 10.2$ Hz, $J = 7.2$ Hz, CH_2=CH), 5.13 (dd, 1H, $J = 10.2$ Hz, $J = 1.2$ Hz, CHH=CH), 5.03 (dd, 1H, $J = 17.2$ Hz, $J = 1.2$ Hz, CHH=CH), 3.91 (m, 2H, Ph–CH). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 178.5 (CO), 138.5, 136.6, 128.9–126.3, (CPh), 132.8 (CH_2=CH), 118.1 (CH_2=CH), 57.2, 52.7 (Ph–CH).

4.9. 2,2-Dimethyl-5-phenyl-pent-4-enoic acid (m.p. 38°C) [41]

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.31–7.11 (m, 5H, Ph), 6.36 (d, 1H, $J = 16$ Hz, Ph–CH=), 6.11 (dt, 1H, $J = 16$ Hz, $J = 7.5$ Hz, Ph–CH=CH), 2.39 (d, 2H, $J = 16$ Hz, CH_2), 1.17 (s, 6H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 184.8 (CO), 137.6, 129.0, 127.5, 126.5 (CPh), 133.7, 126.1 (CH=), 43.9 (CH_2), 43.0 (C–COOH), 25.1 (CH_3). Anal. Calc. for $C_{13}H_{16}O_2$: C, 76.47; H, 7.84. Found: C, 75.85; H, 8.20%. HMRS Calc. for $C_{13}H_{16}O_2$, 204.1229. Found, 204.1226.

4.10. 2,2-Dimethyl-3-phenyl-pent-4-enoic acid

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.40–7.11 (m, 5H, Ph), 6.25 (m, 1H, CH_2=CH), 5.17 (m, 2H, CH_2=CH), 3.67 (d, 1H, $J = 9.9$ Hz, Ph–CH), 1.29, 1.28 (s, 6H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 184.6 (CO), 140.1, 128.4, 127.4, 125.8 (CPh), 136.8 (CH_2=CH), 118.1 (CH_2=CH), 57.5 (Ph–CH), 47.0 (C–COOH), 23.5, 22.0 (CH_3). HMRS Calc. for $C_{13}H_{16}O_2$, 204.1229. Found, 204.1230.

4.11. 2-Methyl-2-(2-phenyl-cyclopropyl)propionic acid (m.p. 48°C)

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.26–7.11 (m, 5H, Ph), 1.92 (dt, $J = 8.86$, 5.42, 5.42, 1H, Ph–CH), 1.41 (dt, $J = 9.36$, 5.90, 5.90, CH–C(Me_2)), 1.19 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 1.02 (dt, $J = 8.86$, 5.41, 5.43, 1H, Ph–CH–CH_2), 0.89 (dt, $J = 8.86$, 5.41, 5.44, 1H, Ph–CH–CH_2). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 183.0 (CO), 142.0, 127.0, 125.0, 124.5 (CPh), 40.5 (C–COOH), 29.7 (Ph–CH), 22.0 (CH_3), 21.5 (CH_3), 18.0 (CH–C(Me_2)), 10.5 (CH_2). HMRS Calc. for $C_{13}H_{16}O_2$, 204.1229. Found, 204.1226.

4.12. 2,2-Cyclohexyl-5-phenyl-pent-4-enoic acid

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.37–7.21 (m, 5H, Ph), 6.44 (d, 1H, $J = 15.2$ Hz, Ph–CH=), 6.19 (dt, 1H,

$J = 15.2$ Hz, $J = 7.6$ Hz, Ph–CH=CH), 2.47 (d, 2H, $J = 7.6$ Hz, CH_2), 1.65–1.58 (m, 4H, CH_2), 1.50–1.25 (m, 6H, CH_2). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 183.4 (CO), 133.2, 128.6, 127.3, 126.3 (CPh), 137.5, 125.2 (CH=), 47.7 (C–COOH), 43.5 (CH_2), 33.6, 25.8, 23.2 (CH_2). HMRS Calc. for $C_{16}H_{20}O_2$, 244.1463. Found, 244.1461.

4.13. 2,2-Cyclohexyl-3-phenyl-pent-4-enoic acid

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.27–7.20 (m, 5H, Ph), 6.30 (m, 1H, CH_2=CH), 5.14 (m, 2H, CH_2=CH), 3.43 (d, 1H, $J = 10.4$ Hz, Ph–CH), 1.65–1.58 (m, 4H, CH_2), 1.50–1.25 (m, 6H, CH_2). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 182.5 (CO), 136.7, 133.2–125.2 (CPh), 140.1 (CH_2=CH), 117.6 (CH_2=CH), 59.6 (Ph–CH), 52.1 (C–COOH), 32.6–23.1 (CH_2).

4.14. Cyclohexyl-(2-phenyl-cyclopropyl) acetic acid

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.10-0.8 (m, 11H), 1.0–0.40 (m, 4H, CH–(CH_2)$_2$). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 183.2 (CO), 46.2 (C–COOH.), 32.2, 25.9, 23.6 ((CH_2)$_5$), 20.9 (CH–(CH_2)$_2$–), 0.9 (CH–(CH_2)$_2$–). HMRS Calc. for $C_{16}H_{20}O_2$, 244.1463. Found, 244.1461.

4.15. 2,2,5-Triphenyl-pent-4-enoic acid (m.p. 147°C)

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.21–7.06 (m, 15H, Ph), 6.14 (d, 1H, $J = 15$,8 Hz, Ph–CH=), 5.86 (dt, 1H, $J = 15.8$ Hz, $J = 7.1$ Hz, Ph–CH=CH), 3.22 (d, 2H, $J = 7.1$ Hz, CH_2). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 180.7 (CO), 142.1, 137.0 (CPh), 129.3–125.8 (CPh + CH=), 60.9 (C–COOH), 41.7 (CH_2). Anal. Calc. for $C_{25}H_{15}O_2$: C, 84.14; H, 6.10. Found: C, 84.02; H, 6.23%.

4.16. 2-Methoxy-5-phenyl-pent-4-enoic acid

^{1}H-NMR (200 MHz, CDC_{l3}) δ: 7.38–7.18 (m, 5H, Ph), 6.50 (d, 1H, $J = 15.7$ Hz, Ph–CH), 6.23 (dt, 1H, $J = 15.7$ Hz, $J = 7.4$ Hz, Ph–CH=CH), 3.93 (t, 1H, $J = 6.8$ Hz, MeO–CH), 3.45 (s, 3H, Me–O), 2.70 (m, 2H, CH_2). ^{13}C-NMR (50 MHz, $CDCl_3$) δ: 177.2 (CO), 137.5 (CPh), 133.2 (Ph–CH), 128.5, 127.3, 126.2 (CPh), 123.9 (Ph–CH=CH), 79.8 (C–COOH), 58.1 (CH_3), 36.0 (CH_2). This acid has been oxydized directly and the resulting lactone characterized fully.

4.17. 2-Methoxy-3-phenyl-pent-4-enoic acid

4.17.1. α and β Diastereoisomers

^{1}H-NMR (200 MHz, $CDCl_3$) δ: 7.35–7.26 (m, 5H, Ph), 6.17 (m, 2H, CH_2=CH), 5.18 (m, 2H, CH_2=), 4.07 (m, 1H, Me–O–CH), 3.81 (m, 1H, Ph–CH), 3.41, 3.40 (s, 3H, Me–O). ^{13}C-NMR (50 MHz, $CDCl_3$) δ: 176.4 (CO), 140.2, 139.1 (CPh), 137.1, 135.6 (CH=), 128.7–127.2 (CPh), 118.2, 117.4 (CH_2=), 84.4, 84.3 (C–COOH), 59.4, 59.3 (Ph–CH), 52.9, 52.6 (Me–O). These acid were converted into the lactone which were characterized further.

