Selective Mono- and Bis(alkoxycarbonylation)s of Olefins Catalyzed by Palladium in the Presence of Cu(I) or Cu(II) Chloride under Remarkably Mild Conditions. Application to the Synthesis of γ-Butyrolactone Derivatives

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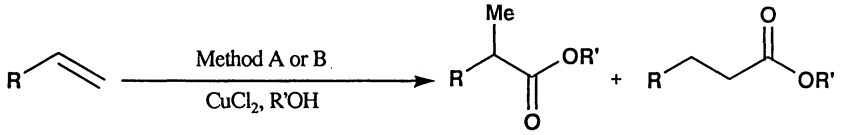
Palladium-catalyzed mono- and bis(alkoxycarbonylation)s of olefins were controlled by the use of copper(II) and copper(I) chloride, respectively, in alcohol under normal pressure of carbon monoxide and oxygen at room temperature without any other additives. 3-Buten-1-ols gave the corresponding γ-butyrolactones and 2-oxotetrahydrofuran-3-acetic acid esters, respectively, in high yields.

It is well-known that palladium chloride can catalyze the hydroesterification[1] and hydrocarboxylation[2] of olefins in acidic alcohols under mild conditions. In the course of our attempts to improve such hydroesterification reaction using various kinds of palladium catalysts in the absence of hydrochloric acid under mild conditions, we realized that palladium(0) black precipitates prior to the beginning or the completion of the reaction whenever the expected monoesters could be obtained in good yields from terminal olefins. On the basis of this observation, we eventually found that Pd–C is a favorable catalyst for the alkoxycarbonylation of olefins, and have briefly reported in the previous paper[3] that mono- and bis(alkoxycarbonylation)s of olefins can be controlled by the use of copper(II) and copper(I) chloride, respectively, together with the Pd–C catalyst in alcohol under normal pressure of carbon monoxide. However, acceleration of the reaction, which required around 8 d for completion, remained as a problem to be solved for wide synthetic applications.

We wish to report here the remarkably improved method which uses palladium(II) and copper(II) or copper(I) chloride under normal pressure of carbon monoxide and oxygen at room temperature comparing with the previous method[3] (Method A in Tables 1 and 2). The present reaction was applied to the synthesis of γ-butyrolactone derivatives.

The monocarbonylation of 1-undecene (**1b**) using various kinds of palladium catalysts (0.02 equiv) and copper(II) chloride (1.5 equiv) was first investigated under CO and O_2 (ca. 1/1, v/v, 1 atm) atmosphere in methanol at 25 °C without addition of an acid. It was found that (1) $PdCl_2$ and $[PdCl_2(CH_3CN)_2]$ are catalysts of choice, (2) the latter is better in view of selectivity of **2b**/**3b** [form of Pd catalyst, reaction time, total yields of **2b** and **3b**, and ratio of **2b**/**3b** were as follows: $PdCl_2$, 23 h, quant., 49/51; $[PdCl_2(CH_3CN)_2]$, 40 h, 90%, 86/14; $[PdCl_2(PhCN)_2]$ 42 h, 74%, 86/14; $[PdCl_2(PPh_3)_2]$,

Table 1. Mono(alkoxycarbonylation) of Terminal Olefins with $CuCl_2$



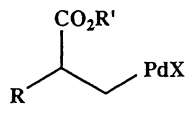
1 2 3

1	R	Method A[a] Solv.	Yield of 2+3/%	Ratio of 2/3[c]	1	Method B[b] Time/h	Yield of 2+3/%	Ratio of 2/3[c]
a,	$CH_3(CH_2)_7$	—	—	—	**a**,	24	92	85/15
b,	$CH_3(CH_2)_8$	MeOH	Quant.	81/19	**b**,	24	Quant.	80/20
c,	$CH_3(CH_2)_9$	MeOH	Quant.	78/22	**c**,	96	96	87/13
d,	$CH_3(CH_2)_{11}$	EtOH	Quant.	72/28	**d**,	74	99	85/15
e,	$CH_3(CH_2)_{15}$	EtOH	82	77/23	**e**,	73	94	83/17
f,	$Ph(CH_2)_2$	MeOH	Quant.	96/4	**f**,	43	90	90/10
g,	$PhOCH_2$	—	—	—	**g**,	96	68	85/15
h,	$TsCH_2$	—	—	—	**h**,	120	Quant.	81/19
i,	$Ts(CH_2)_2$	—	—	—	**i**,	41	91	67/33

a) Pd–C (0.11 equiv), $CuCl_2$ (3 equiv), CO (1 atm), for 8 d at 25 °C. b) $[PdCl_2(CH_3CN)_2]$ (0.02 equiv), $CuCl_2$ (1.5 equiv), CO/O_2 (ca. 1/1, v/v, 1 atm), in MeOH/THF (1/1) at 25 °C. c) Determined by 400 MHz ^{1}H NMR spectra.

43 h, 14%, 44/56; [$PdCl_2$(dppe)] (dppe=1,2-bis (diphenylphosphino)ethane), 42 h, no reaction; [$PdCl_2$(dppp)] (dppp=1,3-bis(diphenylphosphino)propane), 38 h, no reaction; [$Pd(PPh_3)_4$], 48 h, 37%, 25/75], and (3) phos phine ligands retarded the reaction and gave the linear esters in preference. Regarding solvent systems, it was found that the use of THF, CH_2Cl_2, ether, or benzene as co-solvent with methanol is effective probably because of high solubility of olefin in them, but polar solvents retard the reaction [solvent, reaction time, total yields of **2b** and **3b**, and ratio of **2b**/**3b** were as follows, when [$PdCl_2(CH_3CN)_2$] (0.02 equiv) and $CuCl_2$ (1.5 equiv) were used under similar conditions: MeOH, 40 h, 90%, 86/14; MeOH/THF (1/1, v/v), 24 h, quant., 79/21; MeOH/CH_2Cl_2(1/1, v/v), 30 h, 91%, 82/18; MeOH/Et_2O (1/1, v/v), 75 h, 94%, 85/15; MeOH/benzene (1/1, v/v), 29 h, 95%, 76/24; MeOH/CH_3CN (1/1, v/v), 42 h, 50%, 85/15; MeOH/DMF (1/1, v/v), 51 h, 17%, 87/13; MeOH/DMSO (1/1, v/v), 72 h, trace]. Consequently, various kinds of monoesters (**2a**—**i** and **3a**—**i**) were prepared in excellent yields from the corresponding terminal olefins including the functionalized ones (**1g**—**i**) with [$PdCl_2(CH_3CN)_2$] (0.02 equiv) and $CuCl_2$ (1.5 equiv) in MeOH/THF (1/1, v/v) under CO/O_2 (ca. 1/1, v/v, 1 atm)at 25 °C as summarized in Table 1 (Method B).

