Pergamon

Tetrahedron: Asymmetry Vol. 6, No. 6, pp. 1323-1344, 1995

0957-4166/95 $9.50+0.00

0957-4166(95)00166-2

Lipase-catalysed Resolution of 3-(Aryloxy)-1,2-propanediol Derivatives - Towards an Improved Active Site Model of *Pseudomonas cepacia* Lipase (Amano PS)

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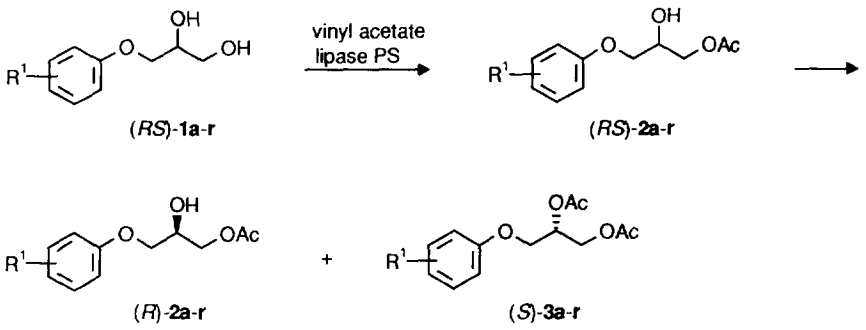
Abstract: A variety of 3-(aryloxy)-1,2-propanediol derivatives with different substituents on the aromatic ring or at the primary hydroxy group were used as substrates in a kinetic resolution by transesterification with vinyl acetate catalysed by lipase from *Pseudomonas cepacia* (Amano PS). Derivatives with substituents in the *para*-position of the aromatic ring were accepted as substrates and resolved with high enantioselectivity. The corresponding derivatives with substituents in the *ortho*-position were much worse substrates for lipase PS or even non-substrates if the substituent was sufficiently space-filling as found for the *tert*-butyl, phenyl, benzyl or benzoyl residue. Otherwise, if the primary hydroxy group was substituted by unbranched long-chain acyl residues very good substrates were resulting. In contrast, derivatives with sterically crowded residues at the primary hydroxy group such as the pivaloyl, *tert*-butyldimethylsilyl, methanesulfonyl, *para*-toluenesulfonyl or trityl groups were non-substrates for lipase PS.

Introduction

Lipase-catalysed kinetic resolutions or asymmetrisations have been established as a suitable approach in the synthesis of enantiomerically pure hydroxy compounds or the corresponding carboxylic ester derivatives.[1] We very recently have chosen acyclic racemic 1,2-diols as substrates for lipase-catalysed transesterifications in order to obtain enantiomerically pure compounds.[2] Particularly, 3-(aryloxy)-1,2-propanediols in enantiomerically pure form are of interest as pharmaceuticals, as intermediates in the synthesis of β-receptor blockers or for other synthetic purposes such as chiral ligands for transition metal complexes or building blocks for crown ethers.



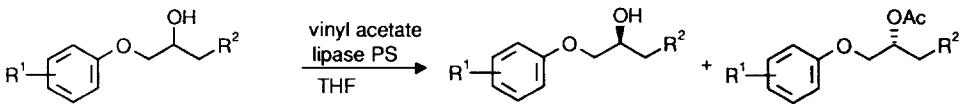
Scheme 1

1,2-Diols are acylated in the presence of lipase from *Pseudomonas cepacia* (Amano PS; formerly called lipase P from *Pseudomonas fluorescens*) in two sequential steps. In the first step the racemic 1,2-diols are acylated regioselectively at the primary hydroxy group without enantioselection. The subsequent acylation at the secondary hydroxy group of the formed racemic primary monoacetate is responsible for the high enantioselection. We found, the enantioselectivity of this transformation significantly depends on the substitution pattern of the aryl ring and the organic solvent used. 3-(Aryloxy)-1,2-propanediols with substituents in the *para*-position showed a much higher enantioselectivity than the corresponding derivatives with *ortho*-substituents.[2]

This behaviour was the starting-point for a broadly extended substrate-mapping in two directions: Further variation of the substitution pattern of the aryl ring and introduction of substituents at the primary hydroxy group. The aim of this investigation was to get more information on the structural requirements of the substrate regarding enantioselectivity and reactivity of the transesterification catalysed by lipase PS. Furthermore, it was of interest to discover non-substrates. In future, based on these results we hope to improve the existing active site models of lipase PS.[3] According to these models the active site of lipase PS contains three domains, the catalytic site and two hydrophobic pockets, realising the interaction with the substrate and its enantioselective conversion.

Results and Discussion

In order to investigate the influence of the substituents R^1 and R^2 all reactions were carried out under standard conditions using 7 equivalents of vinyl acetate, 100 mg of lipase PS and 2.5 ml of dry THF per mmol of substrate until *ca.* 50 % of the alcohol was converted into the corresponding acetate (Scheme 2). The products were separated and their enantiomeric excess (ee) was determined by HPLC on chiral phases.[4]



1. Series: R^2 = OAc, R^1 see Table 1

(*RS*)-**2a-r** (*R*)-**2a-r** (*S*)-**3a-r**

2. Series: R^1 = H, R^2 see Tables 2, 3 and 4

(*RS*)-**4a-x** (*R*)-**4a-v**, (*S*)-**4w**, **x** (*S*)-**5a-v**, (*R*)-**5w**, **x**

3. Series: R^1 = *tert*-Octyl, R^2 see Table 5

(*RS*)-**6a-i** (*S*)-**6a**, (*R*)-**6b-i** (*R*)-**7a**, (*S*)-**7b-i**

Scheme 2

In the first series R^2 was the acetoxy group, whereas R^1 were altered. In the second series R^1 was hydrogen and R^2 was varied. In the third series R^1 was the 4-*tert*-octyl residue and again R^2 was altered (Scheme 2).

The Influence of the Substituent R^1 at the Aryl Ring

These resolutions were performed using the sequential procedure starting from the corresponding racemic diols (*RS*)-**1a-r** as very recently described.[2] However, reactions were run without triethylamine as co-solvent. In this one-pot two-step procedure the substrates for the enantioselective acylation step are the corresponding racemic primary monoacetates (*RS*)-**2a-r**. Due to the significantly distinct behaviour regarding the enantioselectivity, compounds with substituents in *ortho*- or *para*-position of the aromatic ring were selected as substrates. A few examples of 2,4-disubstituted derivatives were included in these investigations. The results demonstrating the influence of the substituents at the aromatic ring are depicted in Table 1.

The results tabulated in Table 1 clearly indicate that substrates with substituents in the *para*-position of the aromatic ring are much better substrates than the corresponding *ortho*-derivatives as already found in our earlier investigations for several derivatives.[2] The compounds with spatially less demanding substituents in the *ortho*-position such as the methyl- and chloro derivatives **2b** and **2e** were accepted as substrates, however, with decreased enantioselectivity compared with their *para*-regioisomers **2c** and **2f**. On the other hand, compounds with more space-filling *ortho*-substituents, such as **1h**, **1l**, **1n** and **1p**, were smoothly converted into the corresponding racemic monoacetates **2h**, **2l**, **2n** and **2p**. However, the subsequent enantioselective reaction step at the chiral secondary hydroxy group, which leads to the enantioselection, was almost

completely suppressed. This is a distinct indication for a limited size of one of the pockets belonging to the active site of lipase PS. The influence of the simultaneous presence of two small substituents as realised in the 2,4-dimethyl- and 2,4-dichloroderivatives **1d** and **1g**, respectively, on the E value of the reaction is difficult to explain. On the other hand, the behaviour of the di-*tert*-butyl derivative **1j** was determined by the sterically crowded substituent in *ortho*-position that causes **2j** to be a non-substrate for lipase PS. Regarding the enantioselectivity of the crucial second reaction step, the derivatives **2i** and **2k** with the branched alkyl substituents in *para*-position were found to be the best ones.

Table 1: Kinetic Resolution of the Diols (*RS*)-**1a-r**

			Monoacetate (*R*)-**2**		Diacetate (*S*)-**3**			
Substrate	R^1	Time (h)	Yield (%)[a]	ee (%)	Yield (%)[a]	ee (%)	c[b]	E[b]
1a	H	53	51	92.9	49	97.6	0.49	>100 (281)
1b	2-Me	240	65	39.1	35	89.9	0.30	27
1c	4-Me	54	58	65.0	42	99.0	0.40	>100 (391)
1d	2,4-Me_2	264	61	68.0	39	95.0	0.42	80
1e	2-Cl	72	74	28.0	26	90.6	0.24	27
1f	4-Cl	72	62	57.2	38	98.8	0.37	>100 (296)
1g	2,4-Cl_2	96	28	40.2	72	90.4	0.31	29
1h	2-*t*-Bu[c]	100				no substrate		
1i	4-*t*-Bu[c]	100	47	99.1	49	98.4	0.50	>100 (671)
1j	2,4-*t*-Bu_2	168				no substrate		
1k	4-*t*-C_8H_{17}[d]	94	47	93.2	53	98.8	0.48	>100 (574)
1l	2-Ph	96				no substrate		
1m	4-Ph	99	56	73.8	44	91.8	0.44	52
1n	2-CO-Ph	96				no substrate		
1o	4-CO-Ph	96	61	62.6	39	98.6	0.39	>100 (270)
1p	2-CH_2-Ph	72				no substrate		
1q	4-CH_2-Ph	96	65	61.5	35	77.4	0.44	15
1r	4-OPh	144	55	61.8	45	86.4	0.42	26

[a] Determined by HPLC. [b] c = conversion, E = enantiomeric ratio. Determined according to Ref. 5a. [c] Ref. 2b. [d] *t*-C_8H_{17} = 1,1,3,3-tetramethylbutyl

Influence of the Substituents R^2 at the Primary Hydroxy Group

Whilst in the first series the substrates for the enantioselective step were the racemic primary monoacetates (*RS*)-**2a-r**, in the second series the phenoxy residue was unsubstituted but the primary hydroxy group was substituted in order to study the influence of the residue R^2 on the enantioselectivity of this transformation and the reactivity of the derivatives. The results with the substrates (*RS*)-**4a-k** with aliphatic unbranched acyl substituents R^2 are shown in Table 2.

Table 2: Kinetic Resolution of the Alcohols (*RS*) **4a-k**.

			Alcohol (*R*)-**4**		Acetate (*S*)-**5**			
Substrate	R^2	Time (h)	Yield (%)[a]	ee (%)	Yield (%)[a]	ee (%)	*c*	E
2a[b]	OCOMe	53	51	92.9	49	97.6	0.49	>100 (281)
4a	OCOEt	78	55	65.4	44	92.7	0.41	52
4b	OCO*n*-Pr	92	55	69.4	43	79.4	0.47	18
4c	OCO*n*-Bu	48	47	94.7	53	87.4	0.52	54
4d	OCO*n*-C_5H_{11}	73	55	67.1	43	98.2	0.41	>100 (223)
4e	OCO*n*-C_6H_{13}	144	43	86.6	57	80.0	0.52	25
4f	OCO*n*-C_7H_{15}	168	49	81.7	45	91.8	0.47	59
4g	OCO*n*-C_8H_{17}	168	72	28.4	24	91.1	0.24	28
4h	OCO*n*-C_9H_{19}	192	60	67.4	36	97.6	0.41	>100 (167)
4i	OCO*n*-$C_{11}H_{23}$	120	50	78.2	48	91.8	0.46	57
4j	OCO*n*-$C_{13}H_{27}$	120	40	95.1	60	74.2	0.56	25
4k	OCO*n*-$C_{15}H_{31}$	168	52	88.8	48	98.5	0.47	>100 (397)

[a] Isolated yield. [b] The diol (*RS*)-**1a** was used as substrate in a sequential acetylation.

As shown in Table 2, there is a significant influence of the length of the introduced acyl residue R^2 on the E value of the reaction. In this series, in which R^2 varies from acetyl to hexadecanoyl, there exist some optimal side chains regarding the enantioselectivity of the reaction. However, there is no general correlation between the enantioselectivity and the length of the acyl chain at the primary hydroxy group. The best selectivities have been calculated for the derivatives **2a**, **4d**, **4h**, and **4k** with the substituents R^2 bearing 2, 6, 10, and 16 carbon atoms, respectively. The acceptance and highly enantioselective transformation of the extremely long substrate

4k was surprising. An only moderate selectivity was observed for the tetradecanoate **4j** with E = 25 in contrast to the hexadecanoate **4k** with an E value > 100.

