DOI: 10.1002/ejoc.200500966

Synthesis of Highly Functionalized Pentalenes via Intermolecular Pauson–Khand Reaction

Armand Becheanu,[a] Angelika Baro,[a] Sabine Laschat,*[a] and Wolfgang Frey[a]

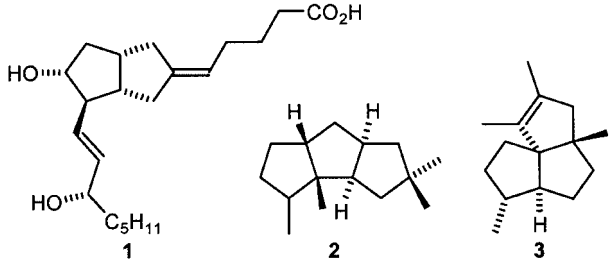
Dedicated to Prof. Siegfried Hünig on the occasion of his 85th birthday

Keywords: Acetylation / Lipases / Organocuprate addition / Pauson–Khand reaction / Pentalenes

A concise synthetic route to highly substituted pentalenones **4** and **5**, respectively, is reported. The key step is a Pauson–Khand reaction of norbornadiene (**7**) with the functionalized acetylenes **8** to give the methanoindenone derivatives **6**. 1,4-Addition of organocuprates resulted in clean formation of 2,3-*trans*-disubstituted methanoindenones **9**. After ozonolysis and reductive workup, the bis(hydroxymethyl)pentalenones **10** were obtained in moderate to good yields. A differentiation of the hydroxy groups became possible by lipase-mediated acetylation with vinyl acetate, giving highly selectively monoacetates **4** with the acetyl group at C-6 of the pentalene system.
(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2006)

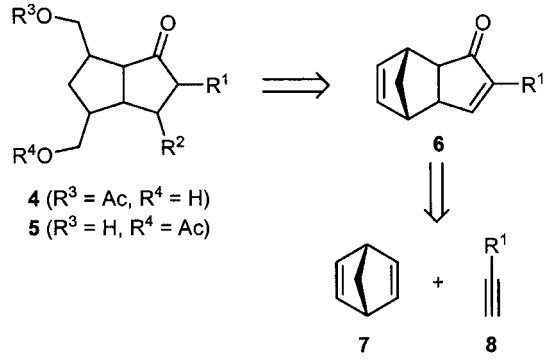
Introduction

Pentalenes, i.e., bicyclo[3.3.0]octanes, constitute important building blocks of many natural products and pharmacologically active compounds such as carbacyclin (**1**) and triquinanes **2**, **3** (Scheme 1). Thus, a lot of efforts has been spent on the synthesis of these compounds.[1,2]



Scheme 1. The bicyclo[3.3.0]octane structural motif in carbacyclin (**1**) and the triquinanes hirsutane (**2**) or silphiperfolene (**3**).

While many pentalene syntheses rely on cationic, anionic, radical or metal mediated cyclization[3–5] as well as Diels–Alder reactions,[6] the intermolecular Pauson–Khand reaction, a [2+2+1]cocyclization of an alkyne, an alkene and carbon monoxide, provides a convergent approach to the pentalene skeleton.[7] Particularly the Pauson–Khand reaction of norbornadiene (**7**) and functionalized acetylenes **8** seemed to be attractive because the resulting tricyclic cyclopentenone **6** can be manipulated by conjugate cuprate addition and furthermore, the alkene moiety can be cleaved oxidatively. We anticipated that subsequent esterification should allow a differentiation between the two hydroxy groups, thus giving access to pentasubstituted bicyclo[3.3.0]-octanes **4** or **5** in a stereoselective fashion (Scheme 2). The results towards this goal are reported below.



Scheme 2. Retrosynthetic route to highly functionalized bicyclooctane derivatives **4** and **5**.

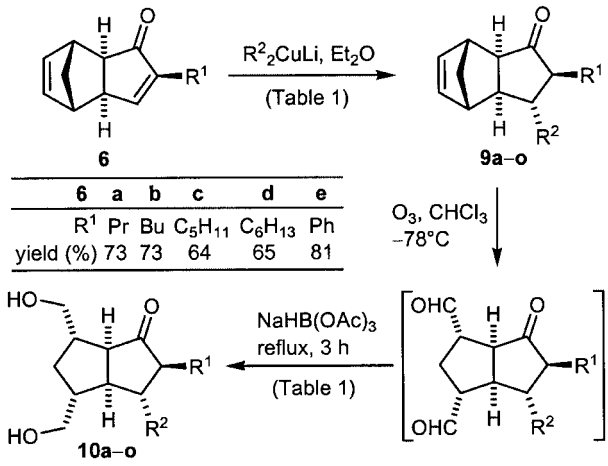
Results and Discussion

The Pauson–Khand cyclization products **6**[8] were treated with diorganocuprates to give the 2,3-*trans*-disubstituted cyclopentenones **9**[9] without any problems. Compounds **9** could be submitted directly to ozonolysis without protection[10] of the keto group. The intermediate dialdehydes

[a] Institut für Organische Chemie der Universität Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany,
Fax: +49-711-685-4285
E-mail: sabine.laschat@oc.uni-stuttgart.de
Supporting information for this article is available on the WWW under http://www.eurjoc.org or from the author.

 © 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

were treated with $NaBH(OAc)_3$[11,12] which was assumed to be mild enough for chemoselective reduction of the aldehyde groups in the presence of a keto function during workup. These conditions resulted in clean formation of the keto diols **10** (Scheme 3, Table 1).



Scheme 3. Cuprate addition to compounds **6** followed by oxidative cleavage of **9** to diols **10**.

Table 1. Addition of organocuprates and oxidative cleavage of cyclopentenones **9** to diols **10**.

Cuprate addition				Cleavage	
9	R^1	R^2	Yield [%]	**10**	Yield [%]
a	Pr	Me	94	**a**[a]	57
b	Pr	Bu	94	**b**	62
c	Pr	Ph	61	**c**	69
d	Bu	Me	98	**d**	22
e	Bu	Bu	93	**e**	53
f	Bu	Ph	62	**f**	75
g	*n*-C_5H_{11}	Me	96	**g**	30
h	*n*-C_5H_{11}	Bu	99	**h**	75
i	*n*-C_5H_{11}	Ph	42	**i**	74
j	*n*-C_6H_{13}	Me	85	**j**	50
k	*n*-C_6H_{13}	Bu	70	**k**	57
l	*n*-C_6H_{13}	Ph	62	**l**	56
m	Ph	Me	87	**m**	34
n	Ph	Bu	69	**n**	38
o	Ph	Ph	68	**o**	43

[a] Crystallization of **10a** from Et_2O gave single crystals which are suitable for X-ray crystallographic analysis (Figure 1).[13] The ORTEP plot clearly shows the *trans* substitution pattern of the butyl and methyl group at C-2 and C-3.

Next, the regio- and diastereoselectivity of the acetylation of diols **10** was investigated. In order to establish proper analytical conditions the chemical acylation[14] was carried out first (Scheme 4, Table 2).

Thus, the derivatives **10** were acetylated with acetic anhydride in the presence of DMAP in pyridine at room temperature to give the regioisomeric monoacetates **4** and **5** in almost quantitative yields (method A, Scheme 4). Regardless of the substituents R^1 and R^2 in the bicyclo[3.3.0]octane moiety only regioselectivities up to 35:65 in favour of the monoacetate **5** were observed (Table 2). The 3-methyl-substituted diols **10a**, **d**, **g**, **m** gave slightly better regioselectivities than the corresponding derivatives **10** with C-3 substituents butyl and phenyl (Entries 1, 4, 7, 13).

The 2-phenyl-substituted monoacetates **4m–o** and **5m–o** turned out to be sensitive to epimerization at C-2 in the presence of acids or bases.

For the enzyme-catalyzed acetylation,[15] first various lipases were screened with diol **10a** as model substrate (Method B, Scheme 4, Table 3).

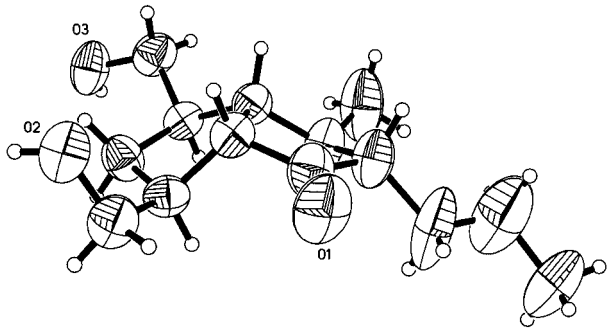
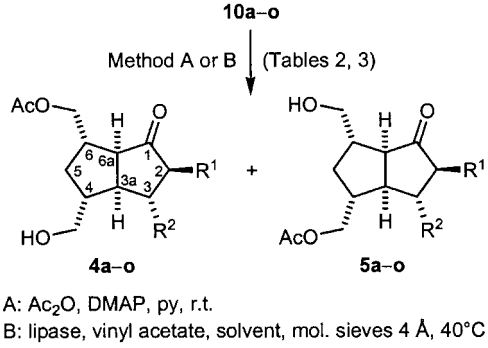


Figure 1. ORTEP view of 2-butyl-4,6-bis(hydroxymethyl)-3-methylhexahydropentalen-1(2*H*)-one (**10a**).



Scheme 4. Acetylation of derivatives **10** for differentiation of the hydroxy groups.

Table 2. Chemical acetylation of diols **10** according to Method A (Scheme 4).

Entry	Diol **10**	R^1	R^2	Acetate **4**, **5**	**4/5**[a]
1	**a**	Pr	Me	**a**	35:65
2	**b**	Pr	Bu	**b**	41:59
3	**c**	Pr	Ph	**c**	46:54
4	**d**	Bu	Me	**d**	36:64
5	**e**	Bu	Bu	**e**	42:58
6	**f**	Bu	Ph	**f**	48:52
7	**g**	C_5H_{11}	Me	**g**	41:59
8	**h**	C_5H_{11}	Bu	**h**	43:57
9	**i**	C_5H_{11}	Ph	**i**	46:54
10	**j**	C_6H_{13}	Me	**j**	42:58
11	**k**	C_6H_{13}	Bu	**k**	39:61
12	**l**	C_6H_{13}	Ph	**l**	45:55
13	**m**	Ph	Me	**m**	43:57
14	**n**	Ph	Bu	**n**	44:56
15	**o**	Ph	Ph	**o**	51:49

[a] Regioisomeric ratios were determined by capillary GC. Details for the assignment of **4** and **5** are given in the supporting information.

 © 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Table 3. Enzymatic acetylation of **10a** with various lipases according to method B.

Entry	Lipase	Time [h]	Conv. [%][a]	**4a/5a**[a]
1	Chirazyme L6	1	32 (60)[b]	87:13
2	Chirazyme L1	1	18 (80)[b]	91:9
3	Lipase L-9518	2	41 (23)[b]	70:30
4	Lipase G	18	26 (2)[b]	47:53
5	Lipase Amano P	18	31 (63)[b]	37:63

[a] Conversion and regioisomeric ratios were determined by capillary GC of the crude products. [b] Diacetate in parenthesis.

The lipases chirazyme L6 and chirazyme L1 gave the best results leading to good regioselectivities of 87:13 and 91:9, respectively, in favour of derivative **4a** (Entries 1, 2). A similar preference for regioisomer **4a** was observed for lipase L albeit with decreased regioselectivity (Entry 3). In contrast, lipase G and lipase Amano P caused a reversed, but low regioselectivity (Entries 4, 5). Surprisingly, lipase-mediated acylations proceeded without any enantioselectivity. Even chirazyme L1 or L6, which clearly favored one regioisomer, gave only racemic monoacetate **4a**.

Next, the time-dependency of the regioselectivity was investigated by treating diol **10a** with chirazyme L1 and vinyl acetate in THF at 40 °C (Table 4). THF was found to work best among the solvents studied (e.g. CH_2Cl_2, acetone, MeCN). The highest regioselectivity of 94:6 in favour of monoacetate **4a** was obtained already after 10 min (Entry 1). At prolonged reaction times the regioselectivity gradually decreased.

Table 4. Enzymatic acetylation of **10a** with lipase chirazyme L1 in dependence on the reaction time.

Entry	Time (min)	Conv. (%)[a][b]	**4a/5a**[a]
1	10	51	94:6
2	20	53	93:7
3	30	52	93:7
4	40	52	91:9
5	50	51	88:12
6	60	51	87:13
7	70	51	87:13

[a] Conversion and regioisomeric ratios were determined by capillary GC of the crude products. [b] The conversion remains constant, however, the amount of diacetate as by-product increases at longer reaction times.

Finally, the optimized reaction conditions were applied to the lipase-mediated acetylation of diols **10a**–**o** (Table 5). In contrast to the chemical reaction, the regioselectivities of the enzymatic acetylations were strongly dependent on the substitution pattern at C-2 and C-3. While the methyl group at C-3 (R^2 = Me) led to regioselectivities between 90:10 and 94:6 in favour of the derivatives **4** (Entries 1, 4, 7, 10, 13), the corresponding 3-butyl- and 3-phenyl-substituted diols **10** resulted in improved regioisomeric ratios up to >99:1 (Table 5).

Table 5. Substituent influence on the enzymatic acetylation of diols **10** with chirazyme L1 and vinyl acetate in THF at 40 °C.

Entry	Diol **10**	R^1	R^2	Acetate **4**, **5**	**4/5**[a]	Yield of **4** (%)[b]
1	**a**	Pr	Me	**a**	94:6	35
2	**b**	Pr	Bu	**b**	>99:1	87
3	**c**	Pr	Ph	**c**	>99:1	84
4	**d**	Bu	Me	**d**	92:8	43
5	**e**	Bu	Bu	**e**	>99:1	79
6	**f**	Bu	Ph	**f**	>99:1	74
7	**g**	C_5H_{11}	Me	**g**	91:9	36
8	**h**	C_5H_{11}	Bu	**h**	>99:1	82
9	**i**	C_5H_{11}	Ph	**i**	>99:1	83
10	**j**	C_6H_{13}	Me	**j**	94:6	49
11	**k**	C_6H_{13}	Bu	**k**	>99:1	68
12	**l**	C_6H_{13}	Ph	**l**	99:1	81
13	**m**	Ph	Me	**m**	90:10	49[c]
14	**n**	Ph	Bu	**n**	99:1	32[c]
15	**o**	Ph	Ph	**o**	99:1	79[c]

[a] Regioisomeric ratios were determined by capillary GC of the crude products. [b] Yields refer to isolated yields. [c] Rapid epimerization of **4** was observed under acidic and basic conditions, respectively.

In order to explain the reversed regioisomeric preference of chemical and enzymatic acetylation we propose the following mechanistic model. The primary hydroxy groups in diols **10** differ in their chemical reactivity towards acylation reagents such as acetic anhydride because the hydroxymethyl group at C-6 might be capable of forming an intramolecular hydrogen bond to the keto group at C-1, whereas the hydroxymethyl group at C-4 is too far away. Thus, the reduced nucleophilicity of the hydrogen-bonded hydroxymethyl group leads to preferred acylation of the hydroxy function at C-4 giving monoacetate **5**. In contrast, the active site of the lipase seems to interfere with intramolecular hydrogen bonding presumably due to competing hydrogen bonds between the enzyme and the keto group in diol **10**, bringing the hydroxymethyl group at C-6 much closer to the active site than the corresponding group at C-4. Thus, the formation of monoacetate **4** is preferred.