The predominant formation of branched monoesters (**2**) by formal Markovnikov addition of methoxycarbonyl group to olefins can be rationalized on the basis of the formation of carbonium ion intermediate,[4] or acidic decomposition of the intermediate (**4**) formed in preference to the regioisomer (**5**) by HCl evolved in the reaction. The reaction mixture using $CuCl_2$ was actually strongly acidic.



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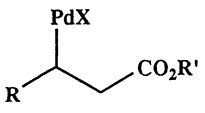

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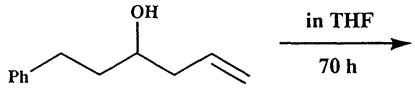
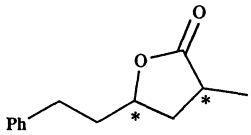
The treatment of 3-buten-1-ols (**6a**,**b**) in THF in a similar manner afforded the corresponding γ-butyrolactones (**7a**,**b**) in good yields as shown in the following Eqs. 1 and 2.[5]

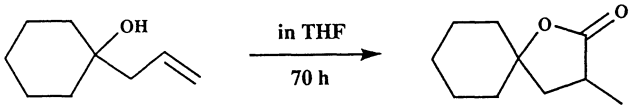


6a



(Eq. 1)

7a, 67%
Ratio of diastereoisomers
63:37

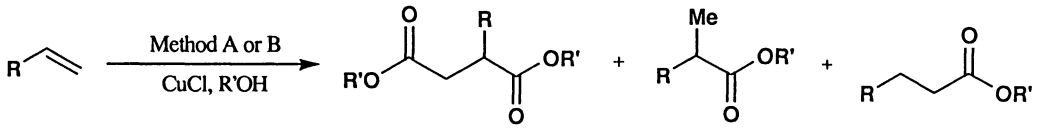


6b

7b, 76%
Mp 67—68 °C

(Eq. 2)

Table 2. Bis(alkoxycarbonylation) of Terminal Olefins with CuCl

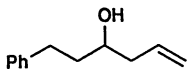
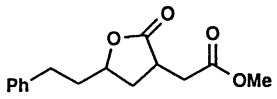
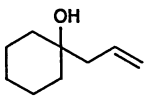
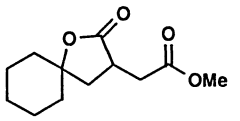
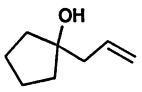
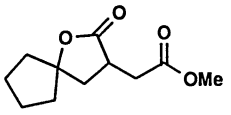
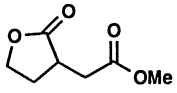
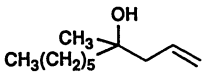
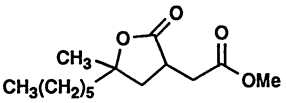
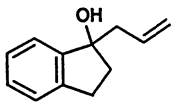
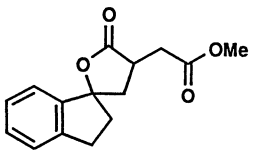


1 **8** **2** **3**

1	R	Method A[a] Solv.	Time/d	Yield of 8/%	1	Method B[b] Solv.	Time/d	Yield of 8/%	Yield of 2+3/%	Ratio of 2/3[c]
a,	$CH_3(CH_2)_7$	—	—	—	**a**,	MeOH	1	70	21	43/57
b,	$CH_3(CH_2)_8$	MeOH	9	Quant.	**b**,	MeOH	1	96	Trace	—
c,	$CH_3(CH_2)_9$	MeOH	8	89	**c**,	MeOH	3	89	11	45/55
d,	$CH_3(CH_2)_{11}$	EtOH	8.5	56	**d**,	MeOH/THF(1/1)	7	90	10	30/70
d,	$CH_3(CH_2)_{11}$	MeOH/THF(1/1)	8	84	**e**,	MeOH/THF(1/1)	7	87	12	10/90
e,	$CH_3(CH_2)_{15}$	EtOH	9	67	**f**,	MeOH	2.5	98	Trace	—
e,	$CH_3(CH_2)_{15}$	MeOH/THF(1/1)	9	92	**g**,	MeOH/THF(1/1)	6	71[d]	—	—
f,	$Ph(CH_2)_2$	MeOH	8	97	**g**,	MeOH	21 h[e]	88	—	—
g,	$PhOCH_2$	—	—	—	**h**,	MeOH/THF(1/1)	6	50[f]	—	—
h,	$TsCH_2$	—	—	—	**h**,	MeOH	18 h[g]	71	—	—
i,	$Ts(CH_2)_2$	—	—	—	**i**,	MeOH	2.5	94	—	—
					i,	MeOH	11 h[g]	87	—	—

a) Pd–C (0.11 equiv), CuCl (3 equiv), CO (1 atm), at 25 °C in the dark. b) $PdCl_2$ (0.02 equiv), CuCl (1.5 equiv), CO/O_2 (ca. 1/1, v/v, 1 atm), at 25 °C. c) Determined by 400 MHz ^{1}H NMR spectra. d) 24% of **1g** was recovered. e) Carried out at 70 °C. f) 50% of **1h** was recovered. g) Carried out at 70 °C with 3.0 equiv of CuCl.

Table 3. Preparation of γ-Butyrolactone 2-Acetic Acid Esters from 3-Butenols[a)]

Entry	3-Butenols	Time	Products	Yield/%
1	**6a**, 	23 h	**9a**, 	90[b)]
2	**6b**, 	20 h	**9b**, 	80
3	**6c**, 	18 h	**9c**, 	86
4	**6d**, 	16 h	**9d**, 	76[c)]
5	**6e**, 	7 d	**9e**, 	94[b)]
6	**6f**, 	2 d	**9f**, 	80[b)]

a) $PdCl_2$ (0.1 equiv), CuCl (1.5 equiv), CO/O_2 (ca. 1/1, v/v, 1 atm), in MeOH at 25 °C. b) Ratios of diastereoisomers were determined by 400 MHz ^1H NMR spectra as follows: **9a** (68/32), **9e** (58/42), **9f** (54/46). c) Determined by GC [OV-17, 2 m×3 mm, N_2, 20 ml min^{-1}, 100—170 °C (20 °C min^{-1})] with internal standard, 1,2,3,4-tetrahydronaphthalene.

