A Convenient Synthesis of the (*E*)-Monoacetates of 2-Alkylidenepropane-1,3-diols

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The authors dedicate this article to Professor E. J. Corey at Harvard University on the occasion of his 80th birthday.

Abstract: Various kinds of 3-substituted (*E*)-2-(hydroxymethyl)prop-2-enyl acetates were conveniently obtained in excellent yields by the regiospecific acetylation of 2-alkylidenepropane-1,3-diols with 10 equivalents of vinyl acetate in the presence of 50% w/w porcine pancreatic lipase (PPL) type II; the starting materials or (*Z*)-monoacetate or diacetate byproducts were generally not present.

Key words: (*E*)-monoacetates, acetylation, diols, regioselectivity, lipase

The development of highly selective acetylation reactions is an attractive research field because the acetyl group, as one of the most popular protecting groups, plays an important role in organic synthesis.[1] Enzymatic acetylation using lipase and vinyl acetate is an excellent methodology, and many papers have reported the enantioselective acetylation of racemic alcohols in the presence of lipase.[2] In the case of the unique highly regioselective acetylation of 2-benzylidenepropane-1,3-diols using several kinds of lipases reported by Takabe and co-workers,[3] diacetates and (*Z*)-monoacetates were obtained as byproducts in all cases, and 1 equivalent of vinyl acetate had to be used to avoid the production of the diacetates. We recently developed and reported in a preliminary communication the preparation of 3-substituted (*E*)-2-(hydroxymethyl)prop-2-enyl acetates by the regiospecific acetylation of 2-alkylidenepropane-1,3-diols with vinyl acetate using 50% w/w porcine pancreatic lipase (PPL) type II,[4] and the preparation of 3-substituted (*Z*)-2-(hydroxymethyl)prop-2-enyl acetates by the highly regioselective hydrolysis of 2-alkylidene-1,3-propylene diacetates using 100% w/w PPL type II.[5] Herein, we report the details of a regiospecific acetylation of 2-alkylidenepropane-1,3-diols with vinyl acetate using 50% w/w PPL type II.

2-Alkylidenepropane-1,3-diols **2** were easily prepared in 20–62% yield from diethyl 2-alkylidenemalonates **1**, which can be obtained from the Knoevenagel condensation of the corresponding aldehydes with diethyl malonate,[6] by reduction using diisobutylaluminum hydride (DIBAL-H) (Table 1).[7]

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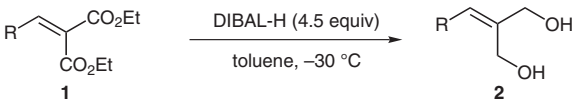
Table 1 Preparation of 2-Alkylidenepropane-1,3-diols **2** from Diethyl 2-Alkylidenemalonates **1**[a]



Entry	R	Time (h)	Product **2**	Yield (%)
1	Ph	2	**2a**	62
2	4-$MeOC_6H_4$	3	**2b**	48
3	4-$F_3CC_6H_4$	3	**2c**	34
4	4-ClC_6H_4	3	**2d**	53
5	4-Tol	3	**2e**	57
6	3-Tol	2	**2f**	55
7	2-Tol	3	**2g**	57
8	Mes	3	**2h**	58
9	$PhCH_2CH_2$	3	**2i**	20
10	2-naphthyl	3	**2j**	47
11	2-furyl	3	**2k**	44
12	2-thienyl	3	**2l**	51
13	3-thienyl	2	**2m**	47

[a] All reactions were carried out with diethyl 2-alkylidenemalonate **1** (1 equiv) and DIBAL-H (4.5 equiv) in toluene at –30 °C.

In a preliminary investigation, the reaction of 2-benzylidenepropane-1,3-diol (**2a**)[3a] with vinyl acetate in the presence of 50% w/w PPL in 1,4-dioxane afforded the corresponding *E*-isomer **3a** as the sole product in 95% yield, as indicated in Table 2, entry 1. The overacetylated product and the *Z*-isomer were not detected in the ^1H NMR spectroscopic analysis of the crude product. We examined the regioselective acetylation of 2-benzylidenepropane-1,3-diols substituted on the benzene ring by electron-donating or electron-withdrawing groups. The results from the acetylation of various substituted 2-benzylidenepropane-1,3-diols **2b–h** and that of 2-alkylidene derivative **2i** with vinyl acetate in the presence of 50% w/w PPL in 1,4-dioxane are collated in Table 2. We selected methoxy and methyl substituents as representative electron-donating groups (entries 2 and 5–8, respec-

