



Towards the catalytic formation of α,β -vinylesters and alkoxy substituted γ -lactones

Pradeep Mathur^{a,b,c,*}, Raj Kumar Joshi^a, Badrinath Jha^a, Amrendra K. Singh^a, Shaikh M. Mobin^b

^a Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India

^b National Single Crystal X-ray Diffraction Facility, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India

^c School of Sciences, Indian Institute of Technology Indore, Khandwa Road, Indore 452017, India

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ABSTRACT

A facile, one pot, high yield synthesis of α,β -vinylester (**1–14**) and alkoxy substituted γ -lactones (**15–28**) has been achieved by the photochemical reaction of terminal acetylene (ferrocenyl phenyl trimethylsilyl, hexyl and cyclohexyl) with alcohol (methanol, ethanol and isopropanol) and carbon monoxide in presence of iron pentacarbonyl as a catalyst. The selectivity of the compounds depends on the time of photolysis of the reaction as well as the solvent used. A stable reaction intermediate ferrole was isolated, and further photolysis with alcohols, resulted in the formation of α,β -vinylester. All the compounds were fully characterised by spectroscopic methods and the molecular structures of compounds **1**, **16**, **17** and **20** were established crystallographically.

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1. Introduction

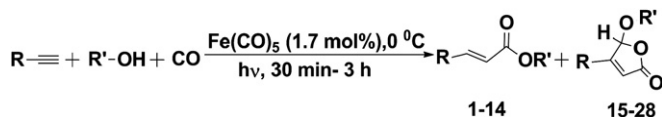
Catalytic synthesis of vinylesters and lactones from oxidative carbonylation of terminal acetylenes is of great significance as these are important building blocks in synthetic chemistry [1]. A wide variety of products resulting from the mono- and dicarbonylation of terminal acetylenes have been obtained from such reactions, using some Pd(II) complexes as catalyst [2,3].

Although several methods exist for the preparation of γ -lactones [4], they suffer from limitation of being multistep or weakly feasible. Also, the reactants need to be selected such that they contain easily cyclisable functionalities. Takashi et al. [5] reported a single step synthesis of γ -lactone, where ethyne undergoes lactonisation under high pressure (100 atm) of CO and $\text{Rh}_6(\text{CO})_{16}$ catalyst; however, the yields are rather modest. Synthesis of α,β -unsaturated esters can be carried out by Heck reaction [6,7], transesterification [8] and a range of other methods [9,10]. However, none of these offer a single step approach towards conversion of terminal acetylene to α,β -unsaturated vinylesters. The lactone ring [furan-2(5H)-one (but-2-en-4-olide)] is an important bioactive component in several medicinal

precursors. Compounds containing these units are highly efficient in antitumor activity, [11,12] intestinal carcinogenesis inhibition [13] antifungal activities, [14] and significantly active against lymphatic leukemia [15] as well as HIV-1 protease inhibition [16]. α,β -Vinylester derivatives of ferrocene are used in the design of organometallic liquid crystals [17], electrochemical redox-receptors, SAM-forming substances, propellants and in asymmetric catalysis [18]. Ferrocenes with open-arms having ene-backbones, and functionalized chromophores [19] are known for their NLO and redox switching properties [20].

In spite of obvious economic advantage, until recently, iron-catalyzed processes were rare in organic synthesis. However, within the last few years, there have been a number of reports on the potential of iron catalysis for reduction, oxidation and coupling reactions [21,22]. Periasamy et al. [23,24] have worked and reported extensively on stoichiometric carbonylation of alkynes. We have been involved in the investigation of reactivity of ferrocenyl substituted terminal and internal acetylenes towards simple metal carbonyl complexes under varying reaction conditions [25]. Very recently, we observed the formation of ferrocenyl substituted esters formed as a result of addition of CO and MeOH to 1,3-diynes supported on carbonyl cluster [26]. In this paper we report the photochemical reaction of different terminal acetylenes (ferrocenyl, phenyl, trimethylsilyl, cyclohexyl, and hexyne) with three different alcohols (methanol, ethanol and isopropanol) and CO in

* Corresponding author. Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India. Tel.: +91 22 25767180; fax: +91 22 25767152.
E-mail address: mathur@iitb.ac.in (P. Mathur).



Scheme 1. Formation of α,β -vinylester and lactones.

presence of catalytic amount (1.7 mol%) of iron pentacarbonyl, which leads to the formation of α,β -vinylester and alkoxy γ -lactone in a single step.

2. Results and discussions

Photolysis of a solution of terminal acetylene (ferrocenyl, phenyl, trimethylsilyl, cyclohexyl, hexyne), alcohols (methanol, ethanol and isopropanol) and CO in presence of $\text{Fe}(\text{CO})_5$ resulted in the formation of ferrocenyl/alkyl/aryl substituted α,β -vinylester (**1–14**), and alkoxy γ -lactone (**15–28**) (Scheme 1). In the reactions of phenylacetylene with alcohols, formation of diphenylquinone was also observed in trace amount. Similar reactions in presence of other metal carbonyls, $\text{M}(\text{CO})_6$ ($\text{M} = \text{Mo}, \text{Cr}, \text{W}$), $\text{Ru}(\text{CO})_5$ and $\text{Ru}_3(\text{CO})_{12}$ did not give these products. Use of visible light in place of UV decreased the yield of esters and lactones. Improved yield of esters and lactones were observed when the photolysis reactions were carried out under continuous bubbling of CO and 1.7 mol% of $\text{Fe}(\text{CO})_5$. In the absence of $\text{Fe}(\text{CO})_5$, and prolonged photolysis of alcoholic solution of terminal acetylene (except ferrocenyl acetylene) with continuous CO bubbling did not yield vinylesters and lactones. In the case of photolysis of ferrocenylacetylene with alcohols in CO presence, some decomposition occurs and liberated Fe^{2+} probably functions as a catalyst, resulting in formation of trace amounts of the vinylester and lactone (less than 10% and 5% respectively). In general, yields of ferrocenyl substituted esters and lactones are better than those of the alkyl/aryl substituted ones. Yields of esters and lactones are susceptible to the type of alcohol as well as duration of UV irradiation (Table 1). The yield of lactones increases and that of ester decreases with increasing reaction time. The yield of esters vary for the alcohols as methanol > ethanol > isopropanol. In case of lactones, a reverse

Table 1
 $\text{Fe}(\text{CO})_5$ catalyzed esterification and lactonization by addition of CO and alcohols to the terminal acetylene.

Run	Acetylene (7.5 mmol)	Solvent	Photolysis (0.5 h) ^{a,b}		Photolysis (3 h) ^{a,b}	
			Ester (Compound no.)	Lactone (Compound no.)	Ester	Lactone
1	FcC≡CH	MeOH	89 (1)	7 (15)	37	60
2	FcC≡CH	EtOH	61 (2)	28 (16)	23	74
3	FcC≡CH	ⁱ PrOH	49 (3)	35 (17)	8	88
4	PhC≡CH	MeOH	57 (4)	9 (18)	34	59
5	PhC≡CH	EtOH	48 (5)	10 (19)	29	63
6	PhC≡CH	ⁱ PrOH	40 (6)	27 (20)	23	71
7	TMSC≡CH	MeOH	54 (7)	12 (21)	26	71
8	TMSC≡CH	EtOH	47 (8)	16 (22)	31	67
9	TMSC≡CH	ⁱ PrOH	44 (9)	32 (23)	17	82
10	C ₄ H ₉ C≡CH	MeOH	58 (10)	12 (24)	29	52
11	C ₄ H ₉ C≡CH	EtOH	44 (11)	19 (25)	21	76
12	C ₄ H ₉ C≡CH	ⁱ PrOH	51 (12)	25 (26)	12	76
13	C ₆ H ₁₁ C≡CH	MeOH	66 (13)	14 (27)	32	60
14	C ₆ H ₁₁ C≡CH	ⁱ PrOH	45 (14)	31 (28)	15	79

Yields are based on the amount of acetylene reacted.