On the other hand, when copper(I) chloride was used in place of copper(II) chloride in the above reaction, diesters (succinates, **8a**—**i**) were selectively formed in high yields as well as the case of Pd–C catalyst (Method A) as shown in Table 2 (Method B). The reaction mixture was faintly acidic in contrast to the case of copper(II) chloride. Although the active species formed from copper(I) chloride in the present reaction is not yet clear, the pale green coloration suggests the formation of copper(II) species, at least in part, by oxidation with molecular oxygen. It is likely that the copper(II) species reacts further with carbon monoxide to afford (alkoxycarbonyl)chlorocopper [Cu(Cl)COOR] which is probably involved in the carbonylation of olefins under neutral conditions as described in the literature.[6)] It is noteworthy that the carbonylation reaction was remarkably retarded by the addition of equimolar amount of LiCl, NaCl, or KCl under similar conditions.

Recently Tamaru and his co-workers reported the interesting inter- and intramolecular bis(alkoxycarbonylation) of 3-buten-1-ols catalyzed by palladium(II).[7)] It prompted us to apply the present bis(alkoxycarbonylation) system to 3-buten-1-ols (**6a**—**f**). The results are summarized in Table 3. The reaction proceeded selectively to give the corresponding 2-oxotetrahydrofuran-3-acetic acid esters (**9a**—**f**) in high yields by the use of 0.1 equiv of $PdCl_2$ and 1.5 equiv of CuCl in spite of the absence of additives such as propylene oxide, triethyl orthoacetate, or *N*,*N*,*N*′,*N*′-tetramethylurea employed in the reported procedure.[7)]

Now it has become possible to control the mono- and bis(alkoxycarbonylation)s of olefins catalyzed by palladium(0) or palladium(II) simply employing copper(II) or copper(I) chloride under remarkably mild conditions.

Mechanistic studies and applications of the present carbonylation reactions are now in progress.

Experimental

All the melting points were determined with a micro melting apparatus (Yanagimoto-Seisakusho) and were uncorrected. The ^1H NMR, IR, and MS spectra were recorded on JEOL JNM-GX 400(400 MHz) FT-NMR spectrometer, JASCO IRA-1 diffraction grating infrared spectrometer, and Hitachi M-80 mass spectrometer, respectively. The chemical shifts of NMR are reported in the δ-scale relative to TMS as an internal standard.

Materials. All the solvents were distilled and stored over a drying agent. Thin-layer chromatography (TLC) was performed on Merck's silica gel 60 PF_{254} (Art. 7749). Terminal olefins (**1a**—**e**) were purified by distillation over active

carbon before use. CuCl was freshly prepared from copper sulfate.[8]

Mono(alkoxycarbonylation) of 1b with $CuCl_2$ (Method A). In a flask equipped with a balloon containing carbon monoxide (1 atm), 1-undecene (**1b**, 39 mg, 0.25 mmol) was added to a mixed dispersion of 5% Pd-C (58 mg, 0.11 equiv of Pd) and anhydrous $CuCl_2$ (from Wako Pure Chemical Industries, Ltd., 95% purity, 106 mg, 3.0 equiv) in absolute methanol (4 ml) at 25 °C. After stirring for 8 d at 25 °C, the reaction mixture was added dropwise to aqueous 10% $NaHCO_3$ solution. The filtrate through Celite was diluted by ethyl acetate. The organic layer was separated and successively washed with water and brine, and dried over sodium sulfate. The residue obtained by evaporation of the solvent was subjected to preparative TLC (SiO_2, hexane/ethyl acetate=10/1, v/v) to afford 54 mg of a mixture of regioisomeric monoesters (**2b**/**3b**=81/19, quantitative yield) as a colorless oil. MS *m/z* 214 (M^+, 2.02%), 101 (29.47), 88(100.00), 87 (11.00), 74 (11.53), 57 (10.00), 43 (10.46); IR (neat) 2920, 2850, 1730, 1460, 1425, 1365, 1250, 1185, 1155, 725 cm^{-1};^1H NMR of **2b** (R′=Me) ($CDCl_3$) δ=0.88 (t, *J*=6.87 Hz, 3H), 1.14 (d, *J*=7.02 Hz, 3H), 1.26 (s, 14H), 1.40 (m, 1H), 1.65 (m, 1H), 2.43 (sextuplet, *J*=7.02 Hz, 1H), 3.66 (s, 3H);^1H NMR of **3b** (R′=Me) ($CDCl_3$) δ=0.88 (t, *J*=6.87 Hz, 3H), 1.26 (s, 16H), 1.65 (m, 2H), 2.31 (t, *J*=7.48 Hz, 2H), 3.66 (s, 3H).

In a similar manner, other monoesters (**2c—f**/**3c—f**) were prepared from the corresponding terminal olefins (**1c—f**).

Methyl 2-Methyldodecanoate (2c, R′=Me) and Methyl Tridecanoate (3c, R′=Me): An oil (a mixture of regioisomers); MS *m/z* 229 (M^++1, 0.89%), 228 (M^+, 3.79), 143 (7.44), 115 (5.59), 101 (33.75), 88 (100.00), 87 (15.29), 74 (6.27); IR (neat) 2920, 2840, 1730, 1455, 1420, 1370, 1185, 1150, 710 cm^{-1}; ^1H NMR of **2c** ($CDCl_3$) δ=0.88 (t, *J*=7.02 Hz, 3H), 1.14 (d, *J*=7.02, 3H), 1.26 (s, 16H), 1.40 (m, 1H), 1.65 (m, 1H), 2.43 (sextuplet, *J*=7.02 Hz, 1H), 3.67 (s, 3H); ^1H NMR of **3c** ($CDCl_3$) δ=0.88 (t, *J*=7.02 Hz, 3H), 1.26 (s, 18H), 1.65 (m, 2H), 2.31 (t, *J*=7.02 Hz, 2H), 3.67 (s, 3H); **2c**/**3c**=78/22.

