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Supporting Information

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Palladium-Catalyzed Selective Anti-Markovnikov Oxidation of Allylic Esters**

Jia Jia Dong, Martín Fañanás-Mastral, Paul L. Alsters, Wesley R. Browne, and Ben L. Feringa**

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Note. All reagents are of commercial grade and used as received unless stated otherwise.

1. General Procedures and methods

Chromatography: Merck silica gel type 9385 230–400 mesh, TLC: Merck silica gel 60, 0.25 mm, with visualization by UV and cerium/molybdenum or potassium permanganate staining. Mass spectra were recorded on an AEI-MS-902 mass spectrometer (EI+) or a LTQ Orbitrap XL (ESI+). ¹H- and ¹³C-NMR spectra were recorded on a Varian AMX400 (400 and 100.59 MHz, respectively) using CDCl₃ as solvent. Chemical shift values are reported in ppm with the solvent resonance as the internal standard (CHCl₃: 7.26 for ¹H, 77.0 for ¹³C). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. ¹³C spectra were assigned based on APT ¹³C-NMR spectroscopy. All reactions were carried out under a nitrogen atmosphere using oven dried glassware and using standard Schlenk techniques.

2. Preparation of substrates

See section 7 for characterization data for all allylic esters.

Preparation and protection of branched allylic esters

A dry Schlenk tube was charged with aldehyde (10 mmol) and dry THF (40 mL) and cooled to 0 °C. Vinylmagnesium bromide (12 mL, 1.0 M in THF) was added dropwise to the mixture. Upon complete conversion (2 h), the reaction was quenched with saturated aqueous NH₄Cl (50 mL). The aqueous layer was extracted with EtOAc (2 x 50 mL). The combined organic layers were washed with brine (50 mL), dried over Na₂SO₄, and concentrated under reduced pressure. Purification by flash silica-gel chromatography (pentane / ether) yielded the desired allylic alcohol.

The allylic alcohol (10 mmol) and pyridine (20 mmol) were dissolved in CH₂Cl₂ (5.0 mL). The reaction mixture was cooled to 0 °C and charged dropwise with the acid chloride (10.3 mmol). Upon complete addition, the reaction mixture was allowed to warm to r.t. and conversion verified by TLC. The mixture was diluted with EtOAc (100 mL) and washed with aqueous 1N HCl (30 mL), water (30 mL) and brine (30 mL). The solution was concentrated under reduced pressure. Purification by flash silica-gel chromatography (pentane / ether) yielded the desired allylic ester.

Protection of linear allylic alcohols

Linear allylic alcohols were protected as for branched allylic alcohols where the corresponding allylic alcohols were available from commercial sources.

Preparing of protected linear allylic esters from their corresponding branched allylic esters

A solution of the allylic ester (5 mmol) in tBuOH (9.52 mL) and acetone (0.48 mL) under argon was treated with $[\text{PdCl}_2(\text{MeCN})_2]$ (10 mol%). The solution was stirred overnight after which conversion had reached in excess of 50 %. The solution was concentrated in vacuo. Purification by flash silica-gel chromatography (pentane / ether) yielded the linear allylic ester.

3. Optimization of conditions for catalyzed oxidation reactions

Table S1. Selectivity and conversion achieved in the oxidation of allylic esters with oxygen as terminal oxidant

a)

Entry	Conditions	Reaction time	A : M ^a	Comments
1	PdCl ₂ (10 mol%), CuCl (100 mol%), DMF:H ₂ O 7:1	3 days	1 : 5.5	73% isolated yield
2	PdCl ₂ (10 mol%), CuCl ₂ (50 mol%), DMF:H ₂ O 4:1	3 days	0 : 100	Reaction stops at 62% conv.
3	Na ₂ PdCl ₄ (10 mol%), CuCl (100 mol%), DMF:H ₂ O 1:1	5 days	0 : 100	----

^a Determined by ¹H-NMR spectral analysis of the crude reaction mixture

b)