4.18. 2-Phenoxy-5-phenyl-pent-4-enoic acid

^{1}H-NMR (200 MHz, $CDCl_3$) δ: 7.38–7.21(m, 7H, Ph), 7.04–6.89 (m, 3H, Ph), 6.55 (d, 1H, $J = 15.8$ Hz, Ph–CH), 6.28 (dt, 1H, $J = 15.7$ Hz, $J = 6.9$ Hz, Ph–CH=CH), 4.78 (dd, 1H, $J = 6.4$ Hz, $J = 5.9$ Hz, CH–COOH), 2.89 (dd, $J = 6.6$ Hz, $J = 5.9$ Hz, 2H, CH_2). ^{13}C-NMR (50 MHz, $CDCl_3$) δ: 176.7 (CO), 157.4, 136.9 (CPh), 134.0 (Ph–CH), 129.8, 122.1, 114.7 (CPh), 128.6, 127.6, 126.4 (CPh), 123.4 (Ph–CH=CH), 76.1 (C–COOH), 36.3 (CH_2). This acid has been converted to the lactone which was characterized.

4.19. 2-Ethyl-pent-4-enoic acid [42]

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 5.78 (dddd, 1H, $J = 17.0$ Hz, $J = 10.2$ Hz, $J = 6.6$ Hz, $J = 6.6$ Hz, CH_2=CH), 5.09 (dd, 1H, $J = 16.8$ Hz, $J = 10.2$ Hz, CHH=CH), 5.04 (dd, 1H, $J = 10.2$ Hz, $J = 1.0$ Hz, CHH=CH), 2.40 (m, 2H, CH_2–CH=), 2.27 (d, 1H, $J = 9.1$ Hz, CH–COOH), 1.48–1.73 (m, 2H, CH_2–CH_3), 0.96 (t, 3H, $J = 7.6$ Hz, CH_2–CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 182.4 (CO), 135.2 (CH_2=CH), 116.9 (CH_2=CH), 46.8 (CHCO$_2$H), 35.7 (CH_2–CH=), 24.6 (CH_2CH_3), 11.56 (CH_2CH_3). HMRS Calc. for $C_7H_{13}O_2$, 129.0916. Found, 129.0918.

4.20. 2-Cyclopropyl-butanoic acid

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.48–1.73 (m, 3H, CH–COOH + CH_2–CH_3), 0.96 (t, 3H, $J = 7.6$ Hz, CH_2–CH_3), 0.97–1.02 (m, 1H, CH–CH–COOH), 0.48–0.62 (m, 2H), 0.28–0.34 (m, 1H), 0.14–0.20 (m, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 182.4 (CO), 52.3 (CHCO$_2$H), 25.4 (CH_2CH_3), 13.2 (CH), 11.8 (CH_2CH_3), 4.58, 3.31 (CH_2)$_2$. HMRS Calc. for $C_7H_{13}O_2$, 129.0916. Found, 129.0918.

4.21. 2-Phenyl-pent-4-enoic acid [42]

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.23–7.14 (m, 5H, Ph), 5.62 (ddt, 1H, $J = 17.3$ Hz, $J = 10.1$ Hz, $J = 9.1$ Hz, CH_2=CH) 4.98 (dd, 1H, $J = 10.1$ Hz, $J = 1.0$ Hz, CHH=CH), 4.91 (dd, 1H, $J = 17.3$ Hz, $J = 1.0$ Hz, CHH=CH), 3.55 (t, 1H, Ph–CH), 2.43 (m, 2H, CH_2). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 178.9 (CO), 136.7, 127.6–126.5 (CPh), 133.8 (CH_2=CH), 116.2 (CH_2=CH), 50.4 (Ph–CH), 37.0 (CH_2).

4.22. 2,2-Dimethyl-pent-4-enoic acid [43]

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 5.76 (m, 1H, CH_2=C$\underline{H}$), 5.07 (m, 2H, C$\underline{H}_2$=CH), 3.67 (m, 2H, C$\underline{H}_2$), 1.18 (s, 6H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 184.4 (CO), 133.9 (CH_2=$\underline{C}$H), 118.3 ($\underline{C}H_2$=CH), 44.5 (CH_2), 42.2 ($\underline{C}$–COOH), 24.6 (CH_3).

4.23. 2-Methyl-2-(cyclopropyl)propionic acid [44]

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.06 (s, 6H, CH_3), 1.18 (m, 1H, C$\underline{H}$–$(CH_2)_2$), 0.36 (m, 4H, CH–(C$\underline{H}_2$)$_2$). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 184.8 (CO), 41.1 ($\underline{C}$–COOH), 22.6(CH_3), 19.4 ($\underline{C}$H–$(CH_2)_2$), 0.85 (CH–($\underline{C}H_2$)$_2$).

4.24. 1-Allyl-cyclohexane carboxylic acid [42]

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 5.75 (m, 1H, CH_2=C$\underline{H}$), 5.06 (m, 2H, C$\underline{H}_2$=CH), 2.28 (d, 1H, J = 7.4 Hz, CH_2), 2.03–1.02 (m, 10H, $(CH_2)_5$). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 182.9 (CO), 133.3 (CH_2=$\underline{C}$H), 111.9 ($\underline{C}H_2$=CH), 47.2 ($\underline{C}$–COOH), 33.5 (CH_2=CH–$\underline{C}H_2$), 28.8, 25.7, 25.4 (($\underline{C}H_2$)$_5$).

4.25. 1-Cyclopropyl-cyclohexane carboxylic acid

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.10–0.8 (m, 11H), 0.40 (m, 4H, CH–(C$\underline{H}_2$)$_2$). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 183.2 (CO), 46.2 ($\underline{C}$–COOH), 32.2, 25.9, 23.6 (($\underline{C}H_2$)$_5$), 20.9 ($\underline{C}$H–$(CH_2)_2$–), 0.9 (CH–($\underline{C}H_2$)$_2$–). HMRS Calc. for $C_{10}H_{16}O_2$, 168.1229. Found, 168.1224.

4.26. 2,2-Diphenyl-pent-4-enoic acid (m.p. 142°C) [45]

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.38–7.28 (m, 10H, Ph), 6.5 (m, 1H, CH_2=C$\underline{H}$), 4.98 (m, 2H, C$\underline{H}_2$=CH), 3.19 (d, 2H, J = 7.0, Hz, CH_2). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 180.2 (CO), 142.0 (CPh), 134.0 ($\underline{C}H_2$=CH), 129.2–128.0–127.2, (CPh), 118.6 (CH_2=$\underline{C}$H), 60.3 ($\underline{C}$–COOH), 42.6 (CH_2).

4.27. 2-Methoxy-pent-4-enoic acid

^{1}H-NMR (200 MHz, $CDCl_3$) δ: 5.68 (dddd, 1H, J = 23.6 Hz, J = 13.7 Hz, J = 9.8 Hz, J = 6.9 Hz, CH_2=C$\underline{H}$–), 5.04–4.95 (m, 2H, C$\underline{H}_2$=CH–), 3.75 (dd, 1H, J = 6.9 Hz, J = 5.4 Hz, Me–O–C$\underline{H}$), 3.29 (s, 3H, CH_3–O), 2.37 (m, 2H, CH_2). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 177.3 (CO), 132.5($\underline{C}H_2$=CH–), 118.4 (CH_2=$\underline{C}$H), 79.7 ($\underline{C}$–COOH), 58.2 (CH_3–O), 36.8 (CH_2). Anal. Calc. for $C_6H_{10}O_3$: C, 55.32; H, 7.68. Found: C, 55.21; H, 8.13.