Conclusion

The Pauson–Khand reaction of norbornadiene (**7**) and substituted acetylenes **8** gives convenient access to methanoindenones **6** which are starting materials for further functionalization. The synthesis of the target compounds **4** was accomplished by lipase-mediated acetylation with vinyl acetate in THF. Despite the excellent regioselectivity it is not clear why the lipase does not exert any stereochemical control. A more efficient approach to the stereoselectivity might be achieved directly during the Pauson–Khand reaction or the cuprate addition. Nevertheless, the sequence of Pauson–Khand reaction, subsequent tandem cuprate 1,4-addition/enolate quenching, oxidative cleavage and enzymatic esterification allows access to highly functionalized bicyclo[3.3.0]octane systems which can be further elaborated.

 © 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Experimental Section

General: The following compounds were prepared according to literature procedures: **6b–e**,[8] **9d–f**, **h**, **k**, **m–o**.[9] Melting points were measured with differential scanning calorimetry and are uncorrected. Column chromatography was carried out using Merck SiO_2 60 (grain size 0.040–0.063 mm) with hexanes (PE, b.p. 40–60 °C), pentane and ethyl acetate (EtOAc) as eluents. ^{1}H NMR spectra were recorded with a Bruker ARX 500 (500 MHz), a Bruker ARX 300 (300 MHz) or a Bruker AC 250 (250 MHz). ^{13}C NMR spectra were recorded with a Bruker ARX 500 (125 MHz), a Bruker ARX 300 (75 MHz) or a Bruker AC 250 (63 MHz). Multiplicities were determined with DEPT experiments. GC was carried out with a Hewlett Packard HP 6890 using an Agilent Technologies HP-5 TA column (30 m) and hydrogen as the carrier gas. Lipases chirazyme L1 and L6 were purchased from Boehringer, lipase P and G from Amano and lipase L-9518 from Sigma.

General Procedure for the Cuprate Addition to 2,3-Disubstituted Methanoindenones 9: A suspension of copper iodide (104 mg, 0.54 mmol) in Et_2O (5 mL) under N_2 was stirred for 10 min at 0 °C or –20 °C (for Bu_2CuLi). Then the organolithium compound (1.08 mmol) was added dropwise and the reaction mixture stirred for a further 10 min at 0 °C or –20 °C. The respective compound **6** (0.45 mmol) was added dropwise and after complete conversion (0.5–2 h, TLC control), the reaction mixture was hydrolyzed with a satd. solution of NH_4Cl (5 mL). The aqueous layer was extracted with Et_2O (5 × 10 mL), and the combined organic layers were dried (K_2CO_3) and concentrated. The crude products **9** were purified by chromatography on SiO_2 with pentane/Et_2O, 12:1.

9a: Yield: 1.92 g, 94%. R_f = 0.46. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.91 (t, J = 7.2 Hz, 3 H, 3′-H), 1.07 (d, J = 9.1 Hz, 1 H, 10-H_a), 1.23 [d, J = 6.6 Hz, 3 H, (C-5)CH_3], 1.25–1.48 (m, 5 H, 1′-H_a, 2′-H, 5-H, 10-H_b), 1.55–1.63 (m, 1 H, 1′-H_b), 1.80–1.85 (m, 1 H, 6-H), 2.12–2.18 (m, 1 H, 4-H), 2.28–2.32 (m, 1 H, 2-H), 2.73–2.75 (m, 1 H, 7-H), 3.10–3.13 (m, 1 H, 1-H), 6.13 (dd, J = 3.0 Hz, J = 5.7 Hz, 1 H, 9-H), 6.17 (dd, J = 3.0 Hz, J = 5.7 Hz, 1 H, 8-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.3 (C-3′), 20.2 (C-2′), 21.0 [(C-5) CH$_3$], 29.7 (C-1′), 40.2 (C-5), 44.5 (C-1), 44.8 (C-10), 46.7 (C-7), 48.8 (C-6), 54.3 (C-2), 60.6 (C-4), 137.4, 138.2 (C-8, C-9), 218.4 (C-3) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2956 cm^{-1} (s), 2928 (s), 2871 (m), 1730 (vs), 1458 (m), 1352 (m), 1216 (m), 707 (s) cm^{-1}. GC-MS (EI): m/z (%) = 204.1 (12) [M$^+$], 139.1 (100), 96.0 (12), 66.0 (65). HRMS (EI): calcd. for $C_{14}H_{20}O$ 204.1514, found 204.1514 [M$^+$].

9b: Yield: 602 mg, 94%. R_f = 0.54. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, J = 7.1 Hz, 3 H, 4′′-H), 0.95 (t, J = 7.1 Hz, 3 H, 3′-H), 1.07 (d, J = 9.1 Hz, 1 H, 10-H_a), 1.19–1.61 (m, 11 H, 1′-H_a, 1′′-H, 2′-H, 2′′-H, 3′′-H, 5-H, 10-H_b), 1.66–1.74 (m, 1 H, 1′-H_b), 1.89 (dd, J = 5.4 Hz, J = 8.9 Hz, 1 H, 6-H), 2.17–2.22 (m, 1 H, 4-H), 2.28–2.32 (m, 1 H, 2-H), 2.69–2.71 (m, 1 H, 7-H), 3.10–3.13 (m, 1 H, 1-H), 6.13 (dd, J = 3.0 Hz, J = 5.7 Hz, 1 H, 9-H), 6.19 (dd, J = 3.0 Hz, J = 5.7 Hz, 1 H, 8-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 (C-4′′), 14.4 (C-3′), 20.3 (C-3′′), 29.6, 30.1, 36.4 (C-1′, C-1′′, C-2′, C-2′′), 44.7 (C-1), 44.8 (C-5, C-10), 47.0 (C-6), 48.2 (C-7), 54.4 (C-2), 59.2 (C-4), 137.4, 138.3 (C-8, C-9), 218.9 (C-3) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2957 cm^{-1} (s), 2925 (s), 2871 (s), 2859 (s), 1729 (vs), 1458 (s), 1378 (m), 1325 (m), 706 (vs) cm^{-1}. GC-MS (EI): m/z (%) = 246.2 (6) [M$^+$], 181.1 (100), 125.1 (4), 95.0 (7), 66.0 (41). HRMS (EI): calcd. for $C_{17}H_{26}O$ 246.1984, found 246.1984 [M$^+$]. $C_{17}H_{26}O$ (246.4): calcd. C 82.87, H 10.64; found C 82.86, H 10.76.

9c: Yield: 866 mg, 61%. R_f = 0.37. ^{1}H NMR (500 MHz, $(CD_3)_2$-CO): δ = 0.72 (t, J = 7.2 Hz, 3 H, 3′-H), 1.05–1.15 (m, 1 H, 2′-H_a), 1.20–1.33 (m, 3 H, 1′-H_a, 2′-H_b, 10-H_a), 1.38–1.43 (m, 1 H, 10-H_b), 1.56–1.60 (m, 1 H, 1′-H_b), 2.26 (t, J = 8.4 Hz, 1 H, 6-H), 2.50–2.53 (m, 1 H, 2-H), 2.54 (d, J = 7.6 Hz, 1 H, 4-H), 2.78–2.80 (m, 1 H, 7-H), 2.94–3.00 (m, 1 H, 5-H), 3.07–3.09 (m, 1 H, 1-H), 6.12 (dd, J = 3.1 Hz, J = 5.6 Hz, 1 H, 9-H), 6.17 (dd, J = 2.9 Hz, J = 5.7 Hz, 1 H, 8-H), 7.23–7.27 (m, 1 H, 4′′-H), 7.34–7.46 (m, 4 H, 2′′-H, 3′′-H, 5′′-H, 6′′-H) ppm. ^{13}C NMR (125 MHz, $(CD_3)_2$-CO): δ = 15.4 (C-3′), 21.7 (C-2′), 31.6 (C-1′), 46.0, 46.1 (C-1, C-10), 48.1 (C-7), 51.8 (C-6), 54.2 (C-2), 55.4 (C-4), 61.6 (C-5), 128.3 (C-4′′), 129.5, 130.5 (C-2′′, C-3′′, C-5′′, C-6′′), 139.2, 139.9 (C-8, C-9), 146.9 (C-1′′), 217.2 (C-3) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2957 cm^{-1} (s), 2930 (s), 2871 (m), 1728 (vs), 1493 (m), 1453 (s), 1324 (m), 1284 (m), 1063 (m), 756 (s), 698 (vs) cm^{-1}. GC-MS (EI): m/z (%) = 266.4 (2) [M$^+$], 201.2 (65), 158.2 (22), 128.1 (9), 115.1 (12), 91.1 (16), 66.1 (100). HRMS (CI, CH_4): calcd. for $C_{19}H_{22}O$ 266.1671, found 266.1668 [M$^+$].

9g: Yield: 324 mg, 96%. R_f = 0.51. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 3 H, 5′-H), 1.07 (d, J = 9.2 Hz, 1 H, 10-H_a), 1.23 [d, J = 6.5 Hz, 3 H, (C-5)CH_3], 1.31–1.49 (m, 9 H, 1′-H_a, 2′-H, 3′-H, 4′-H, 5-H, 10-H_b), 1.53–1.66 (m, 1 H, 1′-H_b), 1.79–1.86 (m, 1 H, 6-H), 2.14 (dddd, J = 2.0 Hz, J = 4.4 Hz, J = 6.2 Hz, J = 12.5 Hz, 1 H, 4-H), 2.30 (d, J = 9.2 Hz, 1 H, 2-H), 2.72–2.76 (m, 1 H, 7-H), 3.10–3.14 (m, 1 H, 1-H), 6.13 (dd, J = 2.9 Hz, J = 5.7 Hz, 1 H, 9-H), 6.17 (dd, J = 2.9 Hz, J = 5.7 Hz, 1 H, 8-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 (C-5′), 21.0 [(C-5) CH$_3$], 22.4 (C-4′), 26.6, 27.2 (C-1′, C-2′), 32.1 (C-3′), 40.0 (C-5), 44.4 (C-1), 44.8 (C-10), 46.6 (C-7), 48.6 (C-6), 54.2 (C-2), 60.6 (C-4), 137.3, 138.1 (C-8, C-9), 218.4 (C-3) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2954 cm^{-1} (s), 2926 (s), 2870 (m), 2858 (m), 1731 (vs), 1459 (m), 1324 (m), 1217 (m), 707 (s) cm^{-1}. MS (EI): m/z (%) = 232.1 (6) [M$^+$], 167.1 (100), 96.0 (19), 66.0 (74), 41.0 (10). HRMS (EI): calcd. for $C_{16}H_{24}O$ 232.1827, found 232.1827 [M$^+$].

9i: Yield: 161 mg, 42%. R_f = 0.42. ^{1}H NMR (500 MHz, $(CD_3)_2$-CO): δ = 0.76 (t, J = 7.0 Hz, 3 H, 5′-H), 1.12–1.19 (m, 5 H, 2′-H_a, 3′-H, 4′-H), 1.22–1.32 (m, 3 H, 1′-H_a, 2′-H_b, 10-H_a), 1.38–1.42 (m, 1 H, 10-H_b), 1.51–1.61 (m, 1 H, 1′-H_b), 2.27 (t, J = 8.3 Hz, 1 H, 6-H), 2.50–2.56 (m, 2 H, 2-H, 4-H), 2.77–2.80 (m, 1 H, 7-H), 2.93–2.99 (m, 1 H, 5-H), 3.07–3.10 (m, 1 H, 1-H), 6.12 (dd, J = 3.0 Hz, J = 5.6 Hz, 1 H, 9-H), 6.17 (dd, J = 2.9 Hz, J = 5.6 Hz, 1 H, 8-H), 7.23–7.28 (m, 1 H, 4′′-H), 7.34–7.46 (m, 4 H, 2′′-H, 3′′-H, 5′′-H, 6′′-H) ppm. ^{13}C NMR (125 MHz, $(CD_3)_2$CO): δ = 15.1 (C-5′), 23.9 (C-4′), 28.1 (C-2′), 29.1 (C-1′), 33.5 (C-3′), 46.0 (C-1), 46.1 (C-10), 48.1 (C-7), 51.8 (C-6), 54.2 (C-2), 55.4 (C-4), 61.8 (C-5), 128.3 (C-4′′), 129.6, 130.4 (C-2′′, C-3′′, C-5′′, C-6′′), 139.2, 139.9 (C-8, C-9), 146.9 (C-1′′), 217.2 (C-3) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2955 cm^{-1} (s), 2928 (s), 2871 (m), 2856 (s), 1730 (vs), 1493 (m), 1452 (s), 1324 (m), 1284 (m), 1271 (m), 1204 (m), 1072 (m), 754 (s), 698 (vs) cm^{-1}. GC-MS (EI): m/z (%) = 294.4 (1) [M$^+$], 229.3 (69), 158.1 (31), 128.1 (10), 115.0 (14), 91.0 (18), 66.0 (100). HRMS (CI, CH_4): calcd. for $C_{21}H_{26}O$ 294.1984, found 294.1984 [M$^+$].

9j: Yield: 309 mg, 85%. R_f = 0.51. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, J = 6.7 Hz, 3 H, 6′-H), 1.07 (d, J = 9.2 Hz, 1 H, 10-H_a), 1.23 [d, J = 6.5 Hz, 3 H, (C-5)CH_3], 1.25–1.49 (m, 11 H, 1′-H_a, 2′-H, 3′-H, 4′-H, 5-H, 5′-H, 10-H_b), 1.51–1.62 (m, 1 H, 1′-H_b), 1.79–1.86 (m, 1 H, 6-H), 2.10–2.18 (m, 1 H, 4-H), 2.27–2.33 (m, 1 H, 2-H), 2.72–2.76 (m, 1 H, 7-H), 3.10–3.14 (m, 1 H, 1-H), 6.13 (dd, J = 2.9 Hz, J = 5.7 Hz, 1 H, 9-H), 6.17 (dd, J = 2.9 Hz, J = 5.7 Hz, 1 H, 8-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 (C-6′), 21.0 [(C-5) CH$_3$], 22.5 (C-5′), 26.9, 27.3 (C-1′, C-2′), 29.6 (C-3′), 31.6 (C-4′), 40.0 (C-5), 44.4 (C-1), 44.8 (C-10), 46.6 (C-7), 48.7 (C-6), 54.2 (C-2), 60.7 (C-4), 137.4, 138.2 (C-8, C-9), 218.4 (C-3) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2954 cm^{-1} (s), 2925 (s), 2870 (m), 2856 (m), 1732

 © 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

(vs), 1458 (m), 1324 (m), 1217 (m), 707 (s) cm^{-1}. GC-MS (EI): *m/z* (%) = 246.2 (12) [M^+], 181.1 (100), 96.0 (12), 66.1 (40), 41.0 (4). HRMS (EI): calcd. for $C_{17}H_{26}O$ 246.1984, found 246.1988 [M^+].

9l: Yield: 1.13 g, 62%. R_f = 0.31. ^1H NMR (500 MHz, $(CD_3)_2CO$): δ = 0.80 (t, *J* = 7.2 Hz, 3 H, 6′-H), 1.05–1.31 (m, 10 H, 1′-H_a, 2′-H, 3′-H, 4′-H, 5′-H, 10-H_a), 1.39–1.43 (m, 1 H, 10-H_b), 1.51–1.61 (m, 1 H, 1′-H_b), 2.27 (t, *J* = 8.4 Hz, 1 H, 6-H), 2.51–2.56 (m, 2 H, 2-H, 4-H), 2.78–2.80 (m, 1 H, 7-H), 2.93–3.00 (m, 1 H, 5-H), 3.07–3.10 (m, 1 H, 1-H), 6.12 (dd, *J* = 3.0 Hz, *J* = 5.6 Hz, 1 H, 9-H), 6.17 (dd, *J* = 2.9 Hz, *J* = 5.7 Hz, 1 H, 8-H), 7.23–7.28 (m, 1 H, 4′′-H), 7.34–7.46 (m, 4 H, 2′′-H, 3′′-H, 5′′-H, 6′′-H) ppm. ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ = 15.2 (C-6′), 24.1 (C-5′), 28.4, 29.2, 31.0, 33.2 (C-1′, C-2′, C-3′, C-4′), 46.0 (C-1), 46.1 (C-10), 48.1 (C-7), 51.8 (C-6), 54.2 (C-2), 55.4 (C-4), 61.8 (C-5), 128.3 (C-4′′), 129.6, 130.4 (C-2′′, C-3′′, C-5′′, C-6′′), 139.2, 139.9 (C-8, C-9), 147.0 (C-1′′), 217.2 (C-3) ppm. FT-IR (ATR): $\tilde{\nu}$ = 2955 cm^{-1} (s), 2926 (s), 2870 (m), 2855 (s), 1731 (vs), 1493 (m), 1452 (s), 1324 (m), 1284 (m), 1207 (m), 1067 (m), 754 (s), 698 (vs) cm^{-1}. GC-MS (EI): *m/z* (%) = 306.9 (1) [(M – H)$^+$], 243.3 (70), 158.1 (26), 128.1 (8), 115.1 (12), 91.1 (17), 66.0 (100). HRMS (CI, CH_4): calcd. for $C_{22}H_{28}O$ 308.2140, found 308.2137 [M^+].

