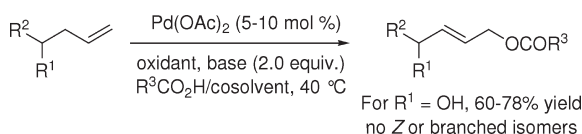


Palladium-Catalyzed Allylic Acyloxylation of Terminal Alkenes in the Presence of a Base

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The efficiency and the selectivity of the Pd-catalyzed oxidation, in carboxylic acids, of terminal alkenes are strongly improved in the presence of a base. The methodology is particularly well adapted for the oxidation of homoallylic alcohols, for which the resulting acyloxylation products are obtained selectively as *E*-isomers in fair to good yields.

Palladium(II)-catalyzed allylic oxidation of internal or cyclic olefins in acetic acid is an efficient process for the synthesis of allylic acetates.¹ On the other hand, terminal olefins generally yield mixtures of allylic acetates, vinyl acetates, and ketones.² Recently, two important progresses have been achieved toward more selective transformations. White et al. demonstrated that the association of Pd(OAc)₂, benzoquinone (BQ), and DMSO or a bis(sulfoxide) ligand promoted the regio- and stereoselective allylic acetoxylation of terminal alkenes. In addition, either linear or branched

products were selectively obtained depending on the reaction conditions.³ This methodology has been applied in the total synthesis of 6-deoxyerythronolide B, through a C–H oxidative macrolactonization, increasing the overall efficiency of the synthesis and providing stereochemical control at a key lactone position.⁴ Kaneda and co-workers described a regioselective process leading to linear allylic acetates using *N,N*-dimethylacetamide (DMA) as solvent and molecular oxygen as the sole oxidant, high pressures of O₂ (6 atm) being required, however.⁵ Bipyrimidines as ligands were also found to improve the allylic acetoxylation of olefins.⁶ The proposed mechanism of such transformations generally involves π -allyl-Pd(II) intermediates.^{3f,6,7} Surprisingly, the influence of additives, such as acetate salts, has not received so much attention for the oxidation of terminal olefins.⁸ Such compounds could act as bases to facilitate the formation of π -allyl complexes,⁹ and as nucleophiles on such complexes. Herein, we disclose our results on the use of bases for the Pd-catalyzed oxidation of terminal alkenes.

The oxidation of allylbenzene (**1a**) in the presence of Pd(OAc)₂ (0.05 equiv) and BQ (2.0 equiv) in AcOH at 40 °C for 24 h led to a high conversion, but as observed before,^{3g} to a low yield of cinnamyl acetate (**2a**) (Table 1, entry 1). The use of DMSO or DMA as the cosolvent improved the selectivity of the reaction, but dropped the conversion (entries 2 and 3). Almost full conversion was observed with CH₃CN as cosolvent, leading to **2a** in 54% yield (entry 4). CH₂Cl₂ was not an efficient cosolvent (entry 5). In AcOH containing NaOAc as additive, **2a** can be produced in high yields but the results were inconsistent (entry 6). In contrast, reproducible results were obtained in EtCO₂H containing LiOH·H₂O as a base,¹⁰ affording **3a** in up to 75% yield, with high regioselectivity and good stereoselectivity (entries 7 and 8). The use of MnO₂, MnO₂/BQ, O₂/Cu(OAc)₂, or O₂ as oxidizing agents led to lower conversions and yields, but in some cases to higher L/B and *E/Z* ratios (entries 9–12).