4.28. 2-Phenoxy-pent-4-enoic acid (m.p. 60°C)

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.19–7.16 (m, 2H, H *ortho*), 6.91–6.76 (m, 3H, H *meta* and *para*), 5.81 (m, 1H, CH_2=C$\underline{H}$–), 5.09 (m, 2H, C$\underline{H}_2$=CH–), 4.62 (dd, 1H, J = 6.1 Hz, J = 5.6 Hz, Ph–O–C$\underline{H}$), 2.64 (dd, 2H, J = 6.1 Hz, J = 5.6 Hz, CH_2). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 176.4 (CO), 156.3 (CPh), 130.9 (CH_2=$\underline{C}$H), 128.6, 120.9, 114.1 (CPh), 117.9 ($\underline{C}H_2$=CH), 74.6 ($\underline{C}$–COOH), 35.8 (CH_2). Anal. Calc. for $C_{11}H_{12}O_3$: C, 68.75; H, 6.25. Found: C, 68.71; H, 6.30%.

4.29. 2-Cyclopropyl-2-phenoxy-acetic acid

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.19–7.16 (m, 2H, H *ortho*), 6.91–6.76 (m, 3H, H *meta* and *para*), 3.99 (d, 1H, J = 7.6 Hz, C$\underline{H}$–COOH), 1.35–1.27 (m, 1H, $(CH_2)_2$–C$\underline{H}$), 0.62–0.45 (m, 4H, (C$\underline{H}_2$)$_2$–CH). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 176.7 (CO), 156.4, 128.3, 121.2, 114.0 (CPh), 78.0 ($\underline{C}$–COOH), 12.5 (CH_2)$_2$–$\underline{C}$H), 2.7, 1.3 (($\underline{C}H_2$)$_2$–CH). HMRS Calc. for $C_{11}H_{12}O_3$, 192.0786. Found, 192.0792.

4.30. 2-Methyl-2-phenoxy-pent-4-enoic acid [46]

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.22–7.17 (m, 2H, Ph *ortho*), 7.04–6.89 (t, 1H, J = 7.2 Hz, Ph *meta*), 6.88 (d, 2H, J = 8 Hz, H *para*), 5.81 (m, 1H, CH_2=C$\underline{H}$), 5.10 (m, 2H, C$\underline{H}_2$ = CH), 2.70 (dd, 1H, J = 14.1 Hz, J = 7.1 Hz, =CH–CH$\underline{H}$), 2.60 (dd, 1H, J = 14.1 Hz, J = 7.1 Hz, =CH–C$\underline{H}$H), 1.44 (s, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 177.9 (CO), 154.4, 129.3, 123.1, 120.2 (CPh), 133.2 (CH_2=$\underline{C}$H), 119.7 ($\underline{C}H_2$=CH), 81.7 ($\underline{C}$–COOH), 43.4 (CH_2), 21.3 (CH_3). HMRS Calc. for $C_{12}H_{14}O_3$, 206.0943. Found, 206.0937.

4.31. 2-Cyclopropyl-2-phenoxy-propionic acid

^{1}H-NMR (200 MHz, $CDCl_3$) δ: 7.29–6.92 (m, 5H, Ph), 1.45 (s, 3H, CH_3), 1.40 (m, 1H, CH), 0.66 (m, 4H, $2CH_2$). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 177.9 (CO), 154.4, 129.2, 123.1, 120.6 (CPh), 81.0 ($\underline{C}$–COOH), 22.0 (CH_3), 21.3 (CH_3), 19.6 (–$\underline{C}$H((CH_2)$_2$), 2.0, 1.6 (–CH(($\underline{C}H_2$)$_2$). HMRS Calc. for $C_{12}H_{14}O_3$, 206.0943. Found, 206.0937.

4.32. 2-Methyl-oct-4-enoic acid (cis and trans)

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 5.48 (dt, 1H, J = 15.2 Hz, J = 7.1 Hz, CH=), 5.36 (dt, 1H, J = 15.2 Hz, J = 7.1 Hz, CH=), 2.50 (m, 1H, C$\underline{H}$–COOH), 2.33–2.44 (m, 1H, C$\underline{H}$H–CH=), 2.14–2.26 (m, 1H, CH$\underline{H}$–CH=), 1.97 (q, 2H, J = 7.1 Hz, CH_3–CH_2–C$\underline{H}_2$), 1.36 (m, 2H, CH_3–C$\underline{H}_2$), 1.16 (d, 3H, J = 7.1 Hz, C$\underline{H}_3$–CH), 0.90 (t, 3H, J = 7,1 Hz, CH_3 *cis*) 0.87 (t, 3H,

$J = 7{,}1$ Hz, CH_3 *trans*). ^{13}C-NMR (50 MHz, $CDCl_3$) δ: 180.1 (CO), 133.0 (=CH *trans*), 132.3 (=CH *cis*), 126.4 (=CH *trans*), 125.8 (=CH *cis*), 36.4 (CH_2–CH=CH *trans*), 34.6, 30.9, 29.3, 22.7, 22.5 (CH_2), 16.24 (CH_3–CH–COOH *cis*), 16.15 (CH_3–CH–COOH *trans*), 13.7 (CH_3 *cis*), 13.5 (CH_3 *trans*). HMRS Calc. for $C_9H_{15}O_2$ (MH), 157.1229. Found, 157.1232.

4.33. 2-Phenyl-oct-4-enoic acid

^{1}H-NMR (200 MHz, $CDCl_3$) δ: 7.37–7.31 (m, 5H, Ph), 5.52 (m, 1H, CH=), 5.34 (m, 1H, CH=), 3.65 (m, 1H, Ph–CH), 2.21 (d, 2H, $J = 5.6$ Hz, $C(Me_2)$–CH_2–CH=), 2.51 (m, 1H, Ph–CH–CHH), 2.81 (m, 1H, Ph–CH–CHH), 1.96 (m, 2H, CH_3–CH_2–CH_2), 1.34 (m, 2H, CH_3–CH_2), 0.86 (t, 3H, $J = 7{,}2$ Hz, CH_3). ^{13}C-NMR (50 MHz, $CDCl_3$) δ: 180.3 (CO), 138.2 (CPh), 133.6 (CH(Ph)–CH_2–CH=), 128.7, 128.2, 127.6 (CPh), 126.3 ($C(Ph_2)$–CH_2–CH=CH), 52.2 (Ph–CH), 36.3 (CH(Ph)–CH_2–CH=CH), 42.5 (C–COOH), 34.7 (CH_3–CH_2–CH_2), 22.6 (CH_3–CH_2),13.6 (CH_3). HMRS Calc. for $C_{14}H_{18}O_2$, 219.1385. Found, 219.1379.