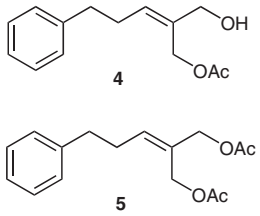


Figure 1 Byproducts of the acetylation of 2-alkylidenepropane-1,3-diol **2i**

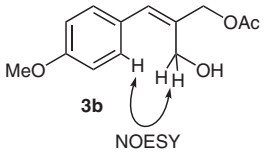
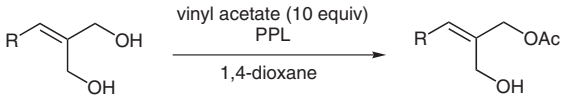


Figure 2 Determination of the structure of monoacetate **3b**

tively), trifluoromethyl and chloro substituents as electron-withdrawing groups (entries 3 and 4, respectively), and 2-(3-phenylpropylidene)propane-1,3-diol (**2i**) for the reaction of an aliphatic species (entry 9). Fortunately, all *para*-monosubstituted 2-benzylidenepropane-1,3-diols **2b–e** reacted under the above conditions to afford the corresponding (*E*)-monoacetylated products **3b–e** in excellent yields with complete regioselectivity. High regioselectivity was also observed in the reactions of the more-hindered substrates **2f** and **2g** containing methyl groups at the *meta*- and *ortho*-positions of the benzene ring (entries 6 and 7, respectively). 2-(2,4,6-Trimethylbenzylidene)propane-1,3-diol (**2h**) was a poor substrate for acetylation using PPL, probably because of the steric hindrance of the *ortho*-substituents on the benzene ring, and its corresponding (*E*)-monoacetate **3h** was obtained in only 30% yield (entry 8). The reaction of 2-(3-phenylpropylidene)propane-1,3-diol (**2i**) (entry 9) afforded the (*E*)-monoacetate with lower regioselectivity than that observed for the reactions of substituted 2-benzylidenepropane-1,3-diols **2a–h**. Although the corresponding *E*-isomer **3i** was obtained in 80% yield, *Z*-isomer **4** and diacetate **5** were produced as byproducts in 5 and 6% yield, respectively (Figure 1). In addition to the above reactions, polycyclic and heterocyclic aromatic diols **2j–m** were converted into the corresponding *E*-monoacetates **3j–m** with high regioselectivity (entries 10 and 11–13, respectively); however, the reaction of polycyclic diol **2j** containing a 2-naphthyl group gave a lower yield because of steric hindrance similar to that mentioned above for entry 8.

The structure of monoacetate **3b** was determined as the *E*-isomer by nuclear Overhauser effect spectroscopy (NOESY) (Figure 2). A NOESY relationship was observed between the aromatic and the methylene protons adjacent to the hydroxy group. All the other monoacetates **3a** and **3c–m** were also determined to be the *E*-isomers by NOESY analysis.

Table 2 *E*-Acetylation of 2-Alkylidenepropane-1,3-diols **2** in the Presence of Porcine Pancreatic Lipase[a]



2 **3**

Entry	R	Time (h)	Product **3**	Yield (%)
1	Ph	23	**3a**	95
2	4-$MeOC_6H_4$	23	**3b**	94
3	4-$F_3CC_6H_4$	47	**3c**	90
4	4-ClC_6H_4	48	**3d**	94
5	4-Tol	31	**3e**	97
6	3-Tol	20	**3f**	92
7	2-Tol	26	**3g**	95
8	Mes	72	**3h**	30[b]
9	$PhCH_2CH_2$	28	**3i**	80[c]
10	2-naphthyl	24	**3j**	38[d]
11	2-furyl	24	**3k**	65[e]
12	2-thienyl	24	**3l**	82
13	3-thienyl	24	**3m**	97

[a] All reactions were carried out with 2-alkylidenepropane-1,3-diol **2** (1 equiv), vinyl acetate (10 equiv), and 50% w/w PPL in 1,4-dioxane (3 mL) at r.t.
[b] Starting material **2h** was recovered in 61% yield.
[c] Starting material **2i** was recovered in 4% yield, and *Z*-isomer **4** and diacetate **5** were obtained in 5 and 6% yield, respectively.
[d] Starting material **2j** was recovered in 37% yield.
[e] Starting material **2k** was recovered in 14% yield.

