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Tetrahedron 61 (2005) 11952–11964

Oxidative nucleophilic substitution of hydrogen in nitroarenes with phenylacetic acid derivatives

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Received 9 June 2005; revised 1 September 2005; accepted 15 September 2005

Available online 10 October 2005

Dedicated to Professor V. I. Minkin on the occasion of his 70th birthday

Abstract—Oxidative nucleophilic substitution of hydrogen (ONSH) in nitroarenes with carbanion of isopropyl phenyl acetate gives various products depending on the conditions and oxidant. The reaction carried out in liquid ammonia and $KMnO_4$ oxidant gives *iso*-propyl α-hydroxy-α-nitroarylphenylacetates formed via hydroxylation of the initial ONSH products. In some cases additionally dimeric, trimeric and tetrameric products are formed. In THF and $Bu_4N^+MnO_4^-$ or DDQ oxidants simple ONSH products are formed whereas oxidation by dimethyl dioxirane (DMD) gave *iso*-propyl hydroxyaryl phenyl acetates. The dimeric and trimeric products are apparently formed via coupling of nitrobenzylic radicals generated in course of oxidation with nitrobenzylic carbanions of the ONSH products.

1. Introduction

Oxidative nucleophilic substitution of hydrogen (ONSH), in nitroarenes and other electron deficient arenes is presently a well recognized process.[1–6] Of particular interest and value is introduction of carbon substituents into nitroaromatic rings via oxidation of σ^H adducts of carbon nucleophiles such as Grignard reagents[7–9] and carbanions[10] to nitroarenes. In our recent studies we have shown that this reaction proceeds efficiently between nitroarenes and tertiary (methinic) carbanions generated from 2-phenylalkanenitriles[11] and esters of *iso*-butyric[12] and 2-phenylpropionic acids.[13] Addition of these carbanions to nitroarenes proceeds mainly *para* to the nitro group and the produced σ^H adducts are oxidized by $KMnO_4$[11–13] in liquid ammonia or DDQ in THF giving products of ONSH in *para* positions. It should be noted that oxidation with $KMnO_4$ is sensitive to steric hindrances, bulky substituents *ortho* to the addition site (*meta* to the nitro group) hinder or inhibit the oxidation process.[11] On the other hand, oxidation of these σ^H adducts with dimethyl dioxirane (DMD) in THF gives *para* substituted phenols.[14,15] This oxidant reacts directly with negatively charged nitro group of the σ^H adducts in a process analogous to the Nef reaction.[15]

Oxidation of σ^H adducts of secondary (methylenic) carbanions to nitroarenes is somewhat more complicated process because the addition can take place at *ortho* and *para* positions so isomeric σ^H adducts and subsequently ONSH products can be formed. Moreover the products in which hydrogen of the methylenic group is replaced with a nitroaromatic ring are much stronger CH acids than the carbanion precursors thus in the case the reaction media contain basis agents, the ONSH products could be deprotonated and further oxidized. The highly stabilized nitrobenzylic carbanions of the ONSH products are weak nucleophiles and do not form σ^H adducts with nitroarenes so disubstitution via ONSH is not observed. There are many reported examples of ONSH process with secondary carbanions in which atmospheric oxygen acted as the oxidant, usually in these cases the reaction requires excess of base.[10,16,17] It is therefore supposed that σ^H adducts of such carbanions are further deprotonated before being oxidized with oxygen. The reaction of secondary carbanion of phenylacetonitrile with nitrobenzene in liquid ammonia and $KMnO_4$ oxidant gave a mixture of *o*- and *p*-nitrobenzophenones.[18] It seems that the initial ONSH products formed by oxidation of the σ^H adducts *ortho* and *para* to the nitrogroup were deprotonated and the produced carbanions oxidized to cyanohydrines that dissociated to benzophenones.

Keywords: Carbanions; Nitroarenes; σ-Adducts; Oxidation; Nucleophilic substitution.
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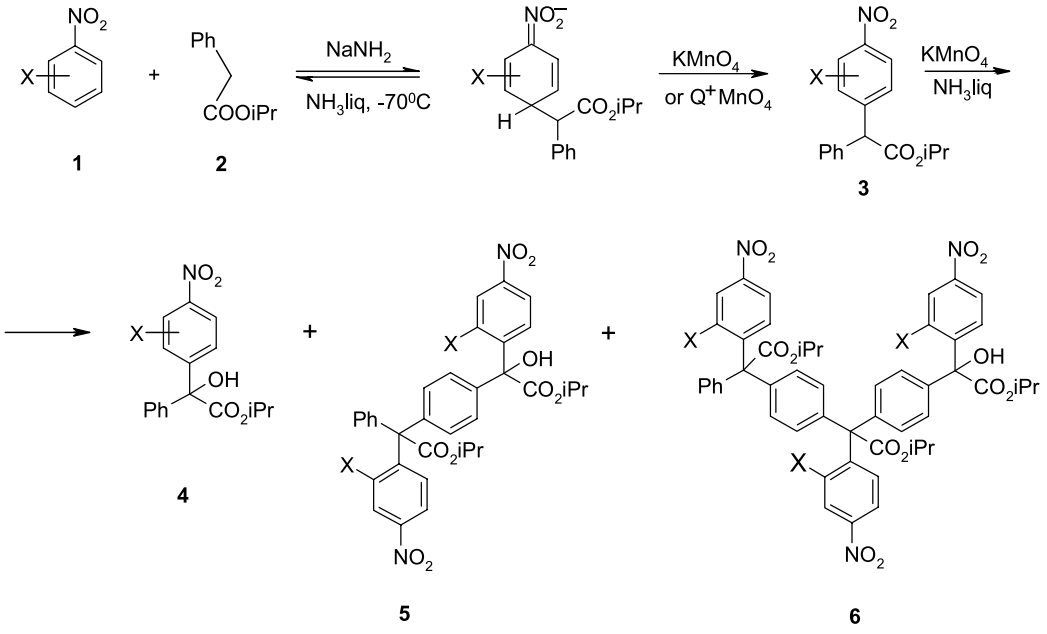
doi:10.1016/j.tet.2005.09.053



Scheme 1.

2. Results and discussion

The products of ONSH reaction in nitroarenes by carbanions of alkyl phenylacetates—esters of nitroaryl phenylacetic acids—upon deprotonation and further oxidation should form esters of α-hydroxy nitroaryl phenylacetic acids. Since such esters should be stable under these conditions we have studied ONSH reaction in a series of substituted nitrobenzenes **1a–o** with carbanion of *iso*-propyl phenylacetate **2**. The reactions were carried out in liquid ammonia, the carbanions generated by action of $NaNH_2$ and the intermediate σ^H adducts oxidized with $KMnO_4$. Since the expected ONSH products **3a** should be strong CH acids the base was used in excess. The reaction of **2** with nitrobenzene **1a** in ratio 1:1 gave not a simple ONSH product **3a**, but *iso*-propyl 2-phenyl-2-*p*-nitrophenyl-2-hydroxypropionate **4a**, in moderate yield 40%. Obviously, the expected initially formed ONSH product was further deprotonated and oxidized in form of nitrobenzylic carbanion to the hydroxy ester. When nitrobenzene was used in an excess (2 equiv) yield of **4a** was much higher: 78%. It seems therefore that in the former case, due to moderate electrophilicity of **1a**, the addition equilibrium was not sufficiently shifted to the σ^H adducts, hence in further experiments nitroarenes were used in excess. It should be mentioned that under these conditions the ONSH reaction proceeded only *para* to the nitro group. Similar products were formed in the reaction of **2** with a series of nitroarenes **1b–m**.