Considering the above described results, it can be concluded: If a given substrate exhibits poor or moderate enantioselectivity there is a real chance of increasing the enantioselectivity by substitution of the diol at the primary hydroxy group by a long chain acyl residue. However a long chain substituent is no prerequisite for high enantioselection as evidenced by comparison of the acetate **2a** and the hexadecanoate **4k**.

Table 3 depicts the results obtained in the lipase-catalysed enantioselective transesterification of the substrates (*RS*)-**4l-o** with branched aliphatic acyl residues R^2. A remarkable difference was observed for the reactivity of the isobutanoate **4l** and the pivaloate **4n**. Whilst the former derivative was a good substrate for lipase PS with high enantioselectivty (E = 78), the latter one was not accepted as a substrate in the lipase-catalysed transesterification by lipase PS. This is an evidence for the limited size of the third dimension of the second hydrophobic pocket in the active site of lipase PS. The *iso*-compounds **4m** and **4o** were less selectively resolved than the corresponding unbranched *n*-butanoate **4c** and the *n*-hexanoate **4d** (Table 2). Table 4 shows results with the further derivatives **4p-x**. The most remarkable results from Table 4 are that the *tert*-butyldimethylsilyl ether **4s**, the methanesulfonate **4t**, the *p*-toluenesulfonate **4u** and the tritylether **4v** are non-substrates, as well due to the size of the substituents at the primary hydroxy group. These findings are in accordance with the result for the pivaloate **4n** (Table 3). Surprisingly, the aminoalcohol **4x** was smoothly acylated but completely non-selective under the reaction conditions.

Table 3: Kinetic Resolution of the Alcohols (*RS*)-**4l-o**

			Alcohol (*R*)-**4**		Acetate (*S*)-**5**			
Substrate	R^2	Time (h)	Yield (%)[a]	ee (%)	Yield (%)[a]	ee (%)	*c*	E
4l	OCO*i*-Pr	100	58	51.8	42	95.8	0.35	78
4m	OCO*i*-Bu	96	61	32.4	39	84.4	0.28	16
4n	OCO*t*-Bu	192			no substrate			
4o	OCO*i*-C_5H_{11}	192	53	41.2	46	46.0	0.47	4

[a] Isolated yield

Table 4: Kinetic Resolution of the Alcohols (*RS*)-**4p-x**

Substrate	R^2	Time (h)	Alcohol (*R*)-**4**		Acetate (*S*)-**5**		*c*	E
			Yield (%)[a]	ee (%)	Yield (%)[a]	ee (%)		
4p	OCO*c*-C_6H_{11}	144	78	20.8	22	76.0	0.21	9
4q	OCOPh	162	78	19.4	17	95.2	0.17	47
4r	OCOBn	336	84	10.0	14	78.5	0.11	9
4s	OSi*t*-BuMe_2	192				no substrate		
4t	OSO_2Me	94				no substrate		
4u	OSO_2Tol	260				no substrate		
4v	$OCPh_3$	168				no substrate		
4w	N_3	172	58	67.6[b]	42	78.6[c]	0.46	17
4x	N(*i*-Pr_2)	168	40	0.9[d]	58	0.5[e]	0.54	1

[a] Isolated yield. [b] (*S*)-**4w**. [c] (*R*)-**5w**. [d] (*S*)-**4x**, [e] (*R*)-**5x**.

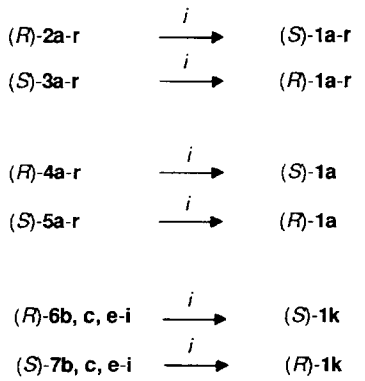
Table 5: Kinetic Resolution of the Alcohols (*RS*)-**6a-i**

Substrate	R^2	Time (h)	Alcohol (*R*)-**6**		Acetate (*S*)-**7**		*c*	E
			Yield (%)[a]	ee (%)	Yield (%)[a]	ee (%)		
2k[b]	OCOMe	94	47	93.2	53	98.8	0.48	>100 (574)
6a	N_3	264	64	66.0[c]	33	87.1[d]	0.43	29
6b	OCOPh	115	58	59.0	41	98.9	0.37	>100 (330)
6c	OCOEt	72	47	66.9	52	89.4	0.43	36
6d	OCO*t*-Bu	192				no substrate		
6e	OCO*n*-C_5H_{11}	168	47	99.9	53	67.5	0.60	36
6f	OCO*i*-C_5H_{11}	72	44	97.2	54	66.9	0.59	20
6g	OCO*n*-C_9H_{19}	72	48	88.0	48	74.7	0.54	20
6h	OCO*n*-$C_{11}H_{23}$	72	51	76.6	49	85.1	0.48	29
6i	OCO*n*-$C_{15}H_{31}$	144	42	88.2	58	60.6	0.59	11

[a] Isolated yield. [b] The diol (*RS*)-**1k** was used as substrate in a sequential acetylation. [c] (*S*)-**6a**. [d] (*R*)-**7a**.

In Table 5 the results of the third series are depicted using the substrates (*RS*)-**6a-i** with the *tert*-octyl-residue in *para*-position of the aromatic ring and a few selected substituents R^2 at the primary hydroxy group. Compared with the unsubstituted derivatives at the aromatic ring, there is no general correlation caused by adding of the *tert*-octyl residue to substrates of type **4**. In some cases, in which the unsubstituted derivatives such as **4o**, **4q**, and **4w** showed poor or moderate selectivity, the E value was increased using the derivatives **6a**, **6b**, and **6f**. In other cases, like **6e**, **6g**, and **6i** compared with their unsubstituted counterparts **4d**, **4h**, and **4k**, respectively, the additional presence of the *tert*-octyl substituent in *para*-position of the aromatic ring caused a significant decrease of the enantioselectivity. Nevertheless, all examples investigated with either high or poor selectivity show that extremely long derivatives are accepted as substrates by lipase PS.

The absolute configuration of the reaction products was assigned after deacylation furnishing the corresponding diols **1a-r** on the basis of their specific rotation in ethanol and their CD spectra in Cupra A solution (Scheme 3).



Scheme 3: *i*: basic ion-exchange resin/MeOH

The monoacetates (*R*)-**2a-r** afforded the diols (*S*)-**1a-r** with a positive optical rotation and a positive Cotton effect at 265 - 280 nm. The diacetates (*S*)-**3a-r** furnished the diols (*R*)-**1a-r** with a negative optical rotation and a negative Cotton effect. In the case of **1o** no Cotton effect was observed and the enantiomeric diols of **1m** were insoluble in Cupra A solution. The monoacyl derivatives (*R*)-**4a-r** and the diacyl derivatives (*S*)-**5a-r** were converted into the known diols (*S*)-**1a** and (*R*)-**1a**, respectively. In analogy, the monoacyl derivatives (*R*)-**6b**, **c**, **e-i** and the diacyl derivatives (*S*)-**7b**, **c**, **e-i** were deacylated to give the diols (*S*)-**1k** and (*R*)-**1k**, respectively. The measured optical rotations and CD spectra were in accordance with our earlier results.[2b]

In the case of the azidoalcohols **4w** and **6a** the absolute configuration of the products was assigned on the basis of the different reactivity of the enantiomers in the assumption that their reactivity was the same as that of the corresponding monoacyl derivatives. This assumption is in accordance with Kazlauskas rule.[6] The slow-reacting enantiomer of **4w** was assigned the (*S*)-configuration affording (*S*)-**4w** and the fast-reacting enantiomer the (*R*)-configuration yielding (*R*)-**5w**. On the same basis the configuration of **6a** was assigned.

Conclusions

The enantioselectivity and reactivity of the lipase PS-catalysed transesterification in a series of 3-(aryloxy)-1,2-propanediol derivatives strongly depend on the substituents R^1 at the aryl ring and the substituents R^2 replacing the primary hydroxy group. In general, *para*-substitution at the aryl ring gave substrates which were kinetically resolved with high enantioselectivity. In contrast, *ortho*-substitution by large substituents such as *tert*-butyl, phenyl, benzoyl or benzyl furnished non-substrates for lipase PS. 3-(Aryloxy)-1,2-propanediols with large *ortho*-substituents are not able to fit with the active site of lipase PS. These substrates led to neither enantioselective nor non-enantioselective transesterification due to the spatial limits of the appropriate hydrophobic pocket. The second hydrophobic pocket, which usually interacts with the substituent at the primary hydroxy group, exhibits strongly spatial limitations as well. Unbranched acyl residues reaching from acetyl to hexadecanoyl interact with the second hydrophobic pocket realising enantioselectivities from moderate to very high. This fact is hardly to explain with Kazlauskas' rule.[6] According to this empirical rule, valid also for lipase PS, high enantioselection in the lipase-catalysed kinetic resolution of secondary alcohols requires a large difference in the size of both substituents connected with the chiral centre. The second hydrophobic pocket seems to be a long flat tube. But it seems not to be necessary that this tube must be completely filled with a substituent of the substrate. Moreover, a derivative with a *para*-(*tert*-octyl)-substituent and the hexadecanoyl residue at the primary hydroxy group as an extremely long molecule was accepted as a substrate by lipase PS. On the other hand, sterically more crowded substituents such as pivaloyl, *tert*-butyldimethylsilyl or *para*-toluenesulfonyl instead of unbranched acyl residues led to non-substrates due to the sterical limitation of the second hydrophobic pocket. Surprisingly, a derivative with the diisopropylamino residue instead of, for instance, the acetoxy or the isobutanoyloxy residue at the methylene carbon was a reactive substrate but without any enantioselectivity due to the lacking ability for the chiral recognition of lipase PS for this type of substrate. It is our aim to continue this investigation in order to quantify the spatial requirements of the active site of lipase PS.

Acknowledgement: This work was supported by the Deutsche Forschungsgemeinschaft (DFG) (Th 562/1-1), the Deutsche Akademie der Naturforscher - Leopoldina and the Fonds der Chemischen Industrie. A gift of lipase PS from Amano Pharmaceutical Co. is gratefully acknowledged.

Experimental

General. THF was dried over sodium wire. All reactions were monitored by thin-layer chromatography on glass plates coated with a 0.25 mm layer of silica gel or by HPLC on Lichrosorb Si 60, 7 µm (120×4 mm). Compounds were visualised in the TLC in UV and with a 3.5 % solution of molybdatophosphoric acid in ethanol. Flash chromatography was performed with silica gel 60 (0.063-0.040 mm). ^{1}H NMR spectra were recorded on a Bruker WP 200 SY or on a Varian Gemini 300 spectrometer. ^{13}C NMR spectra were obtained on a Varian Gemini 300 spectrometer. Mass spectra were recorded on the GC/MS-Datensystem HP 5985B or on the Autospec, VG, and if not otherwise indicated, they were obtained by electron impact. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. CD spectra were recorded on a Jasco J-710 spectrometer. The substrates were prepared by standard procedures.

General Procedure for the Kinetic Resolution of the Derivatives (*RS*)-1a-r, (*RS*)-4a-w and (*RS*)-6a-i. A solution of the corresponding alcohol (1 mmol) in THF (2.5 ml) was treated with vinyl acetate (7 mmol) and lipase Amano PS (100 mg). The suspension was stirred at room temperature for the time indicated in the Tables 1 - 5. After filtration through Celite the filter cake was washed with THF (3×5 ml). The solvent was distilled off under reduced pressure, and the residue was separated by flash chromatography.

(*R*)-1-Acetoxy-3-(2,4-dimethylphenoxy)-2-propanol [(*R*)-2d]: ^{1}H NMR: 2.04 (s, 3H), 2.10 (s, 3H), 2.19 (s, 3H), 2.61 (d, 1H, J = 4), 3.90-4.25 (m, 5H), 6.64 (d, 1H, J = 9), 6.87 (m, 2H); ^{13}C NMR: 16.06, 20.39, 20.80, 65.49, 68.47, 68.77, 111.24, 126.48, 126.99, 130.24, 131.61, 154.21, 171.24; MS (*m/z*): 238 (M^+), 122, 117 (100), 107, 91, 77; calcd.: C 65.53, H 7.61 for $C_{13}H_{18}O_4$, found: C 65.55, H 7.77.

