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Catalytic asymmetric epoxidation of alkenes with arabinose-derived ketones containing a cyclohexane-1,2-diacetal

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Dedicated to George W. J. Fleet on the occasion of his 65th birthday

ABSTRACT

The effect of diol blocking groups, cyclohexane-1,2-diacetal verses butane-1,2-diacetal, on the asymmetric epoxidation of *trans*- and *cis*-alkenes by arabinose-derived ketones is reported. The ketone catalysts with a cyclohexane-1,2-acetal display similar asymmetric induction as those catalysts with a butane-1,2-diacetal in most cases. For (*E*)-1-benzyloxy-4-hexene, the ee of the enantioselective epoxidation has reached 61% with the cyclohexane-1,2-dineopentyl acetal ketone catalyst.

1. Introduction

The catalytic asymmetric epoxidation of olefins is an important synthetic method to induce chirality into organic molecules; the resultant epoxides therefore provide versatile intermediates for natural products or pharmaceutical synthesis. Catalytic enantioselective epoxidation using transition metal complexes is well established and chiral oxiranes are obtained from allylic alcohols[1] and from unfunctionalized *cis*-alkenes[2] with excellent asymmetric induction. In recent years, chiral dioxiranes,[3] generated in situ from Oxone® and chiral ketones, have become promising reagents for the asymmetric epoxidation of unfunctionalized alkenes. This organocatalytic epoxidation using chiral ketone catalysts was pioneered by Curci in 1984.[4] Subsequently, elegant 11-membered C_2-symmetry biaryl ketones developed by Yang et al.[5] afforded enantioselectivities which have stimulated worldwide investigations on the subject. There are now many research groups which have achieved impressive results using different chiral ketone/Oxone® systems.[6] Our long-term interest in the application of carbohydrates in asymmetric synthesis has prompted us to search for a readily prepared ketone catalyst to induce chirality with high ee in the asymmetric epoxidation. Arabinose, available commercially in large quantities for both enantiomers, has been the first choice for our studies. Over the years, we had described the use of arabinose-derived alcohols as chiral auxiliaries in asymmetric Diels–Alder reactions[7] and in asymmetric Hosomi–Sakurai reaction.[8] Our efforts towards the enantioselective epoxidation of alkenes have provided chiral ketone organocatalysts derived from D-glucose;[9] 2-uloses and 3-uloses derived from L-arabinose;[10] and arabinose-derived 4-uloses[11] containing a tunable butane-2,3-diacetal[12] as the steric blocker. These ketone catalysts have been employed for the asymmetric epoxidation of *trans*-disubstituted, *trans*-trisubstituted and *cis*-alkenes. For arabinose-derived 4-uloses, the enantioselectivity increases with the size of the acetal alkoxy group for both *trans*-disubstituted and -trisubstituted alkenes.[11b,c] Interestingly, an inverse relationship with the size of the alkoxy group was observed for *cis*-alkenes.[11a] Herein, we report the effect of diol blocking groups, cyclohexane-1,2-diacetal verses butane-1,2-diacetal, on the asymmetric epoxidation of *trans*- and *cis*-alkenes.

2. Results and discussion

In order to study the effect of a cyclic as opposed to an acyclic diketone blocking group for the *trans*-1,2-diol on asymmetric epoxidation, we employed 1,1,2,2-tetramethoxycyclohexane instead of 2,2,3,3-tetramethoxybutane (TMB) in the acetalization reaction. Two new uloses, **1** and **2**, were prepared and the syntheses are shown in Scheme 1 and 2, respectively.

The benzyl arabinopyranoside **3**[11b] was acetalized with 1,1,2,2-tetramethoxy-cyclohexane[12] and the *trans*-diequatorial diol moiety in **3** was protected to afford cyclohexane-1,2-diacetal **4** in 51% yield (Scheme 1). Oxidation of the free alcohol in dimethyl acetal **4** with pyridinium dichromate (PDC) gave ketone **1** in excellent yield. The methoxy substituents in dimethyl acetal **4** were exchanged to neopentyl groups by transacetalization[11b] under acidic conditions with neopentyl alcohol to give di-neopentyl acetal **5** in 87% yield (Scheme 2). The PDC oxidation of the C-4 hydroxyl group in **5** furnished cyclohexane-1,2-dineopentyl acetal ketone **2** in 92% yield.

