

Supporting Information

Enantioselective Acylation of Secondary Alcohols Catalyzed by Chiral *N*-Heterocyclic Carbenes

Taichi Kano, Kouji Sasaki and Keiji Maruoka*

*Department of Chemistry, Graduate School of Science, Kyoto University
Sakyo, Kyoto 606-8502, Japan*

General Information. Infrared (IR) spectra were recorded on a Shimadzu IRPrestige-21 spectrometer. ^1H and ^{13}C NMR spectra were measured on a JEOL JNM-FX400 NMR spectrometer at ambient temperature. ^1H NMR data were reported as follows: chemical shift in ppm from tetramethylsilane as an internal standard, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, hept = heptet, m = multiplet, br = broad), coupling constants (Hz), and assignment. ^{13}C NMR spectra were determined with complete proton decoupling. Chemical shifts are reported in ppm from the residual solvent as an internal standard. High performance liquid chromatography (HPLC) was performed on Shimadzu 10A instruments using a Daicel CHIRALPAK or CHIRALCEL, 4.6 mm \times 25 cm column. Gas chromatography (GC) was performed on Shimadzu GC-14B instruments using CHIRALDEX, 20 m \times 0.25 mm column. High-resolution mass spectra (HRMS) were performed on Applied Biosystems Mariner biospectrometry workstation. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter. For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF₂₅₄, 0.25 mm) were used. The products were purified by flash column chromatography on silica gel 60 (Merck 1.09386.9025, 230-400 mesh).

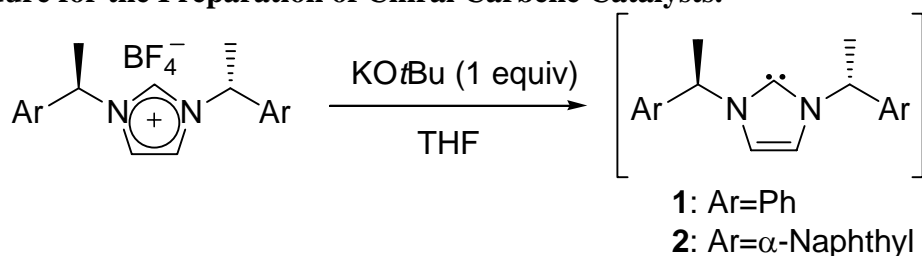
Tetrahydrofuran was distilled from sodium/benzophenone. 1,3-Bis-(1-(*R*)-phenylethyl)-imidazolium tetrafluoroborate and 1,3-bis-(1-(*R*)-(1-naphthyl)ethyl)imidazolium tetrafluoroborate were synthesized according to the literature procedure¹ and purified by flash column chromatography. 1-Phenylethanol (TCI) was purified by distillation prior to use. α -Methyl-1-naphthalenemethanol, α -methyl-2-naphthalenemethanol, 1-(4-fluorophenyl)ethanol, 1-(4-methoxyphenyl)ethanol and 1-phenylpropanol were prepared by reduction of corresponding ketones with NaBH₄ and were purified by flash column chromatography and/or distillation. (*E*)-4-Phenyl-3-buten-2-ol and (*E*)-3-methyl-4-phenyl-3-buten-2-ol were prepared by methylation of *trans*-cinnamaldehyde and α -methyl-*trans*-cinnamaldehyde with methyllithium, respectively, and were purified by flash column chromatography and/or distillation. Other simple chemicals were purchased and used as such.

Preparation of Vinyl Diphenylacetate.²

A mixture of diphenylacetic acid (6.37 g, 30 mmol), diacetato(1,10-phenanthroline)palladium(II)