In summary, PPL works efficiently as a catalyst in the regiospecific acetylation of 2-alkylidenepropane-1,3-diols. Although a large excess of vinyl acetate (10 equiv) was used in the reaction, the corresponding (*E*)-monoacetates were generally obtained as the sole products in high yields without overacetylation. 3-Substituted (*E*)-2-(hydroxymethyl)prop-2-enyl acetates are potentially useful intermediates in organic synthesis and may be used as building blocks in the syntheses of natural products. Using our procedure, it is possible to prepare various kinds of (*E*)-monoacetates.

The ^1H NMR spectra were measured with a Bruker Ultrashield 400 Plus (400 MHz) spectrometer, with TMS as an internal standard. ^{13}C NMR spectroscopy was performed on a Bruker Ultrashield 400 Plus (100 MHz) spectrometer, with TMS as an internal standard. High-resolution mass spectra (HRMS) were recorded using a Waters LCT Premier (ESI-TOF-MS) spectrometer. For TLC, Merck precoated TLC plates (silica gel 60 F_{254}, Art 5715) were used. Porcine pancreatic lipase type II was commercially available from Sigma.

Diethyl 2-[4-(Trifluoromethyl)benzylidene]malonate (1c); Typical Procedure

A clear, colorless solution of 4-(trifluoromethyl)benzaldehyde (4.00 mL, 30.0 mmol, 1.00 equiv), diethyl malonate (4.76 mL, 31.5 mmol, 1.05 equiv), and benzoic acid (403 mg, 3.30 mmol, 0.11 equiv) in benzene (15 mL) was stirred at 120 °C for 17 h using a Dean–Stark trap. The mixture was then diluted with EtOAc (200 mL), washed with sat. aq $NaHCO_3$ (100 mL) and sat. aq NaCl (100 mL), and dried (anhyd $MgSO_4$). The crude product was chromatographed (silica gel, EtOAc–hexane, 1:10) to afford **1c**. Yield: 8.99 g (95%); colorless plate crystals; mp 49–50 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (t, *J* = 7.1 Hz, 3 H, CH_2CH_3), 1.35 (t, *J* = 7.1 Hz, 3 H, CH_2CH_3), 4.33 (q, *J* = 7.1 Hz, 2 H, CH_2CH_3), 4.34 (q, *J* = 7.1 Hz, 2 H, CH_2CH_3), 7.57 (d, *J* = 8.4 Hz, 2 H, ArH), 7.64 (d, *J* = 8.4 Hz, 2 H, ArH), 7.75 (s, 1 H, =CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 14.1, 61.97, 61.99, 123.7 (q, $^1J_{C–F}$ = 272 Hz), 125.7 (q, $^3J_{C–F}$ = 3.7 Hz), 128.8, 129.5, 131.9 (q, $^2J_{C–F}$ = 32.8 Hz), 136.5, 140.2, 163.7, 166.0.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{15}F_3O_4$: 339.0815; found: 339.0808.

Diethyl 2-(2,4,6-Trimethylbenzylidene)malonate (1h)

Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (t, *J* = 7.1 Hz, 3 H, CH_2CH_3), 1.35 (t, *J* = 7.1 Hz, 3 H, CH_2CH_3), 2.17 (s, 6 H, 2 CH_3), 2.26 (s, 3 H, CH_3), 4.02 (q, *J* = 7.1 Hz, 2 H, CH_2CH_3), 4.32 (q, *J* = 7.1 Hz, 2 H, CH_2CH_3), 6.82 (s, 2 H, ArH), 7.87 (s, 1 H, =CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.6, 14.2, 20.1, 21.0, 61.0, 61.6, 127.9, 130.5, 131.1, 135.1, 137.7, 145.5, 163.7, 165.2.

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{22}O_4$: 291.1591; found: 291.1617.