Ethyl 2-Methyltetradecanoate (2d, R′=Et) and Ethyl Pentadecanoate (3d, R′=Et): An oil (a mixture of regioisomers); MS *m/z* 271 (M^++1, 18.60%), 270 (M^+, 31.28), 227 (11.02), 225 (11.97), 213 (12.90), 157 (14.59), 116 (11.24), 115 (32.30), 102 (100.00), 101 (15.93), 88 (12.68), 74 (11.18), 43 (10.07); IR (neat) 2935, 2860, 1740, 1465, 1380, 1180, 1160 cm^{-1}; ^1H NMR of **2d** ($CDCl_3$) δ=0.92 (t, *J*=7.02 Hz, 3H), 1.17 (d, *J*=7.02 Hz, 3H), 1.29 (m, 23H), 1.43 (m, 1H), 1.65 (m, 1H), 2.44 (sextuplet, *J*=7.02 Hz, 1H), 4.16 (q, *J*=7.02 Hz, 2H); ^1H NMR of **3d** ($CDCl_3$) δ=0.92 (t, *J*=7.02 Hz, 3H), 1.29 (m, 25H), 1.65 (m, 2H), 2.32 (t, *J*=7.32 Hz, 2H), 4.16 (q, *J*=7.02 Hz, 2H); **2d**/**3d**=72/28.

Methyl 2-Methyltetradecanoate (2d, R′=Me) and Methyl Pentadecanoate (3d, R′=Me): An oil (a mixture of regioisomers); MS *m/z* 257 (M^++1, 1.31%), 256 (M^+, 5.60), 101 (16.82), 88 (100.00); IR (neat) 2930, 2860, 1740, 1455, 1370, 1190, 1160 cm^{-1}; ^1H NMR of **2d** ($CDCl_3$) δ=0.88 (t, *J*=7.02 Hz, 3H), 1.14 (d, *J*=7.02 Hz, 3H), 1.26 (s, 20H), 1.40 (m, 1H), 1.65 (m, 1H), 2.43 (sextuplet, *J*=7.02 Hz, 1H), 3.66 (s, 3H); ^1H NMR of **3d** ($CDCl_3$) δ=0.88 (t, *J*=7.02 Hz, 3H), 1.26 (s, 22H), 1.65 (m, 2H), 2.30 (t, *J*=7.32 Hz, 2H), 3.67 (s, 3H); **2d**/**3d**=85/15 (by Method B).

Ethyl 2-Methyloctadecanoate (2e, R′=Et) and Ethyl Nonadecanoate (3e, R′=Et): An oil (a mixture of regioisomers); MS *m/z* 327 (M^++1, 14.03%), 326 (M^+, 31.35), 269 (12.02), 185 (13.25), 157 (22.19), 129 (19.18), 115 (45.77), 102 (100.00), 101 (22.53), 83 (14.64), 74 (17.62), 57 (21.55); IR (neat) 2920, 2850, 1725, 1460, 1370, 1175 cm^{-1}; ^1H NMR of **2e** ($CDCl_3$) δ=0.88 (t, *J*=6.72 Hz, 3H), 1.13 (d, *J*=7.02 Hz, 3H), 1.25 (m, 31H), 1.40 (m, 1H), 1.64 (m, 1H), 2.40 (sextuplet, *J*=7.02 Hz, 1H), 4.10 (q, *J*=7.02 Hz, 2H); ^1H NMR of **3e** ($CDCl_3$) δ=0.88 (t, *J*=6.72 Hz, 3H), 1.25 (m, 33H), 1.64 (m, 2H), 2.28 (t, *J*=7.32 Hz, 2H), 4.10 (q, *J*=7.02 Hz, 2H); **2e**/**3e**=77/23.

Methyl 2-Methyloctadecanoate (2e, R′=Me) and Methyl Nonadecanoate (3e, R′=Me): An oil (a mixture of regioisomers); MS *m/z* 313 (M^++1, 5.49%), 312 (M^+, 21.71), 101 (36.66), 88 (100.00); IR (neat) 2930, 2860, 1735, 1455, 1190, 1160 cm^{-1}; ^1H NMR of **2e** ($CDCl_3$) δ=0.88 (t, *J*=7.02 Hz, 3H), 1.13 (d, *J*=7.02 Hz, 3H), 1.26 (s, 28H), 1.40 (m, 1H), 1.65 (m, 1H), 2.42 (sextuplet, *J*=7.02 Hz, 1H), 3.66 (s, 3H); ^1H NMR of **3e** ($CDCl_3$) δ=0.88 (t, *J*=7.02 Hz, 3H), 1.26 (s, 30H), 1.65 (m, 2H), 2.30 (t, *J*=7.63 Hz, 2H), 3.66 (s, 3H); **2e**/**3e**=83/17 (by Method B).

Methyl 2-Methyl-4-phenylbutanoate (2f, R′=Me) and Methyl 5-Phenylpentanoate (3f, R′=Me): An oil (a mixture of regioisomers); MS *m/z* 192 (M^+, 5.96%), 105 (8.13), 104 (9.52), 91 (33.28), 88 (100.00), 57 (15.07); IR (neat) 3000, 2900, 1720, 1590, 1480, 1440, 1420, 1365, 1230, 1190, 1150, 1040, 735, 690 cm^{-1}; ^1H NMR of **2f** ($CDCl_3$) δ=1.18 (d, *J*=7.02 Hz, 3H), 1.71 (m, 1H), 2.04 (m, 1H), 2.47 (sextuplet, *J*=7.02 Hz, 1H), 2.60 (t, *J*=7.93 Hz, 2H), 3.67 (s, 3H), 7.17 (m, 3H), 7.27 (m, 2H); ^1H NMR of **3f** ($CDCl_3$) δ=1.66 (m, 4H), 2.32 (t,*J*=7.02 Hz, 2H), 2.75 (m, 1H), 2.95 (m, 1H), 2.60 (t, *J*=7.93 Hz, 2H), 3.67 (s, 3H), 7.17 (m, 3H), 7.27 (m, 2H); **2f**/**3f**=96/4.

Mono(alkoxycarbonylation) of 1a with $CuCl_2$ (Method B). In a flask equipped with balloons containing carbon monoxide (1 atm) and oxygen (1 atm), 1-decene (**1a**, 35 mg, 0.25 mmol) was added dropwise to a mixture of $[PdCl_2(CH_3CN)_2]$ (6 mg, 0.02 equiv) and anhydrous $CuCl_2$ (95% purity, 53 mg, 1.5 equiv) in absolute methanol (2 ml) and THF (2 ml) at 25 °C. After stirring for 24 h at 25 °C, the reaction mixture was added dropwise to aqueous 10% $NaHCO_3$ solution. The filtrate through Celite was treated with a small amount of aqueous KCN solution to deactivate palladium catalyst and diluted by ethyl acetate. The organic layer was separated and successively washed with water and brine, and dried over sodium sulfate. The residue obtained by evaporation of the solvent was subjected to preparative TLC (SiO_2, hexane/ethyl acetate=10/1, v/v) to afford 46 mg of a mixture of regioisomeric monoesters (**2a**/**3a**=85/15, 92% yield) as a colorless oil. MS *m/z* 200 (M^+, 5.28%), 101 (29.12), 88 (100.00), 87 (56.67), 74 (79.26); IR (neat) 2940, 2860, 1735, 1455, 1430, 1375, 1190, 1160 cm^{-1}; ^1H NMR of **2a** (R′=Me) ($CDCl_3$) δ=0.88 (t, *J*=7.02 Hz, 3H), 1.13 (d, *J*=7.02 Hz, 3H), 1.26 (s, 12H), 1.40 (m, 1H), 1.64 (m, 1H), 2.43 (sextuplet, *J*=7.02 Hz, 1H), 3.67 (s, 3H) ; ^1H NMR of **3a** (R′=Me) ($CDCl_3$) δ=0.88 (t, *J*=7.02 Hz, 3H), 1.26 (s, 14H), 1.64 (m, 2H), 2.30 (t, *J*=7.62 Hz, 2H), 3.67 (s, 3H).