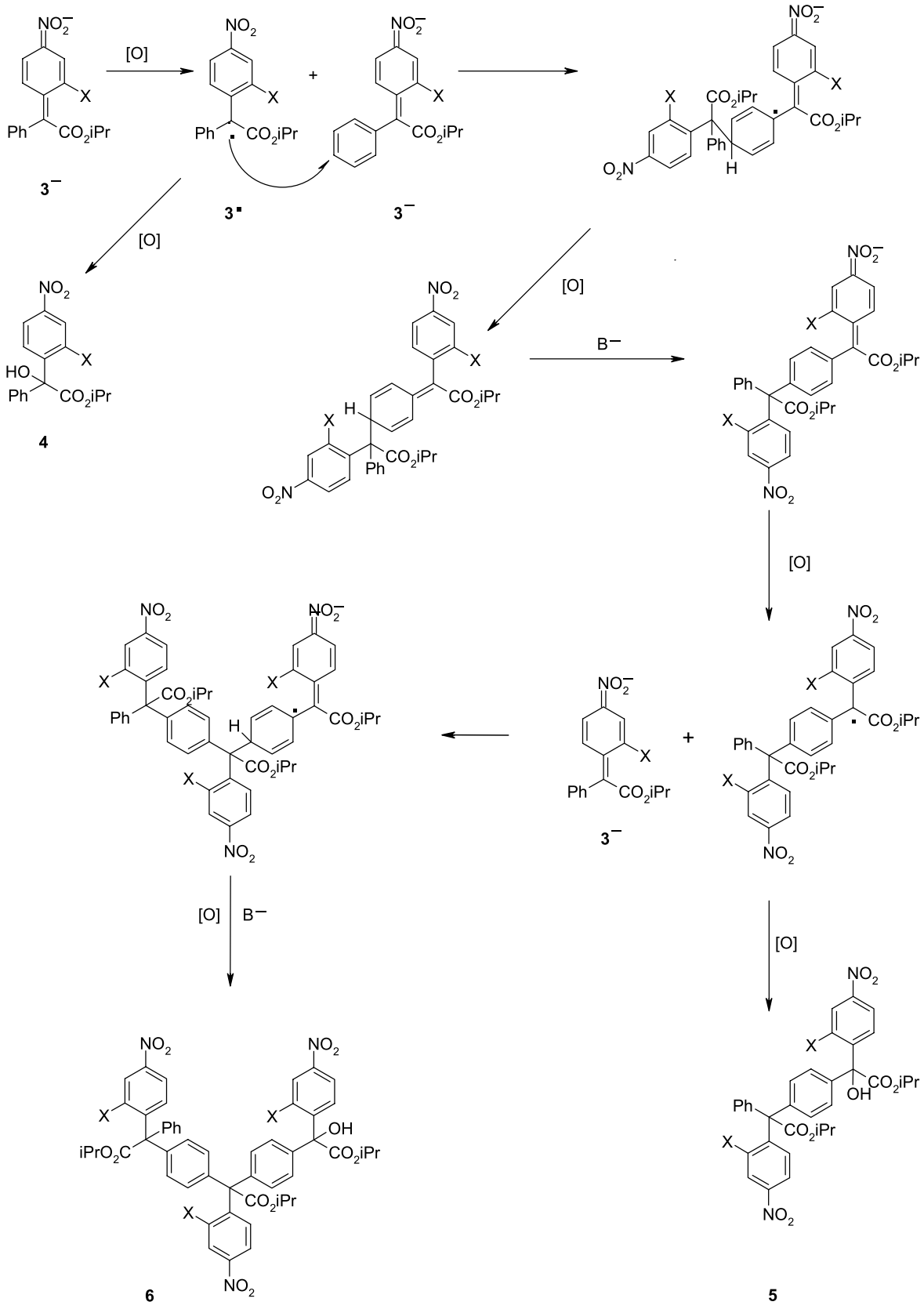
The reaction of **2** with *m*-halonitrobenzenes **1c**,**e**,**g**,**h**, and **j** was more complicated. Besides of the expected α-hydroxyesters **4c**,**e**,**g**,**h**,**j**, produced via hydroxylation of the initial ONSH products, substantial quantities of products of higher molecular weight were isolated from the reaction mixtures. For instance the reaction of **2** with *m*-chloronitrobenzene **1e** gave expected hydroxyester **4e** 29% and two other products **5e** and **6e**. On the basis of detailed MS (EI and ESI experiments), ^1H and ^{13}C NMR analysis including correlation spectra of the compounds **5e** and **6e** they were assigned dimeric and trimeric structures, respectively, as shown in Scheme 1. Detailed analyses of the NMR spectra of compounds **5** and **6** are presented at the end of the paper. Results of the reaction of **2** with nitroarenes and $KMnO_4$ oxidant are given in Table 1

Table 1. Oxidation of σ^H adducts of $\mathbf{2}^-$ to nitroarenes by $KMnO_4$ in NH_3liq and by $Bu_4N^+MnO_4^-$ in THF (Scheme 1)

$ArNO_2$		Products, No. yields							
X	No.	$KMnO_4/NH_3liq$[a]						$Q^+MnO_4^-$/THF[b]	
H	**1a**	**4a**	78						
2-F	**1b**	**4b**	77					**3b**	45
3-F	**1c**	**4c**	39	**5c**	27	**6c**	5	**3c**	20
2-Cl	**1d**	**4d**	57					**3d**	30
3-Cl	**1e**	**4e**	29	**5e**	39	**6e**	15	3e	69
2-Br	**1f**	**4f**	60					**3f**	26
3-Br	**1g**	**4g**	27	**5g**	48	**6g**	17	**3g**	73
3-I	**1h**	**4h**	22	**5h**	37	**6h**	13		
3-MeO	**1j**	**4j**	29	**5j**	19	**6j**	23[c]		
2-CN	**1k**	**4k**	47						
2-NT[d]	**1l**	**4l**	26						
1-NN[e]	**1m**	**4m**	40						

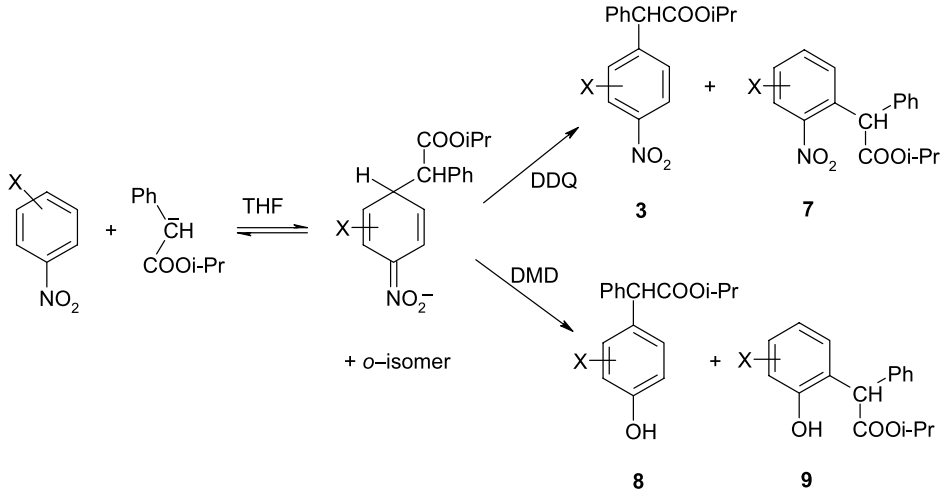
[a] Ratio $ArNO_2$: **2**=2.
[b] Ratio $ArNO_2$: **2**=1.2.
[c] Tetramer **6j′** was also isolated.
[d] 2-Nitrothiophene.
[e] 1-Nitronaphthalene.