2-(4-Methoxybenzylidene)propane-1,3-diol (2b); Typical Procedure[3a]

To a colorless solution of diethyl 2-(4-methoxybenzylidene)malonate (**1b**)[6] (5.44 g, 22.0 mmol, 1.00 equiv) in dry toluene (10 mL) was added dropwise at –30 °C a solution of 0.99 M DIBAL-H in toluene (100 mL, 99.0 mmol, 4.50 equiv) under an argon atmosphere. The mixture was stirred at –30 °C for 3 h, and then quenched at the same temperature with MeOH (10 mL). To the mixture was added a solution of potassium sodium tartrate (126 g) in H_2O (350 mL). After stirring at r.t. for 1 h, the mixture was extracted with EtOAc (3 × 200 mL), and the EtOAc layers were combined, washed with brine, dried (anhyd $MgSO_4$), and evaporated. The crude product was chromatographed (silica gel, EtOAc–hexane, 2:1) to afford **2b**. Yield: 2.04 g (48%); colorless powder; mp 69–70 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.14 (t, *J* = 5.7 Hz, 1 H, OH), 2.21 (t, *J* = 5.4 Hz, 1 H, OH), 3.82 (s, 3 H, OCH_3), 4.39 (d, *J* = 5.4 Hz, 2 H, CH_2), 4.47 (d, *J* = 5.7Hz, 2 H, CH_2), 6.60 (s, 1 H, =CH), 6.89 (d, *J* = 8.8 Hz, 2 H, ArH-3), 7.22 (d, *J* = 8.8 Hz, 2 H, ArH-2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.3, 60.9, 68.0, 113.8, 128.7, 129.8, 130.2, 137.6, 158.9.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_{14}O_3$: 217.0835; found: 217.0820.

2-[4-(Trifluoromethyl)benzylidene]propane-1,3-diol (2c)

Colorless powder; mp 97–99 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.35 (br s, 2 H, 2 OH), 4.36 (s, 2 H, CH_2), 4.38 (s, 2 H, CH_2), 6.64 (s, 1 H, =CH), 7.34 (d, *J* = 8.4 Hz, 2 H, ArH), 7.56 (d, *J* = 8.4 Hz, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 60.4, 67.3, 124.1 (q, $^1J_{C–F}$ = 272 Hz), 125.3 (q, $^3J_{C–F}$ = 3.8 Hz), 128.2, 129.1, 129.3 (q, $^2J_{C–F}$ = 32.5 Hz), 139.7, 141.2.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_{11}F_3O_2$: 255.0603; found: 255.0646.

2-(4-Chlorobenzylidene)propane-1,3-diol (2d)

Colorless cotton crystals; mp 103–105 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.24 (br s, 2 H, 2 OH), 4.40 (s, 2 H, CH_2), 4.42 (s, 2 H, CH_2), 6.60 (s, 1 H, =CH), 7.21 (d, *J* = 8.5 Hz, 2 H, ArH), 7.32 (d, *J* = 8.5 Hz, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 60.6, 67.6, 128.5, 128.6, 130.2, 133.3, 134.6, 139.8.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{10}H_{11}ClO_2$: 221.0340; found: 221.0321.

2-(4-Methylbenzylidene)propane-1,3-diol (2e)

Colorless plate crystals; mp 107–108 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.08 (t, *J* = 4.8 Hz, 1 H, OH), 2.11 (t, *J* = 4.8 Hz, 1 H, OH), 2.36 (s, 3 H, CH_3), 4.41 (d, *J* = 4.8 Hz, 2 H, CH_2), 4.48 (d, *J* = 4.8 Hz, 2 H, CH_2), 6.63 (s, 1 H, =CH), 7.17 (s, 4 H, ArH).

^{13}C NMR (100 MHz, CD_3OD): δ = 21.2, 59.2, 65.5, 129.2, 129.9, 135.2, 137.9, 141.0.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_{14}O_2$: 201.0886; found: 201.0888.

2-(3-Methylbenzylidene)propane-1,3-diol (2f)

Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.30 (s, 3 H, CH_3), 3.50 (br s, 1 H, OH), 3.63 (br s, 1 H, OH), 4.31 (s, 2 H, CH_2), 4.37 (s, 2 H, CH_2), 6.55 (s, 1 H, =CH), 7.01–7.05 (m, 3 H, ArH), 7.18 (t, *J* = 8.0 Hz, 1 H, ArH-5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4, 60.1, 66.9, 125.9, 128.0, 128.2, 129.5, 129.7, 136.1, 137.8, 139.1.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_{14}O_2$: 201.0886; found: 201.0888.