In a similar manner, other monoesters (**2b—i**/**3b—i**) and lactones (**7a,b**) were prepared from the corresponding terminal olefins (**1b—i**) and 3-buten-1-ols (**6a,b**), respectively. Regioisomers, **2g—i** and **3g—i**, could be separated each other by preparative TLC. Their spectral data except **2b—f**/**3b—f**, those of which have been shown above, are given in the following.

Methyl 2-Methyl-3-phenoxypropanoate (2g, R′=Me): An oil; MS *m/z* 194 (M^+, 40.60%), 149 (99.24), 137 (46.36), 101 (29.07), 94 (30.32), 71 (44.86), 69 (100.00), 59 (40.10); IR (neat) 3030, 2980, 2950, 2880, 1730, 1595, 1580, 1490, 1460, 1430,

1240, 1195, 1165, 1030, 745, 680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.30 (d, J=7.02 Hz, 3H), 2.95 (m, 1H), 3.72 (s, 3H), 3.99 (dd, J=9.16, 6.71 Hz, 1H), 4.19 (dd, J=9.16, 6.14 Hz, 1H), 6.90 (m, 2H), 6.95 (m, 1H), 7.27 (m, 2H).

Methy 2-Methyl-3-phenoxybutanoate (3g, R′=Me): An oil; MS m/z 194 (M^+, 12.63%), 163 (15.04), 101 (100.00), 94 (35.12), 59 (42.09), 28 (33.68); IR (neat) 3020, 2920, 1730, 1590, 1580, 1480, 1460, 1430, 1230, 1160, 1070, 1030, 740, 680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.11 (m, 2H), 2.53 (t, J=7.32 Hz, 1H), 3.69 (s, 3H), 4.01 (t, J=6.11 Hz, 2H), 6.88 (m, 2H), 6.94 (m, 1H), 7.26 (m, 2H).

Methyl 2-Methyl-3-(*p*-tolylsulfonyl)propanoate (2h, R′=Me): Mp 86—87 °C (recrystallized from hexane/ethyl acetate); MS m/z 257 (M^++1, 1.98%), 256 (M^+, 12.28), 155 (28.25), 139 (53.38), 132 (13.80), 101 (100.00), 92 (49.40), 91 (78.49), 73 (22.33), 69 (35.37), 59 (70.00); IR (KBr) 2995, 2970, 1735, 1590, 1450, 1430, 1380, 1300, 1140, 880, 830, 810, 760, 680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.31 (d, J=7.02 Hz, 3H), 2.45 (s, 3H), 3.01 (m, 1H), 3.07 (dd, J=14.04, 5.19 Hz, 1H), 3.62 (s, 3H), 3.67 (dd, J=14.04, 7.33 Hz, 1H), 7.36 (d, J=8.24 Hz, 2H), 7.78 (d, J=8.24 Hz, 2H). Found: C, 56.18; H, 6.17%. Calcd for $C_{12}H_{16}O_4S$: C, 56.23; H, 6.29%.

Methyl 4-(*p*-Tolylsulfonyl)butanoate (3h, R′=Me): An oil; MS m/z 257 (M^++1, 0.39%), 256 (M^+, 2.22), 225 (14.38), 183 (6.63), 155 (6.30), 139 (9.18), 101 (100.00), 91 (20.55), 59 (39.90); IR (neat) 2965, 2940, 1735, 1590, 1435, 1310, 1300, 1280, 1140, 1080, 810, 720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.02 (m, 2H), 2.45 (s, 3H), 2.46 (t, J=7.17 Hz, 2H), 3.15 (m, 2H), 3.65 (s, 3H), 7.37 (d, J=8.24 Hz, 2H), 7.79 (d, J=8.24 Hz, 2H).

Methyl 2-Methyl-4-(*p*-tolylsulfonyl)butanoate (2i, R′=Me): An oil; MS m/z 271 (M^++1, 0.35%), 270 (M^+, 0.91), 239 (6.92), 183 (6.33), 157 (6.51), 140 (6.10), 139 (6.53), 115 (100.00), 91 (14.13), 59 (39.85); IR (neat) 3040, 2960, 1730, 1595, 1450, 1380, 1300, 1200, 1140, 1085, 1050, 810, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.16 (d, J=7.01 Hz, 3H), 1.87 (m, 1H), 2.00 (m, 1H), 2.46 (s, 3H), 2.56 (m, 1H), 3.11 (m, 2H), 3.65 (s, 3H), 7.36 (d, J=8.09 Hz, 2H), 7.77 (d, J=8.09 Hz, 2H).

Methyl 5-(*p*-Tolylsulfonyl)pentanoate (3i, R′=Me): An oil; MS m/z 271 (M^++1, 0.28%), 270 (M^+, 1.04), 239 (8.59), 155 (5.98), 115 (100.00), 92 (12.89), 91 (17.87), 83 (26.01), 73 (40.50), 59 (13.91), 55 (41.67); IR (neat) 3040, 2960, 1735, 1600, 1440, 1300, 1285, 1145, 1095, 910, 810, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.72 (m, 4H), 2.30 (t, J=7.02 Hz, 2H), 2.46 (s, 3H), 3.07 (t, J=7.33 Hz, 2H), 3.65 (s, 3H), 7.36 (d, J=8.24 Hz, 2H), 7.78 (d, J=8.24 Hz, 2H).