General Procedure for the Preparation of Bis(hydroxymethyl)hexahydropentalen-1(2*H*)-ones 10: A stream of O_3 was passed through a solution of **9** (2.42 mmol) in $CHCl_3$ (30 mL) at –78 °C until a light blue color was visible. Then N_2 was passed through for 10 min, sodium triacetoxyborohydride (5.31 g, 24.3 mmol) was added portionwise and the reaction mixture warmed to room temperature. After stirring for 0.5 h, the reaction mixture was heated at reflux for 3 h. Then it was hydrolyzed with a satd. solution of NH_4Cl (30 mL), and the aqueous layer was extracted with $CHCl_3$ and EtOAc (3 × 30 mL each). The combined organic layers were dried (K_2CO_3) and concentrated. The residue was chromatographed on SiO_2 with PE/EtOAc, 1:3.

10a: Yield: 2.81 g, 57%. R_f = 0.19. M.p. 87 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.2 Hz, 3 H, 3′-H), 1.18 (d, *J* = 6.5 Hz, 3 H, C*H*$_3$), 1.20–1.37 (m, 2 H, 2′-H_a, 5-H_a), 1.38–1.52 (m, 2 H, 1′-H_a, 2′-H_b), 1.52–1.59 (m, 1 H, 1′-H_b), 1.60–1.69 (m, 1 H, 3-H), 1.95–2.01 (m, 1 H, 2-H), 2.03–2.19 (m, 4 H, 3a-H, 4-H, 5-H_b, 6-H), 2.62 (t, *J* = 9.1 Hz, 1 H, 6a-H), 3.55 [dd, *J* = 8.0 Hz, *J* = 10.7 Hz, 1 H, (C-6)C*H*$_a$OH], 3.60 [dd, *J* = 4.0 Hz, *J* = 5.6 Hz, 2 H, (C-4)C*H*$_2$OH], 3.73 [dd, *J* = 4.1 Hz, *J* = 10.6 Hz, 1 H, (C-6)C*H*$_b$OH] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.3 (C-3′), 18.3 (*C*H$_3$), 19.9 (C-2′), 29.2 (C-1′), 34.3 (C-5), 42.8 (C-3), 43.9 (C-6), 47.4 (C-3a), 51.1 (C-4), 57.7, 58.3 (C-2, C-6a), 66.4, 66.7 [(C-4) *C*H$_2$OH, (C-6) *C*H$_2$OH], 222.3 (C-1) ppm. FT-IR (ATR): $\tilde{\nu}$ = 3310 cm^{-1} (s), 2957 (s), 2932 (s), 2898 (s), 2869 (s), 2820 (m), 1722 (vs), 1481 (m), 1449 (m), 1404 (m), 1377 (m), 1338 (m), 1313 (m), 1277 (m), 1225 (m), 1171 (m), 1116 (s), 1082 (s), 1029 (vs), 1003 (s), 989 (s) cm^{-1}. MS (EI): *m/z* (%) = 240.2 (2) [M^+], 222.1 (4), 198.1 (18), 183.1 (100), 165.1 (5), 147.0 (8), 118.0 (22), 91.0 (15), 79.0 (10), 67.0 (7). $C_{14}H_{24}O_3$ (240.3): calcd. C 69.96, H 10.07; found C 70.01, H 10.11.

10b: Yield: 619 mg, 62%. R_f = 0.32. M.p. 51 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.1 Hz, 3 H, 4′′-H), 0.93 (t, *J* = 6.8 Hz, 3 H, 3′-H), 1.20–1.44 (m, 7 H, 2′-H, 2′′-H, 3′′-H, 5-H_a), 1.46–1.62 (m, 4 H, 1′-H, 1′′-H), 1.70–1.77 (m, 1 H, 3-H), 2.00–2.24 (m, 5 H, 2-H, 3a-H, 4-H, 5-H_b, 6-H), 2.63 (t, *J* = 8.7 Hz, 1 H, 6a-H), 3.55 [dd, *J* = 8.1 Hz, *J* = 10.7 Hz, 1 H, (C-6)C*H*$_a$OH], 3.57 [dd, *J* = 5.6 Hz, *J* = 11.1 Hz, 1 H, (C-4)C*H*$_a$OH], 3.67 [dd, *J* = 5.2 Hz, *J* = 10.5 Hz, 1 H, (C-4)C*H*$_b$OH], 3.71 [dd, *J* = 4.5 Hz, *J* = 10.6 Hz, 1 H, (C-6)C*H*$_b$OH] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0 (C-4′′), 14.3 (C-3′), 20.1 (C-2′), 23.1 (C-2′′), 28.5 (C-1′), 30.9 (C-3′′), 33.6 (C-1′′), 34.1 (C-5), 44.0 (C-6), 46.0 (C-3), 48.1, 48.3 (C-3a, C-4), 55.7 (C-2), 57.5 (C-6a), 66.2, 66.5 [(C-4) *C*H$_2$OH, (C-6) *C*H$_2$OH] ppm. FT-IR (ATR): $\tilde{\nu}$ = 3362 cm^{-1} (s), 2955 (s), 2924 (s), 2870 (s), 1718 (vs), 1464 (m), 1378 (m), 1052 (s), 903 (s), 727 (vs), 649 (s) cm^{-1}. GC-MS (EI): *m/z* (%) = 281.1 (1) [(M – H)$^+$], 264.4 (1), 240.4 (3), 183.2 (100), 147.2 (6), 119.2 (5), 91.1 (4), 79.1 (8), 67.1 (8), 55.1 (14). HRMS (CI, CH_4): calcd. for $C_{17}H_{31}O_3$ 283.2273, found 283.2273 [M + H]$^+$.

10c: Yield: 683 mg, 69%. R_f = 0.31. ^1H NMR (500 MHz, $(CD_3)_2CO$): δ = 0.73 (t, *J* = 7.2 Hz, 3 H, 3′-H), 1.05–1.12 (m, 1 H, 2′-H_a), 1.24–1.36 (m, 2 H, 1′-H_a, 2′-H_b), 1.42–1.55 (m, 2 H, 1′-H_b, 5-H_a), 2.08–2.24 (m, 3 H, 4-H, 5-H_b, 6-H), 2.60–2.69 (m, 2 H, 2-H, 3a-H), 2.74 (dt, *J* = 1.2 Hz, *J* = 9.4 Hz, 1 H, 6a-H), 2.82 (dd, *J* = 9.6 Hz, *J* = 12.3 Hz, 1 H, 3-H), 3.21 [dd, *J* = 6.8 Hz, *J* = 10.4 Hz, 1 H, (C-4)C*H*$_a$OH], 3.30 [dd, *J* = 5.2 Hz, *J* = 10.4 Hz, 1 H, (C-4) C*H*$_b$OH], 3.55 [dd, *J* = 5.9 Hz, *J* = 10.3 Hz, 1 H, (C-6)C*H*$_a$OH], 3.69 [dd, *J* = 5.4 Hz, *J* = 10.4 Hz, 1 H, (C-6)C*H*$_b$OH], 7.23–7.26 (m, 1 H, 4′′-H), 7.32–7.36 (m, 2 H, 3′′-H, 5′′-H), 7.39–7.42 (m, 2 H, 2′′-H, 6′′-H) ppm. ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ = 15.4 (C-3′), 21.6 (C-2′), 31.9 (C-1′), 36.2 (C-5), 46.4 (C-6), 49.3 (C-4), 53.2 (C-3a), 56.2 (C-3), 56.9 (C-6a), 59.5 (C-2), 66.8, 67.2 [(C-4) *C*H$_2$OH, (C-6) *C*H$_2$OH], 128.4 (C-4′′), 129.6 (C-2′′, C-6′′), 130.4 (C-3′′, C-5′′), 145.0 (C-1′′) ppm. FT-IR (ATR): $\tilde{\nu}$ = 3359 cm^{-1} (s), 2955 (s), 2915 (s), 2870 (s), 1720 (vs), 1495 (m), 1454 (s), 1374 (s), 1305 (m), 1241 (s), 1158 (m), 1082 (s), 1046 (vs), 917 (m), 760 (s), 736 (m), 699 (vs) cm^{-1}. GC-MS (EI): *m/z* (%) = 302.3 (10) [M^+], 284.3 (11), 273.3 (15), 260.2 (86), 242.2 (31), 201.1 (20), 169.1 (11), 146.1 (20), 131.1 (16), 117.0 (92), 104.1 (41), 91.0 (100), 79.1 (26), 67.1 (16), 55.0 (31). HRMS (CI, CH_4): calcd. for $C_{19}H_{27}O_3$ 303.1960, found 303.1951 [M + H]$^+$.

10d: Yield: 53 mg, 22%. R_f = 0.22. ^1H NMR (500 MHz, $(CD_3)_2CO$): δ = 0.91 (t, *J* = 7.1 Hz, 3 H, 4′-H), 1.19 (d, *J* = 6.5 Hz, 3 H, C*H*$_3$), 1.22–1.52 (m, 6 H, 1′-H_a, 2′-H_a, 2′-H_b, 3′-H, 5-H_a), 1.54–1.62 (m, 1 H, 1′-H_b), 1.64–1.73 (m, 1 H, 3-H), 1.94–1.98 (m, 1 H, 2-H), 1.99–2.16 (m, 4 H, 3a-H, 4-H, 5-H_b, 6-H), 2.55 (t, *J* = 8.7 Hz, 1 H, 6a-H), 3.44–3.74 [m, 4 H, (C-4)C*H*$_2$OH, (C-6)C*H*$_2$OH] ppm. ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ = 15.2 (C-4′), 19.8 (*C*H$_3$), 24.6 (C-3′), 28.9 (C-1′), 30.8 (C-2′), 36.2 (C-5), 44.1 (C-3), 46.2 (C-6), 49.8 (C-3a), 53.0 (C-4), 57.0 (C-6a), 59.6 (C-2), 66.8, 67.8 [(C-4) *C*H$_2$OH, (C-6) *C*H$_2$OH] ppm. FT-IR (ATR): $\tilde{\nu}$ = 3317 cm^{-1} (s), 2956 (s), 2930 (s), 2898 (s), 2857 (s), 1722 (vs), 1481 (m), 1448 (m), 1403 (m), 1377 (m), 1338 (m), 1311 (m), 1276 (m), 1227 (m), 1170 (m), 1115 (s), 1081 (s), 1028 (vs), 1003 (s), 988 (s) cm^{-1}. GC-MS (EI): *m/z* (%) = 254.5 (2) [M^+], 239.3 (6), 198.3 (9), 183.2 (100), 165.2 (6), 147.2 (6), 79.0 (13), 69.1 (11), 55.1 (19). HRMS (CI, CH_4): calcd. for $C_{15}H_{26}O_3$ 254.1882, found 254.1879 [M^+].

10e: Yield: 165 mg, 53%. R_f = 0.35. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.1 Hz, 3 H, 4′′-H), 0.92 (t, *J* = 6.8 Hz, 3 H, 4′-H), 1.18–1.36 (m, 9 H, 2′-H, 2′′-H, 3′-H, 3′′-H, 5-H_a), 1.49–1.62 (m, 4 H, 1′-H, 1′′-H), 1.71–1.78 (m, 1 H, 3-H), 2.02–2.24 (m, 5 H, 2-H, 3a-H, 4-H, 5-H_b, 6-H), 2.63 (t, *J* = 9.4 Hz, 1 H, 6a-H), 3.55 [dd, *J* = 8.0 Hz, *J* = 10.7 Hz, 1 H, (C-6)C*H*$_a$OH], 3.57 [dd, *J* = 6.0 Hz, *J* = 10.8 Hz, 1 H, (C-4)C*H*$_a$OH], 3.67 [dd, *J* = 5.1 Hz, *J* = 10.6 Hz, 1 H, (C-4)C*H*$_b$OH], 3.72 [dd, *J* = 4.5 Hz, *J* = 10.7 Hz, 1 H, (C-6)C*H*$_b$OH] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9, 14.0 (C-4′, C-4′′), 22.9, 23.1 (C-3′, C-3′′), 28.3 (C-1′), 28.5, 29.0 (C-2′, C-2′′), 33.6 (C-1′′), 34.1 (C-5), 44.0 (C-6), 45.9 (C-3), 48.1, 48.3 (C-3a, C-4), 55.8 (C-2), 57.5 (C-6a), 66.2, 66.5 [(C-4) *C*H$_2$OH, (C-6) *C*H$_2$OH] ppm. FT-IR (ATR): $\tilde{\nu}$ = 3362 cm^{-1} (s), 2954 (s), 2925 (s), 2858 (s), 1719 (vs), 1465 (m), 1378 (m), 1053 (s), 1028 (s), 903 (s), 727 (s), 649 (s) cm^{-1}. GC-MS (EI): *m/z* (%) = 296.6 (1) [M^+], 239.4 (7), 183.2 (100), 165.3 (7), 147.2 (8), 119.2 (7), 91.1 (5),

 © 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

79.1 (8), 67.1 (7), 55.1 (15). HRMS (CI, CH_4): calcd. for $C_{18}H_{32}O_3$ 296.2351, found 296.2348 [M^+].

10f: Yield: 190 mg, 75%. R_f = 0.32. ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ = 0.75 (t, J = 7.2 Hz, 3 H, 4′-H), 1.01–1.10 (m, 3 H, 2′-H_a, 3′-H), 1.23–1.30 (m, 1 H, 2′-H_b), 1.36 (tdd, J = 5.0 Hz, J = 10.2 Hz, J = 13.3 Hz, 1 H, 1′-H_a), 1.42–1.51 (m, 2 H, 1′-H_b, 5-H_a), 2.08–2.25 (m, 3 H, 4-H, 5-H_b, 6-H), 2.61–2.68 (m, 2 H, 2-H, 3a-H), 2.74 (dt, J = 1.1 Hz, J = 9.5 Hz, 1 H, 6a-H), 2.80–2.83 (m, 1 H, 3-H), 3.18–3.24 [m, 1 H, (C-4)CH_aOH], 3.28–3.32 [m, 1 H, (C-4)CH_bOH], 3.52–3.58 [m, 1 H, (C-6)CH_aOH], 3.66–3.72 [m, 1 H, (C-6)CH_bOH], 7.22–7.26 (m, 1 H, 4′′-H), 7.32–7.37 (m, 2 H, 3′′-H, 5′′-H), 7.38–7.42 (m, 2 H, 2′′-H, 6′′-H) ppm. ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ = 15.0 (C-4′), 24.4 (C-3′), 29.1 (C-1′), 30.5 (C-2′), 36.2 (C-5), 46.4 (C-6), 49.3 (C-4), 53.1 (C-3a), 56.1 (C-3), 56.9 (C-6a), 59.6 (C-2), 66.8, 67.2 [(C-4) CH$_2$OH, (C-6) CH$_2$OH], 128.4 (C-4′′), 129.6 (C-2′′, C-6′′), 130.3 (C-3′′, C-5′′), 145.0 (C-1′′) ppm. FT-IR (ATR): $\tilde{\nu}$ = 3399 cm^{-1} (s), 2926 (s), 2871 (s), 1726 (vs), 1495 (m), 1454 (s), 1373 (s), 1240 (s), 1158 (m), 1044 (vs), 923 (m), 760 (s), 728 (m), 700 (vs) cm^{-1}. GC-MS (EI): m/z (%) = 316.3 (50) [M^+], 298.3 (6), 273.3 (26), 260.2 (79), 242.3 (34), 201.1 (18), 160.1 (25), 141.2 (13), 131.1 (22), 117.1 (81), 104.1 (81), 91.0 (100), 79.1 (29), 67.1 (28), 55.0 (37). HRMS (EI): calcd. for $C_{20}H_{28}O_3$ 316.2038, found 316.2044 [M^+].