4.34. 2,2-Dimethyl-oct-4-enoic acid (cis and trans)

^{1}H-NMR (200 MHz, $CDCl_3$) δ: 5.49–5.27 (m, 2H, CH=), 2.31 (d, 2H, $J = 7.1$ Hz, CH_2–CH–COOH *cis*), 2.24 (d, 2H, $J = 7.1$ Hz, CH_2–CH–COOH *trans*), 2.01 (m, 2H, CH_3–CH_2–CH_2), 1.38 (m, 2H, CH_3–CH_2), 1.21 (s, 6H, CH_3 *cis*), 1.19 (s, 6H, CH_3 *trans*), 0.91 (t, 3H, $J = 7{,}1$ Hz, CH_3–CH_2 *cis*) 0.89 (t, 3H, $J = 7{,}1$ Hz, CH_3–CH_2 *trans*). ^{13}C-NMR (50 MHz, $CDCl_3$) δ: 184.8 (CO), 134.5 (CH= *trans*), 132.9 (CH= *cis*), 125.2 (=CH *trans*), 125.5 (=CH *cis*), 43.3 ($C(Me_2)$–CH_2–CH *trans*), 42.5 (C–COOH), 37.5 ($C(Me_2)$–CH_2–CH *cis*), 34.7 (CH_3–CH_2–CH_2 *trans*), 29.4 (CH_3–CH_2–CH_2 *cis*), 24.5 ($(Me)_2$), 22.8 (CH_3–CH_2 *cis*), 22.6 (CH_3–CH_2 *trans*), 13.8 (CH_3 *cis*), 13.6 (CH_3 *trans*). HMRS Calc. for $C_{10}H_{18}O_2$, 170.1385. Found, 170.1385.

4.35. 2,2-Diphenyl-oct-4-enoic acid (m.p. 94°C)

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.38–7.32 (m, 10H, Ph), 5.43–5.28 (m, 2H, CH=), 3.19 (d, 2H, $J = 5.6$ Hz, $C(Ph_2)$–CH_2), 1.89 (m, 2H, CH_3–CH_2–CH_2), 1.29 (m, 2H, CH_3–CH_2), 0.84 (t, 3H, $J = 7{,}4$ Hz, CH_3). ^{13}C-NMR (100 MHz, CDCl3) δ: 181.0 (CO), 142,4 (CPh), 135.1 ($C(Ph_2)$–CH_2–CH=), 129.4, 128.9, 128.0 (CPh), 125.2 (Pr–CH=), 60.8 (C–COOH), 41.6 ($C(Ph_2)$–CH_2), 34.9 (CH_3–CH_2–CH_2), 22.6 (CH_3–CH_2),13.7 (CH_3). HMRS Calc. for $C_{20}H_{22}O_2$, (MH) 294.1698. Found, 294.1703.

4.36. 2-Methoxy-oct-4-enoic acid [47]

^{1}H-NMR (200 MHz, $CDCl_3$) δ: 5.60–5.27 (m, 2H, CH=), 3.81 (dd, 1H, $J = 6.4$ Hz, $J = 5.4$ Hz, MeO–CH), 3.41 (MeO), 2.49 (m, 2H, MeO–CH–CH_2), 1.96 (m, 2H, CH_3–CH_2–CH_2), 1.35 (m, 2H, CH_3–CH_2), 0.86 (t, 3H, $J = 7.2$ Hz, CH_3). ^{13}C-NMR (50 MHz, $CDCl_3$) δ: 176.9 (CO), 134.1 (CH= *trans*), 133.5 (CH= *cis*), 123.4 (=CH *trans*), 123.1 (=CH *cis*), 80.1 (C–COOH), 57.8 (OCH_3), 35.4 (CH_2–CH–OMe *trans*), 34.3 (CH_3–CH_2–CH_2 *cis*), 30.5, 29.4 (CH_2 *cis*), 22.7 (CH_3–CH_2 *cis*), 22.1 (CH_3–CH_2 *trans*),13.8 (CH_3 *cis*), 13.2 CH_3 *trans*). HMRS Calc. for $C_9H_{17}O_3$, (MH) 173.1178. Found, 173.1177.

4.37. 2-Methyl-2-phenoxy-oct-4-enoic acid

^{1}H-NMR (200 MHz, $CDCl_3$) δ: 7.17–7.14 (m, 2 H, H *meta*), 6.93 (t, 1H, $J = 7.2$ Hz, H *para*), 6.84 (dd, 2H, $J = 8{,}6$ Hz, $J = 1$ Hz, H *ortho*), 5.44 (m, 2H, CH=), 2.57 (m, 2H, CH_2–C–COOH), 1.91 (m, 2H, CH_3–CH_2–CH_2), 1.40 (s, 3H, CH_3–C–COOH), 1.35 (m, 2H, CH_3–CH_2), 0.79 (t, 3H, $J = 7{,}2$ Hz, CH_3). ^{13}C-NMR (50 MHz, $CDCl_3$) δ: 179.8 (CO), 155.2 (CPh), 136.3 (C(PhO)–CH_2–CH=), 129.6, 123.2, 120.6 (CPh), 120.5 (C(PhO)–CH_2–CH=CH), 82.3 (C–COOH), 43.0 (CH(-PhO)–CH_2), 35.1 (CH_3–CH_2–CH_2), 22.8 (CH_3–CH_2), 21.5 (CH_3–C–COOH), 14.0 (CH_3). Anal. Calc. for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.64; H, 8.30%.

4.38. 2-Phenoxy-oct-4-enoic acid (m.p. 43°C) (NMR for trans)

^{1}H-NMR (200 MHz, $CDCl_3$) δ: 7.22 (t, 2 H, $J = 8.4$ Hz, H *meta*), 6.93 (t, 1H, $J = 7.4$ Hz, H *para*), 6.85 (d, 2H, $J = 8{,}2$ Hz, H *ortho*), 5.38-5.63 (m, 2H, CH=) 4.62 (t, 2H, $J = 6.6$ Hz, CH–COOH), 2.62 (t, 2H, $J = 6.0$ Hz, CH_2–C–COOH), 1.93 (m, 2H, CH_3–CH_2–CH_2), 1.37 (m, 2H, CH_3–CH_2), 0.82 (t, 3H, $J = 7{,}1$ Hz, CH_3). ^{13}C-NMR (50 MHz, $CDCl_3$) δ: 177.3 (CO), 157.6 (CPh), 135.2 (CH=), 127.9, 123.4, 121.9, 115.3 (CPh + =CH), 76.4 (C–COOH), 36.0 (COOH–CH–CH_2), 22.8 (CH_3–CH_2), 13.7 (CH_3). Anal. Calc. for $C_{14}H_{18}O_3$: C, 71.79; H, 7.69. Found: C, 71.68; H, 7.83%.

4.39. 3,5-Diphenyl-2-methyl-pent-4-enoic acid

4.39.1. α Diastereoisomer (m.p. 128°C)

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.20–7.37 (m, 10 H, Ph), 6.49 (d, 1H, $J = 15.8$ Hz, Ph–CH=), 6.42 (dd, 1H, $J = 15.8$ Hz, $J = 7.6$ Hz, Ph–CH=CH), 3.65 (t, 1H, $J = 9.6$ Hz, PhCH), 2.95 (m, 1H, CH–COOH), 1.06 (d, 3H, $J = 6.6$ Hz, CH_3). ^{13}C-NMR (50 MHz, $CDCl_3$) δ: 182.0 (CO), 141.2 (CPh), 137.3 (CH=), 131.1–126.4 (CPh + =CH), 52.6 (CHPh), 45.5 (C–COOH), 16.0 (CH_3).