(126.9 mg, 0.3 mmol) and vinyl acetate (28 mL, 0.3 mol) was stirred at 50 °C for 24 h under argon atmosphere. After cooling to room temperature, the reaction mixture was filtered through celite. The filtrate was poured into saturated aqueous NaHCO₃ and extracted with ethyl acetate. The combined organic layer was dried over Na₂SO₄ and concentrated under vacuum. The residue was purified by column chromatography on silica gel (ether/hexane = 0:1~1:50 as eluent) followed by distillation (130~140 °C, 0.05 mmHg) to give vinyl diphenylacetate (6.17 g, 25.9 mmol) as a colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 7.35-7.23 (11H, m, Ar-H, CO₂CHCH₂), 5.07 (1H, s, Ph₂CHCO₂), 4.90 (1H, dd, *J* = 14.4, 1.6 Hz, CHCH₂), 4.60 (1H, dd, *J* = 6.4, 1.6 Hz, CHCH₂); ¹³C NMR (100 MHz, CDCl₃) δ 169.4, 141.2, 137.9, 128.6, 128.5, 127.4, 98.4, 56.8; IR (neat) 1749, 1645, 1497, 1454, 1182, 1132, 945, 878, 743, 696, 632 cm⁻¹; HRMS (ESI-TOF) Calcd for C₁₆H₁₄O₂Na: 261.0886 ([M+Na]⁺), Found: 261.0884 ([M+Na]⁺).

General Procedure for the Preparation of Chiral Carbene Catalysts.³



A solution of 1,3-bis-(1-(*R*)-phenylethyl)imidazolium tetrafluoroborate (10.9 mg, 0.03 mmol) in freshly distilled THF (2 mL) was carefully degassed with argon at -78 °C. To the solution was added a 1.0 M THF solution of potassium *tert*-butoxide (30 μL, 0.03 mmol) dropwise at room temperature. After stirring for 0.5 h, the catalyst solution was used for the following reactions.

Acylation of 1-Phenylethanol with Methyl Acetate by Chiral Carbene Catalyst 1.

To a mixture of 1-phenylethanol (72 μL, 0.6 mmol), methyl acetate (0.5 mL, 6.3 mmol) and MS 4Å (200 mg) in THF (0.5 mL) at -78 °C under argon atmosphere was added a THF solution of the catalyst **1** which was prepared under the same conditions as described above except for using 1 mL of THF as solvent. The flask was rinsed with THF (0.5 mL) and the THF solution was also transferred to the reaction mixture at -78 °C. After stirring under the conditions as indicated in Table 1, the reaction mixture was then treated with 0.1 N HCl and filtered through celite. The filtrate was extracted with ether. The combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated under vacuum. The residue was purified by column chromatography on silica gel (ether/hexane = 1:50~1:2 as eluent) to give the corresponding ester (59.8 mg, 0.364 mmol) and the remaining alcohol (26.1 mg, 0.214 mmol), respectively. The optical purities of the ester and the alcohol were determined by chiral GC and HPLC analysis (Table 3).

General Procedure for Enantioselective Acylation of Secondary Alcohols with Vinyl Esters by

Chiral Carbene Catalyst 1 or 2.

To a solution of catalyst **1** or **2** and a secondary alcohol (0.6 mmol) in THF (2 mL) was added a vinyl ester dropwise at -78 °C. The reaction mixture was stirred under the conditions as indicated in Table 1 or Table 2. The resulting mixture was then treated with 0.1 N HCl and extracted with ether. The combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated under vacuum. The residue was purified by column chromatography on silica gel (ether/hexane = 1:50~1:2 as eluent) to give the corresponding ester and the remaining alcohol, respectively. The optical purities of the esters and the alcohols were determined by chiral GC and HPLC analysis (Table 3).

Table 1: Enantioselective Acylation of 1-Phenylethanol with Chiral Carbene Catalyst **1**.

$\text{Ph-CH(OH)-CH}_3 + \text{R}^1\text{CO}_2\text{R}^2 \xrightarrow[\text{THF}]{5 \text{ mol\% } \mathbf{1}}$

$\text{Ph-CH(O-C(=O)R}^1\text{)-CH}_3 + \text{Ph-CH(OH)-CH}_3$

(R)-Ester **(S)-Alcohol**

Entry	R ¹ CO ₂ R ²	(equiv)	Conditions [°C, h]	(R)-Ester [% ee (% yield)]	(S)-Alcohol [% ee (% yield ^a)]	<i>s</i> ^b
1	MeCO ₂ Me	10.5	-78~-20, 5; 0, 2	0 (61)	0 (36)	1.0
2	MeCO ₂ (vinyl)	0.5	-78, 1	29 (36)	20 (56)	2.2
3	<i>i</i> PrCO ₂ (vinyl)	0.5	-78, 1	67 (37)	43 (55)	7.8
4	<i>t</i> BuCO ₂ (vinyl)	1.5	-78, 1	76 (40)	50 (57)	12
5	Ph ₂ CHCO ₂ (vinyl)	0.75	-78, 3	93 (33)	52 (61)	46