It should be stressed that compounds **5** and **6** were formed only when the reacting nitroarene contained a substituent X located *meta* to the nitro group. It appears that this substituent affects the reaction course due to its steric, not electronic, effects because products **5** and **6** were formed also in the reaction of **2** with nitrobenzene substituted in *meta* position not only with halogens but also with electrodonating group (X=OMe), *m*-nitroanisole **1j**. It appears that hydroxy esters **3** and dimeric and trimeric products **5** and **6** are formed as a result of oxidation of



Scheme 2.

carbanions of initial ONSH products **3**. In the oxidation of the initial products of ONSH in nitroarenes containing substituents X in *meta* position formation of dimeric products **5** competes with the hydroxylation reaction. In order to confirm that products **4**, **5** and **6** are indeed formed via oxidation of nitrobenzylic carbanions of the initial ONSH products, **3a** and **3e** were prepared independently via S_NAr of halogen in 4-fluoro and 3,4-dichloronitrobenzene



Scheme 3.

with carbanion of **2**. These nitroarylated esters **3a** and **3e** dissolved in liquid ammonia are deprotonated by the solvent to a low degree, addition of $NaNH_2$ to such solutions converts **3a** and **3e** into carbanions $\mathbf{3a}^-$ and $\mathbf{3e}^-$ that are stable and can be recovered upon acidification of the solution with NH_4Cl. Treatment of a solution of carbanion of **3a** in NH_3 liquid with $KMnO_4$ gave **4a** whereas carbanion of **3e** gave a mixture of **4e**, **5e** and **6e**, respectively. Composition of the latter mixture was similar to that obtained in the direct reaction of **2** with 3-chloronitrobenzene. These results confirm that of **4**, **5** and **6** are produced by further conversion of **3** as shown in Scheme 1.

It appears that compounds **5** and **6** are formed via coupling of carbanions $\mathbf{3}^-$ with free radicals of **3**, produced by oxidation of carbanions of **3** by $KMnO_4$. A speculative pathway of formation of **4** and **5** is shown in Scheme 2. Perhaps substituents X hinder conjugation of the carboanionic and free radical centers in $\mathbf{3}^-$ and $\mathbf{3}^{\cdot}$ with the nitroaryl rings, whereas steric hindrances prevent addition of $\mathbf{3}^{\cdot}$ to the carbanion α- to the alkoxycarbonyl group. Thanks to the increased electron density on unsubstituted phenyl ring of $\mathbf{3}^-$ it adds electrophilic radical $\mathbf{3}^{\cdot}$ giving anion-radical, that is subsequently oxidized, deprotonated and hydroxylated to **5**. On the other hand, direct oxidation of $\mathbf{3}^{\cdot}$ with $KMnO_4$ gave **4**. Thus competition between formation of **4** and **5** seems to depend on relation of rates of direct oxidation $\mathbf{3}^{\cdot} \rightarrow \mathbf{4}$ and addition of $\mathbf{3}^{\cdot}$ to $\mathbf{3}^-$, that is affected by steric effects of substituents X. Similar carbanion coupling under oxidative condition has been previously observed.[19,20]

In order to verify this hypothesis we have done additional experiments changing ratio and order of mixing of the reactants. However changes of the procedure, for example, slow addition of a solution of σ^H adducts to a solution of $KMnO_4$ did not change the outcome of the reaction. Attempts to arrest the reaction of $\mathbf{2}^-$ with $ArNO_2$, carried out in NH_3 and $KMnO_4$ oxidant, on the stage of **3** by using small amounts of the base and oxidant gave negative results. In such experiments mixtures of starting materials and products **3**, **4** (and **5** and **6**) were produced.

Formation and oxidation of σ^H adducts with permanganate anions can be carried out not only in liquid NH_3 but also in moderately polar solvents, for example, THF, provided a soluble salt of this anion is used. Indeed, treatment of **2** with *t*-BuOK in THF produced carbanions that form σ^H adducts upon addition of $ArNO_2$. Oxidation of such system with tetrabutylammonium permanganate, results in formation of ONSH products **3** in moderate to good yields. Interestingly no hydroxylated esters **4** were formed under these conditions and the reaction proceeded only *para* to the nitro group. Results of these reactions are presented in Table 1.

Another oxidant, widely used for oxidation of the anionic σ^H adducts, is DDQ. For obvious reasons it cannot be used in the reactions carried out in liquid ammonia. Oxidation of σ^H adducts of $\mathbf{2}^-$ to nitroarenes generated in THF with DDQ gave somewhat different results as compared with oxidation by $Q^+MnO_4^-$. As it was mentioned earlier, permanganate anions oxidize efficiently only σ^H adducts *para* to the nitro group so with $KMnO_4$ and $Q^+MnO_4^-$ oxidants the reaction of **2** with nitroarenes **1** gave products **3**, **4** (and **5** and **6**), in which hydrogen located *para* to the nitro group was substituted by the carbanion moiety. Oxidation of σ^H adducts with DDQ is less sensitive to steric hindrances and the reaction of $\mathbf{2}^-$ with nitroarenes and DDQ oxidant always gives mixtures of *para* and *ortho* isomers of the ONSH products **3** and **7**, respectively (Scheme 3, Table 2).

Since oxidation of the σ^H adducts of $\mathbf{2}^-$ and nitroarenes by DDQ in THF is not accompanied with hydroxylation we have applied this system for the ONSH in nitrobenzene **1a** and 4-chloronitrobenzene **1o** with phenylacetonitrile carbanion. This reaction proceeded efficiently giving a mixture of 2-nitrophenyl and 4-nitrophenyl phenylacetonitrile **10a** and **11a** and 2-nitro-5-chlorophenyl acetonitrile **11o**, respectively. Further hydroxylation of the ONSH products was not observed (Scheme 4).

Although oxygen is a moderately active oxidant, it can oxidize σ^H adducts, particularly those produced by

Table 2. Oxidation of σ^H adducts of $\mathbf{2}^-$ to nitroarenes by DDQ in THF (Scheme 3)

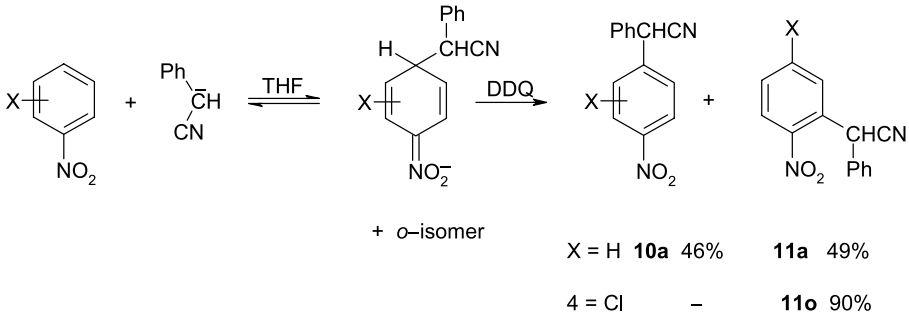
$ArNO_2$		Products			
X	No.	No. yield			
H	**1a**	**3a**	16	**7a**	30[a]
2-F	**1b**	**3b**	36	**7b**	17[b]
3-F	**1c**	**3c**[c]	54		
2-Cl	**1d**	**3d**	44	**7d**	23[a]
3-Cl	**1e**	**3e**	59	**7e**	10[a]
2-Br	**1f**	**3f**	32	**7f**	24[b]
3-Br	**1g**	**3g**	56	**7g**	9[b]
1-NN[d]	**1m**	**3m**	12	**7m**	75[a]
3-CN	**1n**	**3n**	32	**7n**	53[a]
4-Cl	**1o**			**7o**	78[a]

[a] Ratio $ArNO^2$: **2**=2.
[b] Ratio $ArNO^2$: **2**=1.2.
[c] Small amount of a mixture containing isomeric products *ortho*-substitution was formed but not separated.
[d] 1-Nitronaphthalene.

o- and *p*-isomers of substituted phenols usually in good yields (Table 3).