4.39.2. β Diastereoisomer (m.p. 111°C)

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.18–7.35 (m, 10 H, Ph), 6.47 (d, 1H, $J = 15.8$ Hz, Ph–CH=), 6.24 (dd, 1H, $J = 15.8$ Hz, $J = 9.3$ Hz, Ph–CH=CH), 3.65 (t, 1H, $J = 9.3$ Hz, PhCH), 2.86–2.95 (m, 1H, CH–COOH), 1.25 (d, 3H, $J = 7.4$ Hz, CH_3). ^{13}C-NMR (50 MHz, $CDCl_3$) δ: 181.8 (CO), 142.4 (CPh), 137.4 (CH=), 132.4–126.7 (CPh + =CH), 52.7 (CHPh), 45.4 (C–COOH), 16.0 (CH_3). HMRS Calc. for $C_{18}H_{19}O_2$, (MH) 266.1307. Found, 266.1306.

4.40. 3,5-Diphenyl-2,2-dimethyl-pent-4-enoic acid (m.p. 85°C)

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.52–7.32 (m, 10 H, Ph), 6.63 (d, 1H, $J = 15.8$ Hz, Ph–CH=), 6.49 (dd, 1H, $J = 15.8$ Hz, $J = 10.0$ Hz, Ph–CH=CH), 3.93 (d, 1H, $J = 8.0$ Hz, CH–COOH), 1.37 (s, 3H, CH_3), 1.32 (s, 3H, CH_3). ^{13}C-NMR (50 MHz, $CDCl_3$) δ: 184.2 (CO), 140.4 (CPh), 137.5 (CH=), 133.2–126.6 (CPh + =CH), 52.8 (CHPh), 47.3 (C–COOH), 23.5 (CH_3), 22.6 (CH_3). Anal. Calc. for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.24; H, 7.12%.

4.41. 2-Isopropyl-5-phenyl-pent-4-enoic acid

^{1}H-NMR (200 MHz, $CDCl_3$) δ: 7.35–7.20 (m, 5 H, Ph), 6.5 (d, 1H, $J = 16$ Hz, Ph–CH=), 6.15 (dt, 1H, $J = 16$ Hz, $J = 8$ Hz, Ph–CH=CH), 4.98 (s, 2H, CH_2=), 3.24 (t, 1H, $J = 8$ Hz, CH_2=CH), 2.85–2.40 (m, 2H, CH_2), 1_2O_2.80 (s, 3H, CH_3). ^{13}C-NMR (50 MHz, $CDCl_3$) δ: 179.2 (CO), 141.4 (CPh), 137.5 (CH=), 132.2–126.2 (CPh), 114.9 (=CH_2), 53.0 (C–COOH), 33.0 (CH_2), 20.5 (CH_3).

4.42. 5-Phenyl-pent-4-enoic acid

^{1}H-NMR (200 MHz, $CDCl_3$) δ: 7.55–7.15 (m, 5 H, Ph), 6.45 (d, 1H, $J = 16$ Hz, Ph–CH=), 6.20 (dt, 1H, $J = 16$ Hz, $J = 8$ Hz, Ph–CH=CH), 2.55 (m, 4H, CH_2). ^{13}C-NMR (50 MHz, $CDCl_3$) δ: 179.6 (CO), 147.2 (CPh), 142.0 (CH=), 138–120.2 (CPh + =CH), 33.9 (CH_2–CH=), 27.9 (CH_2–COOH). HMRS Calc. for $C_{11}H_{12}O_2$, 176.0837. Found, 176.0843.

4.43. Mixture of 5-phenyl-2-trimethylsilanyl-pent-4-enoic (A) acid and 3-phenyl-2-trimethylsilanyl-pent-4-enoic acid (B)

^{1}H-NMR (200 MHz, $CDCl_3$) δ: 7.40–7.15 (m, Ph), 6.40 (d, $J = 16$ Hz, Ph–CH=, A), 6.20 (dt, $J = 16$ Hz, $J = 8$ Hz, Ph–CH=CH, A), 6.15–5.75 (m, CH=, B), 5.24–4.90 (m, =CH_2, B), 3.85–3.7 (m, Ph–CH, B), 2.75–2.55 (m, CH_2, A and B), 2.35–2.15 CH_2–CH–COOH, A), 0.15 (s, Si–CH_3). HMRS Calc. for $C_{14}H_{20}O_2Si$, 248.1233. Found, 248.1228.

4.44. Typical experimental procedure for the H_2O_2/MTO reactions

The unsaturated acid (1–3 mmol), 31% H_2O_2 (1,1 equivalents) and chloroform (2–5 ml) were placed in a 25 ml flask. MTO (5 mol%) was added and the mixture stirred vigorously at room temperature until the disappearance of the olefinic protons (^{1}H-NMR). Any remaining MTO and/or H_2O_2 were decomposed with the addition of dilute thiosulphite solution. The organic layer was removed and the aqueous layer was extracted with dichloromethane. The combined organic layers were dried ($MgSO_4$) and the products purified by column chromatography. Cyclopropane acids were recovered by acidification of the aqueous layer followed by extraction with dichloromethane.

4.45. 2-Methyl-2-(3-phenyl-oxiran-2-yl)-propionic acid

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.30–7.22 (m, 5H, Ph), 4.93 (d, 1H, $J = 8.6$ Hz, Ph–CH), 3.95 (m, 1H, Ph–CH–CH), 1.95 (d, 2H, $J = 13.2$ Hz, CH_2–$C(Me_3)_2$), 1.33 (s, 6H, CH_3). RMN: ^{13}C (100 MHz, $CDCl_3$) δ: 175 (CO), 131–125 (CPh), 85.0 (Ph–CH), 66.5 (Ph–CH–CH), 41.2 (C–COOH), 28.6 (CH_2), 27.9, 27.5 (CH_3)

4.46. 5-(Hydroxy-phenyl-methyl)-3,3-dimethyl-dihydrofuran-2-one (m.p. 52°C)

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.38–7.29 (m, 5H, Ph), 5.13 (d, 1H, $J = 3$ Hz, Ph–CH), 4.60 (m, 1H, CH–O), 1.67 (dd, 1H, $J = 13$ Hz, $J = 6$ Hz, CH_2), 1.21 (dd, 1H, $J = 13$ Hz, $J = 10$ Hz, CH_2), 1.26 (s, 3H, CH_3), 1.20 (s, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 182.3 (CO), 138, 127.5, 127.2, 125.0 (CPh), 78.7 (Ph–CH), 71.3 (CH–O), 39.2 (C–COO), 34.5 (CH_2), 23.9, 23.7 (CH_3). Anal. Calc. for $C_{13}H_{16}O_3$: C, 70.91; H, 7.27. Found: C, 70.71; H, 7.31%.

4.47. 5-(Hydroxy-methyl)-3,3-dimethyl-4-phenyl-dihydrofuran-2-one (m.p. 51°C)

4.47.1. α Diastereoisomer

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.25–6.96 (m, 5H, Ph), 4.90 (m, 1H, CH–O), 3.61 (dd, 1H, $J = 12.7$ Hz, $J = 8.1$ Hz, CHH–OH), 3.55 (dd, 1H, $J = 12.7$ Hz, $J = 4.8$ Hz, CHH–O), 3.18 (d, 1H, $J = 5.6$ Hz, Ph–CH), 1.42 (s, 3H, CH_3), 0.88 (s, 3H,CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 182.0 (CO), 135.0–128.0 (CPh), 81.1 (Ph–CH), 63.4 (CH_2), 55.8 (CH–O), 45.2 (C–COO), 26.1, 20.6 (CH_3).