^a In presence of 1.7 mol% of $\text{Fe}(\text{CO})_5$.

^b Continuous CO bubbling. Fc = ferrocenyl, Ph = phenyl, TMS = trimethylsilyl, C₄H₉ = *n*-butyl, C₆H₁₁ = cyclohexyl.

trend is observed (Table 1). These observations can be utilized to improve the yield of a particular type of compound selectively by careful tuning of reaction conditions. For example, the best yield for ester ($\text{FcC}_2\text{H}_2\text{CO}_2\text{CH}_3$, 89%) can be achieved using methanol as solvent and a short duration of photolysis (30 min). Similarly, for lactones, the best yield (88%) is obtained when isopropanol is used as a solvent and photolysis carried out for 3 h.

All compounds were characterized by IR, ¹H and ¹³C NMR spectroscopy, mass spectrometry and elemental analyses. Molecular structures of compounds **1**, **16**, **17** and **20** were confirmed by single crystal X-ray diffraction technique. All esters show the characteristic CO stretching in the range 1633–1754 cm⁻¹. In lactones, the CO stretching varies from 1619–1799 cm⁻¹. ¹H NMR spectra of esters show peaks for vinylic protons at δ 7.40–7.71 and δ 6.45–6.94. The coupling constants of the vinylic protons for compounds **4**, **7**, **8**, **9**, and **10** was observed between $J = 3.1$ –7.8 Hz, indicative of a cis configuration of hydrogen atom around the π -electron cloud, whereas, for the remaining vinylesters, having $J = 13.4$ –16.2 Hz, a trans configuration of H atoms around the olefinic bond is suggested. In lactones the vinylic proton signals were observed in the range δ 5.96–6.34, while the CH(OR') proton signal appears at δ 6.02–6.34. Signals for ferrocenyl, phenyl, cyclohexyl, TMS, and butyl groups protons were observed at their usual positions.

Molecular structure of **1** is shown in Fig. 1. The ferrocenyl group is trans to COOR' group. The C–C bond lengths C(2)–C(3) = 1.465(6) Å, C(3)–C(4) = 1.318(6) Å and C(4)–C(5) = 1.442(6) Å indicate delocalization of electrons over the four carbon atoms and ferrocenyl group. Molecular structure of **16** and **17** (Figs. 2 and 3) consists of a lactone ring with ferrocenyl group at position 3 and alkoxy group at position 4 and 2, respectively, while in compound **20** (Fig. 4), the phenyl group is at position 3 and alkoxy group at position 11. In all lactones, both ferrocenyl/phenyl and OR' groups are on the same side of the lactone ring.

In earlier work [27], we have shown that the photochemical reaction of $\text{Fe}(\text{CO})_5$, ferrocenylacetylene and CO in hexane solvent forms diferrocenyl quinone and the reaction proceeds via the ferrole intermediate, $[\text{Fe}(\text{C}(\text{O})\text{C}(\text{H})\text{C}(\text{Fc})\text{C}(\text{O}))(\text{CO})_4]$. Trace amount of quinone formed in our present reaction of acetylene with alcohol and CO in presence of $\text{Fe}(\text{CO})_5$ suggested that here too perhaps a ferrole intermediate might be involved. Indeed, when we investigated the reaction of ferrole $[\text{Fe}(\text{C}(\text{O})\text{C}(\text{H})\text{C}(\text{Fc})\text{C}(\text{O}))(\text{CO})_4]$ with alcohol, we observed a total transformation to vinylesters in all cases, and therefore, the formation of vinylester can be shown to proceed according to the steps depicted in Scheme 2. It can be argued that ferrole to ester conversion is relatively faster than the quinone formation due to high concentration of alcohol (solvent). The ferrole to quinone conversion becomes significant when the reaction is carried out with visible light irradiation at room temperature. Involvement of a carbene intermediate in the formation of alkoxy lactone has been proposed in literature [28]. We suggest that a carbene intermediate is involved in our reaction also leading to the formation of alkoxy lactones, as depicted in Scheme 3.

3. Conclusion

In conclusion, we have demonstrated a one pot synthesis of α,β -vinylesters and alkoxy substituted lactones using iron pentacarbonyl as catalyst. Our facile method, contrasts with a related use of $\text{Fe}(\text{CO})_5$ or $\text{Fe}_3(\text{CO})_{12}$ as catalyst for the formation of succinimides by reaction of alkynes with ammonia or amines with CO at high temperature and pressure [29], and may find general utility in the synthetic methodology of these important organic compounds.

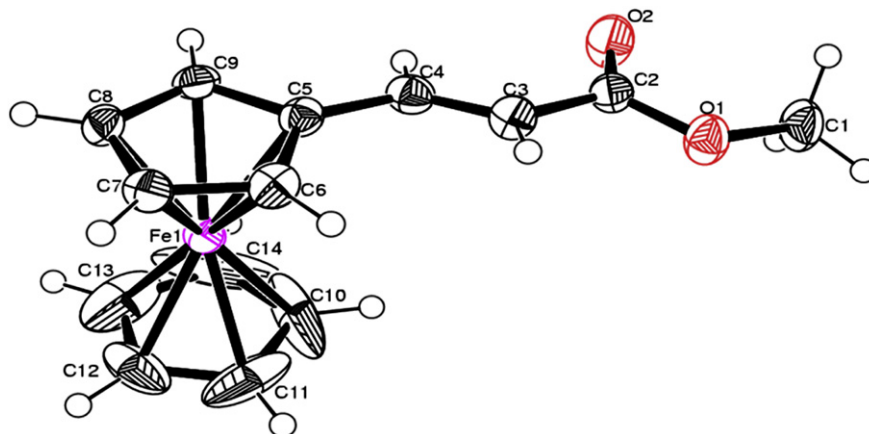


Fig. 1. ORTEP diagram of *Methyl-3-ferrocenyl-2-propenoate* (**1**) with 50% probability ellipsoids, Selected bond distances [Å] and angles [deg]: C(9)–C(5): 1.433(6), O(1)–C(2): 1.340(5), O(1)–C(1): 1.434(5), C(3)–C(4): 1.318(6), C(3)–C(2): 1.465(6), C(2)–O(2): 1.202(5), C(5)–C(6): 1.428(6), C(5)–C(4): 1.442(6); C(2)–O(1)–C(1): 115.3(4), C(4)–C(3)–C(2): 120.2(4), O(2)–C(2)–O(1): 122.7(4), O(2)–C(2)–C(3): 126.2(4), O(1)–C(2)–C(3): 111.1(4), C(6)–C(5)–C(9): 107.6(4), C(6)–C(5)–C(4): 128.5(4), C(9)–C(5)–C(4): 123.7(4), C(3)–C(4)–C(5): 126.2(5).

4. Experimental

4.1. General procedures

Reactions and manipulations were performed using standard Schlenk line technique under argon/nitrogen with a slightly positive pressure. Photochemical reactions were carried out in cooled double walled quartz vessel having a 125-W immersion type mercury lamp manufactured by Applied Photophysics Ltd. Infrared spectra were recorded on Thermo-Nicolet 380 FTIR spectrometer as hexane and dichloromethane solutions in 0.1 mm path length of NaCl, NMR spectra on VARIAN VXRO-400S spectrometer in CDCl₃. Elemental analysis was performed on a Carlo-Erba automatic analyzer. Iron

pentacarbonyl (97% pure) was purchased from Fluka. Phenylacetylene, cyclohexylacetylene and 1-hexyne were purchased from Aldrich. Trimethylsilylacetylene was purchased from Spectrochem Ltd. Ferrocenylacetylene was prepared using reported method [30]. TLC plates were purchased from Merck (20 × 20 cm, silica gel 60 F₂₅₄). Solvents were purchased from Merck and used after purification and drying under argon atmosphere.