10g: Yield: 108 mg, 30%. R_f = 0.32. ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ = 0.89 (t, J = 6.9 Hz, 3 H, 5′-H), 1.19 (d, J = 6.6 Hz, 3 H, CH_3), 1.23–1.38 (m, 7 H, 2′-H, 3′-H, 4′-H, 5-H_a), 1.41–1.50 (m, 1 H, 1′-H_a), 1.51–1.61 (m, 1 H, 1′-H_b), 1.62–1.73 (m, 1 H, 3-H), 1.92–1.98 (m, 1 H, 2-H), 1.99–2.17 (m, 4 H, 3a-H, 4-H, 5-H_b, 6-H), 2.54 (t, J = 9.2 Hz, 1 H, 6a-H), 3.47–3.74 [m, 4 H, (C-4)CH_2OH, (C-6)CH_2OH] ppm. ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ = 15.3 (C-5′), 19.8 (CH$_3$), 24.1 (C-4′), 28.2 (C-2′), 29.2 (C-1′), 33.9 (C-3′), 36.2 (C-5), 44.1 (C-3), 46.2 (C-6), 49.8 (C-3a), 53.0 (C-4), 57.0 (C-6a), 59.6 (C-2), 66.8, 67.8 [(C-4) CH$_2$OH, (C-6) CH$_2$OH] ppm. FT-IR (ATR): $\tilde{\nu}$ = 3317 cm^{-1} (s), 2954 (s), 2926 (s), 2898 (s), 2853 (s), 1722 (vs), 1480 (m), 1448 (m), 1406 (m), 1377 (m), 1337 (m), 1312 (m), 1274 (m), 1224 (m), 1170 (m), 1116 (s), 1082 (s), 1027 (vs), 1002 (s), 989 (s) cm^{-1}. GC-MS (EI): m/z (%) = 268.4 (3) [M^+], 253.4 (12), 198.2 (9), 183.2 (100), 147.2 (6), 91.1 (6), 79.1 (11), 67.0 (11), 55.1 (18). HRMS (CI, CH_4): calcd. for $C_{16}H_{28}O_3$ 268.2038, found 268.2032 [M^+].

10h: Yield: 370 mg, 75%. R_f = 0.21. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.0 Hz, 3 H, 5′-H), 0.92 (t, J = 7.0 Hz, 3 H, 4′′-H), 1.20–1.40 (m, 13 H, 2′-H, 2′′-H, 3′-H, 3′′-H, 4′-H, 4′′-H, 5-H_a), 1.48–1.62 (m, 4 H, 1′-H, 1′′-H), 1.70–1.77 (m, 1 H, 3-H), 2.02–2.24 (m, 5 H, 2-H, 3a-H, 4-H, 5-H_b, 6-H), 2.63 (t, J = 8.7 Hz, 1 H, 6a-H), 3.55 [dd, J = 7.9 Hz, J = 10.6 Hz, 1 H, (C-6)CH_aOH], 3.58 [dd, J = 6.1 Hz, J = 10.5 Hz, 1 H, (C-4)CH_aOH], 3.67 [dd, J = 5.2 Hz, J = 10.5 Hz, 1 H, (C-4)CH_bOH], 3.72 [dd, J = 4.6 Hz, J = 10.6 Hz, 1 H, (C-6)CH_bOH] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0 (C-5′, C-4′′), 22.4 (C-4′), 23.1 (C-3′′), 26.5 (C-2′), 28.5, 28.6 (C-1′, C-2′′), 32.0 (C-3′), 33.5 (C-1′′), 34.2 (C-5), 44.0 (C-6), 46.0 (C-3), 48.1, 48.3 (C-3a, C-4), 55.9 (C-2), 57.5 (C-6a), 66.2, 66.5 [(C-4) CH$_2$OH, (C-6) CH$_2$OH] ppm. FT-IR (ATR): $\tilde{\nu}$ = 3392 cm^{-1} (s), 2954 (s), 2925 (vs), 2858 (s), 1721 (vs), 1465 (m), 1378 (m), 1053 (s), 1028 (s), 903 (s), 726 (s), 650 (s) cm^{-1}. GC-MS (EI): m/z (%) = 311.6 (4) [M + H]$^+$, 253.4 (12), 183.3 (100), 147.3 (6), 119.2 (5), 91.1 (5), 79.1 (8), 67.1 (8), 55.1 (14). HRMS (CI, CH_4): calcd. for $C_{19}H_{34}O_3$ 310.2508, found 310.2564 [M^+].

10i: Yield: 143 mg, 74%. R_f = 0.31. ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ = 0.77 (t, J = 7.1 Hz, 3 H, 5′-H), 1.05–1.19 (m, 4 H, 3′-H, 4′-H), 1.24–1.39 (m, 3 H, 2′-H, 1′-H_a), 1.42–1.52 (m, 2 H, 1′-H_b, 5-H_a), 2.08–2.25 (m, 3 H, 4-H, 5-H_b, 6-H), 2.61–2.69 (m, 2 H, 2-H, 3a-H), 2.74 (dt, J = 1.1 Hz, J = 9.5 Hz, 1 H, 6a-H), 2.80–2.87 (m, 1 H, 3-H), 3.18–3.24 [m, 1 H, (C-4)CH_aOH], 3.30 [td, J = 5.0 Hz, J = 10.1 Hz, 1 H, (C-4)CH_bOH], 3.55 [ddd, J = 6.2 Hz, J = 7.8 Hz, J = 11.2 Hz, 1 H, (C-6)CH_aOH], 3.69 [dd, J = 5.6 Hz, J = 9.2 Hz, 1 H, (C-6)CH_bOH], 7.22–7.26 (m, 1 H, 4′′-H), 7.32–7.36 (m, 2 H, 3′′-H, 5′′-H), 7.39–7.42 (m, 2 H, 2′′-H, 6′′-H) ppm. ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ = 15.1 (C-5′), 23.9 (C-4′), 28.0 (C-2′), 29.4 (C-1′), 33.5 (C-3′), 36.2 (C-5), 46.4 (C-6), 49.3 (C-4), 53.2 (C-3a), 56.2 (C-3), 56.9 (C-6a), 59.7 (C-2), 66.8, 67.2 [(C-4) CH$_2$OH, (C-6) CH$_2$OH], 128.4 (C-4′′), 129.6 (C-2′′, C-6′′), 130.3 (C-3′′, C-5′′), 145.0 (C-1′′) ppm. FT-IR (ATR): $\tilde{\nu}$ = 3371 cm^{-1} (s), 2925 (s), 2858 (s), 1724 (vs), 1495 (m), 1454 (s), 1374 (m), 1240 (s), 1157 (m), 1079 (s), 1047 (vs), 974 (m), 760 (s), 724 (m), 699 (vs) cm^{-1}. GC-MS (EI): m/z (%) = 330.3 (59) [M^+], 273.2 (20), 260.1 (76), 242.2 (41), 229.2 (32), 201.1 (47), 183.0 (20), 155.0 (15), 130.7 (33), 117.0 (46), 104.0 (87), 91.0 (100), 78.9 (32), 67.0 (39), 55.0 (32). HRMS (EI): calcd. for $C_{21}H_{30}O_3$ 330.2195, found 330.2192 [M^+].

10j: Yield: 899 mg, 50%. R_f = 0.27. M.p. 54 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 3 H, 6′-H), 1.18 (d, J = 6.4 Hz, 3 H, CH_3), 1.20–1.34 (m, 8 H, 2′-H_a, 3′-H, 4′-H, 5′-H, 5-H_a), 1.35–1.43 (m, 1 H, 2′-H_b), 1.45–1.52 (m, 1 H, 1′-H_a), 1.53–1.60 (m, 1 H, 1′-H_b), 1.61–1.70 (m, 1 H, 3-H), 1.95–2.00 (m, 1 H, 2-H), 2.01–2.17 (m, 4 H, 3a-H, 4-H, 5-H_b, 6-H), 2.62 (t, J = 9.0 Hz, 1 H, 6a-H), 3.55 [dd, J = 8.0 Hz, J = 10.6 Hz, 1 H, (C-6)CH_aOH], 3.60 [dd, J = 2.6 Hz, J = 5.7 Hz, 2 H, (C-4)CH_2OH], 3.73 [dd, J = 4.0 Hz, J = 5.6 Hz, 1 H, (C-6)CH_bOH] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0 (C-6′), 18.3 (CH$_3$), 22.5 (C-5′), 26.7 (C-2′), 27.0 (C-1′), 29.6 (C-3′), 31.6 (C-4′), 34.4 (C-5), 42.8 (C-3), 43.9 (C-6), 47.5 (C-3a), 51.2 (C-4), 57.8 (C-6a), 58.5 (C-2), 66.5, 66.7 [(C-4) CH$_2$OH, (C-6) CH$_2$OH] ppm. FT-IR (ATR): $\tilde{\nu}$ = 3366 cm^{-1} (s), 2952 (s), 2924 (s), 2856 (s), 1720 (vs), 1458 (m), 1378 (m), 1054 (s), 1016 (s), 903 (vs), 724 (vs) cm^{-1}. GC-MS (EI): m/z (%) = 282.4 (4) [M^+], 267.4 (12), 198.3 (6), 183.2 (100), 147.2 (6), 119.2 (5), 91.1 (6), 79.1 (12), 67.1 (10), 55.1 (18). HRMS (CI, CH_4): calcd. for $C_{17}H_{31}O_3$ 283.2273, found 283.2273 [M + H]$^+$.

10k: Yield: 921 mg, 57%. R_f = 0.28. ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ = 0.88 (t, J = 6.8 Hz, 3 H, 6′-H), 0.89 (t, J = 7.2 Hz, 3 H, 4′′-H), 1.20–1.44 (m, 13 H, 2′-H, 2′′-H, 3′-H, 3′′-H, 4′-H, 5′-H, 5-H_a), 1.46–1.60 (m, 4 H, 1′-H, 1′′-H), 1.70–1.77 (m, 1 H, 3-H), 1.90–2.22 (m, 5 H, 2-H, 3a-H, 4-H, 5-H_b, 6-H), 2.53 (t, J = 8.9 Hz, 1 H, 6a-H), 3.43–3.58 [m, 4 H, (C-4)CH_2OH, (C-6)CH_2OH] ppm. ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ = 15.3 (C-6′, C-4′′), 24.2, 24.8 (C-5′, C-3′′), 28.7 (C-2′), 31.0, 31.2, 31.3 (C-1′, C-2′′, C-3′), 33.4 (C-4′), 35.9, 36.0 (C-1′′, C-5), 45.9 (C-6), 47.0 (C-3), 50.2, 50.4 (C-3a, C-4), 57.0, 57.0 (C-2, C-6a), 67.0, 67.1 [(C-4) CH$_2$OH, (C-6) CH$_2$OH] ppm. FT-IR (ATR): $\tilde{\nu}$ = 3375 cm^{-1} (s), 2954 (s), 2922 (vs), 2856 (s), 1720 (vs), 1458 (m), 1377 (m), 1050 (s), 1026 (s), 724 (m), 620 (m) cm^{-1}. GC-MS (EI): m/z (%) = 324.2 (1) [M^+], 267.1 (16), 183.0 (100), 165.0 (5), 147.0 (7), 119.0 (5), 91.1 (5), 78.9 (7), 66.9 (8), 55.1 (17). HRMS (CI, CH_4): calcd. for $C_{20}H_{37}O_3$ 325.2742, found 325.2742 [M + H]$^+$.

10l: Yield: 606 mg, 56%. R_f = 0.35. ^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ = 0.81 (t, J = 7.2 Hz, 3 H, 6′-H), 1.05–1.17 (m, 7 H, 2′-H_a, 3′-H, 4′-H, 5′-H), 1.24–1.39 (m, 2 H, 1′-H_a, 2′-H_b), 1.41–1.57 (m, 2 H, 1′-H_b, 5-H_a), 2.08–2.26 (m, 3 H, 4-H, 5-H_b, 6-H), 2.61–2.69 (m, 2 H, 2-H, 3a-H), 2.74 (dt, J = 1.4 Hz, J = 9.5 Hz, 1 H, 6a-H), 2.79–2.90 (m, 1 H, 3-H), 3.21 [dd, J = 6.8 Hz, J = 10.1 Hz, 1 H, (C-4)CH_aOH], 3.30 [dd, J = 5.0 Hz, J = 10.3 Hz, 1 H, (C-4)CH_bOH], 3.55 [dd, J = 6.0 Hz, J = 9.5 Hz, 1 H, (C-6)CH_aOH], 3.69 [dd, J = 5.5 Hz, J = 10.5 Hz, 1 H, (C-6)CH_bOH], 7.21–7.26 (m, 1 H, 4′′-H), 7.32–7.37 (m, 2 H, 3′′-H, 5′′-H), 7.39–7.42 (m, 2

 © 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

H, 2′′-H, 6′′-H) ppm. ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ = 15.2 (C-6′), 24.1 (C-5′), 28.3 (C-2′), 29.5 (C-1′), 31.0 (C-3′), 33.2 (C-4′), 36.2 (C-5), 46.4 (C-6), 49.3 (C-4), 53.2 (C-3a), 56.2 (C-3), 56.9 (C-6a), 59.7 (C-2), 66.8, 67.2 [(C-4) *C*H$_2$OH, (C-6) *C*H$_2$OH], 128.4 (C-4′′), 129.6 (C-2′′, C-6′′), 130.3 (C-3′′, C-5′′), 145.0 (C-1′′) ppm. FT-IR (ATR): $\tilde{\nu}$ = 3379 cm^{-1} (s), 2952 (s), 2924 (s), 2856 (s), 1724 (vs), 1495 (m), 1454 (s), 1374 (s), 1241 (s), 1157 (m), 1077 (s), 1046 (vs), 760 (s), 730 (m), 699 (vs) cm^{-1}. GC-MS (EI): *m*/*z* (%) = 344.3 (33) [M$^+$], 273.2 (29), 260.2 (91), 242.1 (30), 229.2 (7), 211.1 (17), 201.1 (21), 183.1 (20), 158.0 (23), 128.9 (19), 117.0 (53), 104.0 (77), 91.0 (100), 79.0 (28), 67.0 (21), 55.0 (40). HRMS (EI): calcd. for $C_{22}H_{32}O_3$ 344.2351, found 344.2357 [M$^+$].