^a Under the reaction conditions, a small amount of acetal esters **3** was generated as a byproduct with very low de and ee in each case,⁴ suggesting very little participation of the catalyst in the formation of **3**. ^b *s* = $\ln[1 - c(1 + ee_{\text{ester}})] / \ln[1 - c(1 - ee_{\text{ester}})]$, $c = \text{yield}_{\text{ester}} / (\text{yield}_{\text{ester}} + \text{yield}_{\text{alcohol}})$.

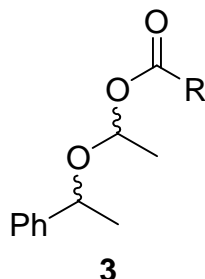


Table 2: Enantioselective Acylation of *sec*-Alcohols with Chiral Carbene Catalysts **1** and **2**.

Entry	Substrate	Catalyst	Conditions	(<i>R</i>)-Ester	(<i>S</i>)-Alcohol	<i>s</i> ^b
			[°C, h]	[% ee (% yield)]	[% ee (% yield ^a)]	
1		1	-78, 3	93 (33)	52 (61)	46
2		2	-78, 3	96 (32)	51 (62)	80
3		2	-78, 3; -20, 3.5	92 (33)	42 (67)	38
4		1	-78, 3	90 (35)	53 (58)	33
5		2	-78, 4	91 (39)	62 (54)	42
6		2	-78, 2; -40, 3	94 (30)	36 (70)	48
7		1	-78, 1.5	93 (35)	50 (63)	46
8		2	-78, 6	95 (27)	36 (71)	56
9		2	-78, 4; -40, 0.5	94 (29)	39 (71)	47
10		1	-78, 3.5	84 (27)	31 (73)	16
11		1	-78, 1; -40, 2	87 (33)	42 (66)	22

^a Under the reaction conditions, a small amount of the corresponding acetal ester was generated as a byproduct with very low de and ee in each case, suggesting very little participation of the catalyst in the formation of the acetal ester. For example, treatment of the acetal ester of α -methyl-2-naphthalenemethanol with *p*-toluenesulfonic acid in MeOH/CH₂Cl₂ at room temperature furnished the secondary alcohol in 6% ee.

^b $s = \ln[1 - c(1 + ee_{\text{ester}})] / \ln[1 - c(1 - ee_{\text{ester}})]$, $c = \text{yield}_{\text{ester}} / (\text{yield}_{\text{ester}} + \text{yield}_{\text{alcohol}})$.

Table 3. GC and HPLC Conditions and Retention Times for the Determination of Enantiomeric Excess.