4.2. Crystal structure determination

Suitable X-ray quality crystals of compounds **1** (0.34 × 0.32 × 0.28 mm³), **16** (0.34 × 0.30 × 0.26 mm³), **17** (0.28 × 0.23 × 0.19 mm³) and **20** (0.32 × 0.28 × 0.15 mm³) were grown by

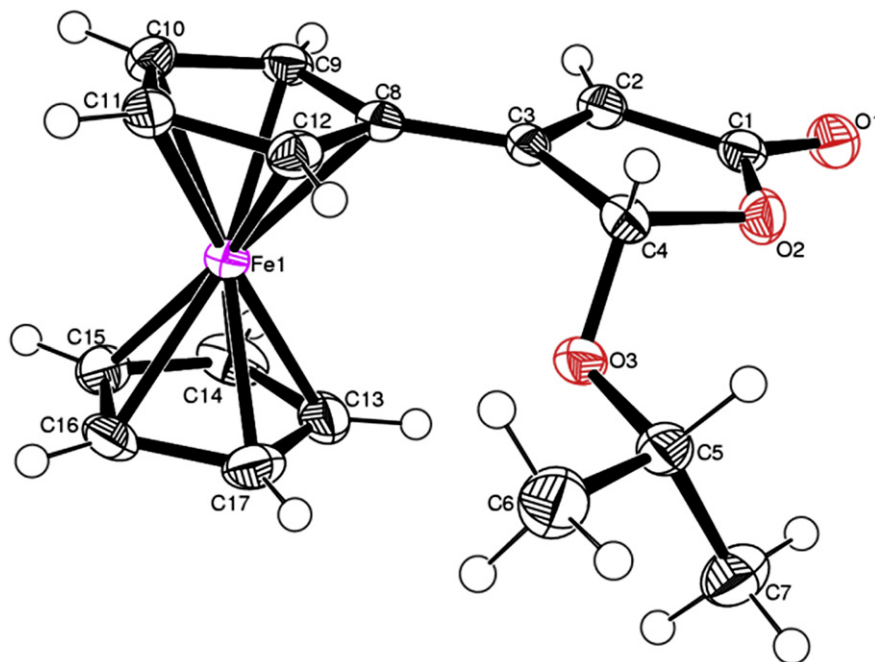


Fig. 2. ORTEP diagram of *3-ferrocenyl-4-ethoxy-2-butenolide* (**16**) with 50% probability ellipsoids, Selected bond distances [Å] and angles [deg]: O(1)–C(1): 1.205(3), O(2)–C(1): 1.374(3), O(2)–C(2): 1.457(3), O(3)–C(2): 1.383(3), O(3)–C(5): 1.456(3), C(1)–C(4): 1.460(4), C(2)–C(3): 1.511(3), C(3)–C(4): 1.340(4), C(3)–C(7): 1.444(3), C(5)–C(6): 1.502(4), C(7)–C(8): 1.434(3), C(7)–C(11): 1.443(3); C(1)–O(2)–C(2): 108.89(19), C(2)–O(3)–C(5): 114.35(18), O(1)–C(1)–O(2): 121.0(3), O(1)–C(1)–C(4): 130.5(3), O(2)–C(1)–C(4): 108.6(2), O(3)–C(2)–O(2): 110.7(2), O(3)–C(2)–C(3): 110.7(2), O(2)–C(2)–C(3): 104.69(19), C(4)–C(3)–C(7): 130.4(2), C(4)–C(3)–C(2): 108.1(2), C(7)–C(3)–C(2): 121.5(2), C(3)–C(4)–C(1): 109.7(2), O(3)–C(5)–C(6): 108.2(2).

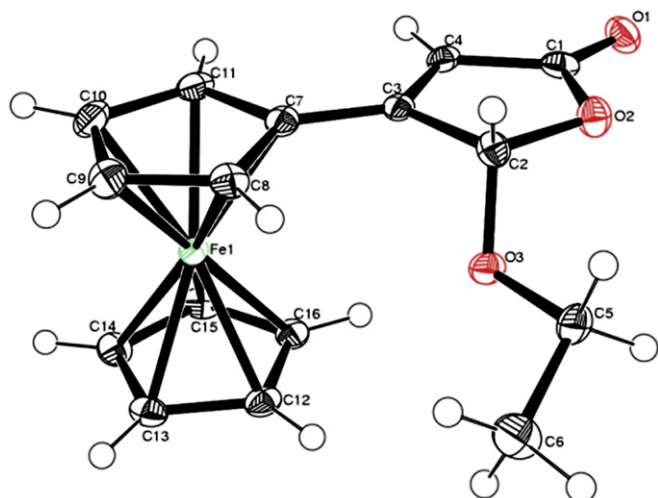


Fig. 3. ORTEP diagram of 3-ferrocenyl-4-isopropoxy-2-butenolide (**17**) with 50% probability ellipsoids. Selected bond length (Å) and bond angles (deg): O(1)–C(1) = 1.211(3), O(2)–C(1) = 1.377(4), O(2)–C(4) = 1.456(3), O(3)–C(4) = 1.386(3), O(3)–C(5) = 1.460(3), C(1)–C(2) = 1.468(4), C(2)–C(3) = 1.342(4), C(3)–C(8) = 1.455(4), C(3)–C(4) = 1.517(4), C(8)–C(9) = 1.445(4), C(8)–C(12) = 1.455(4); C(1)–O(2)–C(4) = 109.1(2), C(4)–O(3)–C(5) = 114.3(2), O(1)–C(1)–O(2) = 120.7(3), O(1)–C(1)–C(2) = 130.9(3), O(2)–C(1)–C(2) = 108.4(2), C(3)–C(2)–C(1) = 109.5(3), C(2)–C(3)–C(8) = 129.8(3), C(2)–C(3)–C(4) = 108.3(2), C(8)–C(3)–C(4) = 121.8(2), O(3)–C(4)–O(2) = 109.9(2), O(3)–C(4)–C(3) = 110.6(2), O(2)–C(4)–C(3) = 104.6(2), C(9)–C(8)–C(12) = 107.1(2), C(9)–C(8)–C(3) = 126.7(3), C(12)–C(8)–C(3) = 126.2(3).

slow evaporation of *n*-hexane and dichloromethane solution at 10 °C–15 °C, and X-ray crystallographic data were collected (Table 2). Oxford Diffraction X calibur-S, CCD system equipped with area detector was used for the cell determination and intensity data collection for compounds **1**, **16**, **17** and **20**. Monochromatic Mo K α radiation (0.71359 Å) was used for the measurements. Absorption corrections using multi ψ -scans were applied. Structures were solved

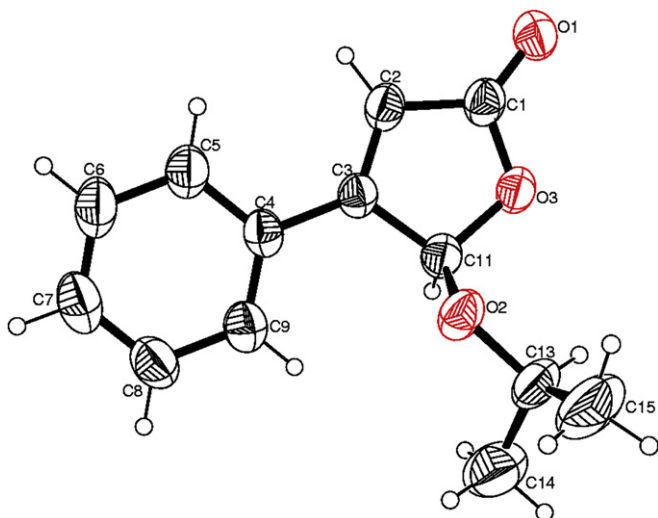
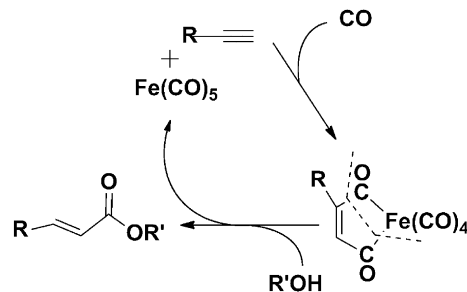