Entry	Solvent	A : M ^a	Comments
1	DMF:H ₂ O 7:1	1 : 3	Full conv. after 2 days; 79% yield
2	DMF:H ₂ O 1:1	0 : 100	82% yield
3	DMF:H ₂ O 7:1 + 2 eq. HMPA	0 : 100	85% yield
4	DMF	--	No reaction, SM recovered
5	Acetonitrile	--	No reaction, SM recovered
6	DMF:H ₂ O 5:1	1 : 4.2	Full conv.
7	DMF:H ₂ O 15:1	1 : 3.7	Slower reaction; Full conv. not reached
8	tBuOH:H ₂ O 9:1	1.8 : 1	85% yield of combined yield (A and M)

^a Determined by ¹H-NMR analysis of the crude reaction mixture

Table S2. Selectivity and conversion achieved in the oxidation of protected allylic ester with various catalysts using *p*-benzoquinone as oxidant

<p>0.05 M</p> <p>cat. (10 mol%) p-benzoquinone (1 equiv.) tBuOH:H₂O 9:1</p> <p>A</p> <p>M</p>				
Entry	catalyst	Conv.	A : M	Comments ^a
1	PdCl ₂	full	2.1 : 1	Side product observed
2	PdCl ₂ (MeCN) ₂	full	3 : 1	Side product observed
3	Pd(OAc) ₂	0 %	-	No conversion
4	PdCl ₂ (o-Tol) ₂	0 %	-	No conversion
5	PdCl ₂ (COD)	0 %	-	No conversion
<p>cat. (10 mol%) p-benzoquinone (1 equiv.) tBuOH : acetone (24 : 1) r.t.</p> <p>2B</p> <p>2A</p> <p>2M</p> <p>2K</p>				
Entry	catalyst	Conv.	2A : 2M : (2L+2K)	
6	PdCl ₂ (MeCN) ₂	full	83 : 11 : 6	
7	none	0 %	---	
8	PdCl ₂	68 %	19 : 7 : 42	
9	PdCl ₂ (PPh ₃) ₂	0 %	---	
10	(η^3 -C ₃ H ₅) ₂ Pd ₂ Cl ₂	full	75 : 9 : 16	
11	PdCl ₂ (PhCN) ₂	full	84 : 10 : 6	

^a side product = corresponding linear alkene and oxidized linear alkene

Table S3. Selectivity and conversion achieved in the oxidation of allylic esters with different amount of water

Entry	Solvent ^c	Conv. ^b	2A : 2M : (2L+2K)
1	tBuOH / 100 eq. H ₂ O	full	71 : 24 : 5
2	tBuOH / 3 eq. H ₂ O	full	75 : 17 : 8
3 ^a	tBuOH / 3 eq. H ₂ O	full	68 : 19 : 13
4	tBuOH / 1.1 eq. H ₂ O	full	75 : 15 : 10
5	tBuOH / acetone (24 : 1) ^d	full	83 : 11 : 6

^a at 40 °C ^b reaction mixtures were stirred at r.t. until completion (by TLC) unless stated otherwise ^c keep the substrate concentrate at 0.025 M ^d volum ratio

Table S4. Selectivity and conversion achieved in the oxidation of allylic ester **2B with various oxidants**

Entry	oxidant	conversion	A : M
1	Benzoquinone (100 mol%)	full	2.9 : 1
3	2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (100 mol%)	0 %	--
4	tBuOOH(70% wt in H ₂ O) (100 mol%)	50 %	1 : 1
5	K ₃ [Fe(CN) ₆] (100 mol%)	0 %	--
6	Benzoquinone (200 mol%)	full	2.9 : 1
7	Benzoquinone (50 mol%)	60%	2.5 : 1
8	Dichloro-benzoquinone (100 mol%)	full	2.9 : 1

Table S5. Screening of solvent, temperature, reaction time and added water in the oxidation of 2B with 10 mol% [PdCl₂(MeCN)₂].