4.47.2. β Diastereoisomer

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.25–6.96 (m, 5H, Ph), 4.90 (ddd, 1H, $J = 11.2$ Hz, $J = 4.6$ Hz, $J = 2.5$ Hz,

CH–O), 3.87 (dd, 1H, $J = 12.7$ Hz, $J = 2.5$ Hz, CHH–O), 3.31 (dd, 1H, $J = 12.2$ Hz, $J = 4.1$ Hz, CHH–O), 3.28 (d, 1H, $J = 11.2$ Hz, Ph–CH), 1.21 (s, 3H, CH_3), 0.88 (s, 3H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 181.0 (CO), 136.0–128.0 (CPh), 80.6 (Ph–CH), 62.4 (CH_2), 53.0 (CH–O), 44.9 (C–COO), 23.8, 21.0 (CH_3). Anal. calc. for $C_{13}H_{16}O_3$: C, 70.91; H, 7.27. Found: C, 70.81; H, 7.49%.

4.48. 5-(Hydroxy-methyl)-3,3-diphenyl-dihydrofuran-2-one (m.p. 72°C) [48]

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.24–7.09 (m, 10H, Ph), 4.29 (m, 1H, CH–O), 3.77 (dd, 1H, $J = 12.7$ Hz, $J = 2.5$ Hz, HOCHH), 3.51 (ddd, 1H, $J = 12.7$, $J = 3.6$ Hz, $J = 1.5$ Hz,, HOCHH), 2.76 (m, 2H, CH_2). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 178.1 (CO), 142.3, 140.2, 129.4, 128.8, 128.2, 127.8, 127.7 (CPh), 78.2 (Ph_2–C), 63.2 (C(OH)H_2–CH–O), 57.0 (CH_2OH), 38.7 (CH_2–CPh_2).

4.49. 5-(Hydroxy-phenyl-methyl)-3,3-diphenyl-dihydrofuran-2-one (m.p. 66°C)

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.28–7.19 (m, 15H, Ph), 5.05 (d, 1H, $J = 3.5$ Hz, Ph–CH), 4.42 (ddd, 1H, $J = 3.5$ Hz, $J = 5.1$ Hz, $J = 10.7$ Hz, CH–O), 3.02 (dd, 1H, $J = 13.2$ Hz, $J = 10.7$ Hz, CH_2), 2.52 (dd, 1H, $J = 12.7$ Hz, $J = 5.1$ Hz, CH_2). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 176.1 (CO), 141.0, 138.4, 137.2, 131.0–125.1 (CPh), 78.9 (Ph_2–CH), 71.1 (CH–O), 57.0 (Ph–C–OH), 35.2 (CH_2). HMRS Calc. for $C_{23}H_{20}O_2$, 344.1491. Found, 344.1498.

4.50. 5-Hydroxymethyl-2-oxa-spiro[4.5]decan-1-one (m.p. 112°C)

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 4.54 (m, 1H, CH–O), 3.89 (dd, 1H, $J = 12.7$ Hz, $J = 3.0$ Hz, (HO)CH$_2$), 3.61 (dd, 1H, $J = 12.7$ Hz, $J = 5.1$ Hz, (HO)CH$_2$), 2.24 (dd, 1H, $J = 6.6$ Hz, $J = 12.7$ Hz, CH$_2$–CH–O), 1.89 (dd, 1H, $J = 9.6$ Hz, $J = 12.7$ Hz, CH$_2$–CH–O), 1.81–1.71 (m, 3H, CH_2), 1.64–1.52 (m, 4H, CH_2), 1,.0–1.24 (m, 3H, CH_2). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 182.0 (CO), 77.8 CH–O), 63.9 (HO)CH_2), 44.9 (Cq), 34.1, 33.9, 32.1, 25.3, 22.2, 22.1 (CH_2). HMRS Calc. for $C_{10}H_{16}O_3$, 184.1178. Found, 184.1173.

4.51. 3-(Hydroxy-phenyl-methyl)-2-oxa-spiro[4.5]decan-1-one

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.38–7.25 (m, 5H, Ph), 5.11 (d, 1H, $J = 3.4$ Hz, (HO)CH), 4.58 (ddd, 1H, $J = 12.3$ Hz, $J = 9.6$ Hz, $J = 3.4$ Hz, CH–O), 2.08 (dd, 1H, $J = 12.8$ Hz, $J = 9.4$ Hz, CH$_2$–CH–O), 1.84 (dd, 1H, $J = 12.7$ Hz, $J = 12.3$ Hz, CH$_2$–CH–O), 1.75–1.18 (m, 10H, $((CH_2)_5)$. ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 181.9 (CO), 138.5, 128.6, 128.1, 126.1 (CPh), 80.3 (CH–O), 72.4 (HO–CH), 44.8 (Cq), 33.7, 32.2, 31.5, 25.3, 22.1, 22.0 (CH_2). Anal. Calc. for $C_{16}H_{20}O_3$: C, 73.84; H, 7.69. Found: C, 73.75; H, 7.85%.

4.52. 3-Tertiobutyl-5-(hydroxy-phenyl-methyl)-dihydrofuran-2-one (m.p. 86°C)

4.52.1. α Diastereoisomer

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.41–7.32 (m, 5H, Ph), 5.12 (d, 1H, $J = 3.6$ Hz, Ph–CH), 4.48 (m, 1H, CH–O), 2.44 (dd, 1H, $J = 12.7$ Hz, $J = 8.6$ Hz, CH–C$(CH_3)_3$), 2.22 (ddd, 1H, $J = 12.7$ Hz, $J = 12.7$, $J = 10.7$ Hz, CH_2), 1.89–1.80 (m, 1H, CH_2), 1.04 (s, 9H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 177.6 (CO), 138.8, 130.0–126.4 (CPh), 80.5 (Ph–CH), 72.6 (CH–O), 50.7 (CH–C$(CH_3)_3$), 32.3 (C$(CH_3)_3$), 27.6 (CH_3), 24.3 (CH_2).

4.52.2. β Diastereoisomer

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.41–7.32 (m, 5H, Ph), 5.10 (d, 1H, $J = 3.1$ Hz, Ph–CH), 4.62 (m, 1H, CH–O), 2.55 (dd, 1H, $J = 10.7$ Hz, $J = 7.9$ Hz, (CH–C$(CH_3)_3$), 2.31 (ddd, 1H, $J = 13.2$ Hz, $J = 10.2$, $J = 4.6$ Hz, CH_2), 1.89–1.80 (m, 1H, CH_2), 1.02 (s, 9H, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 179.1 (CO), 139.4, 130.0–126.4 (CPh), 81.3 (Ph–CH), 74 (CH–O), 50.0 (CH–C$(CH_3)_3$), 33.3 (C$(CH_3)_3$), 27.6 (CH_3), 24.0 (CH_2). HMRS Calc. for $C_{15}H_2OO_3$, 248.1491. Found, 248.1486.

4.53. 5-Hydroxymethyl-3-phenoxy-dihydro-furan-2-one

4.53.1. α Diastereoisomer

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.37–7.32 (m, 5H, Ph), 5.14 (d, 1H, $J = 2.5$ Hz, Ph–CH), 4.76 (ddd, 1H, $J = 8.1$ Hz, $J = 4.1$ Hz, $J = 2.5$ Hz, CH–O), 4.19 (dd, 1H, $J = 8.1$ Hz, $J = 6.6$ Hz, Me–O–CH), 3.53 (s, 3H, Me–O), 2.52 (ddd, 1H, $J = 13.2$ Hz, $J = 8.1$ Hz, $J = 4.1$ Hz, CHH), 1,91 (ddd, 1H, $J = 13.2$ Hz, $J = 8.1$ Hz, $J = 6.6$ Hz, CHH). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 175.4 (CO), 138.8, 128.8, 128.2, 126.0 (CPh), 81.3 (Ph–CH), 75.6 (CH–O), (73.2 (Me–O–CH), 58.3 (Me–O), 28.7 (CH_2).