Alcohol	Chiral column	Conditions	Retention time; (<i>R</i>) isomer (min)	Retention time; (<i>S</i>) isomer (min)
1-phenylethanol ^a	HPLC CHIRALCEL OD-H	9% <i>i</i> PrOH/Hex, 0.5 mL/min	11.4	12.8
	GC CHILDEX B-DM	100 °C	31.5	33.8
1-phenylpropanol ^a	HPLC CHIRALCEL OD-H	9% <i>i</i> PrOH/Hex, 0.5 mL/min	11.5	12.3
1-(4-fluorophenyl)ethanol ^a	HPLC CHIRALPAK AS-H	1% <i>i</i> PrOH/Hex, 1.0 mL/min	15.9	16.8
1-(4-methoxy- phenyl)ethanol ^a	HPLC CHIRALCEL OD-H	4% <i>i</i> PrOH/Hex, 0.5 mL/min	35.1	39.3
α -methyl- 2-naphthalenemethanol ^a	HPLC CHIRALCEL OJ-H	5% <i>i</i> PrOH/Hex, 1.0 mL/min	33.6	25.5
α -methyl- 1-naphthalenemethanol ^b	HPLC CHIRALCEL OD-H	9% <i>i</i> PrOH/Hex, 1.0 mL/min	14.1	9.9
(<i>E</i>)-4-phenyl-3-buten-2-ol ^b	HPLC CHIRALCEL OD-H	9% <i>i</i> PrOH/Hex, 1.0 mL/min	14.8	23.4
(<i>E</i>)-3-methyl- 4-phenyl-3-buten-2-ol ^a	HPLC CHIRALCEL OD-H	4% <i>i</i> PrOH/Hex, 1.0 mL/min	9.5	10.6
Ester	Chiral column	Conditions	Retention time; (<i>R</i>) isomer (min)	Retention time; (<i>S</i>) isomer (min)
1-phenylethyl acetate	HPLC CHIRALCEL OD-H	1% <i>i</i> PrOH/Hex, 0.5 mL/min	16.7	7.9
1-phenylethyl isobutylate	HPLC CHIRALPAK AD-H	1% <i>i</i> PrOH/Hex, 0.5 mL/min	9.1	10.7
1-phenylethyl pivalate	GC CHILDEX B-DM	100 °C	38.2	39.3
1-phenylethyl-diphenylacetate	HPLC CHIRALPAK AD-H	1% <i>i</i> PrOH/Hex, 1.0 mL/min	13.1	24.1
1-phenylpropyl- diphenylacetate	HPLC CHIRALPAK AD-H	1% <i>i</i> PrOH/Hex, 1.0 mL/min	12.4	22.7
α -methyl-4-fluorophenyl- methyl diphenylacetate	HPLC CHIRALPAK AD-H	1% <i>i</i> PrOH/Hex, 0.5 mL/min	25.7	56.8
α -methyl-4-methoxyphenyl- methyl diphenylacetate	HPLC CHIRALPAK AS-H	1% <i>i</i> PrOH/Hex, 0.5 mL/min	17.9	20.1
α -methyl-2-naphthalene- methyl diphenylacetate	HPLC CHIRALPAK AS-H	1% <i>i</i> PrOH/Hex, 0.5 mL/min	15.6	17.9
α -methyl-1-naphthalene- methyl diphenylacetate	HPLC CHIRALPAK AD-H	1% <i>i</i> PrOH/Hex, 0.5 mL/min	31.4	52.5
4-phenyl-3-buten-2-yl- diphenylacetate	HPLC CHIRALPAK AS-H	1% <i>i</i> PrOH/Hex, 0.5 mL/min	12.7	14.3
3-methyl-4-phenyl-3-buten- 2-yl diphenylacetate	HPLC CHIRALCEL OD-H	1% <i>i</i> PrOH/Hex, 0.5 mL/min	22.7	16.5

^a Absolute configuration; See ref 5. ^b Absolute configuration; See ref 6.

Hydrolysis of a Diphenylacetate Ester

To a solution of (*R*)-1-phenylethyl diphenylacetate (96% ee, 42.5 mg, 0.134 mmol) in THF/MeOH (1 mL/1 mL) was added aqueous 15 wt% NaOH (0.5 mL) at 0 °C. After stirring at 0 °C for 0.5 h and at room temperature for 1 h, the mixture was poured into saturated aqueous NH₄Cl and extracted with ether. The combined organic layer was dried over Na₂SO₄ and concentrated under vacuum. The residue was purified by column chromatography on silica gel (ether/hexane = 1:5 as eluent) to give (*R*)-1-phenylethanol (15.4 mg, 0.126 mmol, 94%) without loss of optical purity (96% ee).

Characterization of the Diphenylacetates

1-Phenylethyl Diphenylacetate. $[\alpha]_D^{29} +40.6^\circ$ [*c* 0.94, CHCl₃ (96% ee)]; ¹H NMR (400 MHz, CDCl₃) δ 7.35-7.21 (15H, m, Ar-H), 5.94 (1H, q, *J* = 6.8 Hz, PhCHCH₃), 5.05 (1H, s, Ph₂CHCO₂), 1.51 (3H, d, *J* = 6.8 Hz, PhCHCH₃); ¹³C NMR (100 MHz, CDCl₃) δ 171.4, 141.2, 138.6, 138.4, 128.6, 128.40, 128.38, 128.3, 127.7, 127.1, 127.0, 126.0, 73.2, 57.3, 22.2 ; IR (neat) 1734, 1495, 1452, 1186, 1148, 1060, 1030, 756, 745, 649 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₂₂H₂₀O₂Na: 339.1356 ([M+Na]⁺), Found: 339.1356 ([M+Na]⁺).