(*S*)-1,2-Diacetoxy-3-(2,4-dimethylphenoxy)propane [(*S*)-3d]: ^{1}H NMR: 2.01 (s, 3H), 2.03 (s, 3H), 2.11 (s, 3H), 2.18 (s, 3H), 4.01 (d, 2H, J = 5), 4.23 (dd, 1H, J = 12, 6), 4.38 (dd, 1H, J = 12, 4), 5.33 (m, 1H), 6.62 (d, 1H, J = 9), 6.86 (m, 2H); ^{13}C NMR: 15.98, 20.40, 20.72, 20.92, 62.62, 66.20, 69.38, 111.02, 126.67, 126.92, 130.24, 131.60, 154.21, 170.24, 170.58; MS (*m/z*): 280 (M^+), 159 (100), 122, 107, 99, 91, 77; calcd.: C 64.27, H 7.19 for $C_{15}H_{20}O_5$, found: C 64.27, H, 7.36.

(*R*)-1-Acetoxy-3-(2,4-dichlorophenoxy)-2-propanol [(*R*)-2g]: ^{1}H NMR: 2.05 (s, 3H), 2.63 (d, 1H, J = 4.5), 3.90-4.30 (m, 5H), 6.80 (d, 1H, J = 9), 7.05-7.35 (m, 2H); ^{13}C NMR: 20.81, 65.13, 68.25, 70.22, 114.48,

123.87, 126.48, 127.65, 129.99, 152.66, 171.22; MS (*m/z*): 278 (M^+), 162, 117 (100); calcd.: C 47.33, H, 4.33 for $C_{11}H_{12}Cl_2O_4$, found: C 47.30, 4.35.

(*S*)-1,2-Diacetoxy-3-(2,4-dichlorophenoxy)propane [(*S*)-3g]: ^{1}H NMR: 2.02 (s, 3H, 2.05 (s, 3H), 4.09 (d, 2H, *J* = 5), 4.25 (dd, 1H, *J* = 12, 6), 4.41 (dd, 1H, *J* = 12, 4), 5.33 (m, 1H), 6.80 (d, 1H, *J* = 8.5), 7.12 (dd, 1H, *J* = 8.5, 2.5), 7.30 (d, 1H, *J* = 2.5); ^{13}C NMR: 20.70, 20.89, 62.33, 67.50, 69.35, 114.58, 124.19, 126.61, 127.59, 130.01, 152.69, 170.18, 170.50; MS (*m/z*): 320 (M^+), 159 (100), 99; calcd.: C 48.62, H 4.39 for $C_{13}H_{14}Cl_2O_5$, found: C 48.87, H 4.44.

(*RS*)-1-Acetoxy-3-(2,4-di-*tert*-butylphenoxy)-2-propanol [(*RS*)-2j]: ^{1}H NMR: 1.24 (s, 9H), 1.33 (s, 9H), 2.05 (s, 3H), 2.44 (d, 1H, *J* = 5), 3.99 (d, 2H, *J* = 4.5), 4.08-4.35 (m, 3H), 6.73 (d, 1H, *J* = 8.5), 7.11 (dd, 1H, *J* = 8.5, 2.5), 7.28 (d, 1H, *J* = 2.5); ^{13}C NMR: 20.80, 30.02, 31.52, 34.25, 34.96, 65.72, 68.56, 68.79, 111.41, 123.41, 124.08, 137.18, 143.25, 154.66, 171.21; MS (*m/z*): 322 (M^+), 307, 191, 175, 117 (100); calcd.: C 70.78, H 9.38 for $C_{19}H_{30}O_4$, found C 70.83, H 9.56.

(*R*)-1-Acetoxy-3-[4-(1,1,3,3-tetramethylbutyl)phenoxy]-2-propanol [(*R*)-2k]: ^{1}H NMR: 0.64 (s, 9H), 1.28 (s, 6H), 1.64 (s, 2H), 2.05 (s, 3H), 2.53 (d, 1H, *J* = 4.5), 3.90-4.25 (m, 5H), 6.75 (d, 2H, *J* = 8.5), 7.21 (d, 2H, *J* = 8.5); ^{13}C NMR: 20.81, 31.64, 31.73, 32.26, 37.90, 56.87, 63.39, 68.42, 68.56, 113.65, 127.08, 142.85, 155.88, 171.18; MS (*m/z*): 322 (M^+), 251, 135, 117 (100); calcd.: C 70.78, H 9.38 for $C_{19}H_{30}O_4$, found: C 70.71, H 9.64.

(*S*)-1,2-Diacetoxy-3-[4-(1,1,3,3-tetramethylbutyl)phenoxy]propane [(*S*)-3k]: ^{1}H NMR: 0.64 (s, 9H), 1.27 (s, 6H), 1.63 (s, 2H), 2.01 (s, 3H9, 2.03 (s, 3H), 4.03 (d, 2H, *J* = 5), 4.22 (dd, 1H, *J* = 12, 6), 4.37 (dd, 1H, *J* = 12, 4), 5.28 (m, 1H), 6.74 (dd, 2H, *J* = 8.5, 2.5), 7.20 (dd, 2H, *J* = 8.5, 2.5); ^{13}C NMR: 20.73, 20.95, 31.64, 31.73, 37.92, 56.86, 62.57, 65.92, 69.80, 113.70, 127.08, 142.92, 155.80, 170.26, 170.57; MS (*m/z*): 364 (M^+), 293, 159 (100), 135; calcd.: C 69.20, H 8.85 for $C_{21}H_{32}O_5$, found: C 69.14, H, 8.96.

(*RS*)-1-Acetoxy-3-(2-phenylphenoxy)-2-propanol [(*RS*)-2l]: ^{1}H NMR: 1.97 (s, 3H), 2.50 (br s, 1H), 3.80-4.15 (m, 5H), 6.80-7.50 (m, 9H); ^{13}C NMR: 20.73, 65.18, 68.29, 69.49, 113.17, 121.79, 127.04, 128.05, 128.67, 129.33, 130.89, 131.37, 138.15, 155.09, 171.06; MS (*m/z*): 212, 197, 152, 121, 117, 91, 77, 43 (100); calcd. C 7.15, H 6.40 for $C_{17}H_{18}O_4 \times 0.25\ H_2O$, found C 70.09, H 6.56.

(*R*)-1-Acetoxy-3-(4-phenylphenoxy)-2-propanol [(*R*)-2m]: ^{1}H NMR: 2.06 (s, 3H), 2.51 (d, 1H, *J* = 4.5), 3.90-4.30 (m, 5H), 6.90 (m, 2H), 7.15-7.55 (m, 7H); ^{13}C NMR: 20.82, 65.34, 68.48, 68.70, 114.77, 126.68, 128.18, 128.70, 134.40, 140.51, 157.78, 171.20; MS (*m/z*): 286 (M^+), 244, 170, (100), 152, 141, 117; calcd.: C 71.32, H 6.34 for $C_{17}H_{18}O_4$, found: 71.23, H 6.37.

(*S*)-1,2-Diacetoxy-3-(4-phenylphenoxy)propane [(*S*)-3m]: ^{1}H NMR: 2.02 (s, 3H), 2.05 (s, 3H), 4.09 (2H, *J* = 5), 4.24 (dd, 1H, *J* = 12, 6), 4.40 (dd, 1H, *J* = 12, 4), 5.33 (m, 1H), 6.90 (m, 2H), 7.15-7.55 (m, 7H); ^{13}C NMR: 20.72, 20.94, 62.49, 66.05, 69.68, 114, 81, 126.69, 126.76, 128.18, 128.70, 134.40, 140.54, 157.76,

170.26, 170.72; MS (*m/z*): 328 (M^+), 170, 159 (100), 115, 99; calcd.: C 69.49, H 6.14 for $C_{19}H_{20}O_5$, found: C 69.64, H 6.17.

(*RS*)-1-Acetoxy-3-(2-benzoylphenoxy)-2-propanol [(*RS*)-2n]: ^{1}H NMR: 1.98 (s, 3H), 2.59 (s, 1H), 3.70-4.10 (m, 5H), 6.90-7.05 (m, 2H), 7.20-7.55 (m, 5H), 7.70-7.75 (m, 2H); ^{13}C NMR: 20.76, 64.65, 68.07, 70.03, 113.24, 121.27, 128.40, 128.63, 129.52, 130.42, 132.58, 133.08, 138.21, 156.71, 170.87, 196.38; MS (*m/z*): 314 (M^+), 224, 212, 197 (100), 181, 167, 152, 135, 117, 105; calcd.: C 69.23, H 5.16 for $C_{18}H_{18}O_5$, , found: C 69.27, H 5.88.

(*R*)-1-Acetoxy-3-(4-benzoylphenoxy)-2-propanol [(*R*)-2o]: ^{1}H NMR: 2.05 (s, 3H), 2.80 (br s, 1H), 4.05 (m, 2H), 4.20 (m, 3H), 6.91 (d, 2H, J = 9), 7.35-7.50 (m, 3H), 7.65-7.80 (m, 4H); ^{13}C NMR: 20.82, 65.28, 68.31, 68.86, 114.07, 128.21, 129.72, 130.72, 130.63, 132.63, 132.04, 132.55, 138.02, 161.92, 171.19, 195.58; MS (*m/z*): 314 (M^+), 253, 241, 198, 117 (100), 105; calcd.: C 69.23, H 5.16 for $C_{18}H_{18}O_5$; found: C 69.18, 5.85.

(*S*)-1,2-Diacetoxy-3-(4-benzoylphenoxy)propane [(*S*)-3o]: ^{1}H NMR: 2.03 (s, 3H), 2.05 (s, 3H), 4.14 (d, 2H, J = 5), 4.24 (dd, 1H, J = 12, 6), 4.39 (dd, 1H, J = 12, 4), 5.34 (m, 1H), 6.85-6.95 (m, 2H),7.35-7.55 (m, 3H), 7.65-7.80 (m, 4H); ^{13}C NMR: 20.71, 20.92, 62.33, 66.13, 69.44, 114.07, 128.20, 129.70, 130.75, 131.98, 132.50, 138.06, 161.71, 170.19, 170.51, 195.37; MS (*m/z*): 356 (M^+), 267, 255, 241, 225, 159, (100), 121, 105; calcd.: C 67.41 for $C_{20}H_{20}O_6$, found: 67.57, H 5.71.

(*RS*)-1-Acetoxy-3-(2-benzylphenoxy)-2-propanol [(*RS*)-2p]: ^{1}H NMR: 1.92 (s, 1H), 2.01 (s, 3H), 3.75-4.15 (m, 7H), 6.75 (d, 1H, J = 8), 6.88 (t, 1H, J = 8), 7.05-7.25 (m, 7H); ^{13}C NMR: 20.79, 36.87, 65.06, 68.34, 68.53, 111.17, 121.08, 125.99, 127.73, 128.28, 128.41, 129.27, 130.98, 141.01, 156.04, 171.01; MS (*m/z*): 300 (M^+), 238, 165, 117 (100), 105; calcd.: C 71.97, H 6.71 for $C_{18}H_{20}O_4$, found: C 72.16, H 6.94.

(*R*)-1-Acetoxy-3-(4-benzylphenoxy)-2-propanol [(*R*)-2q]: ^{1}H NMR: 2.02 (s, 3H), 2.48 (s, 1H), 3.75-4.25 (m, 7H), 6.75 (d, 2H, J = 8.5), 7.00-7.25 (m, 7H); ^{13}C NMR: 20.80, 40.97, 65.34, 68.48, 68.66, 114.51, 125.98, 128.41, 128.75, 129.92, 134.01, 141.35, 156.65, 171.16; MS (*m/z*): 300 (M^+), 197, 184, 183, 165, 152, 117 (100), 107, 91; calcd.: C 71.97, H 6.71 for $C_{18}H_{20}O_4$, found: C 71.92, H 6.79.