Ketones **6** and **7** containing an acyclic butane diacetal were prepared in a similar manner with 2,2,3,3-tetramethoxybutane and transacetalization (for **7**) as reported by us previously.[11b] Ketones **1**, **2**, **6** and **7** were used as catalysts in the asymmetric epoxidation of different alkenes and the results are summarized in Table 1.

In the comparison of the enantioselectivities between ketones **6** and **1**, it was found that changing the *trans*-diol-protecting group from butane-1,2-diacetal to cyclohexane-1,2-diacetal, did not affect the enantioselectivity appreciably (Table 1, entries 1,2; 5,6;

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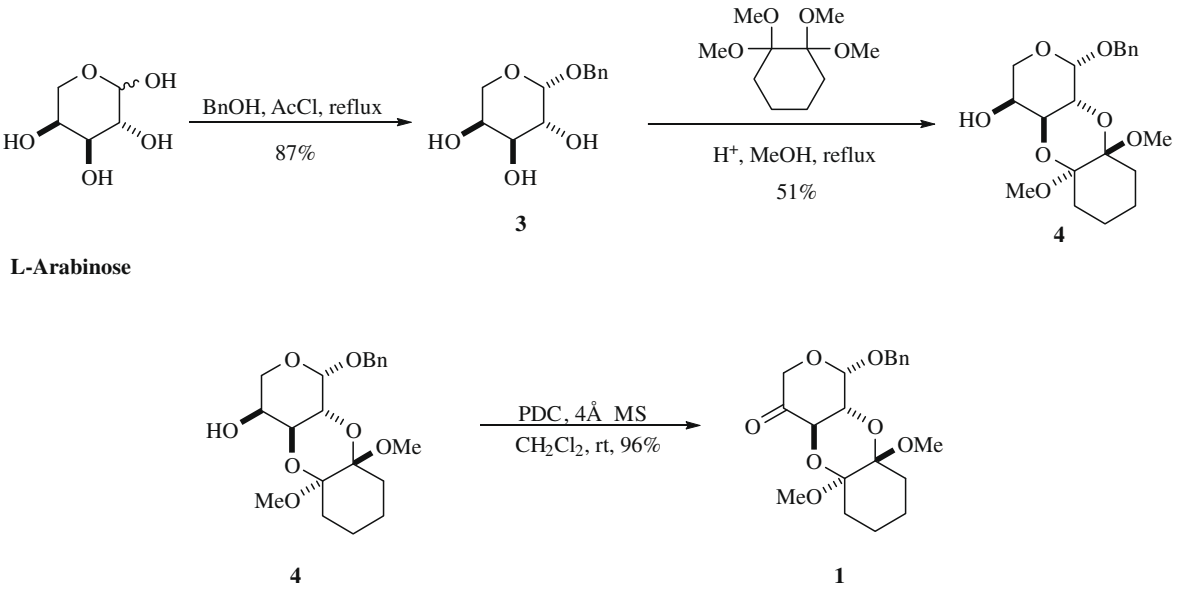
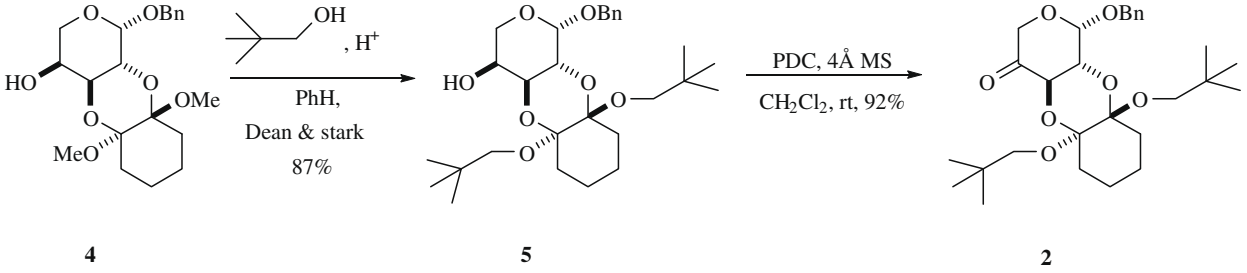


Scheme 1. Synthesis of ulose **1**.



Scheme 2. Synthesis of ulose **2**.

9,10; 13,14; 17,18). Similar asymmetric induction was obtained in all cases.