2-(2-Methylbenzylidene)propane-1,3-diol (2g)

Colorless powder; mp 61–62 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.23 (s, 3 H, CH_3), 3.05 (br s, 1 H, OH), 3.15 (br s, 1 H, OH), 4.29 (s, 2 H, CH_2), 4.39 (s, 2 H, CH_2), 6.62 (s, 1 H, =CH), 7.12–7.20 (m, 4 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.9, 60.5, 66.9, 125.6, 127.6, 128.6, 129.1, 129.9, 135.3, 136.4, 139.2.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_{14}O_2$: 201.0886; found: 201.0888.

2-(2,4,6-Trimethylbenzylidene)propane-1,3-diol (2h)

Colorless powder; mp 88–89 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.11 (s, 6 H, 2 CH_3), 2.25 (s, 3 H, CH_3), 2.93 (br s, 1 H, OH), 3.27 (br s, 1 H, OH), 4.01 (s, 2 H, CH_2), 4.38 (s, 2 H, CH_2), 6.37 (s, 1 H, =CH), 6.83 (s, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.3, 20.9, 60.8, 66.1, 127.3, 128.0, 132.2, 135.9, 136.5, 139.8.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{18}O_2$: 229.1199; found: 229.1197.

2-(3-Phenylpropylidene)propane-1,3-diol (2i)

Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.39 (q, *J* = 7.6 Hz, 2 H, CH_2CH=), 2.59 (br s, 1 H, OH), 2.67 (t, *J* = 7.6 Hz, 2 H, $PhCH_2$), 3.01 (br s, 1 H, OH), 4.11 (s, 4 H, 2 CH_2), 5.56 (t, *J* = 7.6 Hz, 1 H, =CH), 7.15–7.20 (m, 3 H, ArH), 7.24–7.29 (m, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.3, 35.6, 59.4, 66.9, 126.0, 128.4, 128.5, 129.5, 137.9, 141.4.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_{16}O_2$: 215.1043; found: 215.1061.

2-(2-Naphthylmethylene)propane-1,3-diol (2j)
Colorless powder; mp 107–108 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.21 (br s, 2 H, 2 OH), 4.47 (s, 2 H, CH_2), 4.55 (s, 2 H, CH_2), 6.81 (s, 1 H, =CH), 7.40 (dd, *J* = 1.6, 8.4 Hz, 1 H, ArH), 7.45–7.51 (m, 2 H, ArH), 7.72 (s, 1 H, ArH), 7.80–7.84 (m, 3 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 60.9, 67.7, 126.1, 126.3, 126.9, 127.6, 127.8, 127.9, 128.1, 129.8, 132.5, 133.2, 133.6, 139.6.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{14}O_2$: 237.0886; found: 237.0865.

2-(2-Furylmethylene)propane-1,3-diol (2k)
Pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.04 (br s, 1 H, OH), 2.22 (br s, 1 H, OH), 4.37 (s, 2 H, CH_2), 4.65 (s, 2 H, CH_2), 6.32 (d, *J* = 3.3 Hz, 1 H, ArH-3), 6.35 (s, 1 H, =CH), 6.42 (dd, *J* = 1.8, 3.3 Hz, 1 H, ArH-4), 7.42 (d, *J* = 1.8 Hz, 1 H, ArH-5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 60.8, 66.6, 110.8, 111.5, 116.1, 137.8, 142.5, 151.7.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_8H_{10}O_3$: 177.0522; found: 177.0517.

2-(2-Thienylmethylene)propane-1,3-diol (2l)
Colorless powder; mp 51–52 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.17 (t, *J* = 5.2 Hz, 1 H, OH), 2.24 (t, *J* = 4.8 Hz, 1 H, OH), 4.40 (d, *J* = 5.2 Hz, 2 H, CH_2), 4.65 (d, *J* = 4.8Hz, 2 H, CH_2), 6.69 (s, 1 H, =CH), 7.01–7.04 (m, 2 H, ArH), 7.30–7.32 (m, 1 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 61.2, 67.4, 121.5, 126.3, 127.3, 128.3, 137.9, 138.6.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_8H_{10}O_2S$: 193.0294; found: 193.0312.