10m: Yield: 100 mg, 34%. R_f = 0.25. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.10 (d, *J* = 6.4 Hz, 3 H, C*H*$_3$), 1.31–1.39 (m, 1 H, 5-H$_a$), 1.98–2.05 (m, 1 H, 3-H), 2.09–2.19 (m, 2 H, 4-H, 5-H$_b$), 2.20–2.34 (m, 2 H, 3a-H, 6-H), 2.76 (t, *J* = 9.8 Hz, 1 H, 6a-H), 3.14 (dd, *J* = 0.8 Hz, *J* = 12.6 Hz, 1 H, 2-H), 3.20–3.57 [dd, *J* = 3.9 Hz, *J* = 5.8 Hz, 2 H, (C-4)C*H*$_2$OH], 3.63 [dd, *J* = 7.1 Hz, *J* = 10.8 Hz, 1 H, (C-6)C*H*$_a$OH], 3.73 [dd, *J* = 4.6 Hz, *J* = 10.9 Hz, 1 H, (C-6) C*H*$_b$OH], 7.03–7.06 (m, 2 H, 2′-H, 6′-H), 7.21–7.35 (m, 3 H, 3′-H, 4′-H, 5′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.4 (*C*H$_3$), 34.1 (C-5), 44.0 (C-6), 45.9 (C-3), 47.0 (C-4), 50.9 (C-3a), 57.1 (C-6a), 65.7 [(C-6) *C*H$_2$OH], 65.9 (C-2), 66.5 [(C-4) *C*H$_2$OH], 127.1 (C-4′), 128.5, 128.7 (C-2′, C-3′, C-5′, C-6′), 136.5 (C-1′) ppm. FT-IR (ATR): $\tilde{\nu}$ = 3364 cm^{-1} (s), 2951 (s), 2921 (s), 2870 (s), 1721 (vs), 1496 (m), 1451 (s), 1377 (s), 1051 (vs), 908 (vs), 754 (vs), 646 (s) cm^{-1}. GC-MS (EI): *m*/*z* (%) = 274.4 (18) [M$^+$], 243.4 (11), 173.3 (23), 118.1 (100), 91.1 (38), 79.1 (25), 67.1 (11), 55.1 (8). HRMS (EI): calcd. for $C_{17}H_{22}O_3$ 274.1569, found 274.1552 [M$^+$].

10n: Yield: 115 mg, 38%. R_f = 0.29. ^{1}H NMR (500 MHz, $(CD_3)_2$-CO): δ = 0.77 (t, *J* = 7.0 Hz, 3 H, 4′-H), 1.11–1.30 (m, 4 H, 2′-H, 3′-H), 1.44 (dd, *J* = 4.6 Hz, *J* = 10.2 Hz, 1 H, 5-H$_a$), 1.57–1.63 (m, 2 H, 1′-H), 2.14–2.37 (m, 4 H, 3-H, 4-H, 5-H$_b$, 6-H), 2.41 (dt, *J* = 3.4 Hz, *J* = 9.3 Hz, 1 H, 3a-H), 2.69 (t, *J* = 9.6 Hz, 1 H, 6a-H), 2.79–2.92 (m, 2 H, OH), 3.35 (dd, *J* = 0.9 Hz, *J* = 11.9 Hz, 1 H, 2-H), 3.51–3.59 [m, 3 H, (C-4)C*H*$_2$OH, (C-6)C*H*$_a$OH], 3.69 [dd, *J* = 5.3 Hz, *J* = 10.4 Hz, 1 H, (C-6)C*H*$_b$OH], 7.13–7.17 (m, 2 H, 2′-H, 6′-H), 7.20–7.34 (m, 3 H, 3′-H, 4′-H, 5′-H) ppm. ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ = 15.1 (C-4′), 24.6 (C-3′), 29.4 (C-2′), 34.9 (C-1′), 36.1 (C-5), 46.3, 49.8 (C-4, C-6), 50.6 (C-3a), 51.2 (C-3), 57.1 (C-6a), 65.6 (C-2), 66.6, 67.6 [(C-4) *C*H$_2$OH, (C-6) *C*H$_2$OH], 128.3 (C-4′), 130.0, 130.9 (C-2′, C-3′, C-5′, C-6′), 141.1 (C-1′), 219.3 (C-1) ppm. FT-IR (ATR): $\tilde{\nu}$ = 3375 cm^{-1} (s), 2954 (s), 2924 (s), 2859 (s), 1724 (vs), 1496 (m), 1452 (m), 1374 (m), 1240 (s), 1045 (vs), 755 (s), 698 (vs) cm^{-1}. GC-MS (EI): *m*/*z* (%) = 316.2 (34) [M$^+$], 298.2 (5), 267.2 (10), 259.1 (25), 241.2 (10), 225.1 (12), 215.1 (39), 160.0 (26), 149.0 (20), 129.1 (16), 118.0 (100), 116.0 (80), 104.0 (69), 91.1 (95), 78.9 (35), 66.9 (24), 55.1 (21). HRMS (EI): calcd. for $C_{20}H_{28}O_3$ 316.2038, found 316.2037 [M$^+$].

10o: Yield: 861 mg, 43%. R_f = 0.26. ^{1}H NMR (500 MHz, $(CD_3)_2$-CO): δ = 1.57 (dd, *J* = 5.0 Hz, *J* = 10.2 Hz, 1 H, 5-H$_a$), 2.23–2.31 (m, 2 H, 4-H, 5-H$_b$), 2.42–2.51 (m, 1 H, 6-H), 2.82–2.91 (m, 2 H, 3a-H, 6a-H), 3.24–3.91 [m, 1 H, (C-4)C*H*$_a$OH], 3.32–3.39 [m, 2 H, 3-H, (C-4)C*H*$_b$OH], 3.58–3.63 [m, 1 H, (C-6)C*H*$_a$OH], 3.76–3.80 [m, 1 H, (C-6)C*H*$_b$OH], 3.99 (dd, *J* = 0.8 Hz, *J* = 13.2 Hz, 1 H, 2-H), 7.06–7.09 (m, 2 H, 4′-H, 4′′-H), 7.12–7.39 (m, 8 H, 2′-H, 2′′-H, 3′-H, 3′′-H, 5′-H, 5′′-H, 6′-H, 6′′-H) ppm. ^{13}C NMR (125 MHz, $(CD_3)_2CO$): δ = 36.1 (C-5), 46.6 (C-6), 48.8 (C-4), 52.9 (C-3a), 56.8 (C-6a), 58.0 (C-3), 66.5 [(C-6) *C*H$_2$OH], 66.9 (C-2), 67.3 [(C-4) *C*H$_2$OH], 128.3, 128.4 (C-4′, C-4′′), 129.6, 129.9, 130.2, 130.9 (C-2′, C-2′′, C-3′, C-3′′, C-5′, C-5′′, C-6′, C-6′′), 139.4 (C-1′′), 143.5 (C-1′), 217.9 (C-1) ppm. FT-IR (ATR): $\tilde{\nu}$ = 3363 cm^{-1} (s), 3028 (m), 2918 (s), 2871 (s), 1724 (vs), 1601 (m), 1495 (s), 1451 (s), 1374 (m), 1278 (m), 1134 (m), 1074 (s), 1045 (vs), 1025 (s), 968 (m), 929 (m), 753 (s), 696 (vs) cm^{-1}. GC-MS (EI): *m*/*z* (%) = 336.1 (80) [M$^+$], 206.3 (12), 179.0 (48), 165.0 (25), 118.0 (100), 105.0 (16), 91.0 (52), 79.0 (14), 67.0 (14). HRMS (EI): calcd. for $C_{22}H_{24}O_3$ 336.1725, found 336.1726 [M$^+$].

General Procedure for the Enzymatic Esterification to 4,5-Disubstituted [3-(Hydroxymethyl)-6-oxooctahydropentalen-1-yl]methyl Acetates 4 and 5,6-Disubstituted [3-(Hydroxymethyl)-4-oxooctahydropentalen-1-yl]methyl Acetates 5: A mixture of the appropriate **10** (1.13 mmol), molecular sieves (62 pellets, 4 Å), vinyl acetate (94 μL, 87 mg, 1.01 mmol) and lipase (34 mg) in freshly distilled absolute THF (12 mL) was heated at 40 °C for 5–30 min (GC control). The reaction mixture was filtered through cellulose, the filtrate concentrated and chromatographed on SiO_2 with PE/EtOAc, 1:1. GC: HP-5 TA column, gradient 16 °C min^{-1} from 80 °C to 300 °C, then 300 °C for 17 min.

4a: Yield: 182 mg, 15%, colorless oil; R_f = 0.30; t_R = 10.17 min. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.2 Hz, 3 H, 3′-H), 1.17 [d, *J* = 6.4 Hz, 3 H, (C-3)C*H*$_3$], 1.22–1.31 (m, 2 H, 2′-H$_a$, 5-H$_a$), 1.34–1.48 (m, 2 H, 1′-H$_a$, 2′-H$_b$), 1.53–1.68 (m, 2 H, 1′-H$_b$, 3-H), 1.89 (ddd, *J* = 1.4 Hz, *J* = 5.9 Hz, *J* = 11.2 Hz, 1 H, 2-H), 2.00–2.15 (m, 6 H, 3a-H, 4-H, 5-H$_b$, C*H*$_3$COO), 2.22–2.32 (m, 1 H, 6-H), 2.53 (td, *J* = 9.2 Hz, *J* = 1.1 Hz, 1 H, 6a-H), 3.57 (dd, *J* = 6.5 Hz, *J* = 10.5 Hz, 1 H, C*H*$_a$OH), 3.61 (dd, *J* = 6.5 Hz, *J* = 10.5 Hz, 1 H, C*H*$_b$OH), 4.06 (dd, *J* = 7.1 Hz, *J* = 10.9 Hz, 1 H, C*H*$_a$OOC), 4.24 (dd, *J* = 5.2 Hz, *J* = 10.9 Hz, 1 H, C*H*$_b$OOC) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.3 (3′-C), 19.0 [(C-3) *C*H$_3$], 20.1 (C-2′), 20.9 (*C*H$_3$COO), 30.0 (C-1′), 34.5 (C-5), 40.7, 41.7 (C-3, C-4), 47.5 (C-6), 50.9 (C-3a), 54.3 (C-6a), 57.8 (C-2), 66.5, 66.6 (*C*H$_2$OOC, *C*H$_2$OH), 171.1 (*C*OO) ppm. FT-IR (ATR): $\tilde{\nu}$ = 3453 cm^{-1} (m), 2955 (s), 2928 (s), 2870 (s), 1728 (vs), 1457 (m), 1366 (s), 1233 (vs), 1167 (m), 1033 (vs), 971 (m), 909 (m), 734 (m), 605 (m) cm^{-1}. GC-MS (EI): *m*/*z* (%) = 240.1 (14) [(M – CH$_3$COO)$^+$], 225.0 (100), 222.1 (35), 183.0 (72), 180.1 (44), 165.0 (62), 147.0 (32), 119.9 (23), 91.0 (29), 78.9 (58), 68.9 (48), 54.9 (67). HRMS (CI, CH$_4$): calcd. for $C_{16}H_{27}O_4$ 283.1909, found 283.1909 [M + H]$^+$.

5a: Yield: 326 mg, 27%, R_f = 0.37; t_R = 10.07 min. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 7.1 Hz, 3 H, 3′-H), 1.17 [d, *J* = 6.4 Hz, 3 H, (C-3)C*H*$_3$], 1.22–1.33 (m, 2 H, 2′-H$_a$, 5-H$_a$), 1.36–1.52 (m, 2 H, 1′-H$_a$, 2′-H$_b$), 1.53–1.70 (m, 2 H, 1′-H$_b$, 3-H), 1.97–2.02 (m, 1 H, 2-H), 2.04–2.16 (m, 6 H, 3a-H, 4-H, 5-H$_b$, C*H*$_3$COO), 2.18–2.25 (m, 1 H, 6-H), 2.63 (t, *J* = 8.7 Hz, 1 H, 6a-H), 3.55 (dd, *J* = 8.2 Hz, *J* = 10.6 Hz, 1 H, C*H*$_a$OH), 3.73 (dd, *J* = 4.2 Hz, *J* = 10.6 Hz, 1 H, C*H*$_b$OH), 4.01 (dd, *J* = 6.1 Hz, *J* = 9.8 Hz, 1 H, C*H*$_a$OOC), 4.03 (dd, *J* = 5.4 Hz, *J* = 9.8 Hz, 1 H, C*H*$_b$OOC) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.3 (C-3′), 18.2 [(C-3) *C*H$_3$], 19.9 (C-2′), 20.9 (*C*H$_3$COO), 29.1 (C-1′), 34.9 (C-5), 43.0 (C-3), 43.8, 44.2 (C-4, C-6), 51.4 (C-3a), 57.9, 58.3 (C-2, C-6a), 66.5 (*C*H$_2$OOC), 67.8 (*C*H$_2$OH), 171.0 (*C*OO) ppm. FT-IR (ATR): $\tilde{\nu}$ = 3447 cm^{-1} (m), 2955 (s), 2928 (s), 2871 (s), 1728 (vs), 1457 (m), 1368 (s), 1229 (vs), 1171 (m), 1032 (vs), 973 (m), 901 (m) cm^{-1}. GC-MS (EI): *m*/*z* (%) = 282.0 (1) [M$^+$], 267.0 (2), 240.1 (22), 225.0 (100), 180.1 (13), 165.0 (16), 146.9 (17), 139.0 (13), 119.0 (8), 90.9 (10), 78.9 (18), 68.9 (11), 54.9 (23). HRMS (CI, CH$_4$): calcd. for $C_{16}H_{27}O_4$ 283.1909, found 283.1909 [M + H]$^+$.

4b: Yield: 80.7 mg, 87%, colorless oil; R_f = 0.37; t_R = 11.37 min. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.91 (t, *J* = 6.0 Hz, 3 H, 4′′-H), 0.93 (d, *J* = 6.7 Hz, 3 H, 3′-H), 1.18–1.56 (m, 10 H, 1′-H$_a$, 1′′-H, 2′-H, 2′′-H, 3′′-H, 5-H$_a$), 1.58–1.65 (m, 1 H, 1′-H$_b$), 1.68–1.74 (m, 1 H, 3-H), 1.88–1.96 (m, 1 H, 4-H), 1.99–2.03 (m, 1 H, 2-H), 2.05–

 © 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

2.10 (m, 4 H, CH_3COO, 5-H$_b$), 2.11–2.17 (m, 1 H, 3a-H), 2.34–2.42 (m, 1 H, 6-H), 2.55 (dt, J = 0.9 Hz, J = 8.0 Hz, 1 H, 6a-H), 3.56 [dd, J = 6.9 Hz, J = 10.5 Hz, 1 H, (C-4)CH_a], 3.69 [dd, J = 5.6 Hz, J = 10.6 Hz, 1 H, (C-4)CH_b], 4.07 [dd, J = 6.9 Hz, J = 11.0 Hz, 1 H, (C-6)CH_a], 4.14 [dd, J = 5.9 Hz, J = 10.9 Hz, 1 H, (C-6)CH_b] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0, 14.2 (C-3′, C-4′′), 20.4 (C-3′′), 20.9 (COOCH$_3$), 23.0 (C-2′), 29.0 (C-2′′), 32.1 (C-1′), 34.0 (C-5), 35.1 (C-1′′), 40.3 (C-6), 44.7 (C-3), 48.0, 48.3 (C-3a, C-4), 54.8, 55.1 (C-2, C-6a), 65.7, 67.0 (CH$_2$OOC, CH$_2$OH), 171.1 (COO) ppm. FT-IR (ATR): $\tilde{\nu}$ = 3460 cm^{-1} (m), 2956 (s), 2927 (s), 2871 (s), 1728 (vs), 1464 (m), 1366 (s), 1234 (vs), 1034 (s), 905 (m), 730 (s), 648 (m), 606 (m) cm^{-1}. GC-MS (EI): m/z (%) = 281.1 (3) [(M – CH$_3$CO)$^+$], 264.1 (15), 225.2 (100), 183.1 (44), 165.1 (58), 147.0 (20), 118.9 (12), 105.0 (12), 93.1 (17), 79.0 (33), 67.0 (16), 55.0 (32). HRMS (EI): calcd. for $C_{19}H_{32}O_4$ 324.2301, found 324.2285 [M$^+$].