In the comparison of the enantioselectivity shown between ketones **7** and **2**, it was also found that changing the *trans*-diol protecting group from butane-1,2-diacetal to cyclohexane-1,2-diacetal did not affect the enantioselectivity [Table 1, (entries 3,4; 11,12; 15,16; 19,20) except for (*E*)-1-benzyloxy-4-hexene (entries 7 and 8)]. Cyclohexane-1,2-dineopentyl acetal ketone catalyst **2** improves the ee of the asymmetric epoxidation from 45% to 61% for this long-chain disubstituted *trans*-alkene (entry 8). This finding is close to the best result reported by Denmark (68% ee).[17] We suggest that, in ketone **2**, the cyclohexyl group causes the branched neopentyl acetal to be more rigid than that in ketone **7**. Hence, the spatial disorder of the neopentyl acetal moiety in ketone **2** is smaller than that in ketone **7**. This parameter may cause a stronger steric effect for long-chain disubstituted alkenes rather than for simple alkenes. Further investigation in this direction is currently in progress.

We previously reported[11a] that in the epoxidation of *cis*-alkenes, the ee increased inversely with the size of the blocking groups in our arabinose-derived ketones. In the present study, cyclohexane-1,2-dineopentyl acetal ketone **2** has the more bulky blocking group and displays the poorest ee with *cis*-alkenes (entries 16 and 20).

3. Conclusion

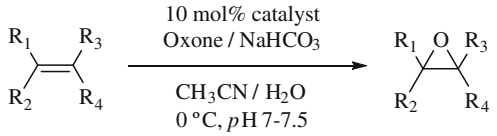
In conclusion, all the ketone catalysts were easily prepared from L-arabinose in four steps and afforded good chemical yields (81–96%) of epoxides in the catalytic asymmetric epoxidation of alkenes. The new cyclohexane-1,2-dineopentyl acetal ketone **2** was found to be the best enantioselective catalyst for the epoxidation of *trans*-alkenes. The more rigid structure of **2** is believed to cause a stronger steric interaction with long-chain disubstituted *trans*-alkenes, rather than with simple *trans*-alkenes. Hence, a good ee of 61% was obtained for (*E*)-1-benzyloxy-4-hexene that compares favourably with the best ee of 68% reported for this substrate. In line with our previous finding, the ee of the asymmetric epoxidation of *cis*-alkenes decreased with the size of the acetal-blocking group.

4. Experimental

4.1. General

Melting points were reported in degrees Celsius and are uncorrected. Optical rotations were measured at 589 nm. Infrared (IR) spectra were recorded on an FT-IR spectrophotometer as thin films on KBr discs. Nuclear magnetic resonance (NMR) spectra were measured at 300.13 MHz (^{1}H) or at 75.47 MHz (^{13}C) in $CDCl_3$ solutions, unless stated otherwise. All chemical shifts were recorded in ppm relative to tetramethylsilane ($\delta = 0.0$). Spin–spin coupling constants (J) in hertz were measured directly from the spectra. MS and HRMS were performed at the Department of Chemistry, The Chinese University of Hong Kong, Hong Kong, China. Carbon and hydrogen elemental analyses were carried out by the Department of Chemistry, Brunel University, Uxbridge, U.K. All reactions

Table 1
The effect of *trans*-diequatorial diol blocking group on asymmetric epoxidation of alkenes catalyzed by ketones **1**, **2**, **6** and **7**



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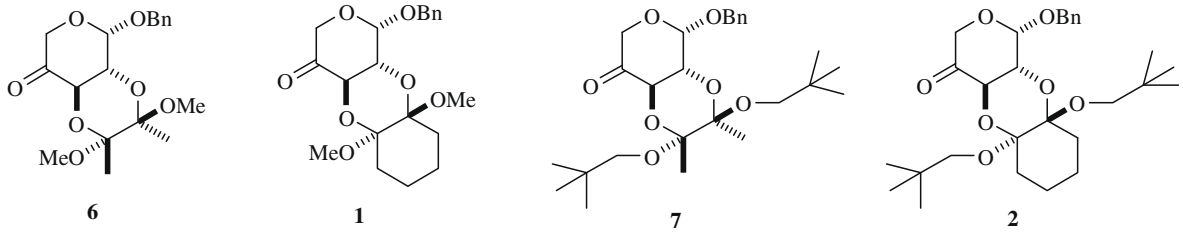
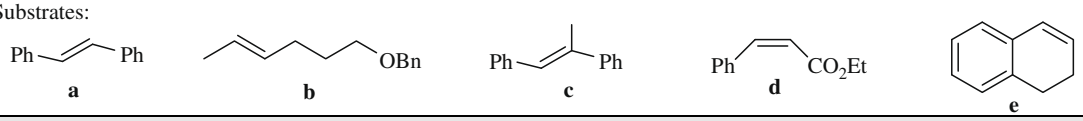