entry	time	H ₂ O	solvent	Temp.	result ^a
1	5 h	3.0 equiv.	t-amyl alcohol	r.t.	Low conversion
2	20 h	3.0 equiv.	t-amyl alcohol	r.t.	Full conv. A: M / 2.5 : 1
3	18 h	1.1 equiv.	t-amyl alcohol	r.t.	Full conv. A:M / 3.2:1
4	18 h	1.1 equiv.	tBuOH : t-amyl alcohol 24 : 1	r.t.	Full conv. A:M / 3.3:1
5	3 h	100 equiv	tBuOH	r.t.	Full conv. A:M / 2.2:1
6	5 h	3.0 equiv	tBuOH	r.t.	Full conv. A:M / 4.4:1 side products less than 10%
7	5.5 h	3.0 equiv	tBuOH (0.025 M)	r.t.	Full conv. A:M / 4.4:1 more than 10% side product
8	3 h	3.0 equiv	tBuOH	40 °C	Full conv. A:M / 3.5:1
9	5.5 h	1.1 equiv.	tBuOH	r.t.	Full conv. A : M / 4.9 : 1 10% side product
10	20 h 5 mol% Pd	1.1 equiv.	tBuOH	r.t.	Full conv. A : M / 4.2 : 1 17% side product
11	20 h 1 mol% Pd	1.1 equiv.	tBuOH	r.t.	Full conv. A : M / 4.8 : 1 10% side product
12	5.5 h	3.0 equiv.	tBuOH : iPrOH 24 : 1	r.t.	Full conv. A : M / 4.4 : 1
13	5.5 h	3.0 equiv	tBuOH : EtOH 24 : 1	r.t.	Full conv. A : M / 3.5 : 1
14	4 h	1.0 equiv.	tBuOH : iPrOH 24 : 1	r.t.	Full conv. A : M / 5 : 1 14.5% side product
15	4 h	1.0 equiv.	tBuOH : acetone 24 : 1	r.t.	Full conv. A : M / 6.3 : 1 9% side product
16	5 h	1.0 equiv.	tBuOH : acetone 4 : 1	r.t.	Full conv. A : M / 6.3 : 1 9% side product
17	4h	1.0 equiv.	tBuOH : butanone 4 : 1	r.t.	Full conv. A : M / 6.0 : 1 7% side product
18	4h	1.0 equiv.	tBuOH : butanedione (4 equiv.)	r.t.	Full conv. A : M / 6.4 : 1 Less than 5% side product
19	4.5 h	1.1 equiv.	Acetone	r.t.	55% conv. Only rearrangement side product (i.e. the corresponding linear alkene)

^a side product = corresponding linear alkene and oxidized linear alkene

Table S6. Oxidation of 2B with co-solvents, at r.t. using 10 mol% [PdCl₂(CH₃CN)₂]

entry	time	solvent	H ₂ O	result ^a
1	6 h	tBuOH/tBuCN (24 : 1)	0	74% conv. 40% side product 26% aldehyde 8% ketone
2	6 h	tBuOH CH ₂ Cl ₂ (24 : 1)	0	Full conv. A : M / 6.3 : 1 5% side product
3	6 h	tBuOH Diethyl ether (24 : 1)	0	90% con. 10% side product A : M / 6.5 : 1
4	5h	tBuOH Pentane (24 : 1)	0	Full conv. A : M / 5.7 : 1 6% side product
5	6h	tBuOH Acetone (24 : 1)	0	full conv. A : M / 7.5 : 1 6% side product

^aside product = corresponding linear alkene and oxidized linear alkene

4. General procedures for catalyzed oxidation of allylic esters

Oxidation of branched allylic esters (Table 2, Scheme 4)

[PdCl₂(PhCN)₂] (0.005 mmol to 0.025 mmol) and *p*-benzoquinone (1 mmol) were dissolved in a 2 ml mixture of tBuOH and acetone (v : v / 24 : 1). The branched allylic ester (1 mmol, 0.5 M) was added to the mixture under N₂ and stirred at room temperature until the reaction was complete by T.L.C. analysis. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated in vacuo. Purification by flash silica-gel chromatography yielded the desired aldehyde.

Oxidation of linear allylic esters (Table 3)

[PdCl₂(PhCN)₂] (0.005 mmol to 0.05 mmol) and linear allylic alcohol (0.5 mmol, 0.5 M) were dissolved in the 1 ml mixture of tBuOH and acetone (v : v / 24 : 1). *p*-Benzoquinone (0.5 mmol) was added in the solution. The reaction mixture was protected by nitrogen and stirred at room temperature until the reaction was complete. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated in vacuo. Purification by silica-gel flash chromatography yielded the desired aldehyde.