The scope of the process was then examined, under the experimental conditions of entry 8 of Table 1 (namely afterward, method A). An electron donating group on the arene decreases the regioselectivity of the oxidation (Table 2, **3b** and **3c**), while an electron withdrawing group did not affect it (**3d**). The methodology was found to be particularly well adapted to homoallylic alcohols and their derivatives. A protected homoallylic alcohol, such as 1-phenylbut-3-enyl acetate (**1e**), was regio- and stereoselectively oxidized into

(1) (a) Beccalli, E. M.; Broggini, G.; Martinelli, M.; Sottocornola, S. *Chem. Rev.* **2007**, *107*, 5318. (b) Frison, J.-C.; Legros, J.; Bolm, C. *Copper- and Palladium-Catalyzed Allylic Acyloxylation*; Wiley-VCH Verlag GmbH & Co: Weinheim, Germany, 2005; Vol. 2. (c) Grennberg, H.; Bäckvall, J.-E. *Allylic oxidations: palladium-catalyzed allylic oxidation of olefins*; Wiley-VCH Verlag GmbH & Co: Weinheim, Germany, 2004; Vol. 2. (d) Muzart, J. *Bull. Soc. Chim. Fr.* **1986**, 65.

(2) (a) Tsuji, J. *Palladium Reagents and Catalysts: New Perspectives for the 21st Century*; Wiley and Sons: New York, 2004. (b) Åkermark, B.; Larsson, E. M.; Oslob, J. D. *J. Org. Chem.* **1994**, *59*, 5729. (c) Kitching, W.; Rappoport, Z.; Winstein, S.; Yong, W. G. *J. Am. Chem. Soc.* **1966**, *88*, 2054.

(3) (a) Covell, D. J.; White, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 6448. (b) Fraunhoffer, K. J.; Prabakaran, N.; Sirois, L. E.; White, M. C. *J. Am. Chem. Soc.* **2006**, *128*, 9032. (c) Delcamp, J. H.; White, M. C. *J. Am. Chem. Soc.* **2006**, *128*, 15076. (d) Covell, D. J.; Vermeulen, N. A.; Labenz, N. A.; White, M. C. *Angew. Chem., Int. Ed.* **2006**, *45*, 8217. (e) Fraunhoffer, K. J.; Bachovchin, D. A.; White, M. C. *Org. Lett.* **2005**, *7*, 223. (f) Chen, M. S.; Prabakaran, N.; Labenz, N. A.; White, M. C. *J. Am. Chem. Soc.* **2005**, *127*, 6970. (g) Chen, M. S.; White, M. C. *J. Am. Chem. Soc.* **2004**, *126*, 1346.

(4) Stang, E. M.; White, M. C. *Nat. Chem.* **2009**, *1*, 547.

(5) Mitsudome, T.; Umetani, T.; Nosaka, N.; Mori, K.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 481.

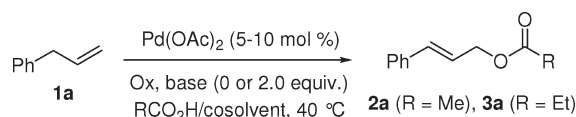
(6) Lin, B.-L.; Labinger, J. A.; Bercaw, J. E. *Can. J. Chem.* **2009**, *87*, 264.

(7) Grennberg, H.; Bäckvall, J.-E. *Chem.—Eur. J.* **1998**, *4*, 1083.

(8) A noncoordinating base was recently used as additive, but its exact role is unclear, see ref 3d. AcO[−] anions accelerate the reaction of Pd(OAc)₂ with alkenes in apolar solvents, due to better solubility of Pd(II) species in the presence of (R₄N)⁺AcO[−], see: Kozitsyna, N. Y.; Bukharkina, A. A.; Martens, M. V.; Vargaftik, M. N.; Moiseev, I. I. *J. Organomet. Chem.* **2001**, *636*, 69.

(9) Trost, B. M.; Strege, P. E.; Weber, L.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3407.

(10) NaOH and LiOH·H₂O afforded similar results, but the latter which is less hygroscopic was used for easier handling.