Fig. 4. ORTEP diagram of 3-phenyl-4-isopropoxy-2-butenolide (**20**) with 50% probability ellipsoids. Selected bond length (Å) and bond angles (deg): O(1)–C(1) = 1.208(4), O(2)–C(11) = 1.379(4), O(2)–C(13) = 1.454(4), O(3)–C(1) = 1.357(4), O(3)–C(11) = 1.449(3), C(1)–C(2) = 1.457(5), C(2)–C(3) = 1.323(4), C(3)–C(4) = 1.458(4), C(3)–C(11) = 1.511(5), C(4)–C(9) = 1.367(4), C(4)–C(5) = 1.396(5); C(11)–O(2)–C(13) = 114.2(3), C(1)–O(3)–C(11) = 110.1(3), O(1)–C(1)–O(3) = 122.3(3), O(1)–C(1)–C(2) = 130.0(4), O(3)–C(1)–C(2) = 107.7(3), C(3)–C(2)–C(1) = 110.2(3), C(2)–C(3)–C(4) = 128.6(3), C(2)–C(3)–C(11) = 108.2(3), C(4)–C(3)–C(11) = 123.2(3), C(9)–C(4)–C(5) = 118.4(3), C(9)–C(4)–C(3) = 121.8(4), C(5)–C(4)–C(3) = 119.8(3), O(2)–C(11)–O(3) = 109.3(3), O(2)–C(11)–C(3) = 109.7(3), O(3)–C(11)–C(3) = 103.7(3).



Scheme 2. Mechanism for the formation of α,β -vinylester.

by direct methods (SHELXS) and refined by full-matrix least squares against F_o^2 using SHELXL-97 software [31]. Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were geometrically fixed and allowed to refine using a riding model.

4.3. General procedure for ironpentacarbonyl catalyzed photolysis of terminal acetylene, CO and alcohols

To a 60 mL alcoholic solution (methanol, ethanol or isopropanol) of different terminal acetylene (7.5 mmol), $\text{Fe}(\text{CO})_5$ (0.1 mL, 0.1 mmol) was added. This reaction mixture was photolysed for 30 min to 3 h at 0 °C in a photochemical vessel with continuous bubbling of CO. After removal of volatiles, the residue was subjected to chromatographic work up. Ethyl acetate/hexane (5:95 v/v) solvent mixture eluted the orange red (ferrocenyl substituted vinylesters) or light yellow band (remaining products). Further elution with (10:90 v/v) solvent mixture yielded the dark red band of the ferrocenyl substituted lactone or a light yellow band of the other organic derivatives of lactones.

4.3.1. Methyl-3-ferrocenyl-2-propenoate (**1**)

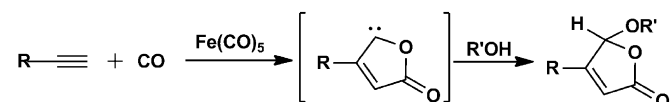
Yield: 582 mg (37%) as an orange red solid. ^1H NMR (CDCl_3 , 400 MHz, 298 K) δ 7.51 (d, J = 15.9 Hz, 1H, Fc–CH=CH–), 6.05 (d, J = 15.9 Hz, 1H, Fc–CH=CH–), 3.70 (s, 3H, –CH₃), 4.11 (s, 5H, C₅H₅–), 4.39–4.48 (m, 4H, C₅H₄–). ^{13}C NMR (CDCl_3) δ 167.7 (CO), 146 (Fc–CH=CH–), 114.62 (Fc–CH=CH–), 70.99 (C₅H₅–), 69.80–68.73 (C₅H₄–), 51.53 (CH₃O–). IR (Hexane, cm^{-1}): 1727, 1635 (ν_{CO}); MS (m/z , ES⁺): 271 (M + H)⁺; M.P. 84–86 °C. Anal. Calc. for C₁₄H₁₄O₂Fe: C, 62.21, H, 5.22. Found: C, 62.14; H 5.20.

4.3.2. Ethyl-3-ferrocenyl-2-propenoate (**2**)

Yield: 362 mg (23%) as an orange red solid. ^1H NMR (CDCl_3 , 400 MHz, 298 K) δ 7.43 (d, J = 15.6, 1H, Fc–CH=CH–), 5.94 (d, J = 15.9, 1H, Fc–CH=CH–), 4.12 (q, J = 7.3, 2H, –OCH₂CH₃), 1.25 (t, J = 7.0, 3H, –CH₃), 4.09 (s, 5H, C₅H₅–), 4.32–4.42 (m, 4H, C₅H₄–). ^{13}C NMR (CDCl_3) δ 167.27 (CO), 145.6 (Fc–CH=CH–), 115.03 (Fc–CH=CH–), 70.83 (C₅H₅–), 69.69–68.61 (C₅H₄–), 60.19 (–OCH₂), 14.42 (CH₃–). IR (Hexane, cm^{-1}) 1723, 1637 (ν_{CO}). MS (m/z , ES⁺): 285 (M + H)⁺. M.P. 65–67 °C. Anal. Calc. for C₁₅H₁₆O₂Fe: C, 63.40, H, 5.76. Found: C, 63.26; H, 5.75.

4.3.3. Isopropyl-3-ferrocenyl-2-propenoate (**3**)

Yield: 126 mg (8%) as an orange red solid. ^1H NMR (CDCl_3 , 400 MHz, 298 K) δ 7.49 (d, J = 15.6, 1H, Fc–CH=CH–), 5.96 (d,



Scheme 3. Mechanism for the formation of alkoxy γ -lactone.

Table 2
Crystal data and structure refinement parameters for compounds **1**, **16**, **17** and **20**.

	1	16	17	20
Empirical formula	C ₁₄ H ₁₄ FeO ₂	C ₁₆ H ₁₆ FeO ₃	C ₁₇ H ₁₈ FeO ₃	C ₁₃ H ₁₄ O ₃
Formula weight	270.10	312.14	326.16	218.24
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ /c	<i>P</i> - 1	<i>P</i> 2 ₁ /n	<i>P</i> 2 ₁ /c
<i>a</i> , Å	14.814 (5)	9.9547 (14)	13.771 (3)	6.0897 (17)
<i>b</i> , Å	7.579 (3)	10.0955 (12)	9.4798 (18)	22.819 (8)
<i>c</i> , Å	10.863 (4)	13.2895 (15)	11.840 (2)	8.704 (2)
α deg	90	90	90	90
β deg	106.96 (3)	90	108.773 (18)	96.29 (3)
γ deg	90	90	90	90
<i>V</i> , Å ³	1166.6 (8)	1335.6 (3)	1463.5 (5)	1202.3 (6)
<i>Z</i>	4	4	4	4
D _{calc} , mg m ⁻³	1.538	1.552	1.480	1.206
Abs coeff, mm ⁻¹	1.277	1.133	1.037	0.085
<i>F</i> (000)	560	648	680	464
Cryst size, mm	0.34 × 0.32 × 0.28	0.28 × 0.23 × 0.19	0.34 × 0.30 × 0.26	0.32 × 0.28 × 0.15
θ range, deg	3.33 to 24.99	3.07 to 25.00	3.13 to 30.00	3.37 to 25.00
Index ranges	-17 ≤ <i>h</i> ≤ 17 -6 ≤ <i>k</i> ≤ 9 -10 ≤ <i>l</i> ≤ 12	-11 ≤ <i>h</i> ≤ 11 -12 ≤ <i>k</i> ≤ 5 -15 ≤ <i>l</i> ≤ 14	-19 ≤ <i>h</i> ≤ 19 -13 ≤ <i>k</i> ≤ 12 -16 ≤ <i>l</i> ≤ 15	-7 ≤ <i>h</i> ≤ 7 -27 ≤ <i>k</i> ≤ 27 -10 ≤ <i>l</i> ≤ 10
Reflections collected/unique	6039/2051 [R(int) = 0.0705]	5833/2331 [R(int) = 0.0268]	12981/4250 [R(int) = 0.1140]	9885/2116 [R(int) = 0.1052]
Data/restraints/parameters	2051/0/164	2331/0/182	4250/0/200	2116/0/147
Goodness-of-fit on <i>F</i> ²	0.924	0.932	1.040	0.836
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0526, <i>wR</i> 2 = 0.1201	<i>R</i> 1 = 0.0255, <i>wR</i> 2 = 0.0623	<i>R</i> 1 = 0.0463, <i>wR</i> 2 = 0.1154	<i>R</i> 1 = 0.0592, <i>wR</i> 2 = 0.1269
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0772, <i>wR</i> 2 = 0.1309	<i>R</i> 1 = 0.0273, <i>wR</i> 2 = 0.0630	<i>R</i> 1 = 0.0777, <i>wR</i> 2 = 0.1542	<i>R</i> 1 = 0.1682, <i>wR</i> 2 = 0.1593
Largest diff peak and hole, eÅ ⁻³	0.578 and -0.692	0.348 and -0.375	0.949 and -0.769	0.161 and -0.157