2.1. Detailed analysis of the NMR spectra of compounds 5–6

The structures of compounds **3**, **4**, **7**, **8** and **9** (see Schemes 1 and 3) could be easily established on the basis of ^{1}H NMR spectra only, but a special effort has to be made in order to prove the structures of the products of higher molecular weight (**5** and **6**), which were obtained when $KMnO_4$ was used as the oxidizing agent (see Scheme 1). For all these compounds a meticulous analysis of the ^{1}H and ^{13}C NMR data including *g*-HSQC and *g*-HMQC spectra has to be performed. A similar analysis has to be made also for compounds **4c**, **4e**, **4g**, **4h** and **4j** which served as the model compounds.



Scheme 4.

secondary carbanions that under the reaction conditions can be deprotonated to dianions. We have made a few experiments in order to oxidize σ^H adducts of $\mathbf{2}^-$ to nitroarenes in liquid ammonia and in THF bubbling oxygen through the reaction mixtures. Indeed under these conditions the oxidation proceeded giving mixtures of ONSH products **3**, and hydroxylated products **4** but usually in low overall yields so this line of experiments was not pursued.

As it was mentioned earlier oxidation of the σ^H adducts of tertiary carbanions to nitroarenes with dimethyldioxirane, DMD, gave *p*-substituted phenols—the oxidation proceeded at the negatively charged nitro group.[14,15]

In our experiments we have found that oxidation of σ^H adducts of secondary carbanions $\mathbf{2}^-$ to nitroarenes with DMD proceeds also along this pathway to give mixtures of

Table 3. Oxidation of σ^H adducts of 2^- to nitroarenes by DMD in THF (Scheme 3)[a]

$ArNO_2$		Products			
X	No.	No. yield			
2-Cl	**1d**	**8d**	49	**9d**	17
3-Cl	**1e**	**8e**	65	**9e**	12
2-Br	**1f**	**8f**	42	**9f**	18
3-Br	**1g**	**8g**	76	**9g**	20
1-NN	**1m**	**8m**	19	**9m**	42
4-Cl	**1o**			**9o**	60

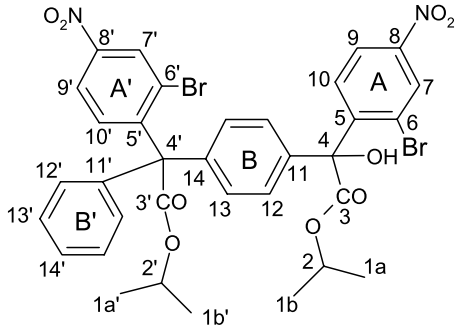
[a] Ratio $ArNO^2$: **2**=1.2.

The ^{1}H and ^{13}C NMR data obtained for compound **5g** has been collected in Table 4, for compounds **4c**, **4e**, **4g**, **4h** and **4j** in Tables 5 and 6, and for compounds **5** in Tables 7 and 8 (Tables 5–8 are available in Supplementary data). This form of the presentation of the vast NMR material revealed the trends occurring in the chemical shifts under the influence of substituents and provided us with an additional check of the correctness of the assignments made on the basis of the correlation spectra.

An analysis of the spectra has been performed in two steps. In the first step, the signals in the ^{1}H and ^{13}C NMR spectra of the 3-substituted α-hydroxyesters, **4c**, **4e**, **4g**, **4h** and **4j**, were assigned on the basis of the general knowledge of substituent effects, and the preliminary assignments have been confirmed by means of the *g*-HSBC and *g*-HMBC spectra.

In the second step the ^{1}H and ^{13}C NMR spectra of the products of the oxidation reaction denoted as **5** have been compared with the spectra of the corresponding compounds **4**. It becomes immediately clear that the spectra of these new compounds contain two fragments which are very similar, in some cases almost identical, to the spectra of compounds **4**. The differences observed can be easily interpreted in terms of the substitution effects. Furthermore, many of the signals are apparent doublets, the differences between them being in the range of several Hz at 11.7 T, which is typical of the pairs of diastereoisomers. A thorough

Table 4. ^{1}H (in parantheses) and ^{13}C NMR spectra of bromo dimer **5g** measured in CDCl3 and acetone-d_6 and the relevant *g*-HMB correlation peaks; all data are in ppm against TMS[a,b,c]



	In $CDCl_3$	In CD_3COCD_3	HMBC	C/HNo.	In $CDCl_3$	In CD_3COCD_3	HMBC
2	72.12; 72.11 (5.22)[dd]	71.58; 71.56 (5.17)[e]		2′	70.69 (5.22)[d]	71.13 (5.17)[e]	
3	172.31; 172.30	172.15; 172.10	2, O*H*, CH3	3′	170.45; 170.41	170.98	2′, CH3
4	80.73; 80.70	81.83; 81.88	10,12	4′	67.10; 67.08	67.83	10′,12′,13
5	147.67	149.54; 149.51	7,9,O*H*	5′	150.69; 150.65	151.60	7′,9′, 10′
6	124.30	124.82	7,9,10	6′	126.84; 126.81	127.35	7′,9′,10′
7	129.32 (8.480)	129.70 (8.445)	9,10	7′	129.00; 128.98 (8.485)	129.45 (8.470; 8.466)	9′
8	147.57; 147.53	148.54	7,9,10	8′	147.00	148.01	7′,9′, 10′
9	121.63; 121.62 (8.015; 8.008)	122.59 (8.133; 8.128)	7,10	9′	121.71 (8.080; 8.076)	122.74 (8.189; 8.187)	7′,10′
10	131.63; 131.60 (7.037; 7.009)	132.19; 132.16 (7.287; 7.264)		10′	132.01 (7.012; 7.009)	133.19 (7.121; 7.119)	
11	138.31; 138.28	140.30; 140.27	12,13,O*H*	11′	141.26; 141.22	141.76; 141.72	13′
12	126.72; 126.67 (7.602)	127.82;1 27.78 (7.657)		12′	129.83 (7.23)	130.73 (7.314)	13′
13	130.42; 130.37 (7.41)	130.97; 130.93 (7.448)		13′	128.52; 128.50 (7.35)[f]	129.21; 129.20 (7.384)[g]	14′
14	140.54; 140.53	142.13; 142.09	12	14′	128.03; 128.00 (7.35)[f]	128.64; 128.63 (7.384)[g]	12′,13′
O*H*	(4.370; 4.357)				(5.8)		

[a] Signals of the protons 1 and 1′ (centred at ca. 1.26 ppm) and carbons 1 and 1′ (centred at ca. 21.5 ppm) are strongly overlapped.
[b] *J*HH coupling values are almost identical with those observed for the corresponding compounds **4** (see Table 5 in Supplementary data) and therefore are not shown in this Table.
[c] *g*-HSQ correlation peaks are shown in Table 8 (see Supplementary data).
[d–g] Signals overlapped.

analysis of the *g*-HSBC and *g*-HMBC spectra performed for compounds **5** indicated that, as a matter of fact, a dimeric structure should be assigned to them (see Scheme 1). As an example the spectra obtained for the bromo derivative **5g**, are discussed below more closely.