2-(3-Thienylmethylene)propane-1,3-diol (2m)
Colorless powder; mp 82–83 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.98 (t, *J* = 5.8 Hz, 1 H, OH), 2.07 (t, *J* = 5.4 Hz, 1 H, OH), 4.39 (d, *J* = 5.8 Hz, 2 H, CH_2), 4.52 (d, *J* = 5.4 Hz, 2 H, CH_2), 6.58 (s, 1 H, =CH), 7.09 (dd, *J* = 1.2, 5.0 Hz, 1 H, ArH), 7.23–7.25 (m, 1 H, ArH), 7.31 (dd, *J* = 3.0, 5.0 Hz, 1 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 61.1, 67.7, 123.8, 124.0, 125.6, 128.5, 137.1, 138.6.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_8H_{10}O_2S$: 193.0294; found: 193.0273.

(*E*)-2-(Hydroxymethyl)-3-(4-methoxyphenyl)prop-2-enyl Acetate (3b); Typical Procedure
A pale-yellow suspension of 2-(4-methoxybenzylidene)propane-1,3-diol (**2b**) (194 mg, 1.00 mmol, 1.00 equiv), vinyl acetate (0.92 mL, 10.0 mmol, 10.0 equiv), and 50% w/w PPL (97 mg) in 1,4-dioxane (3 mL) was stirred at r.t. for 23 h. Then, the resulting suspension was diluted with EtOAc (10 mL) and dried (anhyd $MgSO_4$). The mixture was filtered, and the filtrate was evaporated. The crude product was chromatographed (silica gel, EtOAc–hexane, 2:3) to afford **3b**.[3a] Yield: 222 mg (94%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.13 (s, 3 H, $COCH_3$), 2.23 (br s, 1 H, OH), 3.82 (s, 3 H, OCH_3), 4.33 (s, 2 H, C*H*$_2$OH), 4.80 (s, 2 H, C*H*$_2$OAc), 6.67 (s, 1 H, =CH), 6.89 (d, *J* = 8.7 Hz, 2 H, ArH-3), 7.26 (d, *J* = 8.7 Hz, 2 H, ArH-2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1, 55.3, 59.4, 67.8, 113.8, 128.2, 130.3, 132.8, 133.8, 159.2, 171.4.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{16}O_4$: 259.0941; found: 259.0958.

(*E*)-2-(Hydroxymethyl)-3-phenylprop-2-enyl Acetate (3a)
Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.12 (s, 3 H, $COCH_3$), 2.53 (br s, 1 H, OH), 4.31 (s, 2 H, C*H*$_2$OH), 4.82 (s, 2 H, C*H*$_2$OAc), 6.71 (s, 1 H, =CH), 7.25–7.36 (m, 5 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1, 59.3, 67.2, 127.6, 128.3, 128.9, 132.5, 135.5, 135.7, 171.4.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_{14}O_3$: 229.0835; found: 229.0831.

(*E*)-2-(Hydroxymethyl)-3-[4-(trifluoromethyl)phenyl]prop-2-enyl Acetate (3c)
Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.15 (s, 3 H, $COCH_3$), 2.49 (br s, 1 H, OH), 4.28 (s, 2 H, C*H*$_2$OH), 4.84 (s, 2 H, C*H*$_2$OAc), 6.73 (s, 1 H, =CH), 7.41 (d, *J* = 8.2 Hz, 2 H, ArH-2), 7.60 (d, *J* = 8.2 Hz, 2 H, ArH-3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 58.9, 66.8, 124.1 (q, $^1J_{C-F}$ = 272 Hz), 125.3 (q, $^3J_{C-F}$ = 3.8 Hz), 129.2, 129.6 (q, $^2J_{C-F}$ = 32.5 Hz), 130.7, 137.6, 139.4, 171.4.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{13}F_3O_3$: 297.0709; found: 297.0739.

(*E*)-3-(4-Chlorophenyl)-2-(hydroxymethyl)prop-2-enyl Acetate (3d)
Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.14 (s, 3 H, $COCH_3$), 2.23 (br s, 1 H, OH), 4.28 (s, 2 H, C*H*$_2$OH), 4.81 (s, 2 H, C*H*$_2$OAc), 6.67 (s, 1 H, =CH), 7.24 (d, *J* = 8.4 Hz, 2 H, ArH-2), 7.33 (d, *J* = 8.4 Hz, 2 H, ArH-3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 59.1, 67.1, 128.5, 130.3, 131.3, 133.6, 134.1, 136.1, 171.3.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_{13}ClO_3$: 263.0445; found: 263.0488.