α -Methyl-2-naphthalenemethyl Diphenylacetate. $[\alpha]_D^{30} +39.3^\circ$ [*c* 0.99, CHCl₃ (93% ee)]; ¹H NMR (400 MHz, CDCl₃) δ 7.80-7.78 (1H, m, Ar-H), 7.76 (1H, d, *J* = 8.8 Hz, Ar-H), 7.72-7.69 (1H, m, Ar-H), 7.62 (1H, s, Ar-H), 7.46-7.44 (2H, m, Ar-H), 7.34-7.30 (5H, m, Ar-H), 7.28-7.23 (6H, m, Ar-H), 6.10 (1H, q, *J* = 6.4 Hz, ArCHCH₃), 5.09 (1H, s, Ph₂CHCO₂), 1.60 (3H, d, *J* = 6.4 Hz, PhCHCH₃); ¹³C NMR (100 MHz, CDCl₃) δ 171.4, 138.61, 138.59, 138.4, 133.0, 132.8, 128.60, 128.57, 128.43, 128.41, 128.1, 127.9, 127.5, 127.09, 127.07, 126.0, 125.9, 124.7, 123.9, 73.2, 57.3, 22.2; IR (neat) 1732, 1495, 1452, 1306, 1273, 1188, 1148, 1126, 1061, 858, 818, 745, 698 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₂₆H₂₂O₂Na: 389.1512 ([M+Na]⁺), Found: 389.1512 ([M+Na]⁺).

α -Methyl-1-naphthalenemethyl Diphenylacetate. $[\alpha]_D^{30} +5.9^\circ$ [*c* 1.04, CHCl₃ (94% ee)]; ¹H NMR (400 MHz, CDCl₃) δ 7.96 (1H, dd, *J* = 7.6, 2.0 Hz, Ar-H), 7.83 (1H, dd, *J* = 7.2, 2.4 Hz, Ar-H), 7.75 (1H, dd, *J* = 7.6, 1.6 Hz, Ar-H), 7.47-7.21 (14H, m, Ar-H), 6.70 (1H, q, *J* = 6.8 Hz, ArCHCH₃), 5.10 (1H, s, Ph₂CHCO₂), 1.67 (3H, d, *J* = 6.8 Hz, PhCHCH₃); ¹³C NMR (100 MHz, CDCl₃) δ 171.5, 127.10, 127.07, 126.1, 125.5, 125.1, 123.1, 123.0, 128.7, 128.60, 128.59, 128.43, 128.38, 128.3, 127.10, 127.07, 126.1, 125.5, 125.1, 123.1, 123.0, 70.4, 57.3, 21.7; IR (neat) 1732, 1497, 1452, 1227, 1188, 1150, 1069, 1042, 799, 777, 745, 700 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₂₆H₂₂O₂Na: 389.1512 ([M+Na]⁺), Found: 389.1509 ([M+Na]⁺).

α -Methyl-4-fluorophenylmethyl Diphenylacetate. $[\alpha]_D^{30} +31.7^\circ$ [*c* 1.01, CHCl₃ (91% ee)]; ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.16 (12H, m, Ar-H), 6.96 (2H, t, *J* = 8.4 Hz, Ar-H), 5.91 (1H, q, *J* = 6.8 Hz, ArCHCH₃), 5.03 (1H, s, Ph₂CHCO₂), 1.50 (3H, d, *J* = 6.8 Hz, PhCHCH₃); ¹³C NMR (100 MHz,

CDCl₃) δ 171.4, 160.9, 138.5, 138.3, 137.0, 128.54, 128.50, 128.4, 127.8, 127.7, 127.12, 127.10, 115.2, 115.0, 72.5, 57.2, 22.1; IR (neat) 1732, 1604, 1510, 1452, 1223, 1186, 1148, 1059, 1003, 835, 746, 698, 565 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₂₂H₁₉O₂FNa: 357.1261 ([M+Na]⁺), Found: 357.1265 ([M+Na]⁺).