5b: t_R = 11.22 min. GC-MS (EI): m/z (%) = 282.3 (4) [(M – CH$_2$CO)$^+$], 225.1 (100), 181.1 (6), 165.1 (13), 147.0 (16), 119.0 (6), 105.0 (4), 93.0 (6), 79.0 (11), 67.0 (6), 55.0 (14). HRMS (EI): calcd. for $C_{19}H_{32}O_4$ 324.2301, found 324.2285 [M$^+$].

4c: Yield: 158 mg, 84%, colorless oil; R_f = 0.31; t_R = 12.61 min. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.76 (t, J = 7.1 Hz, 3 H, 3′-H), 1.00–1.44 (m, 4 H, 1′-H$_a$, 2′-H, 5-H$_a$), 1.47–1.64 (m, 1 H, 1′-H$_b$), 2.00–2.24 (m, 5 H, 4-H, 5-H$_b$, CH_3COO), 2.30–2.46 (m, 1 H, 6-H), 2.49–2.62 (m, 2 H, 2-H, 3a-H), 2.64–2.80 (m, 2 H, 3-H, 6a-H), 3.35 [d, J = 6.3 Hz, 2 H, (C-4)CH_2], 4.11 [dd, J = 7.0 Hz, J = 11.0 Hz, 1 H, (C-6)CH_a], 4.30 [dd, J = 5.2 Hz, J = 11.0 Hz, 1 H, (C-6)CH_b], 7.22–7.38 (m, 5 H, 2′′-H, 3′′-H, 4′′-H, 5′′-H, 6′′-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 14.2 (C-3′), 20.0 (C-2′), 21.0 (CH$_3$COO), 30.1 (C-1′), 34.6 (C-5), 41.0 (C-6), 47.6 (C-4), 51.6 (C-3a), 54.4 (C-3, C-6a), 58.2 (C-2), 66.2, 66.6 (CH$_2$OOC, CH$_2$OH), 127.1 (C-4′′), 127.5, 129.0 (C-2′′, C-3′′, C-5′′, C-6′′), 142.3 (C-1′′), 171.2 (COO), 217.7 (C-1) ppm. FT-IR (ATR): $\tilde{\nu}$ = 3440 cm^{-1} (m), 2955 (s), 2928 (s), 2871 (s), 1729 (vs), 1495 (m), 1454 (m), 1366 (s), 1237 (vs), 1158 (m), 1074 (m), 1034 (s), 970 (m), 906 (s), 761 (s), 731 (s), 701 (vs), 648 (m) cm^{-1}. GC-MS (EI): m/z (%) = 302.2 (16) [(M – C$_3$H$_6$)$^+$], 284.1 (57), 242.1 (30), 224.1 (14), 211.0 (12), 182.1 (15), 169.9 (10), 155.0 (12), 146.0 (19), 130.9 (17), 116.9 (74), 104.0 (32), 90.9 (100), 78.9 (35), 67.0 (11), 54.9 (22). HRMS (EI, CH$_4$): calcd. for $C_{21}H_{28}O_4$ 344.1988, found 344.1986 [M$^+$].

5c: t_R = 12.48 min. GC-MS (EI): m/z (%) = 301.2 (70) [(M – C$_3$H$_7$)$^+$], 284.2 (28), 242.2 (46), 225.1 (21), 201.0 (25), 183.0 (25), 167.1 (12), 158.0 (25), 146.0 (32), 117.0 (90), 104.0 (57), 91.0 (100), 79.0 (52), 67.0 (16), 55.0 (28). HRMS (EI, CH$_4$): calcd. for $C_{21}H_{28}O_4$ 344.1988, found 344.1986 [M$^+$].

4d: Yield: 8 mg, 43%, colorless oil; R_f = 0.39; t_R = 10.66 min. ^{1}H NMR (500 MHz, C_6D_6): δ = 0.89 [d, J = 6.3 Hz, 3 H, (C-3)CH_3], 0.91 (t, J = 7.0 Hz, 3 H, 4′-H), 0.94–1.02 (m, 1 H, 5-H$_a$), 1.20–1.32 (m, 3 H, 2′-H$_a$, 3-H, 3′-H), 1.33–1.46 (m, 2 H, 1′-H$_a$, 2′-H$_b$), 1.51–1.62 (m, 4 H, 1′-H$_b$, 2-H, 3a-H, 4-H), 1.69–1.82 (m, 4 H, CH_3COO, 5-H$_b$), 2.09–2.18 (m, 1 H, 6-H), 2.21 (t, J = 9.3 Hz, 1 H, 6a-H), 3.11 [d, J = 5.7 Hz, 2 H, (C-4)CH_2], 4.07 [dd, J = 7.2 Hz, J = 10.9 Hz, 1 H, (C-6)CH_a], 4.33 [dd, J = 5.3 Hz, J = 10.9 Hz, 1 H, (C-6)CH_b] ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 14.1 (C-4′), 18.8 [(C-3) CH$_3$], 20.5 (CH$_3$COO), 23.4 (C-3′), 27.8 (C-1′), 29.4 (C-2′), 34.7 (C-5), 41.1, 41.9 (C-3, C-6), 47.7, 51.0 (C-3a, C-4), 54.4 (C-6a), 57.9 (C-2), 66.4, 66.8 (CH$_2$OOC, CH$_2$OH), 170.2 (COO), 217.2 (C-1) ppm. FT-IR (ATR): $\tilde{\nu}$ = 3439 cm^{-1} (m), 2954 (s), 2927 (s), 2869 (s), 1729 (vs), 1457 (m), 1366 (s), 1234 (vs), 1166 (m), 1034 (vs), 972 (m), 909 (m), 728 (m), 605 (m) cm^{-1}. GC-MS (EI): m/z (%) = 296.4 (4) [M$^+$], 281.0 (10), 236.2 (36), 225.2 (100), 205.1 (8), 183.0 (44), 180.1 (41), 165.0 (48), 147.0 (31), 125.0 (12), 119.1 (16), 93.0 (29), 79.0 (48), 68.9 (40), 55.0 (54). HRMS (EI): calcd. for $C_{17}H_{28}O_4$ 296.1988, found 296.2000 [M + H]$^+$.

5d: t_R = 10.58 min. GC-MS (EI): m/z (%) = 296.3 (4) [M$^+$], 281.2 (9), 240.2 (11), 225.1 (100), 180.1 (10), 165.0 (14), 147.0 (20), 119.0 (10), 93.0 (12), 79.0 (18), 69.0 (10), 55.0 (22). HRMS (EI): calcd. for $C_{17}H_{28}O_4$ 296.1988, found 296.2000 [M + H]$^+$.

4e: Yield: 66.0 mg, 79%, colorless oil; R_f = 0.36; t_R = 11.80 min. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.0 Hz, 3 H, 4′′-H), 0.93 (t, J = 6.8 Hz, 3 H, 4′-H), 1.16–1.56 (m, 12 H, 1′-H$_a$, 1′′-H, 2′-H, 2′′-H, 3′-H, 3′′-H, 5-H$_a$), 1.60–1.67 (m, 1 H, 1′-H$_b$), 1.68–1.74 (m, 1 H, 3-H), 1.88–1.96 (m, 1 H, 4-H), 1.98–2.03 (m, 1 H, 2-H), 2.05–2.10 (m, 4 H, 5-H$_b$, CH_3COO), 2.11–2.17 (m, 1 H, 3a-H), 2.35–2.42 (m, 1 H, 6-H), 2.55 (dt, J = 0.9 Hz, J = 8.7 Hz, 1 H, 6a-H), 3.56 [dd, J = 6.9 Hz, J = 10.6 Hz, 1 H, (C-4)CH_a], 3.69 [dd, J = 5.6 Hz, J = 10.6 Hz, 1 H, (C-4)CH_b], 4.07 [dd, J = 6.9 Hz, J = 10.8 Hz, 1 H, (C-6)CH_a], 4.14 [dd, J = 5.9 Hz, J = 10.8 Hz, 1 H, (C-6)CH_b] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9, 14.0 (C-4′, C-4′′), 20.9 (CH$_3$COO), 22.8, 23.0 (C-3′, C-3′′), 29.0, 29.3, 29.5 (C-1′, C-2′, C-2′′), 34.1 (C-5), 35.1 (C-1′′), 40.3 (C-6), 44.6 (C-3), 48.0, 48.3 (C-3a, C-4), 54.8, 55.2 (C-2, C-6a), 65.7, 67.0 (CH$_2$OOC, CH$_2$OH), 171.1 (COO) ppm. FT-IR (ATR): $\tilde{\nu}$ = 3441 cm^{-1} (m), 2955 (s), 2926 (s), 2858 (s), 1732 (vs), 1465 (m), 1366 (s), 1237 (vs), 1035 (s), 904 (s), 727 (s), 649 (m) cm^{-1}. GC-MS (EI): m/z (%) = 338.5 (2) [M$^+$], 278.2 (10), 225.1 (100), 203.1 (10), 183.1 (46), 165.0 (29), 147.0 (12), 132.9 (5), 119.1 (7), 105.0 (8), 91.0 (14), 79.0 (19), 67.0 (15), 55.0 (30). HRMS (EI): calcd. for $C_{20}H_{34}O_4$ 338.2457, found 338.2436 [M$^+$].

5e: t_R = 11.66 min. GC-MS (EI): m/z (%) = 281.1 (8) [(M – C$_4$H$_9$)$^+$], 225.1 (100), 183.1 (5), 165.0 (14), 147.0 (15), 137.0 (4), 118.9 (7), 90.9 (7), 79.0 (14), 67.0 (8), 54.9 (19). HRMS (EI): calcd. for $C_{20}H_{34}O_4$ 338.2457, found 338.2436 [M$^+$].

4f: Yield: 80.1 mg, 74%, colorless oil; R_f = 0.32; t_R = 12.99 min. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.77 (t, J = 6.9 Hz, 3 H, 4′-H), 0.99–1.46 (m, 6 H, 1′-H$_a$, 2′-H, 3′-H, 5-H$_a$), 1.49–1.65 (m, 1 H, 1′-H$_b$), 2.04–2.24 (m, 5 H, 4-H, 5-H$_b$, CH_3COO), 2.32–2.46 (m, 1 H, 6-H), 2.48–2.62 (m, 2 H, 2-H, 3a-H), 2.65–2.80 (m, 2 H, 3-H, 6a-H), 3.35 [d, J = 6.3 Hz, 2 H, (C-4)CH_2], 4.11 [dd, J = 7.0 Hz, J = 11.0 Hz, 1 H, (C-6)CH_a], 4.30 [dd, J = 5.2 Hz, J = 11.0 Hz, 1 H, (C-6)CH_b], 7.22–7.39 (m, 5 H, 2′′-H, 3′′-H, 4′′-H, 5′′-H, 6′′-H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 13.7 (C-4′), 20.9 (CH$_3$COO), 22.6 (C-3′), 27.3 (C-2′), 28.7 (C-1′), 34.5 (C-5), 40.9 (C-6), 47.5 (C-4), 51.5 (C-3a), 54.2, 54.3 (C-3, C-6a), 58.2 (C-2), 66.1, 66.5 (CH$_2$OOC, CH$_2$OH), 127.1 (C-4′′), 127.4, 128.8 (C-2′′, C-3′′, C-5′′, C-6′′), 142.1 (C-1′′), 171.1 (COO), 217.6 (C-1) ppm. FT-IR (ATR): $\tilde{\nu}$ = 3433 cm^{-1} (m), 2954 (s), 2928 (s), 2859 (s), 1730 (vs), 1495 (m), 1454 (m), 1366 (s), 1236 (vs), 1156 (m), 1074 (m), 1033 (s), 967 (m), 905 (s), 760 (s), 727 (s), 701 (vs), 648 (m) cm^{-1}. GC-MS (EI): m/z (%) = 358.3 (6) [M$^+$], 298.2 (45), 242.1 (30), 224.2 (14), 211.1 (16), 183.1 (20), 160.1 (18), 131.0 (23), 117.0 (64), 104.0 (64), 91.0 (100), 79.0 (30), 67.0 (11), 54.9 (26). HRMS (EI, CH$_4$): calcd. for $C_{22}H_{30}O_4$ 358.2144, found 358.2144 [M$^+$].

5f: t_R = 12.87 min. GC-MS (EI): m/z (%) = 358.3 (8) [M$^+$], 301.1 (76), 242.1 (64), 201.1 (25), 183.2 (16), 158.0 (33), 141.0 (14), 117.0 (84), 104.0 (67), 91.0 (100), 79.0 (38), 67.0 (19), 55.0 (43). HRMS (EI, CH$_4$): calcd. for $C_{22}H_{30}O_4$ 358.2144, found 358.2144 [M$^+$].

4g: Yield: 14.9 mg, 36%, colorless oil; R_f = 0.37; t_R = 11.19 min. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.9 Hz, 3 H, 5′-H), 1.17 [d, J = 6.6 Hz, 3 H, (C-3)CH_3], 1.20–1.35 (m, 6 H, 2′-H$_a$, 3′-H, 4′-H, 5-H$_a$), 1.36–1.51 (m, 2 H, 1′-H$_a$, 2′-H$_b$), 1.54–1.69 (m, 2 H, 1′-H$_b$, 3-H), 1.86–1.91 (m, 1 H, 3a-H), 2.01–2.16 (m, 6 H, CH_3COO, 2-H, 4-H, 5-H$_b$), 2.23–2.31 (m, 1 H, 6-H), 2.53 (t, J =

 © 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

8.7 Hz, 1 H, 6a-H), 3.55–3.63 [m, 2 H, (C-4)CH_2], 4.07 [dd, J = 7.1 Hz, J = 10.9 Hz, 1 H, (C-6)CH_a], 4.24 [dd, J = 5.2 Hz, J = 10.9 Hz, 1 H, (C-6)CH_b] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0 (C-5′), 19.0 [(C-3) CH$_3$], 20.9 (CH$_3$COO), 22.4 (C-4′), 26.5 (C-2′), 27.7 (C-1′), 32.1 (C-3′), 34.5 (C-5), 40.7 (C-6), 41.7 (C-3), 47.5 (C-4), 50.9 (C-2), 54.3 (C-6a), 57.9 (C-3a), 66.6, 66.7 (CH$_2$OOC, CH$_2$OH), 171.1 (COO) ppm. FT-IR (ATR): $\tilde{\nu}$ = 3448 cm^{-1} (m), 2953 (s), 2926 (s), 2859 (s), 1729 (vs), 1457 (m), 1366 (s), 1235 (vs), 1166 (m), 1035 (vs), 1034 (s), 907 (m), 727 (m), 647 (m), 606 (m) cm^{-1}. GC-MS (EI): m/z (%) = 310.3 (5) [M$^+$], 295.2 (8), 250.2 (22), 225.1 (100), 183.2 (30), 180.0 (22), 165.0 (35), 147.1 (26), 121.0 (10), 107.0 (14), 91.0 (21), 79.0 (32), 68.9 (36), 55.0 (34). HRMS (EI): calcd. for $C_{18}H_{30}O_4$ 310.2144, found 310.2127 [M$^+$].

5g: t_R = 11.11 min. GC-MS (EI): m/z (%) = 310.2 (6) [M$^+$], 295.2 (12), 240.1 (13), 225.1 (100), 180.1 (10), 165.0 (16), 147.0 (20), 119.0 (9), 105.0 (8), 93.0 (12), 79.0 (16), 68.9 (11), 55.0 (19). HRMS (EI): calcd. for $C_{18}H_{30}O_4$ 310.2144, found 310.2127 [M + H]$^+$.