TABLE 1. Optimization of the Oxidation of Allylbenzene (**1a**)^a

entry	RCO ₂ H/cosolvent	Pd(OAc) ₂ , %	Ox (equiv)	base	conv., ^b %	yield, ^c %	L/B, <i>E/Z</i> ^d
1	AcOH	5	BQ (2.0)		70	(12)	
2	AcOH/DMSO, 1:1	5	BQ (2.0)		38	(25)	
3	AcOH/DMA, 1:1	5	BQ (2.0)		29	(18)	
4	AcOH/CH ₃ CN, 1:1	5	BQ (2.0)		97	(54)	
5	AcOH/CH ₂ Cl ₂ , 1:1	5	BQ (2.0)		50	(< 5)	
6	AcOH	5	BQ (2.0)	NaOAc	80–100	60–76 (70–86)	99.9, 21
7	EtCO ₂ H	5	BQ (2.0)	LiOH·H ₂ O	78	(65)	
8	EtCO ₂ H	10	BQ (2.0)	LiOH·H ₂ O	100	75 (86)	99.9, 21
9	EtCO ₂ H	10	MnO ₂ (2.0)	LiOH·H ₂ O	80	57 (67)	99.9, 25
10	EtCO ₂ H	10	BQ (0.05), MnO ₂ (2.0)	LiOH·H ₂ O	92	60 (71)	99.9, 14
11	EtCO ₂ H	10	Cu(OAc) ₂ (0.5), O ₂ ^e	LiOH·H ₂ O	85	61 (71)	99.9, 50
12	EtCO ₂ H	10	O ₂ ^e	LiOH·H ₂ O	45	15 (24)	99.9, 14

^a**1a** (1.0 mmol), Pd(OAc)₂ (0.05 or 0.1 mmol), oxidant (0.5 or 2.0 mmol), base (0 or 2.0 mmol), RCO₂H/cosolvent (2.0 mL), 40 °C, 24 h. ^bDetermined by GC. ^cGC yield in parentheses. ^dDetermined by GC on isolated products. ^eGas bag.

E-3e in medium yield. Interestingly, unprotected alcohols **1f–o** have been directly oxidized into corresponding linear (*E*)-4-hydroxy-esters **3f–o**. No *Z*, or branched isomers were detected by GC analysis. The allylic alcohol group is preserved, its oxidation or isomerization into a ketone function not being observed. Halogenated compounds (**1g–j**) were effectively oxidized allowing the possible elaboration of more complex compounds through further coupling reactions. While most products were isolated in fair to good yields (60–78%), **3k** and **3l** were obtained in low yields (~10%). The oxidation of ether **1p** into **E-3p** was improved from 48% to 74% when the reaction was performed at rt for 72 h.

Oxidation of 1-decene (**1s**) in EtCO₂H led to the expected product **3s** in good yield (Table 3, entry 1), but with low regio- and stereoselectivity (L/B and *E/Z* < 10%). In addition, the product was contaminated with 10% of the homoallylic derivative. We have observed that the use of a higher carboxylic acid as solvent can improve the selectivity, but has a detrimental effect on the conversion, *i*-PrCO₂H leading to only 62% conversion (entry 2). Interestingly, the addition of a cosolvent such as CH₃CN to *i*-PrCO₂H gave almost full conversion leading to **4s** in good yield, regio- and stereoselectivity, the amount of homoallylic derivative remaining relatively unchanged (entry 3), however. Medium conversion was obtained with *t*-BuCO₂H/CH₃CN, even in prolonging the reaction time to 72 h (entries 4 and 5), but the use of MnO₂ as oxidizing agent improved the conversion (entry 6), particularly when associated with BQ (entry 7). This latter acts probably as an electron-transfer mediator between the catalyst and the oxidant, and facilitates the overall transformation.¹¹

5s–v were obtained in fair yields (59–69%) with good regio- and stereoselectivities (L/B 21–34, *E/Z* 12–18), and were contaminated with only low amounts of the homoallylic derivatives (Tables 2 and 3). The new procedure, based on the conditions of Table 3, entry 7 (called method B), is well adapted to the oxidation of homoallylic alcohols. Indeed, the efficiency of the oxidation of **1f** and **1g** was improved (Table 2: **3f**, 64%; **5f**, 78%; **3g**, 60%; **5g**, 77%), and inter-

estingly, **1k** and **1l** could be thus oxidized in high yields and regio- and stereoselectivities (**5k**, 80%; **5l**, 72%). Ethers were obtained in fair yields with method B (Table 2) in 72 (**5q**) or 24 h (**5r**). The oxidation of **1e** was slightly improved (**3e**, 55%; **5e**, 60%), but method B was less efficient than method A with allylarenes (**5a**, 60%; **5c**, 51%).