Oxidation of a mixture of linear and branched allylic esters (Scheme 3)

[PdCl₂(PhCN)₂] (0.025 mmol) and linear allylic alcohol (0.5 mmol, 0.25 M) were dissolved in the 2 ml mixture of tBuOH and acetone (v : v / 24 : 1). After stirring for 30 min, *p*-benzoquinone (1 mmol) was added to the solution. After the *p*-benzoquinone had dissolved, the branched allylic ester (0.5 mmol, 0.25 M) was added. The reaction mixture was kept under N₂ and stirred at room temperature until the reaction was complete. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated in vacuo. Purification by flash silica-gel chromatography (9 : 1 pentane : ether eluent) yielded the desired aldehyde.

5. Characterization of products

3-Oxopropyl furan-2-carboxylate 1A (Table 2, entry 1) Isolated by flash column chromatography on silica gel (pentane/ether = 9:1, R_f = 0.6). The title compound was obtained as a colorless oil (78% yield). HRMS (ESI+) calc. for $C_8H_6O_4$ ($M+H$)⁺ 168.0500, found 169.0494;

1H NMR (400 MHz, $CDCl_3$) δ 9.84 (s, 1H), 7.58 (s, 1H), 7.17 (d, J = 3.5 Hz, 1H), 6.51 (m, 1H), 4.64 (t, J = 6.17 Hz, 1H), 2.90 (dt, J = 1.35 Hz, 6.16, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.0, 158.3, 146.5, 144.1, 118.3, 111.8, 58.3, 42.7.

4-Oxobutan-2-yl furan-2-carboxylate 2A (Table 2, entry 2) Isolated by flash column chromatography on silica gel (pentane/ether = 9:1, R_f = 0.5). The title compound was obtained as a colorless oil (71% yield). HRMS (ESI⁺) calc. for C₉H₁₁O₄ (M+H)⁺ 183.0651, found 183.0651;

¹H NMR (400 MHz, CDCl₃) δ 9.79 (s, 1H), 7.57 (s, 1H), 7.16 (d, *J* = 3.5 Hz, 1H), 6.50 (m, 1H), 5.6 (m, 1H), 2.87 (ddd, *J* = 16.94 Hz, 7.08 Hz, 2.32 Hz, 1H), 2.70 (ddd, *J* = 16.94 Hz, 5.43 Hz, 1.46 Hz, 1H), 1.45 (d, *J* = 6.37 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 199.0, 157.9, 146.4, 144.4, 118.2, 111.8, 66.6, 49.5, 20.2.

1-Oxopentan-3-yl furan-2-carboxylate 3A (Table 2, entry 3) Isolated by flash column chromatography on silica gel (pentane/ether = 8.5:1.5, R_f = 0.55). The title compound was obtained as a colorless oil (79% yield). HRMS (ESI⁺) calc. for $C_{10}H_{13}O_4$ (M+H)⁺ 197.0808, found 197.0808;

¹H NMR (400 MHz, CDCl₃) δ 9.78 (s, 1H), 7.56 (s, 1H), 7.15 (d, J = 3.49 Hz, 1H), 6.49 (m, 1H), 5.46 (m, 1H), 2.80 (ddd, J = 16.8 Hz, 7.26 Hz, 2.56 Hz, 1H), 2.73 (ddd, J = 16.8 Hz, 5.06 Hz, 1.5 Hz, 1H), 1.77 (m, 1H), 0.97 (t, J = 7.4 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 199.3, 158.1, 146.4, 144.3, 118.1, 111.8, 70.9, 47.6, 27.3, 9.4.

1-Oxo-octan-3-yl furan-2-carboxylate 4A (Table 2, entry 4) Isolated by flash column chromatography on silica gel (pentane/ethyl acetate = 8.5:1.5, R_f = 0.45). The title compound was obtained as colorless oil (73% yield). HRMS (ESI⁺) calc. for $C_{13}H_{19}O_4$ (M+H)⁺ 239.1277, found 239.1277;

¹H NMR (400 MHz, CDCl₃) δ 9.79 (s, 1H), 7.57 (s, 1H), 7.16 (d, J = 3.5 Hz, 1H), 6.51 (m, 1H), 5.53 (m, 1H), 2.79 (ddd, J = 16.75 Hz, 7.13 Hz, 2.59 Hz, 1H), 2.74 (ddd, J = 16.75 Hz, 5.12 Hz, 1.6 Hz, 1H), 1.74 (m, 2H), 1.30 (m, 6H), 0.87 (m, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 199.3, 158.1, 146.4, 144.3, 118.2, 111.8, 69.9, 48.1, 34.2, 31.4, 24.8, 22.4, 13.9.