2-Methyl-6-phenyl-4-hexanolide (7a): An oil (a mixture of diastereoisomers); MS m/z 204 (M^+, 43.07%), 131 (42.27), 130 (100.00), 117 (50.72), 92 (75.94), 91 (88.26); IR (neat) 3040, 2940, 1770, 1600, 1490, 1450, 1375, 1355, 1180, 1160, 1020, 925, 745, 695 cm^{-1}; ^{1}H NMR of a major diastereoisomer (**M**) ($CDCl_3$, by COSY) δ=1.27 (d, J=7.02 Hz, 3H), 1.53 (m, 1H), 1.81—2.07 (m, 2H), 2.46 (m, 1H), 2.60—2.78 (m, 3H), 4.31 (m, 1H), 7.20 (m, 3H), 7.28 (m, 2H); ^{1}H NMR of a minor diastereoisomer (**m**) ($CDCl_3$, by COSY) δ=1.28 (d, J=7.33 Hz, 3H), 1.90—2.15 (m, 4H), 2.70—2.87 (m, 3H), 4.49 (m, 1H), 7.20 (m, 3H), 7.28 (m, 2H); **M**/**m**=63/37.

3-Methyl-1-oxaspiro[4.5]decan-2-one (7b): Mp 67—68 °C (recrystallized from hexane, lit, 68—70 °C,[9a] 70.5—71 °C[9b,c]); MS m/z 169 (M^++1, 1.47%), 168 (M^+, 10.80), 125 (100), 124 (31.11), 112 (20.87), 82 (39.66), 81 (28.22), 55 (43.90); IR (KBr) 2940, 2860, 1765, 1440, 1210, 1130, 960, 950, 920 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.27 (d, J=7.33 Hz, 3H), 1.39 (m, 1H), 1.45—1.65 (m, 5H), 1.58 (dd, J=12.81, 11.29 Hz, 1H), 1.65—1.82 (m, 4H), 2.34 (dd, J=12.81, 9.16 Hz, 1H), 2.78 (m, 1H).

Bis(alkoxycarbonylation) of 1b with CuCl (Method A). In a flask equipped with a balloon containing carbon monoxide (1 atm), 1-undecene (**1b**, 39 mg, 0.25 mmol) was added to a mixed dispersion of 5% Pd–C (58 mg, 0.11 equiv of Pd) and CuCl (74 mg, 3.0 equiv) in absolute methanol (4 ml) at 25 °C. After stirring for 9 d at 25 °C, the reaction mixture was added dropwise to aqueous 10% $NaHCO_3$ solution. The filtrate through Celite was diluted by ethyl acetate. The organic layer was successively washed with water and brine, and dried over sodium sulfate. The residue obtained by evaporation of the solvent was subjected to preparative TLC (SiO_2, hexane/ethyl acetate=15/1, v/v) to afford 68 mg of diesters [**8b** (R′=Me), quantitative yield] as a colorless oil. MS m/z 273 (M^++1, 3.75%), 241 (39.63), 199 (43.25), 170 (30.32), 146 (96.68), 138 (23.91), 114 (100.00), 97 (16.45), 87 (20.92), 83 (15.93), 55 (17.30); IR (neat) 2910, 2840, 1730, 1430, 1350, 1250, 1185, 1150, 995, 905, 725 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.88 (t, J=6.71 Hz, 3H), 1.26 (m, 14H), 1.51 (m, 1H), 1.63 (m, 1H), 2.43 (dd, J=16.48, 5.19 Hz, 1H), 2.71 (dd, J=16.48 Hz, 9.15 Hz, 1H), 2.83 (m, 1H), 3.67 (s, 3H), 3.70 (s, 3H).

In a similar manner, other diesters (**8c—f**) were prepared from the corresponding terminal olefins (**1c—f**).

Dimethyl 2-Decylsuccinate (8c, R′=Me): An oil ; MS m/z 287 (M^++1, 2.25%), 286 (M^+, 0.19), 255 (20.54), 213 (31.77), 170 (24.45), 146 (100.00), 138 (16.41), 114 (76.57), 97 (11.86), 87 (12.88), 55 (14.93); IR (neat) 2930, 2860, 1740, 1460, 1435, 1370, 1240, 1200, 1180 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.88 (t, J=6.72 Hz, 3H), 1.25 (s, 16H), 1.50 (m, 1H), 1.62 (m, 1H), 2.43 (dd, J=16.48, 5.19 Hz, 1H), 2.71 (dd, J=16.48, 9.16 Hz, 1H), 2.82 (m, 1H), 3.67 (s, 3H), 3.69 (s, 3H).

Diethyl 2-Dodecylsuccinate (8d, R′=Et): An oil; MS m/z 343 (M^++1, 28.34%), 297 (67.42), 255 (39.36), 184 (37.43), 174 (100.00), 138 (23.41), 128 (84.72), 101 (16.54), 97 (16.71), 55 (17.69), 43 (19.84); IR (neat) 2935, 2860, 1745, 1735, 1465, 1375, 1260, 1175, 1160, 1030 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.83 (t, J=6.72 Hz, 3H), 1.20 (m, 26H), 1.45 (m, 1H), 1.57 (m, 1H), 2.36 (dd, J=16.18, 5.19 Hz, 1H), 2.64 (dd, J=16.18, 9.46 Hz, 1H), 2.76 (m, 1H), 4.09 (m, 4H).

Dimethyl 2-Dodecylsuccinate (8d, R′=Me): Mp 34—35 °C (not recrystallized); MS m/z 315 (M^++1, 0.30%), 283 (10.70), 241 (21.90), 170 (26.96), 156 (10.45), 146 (100.00), 138 (17.03), 114 (60.74), 97 (10.78), 87 (9.44), 83 (9.60), 55 (8.84); IR (neat, melted) 2900, 2830, 1720, 1440, 1420, 1145 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.88 (t, J=6.87 Hz, 3H), 1.25 (s, 20H), 1.50 (m, 1H), 1.63 (m, 1H), 2.43 (dd, J=16.48, 4.89 Hz, 1H), 2.71 (dd, J=16.48, 9.46 Hz, 1H), 2.84 (m, 1H), 3.67 (s, 3H), 3.70 (s, 3H).

Diethyl 2-Hexadecylsuccinate (8e, R′=Et): An oil; MS m/z 399 (M^++1, 0.93%), 398 (M^+, 0.91), 353 (17.41), 311 (16.46), 184 (26.20), 174 (100.00), 138 (15.59), 128 (48.71), 101 (10.99), 97 (12.02), 83 (10.93), 57 (11.50); IR (neat) 2930, 2860, 1735, 1460, 1370, 1250, 1170, 1160, 1025 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.91 (t, J=6.72 Hz, 3H), 1.29 (m, 34H), 1.53 (m, 1H), 1.67 (m, 1H), 2.44 (dd, J=16.33, 5.04 Hz, 1H), 2.72 (dd, J=16.33, 9.32 Hz, 1H), 2.84 (m, 1H), 4.18 (m, 4H).