(*S*)-1,2-Diacetoxy-3-(4-benzylphenoxy)propane [(*S*)-3q]: ^{1}H NMR: 1.99 (s, 3H), 2.02 (s, 3H), 3.84 (s, 2H), 4.01 (d, 2H, J = 5), 4.20 (dd, 1H, J = 12, 6), 4.35 (dd, 1H, J = 12, 4), 5.28 (m, 1H), 6.75 (d, 2H, 2H, J = 8.5), 7.00-7.25 (m, 7H); ^{13}C NMR: 20.70, 20.92, 40.98, 62.51, 66.04, 69.73, 114.56, 125.98, 128.40, 128.74, 129.90, 134.02, 141.36, 156.64, 170.22, 170.54; MS (*m/z*): 342 (M^+), 298, 184, 159 (100), 115; calcd.: C 70.16, H 6.48 for $C_{20}H_{22}O_5$, found: C 70.26, H 6.55.

(*R*)-1-Acetoxy-3-(4-phenoxyphenoxy)-2-propanol [(*R*)-2r]: ^{1}H NMR: 2.05 (s, 3H), 2.57 (br s, 1H), 3.94 (m, 2H), 4.23 (m, 3H), 6.75-7.02 (m, 7H), 7.22 (dd, 2H, J = 12, 2); ^{13}C NMR: 20.81, 65.35, 68.47, 69.22, 115.62, 117.71, 120.71, 122.58, 126.61, 150.73, 154.51, 158.20, 171.19; MS (*m/z*): 302 (M^+), 260, 186, 159, 117 (100); calcd.: C 67.55, H 6.00 for $C_{17}H_{18}O_5$, found: C 67.50, H 6.17.

(*S*)-1,2-Diacetoxy-3-(4-phenoxyphenoxy)propane [(*S*)-3r]: ^{1}H NMR: 2.01 (s, 3H), 2.04 (s, 3H), 4.03 (d, 2H, *J* = 5), 4.22 (dd, 1H, *J* = 12, 6), 4.38 (dd, 1H, *J* = 12, 4), 5.31 (m, 1H), 6.75-7.00 (m, 7H), 7.21 (dd, 2H, *J* = 12, 2); ^{13}C NMR: 20.72, 20.94, 62.51, 66.56, 69.72, 115.69, 117.72, 120.70, 122.57, 129.61, 150.77, 154.60, 158.22, 170.24, 170.55; MS (*m/z*): 344 (M^+), 186, 159 (100), 129, 115, 99; calcd.: C 66.26, H 5.85 for $C_{19}H_{20}O_6$, found: C 66.15, H 5.85.

(*R*)-3-Phenoxy-1-propanoyloxy-2-propanol [(*R*)-4a]: ^{1}H NMR: 1.09 (t, 3H, *J* = 7,5), 2.36 (q, 2H, *J* = 7.5), 2.58 (d, 1H, *J* = 4.5), 3.96-3.98 (m, 2H), 4.16-4.25 (m, 3H), 6.83-6.96 (m, 3H), 7.19-7.27 (m, 2H); ^{13}C NMR: 9.04, 27.40, 65.25, 68.56, 68.61, 114.50, 121.34, 129.55, 158.27, 174.65; MS (*m/z*): 224 (M^+), 131 (100), 107, 94, 77, 65, 57; calcd.: C 64.27, H 7.19 for $C_{12}H_{16}O_4$; found: C 64.29, H 7.25.

(*S*)-2-Acetoxy-3-phenoxy-1-propanoyloxypropane [(*S*)-5a]: ^{1}H NMR: 1.07 (t, 3H, *J* = 7.5), 2.04 (s, 3H), 2.29 (q, 2H, *J* = 7.5), 4.06 (d, 2H, *J* = 5), 4.22 (dd, 1H, *J* = 12, 6), 4.37 (dd, 1H, *J* = 12, 4), 5.31 (m, 1H), 6.82-6.93 (m, 3H), 7.18-7.27 (m, 2H); ^{13}C NMR: 9.01, 20.93, 27.35, 62.36, 65.96, 69.77, 114.55, 121.33, 120.50, 158.24, 170.25, 173.99; MS (*m/z*): 266 (M^+), 173 (100), 94, 77, 65, 57, 43; calcd.: C 63.14, H 6.81 for $C_{14}H_{18}O_5$; found: C 63.02, H 6.78.

(*R*)-1-*n*-Butanoyloxy-3-phenoxy-2-propanol-[(*R*)-4b]: ^{1}H NMR: 0.89 (t, 3H, *J* = 7.5), 1.60 (hex, 2H, *J* = 7.5), 2.28 (t, 2H, *J* = 7.4), 2.64 (d, 1H, *J* = 4), 3.94-3.97 (m, 2H), 4.17-4.25 (m, 3H), 6.83-6.95 (m, 3H), 7.19-7.27 (m, 2H); ^{13}C NMR: 12.05, 18.38, 35.98, 65.14, 68.53, 68.65, 114.50, 121.35, 129.55, 158.26, 173.90; MS (*m/z*): 238 (M^+), 145 (100), 119, 107, 94, 71, 43; calcd.: C 65.53, H 7.61 for $C_{13}H_{18}O_4$; found: C 65.24, H 7.59.

(*S*)-2-Acetoxy-1-*n*-butanoyloxy-3-phenoxypropane [(*S*)-5b]: ^{1}H NMR: 0.88 (t, 3H, *J* = 7.5), 1.58 (hex, 2H, *J* = 7,5), 2.03 (s, 3H), 2.25 (t, 2H, *J* = 7.5), 4.05 (d, 2H, *J* = 5), 4.22 (dd, 1H, *J* = 12, 6), 4.37 (dd, 1H, *J* = 12, 4), 5.31 (m, 1H), 6.83-6.93 (m, 3H), 7.19-7.25 (m, 2H); ^{13}C NMR: 13.89, 18.67, 21.26, 36.26, 62.56, 66.28, 70.12, 114.88, 121.65, 129.83, 158.57, 170.58, 173.52; MS (*m/z*): 280 (M^+), 187 (100), 149, 94, 71, 43; calcd.: C 64.27, H 7.19 for $C_{15}H_{20}O_5$; found: C 64.04, H 7.20.

(*R*)-1-*n*-Pentanoyloxy-3-phenoxy-2-propanol [(*R*)-4c]: ^{1}H NMR: 0.84 (t, 3H, *J* = 7.5), 1.28 (hex, 2H, *J* = 7.5), 1.56 (quin, 2H, *J* = 7.5), 2.31 (t, 2H, *J* = 7.5), 2.67 (d, 1H, *J* = 4.5), 3.92-3.98 (m, 2H), 4.14-4.24 (m, 3H), 6.81-6.94 (m, 3H), 7.17-7.27 (m, 2H); ^{13}C NMR: 13.67, 22.20, 26.93, 33.83, 65.15, 68.57, 114.49, 121.31, 129.52, 158.27, 174.04; MS (*m/z*): 252 (M^+), 159 (100), 107, 94, 77, 65, 57; calcd.: C 66.64, H 7.99 for $C_{14}H_{20}O_4$; found: C 66.55, H 7.94.

(*S*)-2 Acetoxy-1-*n*-pentanoyloxy-3-phenoxypropane [(*S*)-5c]: ^{1}H NMR: 0.83 (t, 3H, *J* = 7), 1.27 (hex, 2H, *J* = 7), 1.54 (quin, 2H, *J* = 7), 2.03 (s, 3H), 2.26 (t, 2H, *J* = 7), 4.05 (d, 2H, *J* = 5), 4.20 (dd, 1H, *J* = 12, 6), 4.35 (dd, 1H, *J* = 12, 4), 5.31 (m, 1H), 6.82-6.93 (m, 3H), 7.18-7.26 (m, 2H); ^{13}C NMR: 13.67, 20.94, 22.16, 26.91, 33.78, 62.24, 65. 93, 69.78, 114.54, 121.32, 129.51, 158.24, 170.25, 173.37; MS (*m/z*): 294 (M^+), 201 (100), 94, 85, 77, 65, 57, 43; calcd.: C 65.29, H 7.56 for $C_{16}H_{22}O_5$; found: C 65.25, H 7.77.

(*R*)-1-*n*-Hexanoyloxy-3-phenoxy-2-propanol [(*R*)-4d]: ^{1}H NMR: 0.82 (t, 3H, *J* = 7), 1.20-1.27 (m, 4H), 1.59 (m, 2H), 2.29 (t, 2H, *J* = 7.5), 2.56 (d, 1H, *J* = 4.5), 3.94-4.24 (m, 5H), 6.83-6.95 (m, 3H), 7.19-7.27 (m, 2H); ^{13}C NMR: 13.88, 22.29, 24.59, 31.26, 34.10, 65.18, 68.63, 114.54, 121.34, 129.55, 158.32, 174.04; MS (*m/z*): 266 (M^+), 173 (100), 107, 94, 77, 71, 55, 43; calcd.: C 67.64, H 8.33 for $C_{15}H_{22}O_4$; found: C 67.59, H 8.54.

(*S*)-2-Acetoxy-1-*n*-hexanoyloxy-3-phenoxypropane [(*S*)-5d]: ^{1}H NMR: 0.82 (t, 3H, *J* = 7), 1.19-1.28 (m, 4H), 1.55 (quin, 2H, *J* = 7), 2.03 (s, 3H), 2.26 (t, 2H, *J* = 7.5), 4.05 (d, 2H, *J* = 5.5), 4.21 (dd, 1H, *J* = 12, 6), 4.36 (dd, 1H, *J* = 12, 4), 5.31 (m, 1H), 6.81-6.93 (m, 3H), 7.20-7.25 (m, 2H); ^{13}C NMR: 13.86, 20.94, 22.27, 24.55, 31.20, 34.03, 62.24, 65.95, 69.80, 114.56, 121.33, 129.51, 158.25, 170.24, 173.37; MS (*m/z*): 308 (M^+), 215 (100), 135, 99, 77, 55, 43; calcd.: C 66.21, H 7.85 for $C_{17}H_{24}O_5$; found: C 66.01, H 7.82.

(*R*)-1-*n*-Heptanoyloxy-3-phenoxy-2-propanol [(*R*)-4e]: ^{1}H NMR: 0.81 (t, 3H, *J* = 6), 1,21-1.23 (m, 6H), 1.57 (m, 2H), 2.29 (t, 2H, *J* = 7.5), 2.67 (d, 1H, *J* = 4), 3.94-3.97 (m, 2H), 4.10-4.25 (m, 3H), 6.83-6.95 (m, 3H), 7.19-7.27 (m, 2H); ^{13}C NMR: 13.99, 22.44, 24.66, 24.85, 28.76, 31.40, 34.13, 65.15, 68.56, 68.63, 114.51, 121.34, 129.53, 158.28, 174.06; MS (*m/z*): 280 (M^+), 187 (100), 168, 113, 94, 77, 55, 43; calcd.: C 68.54, H 8.63 for $C_{16}H_{24}O_4$; found: C 68.74, H 8.76.

(*S*)-2-Acetoxy-1-*n*-heptanoyloxy-3-phenoxypropane [(*S*)-5e]: ^{1}H NMR: 0.81 (t, 3H, *J* = 6.5), 1.18-1.26 (m, 6H), 1.54 (m, 2H), 2.03 (s, 3H), 2.26 (t, 2H, *J* = 7), 4.05 (d, 2H, *J* = 5), 4.22 (dd, 1H, *J* = 12, 6), 4.36 (dd, 1H, *J* = 12, 4), 5.31 (m, 1H), 6.82-6.91 (m, 3H), 7.20-7.26 (m, 2H); ^{13}C NMR: 14.00, 20.94, 22.44, 24.82, 28.72, 31.40, 34.07, 62.24, 65.94, 69.80, 114.56, 121.33, 129.50, 158.25, 170.24, 173.38; MS (*m/z*): 322 (M^+), 229 (100), 193,133, 113, 94, 77, 43; calcd.: C 67.06, H 8.13 for $C_{18}H_{26}O_5$; found: C 66.94, H 8.14.