ESI-MS and the tandem version ESI-MS/MS are well adapted to the observation of short-lived molecular ions issued from metallocatalyzed reactions, and proposed species can be characterized from high resolution (HRMS) and ESI-MS/MS fragmentation.¹² The analysis by ESI/MS(+) of a mixture of Pd(OAc)₂ (0.1 mmol) and LiOH·H₂O (2.0 mmol) in EtCO₂H (2 mL) has shown two clusters at *m/z* 419.0661 and 499.1119, attributed to monomeric palladium species [Li₂Pd(EtCO₂)₄,Li]⁺ and [Li₂Pd(EtCO₂)₄,EtCO₂Li,Li]⁺, respectively. After addition of BQ and **1a**, and 45 min of stirring, two new clusters were observed at *m/z* 457.1002 and 537.1454, and were assigned to [LiPd(**1a**)(EtCO₂)₃,Li]⁺ and [LiPd(**1a**)-(EtCO₂)₃,EtCO₂Li,Li]⁺, respectively (Figures S1–S6, Supporting Information). Palladium acetate exists as a trimer in the solid state, in which the Pd(OAc)₂ units are joined by double OAc bridges.¹³ According to the ESI/MS studies, the acetate anion of the salt can act as a ligand for palladium leading to M₂Pd(OAc)₄ (**A**),¹⁴ then coordination of **1** to **A** affords **B** (Scheme 1). The ligated RCO₂[–] in **B** can act as a base, facilitating the formation of π -allyl complex **C**.^{9,15} Carefull