4-Methyl-1-oxohexan-3-yl furan-2-carboxylate 5A (Table 2, entry 5) Isolated by flash column

chromatography on silica gel (pentane/ether = 8:2, R_f = 0.45). The title compound was obtained as a colorless oil (45% yield).

HRMS (ESI+) calc. for $C_{12}H_{17}O_4$ ($M+H$)⁺ 225.1121, found 225.1120;

1H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 7.58 (s, 1H), 7.16 (d, J = 3.5 Hz, 1H), 6.50 (m, 1H), 5.54 (m, 1H), 2.72 (m, 2H), 1.88-1.16 (m, 3H), 0.94 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.7, 199.6, 158.1, 146.5, 118.1, 118.1, 111.8, 72.9, 72.3, 45.8, 44.8, 38.5, 38.1, 25.3, 24.9, 14.3, 14.1, 11.5, 11.3.

1-(Benzyloxy)-4-oxobutan-2-yl furan-2-carboxylate 6A (Table 2, entry 6) Isolated by flash column chromatography on silica gel (pentane/ether = 7.5:2.5, R_f = 0.4). The title compound was obtained as a colorless oil (71% yield). HRMS (ESI⁺) calc. for $C_{16}H_{17}O_5$ ($M+H$)⁺ 289.1070, found 289.1070;

¹H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.59 (s, 1H), 7.35-7.27 (m, 5H), 7.18 (d, J = 3.5 Hz, 1H), 6.51 (m, 1H), 5.67 (m, 1H), 4.61-4.53 (dd, J = 22.8 Hz, 12.1 Hz, 2H), 3.75-3.67 (ddd, J = 22.5 Hz, 10.5 Hz, 4.7 Hz, 2H), 2.90 (dd, J = 6.2 Hz, 1.6 Hz, 2H); ¹³C NMR (101 MHz, $CDCl_3$) δ 198.7, 157.8, 146.6, 144.1, 137.5, 128.4, 127.8, 127.6, 118.5, 111.9, 73.3, 70.2, 68.5, 45.0, 29.6.

3-Oxo-1-phenylpropyl furan-2-carboxylate 7A (Table 2, entry 7) Isolated by flash column chromatography of silica gel (pentane/ether = 8:2, R_f = 0.5). The title compound was obtained as a colorless oil (52% yield). HRMS (ESI⁺) calc. for C₁₄H₁₃O₄ (M+H)⁺ 245.0808, found 245.0810;

¹H NMR (400 MHz, CDCl₃) δ 9.80 (s, 1H), 7.58 (s, 1H), 7.45-7.30 (m, 5H), 7.21 (d, *J* = 3.5 Hz, 1H), 6.51 (m, 1H), 3.23 (ddd, *J* = 17.0 Hz, 8.3 Hz, 2.2 Hz, 1H), 2.99 (ddd, *J* = 17.0 Hz, 4.9 Hz, 1.3 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 198.3, 157.5, 146.6, 144.2, 138.6, 128.8, 128.6, 126.3, 118.5, 111.9, 70.9, 49.7.

4-Oxo-1-phenylbutan-2-yl furan-2-carboxylate 8A (Table 2, entry 8) Isolated by flash column chromatography on silica gel (pentane/ether = 7:3, R_f = 0.4). The title compound was obtained as a colorless oil (64% yield). HRMS (ESI⁺) calc. for C₁₅H₁₅O₄ (M+H)⁺ 259.0970, found 259.0965;

¹H NMR (400 MHz, CDCl₃) δ 9.73 (s, 1H), 7.58 (s, 1H), 7.32-7.23 (m, 5H), 7.15 (d, *J* = 3.5 Hz, 1H), 5.72 (m, 1H), 3.14 (dd, *J* = 13.7 Hz, 6.0 Hz, 1H), 3.00 (dd, *J* = 13.8 Hz, 6.9 Hz, 1H), 2.78 (ddd, *J* = 17.07 Hz, 7.4 Hz, 2.3 Hz, 1H), 2.72 (ddd, *J* = 17.0 Hz, 5.0 Hz, 0.9 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 198.9, 157.8, 146.5, 144.2, 136.0, 129.5, 128.6, 127.0, 118.3, 111.8, 70.3, 46.9, 40.2.