(*R*)-1-*n*-Octanoyloxy-3-phenoxy-2-propanol [(*R*)-4f]: ^{1}H NMR: 0.81 (t, 3H, *J* = 7), 1.20-1.27 (m, 8H), 1.56 (m, 2H), 2.29 (t, 2H, *J* = 7), 2.63 (d, 1H, *J* = 4), 3.93-3.96 (m, 2H), 4.16-4.24 (m, 3H), 6.82-6.95 (m, 3H), 7.18-7.26 (m, 2H); ^{13}C NMR: 14.04, 22.57, 24.88, 28.88, 29.04, 31.61, 34.12, 65.13, 68.54, 68.59, 114.47, 121.31, 129.52, 158.26, 174.05; MS (*m/z*): 294 (M^+), 201 (100), 168, 127, 107, 94, 77, 65, 43; calcd.: C 69.36, H 8.91 for $C_{17}H_{26}O_4$; found: C 69.12, H 8.95.

(*S*)-2-Acetoxy-1-*n*-octanoyloxy-3-phenoxypropane [(*S*)-5f]: ^{1}H NMR: 0.81 (t, 3H, *J* = 7), 1.20 (m, 8H), 1.57 (m, 2H), 2.03 (s, 3H), 2.26 (t, 2H, *J* = 7.5), 4.05 (d, 2H, *J* = 5), 4.22 (dd, 1H, *J* = 12, 6), 4.36 (dd, 1H, *J* = 12, 4), 5.31 (m, 1H), 6.82-6.93 (m, 3H), 7.19-7.25 (m, 2H); ^{13}C NMR: 14.04, 20.94, 22.57, 24.87, 28.89, 29.12, 31.62, 34.07, 62.23, 65.95, 69.80, 114.56, 121.33, 129.50, 158.26, 170.23, 173.38; MS (*m/z*): 336 (M^+), 243 (100), 135, 105, 94, 77, 65, 57, 43; calcd.: C 67.83, H 8.39 for $C_{19}H_{28}O_5$; found: C 67.53, H 8.40.

(*R*)-1-*n*-Nonanoyloxy-3-phenoxy-2-propanol [(*R*)-4g]: ^{1}H NMR: 0.81 (t, 3H, *J* = 7), 1.20 (m, 10 H), 1.57 (m, 2H), 2.29 (t, 2H, *J* = 7), 2.57 (br s, 1H), 3.89-4.02 (m, 2H), 4.11-4.27 (m, 3H), 6.83-6.95 (m, 3H), 7.19-7.27 (m, 2H); ^{13}C NMR: 14.07, 22.61, 24.89, 29.10, 29.19, 31.78, 34.13, 65.15, 68.61, 114.52, 121.32,

129.53, 158.30, 174.04; MS (*m/z*): 308 (M^+), 215 (100), 168, 141, 107, 94, 77, 57, 43; calcd.: C 70.10, H 9.15 for $C_{18}H_{28}O_4$; found: C 70.30, H 9.41.

(*S*)-2-Acetoxy-1-*n*-nonanoyloxy-3-phenoxypropane [(*S*)-5g]: ^{1}H NMR: 0.81 (t, 3H, *J* = 7), 1.19 (m, 10 H), 1.54 (m, 2H), 2.03 (s, 3H), 2.25 (t, 2H, *J* = 7.5), 4.05 (d, 2H, *J* = 5), 4.20 (dd, 1H, *J* = 12, 6), 4.35 (dd, 1H, *J* = 12, 4), 5.30 (m, 1H), 6.81-6.94 (m, 3H), 7.18-7.26 (m, 2H); ^{13}C NMR: 14.08, 20.94, 22.62, 24.87, 29.08, 29.19, 31.79, 34.07, 62.23, 65.92, 69.79, 114.54, 121.32, 129.50, 158.25, 170.23, 173.38; MS (*m/z*): 350 (M^+), 257 (100), 201, 171, 141, 94, 71, 43; calcd.: C 68.54, H 8.63 for $C_{20}H_{30}O_5$; found: C 68.39, H 8.88.

(*R*)-1-*n*-Decanoyloxy-3-phenoxy-2-propanol [(*R*)-4h]: ^{1}H NMR: 0.81 (t, 3H, *J* = 7), 1.19 (m, 12 H), 1.56 (m, 2H), 2.25 (t, 2H, *J* = 7), 2.60 (d, 1H, *J* = 4), 3.94-3.97 (m, 2H), 4.17-4.25 (m, 3H), 6.83-6.95 (m, 3H), 7.19-7.27 (m, 2H); ^{13}C NMR: 14.09, 22.64, 24.88, 29.09, 29.23, 29.38, 31.82, 34.12, 65.14, 68.56, 114.49, 121.29, 129.51, 158.28, 174.05; MS (*m/z*): 323 (M^+), 305, 229 (100), 168, 155, 121, 107; calcd.: C 70.77, H 9.38 for $C_{19}H_{30}O_4$; found: C 70.52, H 9.55.

(*S*)-2-Acetoxy-1-*n*-decanoyloxy-3-phenoxypropane [(*S*)-5h]: ^{1}H NMR: 0.81 (t, 3H, *J* = 6.5), 1.19 (m, 12H), 1.54 (m, 2H), 2.03 (s, 3H), 2.25 (t, 2H, *J* = 7.5), 4.05 (d, 2H, *J* = 5), 4.20 (dd, 1H, *J* = 12, 6), 4.35 (dd, 1H, *J* = 12, 4), 5.31 (m, 1H), 6.81-6.94 (m, 3H), 7.18-7.26 (m, 2H); ^{13}C NMR: 14.11, 20.97, 22.66, 24.89, 29.09, 29.26, 29.41, 31.85, 34.10, 62.25, 65.96, 69.82, 114.57, 121.35, 129.53, 158.27, 170.26, 173.41; MS (*m/z*): 364 (M^+), 304, 271, 193, 155, 117, 94, 71, 55, 43 (100), 41; calcd.: C 69.21, H 8.85 for $C_{21}H_{32}O_5$; found: C 69.24, H 9.00.

(*R*)-1-*n*-Dodecanoyloxy-3-phenoxy-2-propanol [(*R*)-4i]: ^{1}H NMR: 0.81 (t, 3H, *J* = 6.5), 1.19 (m, 16 H), 1.53-1.59 (m, 2H), 2.29 (t, 2H, *J* = 7.5), 2.56 (d, 1H, *J* = 4.5), 3.94-3.97 (m, 2H), 4.17-4.24 (m, 3H), 6.83-6.95 (m, 3H), 7.19-7.27 (m, 2H); ^{13}C NMR: 14.12, 22.69, 24.92, 29.13, 29.26, 29.33, 29.45, 29.60, 31.91, 34.16, 65.17, 68.57, 68.68, 114.53, 121.36, 129.56, 158.30, 174.05; MS (*m/z*): 350 (M^+), 257 (100), 168, 149, 94, 57, 43; calcd.: C 71.96, H 10.11 for $C_{21}H_{34}O_4$; found: C 72.13, 10.10.

(*S*)-2-Acetoxy-1-*n*-dodecanoyloxy-3-phenoxypropane [(*S*)-5i]: ^{1}H NMR: 0.81 (t, 3H *J* = 6.5), 1.19 (m, 16 H), 1.54 (m, 2H), 2.03 (s, 3H), 2.25 (t, 2H, *J* = 7.5), 4.05 (d, 2H, *J* = 5), 4.23 (dd, 1H, *J* = 12, 6), 4.35 (dd, 1H, *J* = 12, 4), 5.31 (m, 1H), 6.81-6.94 (m, 3H), 7.18-7.26 (m, 2H); ^{13}C NMR : 14.12, 20.96, 22.69, 24.89, 29.09, 29.26, 29.33, 29.46, 29.61, 31.91, 34.10, 62.25, 65.97, 69.82, 114.58, 121.35, 129.52, 158.28, 170.25, 173.40; MS (*m/z*): 392 (M^+), 332, 299 (100), 183, 117, 94, 57; calcd.: C 70.37, H 9.25 for $C_{23}H_{36}O_5$; found: C 70.44, H 9.62.

(*R*)-3-Phenoxy-1-*n*-tetradecanoyloxy-2-propanol [(*R*)-4j]: ^{1}H NMR: 0.81 (t, 3H, *J* = 6.5), 1.18 (m, 20 H), 1.53-1.64 (m, 2H), 2.29 (t, 2H, *J* = 7.5), 2.61 (d, 1H, *J* = 4.5), 3.93-3.96 (m, 2H), 4.07-4.24 (m, 3H), 6.82-6.94 (m, 3H), 7.19-7.26 (m, 2H); ^{13}C NMR: 14.07, 22.63, 24.85, 29.07, 29.20, 29.30, 29.40, 29.59, 31.86, 34.08, 65.11, 68.54, 114.46, 121.25, 129.47, 158.26, 173.99; MS (*m/z*): 378 (M^+), 285 (100), 211, 168, 94, 57; calcd.: C 72.97, H 10.12 for $C_{23}H_{38}O_4$; found: C 73.07, H 10.17.

(*S*)-2-Acetoxy-3-phenoxy-1-*n*-tetradecanoyloxypropane [(*S*)-5j]: ^{1}H NMR: 0.81 (t, 3H, *J* = 6.5), 1.19 (m, 20 H), 1.54 (m, 2H), 2.03 (s, 3H), 2.25 (t, 2H, *J* = 7.5), 4.05 (d, 2H, *J* = 5), 4.20 (dd, 1H, *J* = 12, 6), 4.35 (dd, 1H, *J* = 12, 4), 5.31 (m, 1H), 6.81-6.94 (m, 3H), 7.18-7.26 (m, 2H); ^{13}C NMR: 14.13, 20.97, 22.69, 24.89, 29.09, 29.26, 29.36, 29.46, 29.65, 31.92, 34.10, 62.25, 65.97, 69.82, 114.58, 121.35, 129.53, 158.27, 170.26, 173.41; MS (*m/z*): 420 (M^+), 327 (100), 211, 117, 94, 57, 43; calcd.: C 71.39, H 9.59 for $C_{25}H_{40}O_5$; found: C 71.41, H 9.58.

(*R*)-1-*n*-Hexadecanoyloxy-3-phenoxy-2-propanol [(*R*)-4k]: ^{1}H NMR: 0.81 (t, 3H, *J* = 6.5), 1.19 (m, 24 H), 1.57 (m, 2H), 2.29 (t, 2H, *J* = 7.5), 2.48 (d, 1H, *J* = 4.5), 3.97 (m, 2H), 4.17-4.22 (m, 3H), 6.83-6.95 (m, 3H), 7.19-7.27 (m, 2H); ^{13}C NMR: 14.13, 22.70, 24.93, 29.14, 29.26, 29.37, 29.46, 29.68, 31.93, 34.16, 65.18, 68.58, 68.69, 114.53, 121.37, 129.56, 158.30, 174.06; MS (*m/z*): 406 (M^+), 313 (100), 239, 168, 94, 69, 57; calcd.: C 73.84, H 10.40 for $C_{25}H_{42}O_4$; found: C 73.64, H 10.55.

(*S*)-2-Acetoxy-1-*n*-hexadecanoyloxy-3-phenoxypropane [(*S*)-5k]: ^{1}H NMR: 0.88 (t, 3H, *J* = 6.5), 1.25 (m, 24 H), 1.58-1.63 (m, 2H), 2.10 (s, 3H), 2.32 (t, 2H, *J* = 7.5), 4.11 (d, 2H, *J* = 5), 4.28 (dd, 1H, *J* = 12, 6), 4.41 (dd, 1H, *J* = 12, 4), 5.37 (m, 1H), 6.89-7.00 (m, 3H), 7.26-7.32 (m, 2H); ^{13}C NMR: 14.22, 21.07, 22.79, 24.98, 29.19, 29.36, 29.46, 29.55, 29.77, 32.02, 34.19, 62.34, 66.03, 69.90, 114.65, 121.44, 129.62, 158.35, 170.36, 173.51; MS (CI, NH_3, *m/z*): 466 ($[M+NH_4]^+$), 449 ($[M+H]^+$), 389, 355, 193 (100), 117, 43; calcd.: C 72.28, H 9.89 for $C_{27}H_{44}O_5$; found: C 72.30, H 10.01.