The measurements of the spectra for this compound have been performed in $CDCl_3$ and acetone-d_6 solutions and at two magnetic fields, 9.4 and 11.7 T. This allowed us to clarify the problems when an accidental overlap of the signals occurred and to discriminate between a genuine coupling and a splitting of the signals due to the presence of diastereoisomers.

Out of the two groups of signals corresponding to the quaternary aliphatic carbons, appearing at about 80 and at 67 ppm, those at the lower field should be assigned to carbon 4 and those at the higher field to carbon 4′. The correlation signals observed in the *g*-HMBC spectra recorded in acetone-d_6 between these two carbons and protons at 7.287; 7.264 and 7.121; 7.119 ppm allow one to assign the latter to H10 and H10′, respectively. Subsequent assignment of all the remaining signals of rings A and A′ becomes easy. Further crucial information is provided by the correlations observed in the $CDCl_3$ solution between the proton of the OH group and the carbon signals at 172.31; 172.30, 147.67 and 138.31; 138.28 ppm which can be consequently assigned to carbons C3, C5 and C11, respectively. The correlations (in acetone-d_6) between carbon C4′ and signals at 7.121; 7.119, 7.314 and 7.448 ppm indicate that the latter belong to H10′, H12′ and H13, respectively.

A similar analysis performed for the compounds with still higher molecular weights showed that the trimeric and tetrameric structures should be assigned to them (see Scheme 1). However, a precise assignment of the signals to particular hydrogen and carbon atoms in ^{1}H and ^{13}C NMR spectra, respectively, is rather difficult for obvious reasons. First of all, the number of diastereoisomers increases causing further splitting of the signals and secondly, a discriminating influence of the OH group on the shielding of the atoms in more remote rings is almost negligible. As a result, in many cases a strong overlap of the signals occurs. Therefore, the NMR data for compounds **6** have been included in

Section 3, where only tentative assignments have been proposed.

3. Conclusions

Secondary carbanions of isopropyl phenyl acetate **2** add to nitroarenes in positions of *ortho* and *para* to the nitro group. The produced anionic σ^H adducts can be oxidized by a variety of oxidants. Permanganate anions oxidize only σ^H adducts *para* to the nitro group, the final outcome depends on the conditions. In liquid ammonia the initially formed ONSH products **3** are oxidized further to esters of α-hydroxyacids **4** and, in some cases, undergo dimerization to **5** and trimerization to **6**. This unprecedented process is observed in the reaction of *m*-substituted nitroarenes and proceeds apparently via coupling of carbanions with free radicals, generated during oxidation of the carbanions. On the other hand, oxidation of the σ^H adducts with tetrabutylammonium permanganate carried out in THF gave ONSH products **3**, under these conditions only σ^H adducts in *para* positions are oxidized. DDQ oxidizes both *ortho* and *para* σ^H adducts thus in the reaction of $\mathbf{2}^-$ with nitroarenes and DDQ oxidant mixtures of isomeric ONSH products are formed. Oxidation of σ^H adducts of $\mathbf{2}^-$ to nitroarenes with DMD proceeds at the negatively charged nitrogroup of the *ortho* and *para* σ^H adducts that results in formation of isomeric substituted phenols.

4. Experimental

4.1. General

^1H and ^{13}C NMR spectra were recorded with a Mercury-400BB (400 MHz) and Bruker DRX 500 instruments. Mass spectra were measured on AMD 604 Inectra GmBH spectrometer using EI or ESI. For analytical TLC Merck alufolien sheets Kieselgel 60 F_{254} were used. For column chromatography silica gel 230–400 mesh Merck was used. DMF was distilled over calcium hydride and stored over molecular sieves, THF was distilled over potassium benzophenone ketyl. Acetone solution of DMD was prepared according to the literature procedure.[21] All reactions were performed under argon atmosphere.

Nitroarenes, DDQ, phenylacetonitryle and potassium *tert*-butoxide were commercial products. Commercially available potassium permanganate was ground. Isopropyl phenylacetate was synthesized from phenylacetic acid and *iso*-propyl alcohol.[13] Tetrabutylamonium permanganate was prepared as follows: To a stirred solution of tetrabutylamonium bromide (5.2 mmol) in water (15 ml) a solution of potassium permanganate 5 mmol in water (100 ml) was added. The precipitated product was filtered, washed with water (10 ml) and dried in vacuum until constant weight. The product can be stored in fridge for no longer then 1 month. Caution: dry tetrabutylamonium permanganate is explosive thus it must not be heated during drying. All usual precautions should be taken. For safety reason we dried the product in small, 3–4 mmol portions.

4.2. Procedures for the oxidative substitution of hydrogen with carbanion of 2

Procedure A. Oxidation with $KMnO_4$ in liquid ammonia. To a suspension of sodium amide freshly prepared from sodium (120 mg, 5.2 mmol) in liquid ammonia (ca 25 ml), at −70 °C, *iso*-propyl phenylacetate **2** (360 mg, 2 mmol) in THF (1.5 ml) was added. After 3 min nitroarene **1** (4 or 2.4 mmol) in THF (1.5 ml) was added dropwise in 1 min. The reaction mixture was stirred for additional 3 min, and solid potassium permanganate (632 mg, 4 mmol) was added in one portion. The reaction mixture was stirred for 4 min and quenched with solid ammonium chloride (ca. 400 mg, 8 mmol). The cooling bath was removed and ammonia was evaporated. To the residue a saturated aqueous solution of oxalic acid was added and the mixture was extracted with ethyl acetate (3×20 ml). The combined organic layers were dried over $MgSO_4$. The solvent was evaporated and the products were purified by column chromatography with AcOEt/hexane as eluent.

Procedure B. Oxidation with DDQ. To a solution of *t*-BuOK (112 mg, 1 mmol) in THF (10 ml) at −70 °C, a solution of *iso*-propyl phenylacetate **2** (1 mmol) in THF (1.5 ml) was added. After 3 min nitroarene **1** (1.2 mmol) in THF (1.5 ml) was added dropwise during 1 min and the mixture was stirred for 3 min at −70 °C. Then solution of DDQ (273 mg, 1.2 mmol) in DMF (2 ml) was added and the reaction mixture was stirred for 5 min, quenched with saturated aqueous NH_4Cl (0.2 ml) and the cooling bath was removed. The reaction mixture was poured to water (100 ml) and extracted with ethyl acetate (3×20 ml) and extracts were washed with brine and dried over $MgSO_4$. The solvent was evaporated and products were purified by column chromatography in AcOEt/hexane. With some cases we were not able to separate the isomeric products **3** and **7** by column chromatography, so compositions of the mixtures were established by ^1H NMR spectroscopy.

Procedure C. Oxidation with $Q^+MnO_4^-$. Experiments were conducted according to procedure B. Instead of DDQ solid $Q^+MnO_4^-$ was added. After quench 10 ml of saturated aqueous solution of oxalic acid was added and procedure B was followed.

Procedure D. Oxidation with DMD. Experiments were conducted according to procedure B. Instead of DDQ water (0.02 ml, 1 mmol) and acetone solution of DMD (ca. 1.2 mmol, 20 ml of ca. 0.06 M) was added to the mixture. The color changed to bright yellow. After 5 min of stirring, saturated aqueous NH_4Cl (0.2 ml) was added the cooling bath was removed and procedure B was followed.