4.53.2. β Diastereoisomer

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.40-7.28 (m, 5H, Ph), 5.10 (d, 1H, $J = 3.5$ Hz, Ph–CH), 4.74 (ddd, 1H, $J = 7.1$ Hz, $J = 5.1$ Hz, $J = 3.5$ Hz, CH–O), 3.92 (dd, 1H, $J = 7.1$ Hz, $J = 6.1$ Hz, Me–O–CH), 3.46 (s, 3H, Me–O), 2.35 (ddd, 1H, $J = 13.5$ Hz, $J = 7.5$ Hz, $J = 5.1$ Hz, CHH), 2.08 (ddd, 1H, $J = 13.5$ Hz, $J = 7.5$ Hz, $J = 6.1$ Hz, CHH). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 173.5 (CO), 137.5, 127.7, 126.0, 125.8 (CPh), 80.0 (HO–CH(Ph)), 74.8 (HO–CH–CH–O), 74.3(Me–O–

C̲H), 57.2 (Me–O), 30.7 (CH_2). HMRS Calc. for $C_{12}H_{15}O_4$, 223.0970. Found, 223.0964.

4.54. 5-Hydroxymethyl-3-phenoxy-dihydro-furan-2-one

4.54.1. α Diastereoisomer

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.30–7.28 (m, 2H, H *ortho*), 7.06–7.01 (m, 3H, H *meta* and *para*), 5.09 (t, 1H, $J = 9.7$ Hz, Ph–O–CH), 4.61 (m, 1H, CH–O), 3.94 (dd, 1H, $J = 12.7$ Hz, $J = 2.5$ Hz, HO–C̲HH), 3.71 (dd, 1H, $J = 12.7$ Hz, $J = 5.1$ Hz, HO–CHH̲), 2.74 (m, 1H, C̲HH–CH(O–Ph)), 2.31 (dt, 1H, $J = 12.7$ Hz, $J = 9,7$ Hz, CHH̲–CH(O–Ph)). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 173.8 (CO), 129.8, 122.6, 116.0, 110.8 (CPh), 77.6 (CH–OH), 73.5 (Ph–O–CH), 63.5 (HO–CH_2), 30.7 (CH_2).

4.54.2. β Diastereoisomer

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.30–7.28 (m, 2H, H *ortho*), 7.06–7.01 (m, 3H, H *meta* and *para*), 5.20 (t, 1H, $J = 7.6$ Hz, Ph–O–CH), 4.77 (m, 1H, CH–O), 3.99 (dd, 1H, $J = 12.7$ Hz, $J = 2.0$ Hz, HO–C̲HH), 3.66 (dd, 1H, $J = 12.7$ Hz, $J = 3.0$ Hz, HO–CHH̲), 2.74 (m, 1H, C̲HH–CH(O–Ph)), 2.31 (dt, 1H, $J = 13.2$ Hz, $J = 7.6$ Hz, CHH̲–CH(O–Ph)). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 174.6 (CO), 129.8, 122.3, 115.9, 110.7 (CPh), 78.6 (CH–O), 72.9 (Ph–O–CH), 63.8 (HO–CH_2), 31.7 (CH_2). HMRS calc. for $C_{11}H_{12}O_3$, 208.0736. Found, 208.0734.

4.55. 5-Hydroxymethyl-3-methyl-3-phenoxy-dihydro-furan-2-one

4.55.1. α Diastereoisomer

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.29 (t, 2H, $J = 7.6$ Hz, Ph *meta*), 7.11 (t, 1H, $J = 7.6$ Hz, Ph *para*), 7.02 (d, 2H, $J = 7.6$ Hz, Ph *ortho*), 4.67 (m, 1H, CH–O), 3.92 (dd, 1H, $J = 12.7$ Hz, $J = 5.6$ Hz, HO–C̲HH), 3.60 (dd, 1H, $J = 12.7$ Hz, $J = 4.6$ Hz, HO–CHH̲), 2.60 (dd, 1H, $J = 13.7$ Hz, $J = 6.1$ Hz, CHH̲–C–Me), 2.23 (dd, 1H, $J = 13.7$ Hz, $J = 9.2$ Hz, C̲HH–C–Me), 1.57 (d, 3H, $J = 2.6$ Hz, Me). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 175.8 (CO), 154.3, 129.5, 124.4, 122.0 (CPh), 81.5 (Ph–O–C), 78.4 (CH–O), 62.7 (HO–CH_2), 36.7 (C̲H$_2$–C–Me), 21.0 (Me). HMRS calc. for $C_{12}H_{14}O_3$, 222.0970. Found, 222.0967.

4.55.2. β Diastereoisomer

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.29 (t, 2H, $J = 7.6$ Hz, Ph *meta*), 7.11 (t, 1H, $J = 7.6$ Hz, Ph *para*), 7.02 (d, 2H, $J = 7.6$ Hz, Ph *ortho*), 4.67 (m, 1H, CH–O), 3.92 (dd, 1H, $J = 12.7$ Hz, $J = 5.6$ Hz, HO–C̲HH), 3.60 (dd, 1H, $J = 12.7$ Hz, $J = 4.6$ Hz, HO–CHH̲), 2.60 (dd, 1H, $J = 13.7$ Hz, $J = 6.1$Hz, CHH̲–C–Me), 2.23 (dd, 1H, $J = 13.7$ Hz, $J = 9.2$Hz, C̲HH–C–Me), 1.62 (d, 3H, $J = 4.6$ Hz, Me). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 176.6 (CO), 154.2, 129.6, 123.7, 121.0 (CPh), 80.4 (Ph–O–C), 77.6 (CH–O), 63.3 (HO–CH_2), 34.9 (C̲H$_2$–C–Me), 22.8 (Me). HMRS calc. for $C_{12}H_{14}O_3$, 222.0970. Found, 222.0967.

4.56. 5-(Hydroxy-propyl-methyl)-3,3-diphenyl-dihydrofuran-2-one

4.56.1. α and β Diastereoisomers (1/1)

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.31–7.25 (m, 5H, Ph), 4.53 (m, CH–O), 4.42 (m, CH–O), 4.16 (m, Ph–C̲H–), 3.99 (m, C̲H–OH), 3.88 (m, Ph–C̲H and C̲H–OH), 2.78 (ddd, $J = 13.2$ Hz, $J = 10.1$ Hz, $J = 4.5$ Hz, CHH̲–C(Ph)), 2.54–2.48 (m, C̲HH̲–C(Ph), 2.30 (dt, $J = 12.7$ Hz, $J = 8.1$ Hz, C̲HH–C(Ph)), 1.59–1.33 (m, CH_3–C̲H$_2$–C̲H$_2$–), 0.97–0.92 (m, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 178.6, 177.7 (CO), 138.0, 136.9, 129.1–127.6 (CPh), 81.5, 81.0 (C–OH), 71.5, 70.1 (CH_2–C̲H–O), 47.0, 46.3 (Ph–C̲H), 34.5, 33.9 (CH_3–CH_2–C̲H$_2$), 30.8, 30.7 (CH_3–C̲H$_2$–CH_2),19.0 (C̲H$_2$–C(Ph)), 14.1 (C̲H$_3$–CH_2–CH_2). Anal. Calc. for $C_{14}H_{18}O_3$: C, 71.79; H, 7.69. Found: C, 71.32; H, 7.89.