4h: Yield: 126 mg, 82%, colorless oil; R_f = 0.35; t_R = 12.24 min. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.0 Hz, 3 H, 5′-H), 0.92 (t, J = 6.8 Hz, 3 H, 4′′-H), 1.18–1.57 (m, 14 H, 1′-H$_a$, 1′′-H, 2′-H, 2′′-H, 3′-H, 3′′-H, 4′-H, 5-H$_a$), 1.58–1.66 (m, 1 H, 1′-H$_b$), 1.68–1.74 (m, 1 H, 3-H), 1.89–1.96 (m, 1 H, 4-H), 1.98–2.03 (m, 1 H, 2-H), 2.05–2.10 (m, 4 H, 5-H$_b$, CH_3COO), 2.11–2.17 (m, 1 H, 3a-H), 2.34–2.41 (m, 1 H, 6-H), 2.55 (dt, J = 0.9 Hz, J = 8.5 Hz, 1 H, 6a-H), 3.56 [dd, J = 6.9 Hz, J = 10.5 Hz, 1 H, (C-4)CH_a], 3.69 [dd, J = 5.6 Hz, J = 10.5 Hz, 1 H, (C-4)CH_b], 4.07 [dd, J = 6.9 Hz, J = 10.8 Hz, 1 H, (C-6)CH_a], 4.14 [dd, J = 5.9 Hz, J = 10.8 Hz, 1 H, (C-6)CH_b] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9 (C-4′′, C-5′), 20.9 (CH$_3$COO), 22.4, 22.9 (C-3′′, C-4′), 26.8, 28.9, 29.8 (C-1′, C-2′, C-2′′), 31.9 (C-3′), 34.0 (C-5), 35.0 (C-1′′), 40.3 (C-6), 44.6 (C-3), 48.0, 48.2 (C-3a, C-4), 54.7, 55.2 (C-2, C-6a), 65.6, 67.0 (CH$_2$OOC, CH$_2$OH), 171.2 (COO) ppm. FT-IR (ATR): $\tilde{\nu}$ = 3437 cm^{-1} (m), 2955 (s), 2926 (s), 2858 (s), 1728 (vs), 1465 (m), 1367 (s), 1238 (vs), 1035 (s), 905 (vs), 728 (vs), 648 (m) cm^{-1}. GC-MS (EI): m/z (%) = 295.4 (12) [(M – C_4H_9)$^+$], 253.2 (14), 225.1 (100), 204.2 (12), 183.1 (43), 165.1 (39), 147.1 (6), 136.9 (7), 116.9 (8), 107.0 (11), 93.0 (20), 78.9 (20), 67.0 (14), 55.0 (24). HRMS (EI): calcd. for $C_{21}H_{36}O_4$ 352.2614, found 352.2613 [M$^+$].

5h: t_R = 12.09 min. GC-MS (EI): m/z (%) = 295.1 (11) [(M – C_4H_9)$^+$], 225.1 (100), 183.0 (6), 165.0 (7), 146.9 (15), 118.9 (5), 105.0 (7), 90.9 (11), 79.0 (10), 67.0 (7), 54.9 (16). HRMS (EI): calcd. for $C_{21}H_{36}O_4$ 352.2614, found 352.2613 [M$^+$].

4i: Yield: 59.0 mg, 83%, colorless oil; R_f = 0.32; t_R = 13.41 min. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.78 (t, J = 6.7 Hz, 3 H, 5′-H), 0.99–1.44 (m, 8 H, 1′-H$_a$, 2′-H, 3′-H, 4′-H, 5-H$_a$), 1.49–1.63 (m, 1 H, 1′-H$_b$), 2.00–2.24 (m, 5 H, 4-H, 5-H$_b$, CH_3COO), 2.32–2.46 (m, 1 H, 6-H), 2.47–2.63 (m, 2 H, 2-H, 3a-H), 2.64–2.80 (m, 2 H, 3-H, 6a-H), 3.34 [d, J = 6.2 Hz, 2 H, (C-4)CH_2], 4.11 [dd, J = 7.0 Hz, J = 11.0 Hz, 1 H, (C-6)CH_a], 4.30 [dd, J = 5.2 Hz, J = 11.0 Hz, 1 H, (C-6)CH_b], 7.21–7.39 (m, 5 H, 2′′-H, 3′′-H, 4′′-H, 5′′-H, 6′′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.8 (C-5′), 20.8 (CH$_3$COO), 22.2 (C-4′), 26.2 (C-2′), 27.6 (C-1′), 31.7 (C-3′), 34.5 (C-5), 40.8 (C-6), 47.5 (C-4), 51.4 (C-3a), 54.2, 54.3 (C-3, C-6a), 58.3 (C-2), 66.0, 66.5 (CH$_2$OOC, CH$_2$OH), 127.1 (C-4′′), 127.4, 128.8 (C-2′′, C-3′′, C-5′′, C-6′′), 142.2 (C-1′′), 171.1 (COO), 217.6 (C-1) ppm. FT-IR (ATR): $\tilde{\nu}$ = 3444 cm^{-1} (m), 2926 (s), 2858 (s), 1730 (vs), 1495 (m), 1454 (m), 1366 (s), 1237 (vs), 1155 (m), 1075 (m), 1033 (s), 966 (m), 906 (s), 760 (s), 727 (s), 700 (vs), 647 (m) cm^{-1}. GC-MS (EI): m/z (%) = 372.2 (8) [M$^+$], 312.2 (34), 302.2 (22), 281.2 (20), 242.1 (35), 224.0 (25), 211.1 (14), 201.1 (34), 181.1 (19), 158.0 (16), 141.0 (14), 130.9 (28), 116.9 (68), 104.0 (65), 91.0 (100), 79.0 (37), 67.0 (11), 55.0 (26). HRMS (EI, CH_4): calcd. for $C_{23}H_{32}O_4$ 372.2301, found 372.2299 [M$^+$].

5i: t_R = 13.30 min. GC-MS (EI): m/z (%) = 372.3 (10) [M$^+$], 312.3 (18), 301.1 (63), 282.0 (10), 271.3 (13), 242.0 (84), 224.2 (12), 211.2 (12), 201.1 (30), 183.1 (19), 158.0 (30), 141.0 (18), 130.9 (24), 117.0 (59), 104.0 (74), 91.0 (100), 78.9 (29), 67.0 (24), 55.0 (34). HRMS (EI, CH_4): calcd. for $C_{23}H_{32}O_4$ 372.2301, found 372.2299 [M$^+$].

4j: Yield: 48.2 mg, 49%, colorless oil; R_f = 0.38; t_R = 11.72 min. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 3 H, 6′-H), 1.17 [d, J = 6.5 Hz, 3 H, (C-3)CH_3], 1.20–1.36 (m, 8 H, 2′-H$_a$, 3′-H, 4′-H, 5′-H, 5-H$_a$), 1.35–1.50 (m, 2 H, 1′-H$_a$, 2′-H$_b$), 1.55–1.68 (m, 2 H, 1′-H$_b$, 3-H), 1.89 (dtd, J = 1.4 Hz, J = 5.7 Hz, J = 6.8 Hz, 1 H, 3a-H), 2.01–2.16 (m, 6 H, CH_3COO, 2-H, 4-H, 5-H$_b$), 2.23–2.31 (m, 1 H, 6-H), 2.53 (t, J = 8.7 Hz, 1 H, 6a-H), 3.55–3.63 [m, 2 H, (C-4)CH_2], 4.06 [dd, J = 7.2 Hz, J = 11.0 Hz, 1 H, (C-6)CH_a], 4.23 [dd, J = 5.2 Hz, J = 10.9 Hz, 1 H, (C-6)CH_b] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0 (C-6′), 19.0 [(C-3) CH$_3$], 20.9 (CH$_3$COO), 22.5 (C-5′), 26.8 (C-2′), 27.7 (C-1′), 29.5 (C-4′), 31.6 (C-3′), 34.5 (C-5), 40.7 (C-6), 41.7 (C-3), 47.5 (C-2), 50.9 (C-4), 54.3 (C-6a), 57.9 (C-3a), 66.5, 66.6 (CH$_2$OOC, CH$_2$OH), 171.1 (COO) ppm. FT-IR (ATR): $\tilde{\nu}$ = 3459 cm^{-1} (m), 2953 (s), 2925 (s), 2856 (s), 1730 (vs), 1457 (m), 1366 (s), 1236 (vs), 1165 (m), 1035 (vs), 907 (s), 728 (s), 648 (m), 606 (m) cm^{-1}. GC-MS (EI): m/z (%) = 324.3 (5) [M$^+$], 309.2 (11), 264.3 (19), 240.1 (14), 225.1 (100), 207.0 (15), 183.0 (42), 165.0 (32), 149.0 (24), 119.1 (7), 105.0 (16), 93.0 (22), 78.9 (31), 68.9 (27), 55.0 (34). HRMS (EI): calcd. for $C_{19}H_{32}O_4$ 324.2301, found 324.2279 [M$^+$].

5j: t_R = 11.64 min. GC-MS (EI): m/z (%) = 324.2 (4) [M$^+$], 309.2 (16), 240.1 (11), 225.1 (100), 207.0 (9), 180.1 (12), 165.0 (16), 147.0 (17), 119.0 (8), 105.0 (10), 93.0 (12), 79.0 (19), 69.0 (11), 55.0 (21). HRMS (EI): calcd. for $C_{19}H_{32}O_4$ 324.2301, found 324.2279 [M$^+$].

4k: Yield: 177 mg, 68%, colorless oil; R_f = 0.37; t_R = 12.69 min. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.8 Hz, 3 H, 6′-H), 0.92 (t, J = 6.8 Hz, 3 H, 4′′-H), 1.20–1.56 (m, 16 H, 1′-H$_a$, 1′′-H, 2′-H, 2′′-H, 3′-H, 3′′-H, 4′-H, 5-H$_a$, 5′-H), 1.59–1.66 (m, 1 H, 1′-H$_b$), 1.68–1.74 (m, 1 H, 3-H), 1.89–1.95 (m, 1 H, 4-H), 1.98–2.03 (m, 1 H, 2-H), 2.04–2.10 (m, 4 H, 5-H$_b$, CH_3COO), 2.11–2.18 (m, 1 H, 3a-H), 2.35–2.42 (m, 1 H, 6-H), 2.55 (dt, J = 0.9 Hz, J = 8.1 Hz, 1 H, 6a-H), 3.56 [dd, J = 6.9 Hz, J = 10.5 Hz, 1 H, (C-4)CH_a], 3.69 [dd, J = 5.5 Hz, J = 10.5 Hz, 1 H, (C-4)CH_b], 4.07 [dd, J = 6.9 Hz, J = 10.9 Hz, 1 H, (C-6)CH_a], 4.14 [dd, J = 5.9 Hz, J = 10.9 Hz, 1 H, (C-6)CH_b] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0 (C-4′′, C-6′), 20.9 (CH$_3$COO), 22.5, 23.0 (C-3′′, C-5′), 27.1, 28.9, 29.4, 29.8 (C-1′, C-2′, C-2′′, C-4′), 31.6 (C-3′), 34.0 (C-5), 35.1 (C-1′′), 40.3 (C-6), 44.6 (C-3), 48.0, 48.3 (C-3a, C-4), 54.7, 55.2 (C-2, C-6a), 65.7, 67.0 (CH$_2$OOC, CH$_2$OH), 171.1 (COO), 220.4 (C-1) ppm. FT-IR (ATR): $\tilde{\nu}$ = 3451 cm^{-1} (m), 2955 (s), 2925 (s), 2856 (s), 1729 (vs), 1458 (m), 1366 (s), 1236 (vs), 1035 (s), 970 (m), 911 (m), 730 (s), 647 (m) cm^{-1}. GC-MS (EI): m/z (%) = 366.5 (2) [M$^+$], 309.2 (14), 267.3 (10), 225.1 (100), 204.2 (4), 183.1 (41), 165.1 (24), 147.1 (9), 132.9 (4), 119.0 (6), 105.0 (8), 91.0 (12), 79.0 (16), 67.0 (12), 55.0 (24). HRMS (EI): calcd. for $C_{22}H_{38}O_4$ 366.2770, found 366.2762 [M$^+$].

5k: t_R = 12.56 min. GC-MS (EI): m/z (%) = 309.2 (13) [(M – C_4H_9)$^+$], 225.1 (100), 165.0 (10), 147.0 (11), 119.1 (5), 105.0 (5), 93.0 (7), 79.0 (7), 69.0 (4), 55.0 (14). HRMS (EI): calcd. for $C_{22}H_{38}O_4$ 366.2770, found 366.2762 [M$^+$].

4l: Yield: 106 mg, 81%, colorless oil; R_f = 0.28; t_R = 13.84 min. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.81 (t, J = 7.1 Hz, 3 H, 6′-H), 1.01–1.41 (m, 10 H, 1′-H$_a$, 2′-H, 3′-H, 4′-H, 5′-H, 5-H$_a$), 1.52–1.60 (m, 1 H, 1′-H$_b$), 2.05–2.21 (m, 5 H, 4-H, 5-H$_b$, CH_3COO), 2.36–2.44

 © 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

(m, 1 H, 6-H), 2.51–2.60 (m, 2 H, 2-H, 3a-H), 2.69 (dd, J = 9.4 Hz, J = 12.1 Hz, 1 H, 3-H), 2.74 (t, J = 9.3 Hz, 1 H, 6a-H), 3.35 [d, J = 6.4 Hz, 1 H, (C-4)CH_2], 4.11 [dd, J = 7.0 Hz, J = 10.9 Hz, 1 H, (C-6)CH_a], 4.30 [dd, J = 5.2 Hz, J = 11.0 Hz, 1 H, (C-6)CH_b], 7.24–7.37 (m, 5 H, 2′′-H, 3′′-H, 4′′-H, 5′′-H, 6′′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9 (C-6′), 20.9 (*C*H$_3$COO), 22.4 (C-5′), 26.5 (C-2′), 27.7 (C-1′), 29.2 (C-4′), 31.4 (C-3′), 34.5 (C-5), 40.9 (C-6), 47.5 (C-4), 51.5 (C-3a), 54.2, 54.3 (C-3, C-6a), 58.3 (C-2), 66.1, 66.5 (*C*H$_2$OOC, *C*H$_2$OH), 127.0 (C-4′′), 127.4, 128.8 (C-2′′, C-3′′, C-5′′, C-6′′), 142.2 (C-1′′), 171.1 (*C*OO), 217.6 (C-1) ppm. FT-IR (ATR): $\tilde{\nu}$ = 3442 cm^{-1} (m), 2925 (s), 2856 (s), 1730 (vs), 1495 (m), 1454 (m), 1366 (s), 1238 (vs), 1156 (m), 1033 (s), 969 (m), 905 (s), 760 (s), 725 (s), 700 (vs), 648 (m) cm^{-1}. GC-MS (EI): *m*/*z* (%) = 386.2 (12) [M$^+$], 344.2 (4), 326.3 (32), 302.2 (33), 259.3 (13), 242.1 (36), 224.2 (21), 215.2 (24), 211.1 (24), 195.1 (11), 183.0 (20), 158.0 (18), 131.0 (32), 116.9 (73), 104.0 (82), 91.0 (100), 79.0 (34), 67.0 (14), 55.0 (34). HRMS (EI, CH_4): calcd. for $C_{24}H_{34}O_4$ 386.2457, found 386.2452 [M$^+$].

5l: t_R = 13.73 min. GC-MS (EI): *m*/*z* (%) = 386.5 (11) [M$^+$], 326.3 (15), 315.4 (11), 301.2 (61), 242.1 (68), 211.1 (16), 201.1 (36), 183.0 (21), 165.0 (14), 158.1 (22), 141.0 (14), 129.1 (18), 116.9 (61), 103.9 (74), 91.0 (100), 79.0 (26), 69.0 (12), 55.0 (25). HRMS (EI, CH_4): calcd. for $C_{24}H_{34}O_4$ 386.2457, found 386.2452 [M$^+$].