J = 15.6, 1H, Fc-CH=CH-), 5.01 (septet, *J* = 6.3, 1H, -OCH(CH₃)₂), 1.17 (d, *J* = 6.4, 6H, CH₃), 4.06 (s, 5H, C₅H₅), 4.31–4.41 (m, 4H, C₅H₄). ¹³C NMR (CDCl₃) δ 166.95 (CO), 145.44 (Fc-CH=CH-), 115.76 (Fc-CH=CH-), 70.89 (C₅H₅-), 69.80 - 68.71 (C₅H₄-), 14.38 (CH₃-). IR (Hexane, cm⁻¹) 1713, 1634 (ν_{CO}); MS (*m/z*, ES⁺): 298 (M)⁺. M.P. 72–74 °C. Anal. Calc. for C₁₆H₁₈O₂Fe: C, 64.45; H, 6.09. Found: C, 64.51; H, 6.14.

4.3.4. Methyl-3-phenyl-2-propenoate (**4**)

Yield: 260 mg (34%) as a light yellow liquid. ¹H NMR (CDCl₃, 400 MHz, 298 K) δ 7.71 (d, *J* = 3.4 Hz, 1H, Ph-CH=CH-), 6.45 (d, *J* = 3.4 Hz, 1H, Ph-CH=CH-), 3.42 (s, 3H, -OCH₃), 7.21–7.43 (m, 5H, C₆H₅-). ¹³C NMR (CDCl₃) δ 167.46 (CO), 144.99 (Ph-CH=CH-), 119.61 (Ph-CH=CH-), 134.58 - 128.19 (C₆H₅-), 51.70 (-OCH₃). IR (Hexane, cm⁻¹) 1730, 1641 (ν_{CO}); MS (*m/z*, ES⁺): 163.0 (M + H)⁺.

4.3.5. Ethyl-3-phenyl-2-propenoate (**5**)

Yield: 222 mg (29%) as a light yellow liquid. ¹H NMR (CDCl₃, 400 MHz, 298 K) δ 7.59 (d, *J* = 16.2 Hz, 1H, Ph-CH=CH-), 6.34 (d, *J* = 16.2 Hz, 1H, Ph-CH=CH-), 4.16 (q, *J* = 7.7 Hz, 2H, -OCH₂-), 1.28 (t, *J* = 7.0 Hz, 3H, CH₃-), 7.31–7.46 (m, 5H, C₆H₅-). ¹³C NMR (CDCl₃) δ 167.17 (CO), 144.75 (Ph-CH=CH-), 118.43 (Ph-CH=CH-), 134.63 - 126.62 (C₆H₅-), 60.66 (-OCH₂-), 14.48 (CH₃-). IR (Hexane, cm⁻¹) 1724, 1641 (ν_{CO}); MS (*m/z*, ES⁺): 176.21 (M)⁺.

4.3.6. Isopropyl-3-phenyl-2-propenoate (**6**)

Yield: 176 mg (23%) as a light yellow liquid. ¹H NMR (CDCl₃, 400 MHz, 298 K) δ 7.68 (d, *J* = 16.2 Hz, 1H, Ph-CH=CH-), 6.32 (d, *J* = 16.2 Hz, 1H, Ph-CH=CH-), 5.10 (septet, *J* = 6.3 Hz, 1H, -OCH-), 1.20 (d, *J* = 6.4 Hz, 6H, -CH₃), 7.34–7.51 (m, 5H, C₆H₅-). ¹³C NMR (CDCl₃) δ 166.59 (CO), 144.42 (Ph-CH=CH-), 118.96 (Ph-CH=CH-), 134.7 - 128.13 (C₆H₅-), 67.87 (-OCH-), 22.05 (CH₃). IR (Hexane, cm⁻¹) 1719, 1640 (ν_{CO}); MS (*m/z*, ES⁺): 191.13 (M + H)⁺.

4.3.7. Methyl-3-trimethylsilyl-2-propenoate (**7**)

Yield: 191 mg (26%) as a light yellow liquid. ¹H NMR (CDCl₃, 400 MHz, 298 K) δ 5.90 (d, *J* = 5.1 Hz, 1H, (CH₃)₃Si-CH=CH-), 3.44 (d, *J* = 5.1 Hz, 1H, (CH₃)₃Si-CH=CH-), 3.56 (s, 3H, -OCH₃), 1.24 (s,

9H, CH₃-). ¹³C NMR (CDCl₃) δ 170.12 (CO), 160.31 ((CH₃)₃Si-CH=CH-), 127.39 ((CH₃)₃Si-CH=CH-), 59.5 (-OCH₃), -1.08 (CH₃). IR (Hexane, cm⁻¹) 1724, 1638 (ν_{CO}); MS (*m/z*, ES⁺): 159.29 (M + H)⁺.

4.3.8. Ethyl-3-trimethylsilyl-2-propenoate (**8**)

Yield: 228 mg (31%) as a light yellow liquid. ¹H NMR (CDCl₃, 400 MHz, CDCl₃, 298 K) δ 5.89 (d, *J* = 5.2 Hz, 1H, (CH₃)₃Si-CH=CH-), 3.44 (d, *J* = 5.2 Hz, 1H, (CH₃)₃Si-CH=CH-), 4.15 (q, *J* = 7.1 Hz, 2H, -OCH₂-), 1.16 (t, *J* = 7.0 Hz, 3H, CH₃-CH₂-), 0.36 (s, 9H, CH₃-). ¹³C NMR (CDCl₃) δ 169.14 (CO), 118.02 ((CH₃)₃Si-CH=CH-), 89.82 ((CH₃)₃Si-CH=CH-), 65.70 (-OCH₂-), 15.07 (CH₃CH₂-), 1.60 (CH₃-). IR (Hexane, cm⁻¹) 1754, 1649 (ν_{CO}); MS (*m/z*, ES⁺): 172.14 (M)⁺.

4.3.9. Isopropyl-3-trimethylsilyl-2-propenoate (**9**)

Yield: 125 mg (17%) as a light yellow liquid. ¹H NMR (CDCl₃, 400 MHz, 298 K) δ 5.87 (d, *J* = 7.8 Hz, 1H, (CH₃)₃Si-CH=CH-), 4.22 (d, 6.1 Hz, 1H, (CH₃)₃Si-CH=CH-), 4.36 (septet, *J* = 6.1 Hz, 1H, -OCH-), 1.28 (d, *J* = 5.2 Hz, 6H, -OCH(CH₃)₂), 0.23 (s, 9H, CH₃-). ¹³C NMR (CDCl₃) δ 184.56 (CO), 124.81 ((CH₃)₃Si-CH=CH-), 97.74 ((CH₃)₃Si-CH=CH-), 71.38 (-OCH-), 21.19 (-OCH(CH₃)₂-), -0.70 (CH₃). IR (Hexane, cm⁻¹) 1744, 1632 (ν_{CO}); MS (*m/z*, ES⁺): 186.19 (M)⁺.