Dimethyl 2-Hexadecylsuccinate (8e, R′=Me): Mp 35 °C (not recrystallized); MS m/z 371 (M^++1, 1.03%), 370 (M^+, 1.09), 339 (15.56), 297 (23.54), 170 (34.56), 156 (12.37), 146 (100.00), 138 (14.95), 114 (37.74), 97 (10.75); IR (KBr) 2920, 2840, 1730, 1720, 1460, 1430, 1370, 1355, 1205, 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.88 (t, J=6.87 Hz, 3H), 1.26 (s, 28H), 1.51 (m, 1H), 1.63 (m, 1H), 2.43 (dd, J=16.33, 4.88 Hz, 1H), 2.71 (dd, J=16.33, 9.46 Hz, 1H), 2.83 (m, 1H), 3.67 (s, 3H),

3.70 (s, 3H).

Dimethyl 2-(2-Phenylethyl)succinate (8f, R′=Me): An oil MS *m/z* 251 (M^++1, 5.36%), 250 (M^+, 8.96), 187 (57.43), 146 (100.00), 144 (11.01), 117 (11.51), 114 (77.49), 104 (31.50), 91 (24.76); IR (neat) 3020, 2950, 2850, 1735, 1600, 1495, 1435, 1365, 1260, 1200, 1160, 730, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.83 (m, 1H), 1.98 (m, 1H), 2.48 (dd, *J*=16.48, 5.19 Hz, 1H), 2.62 (m, 2H), 2.76 (dd, *J*=16.48, 9.16 Hz, 1H), 2.88 (m, 1H), 3.66 (s, 3H), 3.70 (s, 3H), 7.17 (m, 3H), 7.27 (m, 2H).

Bis(alkoxycarbonylation) of 1a with CuCl (Method B). In a flask equipped with balloons containing carbon monoxide (1 atm) and oxygen (1 atm), 1-decene (**1a**, 35 mg, 0.25 mmol) was added to a mixed dispersion of $PdCl_2$ (1 mg, 0.02 equiv) and anhydrous CuCl (37 mg, 1.5 equiv) in absolute methanol (4 ml) at 25 °C. After stirring for 1 d at 25 °C, the reaction mixture was added dropwise to aqueous 10% $NaHCO_3$ solution. The filtrate through Celite was treated with a small amount of aqueous KCN solution to deactivate palladium catalyst and diluted by ethyl acetate. The organic layer was successively washed with water and brine, and dried over sodium sulfate. The residue obtained by evaporation of the solvent was subjected to preparative TLC (SiO_2, hexane/ethyl acetate=10/1, v/v) to afford 45 mg of diester [**8a**(R′=Me), 70%] as a colorless oil accompanied by 10 mg of monoesters (**2a**/**3a**=43/57, 21% yield). **8a**:[10] MS *m/z* 259 (M^++1, 0.59%), 227 (22.03), 185 (44.04), 170 (21.70), 146(100.00), 114 (97.01); IR (neat) 2930, 2860, 1735, 1430, 1160, 1000 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (t, *J*=6.87 Hz, 3H), 1.26 (m, 12H), 1.51 (m, 1H), 1.62 (m, 1H), 2.43 (dd, *J*=16.48, 5.04 Hz, 1H), 2.71 (dd, *J*=16.48, 9.46 Hz, 1H), 2.84 (m, 1H), 3.67 (s, 3H), 3.70 (s, 3H).

In a similar manner, other diesters (**8b**—**i**) and 2-oxotetrahydrofuran-3-acetic acid esters (**9a**—**f**) were prepared from the corresponding terminal olefins (**1b**—**i**) and 3-buten-1-ols (**6a**—**f**), respectively. Their spectral data except **8b**—**f**, those of which have been shown above, are given in the following.

Dimethyl 2-(Phenoxymethyl)succinate (8g, R′=Me): An oil; MS *m/z* 253 (M^++1, 2.86%), 252 (M^+, 18.75), 189 (67.53), 160 (18.92), 159 (100.00), 127 (71.35), 99(29.69), 94 (21.59); IR (neat) 3005, 2960, 1730, 1590, 1580, 1490, 1460, 1435, 1230, 1160, 1070, 1030, 995, 900, 745, 720, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.74 (dd, *J*=17.09, 5.80 Hz, 1H), 2.95 (dd, *J*=17.09, 7.93 Hz, 1H), 3.33 (m, 1H), 3.70 (s, 3H), 3.74 (s, 3H), 4.21 (d, *J*=5.81 Hz, 2H), 6.88 (d, *J*=7.63 Hz, 2H), 6.96 (t, *J*=7.33 Hz, 1H), 7.27 (m, 2H).

Dimethyl 2-(*p*-Tolylsulfonylmethyl)succinate (8h, R′=Me): An oil ; MS *m/z* 315 (M^++1, 0.51%), 314 (M^+, 1.62), 159 (100.00), 139 (25.31), 127 (65.85), 99 (20.52), 91 (26.04); IR (neat) 3020, 2960, 2840, 1730, 1660, 1585, 1430, 1400, 1360, 1310, 1290, 1280, 1200, 1140, 1080, 1030, 820, 800, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.46 (s, 3H), 2.91 (d, *J*=6.10 Hz, 2H), 3.29 (m, 1H), 3.38 (dd, *J*=14.35, 7.63 Hz, 1H), 3.67 (dd, *J*=14.35, 5.19 Hz, 1H), 3.67 (s, 3H), 3.68 (s, 3H), 7.37 (d, *J*=8.09 Hz, 2H), 7.79 (d, *J*=8.09 Hz, 2H).

Dimthyl 2-[2-(*p*-Tolylsulfonyl)ethyl]succinate (8i, R′=Me): An oil; MS *m/z* 329 (M^++1, 0.09%), 328 (M^+, 0.16), 297 (13.25), 173 (100.00), 141 (26.60), 139 (13.24), 113 (28.99), 91 (9.46), 71 (18.36); IR (neat) 3000, 2960, 1730, 1590, 1430, 1400, 1310, 1295, 1280, 1200, 1160, 1140, 1080, 1010, 910, 805, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.00 (m, 2H), 2.44 (dd, *J*=16.78, 5.80 Hz, 1H), 2.45 (s, 3H), 2.70 (dd, *J*=16.78, 8.24 Hz, 1H), 2.93 (m, 1H), 3.14 (m, 2H), 3.65 (s, 3H), 3.67 (s, 3H), 7.36 (d, *J*=8.09 Hz, 2H). 7.76 (d, *J*=8.09 Hz, 2H).