Substrates:



Entry[a]	Catalysts	Substrates	Yield[b] (%)	ee (%)	Config.[e]
1	**6**	a	96	47[c]	(−)-(*S*,*S*)[13]
2	**1**	a	85	46[d]	(−)-(*S*,*S*)13
3	**7**	a	91	83[d]	(−)-(*S*,*S*)[13]
4	**2**	a	91	77[d]	(−)-(*S*,*S*)[13]
5	**6**	b	84	10[d]	(−)-(*S*,*S*)[f]
6	**1**	b	93	13[d]	(−)-(*S*,*S*)[f]
7	**7**	b	88	45[d]	(−)-(*S*,*S*)[f]
8	**2**	b	92	61[d]	(−)-(*S*,*S*)[f]
9	**6**	c	80	75[c]	(−)-(*S*,*S*)[14]
10	**1**	c	92	72[d]	(−)-(*S*,*S*)[14]
11	**7**	c	84	88[d]	(−)-(*S*,*S*)[14]
12	**2**	c	89	89[d]	(−)-(*S*,*S*)[14]
13	**6**	d	96	63[c]	(+)-(2*R*,3*R*)[15]
14	**1**	d	94	64[c]	(+)-(2*R*,3*R*)[15]
15	**7**	d	94	36[c]	(+)-(2*R*,3*R*)[15]
16	**2**	d	87	34[c]	(+)-(2*R*,3*R*)[15]
17	**6**	e	93	32[c]	(−)-(1*S*,2*R*)[16]
18	**1**	e	82	27[c]	(−)-(1*S*,2*R*)[16]
19	**7**	e	85	11[c]	(−)-(1*S*,2*R*)[16]
20	**2**	e	81	7[c]	(−)-(1*S*,2*R*)[16]

[a] Procedures are described in Section 4.
[b] Isolated yield.
[c] Enantioselectivity was determined by HPLC using a Chiralcel OD-H column.
[d] Enantioselectivity was determined by ^{1}H NMR analysis of the epoxide products directly with the shift reagent Eu(hfc)$_3$.
[e] The absolute configurations were determined by comparing the measured specific rotations with the reported ones.
[f] The absolute configuration was tentatively assigned by analogy on the basis of the spiro transition state.[11]

were monitored by analytical thin-layer chromatography (TLC) on aluminium-precoated plates of silica gel 60 F_{254} and compounds were visualized with a spray of 5% w/v dodecamolybdophosphoric acid in EtOH and subsequent heating. Silica gel 60 (230–400 mesh) was used for all flash column chromatographies. The reaction pH was monitored by a pH meter with a pH triode electrode. All solvents were reagent grade unless otherwise stated. Toluene, benzene and THF were fleshly distilled from Na/benzophenone ketyl under nitrogen. CH_2Cl_2 was freshly distilled from CaH_2 under N_2. Other reagents were purchased from commercial suppliers and used without purification. All hexanes used are *n*-hexane.

4.1.1. General in situ epoxidation procedure at 0 °C

To a stirred solution of 1,2-dihydronaphthalene (0.1 mmol), ketone (10 mol %) and *n*-Bu_4NHSO_4 (0.5 mg) in CH_3CN (10 mL) was added an aqueous buffer (5 mL, 4×10^{-4} M aqueous EDTA). The resulting solution was cooled to 0 °C (bath temperature). A solution of Oxone® (307 mg, 0.5 mmol) in aqueous EDTA (5 mL, 4×10^{-4} M) and a solution of $NaHCO_3$ (252 mg, 3.0 mmol) in H_2O (5 mL) were added dropwise concomitantly via two dropping funnels. The pH of the mixture was maintained at about 7–7.5 over a period of 24 h. The reaction mixture was then poured into water (10 mL) and extracted with Et_2O (3×). The combined extracts were dried with anhydrous magnesium sulfate and filtered. The filtrate was concentrated under reduced pressure to give a residue that was purified by flash column chromatography to give the epoxide.