4.2.1. *iso*-Propyl α-(4-nitrophenyl)phenylacetate 3a. Colourless oil. ^1H NMR (400 MHz, $CDCl_3$): $\delta=1.22$ (d, 3H, $J=6.2$ Hz), 1.25 (d, 3H, $J=6.2$ Hz), 5.06 (s, 1H), 5.06–5.14 (m, 1H), 7.27–7.38 (m, 5H), 7.47–7.51 (m, 2H), 8.15–8.19 (m, 2H). ^{13}C NMR ($CDCl_3$): $\delta=21.54$, 21.63, 56.93, 69.27, 123.66, 127.74, 128.39, 128.89, 129.58, 137.42, 146.14, 147.03, 170.8. MS (EI): m/z (%)=299 (M^+, 6), 212 (100), 196 (28), 165 (66), 105 (29), 43 (79). Anal. Calcd for $C_{17}H_{17}NO_4$: C, 68.22: H, 5.72; N, 4.68. Found: C, 68.17; H, 5.74; N, 4.45.

4.2.1.1. iso-Propyl α-(2-nitrophenyl)phenylacetate 7a. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.17 (d, 1.8H, J=6.2 Hz), 1.23 (d, 1.2H, J=6.2 Hz), 1.25 (d, 1.2H, J=6.2 Hz), 1.28 (d, 1.8H, J=6.2 Hz), 5.06 (s, 0.4H), 5.06–5.17 (m, 1H), 5.62 (s, 0.6), 7.08–7.16 (m, 0.6H), 7.15–7.33 (m, 3H), 7.33–7.45 (m, 3H), 7.46–7.51 (m, 1.5H), 8.02 (dd, 0.6H, J=1.51, 8 Hz), 8.17 (m, 0.6H). ^{13}C NMR ($CDCl_3$): δ=21.41, 21.55, 21.64, 21.68, 53.41, 56.94, 69.17, 69.28, 123.67, 124.81, 127.77, 128.07, 128.4, 128.9, 128.96, 129.16, 129.58, 131.6, 133.07, 134.14, 136.72, 137.42, 146.14, 148.87, 170.82.

4.2.2. *iso*-Propyl α-(3-fluoro-4-nitrophenyl)phenylacetate 3b. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.22 (d, 3H, J=6.3 Hz), 1.26 (d, 3H, J=6.3 Hz), 5.0 (s, 1H), 5.03–5.13 (m, 1H), 7.22–7.26 (m, 1H), 7.28–7.31 (m, 4H), 7.32–7.39 (m, 3H), 7.99–8.06 (m, 1H). ^{13}C NMR ($CDCl_3$): δ=21.51, 21.64, 56.69, 69.54, 118.69 (d, J_{CF}=21.1 Hz), 124.78 (d, J_{CF}=5 Hz), 126.12 (d, J_{CF}=3 Hz), 128.02, 128.33, 129.07, 136.77, 147.83 (d, J_{CF}=9 Hz), 155.4 (d, J_{CF}=265 Hz), 170.3 MS (EI): m/z (%)=317 (M^+, 1), 257 (27), 230 (100), 214 (43), 183 (66), 105 (31), 43 (98). Anal. Calcd for $C_{17}H_{16}FNO_4$: C, 64.35: H, 5.08; N, 4.41. Found: C, 64.4; H, 5.1, N, 4.38.

4.2.3. *iso*-Propyl α-(3-fluoro-2-nitrophenyl)phenylacetate 7b. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.2 (d, 0.9H, J=6.2 Hz), 1.22 (d, 2.1H, J=6.3 Hz), 1.25–1.28 (d+d, 3H, J=6.3, 6.2 Hz), 5.0 (s, 0.7H), 5.03–5.13 (m, 1H), 5.17 (s, 0.3H), 7.06–7.12 (m, 0.3H), 7.12–7.21 (m, 0.3H), 7.21–7.31 (m, ~4H), 7.31–7.45 (m, ~4H), 7.97–8.06 (m, 0.7H). ^{13}C NMR ($CDCl_3$): δ=21.44, 21.52, 21.57, 21.64, 51.85, 51.86, 56.69, 69.55, 69.63, 115.91, 116.1, 118.58, 118.8, 124.75, 124.8, 126.1, 126.13, 127.97, 128.03, 128.34, 128.64, 128.99, 129.07, 129.16, 131.79, 131.87, 136.21, 136,77, 147.78, 147,86, 152.62, 154.11, 156.75, 169.96, 170.3.

4.2.4. *iso*-Propyl α-(2-fluoro-4-nitrophenyl)phenylacetate 3c. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.21 (d, 3H, J=6.24 Hz), 1.26 (d, 3H, J=6.23 Hz), 5.11 (m, 1H), 5.28 (s, 1H), 7.28–7.44 (m, 6H), 7.91–7.99 (m, 2H). ^{13}C NMR ($CDCl_3$): δ=21.46, 21.59, 50.21, 69.5, 111.09 (d, J_{CF}=27 Hz), 119.2 (d, J_{CF}=4 Hz), 128.03, 128.63, 129.07, 130.8 (d, J_{CF}=4 Hz), 134.07 (d, J_{CF}=15 Hz), 135.79, 147.78 (d, J_{CF}=9 Hz), 159.83 (d, J_{CF}=251.5 Hz), 170.1. MS (EI): m/z (%)=317 (M^+, 2), 230 (100), 214 (18), 183 (44), 105 (9), 43 (71). HRMS (ES) calcd for $C_{17}H_{16}FNO_4Na$: 340.0956. Found: 340.0976.

4.2.5. *iso*-Propyl α-(3-chloro-4-nitrophenyl)phenylacetate 3d. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.22 (d, 3H, J=6.2 Hz), 1.27 (d, 3H, J=6.2 Hz), 4.99 (s, 1H), 5.04–5.14 (m, 1H), 7.26–7.4 (m, 6H), 7.51 (d, 1H, J=1.9 Hz), 7.84 (d, 1H, J=8.4 Hz). ^{13}C NMR ($CDCl_3$): δ=21.52, 21.65, 56.46, 69.52, 125.72, 127.27, 127.87, 127.97, 128.32, 129.05, 132.06, 136.89, 145.08, 146.63, 170.39. MS (EI): m/z (%)=333 (M^+, 1), 273 (16), 246 (100), 230 (33), 165 (62), 105 (29), 43 (82). Anal. Calcd for $C_{17}H_{16}ClNO_4$: C, 61.18; H, 4.83; N, 4.2; Cl, 10.62. Found: C, 61.25; H, 4.86; N, 4.33; Cl, 10.52.

4.2.5.1. iso-Propyl α-(3-chloro-2-nitrophenyl) phenylacetate 7d. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.16–1.24 (m, 3H), 1.26 (d, 3H, J=6.3 Hz), 4.95 (s, 0.3H), 4.99 (s, 0.7H), 5.04–5.14 (m, 1H), 7.26–7.4 (m, 5H), 7.4–7.44 (m, 0.3H), 7.51 (d, 0.7H, J=1.9 Hz), 7.84 (d, 0.7H, J=8.4 Hz). ^{13}C NMR ($CDCl_3$): δ=21.47, 21.52, 21.65, 51.78, 56.46, 69.52, 69.7, 124.99, 125.72, 127.27, 127.87, 127.95, 127.98, 128.32, 128.35, 128.98, 129.05, 129.15, 129.43, 130.72, 132.06, 132.68, 136.27, 136.88, 169.8, 170.4.