(*R*)-1-(2-Methylpropanoyloxy)-3-phenoxy-2-propanol [(*R*)-4l]: ^{1}H NMR: 1.12 (d, 6H, *J* = 7), 2.48-2.58 (m, 2H), 3.94-3.98 (m, 2H), 4.13-4.25 (m, 3H), 6.83-6.96 (m, 3H), 7.18-7.27 (m, 2H); ^{13}C NMR: 18.94, 33.89, 65.17, 68.62, 114.51, 121.30, 129.52, 158.30, 177.32; MS (m/z): 238 (M^+), 145, 94, 71, 43 (100); calcd.: C 65.53, H 7.61 for $C_{13}H_{18}O_4$; found: C 65.51, H 7.67.

(*S*)-2-Acetoxy-1-(2-methylpropanoyloxy)-3-phenoxypropane [(*S*)-5l]: ^{1}H NMR: 1.10 (d, 6H, *J* = 7), 2.03 (s, 3H), 2.51 (sept, 1H, *J* = 7), 4.05 (d, 2H, *J* = 5), 4.22 (dd, 1H, *J* = 12, 6), 4.36 (dd, 1H, *J* = 12, 4), 5.33 (m, 1H), 6.82-6.93 (m, 3H), 7.20-7.25 (m, 2H); ^{13}C NMR: 19.41, 21.44, 34.40, 62.79, 66.54, 70.32, 115.10, 121.87, 130.05, 158.80, 170.75, 177.12; MS (m/z): 280 (M^+), 187 (100), 94, 77, 71, 43; calcd.: C 64.50, H 6.86 for $C_{15}H_{19}O_5$; found: C 64.44, H 7.03.

(*R*)-1-(3-Methylbutanoyloxy)-3-phenoxy-2-propanol [(*R*)-4m]: ^{1}H NMR: 0.89 (d, 6H, *J* = 6.5), 1.87-2.18 (m, 3H), 2.79 (d, 1H, *J* = 4.5), 3.93-3.96 (m, 2H), 4.12-4.24 (m, 3H), 6.81-6.94 (m, 3H), 7.18-7.26 (m, 2H); ^{13}C NMR: 22.33, 25.65, 43.15, 65.05, 68.52, 68.57, 114.48, 121.26, 129.50, 158.28, 173.31; MS (m/z): 252 (M^+), 214, 168, 159 (100), 107, 94, 85, 77, 57; calcd.: C 66.64, H 7.99 for $C_{14}H_{20}O_4$; found: C 66.40, H 8.02.

(*S*)-2-Acetoxy-1-(3-methylbutanoyloxy)-3-phenoxypropane [(*S*)-5m]: ^{1}H NMR: 0.88 (d, 6H, *J* = 6.5), 1.99-2.17 (m, 6H), 4.05 (d, 2H, *J* = 5), 4.22 (dd, 1H, *J* = 12, 6), 4.36 (dd, 1H, *J* = 12, 4), 5.31 (m, 1H), 6.82-6.94 (m, 3H), 7.19-7.26 (m, 2H); ^{13}C NMR: 20.96, 22.34, 25.68, 43.16, 62.17, 65.95, 69.82, 114.57, 121.35,

129.53, 158.27, 170.26, 172.66; MS (m/z): 294 (M^+), 252, 201, 94, 85, 77, 57, 43 (100); calcd.: C 65.29, H 7.48 for $C_{16}H_{22}O_5$; found: C 65.36, H 7.53.

(*RS*)-3-Phenoxy-1-trimethylacetoxy-2-propanol [(*RS*)-4n]: ^{1}H NMR: 1.16 (s, 9H), 2.57 (d, 1H, J = 4.5), 3.94-3.97 (m, 2H), 4.15-4.21 (m, 3H), 6.83-6.95 (m, 3H), 7.19-7.27 (m, 2H); ^{13}C NMR: 27.15, 38.86, 65.23, 68.58, 68.74, 114.50, 121.31, 129.54, 158.30, 178.74; MS (m/z): 252 (M^+), 159 (100), 107, 94, 77, 57, 41; calcd.: C 66.64, H 7.99 for $C_{14}H_{20}O_4$; found: C 66.80, H 8.06.

(*R*)-1-(4-Methylpentanoyloxy)-3-phenoxy-2-propanol [(*R*)-4o]: ^{1}H NMR: 0.83 (d, 6H, J = 6), 1.48 (m, 3H), 2.30 (t, 2H, J = 7.5), 2.58 (d, 1H, J = 4.5), 3.94-3.97 (m, 2H), 4.17-4.24 (m, 3H), 6.83-6.95 (m, 3H), 7.19-7.27 (m, 2H); ^{13}C NMR: 22.18, 27.62, 32.18, 33.64, 65.18, 68.53, 68.60, 114.48, 121.32, 129.53, 158.25, 174.23; MS (m/z): 266 (M^+), 173 (100), 107, 94, 77, 55; calcd.: C 67.64, H 8.33 for $C_{15}H_{22}O_4$; found: C 67.55, H 8.53.

(*S*)-2-Acetoxy-1-(4-methylpentanoyloxy)-3-phenoxypropane [(*S*)-5o]: ^{1}H NMR: 0.82 (d, 6H, J = 6), 1.46 (m, 3H), 2.03 (s, 3H), 2.27 (t, 2H, J = 7.5), 4.05 (d, 2H, J = 5), 4.21 (dd, 1H, J = 12, 6), 4.35 (dd, 1H, J = 12, 4), 5.32 (m, 1H), 6.82-6.94 (m, 3H), 7.19-7.27 (m, 2H); ^{13}C NMR: 20.97, 22.19, 27.60, 32.16, 33.66, 62.30, 65.96, 69.81, 114.58, 121.36, 129.53, 158.27, 170.27, 173.60; MS (m/z): 308 (M^+), 252, 215 (100), 193, 117, 99, 94, 81, 43; calcd.: C 66.21, H 7.84 for $C_{17}H_{24}O_5$; found: C 66.36, H 8.08.

(*R*)-1-Cyclohexanoyloxy-3-phenoxy-2-propanol [(*R*)-4p]: ^{1}H NMR: 1.15-1.86 (m, 10H), 2.29 (m, 1H), 2.71 (d, 1H, J = 5), 3.93-3.96 (m, 2H), 4.13-4.22 (m, 3H), 6.82-6.93 (m, 3H), 7.12-7.25 (m, 2H); ^{13}C NMR: 25.34, 25.65, 28.97, 43.04, 65.01, 68.60, 114.51, 121.27, 129.52, 158.32, 176.29; MS (*m/z*): 278 (M^+), 185 (100), 94, 77, 55, 41; calcd.: C 69.04, H 7.97 for $C_{16}H_{22}O_4$; found: C 68.83, H 7.80.

(*S*)-2-Acetoxy-1-cyclohexanoyloxy-3-phenoxypropane [(*S*)-5p]: ^{1}H NMR: 1.18-1.85 (m, 10H), 2.03 (s, 3H), 2.26 (m, 1H), 4.05 (d, 2H, J = 5), 4.20 (dd, 1H, J = 12, 6), 4.34 (dd, 1H, J = 12, 4), 5.31 (m, 1H), 6.81-6.94 (m, 3H), 7.19-7.26 (m, 2H); ^{13}C NMR: 20.95, 25.32, 25.65, 28.89, 42.96, 62.09, 65.99, 69.80, 114.55, 121.31, 129.50, 158.25, 170.25, 175.57; MS (*m/z*): 320 (M^+), 227 (100), 201, 135, 111, 83, 55, 43; calcd.: C 67.48, H 7.55 for $C_{18}H_{24}O_5$; found: C 67.42, H 7.45.

(*R*)-1-Benzoyloxy-3-phenoxy-2-propanol [(*R*)-4q]: ^{1}H NMR: 2.65 (d, 1H; J = 5), 4.07 (m, 2H), 4.33 (m, 1H), 4.47-4.50 (m, 2H), 6.85-6.95 (m, 3H), 7.19-7.97 (m, 5H), 8.02 (m, 2H); ^{13}C NMR: 65.84, 68.69, 68.73, 114.54, 121.35, 128.43, 129.55, 129.70, 133.24, 158.29, 166.72; MS (*m/z*): 272 (M^+), 179 (100), 123, 105, 94, 77, 51; calcd.: C 70.55, H 5.92 for $C_{16}H_{16}O_4$; found: C 70.68, H 5.99.

(*S*)-2-Acetoxy-1-benzoyloxy-3-phenoxypropane [(*S*)-5q]: ^{1}H NMR: 2.04 (S, 3H), 4.14 (d, 2H, J = 5.5), 4.47 (dd, 1H, J = 12, 6), 4.59 (dd, 1H, J = 12, 4), 5.47 (m, 1H), 6.84-6.93 (m, 3H), 7.18-7.25 (m, 2H), 7.35-7.40 (m, 2H), 7.47-7.53 (m, 1H), 7.94-7.97 (m, 2H); ^{13}C NMR: 20.92, 63.06, 66.09, 69.78, 114.59, 121.36, 128.42, 129.51, 129.64, 133.17, 158.25, 166.06, 170.24; MS (*m/z*): 314 (M^+), 221 (100), 105, 94, 77, 43; calcd.: C 68.78, H 5.77 for $C_{18}H_{18}O_5$; found: C 69.04, H 5.87.

(*R*)-3-Phenoxy-1-phenylacetoxy-2-propanol [(*R*)-4r]: ^{1}H NMR: 2.61 (br s, 1H), 3.58 (s, 2H), 3.83-3.97 (m, 2H), 4.04-4.22 (m, 3H), 6.75-6.93 (m, 3H), 7.09-7.31 (m, 7H); ^{13}C NMR: 41.14, 65.56, 68.37, 114.46, 121.27, 127.18, 128.59, 129.17, 129.48, 133.63, 158.18, 171.66; MS (*m/z*): 286 (M^+), 193, 119, 91 (100), 77, 65; calcd.: C 71.31, H 6.34 for $C_{17}H_{18}O_4$; found: C 71.34, H 6.55.

(*S*)-2-Acetoxy-3-phenoxy-1-(phenylacetoxy)propane [(*S*)-5r]: ^{1}H NMR: 1.96 (s, 3H), 3.57 (s, 2H), 3.96 (d, 2H, *J* = 5), 4.23 (dd, 1H, *J* = 12, 6), 4.36 (dd, 1H, J = 12, 4), 5.29 (m, 1H), 6.76-6.94 (m, 3H), 7.14-7.27 (m, 7H); ^{13}C NMR: 20.87, 41.21, 62.74, 65.81, 69.62, 114.55, 121.34, 127.17, 128.58, 129.22, 129.50, 133.68, 158.19, 170.21, 171.08; MS (*m/z*): 328 (M^+), 268, 235, 91 (100), 77, 43; calcd.: C 69.50, H 6.14 for $C_{19}H_{20}O_5$; found: C 69.48, H 6.17.

(*RS*)-1-*tert*-Butyldimethylsilyloxy-3-phenoxy-2-propanol [(*RS*)-4s]: ^{1}H NMR: -0.02 (s, 6H), 0.81 (s, 9H), 2.46 (d, 1H, *J* = 5), 3.68 (d, 2H, *J* = 4), 3.92 (m, 3H), 6.80-6.86 (m, 3H), 7.15-7.23 (m, 2H); ^{13}C NMR: -5.46, 18.25, 25.82, 63.72, 68.34, 70.15, 114.48, 120.96, 129.43, 158.58; MS (*m/z*): 225 (M^+ - 57), 207, 151, 75 (100); calcd.: C 63.78, H 9.28 for $C_{15}H_{26}O_3Si$; found: C 64.03, H 9.37.

(*RS*)-1-Methanesulfonyloxy-3-phenoxy-2-propanol [(*RS*)-4t]: ^{1}H NMR: 2.64 (d, 1H, *J* = 5.5), 3.01 (s, 3H), 4.00 (d, 2H, *J* = 5), 4.20-4.39 (m, 3H), 6.83-6.97 (m, 3H), 7.20-7.28 (m, 2H); ^{13}C NMR: 37.47, 67.78, 68.19, 70.39. 114.50, 121.55, 129.61, 158.02; MS (*m/z*): 246 (M^+), 153, 107, 94 (100), 79, 57; calcd.: C 48.77, H 5.73 for $C_{10}H_{14}O_5S$; found: C 48.79, H 5.81.