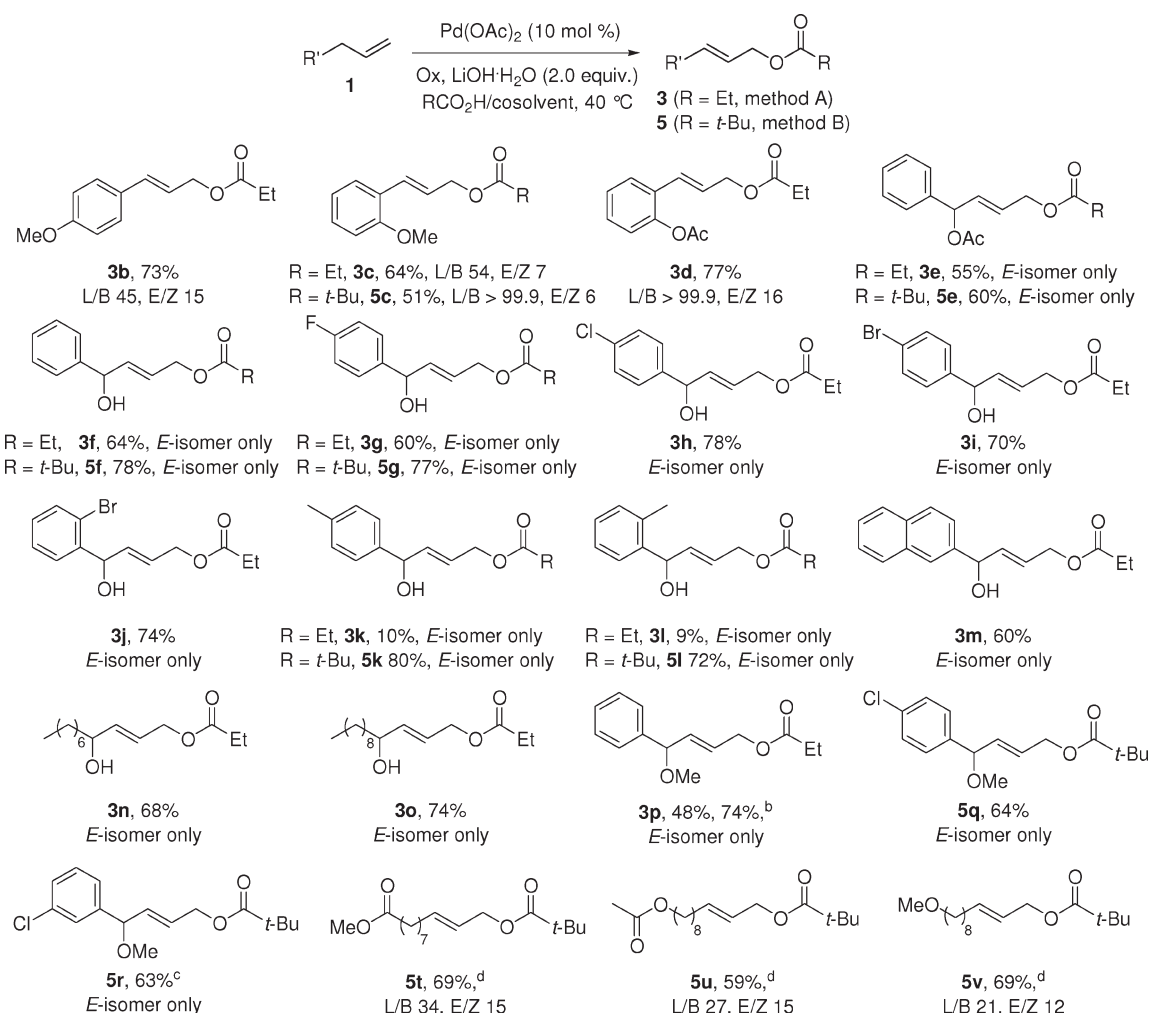
(12) (a) Santos, L. S. *Eur. J. Org. Chem.* **2008**, 235. (b) Svennebring, A.; Sjöberg, P. J. R.; Larhed, M.; Nilsson, P. *Tetrahedron* **2008**, *64*, 1808. (c) Thierry, E.; Harakat, D.; Le Bras, J.; Muzart, J. *Organometallics* **2008**, *27*, 3996. (d) Thierry, E.; Chevrin, C.; Le Bras, J.; Harakat, D.; Muzart, J. *J. Org. Chem.* **2007**, *72*, 1859. (e) Chevrin, C.; Le Bras, J.; Roglans, A.; Harakat, D.; Muzart, J. *New J. Chem.* **2007**, *31*, 121. (f) Markert, C.; Neuburger, M.; Kuliche, K.; Meuwly, M.; Pfaltz, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 5892. (g) Taccardi, N.; Paolillo, R.; Gallo, V.; Mastroianni, P.; Nobile, C. F.; Räisänen, M.; Repo, T. *Eur. J. Inorg. Chem.* **2007**, 4645. (h) Santos, L. S.; Rosso, G. B.; Pilli, R. A.; Eberlin, M. J. *J. Org. Chem.* **2007**, *72*, 5809. (i) Neto, B. A. D.; Alves, M. B.; Lapis, A. A. M.; Nachtigall, F. M.; Eberlin, M. N.; Dupont, J.; Suarez, P. A. Z. *J. Catal.* **2007**, *249*, 154. (j) Masllorens, J.; González, I.; Roglans, A. *Eur. J. Org. Chem.* **2007**, 158.

(13) Skapski, A. C.; Smart, M. L. *J. Chem. Soc., Chem. Commun.* **1970**, 658.

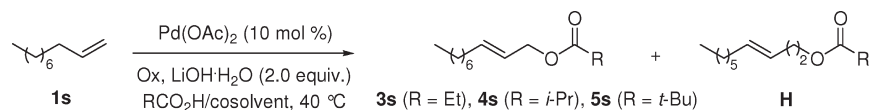
(14) Pandey, R. N.; Henry, P. M. *Can. J. Chem.* **1974**, *52*, 1241.

(15) Tsuji, J. *Palladium Reagents and Catalysts*; Wiley: Chichester, UK, 1995; p 62.