4.3.10. Methyl-2-heptenoate (**10**)

Yield: 178 mg (29%) as a light yellow liquid. ¹H NMR (CDCl₃, 400 MHz, 298 K) δ 7.70 (m, *J* = 3.5 Hz, 1H, C₄H₉-CH=CH-), 7.52 (d, *J* = 3.1 Hz, 1H, C₄H₉-CH=CH-), 3.80 (s, 3H, -OCH₃), 0.90–2.17 (m, 9H, C₄H₉-). ¹³C NMR (CDCl₃) δ 169.01 (CO), 138.41 (C₄H₉-CH=CH-), 121.67 (C₄H₉-CH=CH-), 53.91 (-OCH₃), 33.41 - 14.21 (C₄H₉-). IR (Hexane, cm⁻¹) 1739, 1654 (ν_{CO}); MS (*m/z*, ES⁺): 141.94 (M)⁺.

4.3.11. Ethyl-2-heptenoate (**11**)

Yield: 129 mg (21%) as a light yellow liquid. ¹H NMR (CDCl₃, 400 MHz, 298 K) δ 6.95 (m, *J* = 13.4 Hz, 1H, C₄H₉-CH=CH-), 6.63 (d, *J* = 15.8 Hz, 1H, C₄H₉-CH=CH-), 4.41 (q, *J* = 6.4 Hz, 2H, -OCH₂CH₃), 0.91–2.29 (m, 9H, C₄H₉-). ¹³C NMR (CDCl₃) δ 169.13 (CO), 161.18 (C₄H₉-CH=CH-), 121.17 (C₄H₉-CH=CH-), 58.41 (-OCH₂CH₃), 32.04 - 14.38 (C₄H₉-). IR (Hexane, cm⁻¹) 1734, 1654 (ν_{CO}); MS (*m/z*, ES⁺): 155.10 (M + H)⁺.

4.3.12. Isopropyl-2-heptenoate (12)

Yield: 73 mg (12%) as a light yellow liquid. ^1H NMR (CDCl_3 , 400 MHz, 298 K) δ 6.91 (m, 1H, $\text{C}_4\text{H}_9\text{-CH=CH-}$), 5.82 (d, $J = 14.1$, Hz, 1H, $\text{C}_4\text{H}_9\text{-CH=CH-}$), 2.19 (m, 2H, $-\text{CH}_2-$), 1.31 (m, 2H, $-\text{CH}_2-$), 1.17 (t, 3H, CH_3-). ^{13}C NMR (CDCl_3) δ 165.21 (CO), 137.89 ($\text{C}_4\text{H}_9\text{-CH=CH-}$), 125.41 ($\text{C}_4\text{H}_9\text{-CH=CH-}$), 68.91 ($-\text{OCH}(\text{CH}_3)_2$), 32.44 – 13.84 (C_4H_9-). IR (Hexane, cm^{-1}) 1729, 1633 (ν_{CO}); MS (m/z , ES+): 170.15 (M^+).

4.3.13. Methyl-3-cyclohexyl-2-propenoate (13)

Yield: 259 mg (32%) as a light yellow liquid. ^1H NMR (CDCl_3 , 400 MHz, 298 K) δ 6.89 (q, $J = 6.9$ Hz, 1H, $\text{C}_6\text{H}_{11}\text{CH=CH-}$), 5.78 (d, $J = 14.2$ Hz, 1H, $\text{C}_6\text{H}_{11}\text{CH=CH-}$), 3.72 (s, 3H, $-\text{OCH}_3$), 2.12 (m, 1H, C_6H_{11}), 0.86–1.54 (m, 10H, C_6H_{11}). ^{13}C NMR (CDCl_3) δ 167.91 (CO), 152.20 ($\text{C}_6\text{H}_{11}\text{CH=CH-}$), 121.47 ($\text{C}_6\text{H}_{11}\text{CH=CH-}$), 51.97 ($-\text{OCH}_3$), 39.94 – 25.89 ($\text{C}_6\text{H}_{11}-$). IR (Hexane, cm^{-1}) 1736, 1620 (ν_{CO}); MS (m/z , ES+): 169.11 ($\text{M} + \text{H}^+$).

4.3.14. Isopropyl-3-cyclohexyl-2-propenoate (14)

Yield: 121 mg (15%) as a light yellow liquid. ^1H NMR (CDCl_3 , 400 MHz, 298 K) δ 6.86 (q, $J = 6.7$ Hz, 1H, $\text{C}_6\text{H}_{11}\text{CH=CH-}$), 5.70 (d, $J = 15.8$ Hz, 1H, $\text{C}_6\text{H}_{11}\text{CH=CH-}$), 5.01 (septet, $J = 6.4$ Hz, 1H, $-\text{OCH}(\text{CH}_3)_2$), 1.24 (d, $J = 5.8$ Hz, 6H, $-\text{OCH}(\text{CH}_3)_2$), 2.02 (m, 1H, C_6H_{11}), 0.96–1.54 (m, 10H, $\text{C}_6\text{H}_{11}-$). ^{13}C NMR (CDCl_3) δ 168.82 (CO), 154.08 ($\text{C}_6\text{H}_{11}\text{CH=CH-}$), 119.46 ($\text{C}_6\text{H}_{11}\text{CH=CH-}$), 67.97 ($-\text{OCH}(\text{CH}_3)_2$), 40.49 – 21.94 ($\text{C}_6\text{H}_{11}-$). IR (Hexane, cm^{-1}) 1707, 1580 (ν_{CO}); MS (m/z , ES+): 197.18 ($\text{M} + \text{H}^+$).

4.3.15. 3-Ferrocenyl-4-methoxy-2-butenolide (15)

Yield: 945 mg (60%) as a dark red solid. ^1H NMR (CDCl_3 , 400 MHz, 298 K) δ 6.18 (s, 1H, Fc-C=CH-), 6.16 (s, 1H, $-\text{CH}(\text{OCH}_3)$), 3.59 (s, 3H, $-\text{OCH}_3$), 4.18 (s, 5H, C_5H_5-), 4.53–4.80 (m, 4H, C_5H_4-). ^{13}C NMR (CDCl_3) δ 171.24 (CO), 165.08 (Fc-C=CH-), 111.36 (Fc-C=CH-), 103.20 ($-\text{CH}(\text{OCH}_3)$), 71.49 (C_5H_5-), 68.65 – 68.18 (C_5H_4-), 55.81 ($-\text{OCH}_3$). IR (Hexane, cm^{-1}) 1793, 1619 (ν_{CO}); MS (m/z , ES+): 299 ($\text{M} + \text{H}^+$). M.P. 96–98 °C. Anal. Calc. for $\text{C}_{15}\text{H}_{14}\text{O}_3\text{Fe}$: C, 60.43; H, 4.73. Found: C, 60.39; H, 4.81.

4.3.16. 3-Ferrocenyl-4-ethoxy-2-butenolide (16)

Yield: 1165 mg (74 %) as a dark red solid. ^1H NMR (CDCl_3 , 400 MHz, 298 K) δ 5.96 (s, 1H, $-\text{CH}(\text{OCH}_2\text{CH}_3)$), 6.03 (s, 1H, Fc-C=CH-), 3.79 (m, 2H, $-\text{OCH}_2\text{CH}_3$), 1.34 (t, $J = 7.4$ Hz, 3H, $-\text{OCH}_2\text{CH}_3$), 4.18 (s, 5H, C_5H_5-), 4.53–4.68 (m, 4H, C_5H_4-). ^{13}C NMR (CDCl_3) δ 171.53 (CO), 165.42 (Fc-C=CH-), 111.5 (Fc-C=CH-), 102.66 ($-\text{CH}(\text{OCH}_2\text{CH}_3)$), 71.91 (C_5H_5-), 69.8 – 65.2 (C_5H_4-), 50.99 ($-\text{OCH}_2\text{CH}_3$), 15.37 ($-\text{OCH}_2\text{CH}_3$). IR (Hexane, cm^{-1}) 1793, 1625 (ν_{CO}); MS (m/z , ES+): 313 ($\text{M} + \text{H}^+$). M.P. 98–100 °C. Anal. Calc. for $\text{C}_{16}\text{H}_{16}\text{O}_3\text{Fe}$: C, 61.34; H, 5.11. Found: C, 61.30; H, 5.09.