6. (^1H)NMR spectra of crude products

(^1H)NMR spectrum, Table 2, entry 1

Crude (^1H)NMR spectrum, Table 2, entry 2

Crude (^1H)NMR spectrum, Table 2, entry 3

Crude (^1H)NMR spectrum, Table 3, entry 4

Crude (^1H)NMR spectrum, Table 2, entry 5

Crude (^1H)NMR spectrum, Table 2, entry 6

Crude (^1H)NMR spectrum, Table 2, entry 7

Crude (^1H)NMR spectrum, Table 2, entry 8

Crude (^1H)NMR spectrum, Table 3, entry 1

Crude (^1H)NMR spectrum, Table 3, entry 2

Crude (^1H)NMR spectrum, Table 3, entry 3

Crude (^1H)NMR spectrum, Table 3, entry 4

Crude (^1H)NMR spectrum, Table 3, entry 5

Crude (^1H)NMR spectrum, Scheme 3

Crude (^1H)NMR spectrum, Scheme 4a, oxidation of 4-vinyl-1,3-dioxolan-2-one (0.5 equiv. of 1,2-dichlorobenzene was added as internal standard)

Crude (^1H)NMR spectrum, Scheme 4b, oxidation of 2-furoyl protected pent-1-en-4-ol

Crude (^1H)NMR spectrum, Scheme 4b, oxidation of 2-furoyl protected 5-phenyl-pent-1-en-4-ol

7. Characterization of substrates

Allyl furan-2-carboxylate 1B (Table 2, entry 1) Isolated by flash column chromatography on silica gel (8 : 2 / pentane : ether eluent). The title compound was obtained as a colorless oil (91% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.54 (s, 1H), 7.16 (d, $J = 3.5$ Hz, 1H), 6.46 (m, 1H), 5.97 (m, 1H), 5.37 (d, $J = 7.17$ Hz, 1H), 5.25 (d, $J = 10.41$ Hz, 1H), 4.76 (d, $J = 5.7$ Hz, 2H)

But-3-en-2-yl furan-2-carboxylate 2B (Table 2, entry 2) Isolated by flash column chromatography on silica gel (7.5 : 2.5 / pentane : ether eluent). The title compound was obtained as a colorless oil (93% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.51 (s, 1H), 7.12 (d, $J = 3.5$ Hz, 1H), 6.44 (m, 1H), 5.87 (m, 1H), 5.51 (m, 1H), 5.29 (d, $J = 7.2$ Hz, 1H), 5.13 (d, $J = 10.5$ Hz, 1H), 1.36 (d, $J = 6.5$ Hz, 3H).

Pent-1-en-3-yl furan-2-carboxylate 3B (Table 2, entry 3) Isolated by flash column chromatography on silica gel (8.5 : 1.5 / pentane : ether eluent). The title compound was obtained as a colorless oil (90% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.53 (s, 1H), 7.13 (d, $J = 3.5$ Hz, 1H), 6.45 (m, 1H), 5.82 (m, 1H), 5.36 (m, 1H), 5.30 (d, $J = 7.2$ Hz, 1H), 5.18 (d, $J = 10.5$ Hz, 1H), 1.73 (m., 2H), 0.91 (t, $J = 7.4$ Hz, 3H).