α -Methyl-4-methoxyphenylmethyl Diphenylacetate. [α]_D²⁹ +45.5° [*c* 0.86, CHCl₃ (94% ee)]; ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.16 (12H, m, Ar-H), 6.82 (2H, d, *J* = 8.8 Hz, Ar-H), 5.91 (1H, q, *J* = 6.8 Hz, ArCHCH₃), 5.02 (1H, s, Ph₂CHCO₂), 5.79 (3H, s, CH₃O), 1.50 (3H, d, *J* = 6.8 Hz, PhCHCH₃); ¹³C NMR (100 MHz, CDCl₃) δ 171.5, 159.1, 138.7, 138.5, 133.3, 128.5, 128.4, 128.3, 127.5, 127.03, 126.98, 113.7, 72.9, 57.3, 55.3, 21.9; IR (neat) 1732, 1612, 1514, 1452, 1248, 1179, 1150, 1057, 1032, 831, 746, 700 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₂₃H₂₂O₃Na: 369.1461 ([M+Na]⁺), Found: 369.1465 ([M+Na]⁺).

1-Phenylpropyl Diphenylacetate. [α]_D³⁰ +44.0° [*c* 0.94, CHCl₃ (93% ee)]; ¹H NMR (400 MHz, CDCl₃) δ 7.32-7.18 (15H, m, Ar-H), 5.71 (1H, t, *J* = 7.2 Hz, ArCHCH₂CH₃), 5.06 (1H, s, Ph₂CHCO₂), 1.89 (1H, hept, ArCHCH₂CH₃), 1.78 (1H, hept, ArCHCH₂CH₃), 0.80 (3H, t, *J* = 7.2 Hz, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 171.5, 140.0, 138.7, 138.4, 128.61, 128.58, 128.4, 128.3, 128.1, 127.7, 127.07, 127.00, 126.4, 78.2, 57.4, 29.3, 9.9; IR (neat) 1734, 1495, 1454, 1188, 1146, 976, 912, 745, 696 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₂₃H₂₂O₂Na: 353.1512 ([M+Na]⁺), Found: 353.1513 ([M+Na]⁺).

4-Phenyl-3-buten-2-yl Diphenylacetate. [α]_D³⁰ +48.7° [*c* 0.83, CHCl₃ (84% ee)]; ¹H NMR (400 MHz, CDCl₃) δ 7.32-7.21 (15H, m, Ar-H), 6.48 (1H, dd, *J* = 16, 0.8 Hz, PhCH), 6.13 (1H, dd, *J* = 16, 6.8 Hz, PhCHCH), 5.61 (1H, quint-d, OCHCH₃), 5.04 (1H, s, Ph₂CHCO₂), 1.39 (3H, d, *J* = 6.8 Hz, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ 171.5, 138.7, 138.6, 136.2, 131.4, 128.54, 128.45, 128.41, 128.3, 127.7, 127.1, 126.4, 71.7, 57.3, 20.4; IR (neat) 1732, 1495, 1450, 1188, 1144, 1032, 964, 745, 692 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₂₄H₂₂O₂Na: 365.1512 ([M+Na]⁺), Found: 365.1510 ([M+Na]⁺).

3-Methyl-4-phenyl-3-buten-2-yl Diphenylacetate. [α]_D³⁰ +1.1° [*c* 0.85, CHCl₃ (85% ee)]; ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.17 (15H, m, Ar-H), 6.42 (1H, s, PhCH), 5.48 (1H, q, *J* = 6.8 Hz, OCHCH₃), 5.05 (1H, s, Ph₂CHCO₂), 1.75 (3H, s, PhCHCCH₃), 1.39 (3H, d, *J* = 6.8 Hz, OCHCH₃); ¹³C NMR (100 MHz, CDCl₃) δ 171.4, 138.7, 138.6, 137.1, 136.8, 128.9, 128.57, 128.55, 128.45, 128.4, 127.9, 127.08, 127.06, 126.5, 76.16, 57.4, 19.2, 13.9; IR (neat) 1732, 1495, 1452, 1186, 1148, 1065, 743, 696, 563 cm⁻¹; HRMS (ESI-TOF) Calcd. for C₂₅H₂₄O₂Na: 379.1669 ([M+Na]⁺), Found: 379.1668([M+Na]⁺).

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