(*RS*)-3-Phenoxy-1-(4-toluenesulfonyloxy)-2-propanol [(*RS*)-4u]: ^{1}H NMR: 2.35-2.41 (m, 4H), 3.92 (d, 2H, *J* = 5), 4.03-4.14 (m, 3H), 6.75 (d, 2H, *J* = 8), 6.91 (t, 1H, *J* = 7), 7.17-7.26 (m, 4H), 7.73 (d, 2H, *J* = 8); ^{13}C NMR: 21.64, 67.52, 67.96, 70.24, 114.42, 121.39, 127.94, 129.49, 129.93, 132.32, 145.15, 157.96; MS (*m/z*): 322 (M^+), 229, 155 (100), 107, 91, 77, 65; calcd.: C 59.61, H 5.63 for $C_{16}H_{18}O_5S$; found: C 59.53, H 5.67.

(*RS*)-3-Phenoxy-1-triphenylmethoxy-2-propanol [(*RS*)-4v]: ^{1}H NMR: 2.45 (d, 1H, *J* = 5), 3.34 (dd, 2H, *J* = 5, 2), 4.04-4.15 (m, 3H), 6.87-6.98 (m, 3H), 7.21-7.32 (m, 12H), 7.41-7.45 (m, 5H); ^{13}C NMR: 64.21, 68.93, 69.48, 86.81, 114.54, 121.05, 127.12, 127.88, 128.63, 128.78, 129.46, 143.69, 158.47; MS (*m/z*): 410 (M^+), 259, 243 (100), 165, 105, 94, 77; calcd.: C 81.92, H 6.39 for $C_{28}H_{26}O_3$; found: C 81.95, H 6.56.

(*R*)-1-Azido-3-phenoxy-2-propanol [(*R*)-4w]: ^{1}H NMR: 2.40 (d, 1H, *J* = 5), 3.38-3.48 (m, 2H), 3.96 (m, 2H), 4.10 (m, 1H), 6.83-6.96 (m, 3H), 7.20-7.28 (m, 2H); ^{13}C NMR: 53.36, 68.94, 69.28, 114.50, 121.43, 129.58, 158.15; MS (*m/z*): 193 (M^+), 119, 94 (100), 77, 65, 51, 39; calcd.: C 56.37, H 5.74, N 21.75 for $C_9H_{10}N_3O_2$; found: C 56.57, H 5.87, N 21.94.

(*S*)-2-Acetoxy-1-azido-3-phenoxypropane [(*S*)-5w]: ^{1}H NMR: 2.06 (s, 3H), 3.54 (d, 2H, *J* = 3.5), 4.04 (d, 2H, *J* = 4), 5.21 (m, 1H), 6.82-6.93 (m, 3H), 7.18-7.25 (m, 2H); ^{13}C NMR: 20.88, 50.76, 65.96, 70.73, 114.55, 121.44, 129.55, 158.12, 170.15; MS (*m/z*): 235 (M^+), 142 (100), 94, 77, 43; calcd.: C 56.16, H 5.57, N 17.87 for $C_{11}H_{13}N_2O_3$; found: C 56.14, H 5.59, N 17.84.

(*S*)-1-Diisopropylamino-3-phenoxy-2-propanol [(*S*)-4x]: ^{1}H NMR: 0.95 (d, 6H, *J* = 6.5), 0.99 (d, 6H, *J* = 6.5), 2.37 (dd, 1H, *J* = 13, 9), 2.61 (dd, 1H, *J* = 13, 4), 3.00 (hept, 2H, *J* = 6.5), 3.81-3.95 (m, 3H), 4.03 (s, 1H), 6.83-6.90 (m, 3H), 7.17-7.25 (m, 2H); ^{13}C NMR: 19.58, 22.24, 47.09, 48.26, 65.47, 70.73, 114.51, 120.75, 129.36, 158.91; MS (*m*/z): 251 (M^+),194, 144, 114 (100), 94, 72, 56; calcd.: C 71.67, H 10.03, N 5.57 for $C_{15}H_{25}NO_2$; found: C 71.63, H 10.03, N 5.29.

(*R*)-2-Acetoxy-1-diisopropylamino-3-phenoxypropane [(*R*)-5x]: ^{1}H NMR: 0.99 (d, 12H, *J* = 7), 2.07 (s, 3H), 2.62 (dd, 1H, *J* = 14, 6), 2.73 (dd, 1H, *J* = 14, 8), 3.03 (hept, 2H, *J* = 7), 4.08 (dd, 1H, *J* = 10, 5.5), 4.17 (dd, 1H, *J* = 10, 3.5), 5.16 (m, 1H), 6.90-6.97 (m, 3H), 7.25-7.30 (m, 2H); ^{13}C NMR: 20.47, 21.31, 21.53, 45.07, 48.58, 67.30, 72.11, 114.67, 120.91, 129.48, 158.85, 170.72; MS (CI, NH_3, *m*/z): 294 ([M+H$^+$]), 114 (100), 102, 72, 58, 44; calcd.: C 69.59, H 9.28, N 4.77 for $C_{17}H_{27}O_3N$; found: C 69.65, H 9.28, 4.70.

(*S*)-1-Azido-3-[4-(1,1,3,3-tetramethylbutyl)phenoxy]-2-propanol [(*S*)-6a]: ^{1}H NMR: 0.74 (s, 9H), 1.37 (s, 6H), 1.73 (s, 2H), 2.66 (br s, 1H), 3.52-3.55 (m, 2H), 4.00-4.03 (m, 2H), 4.13-4.18 (m, 1H), 6.85 (d, 2H, *J* = 9), 7.31 (d, 2H, *J* = 9); ^{13}C NMR: 31.66, 31.76, 32.31, 37.99, 53.42, 56.94, 69.01, 69.39, 113.72, 127.19, 143.12, 155.81; MS (*m*/z): 305 (M^+), 234 (100), 135, 107, 57, 41; calcd.: C 66.85, H 8.91, N 13.76 for $C_{17}H_{27}O_2N_3$; found: C 66.64, H 9.17, N 13.53.

(*R*)-2-Acetoxy-1-azido-3-[4-(1,1,3,3-tetramethylbutyl)phenoxy]propane [(*R*)-7a]: ^{1}H NMR: 0.71 (s, 9H), 1.33 (s, 6H), 1.70 (s, 2H), 2.11 (s, 3H), 3.60-3.62 (m, 2H), 4.09 (d, 2H, *J* = 5), 5.27 (quin, 1H, *J* = 5), 6.81 (dd, 2H, *J* = 9, 2), 7.27 (dd, 2H, *J* = 9, 2); ^{13}C NMR: 20.88, 31.62, 31.72, 32.25, 37.92, 50.74, 56.85, 65.95, 70.80, 113.67, 127.10, 143.00, 155.71, 170.12; MS (*m*/z): 347 (M^+), 276, 248, 175, 142 (100), 135, 107; calcd.: C 65.68, H 8.41, N 12.10 for $C_{19}H_{29}N_3O_3$; found: C 65.68, H 8.52, N 12.16.

(*R*)-1-Benzoyloxy-3-[4-(1,1,3,3-tetramethylbutyl)phenoxy]-2-propanol [(*R*)-6b]: ^{1}H NMR: 0.64 (s, 9H), 1.27 (s, 6H), 1.64 (s, 2H), 2.64 (d, 1H, *J* = 4), 4.01-4.05 (m, 2H), 4.29-4.32 (m, 1H), 4.46-4.48 (m, 2H), 6.78 (d, 2H, *J* = 8.5), 7.19-7.24 (m, 2H), 7.34-7.52 (m, 3H), 7.98 (d, 2H, *J* = 8.5); ^{13}C NMR: 31.64, 31.74, 32.28, 37.94, 56.90, 65.85, 68.69, 68.74, 113.70, 127.13, 128.40, 129.70, 133.20, 142.95, 155.90, 166.69; MS (FAB, *m*/z): 385 ([M+H]$^+$), 367, 313, 179 (100), 135; calcd.: C 74.96, H 8.39 for $C_{24}H_{32}O_4$; found: C 75.04, H 8.43.

(*S*)-2-Acetoxy-1-benzoyloxy-3-[4-(1,1,3,3-tetramethylbutyl)phenoxy]propane [(*S*)-7b]: ^{1}H NMR: 0.71 (s, 9H), 1.34 (s, 6H), 1.70 (s, 2H), 2.11 (s, 3H), 4.19 (d, 2H, *J* = 5), 4.54 (dd, 1H, *J* = 12, 6), 4.65 (dd, 1H, *J* = 12, 4), 5.53 (m, 1H), 6.84 (dd, 2H, *J* = 8.5, 4.5), 7.25-7.30 (m, 2H), 7.41-7.47 (m, 2H), 7.54-7.60 (m, 1H), 8.02 (dd, 2H, *J* = 8.5, 4.5); ^{13}C NMR: 21.43, 32.09, 32.20, 32.74, 38.41, 57.35, 63.60, 66.58, 70.34, 114.21, 127.57, 128.87, 130.11, 133.62, 143.46, 156.34, 166.56, 170.76; MS (CI, NH_3, *m*/z): 444 ([M+NH_4]$^+$), 427 ([M+H]$^+$), 367, 305, 221, 105 (100), 91, 57; calcd.: C 73.21, H 8.03 for $C_{26}H_{34}O_5$; found: C 73.32, H 8.25.

(*R*)-1-*n*-Propanoyloxy-3-[4-(1,1,3,3-tetramethylbutyl)phenoxy]-2-propanol [(*R*)-6c]: ^{1}H NMR: 0.40 (s, 9H), 0.85 (t, 3H, *J* = 7.5), 1.03 (s, 6H), 1.39 (s, 2H), 2.08 (q, 2H, *J* = 7.5), 2.34 (d, 1H, *J* = 4.5), 3.71 (m, 2H), 3.92-3.98 (m, 3H), 6.51 (d, 2H, *J* = 9), 6.97 (d, 2H, *J* = 9); ^{13}C NMR: 9.06, 27.43, 31.67, 31.77, 32.32, 37.98,

56.95, 65.30, 68.63, 68.68, 113.72, 127.16, 143.00, 155.94, 174.64; MS (*m/z*): 336 (M^+), 177, 131 (100), 107, 91, 57; calcd.: C 71.39, H 9.59 for $C_{20}H_{32}O_4$; found: C 71.47, H 9.67.

(*S*)-2-Acetoxy-1-*n*-propanoyloxy-3-[4-(1,1,3,3-tetramethylbutyl)phenoxy]propane [(*S*)-7c]: ^{1}H NMR: 0.64 (s, 9H), 1.07 (t, 3H, *J* = 7.5), 1.27 (s, 6H), 1.63 (s, 2H), 2.03 (s, 3H), 2.28 (q, 2H, *J* = 7.5), 4.03 (d, 2H, *J* = 5), 4.20 (dd, 1H, *J* = 12, 6), 4.35 (dd, 1H, *J* = 12, 4), 5.30 (m, 1H), 6.75 (d, 2H, *J* = 9), 7.20 (d, 2H, *J* = 9); ^{13}C NMR: 9.05, 20.99, 27.39, 31.67, 31.76, 32.31, 37.98, 56.92, 62.45, 66.03, 69.91, 113.76, 127.12, 143.00, 155.93, 170.30, 174.04; MS (*m/z*): 378 (M^+), 307, 173 (100), 135, 57, 43; calcd.: C 69.81, H 9.05 for $C_{22}H_{34}O_5$; found: C 69.90, H 9.11.

(*RS*)-1-Trimethylacetoxy-3-[4-(1,1,3,3-tetramethylbutyl)phenoxy]-2-propanol [(*RS*)-6d]: ^{1}H NMR: 0.65 (s, 9H), 1.16 (s, 9H), 1.28 (s, 6H), 1.64 (s, 2H), 2.56 (br s, 1H), 3.92-3.96 (m, 3H), 4.16-4.23 (m, 3H), 6.74 (d, 2H, *J* = 9), 7.21 (d, 2H, *J* = 9); ^{13}C NMR: 27.17, 31.66, 31.76, 32.29, 37.95, 38.85, 56.93, 65.27, 68.69, 113.71, 127.12, 142.87, 155.98, 178.70; MS (*m/z*): 364 (M^+), 293, 159 (100), 135, 107, 57; calcd.: C 72.49, H 9.96 for $C_{22}H_{36}O_4$; found: C 72.63, H 10.02.