(11) Piera, J.; Bäckvall, J.-E. *Angew. Chem., Int. Ed.* **2008**, *47*, 3506.

TABLE 2. Oxidations with Method A or B^a

^aMethod A: **1** (1.0 mmol), Pd(OAc)₂ (0.1 mmol), BQ (2.0 mmol), LiOH·H₂O (2.0 mmol), EtCO₂H (2 mL), 40 °C, 24 h. Method B: **1** (1.0 mmol), Pd(OAc)₂ (0.1 mmol), BQ (0.05 mmol), MnO₂ (2.0 mmol), LiOH·H₂O (2.0 mmol), *t*-BuCO₂H (2 g), CH₃CN (1 mL), 40 °C, 72 h. ^bRoom temperature, 72 h. ^c24 h. ^dPresence of 1–3% of homoallylic derivatives.

TABLE 3. Oxidation of 1-Decene^a

entry	R	cosolvent	Ox (equiv)	time, h	conv., ^b %	yield, %	L/B ^c	E/Z ^c	H ^c
1	Et		BQ (2.0)	24	88	80	8	7	10
2	<i>i</i> -Pr		BQ (2.0)	24	62	42	25	22	11
3	<i>i</i> -Pr	CH ₃ CN	BQ (2.0)	24	94	74	17	19	10
4	<i>t</i> -Bu	CH ₃ CN	BQ (2.0)	24	49	33	50	17	4
5	<i>t</i> -Bu	CH ₃ CN	BQ (2.0)	72	66	43	43	15	4
6	<i>t</i> -Bu	CH ₃ CN	MnO ₂ (2.0)	72	76	54	27	20	3
7	<i>t</i> -Bu	CH ₃ CN	BQ (0.05), MnO ₂ (2.0)	72	90	61	29	18	3

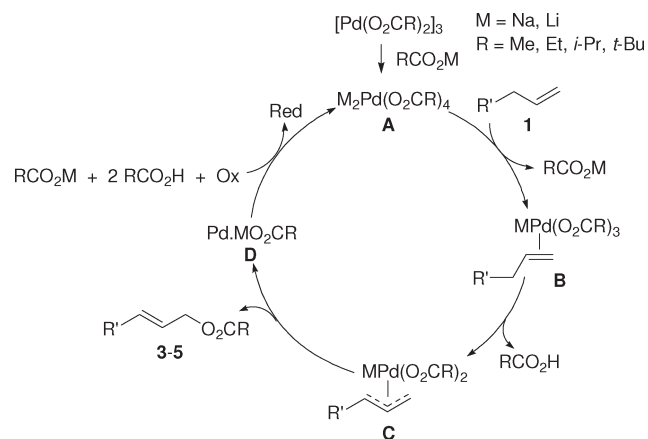
^a**1s** (1.0 mmol), Pd(OAc)₂ (0.1 mmol), LiOH·H₂O (2.0 mmol), RCO₂H (2.0 mL or 2.0 g), cosolvent (1.0 mL), 40 °C. ^bDetermined by GC. ^cDetermined by GC on isolated products (H: homoallylic derivative).

analysis of the ESI/MS spectra did not show the presence of clusters which could be attributed to **C**, suggesting that such a complex evolves rapidly under the reaction conditions. An intramolecular acetoxylation could lead to products **3–5**

and **D**. The reoxidation of Pd(0) would then complete the catalytic cycle.

In conclusion, the use of a base for the Pd-catalyzed allylic oxidation of terminal alkenes in carboxylic acids as solvents

SCHEME 1. Proposed Mechanism



improved the efficiency and the selectivity of the process. The methodology is particularly convenient for the oxidation of homoallylic alcohols, corresponding *E*-acyloxyated products being obtained in fair to good yields.