4.2.6. *iso*-Propyl α-(2-chloro-4-nitrophenyl)phenylacetate 3e. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.21 (d, 3H, J=6.4 Hz), 1.26 (d, 3H, J=6.2 Hz), 5.05–5.19 (m, 1H), 5.49 (s, 1H), 7.26–7.3 (m, 1H), 7.32–7.41 (m, 5H), 8.03 (ddd, 1H, J=0.4, 2.4, 8.6 Hz), 8.27 (d, 1H, J=2.4 Hz). ^{13}C NMR ($CDCl_3$): δ=21.45, 21.61, 54.21, 69.48, 121.67, 124.53, 128.01, 128.76, 129.07, 130.94, 135.11, 135.92, 144.08, 147.19, 170.12. **MS** (EI): m/z (%)=333 (M^+, 1), 273 (9), 246 (100), 230 (22), 165 (59), 43 (74). Anal. Calcd for $C_{17}H_{16}ClNO_4$: C, 61.18; H, 4.83; N, 4.2; Cl, 10.62. Found: C, 61.07, H, 4.93, N, 4.11, Cl, 10.54.

4.2.6.1. iso-Propyl α-(4-chloro-2-nitrophenyl)phenylacetate 7e. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.16 (d, 0.45H, J=6.3 Hz), 1.21 (d, 2.5H, J=6.2 Hz), 1.27 (d, 3H, J=6.3 Hz), 5.08–5.15 (m, 1H), 5.45 (s, 0.85H), 5.57 (s, 0.15H), 7.02–7.05 (d, 0.15H, J=8.5 Hz), 7.22–7.29 (m, 2H), 7.32–7.42 (m, 5H), 7.44 (dd, 0.15H, J=2.2, 8.5 Hz), 8.02–8.06 (m, 0.85H), 8.27 (d, 0.85H, J=2.3 Hz). ^{13}C NMR ($CDCl_3$): δ=21.46, 21.63, 21.63, 21.67, 53.06, 54.22, 69.04, 69.49, 121.68, 124.56, 128, 128.76, 129.09, 129.12, 130.95, 132.75, 132.9, 133.08, 133.92, 135.13, 135.94, 136.25, 144.09, 147.22, 170.14, 170.47.

4.2.7. *iso*-Propyl α-(3-bromo-4-nitrophenyl)phenylacetate 3f. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.23 (d, 3H, J=6.3 Hz), 1.26 (d, 3H, J=6.3 Hz), 4.98 (s, 1H), 5.03–5.16 (m, 1H), 7.27–7.39 (m, 5H), 7.40–7.44 (m, 1H), 7.70 (d, 1H, J=1.8 Hz), 7.80 (d, 1H, J=8.5 Hz). ^{13}C NMR ($CDCl_3$): δ=21.52, 21.65, 56.36, 69.5, 114.63, 125.71, 127.95, 128.31, 128.53, 129.03, 135.02, 136.92, 144.98, 148.5, 170.4. MS (EI): m/z (%)=377 (M^+, 1), 317 (16), 290 (100), 274 (21), 195 (27), 165 (56), 105 (17), 43 (43). Anal. Calcd for $C_{17}H_{16}BrNO_4$: C, 53.99; H, 4.26; N, 3.7. Found: C, 54.2; H, 4.25; N, 3.57.

4.2.7.1. iso-Propyl α-(3-bromo-2-nitrophenyl)phenylacetate 7f. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.2–1.23 (m, 3H), 1.27 (m, 3H), 4.96 (s, 0.4H), 4.98 (s, 0.6H), 5.03–5.16 (m, 1H), 7.23–7.3 (m, 2H), 7.3–7.43 (m, 4H), 7.57 (dd, 0.4H, J=1.3, 8.1 Hz), 7.69–7.71 (m, 0.6H), 7.81 (d, 0.6H, J=8.3 Hz). ^{13}C NMR ($CDCl_3$): δ=21.47, 21.53, 21.65, 51.91, 56.37, 69.5, 69.68, 112.78, 114.63, 125.71, 127.93, 127.95, 128.31, 128.53, 128.97, 129.03, 129.81, 130.95, 132.56, 132.69, 135.2, 136.32, 136.92, 144.98, 148.5, 169.81, 170.4.

4.2.8. *iso*-Propyl α-(2-bromo-4-nitrophenyl)phenylacetate 3g. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.23 (d, 3H, J=6.3 Hz), 1.27 (d, 3H, J=6.2 Hz), 5.06–5.18 (m, 1H), 5.46 (s, 1H), 7.26–7.34 (m, 3H), 7.34–7.42 (m, 3H), 8.08 (ddd, 1H, J=0.4, 2.4, 8.7 Hz), 8.46 (d, 1H, J=2.4 Hz). ^{13}C NMR ($CDCl_3$): δ=21.48, 21.66, 56.67,

69.52, 122.24, 125.17, 127.82, 128.02, 128.75, 129.09, 131.06, 136.2, 145.75, 147.13, 170.11. MS (EI): *m/z* (%)= 377 (M^+, 1), 317 (8), 290 (95), 274 (19), 211 (20), 165 (100), 43 (91). Anal. Calcd for $C_{17}H_{16}BrNO_4$: C, 53.99; H, 4.26; N, 3.7. Found: C, 54.3; H, 4.47; N, 3.58.

4.2.8.1. iso-Propyl α-(4-bromo-2-nitrophenyl)phenylacetate 7g. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.2–1.24 (d+d, 3H, *J*=6.3, 6.3 Hz), 1.26–1.29 (d+d, 3H, *J*=6.2, 6.2 Hz), 5.06–5.18 (m, 1H), 5.46 (s, 0.85H), 5.55 (s, 0.15H), 6.97 (d, 0.15H, *J*=8.5 Hz), 7.22–7.3 (m, ~2H), 7.3–7.44 (m, ~4H), 7.59 (ddd, 0.15H, *J*=0.4, 2.1, 8.5 Hz), 8.08 (ddd, 0.85H, *J*=0.4, 2.5, 8.7 Hz), 2.16 (d, 0.15H, *J*=2.1 Hz), 8.46 (d, 0.85H, *J*=2.5 Hz).

4.2.9. *iso*-Propyl 1-(4-nitronaphthyl)phenylacetate 7m. Yellow crystals, mp 156–158 °C (hexane/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.24 (d, 3H, *J*=6.4 Hz), 1.26 (d, 3H, *J*=6.3 Hz), 5.05–5.19 (m, 1H), 5.21 (s, 1H), 1.29–1.38 (m, 5H), 7.5 (d, 1H, *J*=8.8 Hz), 7.55–7.65 (m, 2H), 7.74–7.76 (m, 1H), 7.84–7.91 (m, 2H). ^{13}C NMR ($CDCl_3$): δ=21.56, 21.58, 51.83, 69.47, 121.77, 124.21, 126.42, 127.51, 127.71, 127.95, 128.12, 128.42, 128.65, 128.89, 130.51, 132.84, 136.98, 147.63, 170.26. MS (EI) *m/z*=303 (13), 262 (37), 261 (48), 218 (52), 105 (100), 77 (22), 43 (29). Anal. Calcd for $C_{21}H_{19}NO_4$: C, 72.19; H, 5.42; N, 4.01. Found: C, 71.47; H, 5.23; N, 3.72.