(*R*)-1-*n*-Hexanoyloxy-3-[4-(1,1,3,3-tetramethylbutyl)phenoxy]-2-propanol [(*R*)-6e]: ^{1}H NMR: 0.65 (s, 9H), 0.83 (t, 3H, *J* = 6), 1.20-1.27 (m, 10H), 1.54-1.58 (m, 4H), 2.29 (t, 2H, *J* = 7.5), 2.53 (br s, 1H), 3.92-3.96 (m, 2H), 4.16-4.24 (m, 3H), 6.76 (d, 2H, *J* = 9), 7.21 (d, 2H, *J* = 9); ^{13}C NMR: 13.88, 22.28, 24.58, 31.25, 31.65, 31.74, 32.30, 34.10, 37.96, 56.92, 65.19, 68.58, 68.69, 113.68, 127.14, 142.98, 155.90, 174.02; MS (FAB, Glycerin, *m/z*): 379 ($[M+H]^+$), 307, 173 (100), 135, 108; calcd.: C 72.97, H 10.12 for $C_{23}H_{38}O_4$; found: C 73.04, H 10.23.

(*S*)-2-Acetoxy-1-*n*-hexanoyloxy-3-[4-(1,1,3,3-tetramethylbutyl)phenoxy]propane [(*S*)-7e]: ^{1}H NMR: 0.65 (s, 9H), 0.82 (t, 3H, *J* = 6), 1.19-1.27 (m, 10H), 1.52-1.63 (m, 4H), 2.02 (s, 3H), 2.27 (t, 2H, *J* = 7.5), 4.03 (d, 2H, *J* = 5), 4.20 (dd, 1H, *J* = 12, 6), 4.34 (dd, 1H, *J* = 12,4), 5.31 (m, 1H), 6.74 (d, 2H, *J* = 9), 7.21 (d, 2H, *J* = 9); ^{13}C NMR: 13.87, 20.87, 22.28, 24.57, 31.25, 31.66, 31.74, 32.29, 34.09, 37.95, 56.94, 62.43, 66.00, 69.13, 113.69, 127.14, 142.99, 155.91, 170.01, 174.24; MS (CI, NH_3, *m/z*): 438 ($[M+NH_4]^+$), 420 (M^+), 349, 215 (100), 135, 57, 43; calcd.: C 71.39, H 9.59 for $C_{25}H_{40}O_5$; found: C 71.59, H 9.81.

(*R*)-1-(4-Methylpentanoyloxy)-3-[4-(1,1,3,3-tetramethylbutyl)phenoxy]-2-propanol [(*R*)-6f]: ^{1}H NMR: 0.64 (s, 9H), 0.83 (d, 6H, *J* = 6), 1.27 (s, 6H), 1.42-1.58 (m, 3H), 1.63 (s, 2H), 2.30 (t, 2H, *J* = 7.5), 2.55 (d, 1H, *J* = 4.5), 3.87-3.95 (m, 2H), 4.11-4.26 (m, 3H), 6.75 (d, 2H, *J* = 9), 7.21 (d, 2H, *J* = 9); ^{13}C NMR: 22.20, 27.64, 31.66, 31.76, 32.20, 32.30, 33.67, 37.97, 56.94, 65.24, 68.62, 68.66, 113.71, 127.13, 142.96, 155.93, 174.21; MS (FAB, MB, *m/z*): 379 ($[M+H]^+$), 361, 245, 174 (100), 133, 117; calcd.: C 72.97, H 10.12 for $C_{23}H_{38}O_4$; found: C 72.85, H 10.20.

(*S*)-2-Acetoxy-1-(4-methylpentanoyloxy)-3-[4-(1,1,3,3-tetramethylbutyl)phenoxy]propane [(*S*)-7f]: ^{1}H NMR: 0.71 (s, 9H), 0.89 (d, 6H, *J* = 6), 1.34 (s, 6H), 1.50-1.59 (m, 3H), 1.70 (s, 2H), 2.10 (s, 3H), 2.33 (t, 2H, *J* = 7.5), 4.10 (d, 2H, *J* = 5), 4.28 (dd, 1H, *J* = 12,6), 4.42 (dd, 1H, *J* = 12, 4), 5.36 (m, 1H), 6.81 (dd,

2H, J = 9, 2), 7.27 (dd, 2H, J = 9, 2); ^{13}C NMR: 20.94, 22.16, 27.55, 31.64, 31.73, 32.11, 32.27, 33.62, 37.92, 56.87, 62.32, 65.95, 69.86, 113.70, 127.07, 142.91, 155.88, 170.22, 173.53; MS (CI, NH_3, *m/z*): 438 ($[M+NH_4]^+$), 426, 420, 349, 305, 215 (100), 135; calcd.: C 71.39, H 9.59 for $C_{25}H_{40}O_5$; found: C 71.61, H 9.85.

(*R*)-1-*n*-Decanoyloxy-3-[4-(1,1,3,3-tetramethylbutyl)phenoxy]-2-propanol [(*R*)-6g]: ^{1}H NMR: 0.32 (s, 9H), 0.49 (t, 3H, J = 6), 0.87 (m, 12H), 0.95 (s, 6H), 1.24 (m, 2H), 1.31 (s, 2H), 1.96 (t, 2H, J = 7.5), 2.36 (d, 1H, J = 4), 3.59-3.65 (m, 2H), 3.79-3.91(m; 3H), 6.43 (d, 2H, J = 9), 6.88 (d, 2H, J = 9); ^{13}C NMR: 14.11, 22.65, 24.90, 29.12, 29.25, 29.40, 31.66, 31.76, 31.85, 32.30, 34.14, 37.96, 56.94, 65.20, 68.64, 113.71, 127.12, 142.93, 155.95, 174.01; MS (*m/z*): 434 (M^+), 363, 229 (100), 209, 135, 57; calcd.: C 74.65, H 10.68 for $C_{27}H_{46}O_4$; found: C 74.77, H 10.88.

(*S*)-2-Acetoxy-1-*n*-decanoyloxy-3-[4-(1,1,3,3-tetramethylbutyl)phenoxy]propane [(*S*)-7g]: ^{1}H NMR: 0.71 (s, 9H), 0.88 (t, 3H, J = 6), 1.26 (m, 12H), 1.34 (s, 6H), 1.61 (m, 2H), 1.70 (s, 2H), 2.10 (s, 3H), 2.32 (t, 2H, J = 7.5), 4.10 (d, 2H, J = 5), 4.28 (dd, 1H, J = 12, 6), 4.42 (dd, 1H, J = 12, 4), 5.36 (m, 1H), 6.81 (dd, 2H, J = 9, 2), 7.27 (dd, 2H, J = 9, 2); ^{13}C NMR: 14.10, 20.98, 22.65, 24.86, 29.07, 29.24, 29.40, 31.65, 31.75, 31.84, 32.29, 34.08, 37.95, 56.89, 62.30, 65.97, 69.90, 113.72, 127.09, 142.94, 155.89, 170.89, 173.40; MS (CI, NH_3, *m/z*): 494 ($[M+NH_4]^+$), 476 (M^+), 405, 305, 271 (100), 135; calcd.: C 73.07, H 10.15 for $C_{29}H_{48}O_5$; found: C 73.36, H 10.35.

(*R*)-1-*n*-Dodecanoyloxy-3-[4-(1,1,3,3-tetramethylbutyl)phenoxy]-2-propanol [(*R*)-6h]: ^{1}H NMR: 0.65 (s, 9H), 0.81 (t, 3H, J = 6), 1.19 (m, 16H), 1.27 (s, 6H), 1.56 (m, 2H), 1.64 (s, 2H), 2.29 (t, 2H, J = 7.5), 2.65 (d, 1H, J = 4), 3.92-3.95 (m, 2H), 4.16-4.23 (m, 3H), 6.75 (d, 2H, J = 9), 7.20 (d, 2H, J = 9); ^{13}C NMR: 14.12, 22.68, 2414.12, 22.68, 24.91, 29.13, 29.25, 29.33, 29.45, 29.60, 31.66, 31.76, 31.90, 32.31, 34.15, 37.96, 56.94, 65.20, 68.62, 68.67, 113.70, 127.13, 142.95, 155.93, 174.03; MS (*m/z*): 462 (M^+), 391, 257 (100), 209, 191, 135, 57; calcd.: C 75.44, H 10.70 for $C_{29}H_{49}O_4$; found: C 75.59, H 10.73.

(*S*)-2-Acetoxy-1-*n*-dodecanoyloxy-3-[4-(1,1,3,3-tetramethylbutyl)phenoxy]propane [(*S*)-7h]: ^{1}H NMR: 0.71 (s, 9H), 0.88 (t, 3H, J = 6.5), 1.26 (m, 16H), 1.34 (s, 6H), 1.61 (m, 2H), 1.70 (s, 2H), 2.09 (s, 3H), 2.32 (t, 2H, J = 7.5), 4.10 (d, 2H, J = 5), 4.27 (dd, 1H, J = 12, 6), 4.42 (dd, 1H, J = 12, 4), 5.36 (m, 1H), 6.81 (dd, 2H, J = 9, 2), 7.27 (dd, 1H, J = 9, 2); ^{13}C NMR: 14.11, 20.97, 22.67, 24.87, 29.08, 29.24, 29.32, 29.44, 29.59, 31.65, 31.75, 31.89, 32.29, 34.08, 37.94, 56.90, 62.30, 65.99, 69.90, 113.72, 127.09, 142.93, 155.90, 170.25, 173.39; MS (FAB, MB, *m/z*): 504 (M^+), 445, 433, 299 (100), 245, 183, 135, 117; calcd.: C 73.76, H 10.39 for $C_{31}H_{52}O_5$; found: C 73.63, H 10.57.

(*R*)-1-*n*-Hexadecanoyloxy-3-[4-(1,1,3,3-tetramethylbutyl)phenoxy]-2-propanol [(*R*)-6i]: ^{1}H NMR: 0.65 (s, 9H), 0.82 (t, 3H, J = 6.5), 1.19 (m, 24H), 1.27 (s, 6H), 1.57 (m, 2H), 1.64 (s, 2H), 2.29 (t, 2H, J = 7.5), 2.58 (br s, 1H), 3.92-3.95 (m, 2H), 4.16-4.20 (m, 3H), 6.76 (d, 2H, J = 8.5), 7.21 (d, 2H, J = 7.5); ^{13}C NMR: 14.13, 22.69, 24.91, 29.13, 29.26, 29.36, 29.46, 29.61, 29.65, 29.68, 31.66, 31.76, 31.92, 32.30, 34.15,

34.33, 37.96, 56.93, 65.19, 68.60, 68.67, 113.69, 127.13, 142.95, 155.91, 174.03; MS (CI, CH_4, *m/z*): 519 ($[M+H]^+$), 501, 447, 313 (100); calcd.: C 76.39, H 11.30 for $C_{33}H_{58}O_4$; found: C 76.46, H 11.53.

(*S*)-2-Acetoxy-1-*n*-hexadecanoyloxy-3-[4-(1,1,3,3-tetramethylbutyl)phenoxy]propane [(*S*)-7i]: ^1H NMR: 0.71 (s, 9H), 0.88 (t, 3H, *J* = 6.5), 1.25 (m, 24H), 1.34 (s, 6H), 1.61 (m, 2H), 1.70 (s, 2H), 2.10 (s, 3H), 2.32 (t, 2H, *J* = 7.5), 4.10 (d, 2H, J = 5), 4.28 (dd, 1H, *J* = 12, 6), 4.42 (dd, 1H, *J* = 12, 4), 5.36 (m, 1H), 6.81 (dd, 2H, *J* = 9, 2), 7.27 (dd, *J* = 9, 2); ^{13}C NMR: 14.13, 20.99, 22.69, 24.88, 29.09, 29.26, 29.36, 29.46, 29.69, 31.66, 31.76, 31.92, 32.30, 34.09, 37.96, 56.91, 62.31, 66.00, 69.91, 113.73, 127.10, 142.96, 155.91, 170.10, 173.42; MS (CI, NH_3, *m/z*): 578 ($[M+NH_4]^+$), 560 (M^+), 545, 501, 489, 355 (100), 305, 135; calc.: C 74.95, H 10.78 for $C_{35}H_{60}O_5$; found: C 75.05, H 10.82.

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(*Received in UK* 18 *April* 1995)