Experimental Section

Method A for the Oxidation of 1. A round-bottomed flask was charged with $LiOH \cdot H_2O$ (2.0 mmol, 84 mg) and $EtCO_2H$ (1 mL) and the mixture was heated (oil bath, 40 °C) for 10 min. BQ (2.0 mmol, 216 mg), $Pd(OAc)_2$ (0.1 mmol, 22.4 mg), and $EtCO_2H$ (1 mL) were added, and the mixture was stirred at rt for 15 min. **1** (1.0 mmol) was added, and the mixture was heated (oil bath, 40 °C) for 24 h. After cooling to rt, the mixture was filtered through a SiO_2 pad, which was washed with Et_2O (50 mL). NaOH (2 M, 25 mL) was added, and the mixture was stirred for 15 min. The organic phase was washed with H_2O (25 mL). The aqueous combined phases were extracted with Et_2O (25 mL). The combined organic phases were dried over $MgSO_4$, and then evaporated to dryness. Flash chromatography (petroleum ether/ $EtOAc$, 95:5–60:40) led to **3**.

Method B for the Oxidation of 1. A round-bottomed flask was charged with $LiOH \cdot H_2O$ (2.0 mmol, 84 mg) and $t\text{-}BuCO_2H$ (2 g), and the mixture was heated (oil bath, 40 °C) for 10 min. BQ (0.05 mmol, 5.5 mg), MnO_2 (2.0 mmol, 174 mg), $Pd(OAc)_2$ (0.1 mmol, 22.4 mg), and CH_3CN (1 mL) were added, and the mixture was stirred at rt for 15 min. **1** (1.0 mmol) was added, and the mixture was heated (oil bath, 40 °C) for 72 h. After cooling to rt, the mixture was filtered through a SiO_2 pad, which was washed with Et_2O (50 mL). NaOH (2 M, 25 mL) was added, and the mixture was stirred for 15 min. The organic phase was washed with H_2O (25 mL). The aqueous combined phases were extracted with Et_2O (25 mL). The combined organic phases were dried over $MgSO_4$, and then evaporated to dryness. Flash chromatography (petroleum ether/ $EtOAc$, 95:52–60:40) led to **5**.

(E)-4-Hydroxy-4-phenylbut-2-enyl propionate (3f): pale yellow oil, 64%, L/B and *E/Z* > 99.9; 1H NMR (250 MHz, $CDCl_3$) δ 1.00 (t, 3H, *J* = 7.6 Hz), 2.20 (q, 2H, *J* = 7.5 Hz), 3.05 (br s, 1H), 4.43 (d, 2H, *J* = 5.0 Hz), 5.05 (d, 1H, *J* = 5.2 Hz), 5.65–5.85 (m, 2H), 7.21 (m, 5H); ^{13}C NMR (63 MHz, $CDCl_3$) δ

9.1, 27.5, 64.1, 74.0, 124.7, 126.3, 127.7, 128.5, 136.2, 142.6, 174.4; IR (film) 3445, 2982, 2942, 1738, 1454, 1382, 1349, 1276, 1186, 1083, 1009, 974, 759, 701. Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.63; H, 7.45.

(E)-4-Hydroxy-4-phenylbut-2-enyl pivalate (5f): colorless oil, 78%, L/B and *E/Z* > 99.9; 1H NMR (250 MHz, $CDCl_3$) δ 1.11 (s, 9H), 2.72 (br s, 1H), 4.46 (d, 2H, *J* = 4.6 Hz), 5.10 (d, 1H, *J* = 4.9 Hz), 5.80 (m, 2H), 7.21 (m, 5H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 27.6, 39.2, 64.5, 74.6, 125.5, 126.8, 128.2, 129.0, 136.2, 143.0, 178.8; IR (film) 3455, 2975, 1728, 1480, 1373, 1283, 1156, 1045, 971, 701; ESHRMS calcd for $C_{15}H_{20}O_3Na$ 271.1310, found 271.1304.