4.57. 5-(Hydroxy-propyl-methyl)-3,3-diphenyl-dihydrofuran-2-one (m.p. 106°C)

^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.14–7.11 (m, 10H, Ph), 4.16 (dt, 1H, $J = 11.6$ Hz, $J = 4.5$ Hz, C̲H–OH), 3.88 (m, 1H, CH–O), 2.96 (dd, 1H, $J = 12.7$ Hz, $J = 10.7$ Hz, CHH̲–C(Ph)$_2$), 2.74 (dd, 1H, $J = 12.7$ Hz, $J = 5.1$ Hz, C̲HH–C(Ph)$_2$), 1.49–1.21 (m, 4H, CH_3–C̲H$_2$–C̲H$_2$), 0.82 (t, 3H, $J = 6.6$ Hz, CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 177.8 (CO), 142.4, 140,2, 129.4–127.8 (CPh), 79.9 (CH–OH), 70.4 (Ph$_2$–CH_2–C̲H), 58.5 (Ph$_2$–C̲), 37.1 (CH_3–CH_2–C̲H$_2$–), 34.4 (CH_3–C̲H$_2$–CH_2–),1 9.3 (C̲H$_2$–C(Ph$_2$)), 14.4 (C̲H$_3$–CH_2–CH_2). Anal. Calc. for $C_{20}H_{22}O_3$: C, 77.92; H, 6.49. Found: C, 77.33; H, 6.86%.

4.58. Typical experimental procedure for palladium oxidation

To the unsaturated acid (500 mg) in DMF (10 ml) was added 25 mg of $PdCl_2(PPh_3)_2$ and 25 mg of $Cu(OAc)_2$. This mixture was heated at 90°C under oxygen. After 24 h the solution was cooled, 30 ml of Et_2O was added and the DMF eliminated by treatment with hydrochloric acid (2 N). The organic phase was dried ($MgSO_4$) and the products purified by column chromatography.

4.59. 5-Methylene-3,3-diphenyl-dihydrofuran-2-one [50]

^{1}H-NMR (200 MHz, $CDCl_3$) δ: 7.28–7.42 (m, 10H, Ph), 4.81 (s, 1H, CHH̲=C), 4.45 (s, 1H, C̲HH=C), 3.56 (s, 2H, C̲H$_2$). ^{13}C-NMR (50 MHz, $CDCl_3$) δ: 175.4

(CO), 152.8 (=C–O), 140.9, 132.4–127.5 (CPh), 89.5 (CH_2=), 57.3 ($C(Ph)_2$), 41.8 (–$\underline{C}H_2$–).

4.60. 5-Methylene-3,3-diphenyl-3H-furan-2-one [51]

^{1}H-NMR (200 MHz, $CDCl_3$) δ: 7.28–7.42 (m, 10H, Ph), 5.73 (s, 1H, =C$\underline{H}$), 2.1 (s, 3H, CH_3). ^{13}C-NMR (50 MHz, $CDCl_3$) δ: 177.9 (CO), 151.5 (=C–O), 140.6, 128.8–127.5 (CPh), 109.8 (=CH), 61.7 ($C(Ph)_2$), 14.2 (CH_3).

4.61. 5-Methylene-3,3-dimethyl-dihydrofuran-2-one [49]

^{1}H-NMR (200 MHz, $CDCl_3$) δ: 4.73 (s, 1H, CH$\underline{H}$=), 4.30 (s, 1H, C$\underline{H}$H=), 2.66 (s, 2H, –CH_2–). 1.28 (s, 6H, CH_3). ^{13}C-NMR (50 MHz, $CDCl_3$) δ: 183.0 (CO), 150.2 (=C–O), 89.3 (CH_2=), 44.6 ($C(Me)_2$), 40.8 (–CH_2–), 13.8 (CH_3).

4.62. Mixture of 3-methylene-2-oxa-spiro[4.5]decan-1-one (A) and 3-methyl-2-oxa-spiro[4.5]dec-3-en-1-one (B)

^{1}H-NMR (200 MHz, $CDCl_3$) δ: 5.37 (s, =CH, B), 4.67 (s, CH$\underline{H}$=, A), 4.27 (s, C$\underline{H}$H=, A), 2.70 (s, 2H, CH_2, A), 1.95 (s, CH_3, B), 1.70–1.05 (m, CH_2). ^{13}C-NMR (50 MHz, $CDCl_3$) δ: 179.7 (CO), 153.9, 151.0 (=C–O), 108.5 (CH=), 88.9 (CH_2=), 44.8 ($C(Me)_2$), 37.19 (CH_2–C=), 33.60, 32.22, 25.10, 24.17, 23.56 (CH_2) MS Calc. for $C_{10}H_{15}O_2$, 167.1067. Found, 167.1072.

4.63. 5-Benzylidene-3,3-diphenyl-dihydrofuran-2-one

^{1}H-NMR (200 MHz, $CDCl_3$) δ: 7.7–7.3 (m, 15 H, Ph), 5.66 (s, 1H, =CH), 3.72 (s, 2H, CH_2). ^{13}C-NMR (50 MHz, $CDCl_3$) δ: 175.3 (CO), 145.4–123.5 (=C–O and CPh), 105.2 (CH=), 57.2 (CPh_2), 43.1 (CH_2). HMRS Calc. for $C_{23}H_{18}O_2$, 326.1307. Found, 326.1308.

4.64. 3,3-Dimethyl-5-methylen-4-phenyl-dihydro-furan-2-one

^{1}H-NMR (200 MHz, $CDCl_3$) δ: 7.2 (m, 5H, Ph), 4.95 (s, 1H, =CH_2), 4.37 (s, 1H, =CH_2), 3.97 (s, 1H, CH), 1.93 (s, 3H, CH_3), 0.89 (s, 3H, CH_3). ^{13}C-NMR (50 MHz, $CDCl_3$) δ: 179.3 (CO), 156.8 (=C–O), 135.4–123.5, (CPh), 90.8 (CH_2=), 56.3 (CMe_2), 44.7 (CH), 25.1 (CH_3), 23.8 (CH_3).

4.65. 3,3,5-Trimethyl-4-phenyl-3H-furan-2-one

^{1}H-NMR (200 MHz, $CDCl_3$) δ: 7.2 (m, 5H, Ph), 1.97 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.27 (s, 3H, CH_3).

4.66. 5-Benzyliden-3,3-dimethyl-dihydro-furan-2-one

^{1}H-NMR (200 MHz, $CDCl_3$) δ: 7.5–7.2 (m, 5H, Ph), 5.54 (s, 1H, =CH), 2.84 (s, 2H, CH_2), 1.34 (s, 3H, CH_3). HMRS Calc. for $C_{13}H_{15}O_2$, 203.1072. Found, 203.1068.

4.67. 5-Benzyl–3,3-dimethyl-3H-furan-2-one

^{1}H-NMR (200 MHz, $CDCl_3$) δ: 7.2 (m, 5H, Ph), 5.05 (s, 1H, =CH), 3.59 (s, 2H, CH_2), 1.26 (s, 3H, CH_3). HMRS Calc. for $C_{13}H_{15}O_2$, 203.1072. Found, 203.1068.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos 156558 and 156557. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

6. Uncited references

[50,51]

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