Oct-1-en-3-yl furan-2-carboxylate 4B (Table 2, entry 4) Isolated by flash column chromatography on silica gel (8 : 2 / pentane : ether eluent). The title compound was obtained as a colorless oil (94% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.49 (s, 1H), 7.09 (d, $J = 3.5$ Hz, 1H), 6.40 (m, 1H), 5.79 (m, 1H), 5.35 (d, $J = 7.2$ Hz, 1H), 5.12 (d, $J = 10.5$ Hz, 1H), 1.64 (m, 2H), 1.28 (m, 6H), 0.78 (m, 3H)

4-Methylhex-1-en-3-yl furan-2-carboxylate 5B (Table 2, entry 5) Isolated by flash column chromatography on silica gel (9 : 1 / pentane : ether eluent). The title compound was obtained as a colorless oil (88% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.57 (s, 1H), 7.17 (d, $J = 3.5$ Hz, 1H), 6.49 (m, 1H), 5.86 (m, 1H), 5.39 (d, $J = 7.2$ Hz, 1H), 5.41-5.20 (m, 3H), 1.74-1.69 (m, 1H), 1.57-1.50 (m, 1H), 1.25-1.15 (m, 1H), 0.97-0.82 (m, 6H).

1-(Benzyloxy)but-3-en-2-yl furan-2-carboxylate 6B (Table 2, entry 6) Isolated by flash column

chromatography on silica gel (8.5 : 1.5 / pentane : ether eluent). The title compound was obtained as a colorless oil (85% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.59 (s, 1H), 7.33-7.21 (m, 6H), 6.52 (m, 1H), 5.93 (m, 1H), 5.74 (m, 1H), 5.44 (d, $J = 7.2$ Hz, 1H), 5.31 (d, $J = 10.5$ Hz, 1H), 4.61 (dd, $J = 2.2$ Hz, 22.7 Hz, 2H), 3.73-3.64 (m, 2H).

1-Phenylallyl furan-2-carboxylate 7B (Table 2, entry 7) Isolated by flash column chromatography on silica gel (8 : 2 / pentane : ether eluent). The title compound was obtained as a colorless oil (85% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.58 (s, 1H), 7.46-7.32 (m, 5H), 7.24 (d, $J = 3.5$ Hz, 1H), 6.50 (m, 1H), 6.14 (m, 1H), 5.43 (d, $J = 7.2$ Hz, 1H), 5.33(d, $J = 10.5$ Hz, 1H).

1-Phenylbut-3-en-2-yl furan-2-carboxylate 8B (Table 2, entry 8) Isolated by flash column chromatography on silica gel (9 : 1 / pentane : ether eluent). The title compound was obtained as a colorless oil (87% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.57 (s, 1H), 7.31-7.17 (m, 6H), 6.49 (m, 1H), 5.91 (m, 1H), 5.71 (m, 1H), 5.33 (d, $J = 7.2$ Hz, 1H), 5.23 (d, $J = 10.5$ Hz, 1H), 3.13 (dd, $J = 7.1$ Hz, 13.7 Hz, 1H), 3.02 (dd, $J = 6.3$ Hz, 13.7 Hz, 1H)

(E)-but-2-en-1-yl furan-2-carboxylate 2L (Table 3, entry 1) Isolated by flash column chromatography on silica gel (8.5 : 1.5 / pentane : ether eluent). The title compound was obtained as a colorless oil (93% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.50 (s, 1H), 7.11 (d, $J = 3.5$ Hz, 1H), 6.43 (m, 1H), 5.80 (m, 1H), 5.59 (m, 1H), 4.66 (d, $J = 6.5$ Hz, 1H), 1.66 (d, $J = 6.4$ Hz, 1H).

(E)-pent-2-en-1-yl furan-2-carboxylate 3L (Table 3, entry 2) Isolated by flash column chromatography on silica gel (9 : 1 / pentane : ether eluent). The title compound was obtained as a colorless oil (91% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.53 (s, 1H), 7.14 (d, $J = 3.5$ Hz, 1H), 6.46 (m, 1H), 5.83 (m, 1H), 5.56 (m, 1H), 4.72 (d, $J = 6.3$ Hz, 2H), 2.02 (m, 2H), 0.97 (m, 3H).

(E)-oct-2-en-1-yl furan-2-carboxylate 4L (Table 3, entry 3) Isolated by flash column chromatography on silica gel (8 : 2 / pentane : ether eluent). The title compound was obtained as a colorless oil (95% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.55 (s, 1H), 7.17 (d, $J = 3.5$ Hz, 1H), 6.48 (m, 1H), 5.83 (m, 1H), 5.62 (m, 1H), 4.73 (d, $J = 6.4$ Hz, 2H), 2.03 (m, 2H), 1.27 (m, 6H), 0.86 (m, 3H).