4.1.2. Cyclohexane-dimethyl acetal 4

To a solution of the benzyl β-L-arabinopyranoside **3** (90 mg, 0.42 mmol), trimethyl orthoformate (0.23 mL, 2.09 mmol), 1,1,2,2-tetramethoxycyclohexane[12] (170 mg, 0.83 mmol), in methanol (10 mL) was added 10-camphorsulfonic acid (10 mg,

10 mol %). Upon refluxing for 12 h, the cooled reaction mixture was neutralized with powdered $NaHCO_3$ (200 mg) and filtered. The filtrate was concentrated under reduced pressure. The crude residue was purified by flash column chromatography to afford cyclohexane-dimethyl acetal **4** as a colourless syrup (81 mg, 51%): R_f 0.36 (hexane–EtOAc, 1:1); $[\alpha]_D^{20} = +38.7$ (*c* 0.83, $CHCl_3$); IR (thin film) 3472 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40–7.25 (5H, m), 4.97 (1H, d, *J* = 3.0 Hz), 4.76 (1H, d, *J* = 12.3 Hz), 4.69 (1H, d, *J* = 12.3 Hz), 4.41 (1H, dd, *J* = 10.8, 3.3 Hz), 4.33 (1H, dd, *J* = 10.8, 3.3 Hz), 3.95 (1H, t, *J* = 1.2 Hz), 3.83 (1H, dd, *J* = 12.8, 1.2 Hz), 3.72 (1H, dd, *J* = 12.6, 1.8 Hz), 3.21 (3H, s), 3.17 (3H, s), 3.04 (1H, br s), 1.81–1.77 (4H, m), 1.49–1.38 (2H, m), 1.38–1.35 (2H, m); ^{13}C NMR ($CDCl_3$) δ 137.9, 128.5, 128.2, 127.8, 99.3, 99.2, 97.5, 69.6, 68.6, 66.9, 66.1, 63.7, 47.1, 47.0, 27.2, 21.6; MS (EI) *m*/*z* (relative intensity) 380 ([M]$^+$, 100), 381 (25); HRMS (EI) calcd for $C_{20}H_{28}O_7$ [M]$^+$ 380.1830, found 380.1833; Anal. Calcd for $C_{20}H_{28}O_7$: C, 63.14; H, 7.42. Found: C, 63.25; H, 7.65.

4.1.3. Cyclohexane-dimethyl acetal ketone 1

To a solution of alcohol **4** (50 mg, 0.13 mmol) in dry CH_2Cl_2 (10 mL) were added slowly PDC (74 mg, 0.20 mmol) and powdered 4 Å molecular sieves (80 mg). The mixture was stirred at room temperature for 12 h. The mixture was suction filtered through a pad of silica gel and the filtrate was concentrated under reduced pressure. The crude residue was purified by flash column chromatography to afford cyclohexane–dimethyl acetal ketone **1** as a colourless syrup (47 mg, 96%): R_f 0.32 (hexane–EtOAc, 1:2); $[\alpha]_D^{20} = +34.2$ (*c* 1.42, $CHCl_3$); IR (thin film) 1743 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.43–7.26 (5H, m), 5.11 (1H, d, *J* = 3.0 Hz), 5.10 (1H, d, *J* = 10.8 Hz), 4.80 (2H, s), 4.26 (1H, dd, *J* = 11.2, 3.3 Hz), 4.13 (1H, d, *J* = 15 Hz), 3.90 (1H, d, *J* = 14.7 Hz), 3.23 (3H, s), 3.18 (3H, s), 1.88–1.80 (4H, m), 1.56–1.53 (2H, m), 1.37–1.36 (2H, m); ^{13}C NMR ($CDCl_3$) δ 200.2, 137.3, 128.8, 128.6, 128.3, 99.6, 98.9, 97.1, 71.9, 70.8, 70.6, 67.6, 47.5, 47.2, 27.3, 27.2, 21.6; MS (ESI) *m*/*z* (relative intensity) 401 ([M+Na]$^+$, 100), 402 (15); HRMS (ESI) calcd for $C_{20}H_{26}O_7$ [M+Na]$^+$ 401.1571, found 401.1564.