(*E*)-2-(Hydroxymethyl)-3-(4-tolyl)prop-2-enyl Acetate (3e)
Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.13 (s, 3 H, $COCH_3$), 2.21 (t, *J* = 5.2 Hz, 1 H, OH), 2.35 (s, 3 H, CH_3), 4.33 (d, *J* = 5.2 Hz, 2 H, C*H*$_2$OH), 4.81 (s, 2 H, C*H*$_2$OAc), 6.70 (s, 1 H, =CH), 7.16 (d, *J* = 8.2 Hz, 2 H, ArH), 7.19 (d, *J* = 8.2 Hz, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1, 21.2, 59.2, 67.4, 128.9, 129.0, 132.6, 132.8, 134.8, 137.5, 171.4.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{16}O_3$: 243.0992; found: 243.1003.

(*E*)-2-(Hydroxymethyl)-3-(3-tolyl)prop-2-enyl Acetate (3f)
Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.12 (s, 3 H, $COCH_3$), 2.35 (s, 3 H, CH_3), 2.40 (br s, 1 H, OH), 4.32 (s, 2 H, C*H*$_2$OH), 4.81 (s, 2 H, C*H*$_2$OAc), 6.69 (s, 1 H, =CH), 7.08–7.10 (m, 3 H, ArH), 7.23 (t, *J* = 7.8 Hz, 1 H, ArH-5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1, 21.4, 59.2, 67.3, 126.0, 128.2, 128.4, 129.6, 132.7, 135.3, 135.7, 137.9, 171.4.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{16}O_3$: 243.0992; found: 243.1003.

(*E*)-2-(Hydroxymethyl)-3-(2-tolyl)prop-2-enyl Acetate (3g)
Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.13 (s, 3 H, $COCH_3$), 2.24 (s, 3 H, CH_3), 2.40 (br s, 1 H, OH), 4.20 (s, 2 H, CH_2OH), 4.85 (s, 2 H, CH_2OAc), 6.71 (s, 1 H, =CH), 7.15–7.22 (m, 4 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.9, 21.1, 59.1, 66.7, 125.6, 127.8, 129.1, 129.9, 131.2, 134.9, 135.6, 136.4, 171.4.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{16}O_3$: 243.0992; found: 243.1003.

(*E*)-2-(Hydroxymethyl)-3-mesitylprop-2-enyl Acetate (3h)
Colorless powder; mp 36–37 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.12 (s, 6 H, 2 CH_3), 2.13 (s, 3 H, $COCH_3$), 2.27 (s, 3 H, CH_3), 3.92 (s, 2 H, CH_2OH), 4.86 (s, 2 H, CH_2OAc), 6.48 (s, 1 H, =CH), 6.85 (s, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.2, 20.96, 21.00, 59.4, 65.9, 128.0, 129.8, 131.8, 135.8, 136.5, 136.7, 171.4.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{20}O_3$: 271.1305; found: 271.1321.

(*E*)-2-(Hydroxymethyl)-5-phenylpent-2-enyl Acetate (3i)
Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.67 (br s, 1 H, OH), 2.06 (s, 3 H, $COCH_3$), 2.44 (q, *J* = 7.5 Hz, 2 H, CH_2CH=), 2.69 (t, *J* = 7.5 Hz, 2 H, CH_2Ph), 4.00 (s, 2 H, CH_2OH), 4.59 (s, 2 H, CH_2OAc), 5.67 (t, *J* = 7.5 Hz, 1 H, =CH), 7.15–7.21 (m, 3 H, ArH), 7.26–7.30 (m, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.9, 29.3, 35.4, 58.1, 66.8, 126.0, 128.3, 128.5, 132.4, 134.4, 141.1, 171.2.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{18}O_3$: 257.1148; found: 257.1150.

(*E*)-2-(Hydroxymethyl)-3-(2-naphthyl)prop-2-enyl Acetate (3j)
Colorless powder; mp 92–93 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.16 (s, 3 H, $COCH_3$), 2.18 (br s, 1 H, OH), 4.41 (s, 2 H, CH_2OH), 4.88 (s, 2 H, CH_2OAc), 6.89 (s, 1 H, =CH), 7.42 (dd, *J* = 1.7, 8.5 Hz, 1 H, ArH), 7.46–7.51 (m, 2 H, ArH), 7.76 (s, 1 H, ArH-1), 7.81–7.85 (m, 3 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1, 59.4, 67.4, 126.28, 126.34, 126.9, 127.6, 127.95, 128.05, 128.13, 132.6, 132.8, 133.17, 133.19, 135.8, 171.4.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{16}O_3$: 279.0992; found: 279.1013.