4m: Yield: 8.52 mg, 49%, colorless oil; R_f = 0.25; t_R = 12.37 min. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.14 (d, J = 6.4 Hz, 3 H, CH_3), 1.52–1.62 (m, 1 H, 5-H$_a$), 2.17 (s, 3 H, CH_3COO), 2.19–2.28 (m, 3 H, 3-H, 4-H, 5-H$_b$), 2.35 (t, J = 7.4 Hz, 1 H, 3a-H), 2.44–2.51 (m, 1 H, 6-H), 2.71 (t, J = 9.7 Hz, 1 H, 6a-H), 3.11 (d, J = 12.6 Hz, 1 H, 2-H), 3.40 [dd, J = 7.7 Hz, J = 10.9 Hz, 1 H, (C-4)CH_a], 3.62–3.66 [m, 1 H, (C-4)CH_b], 4.13 [dd, J = 7.3 Hz, J = 10.9 Hz, 1 H, (C-6)CH_a], 4.32 [dd, J = 5.1 Hz, J = 10.9 Hz, 1 H, (C-6)CH_b], 7.04–7.36 (m, 5 H, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.8 (*C*H$_3$), 20.9 (*C*H$_3$COO), 34.6 (C-5), 41.0 (C-6), 45.5 (C-3), 47.2 (C-4), 50.8 (C-3a), 54.6 (C-6a), 65.8 (C-2), 66.4, 66.6 (*C*H$_2$OOC, *C*H$_2$OH), 127.0 (C-4′), 128.6, 128.7 (C-2′, C-3′, C-5′, C-6′), 136.9 (C-1′), 171.1 (*C*OO), 215.9 (C-1) ppm. FT-IR (ATR): $\tilde{\nu}$ = 3453 cm^{-1} (m), 2955 (s), 2924 (s), 2855 (m), 1736 (vs), 1454 (m), 1376 (s), 1259 (s), 1244 (s), 1125 (m), 1032 (s), 843 (m), 801 (s), 755 (m), 700 (s) cm^{-1}. GC-MS (EI): *m*/*z* (%) = 316.3 (5) [M$^+$], 256.2 (61), 225.2 (32), 209.0 (7), 155.0 (8), 147.1 (11), 118.0 (100), 105.1 (15), 91.0 (44), 79.0 (24), 67.0 (12). HRMS (EI): calcd. for $C_{19}H_{24}O_4$ 316.1675, found 316.1674 [M$^+$].

5m: t_R = 12.29 min. GC-MS (EI): *m*/*z* (%) = 316.2 (42) [M$^+$], 301.1 (7), 258.3 (6), 238.2 (11), 225.2 (12), 197.3 (12), 173.1 (24), 154.9 (17), 143.1 (11), 118.0 (100), 105.1 (26), 91.0 (71), 79.0 (28), 67.0 (12), 55.0 (9). HRMS (EI): calcd. for $C_{19}H_{24}O_4$ 316.1675, found 316.1674 [M$^+$].

4n: Yield: 19.5 mg, 32%, colorless oil; R_f = 0.23; t_R = 13.28 min. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.80 (t, J = 6.7 Hz, 3 H, 4′′-H), 1.09–1.40 (m, 6 H, 1′′-H$_a$, 2′′-H, 3′′-H), 1.56 (dd, J = 7.2 Hz, J = 13.7 Hz, 2 H, 1′′-H$_b$), 2.06 (s, 3 H, CH_3COO), 2.07–2.24 (m, 3 H, 3-H, 4-H, 5-H$_b$), 2.33 (dt, J = 4.1 Hz, J = 9.1 Hz, 1 H, 3a-H), 2.45–2.56 (m, 1 H, 6-H), 2.71 (t, J = 9.1 Hz, 1 H, 6a-H), 3.23 (d, J = 11.2 Hz, 1 H, 2-H), 3.60 [dd, J = 6.5 Hz, J = 10.5 Hz, 1 H, (C-4)CH_a], 3.67 [dd, J = 5.9 Hz, J = 10.5 Hz, 1 H, (C-4)CH_b], 4.12 [dd, J = 7.1 Hz, J = 10.9 Hz, 1 H, (C-6)CH_a], 4.25 [dd, J = 5.5 Hz, J = 10.9 Hz, 1 H, (C-6)CH_b], 7.05–7.35 (m, 5 H, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.8 (C-4′′), 20.9 (*C*H$_3$COO), 22.8 (C-3′′), 28.6 (C-2′′), 33.5 (C-1′′), 34.3 (C-5), 40.8 (C-6), 47.6, 48.2, 48.9 (C-3, C-3a, C-4), 54.8 (C-6a), 63.6 (C-2), 66.1, 66.6 (*C*H$_2$OOC, *C*H$_2$OH), 126.9 (C-4′), 128.6, 128.8 (C-2′, C-3′, C-5′, C-6′), 137.9 (C-1′), 171.1 (*C*OO), 216.5 (C-1) ppm. FT-IR (ATR): $\tilde{\nu}$ = 3440 cm^{-1} (m), 3028 (m), 2954 (s), 2925 (s), 2858 (s), 1732 (vs), 1496 (m), 1453 (m), 1366 (s), 1237 (vs), 1033 (s), 971 (m), 905 (s), 755 (m), 729 (s), 699 (vs), 648 (m) cm^{-1}. GC-MS (EI): *m*/*z* (%) = 358.4 (3) [M$^+$], 298.3 (88), 267.1 (27), 223.2 (22), 189.1 (28), 160.1 (68), 118.0 (91), 104.0 (72), 91.0 (100), 79.0 (33), 67.0 (16). HRMS (CI, CH_4): calcd. for $C_{22}H_{30}O_4$ 358.2144, found 358.2144 [M$^+$].

5n: t_R = 13.13 min. GC-MS (EI): *m*/*z* (%) = 358.0 (36) [M$^+$], 301.2 (15), 267.1 (12), 215.2 (21), 160.0 (35), 149.0 (25), 117.0 (100), 103.9 (62), 90.9 (97), 79.0 (26), 67.0 (16). HRMS (CI, CH_4): calcd. for $C_{22}H_{30}O_4$ 358.2144, found 358.2144 [M$^+$].

4o: Yield: 156 mg, 79%, colorless oil; R_f = 0.22; t_R = 14.53 min. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.42 (ddd, J = 8.0 Hz, J = 10.3 Hz, J = 12.5 Hz, 1 H, 5-H$_a$), 2.08 (s, 3 H, CH_3COO), 2.16–2.24 (m, 1 H, 4-H), 2.27 (td, J = 7.3 Hz, J = 12.5 Hz, 1 H, 5-H$_b$), 2.57–2.65 (m, 1 H, 6-H), 2.82 (dt, J = 3.7 Hz, J = 9.9 Hz, 1 H, 3a-H), 2.91 (t, J = 9.6 Hz, 1 H, 6a-H), 3.13 (dd, J = 9.9 Hz, J = 12.7 Hz, 1 H, 3-H), 3.39 [d, J = 6.3 Hz, 2 H, (C-4)CH_2], 3.73 (dd, J = 0.7 Hz, J = 12.7 Hz, 1 H, 2-H), 4.17 [dd, J = 7.0 Hz, J = 11.0 Hz, 1 H, (C-6)CH_a], 4.36 [dd, J = 5.2 Hz, J = 11.0 Hz, 1 H, (C-6)CH_b], 6.93–7.30 (m, 10 H, 2′-H, 2′′-H, 3′-H, 3′′-H, 4′-H, 4′′-H, 5′-H, 5′′-H, 6′-H, 6′′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.9 (*C*H$_3$COO), 34.4 (C-5), 41.0 (C-6), 47.2 (C-4), 50.7 (C-3a), 54.6 (C-6a), 56.7 (C-3), 65.4 (C-2), 66.0, 66.3 (*C*H$_2$OOC, *C*H$_2$OH), 127.0, 127.1 (C-4′, C-4′′), 127.5, 128.5, 128.6, 128.8 (C-2′, C-2′′, C-3′, C-3′′, C-5′, C-5′′, C-6′, C-6′′), 136.2 (C-1′′), 140.5 (C-1′), 171.1 (*C*OO), 214.8 (C-1) ppm. FT-IR (ATR): $\tilde{\nu}$ = 3443 cm^{-1} (m), 2920 (m), 2891 (m), 1730 (vs), 1602 (m), 1496 (m), 1452 (m), 1386 (m), 1366 (s), 1236 (vs), 1153 (m), 1135 (m), 1074 (m), 1032 (s), 969 (m), 912 (m), 761 (s), 755 (s), 732 (m), 698 (vs), 645 (m), 606 (m) cm^{-1}. GC-MS (EI): *m*/*z* (%) = 378.2 (32) [M$^+$], 318.1 (4), 281.2 (16), 209.1 (12), 179.1 (40), 165.0 (26), 155.1 (13), 118.0 (100), 105.0 (13), 91.0 (43), 79.0 (20), 67.0 (8), 55.1 (3). HRMS (EI, CH_4): calcd. for $C_{24}H_{26}O_4$ 378.1831, found 378.1826 [M$^+$].

5o: t_R = 14.40 min. GC-MS (EI): *m*/*z* (%) = 378.1 (38) [M$^+$], 336.1 (6), 318.3 (5), 281.0 (14), 259.1 (10), 179.1 (48), 165.0 (22), 155.0 (9), 128.9 (10), 117.9 (100), 104.9 (32), 91.0 (43), 78.9 (10). HRMS (EI, CH_4): calcd. for $C_{24}H_{26}O_4$ 378.1831, found 378.1826 [M$^+$].

Supporting Information (see footnote on the first page of this article): Protection of the keto group in some derivatives **9** by using trimethyl orthoformate and Amberlyst-15 to give surprisingly enol ethers instead of *O* protection as well as the assignment of acetates **4** and **5** by NMR experiments.

Acknowledgments

Generous financial support by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the Ministerium für Wissenschaft, Forschung und Kunst des Landes Baden-Württemberg and the Deutsche Akademische Austauschdienst (DAAD award for A. Becheanu) is gratefully acknowledged.

[1] Reviews on pentalene syntheses: a) R. Haag, A. de Meijere, *Top. Curr. Chem.* **1998**, *196*, 137–165; b) U. R. Ghatak, *Proc. Ind. Nat. Sci. Acad. A* **1995**, *61*, 21–36; c) E. Negishi, *Pure Appl. Chem.* **1992**, *64*, 323–334; d) T. Hudlicky, G. Sinai-Zingde, M. G. Natchus, B. C. Ranu, P. Papadopolous, *Tetrahedron* **1987**, *43*, 5685–5721; e) M. Demuth, *Modern Synthetic Methods* **1986**, vol. 4, pp. 89–124; f) S. V. Ley, *Chem. Ind.* **1985**, 101–106.

[2] Reviews on polyquinanes: a) G. Mehta, A. Srikrishna, *Chem. Rev.* **1997**, *97*, 671–719; b) L. A. Paquette, *Top. Curr. Chem.*

 © 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

1984, *119*, 1–160; c) M. Ramaiah, *Synthesis* **1984**, 529–570; d) B. M. Trost, *Chem. Soc. Rev.* **1982**, *11*, 141–170; e) L. A. Paquette, *Top. Curr. Chem.* **1979**, *79*, 41–165.
[3] Triquinane synthesis: S. U. Son, K. H. Park, S. J. Lee, B. M. Kim, Y. K. Chung, *Synlett* **2003**, 1101–1104.
[4] a) N. M. Harrington-Frost, G. Pattenden, *Tetrahedron Lett.* **2000**, *41*, 403–405; b) P. Devin, L. Fensterbank, M. Malacria, *J. Org. Chem.* **1998**, *63*, 6764–6765; c) C.-K. Sha, K. C. Santhosh, S.-H. Lih, *J. Org. Chem.* **1998**, *63*, 2699–2704; d) E. J. Enholm, Z. J. Jia, *J. Org. Chem.* **1997**, *62*, 174–181; e) C. P. Jasperse, D. P. Curran, T. L. Fevig, *Chem. Rev.* **1991**, *91*, 1237–1286.
[5] a) J.-L. Renaud, C. Aubert, M. Malacria, *Tetrahedron* **1999**, *55*, 5113–5128; b) J. Seo, H. Fain, J.-B. Blanc, J. Montgomery, *J. Org. Chem.* **1999**, *64*, 6060–6065; c) J. Tormo, A. Moyano, M. A. Pericas, A. Riera, *J. Org. Chem.* **1997**, *62*, 4851–4856; d) C. Meyer, I. Marek, J.-F. Normant, *Tetrahedron Lett.* **1996**, *37*, 857–860; e) J. Tormo, X. Verdaguer, A. Moyano, M. A. Pericas, A. Riera, *Tetrahedron* **1996**, *52*, 14021–14040; f) F. Saitoh, M. Mori, K. Okamura, T. Date, *Tetrahedron* **1995**, *51*, 4439–4446; g) E. Piers, A. Orellana, *Synthesis* **2001**, 2138–2142.
[6] G. Bahu, V. Sridar, *Ind. J. Chem. B* **1996**, *35*, 711–712.
[7] a) L. V. R. Bonaga, M. E. Krafft, *Tetrahedron* **2004**, *60*, 9795–9833; b) S. E. Gibson, A. Stevenazzi, *Angew. Chem.* **2003**, *115*, 1844–1854; *Angew. Chem. Int. Ed.* **2003**, *42*, 1800–1810; c) B. E. Hanson, *Comments Inorg. Chem.* **2002**, *23*, 289–318; d) K. M. Brummond, J. L. Kent, *Tetrahedron* **2000**, *56*, 3263–3283; e) A. J. Fletcher, S. D. R. Christie, *J. Chem. Soc., Perkin Trans. 1* **2000**, 1657–1668; f) Y. K. Chung, *Coord. Chem. Rev.* **1999**, *188*, 297–341.
[8] a) J. W. Kim, Y. K. Chung, *Synthesis* **1998**, 142–144; b) S. U. Son, S. I. Lee, Y. K. Chung, *Angew. Chem.* **2000**, *112*, 4318–4320; *Angew. Chem. Int. Ed.* **2000**, *39*, 4158–4160; c) S. E. Gibson, C. Johnstone, A. Stevenazzi, *Tetrahedron* **2002**, *58*, 4937–4942.
[9] a) B. Y. Lee, J. W. Han, Y. K. Chung, S. W. Lee, *J. Organomet. Chem.* **1999**, *587*, 181–190; b) N. E. Schore, *Synth. Commun.* **1979**, *9*, 41–47; c) S. U. Son, D. H. Kim, I. G. Jung, Y. K. Chung, S.-G. Lee, S.-H. Chun, *J. Polymer Sci. A* **2002**, *41*, 76–83; d) D. M. Shin, S. U. Son, B. K. Hong, Y. K. Chung, S.-H. Chun, *J. Mol. Catal. A* **2004**, *210*, 35–46; e) K. Hayakawa, H. Schmid, *Helv. Chim. Acta* **1977**, *60*, 2160–2170.
[10] The protection of the keto group with trimethyl orthoformate and Amberlyst-15 resulted in enol ether formation, for details see the Supporting Information.
[11] M. Lautens, J. Mancuso, *Org. Lett.* **2002**, *4*, 2105–2108.
[12] P. A. Wender, H. Kogen, H. Y. Lee, J. D. Munger, R. S. Wilhelm, P. D. Williams, *J. Am. Chem. Soc.* **1989**, *111*, 8957–8958.
[13] CCDC-292008 (for **11a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[14] P. F. Schuda, M. R. Heimann, *Tetrahedron* **1984**, *40*, 2365–2380.
[15] N. Cramer, S. Laschat, A. Baro, *Synlett* **2003**, 2178–2181.

Received: December 9, 2005
Published Online: March 3, 2006

 © 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim