A Concise Diastereoselective Photochemical Synthesis of 3-Hydroxyfuran-2(3*H*)-ones

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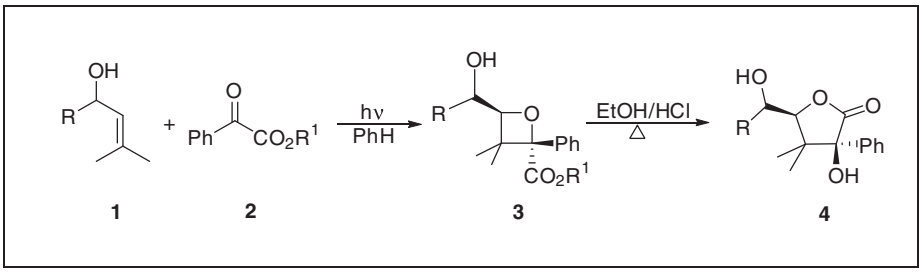

The photocycloaddition of alkyl phenylglyoxylates to allylic alcohols leads to oxetanes **3a–h** with high to moderate (2R*,4R*)-diastereoselectivity that can be easily ring-opened to give 3-hydroxyfuran-2(3H)-ones **4a–b**.

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INTRODUCTION

3-Hydroxyfuran-2(3*H*)-ones are common structural features of many natural and synthetic biologically active compounds and are also versatile synthetic building blocks [1,2]. For example, some (3*S*, 5*R*)-5-alkyl-3-hydroxydihydrofuran-2(3*H*)-ones (I) are excellent food intake-control substances [3]. (3*S*, 5*S*)-3-Hydroxy-5-(hydroxymethyl)dihydrofuran-2(3*H*)-one (II) is a natural hunger substance [4,5]. Racemic (3*R**,5*S**)-3-acetoxy-5-methyldihydrofuran-2(3*H*)-one (III) has been used as a key intermediate in total synthesis of racemic nonactin (Fig. 1) [6]. Moreover, this class of furanones have been used as precursors to 1,3-diols, which are structural fragments frequently found in many natural products [7,8]. Because of the wide range of its utilities, the stereoselective synthesis of this class of compounds has received considerable attention [9–11].

The [2 + 2] photocycloaddition of electronically excited carbonyl substrates to alkenes (*Paternò-Büchi* reaction) is the important synthetic route to oxetanes, which can be subsequently transformed into polyfunctionalized products [12–20]. Concerning the regio- and especially diastereoselectivity of the *Paternò-Büchi* reaction, recent experimental and theoretical work brought a remarkable increase in our understanding of triplet 1,4-biradical behavior [21,22], which also improved the significance of this reaction in synthesis [23].

In continuation of our interest in synthetic application of the *Paternò-Büchi* reaction [24–28], the author reports herein a facial stereoselective synthesis of the title compounds *via* the [2 + 2] photocycloaddition of allylic alcohols **1a–b** with alkyl phenylglyoxylates **2a–d**.

RESULTS AND DISCUSSION

To study the versatility of photocycloaddition reaction of allylic alcohols to α-ketoesters as a synthetic approach to 3-hydroxyfuran-2(3*H*)-ones, the *Paternò-Büchi* reaction of allylic alcohols with alkyl phenylglyoxylates was investigated. The substituents R^1 at alkyl phenylglyoxylate were varied to evaluate the influence of steric bulk and possible electronic effects.

Photolysis of prenol **1a** with alkyl phenylglyoxylates **2a–d** in benzene at 350 nm furnished the oxetanes (±)-**3a–d** with high regio- and moderate (*2R*, 4R**)- diastereoselectivity. The (*2R*,4R**)/(*2R*,4S**)-diastereomeric ratios of the photoadducts were slightly decreased by increasing steric demand of the alkyl phenylglyoxylate substrates (Table 1). When the α-ketoesters, which gave moderate simple diastereoselectivities with prenol, were irradiated with (±)-4-methyl-pent-3-en-2-ol (**1b**), only one (*2R*, 4R**)-diastereomers **3e–h** were obtained in high simple and induced diastereoselectivities (>95/5) from the ^{1}H NMR analysis of the crude reaction mixture (Scheme 1). This result agrees well with the results published by Adam and coworker in the photocycloaddition of triplet excited benzophenone with chiral allylic alcohols [29,30].

The structures of oxetane **3a–d** were assigned on the basis of the spectroscopic analyses (^{1}H NMR and ^{13}C NMR) and mass spectra. In the ^{1}H NMR spectra, the hydrogen on the carbon α- to oxygen of an oxetane ring has a chemical shift of 4.10–4.52 ppm which is in good agreement with the data reported by Arnold [31]. The ^{13}C NMR spectra revealed two significant signals at about 88 and 92 ppm assigned to C-2 and C-4. The mass spectra of compounds **3a–d** also support the

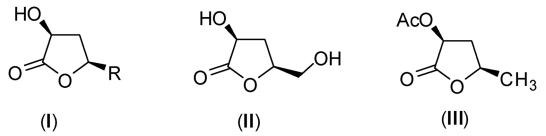


Figure 1. Some important structures of 3-hydroxyfuran-2(3*H*)-ones.

oxetane structure. The molecular ion peaks are not observed (usual situation for oxetane) [32] and the most important fragmentation is cleavage to prenol and a charged carbonyl fragment, the latter then undergoing further decomposition.

The relative configuration of the major diastereoisomer (*2R*, 4R**) was elucidated exemplarily for the (*2R*, 4R**)-oxetane **3h** from the NOE measurements which were detected for one of the geminal methyl groups at oxetane ring by saturation of both the α-hydrogen of the 1-hydroxyethyl group and two phenyl protons at C-4 and C-2. NOE enhancements were also detected for the terminal methyl of 1-hydroxyethyl group and the second geminal methyl group at C-4 and C-3 by saturation of the oxetane 4-H. The pseudoaxial methyl group at C-3 (δ = 0.81 ppm) is shifted upfield by about 0.5 ppm with respect to the other methyl (δ = 1.38 ppm) (Fig. 2). The relative configurations of the remaining oxetanes were assigned by comparison of the ^{1}H NMR data with those of the (*2R*,4R**)-oxetane **3h**.

Hydrolysis of oxetanes **3a-h** in refluxing ethanol containing 1N HCl afforded the 3-hydroxyfuran-2(3*H*)-ones **4a–b** in 75% yield (Scheme 2). Their structures were established on the basis of the spectroscopic data. The IR spectra showed strong absorption bands around 1775 cm^{-1} attributed to the C=O group of γ-lactone. The ^{1}H NMR spectrum of **4a** showed three doublets of doublets at 3.59, 3.80, and 4.46 ppm due to the presence of ($HOCH_2CH$-O) group. In the ^{13}C NMR spectrum, the characteristic signals for the tetrahydrofuranone ring resonate at 34.4, 69.6, 80.4, and 172.8 ppm for C-4, C-5, C-3, and C-2. The relative configuration of compounds **4a–b** was assigned by comparison NMR data with similar compounds in the literature [2]. Furthermore, the author believed that the acid-catalyzed transformation of oxetanes to 3-hydroxyfuran-2(3*H*)-ones **4a-b** proceeded with retention of configuration as evidenced by the neighboring hydroxyl group participation.

The formation of the novel 3-hydroxyfuran-2(3*H*)-ones **4a–b** from oxetanes **3a–h** may be explained mechanistically by protonation of the oxetane O-atom [33] in **3** followed by cleavage of the oxetane ring using anchimeric assistance of the hydroxyl group to form the oxirium intermediate. Then, the ester carbonyl oxygen attacks the three-membered ring, generating a stabilized carbenium/oxonium intermediate which in turn readily undergoes hydrolytic displacement of the alkyl group. The formation of 3-hydroxyfuran-2(3*H*)-ones **4a–b** is also in the line with the published results by Oppenlaender (Scheme 3) [10]. The extraordinary chemical stability of **4** toward acids or bases may be explained in terms of the Bürgi-Dunitz model [34] describing the angular trajectory of the nucleophilic attack to the sp^2-center of a carbonyl group. In **4**, the non-perpendicular attack of a nucleophile is sterically strongly hindered by the methyl groups.

The regioselectivity of the *Paternò-Büchi* reaction of α-ketoesters with prenol as well as 4-methylpent-3-en-2-ol is high and corresponds to the classical 1,4-biradical stablization concept. Indeed, it is known that the irradiation of alkyl phenylglyoxylate results in an efficient conversion to the corresponding nπ* triplet states (T_1) *via* a fast intersystem crossing (ISC) step ($k = 9.4 \times 10^9\ M^{-1}\ S^{-1}$) and the O—C bond formation has been shown to

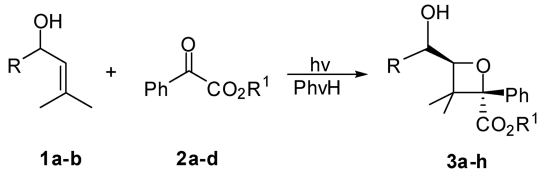
Table 1

Photocycloaddition of allylic alcohols **1a–b** to alkyl phenylglyoxylates **2a-d**.

Entry	R	R[1]	Product	(*2R**, *4R**)/(*2R**, *4S**) d.r.[a]	Yield (%)[b]
1	H	Me	**3a**	79/21	62
2	H	Et	**3b**	77/23	58
3	H	i-Pr	**3c**	71/29	55
4	H	t-Bu	**3d**	67/33	67
5	Me	Me	**3e**	>95/5	64
6	Me	Et	**3f**	>95/5	57
7	Me	i-Pr	**3g**	>95/5	48
8	Me	t-Bu	**3h**	>95/5	65

[a]Diastereomeric ratio (*2R**, *4R**)/(*2R**, *4S**) **3a-h** as determined from ^{1}H-NMR analysis of the crude product mixture.
[b]Yield of the isolated oxetane product.

Scheme 1. Paternò-Büchi reaction of allylic alcohols **1a–b** with alkyl phenylglyoxylates **2a–d**.



be the first step in the *Paternò-Büchi* reaction of electron rich alkenes leading to a triplet 1,4-biradical intermediate [35]. The stereochemistry of the triplet 1,4-biradical is attributed to a conformational memory effect during the ISC process of the triplet 1,4-biradical. According to *Salem-Rowland* rules [36], strong spin-orbit coupling (SOC) occurs when the p-orbitals at the spin-bearing atoms are orthogonal to each other. Two possible conformations of the triplet 1,4-biradical (A and B) can fulfill the *Salem-Rowland* requirement and are able to undergo ISC to singlet states (Fig. 3). Conformers A and B can dissociate to the starting materials or cyclize forming oxetanes. Conformer B is less stable due to steric repulsion between the bulky phenyl group and methyl group and is thus depopulated. ISC from **A** leads to immediate C—C bond formation, and gives the (*2R*,4R**)-diastereomer. When the size of the alkoxy substituent in alkyl phenylglyoxylate is increased (e.g., R^1 = *i*-pr, *t*-Bu), the steric interaction between CO_2R^1 and methyl group disfavor conformer A, and hence the amount of (*2R*,4R**)-oxetane is expected to be decreased. An additional internal hydrogen bond between the primary hydroxyl group and the oxygen atom at position 2 of the triplet 1,4-biradical slightly increases this conformational preference.

In light of the mechanistic picture shown in Figure 3, an increase in bulk of hydroxyalkyl side chain is expected to lead to an increase in simple diastereoselectivity due to increasing steric interactions in one half-space of the ISC-reactive conformer. When allylic 1,3-strain ($A^{1,3}$) between the methyl substituted and the *cis*-methyl group operate as substrate **1b**, an additional diasteroselectivity increase is observed which is connected with hydrogen-bonding interaction with the carbonyl triplet excited state prior to bond formation [37,38] (Fig. 4).

In conclusion, we have shown that the photocycloaddition reaction of allylic alcohols to α-ketoesters serves as an excellent route to the regio- and diastereoselective preparation of 3-hydroxyfuran-2(3*H*)-ones.

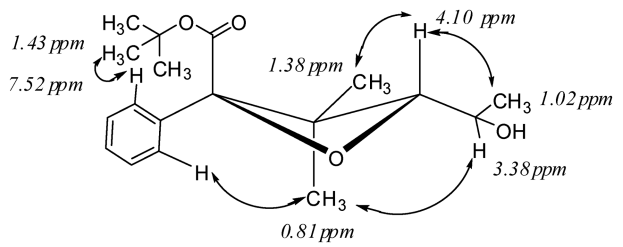


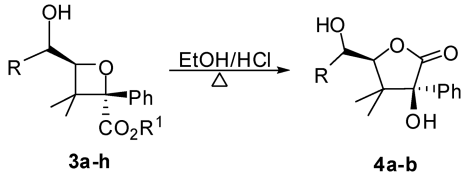
Figure 2. Determination of the configuration of oxetane **3h** by NOE-experiment.

EXPERIMENTAL

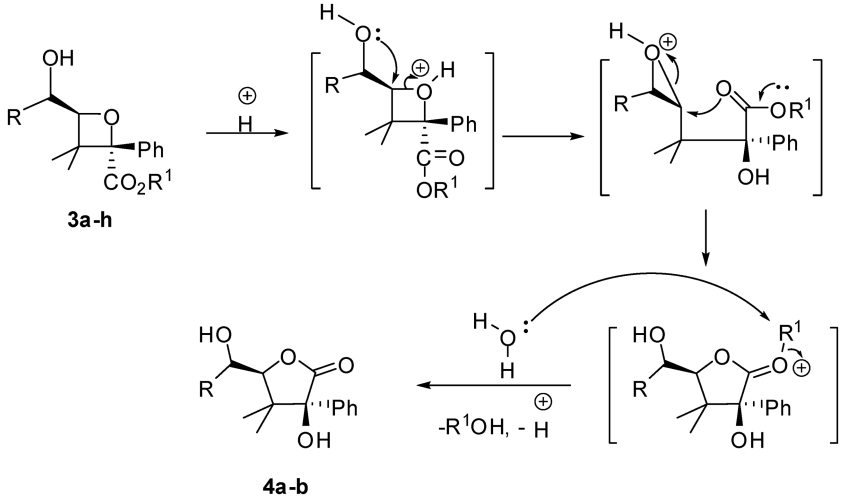
All reactions were carried out in oven-dried glassware (100°C). All solvents were dried before use. Prenol, methyl phenylglyoxylate and ethyl phenylglyoxylate were purchased from Aldrich and were distilled before use. 4-Methyl-pent-3-en-2-ol [39], isopropyl phenylglyoxylate [40] and *tert*-butyl phenylglyoxylate [41] were prepared according to reported methods. Mixtures of ethyl acetate and *n*-hexane were used as eluents. TLC: Commercially precoated polygram© SIL- G/UV 254 plates (Macherey-Nagel). Spots were detected with UV light in an I_2 chamber. IR spectra were recorded on a Mattson 5000 FTIR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AC spectrometer (300 MHz for ^{1}H NMR and 75.5 MHz for ^{13}C NMR), using TMS as an internal standard, and chemical shifts are expressed as δ_{ppm}. Mass spectra were measured on a GCMS-QP1000 EX spectrometer at 70 eV. Preparative thin layer chromatography: Silica gel (2–25 μm) on TLC plates (Fluka); layer thickness 0.25 mm; medium pour diameter 60 Å; 20 × 20 cm on glass plates. Elemental analyses were performed with a Perkin-Elmer elemental analyzer 240-c. A Rayonet® chamber photoreactors equipped with phosphor-coated mercury low-pressure lamps (λ = 350 ± 10 nm) was used for irradiation.

General procedure for photolyses of allylic alcohols with α-ketoesters. In a quartz tube, a mixture of allylic alcohol **1** (0.005 mole) and α-ketoesters **2** (0.005 mole) was dissolved in 50-mL benzene and degassed with a steady stream of N_2. The reaction mixture was irradiated at 10°C in a Rayonet photoreactor (350 nm) for 24 h. The solvent was evaporated under vacuum, and the residue was analyzed by ^{1}H NMR

Scheme 2. Acid catalysed conversion of oxetanes **3a–h** to 3-hydroxyfuran-2(3*H*)-ones **4a-b**.



Scheme 3. Proposed mechanism for the conversion of oxetanes **3a–h** to 3-hydroxyfuran-2(3*H*)-ones **4a–b**.



spectroscopy to determine the simple diastereoselectivity. Purification was carried out by preparative thick layer chromatography using silica gel which was firstly neturalized by elution with 1% TEA/CH_2Cl_2.

(2R*,4R*)-Methyl 4-(hydroxymethyl)-3,3-dimethyl-2-phenyloxetane-2-carboxylate (3a). A solution of 0.82 g (0.005 mole) of methyl phenylglyoxylate and 0.43 g (0.005 mole) of prenol **1a** in 50-mL benzene was irradiated for 24 h according to the above general procedure. The crude product was purified by preparative chromatography to give 0.8 g (62%) **3a** as colorless oil. R_f = 0.43 (*H*:*EA* = 4:1); ir (film): 3450 (OH), 2993, 2986 (C—H sp^3), 1725 (C=O), 1050 (C—O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.81 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.99 (bs, 1H, OH), 3.60 (dd, *J* = 11.9, 5.4 Hz, 1H, CHOH), 3.66 (s, 3H, OCH_3), 3.76 (dd, *J* = 11.9, 6.8 Hz, 1H, CHOH), 4.52 (dd, *J* = 6.8, 5.4 Hz, 1H, H-4), 7.12–7.61 (m, 5H, Ar-H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 18.9 (CH_3), 25.7 (CH_3), 45.0 (C-3), 52.9 (OCH_3), 62.2 (OCH_2), 86.4 (C-2), 90.3 (C-4), 125.4 ($2CH_{Ar}$), 127.4 ($2CH_{Ar}$), 128.1 (CH_{Ar}), 137.7 (Cq_{Ar}), 172.1 (CO) ppm; ms (70 eV): *m/z* 164 (M^+-$C_5H_{10}O$), 149, 133, 105, 86, 77, 57. Anal. Calcd. for $C_{14}H_{18}O_4$ (250.29): C 67.18; H 7.25%, Found: C 67.23; H 7.36%.

(2R*,4R*)-Ethyl 4-(hydroxymethyl)-3,3-dimethyl-2-phenyloxetane-2-carboxylate (3b). A solution of 0.89 g (0.005 mole) of ethyl phenylglyoxylate and 0.43 g (0.005 mole) of prenol **1a** in 50-mL benzene was irradiated for 24 h according to the above general procedure. The crude product was purified by preparative chromatography to give 0.7 g (58%) **3b** as colorless oil. R_f = 0.43 (*H*:*EA* = 4:1); ir (film): 3455 (OH), 2990, 2986 (C—H sp^3), 1718 (C=O), 1080 (C—O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.88 (s, 3H, CH_3), 1.26 (t, *J* = 7.5 Hz, 3H, CH_3), 1.37 (s, 3H, CH_3), 2.05 (bs, 1H, OH), 3.62 (dd, *J* = 11.9, 5.3 Hz, 1H, CHOH), 3.78 (dd, *J* = 11.9, 6.8 Hz, 1H, CHOH), 4.25 (q, *J* = 7.5 Hz, 2H, OCH_2), 4.55 (dd, *J* = 6.8, 5.3 Hz, 1H, H-4), 7.16–7.63 (m, 5H, Ar-H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 13.6 (CH_3), 17.6 (CH_3), 25.4 (CH_3), 45.0 (C-3), 62.3 (t, OCH_2), 63.1 (OCH_2), 86.5 (C-2), 90.3 (C-4), 125.3 ($2CH_{Ar}$), 127.0 ($2CH_{Ar}$), 128.6 (CH_{Ar}), 137.9 (Cq_{Ar}), 171.6 (CO) ppm. Anal.

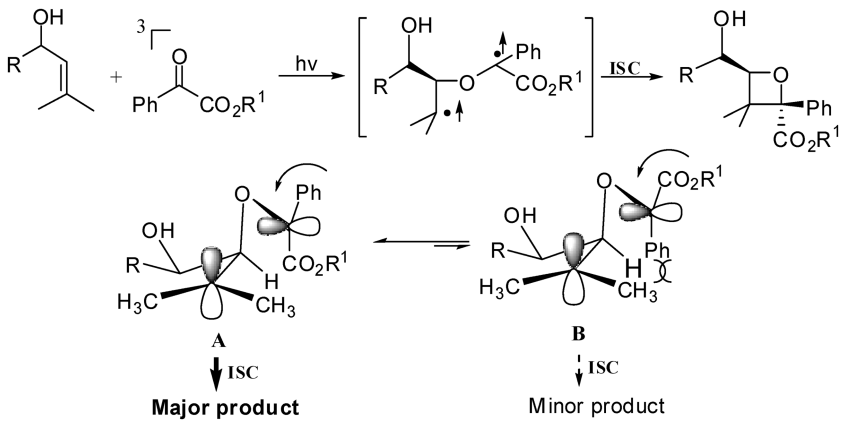


Figure 3. Mechanistic scenario for the photocycloaddition reaction of allylic alcohols to α-ketoesters.

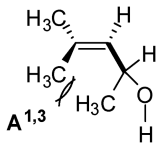


Figure 4. 1,3-Allylic strain in 4-methylpent-3-en-2-ol (**1b**).

Calcd. for $C_{15}H_{20}O_4$ (264.32): C 68.16; H 7.63%, Found: C 68.26; H 7.74%.

(2R*,4R*)-Isopropyl 4-(hydroxymethyl)-3,3-dimethyl-2-phenyloxetane-2-carboxylate (3c). A solution of 0.96 g (0.005 mole) of isopropyl phenylglyoxylate and 0.43 g (0.005 mole) of prenol **1a** in 50-mL benzene was irradiated for 24 h according to the above general procedure. The crude product was purified by preparative chromatography to give 0.7 g (55%) **3c** as colorless oil. R_f = 0.43 (*H*:*EA* = 4:1); ir (film): 3455 (OH), 2990, 2986 (C—H sp^3), 1722 (C=O), 1089 (C—O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85 (s, 3H, CH_3), 1.26 (d, *J* = 6.3 Hz, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.98 (bs, 1H, OH), 3.60 (dd, *J* = 12.0, 4.7 Hz, 1H, CHOH), 3.76 (dd, *J* = 12.0, 6.9 Hz, 1H, CHOH), 4.53 (dd, *J* = 6.9, 4.7 Hz, 1H, H-4), 5.53 (septet, *J* = 6.3 Hz, 1H, OCH), 7.32–7.56 (m, 5H, Ar-H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 19.5 (CH_3), 21.7 (CH_3), 21.9 (CH_3), 26.3 (CH_3), 45.2 (C-3), 62.9 (OCH_2), 69.3 (OCH), 86.6 (C-2), 90.4 (C-4), 125.8 ($2CH_{Ar}$), 127.7 ($2CH_{Ar}$), 128.1 (CH_{Ar}), 138.3 (Cq_{Ar}), 171.2 (CO) ppm. Anal. Calcd. for $C_{16}H_{22}O_4$ (278.34): C 69.04; H 7.97%, Found: C 69.17; H 7.86%.

(2R*,4R*)-*tert*-Butyl-4-(hydroxymethyl)-3,3-dimethyl-2-phenyloxetane-2-carboxylate (3d). A solution of 1.03 g (0.005 mole) of *tert*-butyl phenylglyoxylate and 0.43 g (0.005 mole) of prenol **1a** in 50-mL benzene was irradiated for 24 h according to the above general procedure. The crude product was purified by preparative chromatography to give 1.0 g (67%) **3d** as colorless oil. R_f = 0.43 (*H*:*EA* = 4:1); ir (film): 3465 (OH), 2990, 2986 (C—H sp^3), 1715 (C=O), 1095 (C—O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.83 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 1.44 (s, 9H, $3CH_3$), 1.95 (bs, 1H, OH), 3.60 (dd, *J* = 12.0, 4.7 Hz, 1H, CHOH), 3.72 (dd, *J* = 12.0, 6.9 Hz, 1H, CHOH), 4.52 (dd, *J* = 6.9, 4.7 Hz, 1H, H-4), 7.30–7.51 (m, 5H, Ar-H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 19.5 (CH_3), 26.3 (CH_3), 28.0 ($3CH_3$), 45.0 (C-3), 62.9 (OCH_2), 82.5 (C_q), 86.4 (C-2), 90.4 (C-4), 125.8 ($2CH_{Ar}$), 127.5 ($2CH_{Ar}$), 127.6 (CH_{Ar}), 138.6 (Cq_{Ar}), 170.6 (CO) ppm; ms (70 eV): *m*/*z* 206 (M^+-$C_5H_{10}O$), 150, 133, 105, 86, 77, 57. Anal. Calcd. for $C_{17}H_{24}O_4$ (292.37): C 69.84; H 8.27%, Found: C 69.88; H 8.35%.

(2R*,4R*)-Methyl 4-((R,S)-1-hydroxyethyl)-3,3-dimethyl-2-phenyloxetane-2-carboxylate (3e). A solution of 0.82 g (0.005 mole) of methyl phenylglyoxylate and 0.5 g (0.005 mole) of 4-methylpent-3-en-2-ol **1b** (0.5 g, 5 mmol) in 50-mL benzene was irradiated for 24 h according to the above general procedure. The crude product was purified by preparative chromatography to give 0.8 g (64%) **3e** as colorless oil. R_f = 0.62 (*H*:*EA* = 4:1); ir (film): 3455 (OH), 2994, 2984 (C—H sp^3), 1716 (C=O), 1095 (C—O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86 (s, 3H, CH_3), 1.06 (d, *J* = 6.3 Hz, 3H, CH_3), 1.37 (s, 3H, CH_3), 2.51 (bs, 1H, OH), 3.82 (dq, *J* = 8.8, 6.3 Hz, 1H, CHOH), 3.91 (s, 3H, OCH_3), 4.15 (d, *J* = 8.8 Hz, 1H, H-4), 7.24–7.52 (m, 5H, Ar-H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 17.4 (CH_3), 19.5 (CH_3), 26.6 (CH_3), 44.8 (C-3), 52.5 (OCH_3), 67.9 (CHOH), 89.5 (C-2), 90.6 (C-4), 125.9 ($2CH_{Ar}$), 127.4 (CH_{Ar}), 127.9 ($2CH_{Ar}$), 137.8 (Cq_{Ar}), 171.6 (CO) ppm. Anal. Calcd. for $C_{15}H_{20}O_4$ (264.32): C 68.16; H 7.63%, Found: C 68.24; H 7.74%.

(2R*,4R*)-Ethyl 4-((R,S)-1-hydroxyethyl)-3,3-dimethyl-2-phenyloxetane-2-carboxylate (3f). A solution of 0.89 g (0.005 mole) of ethyl phenylglyoxylate and 0.5 g (0.005 mole) of 4-methylpent-3-en-2-ol **1b** in 50-mL benzene was irradiated for 24 h according to the above general procedure. The crude product was purified by preparative chromatography to give 0.8 g (57%) **3f** as colorless oil. R_f = 0.43 (*H*:*EA* = 4:1); ir (film): 3435 (OH), 2993, 2989 (C—H sp^3), 1720 (C=O), 1092 (C—O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.83 (s, 3H, CH_3), 1.29 (t, *J* = 7.2 Hz, 3H, CH_3), 1.04 (d, *J* = 6.3 Hz, 3H, CH_3), 1.35 (s, 3H, CH_3), 2.50 (bs, 1H, OH), 3.84 (dq, *J* = 8.8, 6.3 Hz, 1H, CHOH), 4.13 (*d*, *J* = 8.8 Hz, 1H, H-4), 4.25 (q, *J* = 7.2 Hz, 2H, OCH_2), 7.31–7.62 (m, 5H, Ar-H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 14.2 (CH_3), 17.9 (CH_3), 19.8 (CH_3), 26.4 (CH_3), 44.9 (C-3), 61.5 (OCH_2), 67.5 (CHOH), 89.4 (C-2), 90.2 (C-4), 125.7 ($2CH_{Ar}$), 127.7 (CH_{Ar}), 127.8 ($2CH_{Ar}$), 137.9 (Cq_{Ar}), 171.7 (CO) ppm. Anal. for $C_{16}H_{22}O_4$ (278.34): Calcd: C 69.04; H 7.97%, Found: C 69.21; H 8.06%.

(2R*,4R*)-Isopropyl 4-((R,S)-1-hydroxyethyl)-3,3-dimethyl-2-phenyl-oxetane-2-carboxylate (3g). A solution of 0.96 g (0.005 mole) of isopropyl phenylglyoxylate and 0.5 g (0.005 mole) of 4-methylpent-3-en-2-ol **1b** in 50-mL benzene was irradiated for 24 h according to the above general procedure. The crude product was purified by preparative chromatography to give 0.7 g (48%) **3g** as colorless oil. R_f = 0.56 (*H*:*EA* = 4:1); ir (film): 3445 (OH), 2997, 2986 (C—H sp^3), 1719 (C=O), 1095 (C—O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85 (s, 3H, CH_3), 1.23 (d, *J* = 6.3 Hz, 3H, CH_3), 1.26 (d, *J* = 6.3 Hz, 3H, CH_3), 1.29 (t, *J* = 6.5 Hz, 3H, CH_3), 1.39 (s, 3H, CH_3), 2.52 (bs, 1H, OH), 3.85 (dq, *J* = 8.8, 6.5 Hz, 1H, CHOH), 4.15 (*d*, *J* = 8.8 Hz, 1H, H-4), 5.11 (septet, *J* = 6.3 Hz, 1H, OCH), 7.33–7.71 (m, 5H, Ar-H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 18.5 (CH_3), 19.5 (CH_3), 21.9 (CH_3), 22.1 (CH_3), 26.5 (CH_3), 45.4 (C-3), 61.9 (CHOH), 69.2 (OCH), 86.2 (C-2), 90.2 (C-4), 126.2 ($2CH_{Ar}$), 127.3 (CH_{Ar}), 128.5 ($2CH_{Ar}$), 138.3 (Cq_{Ar}), 172.1 (CO) ppm. Anal. Calcd. for $C_{17}H_{24}O_4$ (292.37): C 69.84; H 8.27%, Found: C 69.95; H 8.36%.