4.1.4. Cyclohexane-dineopentyl acetal 5

A solution of cyclohexane-dimethyl acetal **4** (100 mg, 0.26 mmol) in benzene (20 mL) containing neopentyl alcohol (93 mg, 1.0 mmol) and *p*-TsOH (2 mg) was heated at reflux with a Dean-Stark trap for 12 h. The cooled reaction mixture was then treated with saturated aqueous $NaHCO_3$ and extracted with Et_2O (3×20 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure. The crude residue was purified by flash column chromatography to afford cyclohexane-dineopentyl acetal **5** as a colourless syrup (111 mg, 87%): R_f 0.33 (hexane–Et_2O, 2:1); $[\alpha]_D^{20} = +36.4$ (*c* 0.66, $CHCl_3$); IR (thin film) 3492 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.34–7.25 (5H, m), 5.01 (1H, d, *J* = 1.8 Hz), 4.76 (1H, d, *J* = 12.0 Hz), 4.61 (1H, d, *J* = 12.0 Hz), 4.42 (2H, m), 3.91 (1H, br s), 3.81 (1H, dd, *J* = 12.6, 1.5 Hz), 3.79 (1H, dd, *J* = 12.6, 1.5 Hz), 3.02 (2H, br s), 2.99 (1H, dd, *J* = 11.4, 8.1 Hz), 2.98 (1H, dd, *J* = 11.4, 8.1 Hz), 2.01 (1H, br s), 1.90–1.77 (4H, m), 1.49–1.48 (2H, m), 1.38–1.25 (2H, m), 0.99 (9H, s), 0.93 (9H, s); ^{13}C NMR ($CDCl_3$) δ 138.4, 128.4, 127.7, 127.6, 98.8, 98.7, 98.5, 69.8, 69.0, 66.5, 66.1, 63.7, 32.0, 27.8, 27.5, 27.4, 21.5; MS (ESI) *m*/*z* (relative intensity) 515 ([M+Na]$^+$, 100), 516 (25); HRMS (ESI) calcd for $C_{28}H_{44}O_7$ [M+Na]$^+$ 515.2979, found 515.2990.

4.1.5. Cyclohexane-dineopentyl acetal ketone 2

To a solution of alcohol **5** (100 mg, 0.20 mmol) in dry CH_2Cl_2 (10 mL) were added slowly PDC (110 mg, 0.30 mmol) and powdered 4 Å molecular sieves (110 mg). The mixture was stirred at room temperature for 12 h. The mixture was suction filtered through a pad of silica gel and the filtrate was concentrated under reduced pressure. The crude residue was purified by flash column chromatography to afford cyclohexane-dineopentyl ketone **2** as a colourless syrup (90 mg, 92%): R_f 0.20 (hexane–Et_2O, 2:1); $[\alpha]_D^{20} = +18.75$ (*c* 1.03, $CHCl_3$); IR (thin film) 1744 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.39–7.26 (5H, m), 5.21 (1H, d, *J* = 11.4 Hz), 5.13 (1H, d, *J* = 3.0 Hz), 4.80 (1H, d, *J* = 11.7 Hz), 4.75 (1H, d, *J* = 11.7 Hz), 4.23 (1H, dd, *J* = 11.4, 3.0 Hz), 4.12 (1H, d, *J* = 14.7 Hz), 3.91 (1H, d, *J* = 15.0 Hz), 3.03 (2H, dd, *J* = 8.4, 1.5 Hz), 2.98 (2H, d, *J* = 8.7 Hz), 1.89–1.83 (4H, m), 1.52–1.50 (2H, m), 1.36–1.25 (2H, m) 0.98 (9H, s), 0.94 (9H, s); ^{13}C NMR ($CDCl_3$) δ 200.7, 137.5, 128.6, 128.1, 128.0, 99.0, 98.4, 97.9, 71.8, 70.9, 70.6, 69.3, 69.2, 67.7, 32.0, 27.7, 27.4, 27.3, 21.5; MS (ESI) *m*/*z* (relative intensity) 513 ([M+Na]$^+$, 100), 514 (30); HRMS (ESI) calcd for $C_{28}H_{42}O_7$ [M+Na]$^+$ 513.2823, found 513.2829.

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