(E)-4-(benzyloxy)but-2-en-1-yl furan-2-carboxylate 6L (Table 3, entry 4) Isolated by flash column chromatography of silica gel (9.5 : 0.5 to 8.5 : 1.5 / pentane : ether eluent). The title compound was obtained as a colorless oil (61% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.53 (s, 1H), 7.30-7.21 (m, 5H), 7.15 (d, $J = 3.5$ Hz, 1H), 6.46 (m, 1H), 5.92 (m, 2H), 4.78 (d, $J = 4.3$ Hz, 2H), 4.48 (s, 2H), 4.02 (d, $J = 3.5$ Hz, 2H).

(E)-4-phenylbut-2-en-1-yl furan-2-carboxylate 8L (Table 3, entry 5) Isolated by flash column chromatography on silica gel (9.7 : 0.3 to 8.5 : 1.5 / pentane : ether eluent). The title compound was obtained as a colorless oil (56% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.57 (s, 1H), 7.32-7.18 (m, 6H), 6.51 (m, 1H), 6.02 (m, 1H), 5.73 (m, 1H), 4.79 (d, $J = 6.3$ Hz, 2H), 3.42 (d, $J = 6.7$ Hz, 2H).

8. Offline (^1H)NMR spectroscopic analysis

Reaction progress in the oxidation of allylic ester **2B** (Scheme 2) was studied by off-line ^1H NMR spectroscopy.

t0 = 0 h (only starting material **2B**), t1 = 1 h (starting material **2B**, linear allylic ester **2L**, aldehyde **2A**), t2 = 5 h (starting material **2B**, linear allylic ester **2L**, aldehyde **2A**), t3 = 16 h (starting material **2B**, linear allylic ester **2L**, aldehyde **2A**), t4 = 36 h (aldehyde **2A**, ketone **2M**, ketone **2K**)

9. Oxidation of enantiopure protected allylic alcohol

Retention of configuration in the oxidation of enantiopure benzyl protected pent-1-ene-3-ol determined by chiral HPLC (ODH – iPrOH/Heptane, 1:99).

PDA Ch1 220nm			
Peak#	Ret. Time	Area	Area%
1	23.030	575326	48.847
2	24.886	602482	51.153
Total		1177808	100.000

HPLC chromatogram of racemic benzyl protected 3-hydroxypentanal

PDA Ch1 220nm			
Peak#	Ret. Time	Area	Area%
1	23.061	786389	64.859
2	24.682	426064	35.141
Total		1212454	100.000

HPLC chromatogram of benzyl protected 3-hydroxypentanal prepared by oxidation of (*S*)-benzyl-pent-1-ene-3-ol ester

10. Expansion of Tables 2 and 3 Details indicating selectivity

Table 2. Pd(II)-catalysed oxidation of branched allylic esters

Entry	R	compound	Conv. ^{[a], [b]}	A : M : (L +K)	Isolated yield(A)
1	H	1B	full	86 : 14 : 0	78%
2	CH ₃	2B	full	83 : 11 : 6	71 %
3	C ₂ H ₅	3B	full	92 : 4 : 4	79 %
4	C ₅ H ₁₁	4B	full	91 : 4 : 5	73%
5		5B	95%	56 : 3 : 41	45%
6		6B	full	90 : 4 : 6	71%
7	Ph	7B	full	57 : 3 : 40	52%
8	Bn	8B	95%	76 : 4 : 20	64%

Entry	R	compound	Conv. ^{[a][b]}	A:M:K	isolated yield(A)
1 ^[c]	CH ₃	2L	full	77 : 11 : 12	70%
2 ^[d]	C ₂ H ₅	3L	full	79 : 5 : 16	74%
3 ^[d]	C ₅ H ₁₁	4L	95%	80 : 5 : 15	72%
4 ^[c]		6L	full	81 : 4 : 15	71%
5 ^{[e], [f]}	Bn	8L	85%	75 : 6 : 19	43%