(*E*)-3-(2-Furyl)-2-(hydroxymethyl)prop-2-enyl Acetate (3k)
Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.12 (s, 3 H, $COCH_3$), 2.30 (br s, 1 H, OH), 4.55 (s, 2 H, CH_2OH), 4.78 (s, 2 H, CH_2OAc), 6.38 (d, *J* = 3.4 Hz, 1 H, ArH-3), 6.40 (s, 1 H, =CH), 6.43 (dd, *J* = 1.8, 3.4 Hz, 1 H, ArH-4), 7.44 (d, *J* = 1.8 Hz, 1 H, ArH-5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 60.0, 67.1, 111.6, 111.8, 119.2, 133.5, 142.9, 151.3, 171.2.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{10}H_{12}O_4$: 219.0628; found: 219.0602.

(*E*)-2-(Hydroxymethyl)-3-(2-thienyl)prop-2-enyl Acetate (3l)
Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.11 (t, *J* = 6.0 Hz, 1 H, OH), 2.13 (s, 3 H, $COCH_3$), 4.52 (d, *J* = 6.0 Hz, 2 H, CH_2OH), 4.81 (s, 2 H, CH_2OAc), 6.77 (s, 1 H, =CH), 7.04 (dd, *J* = 3.6, 5.1 Hz, 1 H, ArH-4), 7.08 (d, *J* = 3.6 Hz, 1 H, ArH-3), 7.34 (dd, *J* = 1.1, 5.1 Hz, 1 H, ArH-5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1, 59.9, 67.3, 125.0, 126.9, 127.3, 129.1, 133.9, 138.1, 171.3.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{10}H_{12}O_3S$: 235.0399; found: 235.0360.

(*E*)-2-(Hydroxymethyl)-3-(3-thienyl)prop-2-enyl Acetate (3m)
Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.09 (s, 3 H, $COCH_3$), 3.11 (br s, 1 H, OH), 4.34 (s, 2 H, CH_2OH), 4.76 (s, 2 H, CH_2OAc), 6.60 (s, 1 H, =CH), 7.08–7.10 (m, 1 H, ArH-4), 7.26–7.28 (m, 2 H, ArH-2, ArH-5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 59.3, 67.3, 124.5, 125.5, 126.4, 128.5, 134.6, 136.7, 171.4.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{10}H_{12}O_3S$: 235.0399; found: 235.0399.

(*Z*)-2-(Hydroxymethyl)-5-phenylpent-2-enyl Acetate (4)
Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.04 (s, 3 H, $COCH_3$), 2.19 (br s, 1 H, OH), 2.46 (q, *J* = 7.4 Hz, 2 H, CH_2CH=), 2.69 (t, *J* = 7.4 Hz, 2 H, CH_2Ph), 4.07 (s, 2 H, CH_2OH), 4.61 (s, 2 H, CH_2OAc), 5.74 (t, *J* = 7.4 Hz, 1 H, =CH), 7.15–7.20 (m, 3 H, ArH), 7.25–7.30 (m, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.9, 29.5, 35.6, 60.1, 65.6, 126.0, 128.38, 128.44, 132.2, 134.3, 141.3, 171.3.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{18}O_3$: 257.1148; found: 257.1107.

2-[(Acetyloxy)-methyl]-5-phenylpent-2-en-1-yl Acetate (5)
Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.03 (s, 3 H, $COCH_3$), 2.06 (s, 3 H, $COCH_3$), 2.45–2.50 (m, 2 H, CH_2CH=), 2.70 (t, *J* = 7.3 Hz, 2 H, CH_2Ph), 4.55 (s, 4 H, 2 × CH_2OAc), 5.81 (t, *J* = 7.5 Hz, 1 H, =CH), 7.16–7.21 (m, 3 H, ArH), 7.26–7.30 (m, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.9, 21.0, 29.6, 35.4, 59.7, 66.5, 126.1, 128.4, 128.5, 129.8, 153.2, 141.0, 170.7, 170.8.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{20}O_4Na$: 299.1254; found: 299.1215.

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