4.3.17. 3-Ferrocenyl-4-isopropoxy-2-butenolide (17)

Yield: 1386 mg (88%) as a dark red solid. ^1H NMR (CDCl_3 , 400 MHz, 298 K) δ 5.96 (s, 1H, $-\text{CH}(\text{OCH}(\text{CH}_3)_2)$), 6.02 (s, 1H, Fc-C=CH-), 4.18 (m, 1H, $-\text{CH}(\text{OCH}(\text{CH}_3)_2)$), 1.2 (d, $J = 6.2$ Hz, 6H, $-\text{OCH}(\text{CH}_3)_2$), 4.18 (s, 5H, C_5H_5-), 4.52–4.66 (m, 4H, C_5H_4-). ^{13}C NMR (CDCl_3) δ 171.68 (CO), 165.60 (Fc-C=CH-), 111.40 (Fc-C=CH-), 101.39 ($-\text{CH}(\text{OCH}(\text{CH}_3)_2)$), 71.76 (C_5H_5-), 68.56 – 68.52 (C_5H_4-), 22.07 (CH_3-). IR (Hexane, cm^{-1}) 1796, 1630 (ν_{CO}); MS (m/z , ES+): 327 ($\text{M} + \text{H}^+$). M.P. 90–94 °C. Anal. Calc. for $\text{C}_{17}\text{H}_{18}\text{O}_3\text{Fe}$: C, 62.57; H, 5.52. Found: C, 62.49; H, 5.54.

4.3.18. 3-Phenyl-4-methoxy-2-butenolide (18)

Yield: 451 mg (59%) as a light yellow liquid. ^1H NMR (CDCl_3 , 400 MHz, 298 K) δ 6.43 (s, 1H, Ph-C=CH-), 6.25 (s, 1H, $-\text{CH}(\text{OCH}_3)$), 3.58 (s, 3H, $-\text{OCH}_3$), 7.26–7.74 (m, 5H, C_6H_5-). ^{13}C NMR (CDCl_3) δ 169.2 (CO), 159.83 (Ph-C=CH-), 114.93 (Ph-C=

CH-), 102.51 ($-\text{CH}(\text{OCH}_3)$), 135.71 – 128.21 (C_6H_5-), 53.47 ($-\text{OCH}_3$). IR (Hexane, cm^{-1}) 1739, 1656 (ν_{CO}); MS (m/z , ES+): 190.09 (M^+).

4.3.19. 3-Phenyl-4-ethoxy-2-butenolide (19)

Yield: 482 mg (63%) as a yellow liquid. ^1H NMR (CDCl_3 , 400 MHz, 298 K) δ 6.29 (s, 1H, $-\text{CH}(\text{OCH}_2\text{CH}_3)$), 6.42 (s, 1H, Ph-C=CH-), 4.01 (q, $J = 6.1$ Hz, 2H, $-\text{OCH}_2\text{CH}_3$), 7.21–7.73 (m, 5H, C_6H_5-), 1.20 (d, $J = 6.1$ Hz, 3H, $-\text{OCH}_2\text{CH}_3$). ^{13}C NMR (CDCl_3) δ 167.09 (CO), 151.14 (Ph-C=CH-), 140.02 (Ph-C=CH-), 128.61 – 126.85 (C_6H_5-), 61.38 ($-\text{OCH}_2\text{CH}_3$), 14.01 ($-\text{OCH}_2\text{CH}_3$). IR (Hexane, cm^{-1}) 1743, 1629 (ν_{CO}); MS (m/z , ES+): 204.81 (M^+).

4.3.20. 3-Phenyl-4-isopropoxy-2-butenolide (20)

Yield: 543 mg (71%) as a yellow liquid. ^1H NMR (CDCl_3 , 400 MHz, 298 K) δ 6.34 (s, 1H, $-\text{CH}(\text{OCH}(\text{CH}_3)_2)$), 6.43 (s, 1H, Ph-C=CH-), 4.20 (septet, $J = 7.0$ Hz, 1H, $-\text{CH}(\text{OCH}(\text{CH}_3)_2)$), 1.30 (d, $J = 6.2$ Hz, 6H, $-\text{OCH}(\text{CH}_3)_2$), 7.20–7.6 (m, 5H, C_6H_5-). ^{13}C NMR (CDCl_3) δ 170.99 (CO), 161.62 (Ph-C=CH-), 115.92 (Ph-C=CH-), 101.48 ($-\text{CH}(\text{OCH}(\text{CH}_3)_2)$), 133.82 – 127.79 (C_6H_5-), 22.14 ($-\text{OCH}(\text{CH}_3)_2$). IR (Hexane, cm^{-1}): 1750, 1625 (ν_{CO}); MS (m/z , ES+): 219.14 ($\text{M} + \text{H}^+$).

4.3.21. 3-Trimethylsilyl-4-methoxy-2-butenolide (21)

Yield: 523 mg (71%) as a light yellow liquid. ^1H NMR (CDCl_3 , 400 MHz, 298 K) δ 5.30 (s, 1H, $-\text{CH}(\text{OCH}_3)$), 5.52 (s, 1H, $(\text{CH}_3)_3\text{SiC=CH-}$), 3.55 (s, 3H, $-\text{OCH}_3$), 0.24 (s, 9H, $-\text{Si}(\text{CH}_3)_3$). ^{13}C NMR (CDCl_3) δ 170.12 (CO), 160.31 ($(\text{CH}_3)_3\text{SiC=CH-}$), 127.39 ($(\text{CH}_3)_3\text{SiC=CH-}$), 89.5 ($-\text{CH}(\text{OCH}_3)$), -1.86 ($-\text{Si}(\text{CH}_3)_3$). IR (Hexane, cm^{-1}) 1748, 1663 (ν_{CO}); MS (m/z , ES+): 185.01 ($\text{M} - \text{H}^+$).

4.3.22. 3-Trimethylsilyl-4-ethoxy-2-butenolide (22)

Yield: 493 mg (67%) as a light yellow liquid. ^1H NMR (CDCl_3 , 400 MHz, 298 K) δ 5.67 (s, 1H, $(\text{CH}_3)_3\text{SiC=CH-}$), 5.30 (s, 1H, $-\text{CH}(\text{OCH}_2\text{CH}_3)$), 4.13 (q, $J = 5.0$ Hz, 2H, $-\text{OCH}_2\text{CH}_3$), 1.20 (t, $J = 7.0$ Hz, 3H, $-\text{OCH}_2\text{CH}_3$). ^{13}C NMR (CDCl_3) δ 173.44 (CO), 130.80 ($(\text{CH}_3)_3\text{SiC=CH-}$), 96.47 ($-\text{CH}(\text{OCH}_2\text{CH}_3)$), 64.35 ($-\text{OCH}_2\text{CH}_3$), 14.88 ($-\text{OCH}_2\text{CH}_3$), -0.56 ($-\text{Si}(\text{CH}_3)_3$). IR (Hexane, cm^{-1}) 1754, 1652 (ν_{CO}); MS (m/z , ES+): 200.17 (M^+).