(2R*,4R*)-*tert*-Butyl 4-((R,S)-1-hydroxyethyl)-3,3-dimethyl-2-phenyl-oxetane-2-carboxylate (3h). A solution of 1.03 g (0.005 mole) of *tert*-butyl phenylglyoxylate and 0.5 g (0.005 mole) of 4-methylpent-3-en-2-ol **1b** in 50-mL benzene was irradiated for 24 h according to the above general procedure. The crude product was purified by preparative chromatography to give 1.0 g (65%) **3h** as colorless oil. R_f = 0.52 (*H*:*EA* = 4:1); ir (film): 3455 (OH), 2993, 2982 (C—H sp^3), 1718 (C=O), 1098 (C—O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.81 (s, 3H, CH_3), 1.02 (d, *J* = 6.2 Hz, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.45 (s, 9H, $3CH_3$), 2.47 (bs, 1H, OH), 3.80 (dq, *J* = 8.8, 6.2 Hz, 1H, CHOH), 4.10 (*d*, *J* = 8.8 Hz, 1H, H-4), 7.23–7.45 (m, 5H, Ar-H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 17.9 (CH_3), 19.9 (CH_3), 26.4 (CH_3), 28.0 ($3CH_3$), 44.6 (C-3), 67.4 (OCH), 82.5 (C_q), 89.9 (C-2), 90.6 (C-4), 125.8 ($2CH_{Ar}$), 127.4 (CH_{Ar}), 127.6 ($2CH_{Ar}$), 138.3 (Cq_{Ar}), 170.5 (CO) ppm. Anal. Calcd. for $C_{18}H_{26}O_4$ (306.4): C 70.56; H 8.55%, Found: C 70.67; H 8.64%.

General procedure for the synthesis of 3-hydroxyfuran-2(3*H*)-ones (4a-b). A solution of 1.18 g (0.005 mole) of oxetane **3a** in a mixture of 50-mL 1N HCl/EtOH (1:1) was refluxed for 24 h. After cooling to room temperature, the mixture was extracted with Et_2O (4 × 50 mL), the organic phase washed with saturated aqueous $NaHCO_3$ solution and H_2O, dried (Na_2SO_4) and evaporated under *vacuo*, pale yellow oil obtained, was subjected to column chromatography using a mixture of ethyl acetate and *n*-hexane (1:3) as eluent to give compounds **4a-b**.

(3R*,5R*)-Dihydro-3-hydroxy-5-(hydroxylmethyl)-4,4-dimethyl-3-phenylfuran-2(3*H*)-one (4a). Colorless oil; 0.8 g (72%); ir (film): 3372 (OH), 2947, 2835 (C—H sp^3), 1775 (C=O), 1165 (C—O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.92 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 2.27 (s, 1H, OH), 3.59 (dd, *J* = 12.75, 5.04 Hz, 1H, CHOH), 3.82 (dd, *J* = 12.75, 3.2 Hz, 1H, CHOH), 4.53 (dd, *J* = 5.04, 3.2 Hz, 1H, H-5), 7.25–7.62 (m, 5H, Ar-H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 19.2 (CH_3), 21.6 (CH_3), 33.6 (C-4), 63.8 (CH_2OH), 69.3 (C-5), 78.6 (C-3), 121.3 (CH_{Ar}), 125.6 ($2CH_{Ar}$), 129.4 ($2CH_{Ar}$), 134.5 (C_{Ar}), 172.4 (C-2) ppm; ms (70 eV): *m/z* 236 (M^+), 219, 192, 176, 149, 105, 87, 77. Anal. Calcd. for $C_{13}H_{16}O_4$ (236.26): C 66.09; H 6.83%, Found: C 66.14; H 6.95%.

(3R*,5R*)-Dihydro-3-hydroxy-5-((R,S)-1-hydroxyethyl)-4,4-dimethyl-3-phenylfuran-2(3*H*)-one (4b). Colorless oil; 0.9 g (75%); ir (film): 3379 (OH), 2966, 2889 (C—H sp^3), 1782 (C=O), 1155 (C—O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 0.86 (s, 3H, CH_3), 1.12 (t, *J* = 7.5 Hz, 3H, CH_3), 1.32 (s, 3H, CH_3), 2.45 (s, 1H, OH), 3.62 (m, 1H, CH), 4.52 (d, *J* = 6.2 Hz, 1H, H-5), 7.34–7.56 (m, 5H, Ar-H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 14.6 (CH_3), 19.6 (CH_3), 22.2 (CH_3), 35.2 (C-4), 64.7 (CHOH), 70.8 (C-5), 79.9 (C-3), 121.5 (CH_{Ar}), 126.2 ($2CH_{Ar}$), 129.6 ($2CH_{Ar}$), 134.8 (C_{Ar}), 172.7 (C-2) ppm; ms (70 eV): *m/z* 250 (M^+), 232, 206, 205, 150, 107, 100, 77. Anal. Calcd. for $C_{14}H_{18}O_4$ (250.29): C 67.18; H 7.25%, Found: C 67.29; H 7.34%.

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