2-(Methoxycarbonymethyl)-6-phenyl-4-hexanolide (9a):[7b] An oil (a mixture of diastereoisomers); MS *m/z* 263 (M^++1, 5.73%), 262 (M^+, 29.12), 230 (15.66), 170 (18.43), 132 (27.07), 131 (21.43), 130 (100.00), 92 (44.47), 91 (53.42), 59 (6.81); IR (neat) 3000, 2920, 1760, 1725, 1590, 1480, 1425, 1360, 1250, 1150, 1020, 980, 900, 720, 690 cm^{-1}; ^1H NMR of a major diastereoisomer (**M**) ($CDCl_3$) δ=1.82—2.25 (m, 4H), 2.50—2.93 (m, 4H), 2.93—3.10 (m, 1H), 3.70 (s, 3H), 4.54 (m, 1H), 7.20 (m, 3H), 7.29 (m, 2H); ^1H NMR of a minor diastereoisomer (**m**) ($CDCl_3$) δ=1.82—2.25 (m, 4H), 2.50—2.93 (m, 4H), 2.93—3.10 (m, 1H), 3.70 (s, 3H), 4.38 (m, 1H), 7.20 (m, 3H), 7.29 (m, 2H); **M**/**m**=68/32.

3-(Methoxycarbonylmethyl)-1-oxaspiro[4.5]decan-2-one (9b):[7b] An oil; MS *m/z* 227 (M^++1, 13.04%), 226 (M^+, 79.63), 195 (48.56), 183 (86.10), 166 (100.00), 155 (66.80), 153 (58.32), 151 (35.84), 150 (82.71), 132 (27.67), 123 (22.69), 108 (25.87), 100 (27.57), 67 (25.13); IR (neat) 2960, 2880, 1770, 1740, 1205 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.39—1.84 (m, 10H), 1.69 (t, *J*=12.11 Hz, 1H), 2.44 (dd, *J*=12.11, 9.31 Hz, 1H), 2.53 (dd, *J*=10.04, 9.15 Hz, 1H), 2.90 (dd, *J*=17.04, 4.27 Hz, 1H), 3.13 (m, 1H).

3-(Methoxycarbonylmethyl)-1-oxaspiro[4.4]nonan-2-one (9c): An oil; MS *m/z* 212 (M^+, 1.89%), 183 (41.69), 181 (39.00), 155 (37.14), 152 (100.00), 136 (74.62), 110 (37.98), 94 (56.60), 55 (29.20); IR (neat) 2900, 2840, 1760, 1720, 1420, 1320, 1360, 1260, 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.70—2.09 (m, 9H), 2.45 (dd, *J*=12.51, 8.55 Hz, 1H), 2.50 (dd, *J*=17.09, 9.16 Hz, 1H), 2.92 (dd, *J*=17.09, 3.97 Hz, 1H), 3.13 (m, 1H), 3.71 (s, 3H).

2-(Methoxycarbonylmethyl)-4-butanolide (9d):[7b] An oil; MS *m/z* 159 (M^++1, 1.97%), 127 (37.80), 114 (16.88), 82 (16.91), 72 (22.41), 59 (57.33), 55 (100.00); IR (neat) 2945, 2910, 1760, 1725, 1430, 1360, 1260, 1200, 1145, 1015 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.05 (m, 1H), 2.51—2.59 (m, 2H), 2.89—3.01 (m, 2H), 3.72 (s, 3H), 4.24 (m, 1H), 4.41 (dt, *J*=8.85, 1.83 Hz, 1H).

4-Methy1-2-(methoxycarbonylmethyl)-4-decanolide (9e): An oil (a mixture of diastereoisomers); MS *m/z* 257 (M^++1, 0.38%), 171 (100.00), 143 (25.36), 139 (13.64), 111 (10.33); IR (neat) 2950, 2880, 1770, 1745, 1460, 1440, 1385, 1290, 1240, 1190, 1175, 1140 cm^{-1}; ^1H NMR of a major diastereoisomer (**M**) ($CDCl_3$) δ=0.89 (t, *J*=7.02 Hz, 3H), 1.22—1.40 (m, 8H), 1.44 (s, 3H), 1.55—1.90 (m, 3H), 2.45 (dd, *J*=11.81, 8.85 Hz, 1H), 2.55 (dd, *J*=11.59, 8.85 Hz, 1H), 2.89 (dd, *J*=7.63, 3.96 Hz, 1H), 3.14 (m, 1H), 3.70 (s, 3H); ^1H NMR of a minor diastereoisomer (**m**) ($CDCl_3$) δ=0.89 (t, *J*=7.02 Hz, 3H), 1.22—1.40 (m, 8H), 1.37 (s, 3H), 1.55—1.90 (m, 3H), 2.30 (dd, *J*=12.52, 8.85 Hz, 1H), 2.51 (dd, *J*=11.59, 8.85 Hz, 1H), 2.93 (dd, *J*=7.63, 3.96 Hz, 1H), 3.14 (m, 1H), 3.70 (s, 3H); **M**/**m**=58/42.

4-(Methoxycarbonylmethyl)spiro[furan-2(3*H*),1′-indan]-5(4*H*)-one (9f): An oil (a mixture of diastereoisomers); MS *m/z* 261 (M^++1, 5.08%), 260 (M^+, 27.41), 229 (36.52), 216 (46.17), 184 (67.52), 143 (100.00), 133 (53.64), 128 (80.13), 100 (94.33); IR (neat) 3030, 2960, 1760, 1730, 1600, 1450, 1430, 1360, 1320, 1250, 1210, 1190, 1165, 1140, 980, 900, 750, 720 cm^{-1}; ^1H NMR of a major diastereoisomer (**M**) ($CDCl_3$) δ=2.22—2.43 (m, 2H), 2.56—2.71 (m, 2H), 2.85—3.02 (m, 3H), 3.06—3.15 (m, 1H), 3.48 (m, 1H), 3.73 (s, 3H), 7.24—7.39 (m, 4H); ^1H NMR of a minor diastereoisomer (**m**) ($CDCl_3$) δ=2.22—2.43 (m, 3H), 2.56—2.71 (m, 2H), 2.85—3.02 (m, 2H), 3.06—3.16 (m, 1H), 3.27 (m, 1H), 3.73 (s, 3H), 7.24—7.39

(m, 4H); **M**/**m**=54/46.

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