4.3.23. 3-Trimethylsilyl-4-(2-propoxy)-2-butenolide (23)

Yield: 604 mg (82%) as a light yellow liquid. ^1H NMR (CDCl_3 , 400 MHz, 298 K) δ 5.71 (s, 1H, $(\text{CH}_3)_3\text{SiC=CH-}$), 5.65 (s, 1H, $-\text{CH}(\text{OCH}(\text{CH}_3)_2)$), 4.21 (Septet, $J = 6.1$ Hz, 1H, $-\text{OCH}(\text{CH}_3)_2$), 1.28 (d, $J = 5.2$ Hz, 6H, $-\text{OCH}(\text{CH}_3)_2$), 0.26 (s, 9H, $-\text{Si}(\text{CH}_3)_3$). ^{13}C NMR (CDCl_3) δ 170.31 (CO), 162.26 ($(\text{CH}_3)_3\text{SiC=CH-}$), 130.68 ($(\text{CH}_3)_3\text{SiC=CH-}$), 95.73 ($-\text{CH}(\text{OCH}(\text{CH}_3)_2)$), 68.16 ($-\text{OCH}(\text{CH}_3)_2$), 23.56 ($-\text{OCH}(\text{CH}_3)_2$), -0.78 ($-\text{Si}(\text{CH}_3)_3$). IR (Hexane, cm^{-1}) 1772, 1600 (ν_{CO}); MS (m/z , ES+): 214.19 (M^+).

4.3.24. 3-Butyl-4-methoxy-2-butenolide (24)

Yield: 320 mg (52%) as a light yellow liquid. ^1H NMR (CDCl_3 , 400 MHz, 298 K) δ 5.67 (s, 1H, $\text{C}_4\text{H}_9\text{C=CH-}$), 6.49 (s, 1H, $-\text{CH}(\text{OCH}_3)$), 3.62 (s, 3H, $-\text{OCH}_3$), 2.24 (m, 2H, C_4H_9-), 0.95–2.24 (m, 7H, C_4H_9-). ^{13}C NMR (CDCl_3) δ 173.61 (CO), 162.43 ($\text{C}_4\text{H}_9\text{C=CH-}$), 121.37 ($\text{C}_4\text{H}_9\text{C=CH-}$), 51.49 (s, $-\text{OCH}_3$), 34.55–15.11 (C_4H_9-). IR (Hexane, cm^{-1}) 1748, 1654 (ν_{CO}); MS (m/z , ES+): 171.10 ($\text{M} + \text{H}^+$).

4.3.25. 3-Butyl-4-ethoxy-2-butenolide (25)

Yield: 468 mg (76%) as a light yellow liquid. ^1H NMR (CDCl_3 , 400 MHz, 298 K) δ 5.70 (s, 1H, $\text{C}_4\text{H}_9\text{C=CH-}$), 5.85 (s, 1H, $-\text{CH}(\text{OCH}_2\text{CH}_3)$), 3.96 (q, $J = 2.8$ Hz, 2H, $-\text{OCH}_2\text{CH}_3$), 1.10–2.12 (m, 9H, C_4H_9-), 1.11 (t, $J = 7.0$ Hz, 3H, $-\text{OCH}_2\text{CH}_3$). ^{13}C NMR (CDCl_3) δ 168.27 (CO), 162.31 ($\text{C}_4\text{H}_9\text{C=CH-}$), 117.91 ($\text{C}_4\text{H}_9\text{C=CH-}$), 103.70 ($-\text{CH}(\text{OCH}_2\text{CH}_3)$), 61.01 ($-\text{OCH}_2\text{CH}_3$), 30.04 – 9.81 (C_4H_9-). IR (Hexane, cm^{-1}) 1799, 1638 (ν_{CO}); MS (m/z , ES+): 185.11 ($\text{M} + \text{H}^+$).

4.3.26. 3-Butyl-4-(2-propoxy)-2-butenolide (**26**)

Yield: 529 mg (86%) as a light yellow liquid. ^1H NMR (CDCl_3 , 400 MHz, 298 K) δ 5.98 (s, 1H, $\text{C}_4\text{H}_9\text{C}=\text{CH}-$), 6.94 (s, 1H, $-\text{CH}(\text{OCH}(\text{CH}_3)_2)$), 5.0 (septet, $J = 6.3$ Hz, 1H, $-\text{CH}(\text{OCH}(\text{CH}_3)_2)$), 0.88–2.23 (m, 9H, C_4H_9-), 1.09 (d, $J = 6.1$ Hz, 6H, $-\text{OCH}(\text{CH}_3)_2$). ^{13}C NMR (CDCl_3) δ 171.52 (CO), 164.05 ($\text{C}_4\text{H}_9\text{C}=\text{CH}-$), 119.67 ($\text{C}_4\text{H}_9\text{C}=\text{CH}-$), 104.09 ($-\text{CH}(\text{OCH}(\text{CH}_3)_2)$), 68.71 ($-\text{OCH}(\text{CH}_3)_2$), 31.45 – 14.37 ($-\text{CH}_3$). IR (Hexane, cm^{-1}) 1776, 1640 (ν_{CO}); MS (m/z , ES+): 197.12 (M – H) $^+$.

4.3.27. 3-Cyclohexyl-4-methoxy-2-butenolide (**27**)

Yield: 486 mg (60%) as a light yellow liquid. ^1H NMR (CDCl_3 , 400 MHz, 298 K) δ 6.39 (s, 1H, $\text{C}_6\text{H}_{11}\text{C}=\text{CH}-$), 6.47 (s, 1H, $-\text{CH}(\text{OCH}_3)$), 3.72 (s, 3H, $-\text{OCH}_3$), 2.05 (m, 1H, $\text{C}_6\text{H}_{11}-$), 1.12–1.77 (m, 10H, C_6H_{11}). ^{13}C NMR (CDCl_3) δ 169.01 (CO), 160.27 ($\text{C}_6\text{H}_{11}\text{C}=\text{CH}-$), 128.40 ($\text{C}_6\text{H}_{11}\text{C}=\text{CH}-$), 121.40 ($-\text{CH}(\text{OCH}_3)$), 49.86 ($-\text{OCH}_3$), 40.51 – 26.76 (C_6H_{11}). IR (Hexane, cm^{-1}) 1737, 1654 (ν_{CO}); MS (m/z , ES+): 198.10 (M + 2H) $^+$.

4.3.28. 3-Cyclohexyl-4-(2-propoxy)-2-butenolide (**28**)

Yield: 640 mg (79%) as a light yellow liquid. ^1H NMR (CDCl_3 , 400 MHz, 298 K) δ 7.10 (s, 1H, $-\text{CH}(\text{OCH}(\text{CH}_3)_2)$), 6.36 (s, 1H, $\text{C}_6\text{H}_{11}\text{C}=\text{CH}-$), 5.0 (septet, $J = 6.4$ Hz, 1H, $-\text{OCH}(\text{CH}_3)_2$), 1.25 (d, $J = 3.0$ Hz, 6H, $-\text{OCH}(\text{CH}_3)_2$), 2.17 (m, 1H, $\text{C}_6\text{H}_{11}-$), 1.03–1.81 (m, 10H, C_6H_{11}). ^{13}C NMR (CDCl_3) δ 171.09 (CO), 152.45 ($\text{C}_6\text{H}_{11}\text{C}=\text{CH}-$), 121.98 45 ($\text{C}_6\text{H}_{11}\text{C}=\text{CH}-$), 110.48 ($-\text{CH}(\text{OCH}(\text{CH}_3)_2)$), 76.88 ($-\text{OCH}(\text{CH}_3)_2$), 39.10 – 26.38 (C_6H_{11}). IR (Hexane, cm^{-1}) 1720, 1654 (ν_{CO}); MS (m/z , ES+): 225.01 (M + H) $^+$.

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Appendix. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 736357, 736356, 736354 and 736355 for compounds **1**, **16–17** and **20** respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>). Supplementary data associated with this article can be found in the online version, at [doi:10.1016/j.jorganchem.2010.08.036](https://doi.org/10.1016/j.jorganchem.2010.08.036).

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