(E)-4-(4-Chlorophenyl)-4-hydroxybut-2-enyl propionate (3h): pale yellow oil, 78%, L/B and *E/Z* > 99.9; 1H NMR (250 MHz, $CDCl_3$) δ 1.09 (t, 3H, *J* = 7.3 Hz), 2.30 (q, 2H, *J* = 7.3 Hz), 3.19 (br s, 1H), 4.53 (d, 2H, *J* = 4.0 Hz), 5.12 (d, 1H, *J* = 4.1 Hz), 5.84 (m, 2H), 7.25 (m, 4H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 8.9, 27.3, 63.8, 73.2, 125.0, 127.6, 128.5, 133.2, 135.6, 140.8, 174.2; IR (film) 3417, 2979, 1731, 1491, 1383, 1187, 1090, 1014, 911, 735; ESHRMS calcd for $C_{13}H_{15}O_3NaCl$ 277.0607, found 277.0614.

(E)-4-(2-Bromophenyl)-4-hydroxybut-2-enyl propionate (3j): pale yellow oil, 74%, L/B and *E/Z* > 99.9; 1H NMR (250 MHz, $CDCl_3$) δ 0.88 (t, 3H, *J* = 7.6 Hz), 2.08 (q, 2H, *J* = 7.5 Hz), 3.11 (br, 1H), 4.31 (m, 2H), 5.35 (s, 1H), 5.66 (m, 2H), 6.89 (dt, 1H, *J* = 1.5 Hz, *J* = 7.9 Hz), 7.08 (dd, 1H, *J* = 4.6 Hz, *J* = 9.6 Hz), 7.28 (m, 2H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 8.9, 27.3, 64.0, 72.1, 122.1, 125.0, 127.6, 127.7, 128.9, 132.5, 134.0, 141.3, 174.2; IR (film) 3436, 2980, 1729, 1465, 1349, 1190, 1084, 1016, 910, 733; ESHRMS calcd for $C_{13}H_{15}O_3NaBr$ 321.0102, found 321.0095.

(E)-4-Hydroxy-4-*p*-tolylbut-2-enyl pivalate (5k): colorless oil, 80%, L/B and *E/Z* > 99.9; 1H NMR (250 MHz, $CDCl_3$) δ 1.08 (s, 9H), 2.21 (s, 3H), 3.23 (br s, 1H), 4.41 (d, 2H, *J* = 4.8 Hz), 5.00 (d, 1H, *J* = 4.4 Hz), 5.71 (td, 1H, *J* = 4.9 Hz, *J* = 15.6 Hz), 5.79 (dd, 1H, *J* = 5.2 Hz, *J* = 15.7 Hz), 7.01 (d, 2H, *J* = 7.6 Hz), 7.10 (d, 2H, *J* = 7.8 Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 20.8, 27.0, 38.5, 64.0, 73.5, 124.3, 126.0, 128.9, 135.8, 137.0, 139.5, 178.1; IR (film) 3439, 2973, 1728, 1480, 1397, 1283, 1156, 1088, 970, 819; ESHRMS calcd for $C_{16}H_{22}O_3Na$ 285.1467, found 285.1457.

(E)-4-(4-Chlorophenyl)-4-methoxybut-2-enyl pivalate (5q): colorless oil, 64%, L/B and *E/Z* > 99.9; 1H NMR (250 MHz, $CDCl_3$) δ 1.13 (s, 9H), 3.23 (s, 3H), 4.53 (m, 3H), 5.74 (m, 2H), 7.21 (m, 4H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 27.0, 38.5, 56.2, 63.6, 82.5, 126.6, 128.0, 128.5, 133.2, 133.5, 139.0, 177.8; IR (film) 2976, 1729, 1482, 1462, 1282, 1152, 1090, 1015, 968, 824; ESHRMS calcd for $C_{16}H_{21}O_3NaCl$ 319.1077, found 319.1082.

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Supporting Information Available: General information, analytical data of compounds **3a–3e**, **3g**, **3i**, **3m–3p**, **5a**, **5c**, **5e**, **5g**, **5i**, and **5r–5v**, ESI/MS(+) spectra (Figures S1–S6), and the copies of 1H NMR and ^{13}C NMR. This material is available free of charge via the Internet at <http://pubs.acs.org>.