4.2.10. *iso*-Propyl α-(2-cyano-4-nitrophenyl)phenylacetate 3n. Colourless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.16 (d, 3H, *J*=6.2 Hz), 1.28 (d, 3H, *J*=6.2 Hz), 5.05–5.15 (m, 1H), 5.62 (s, 1H), 7.04 (dd, 1H, *J*=2.3 Hz), 7.23–7.27 (m, 1H), 7.35–7.44 (m, 5H), 8.01 (d, 1H, *J*=8.8 Hz). ^{13}C NMR ($CDCl_3$): δ=21.37, 21.68, 53.48, 69.46, 126.34, 128.17, 128.3, 129.18, 129.23, 131.76, 135.88, 136.32, 139.75, 147.07, 170.34. MS (ES, MeOH): *m/z* (%)=347 (M^++ Na), HRMS (ES) calcd for $C_{18}H_{16}N_2O_4Na$: 347.1002. Found: 347.1019.

4.2.11. *iso*-Propyl α-(4-cyano-2-nitrophenyl)phenylacetate 7n. Colourless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.16 (d, 3H, *J*=6.2 Hz), 1.28 (d, 3H, *J*=6.2 Hz), 5.05–5.15 (m, 1H), 5.65 (s, 1H), 7.22–7.27 (m, 2H), 7.25 (d, 1H, *J*=8.1 Hz), 7.38–7.45 (m, 3H), 7.74 (dd, 1H, *J*=8.1, 1.6 Hz), 8.31 (d, 1H, *J*=1.6 Hz). ^{13}C NMR ($CDCl_3$): δ= 21.6, 21.91, 53.88, 70.1, 112.81, 116.62, 128.56, 128.64, 129.33, 129.63, 133.26, 135.7, 136.02, 139.48, 149.22, 170.1. MS (ES, MeOH): *m/z* (%)=347 (M^++ Na), HRMS (ES) calcd for $C_{18}H_{16}N_2O_4Na$: 347.1002. Found: 347.1017.

4.2.12. *iso*-Propyl α-(5-chloro-2-nitrophenyl)phenylacetate 7o. White crystals, mp 133–134 °C (heptane). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.16 (d, 3H, *J*=6.2 Hz), 1.28 (d, 3H, *J*=6.2 Hz), 5.05–5.15 (m, 1H), 5.62 (s, 1H), 7.04 (dd, 1H, *J*=2.3 Hz), 7.23–7.27 (m, 1H), 7.35–7.44 (m, 5H), 8.01 (d, 1H, *J*=8.8 Hz). ^{13}C NMR ($CDCl_3$): δ=21.37, 21.68, 53.48, 69.46, 126.34, 128.17, 128.3, 129.18, 129.23, 131.76, 135.88, 136.32, 139.75, 147.07, 170.34. MS (EI): *m/z* (%)=315 (2), 273 (37), 246 (48), 229 (34), 194 (24), 165 (41), 105 (58), 77 (37), 43 (100). HRMS (EI) calcd for $C_{17}H_{16}N_2O_4Cl$: 333.07679. Found: 333.07717. Anal. Calcd for $C_{17}H_{16}ClNO_4$: C, 61.16; H, 4.83; N, 4.2; Cl, 10.62. Found: C, 61.2; H, 4.86; N, 4.03; Cl, 10.55.

4.2.13. α-(4-Nitrophenyl)phenyloacetonitrile 10a. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=5.25 (s, 1H), 7.3–7.47 (m, 5H), 7.52–7.57 (m, 2H), 8.2–8.28 (m, 2H). ^{13}C NMR ($CDCl_3$): δ=42.27, 118.46, 124.39, 126.61, 127.69, 128.7, 128.91, 129.58, 134.35, 142.7. MS (EI): *m/z* (%)=238 (M^+, 100), 221 (17), 192 (37), 165 (58). Anal. Calcd for $C_{14}H_{10}N_2O_4$: C, 70.58; H, 4.23; N, 11.76. Found: C, 70.72; H, 4.5; N, 11.53.

4.2.14. α-(2-Nitrophenyl)phenylacetonitrile 11a. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=6.17 (s, 1H), 7.3–7.4 (m, 5H), 7.53–7.58 (m, 1H), 7.68–7.75 (m, 2H), 8.07 (dd, 1H, *J*=1.3, 8.2 Hz). ^{13}C NMR ($CDCl_3$): δ=38.3, 118.61, 125.77, 127.87, 128.51, 129.31, 129.68, 130.53, 130.94, 134.07, 134.14, 147.66. MS (EI): *m/z* (%)=238 (M^+, 1), 221 (100), 204 (90), 190 (70), 167 (72), 77 (30). Anal. Calcd for $C_{14}H_{10}N_2O_4$: C, 70.58; H, 4.23; N, 11.76. Found: C, 70.6; H, 4.49; N, 11.74.

4.2.15. α-(5-Chloro-2-nitrophenyl)phenylacetonitrile 11o. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=6.19 (s, 1H), 7.29–7.35 (m, 2H), 7.35–7.44 (m, 3H), 7.52 (dd, 1H, *J*=8.8, 2.4 Hz), 7.69 (d, 1H, *J*=2.4 Hz), 8.04 (d, 1H, *J*= 8.8 Hz). ^{13}C NMR ($CDCl_3$): δ=38.17, 118.08, 127.3, 127.87, 129.01, 129.5, 129.89, 130.93, 132.55, 133.33, 140.85, 145.8. MS (EI): *m/z* (%)=271 (M^+ − 1, 1), 255 (71), 238 (94), 229 (36), 201 (39), 190 (100), 166 (88), 77(57). Anal. Calcd for $C_{14}H_9ClN_2O_2$: C, 61.66; H, 3.33; N, 10.27; Cl, 13. Found: C, 61.59; H, 3.33; N, 10.06; Cl, 13.04.

4.2.16. *iso*-Propyl α-hydroxy-α-(4-nitrophenyl)phenylacetate 4a. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.23 (d, 3H, *J*=6.2 Hz), 1.3 (d, 3H, *J*=6.4 Hz), 4.42 (s, 1H), 5.14–5.24 (m, 1H), 7.32–7.39 (m, 5H), 7.68 (m, 2H), 8.18 (m, 2H). ^{13}C NMR ($CDCl_3$): δ=21.46, 21.51, 71.95, 80.37, 123.03, 126.96, 128.47, 128.51, 128.58, 131.74, 132.03, 141.41, 147.48, 148.77, 172.68. MS (EI): *m/z* (%)= 315 (M^+, 1), 228 (100), 150 (67). Anal. Calcd for $C_{17}H_{17}NO_5$: C, 64.75; H, 5.43; N, 4.44. Found: C, 64.9; H, 5.25; N, 4.31.

4.2.17. *iso*-Propyl α-hydroxy-α-(3-fluoro-4-nitrophenyl) phenylacetate 4b. White crystals, mp 69–75 °C (hexane/AcOEt). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.25 (d, 3H, *J*= 6.2 Hz), 1.32 (d, 3H, *J*=6.3 Hz), 4.42 (s, 1H), 5.11–5.29 (m, 1H), 7.35–7.38 (m, 5H), 7.44 (ddd, 1H, *J*=8.7, 1.9, 0.96 Hz), 7.5 (dd, 1H, *J*=12.2, 1.9 Hz), 8.02 (dd, 1H, *J*= 8.7, 7.6 Hz) ^{13}C NMR ($CDCl_3$): δ=21.47, 21.52, 72.28, 79.99, 117.76 (d, J_{CF}=22.1 Hz), 123.75 (d, J_{CF}=3 Hz), 125.47(d, J_{CF}=2 Hz), 126.77, 128.62, 128.73, 126.51(d, J_{CF}=8 Hz), 141, 150.44 (d, J_{CF}=4 Hz), 155.02 (d, J_{CF}= 264.5 Hz), 172.09. HRMS (ES) calcd for $C_{17}H_{15}FNO_5$: 332.0929. Found: 332.0910.

4.2.18. *iso*-Propyl α-hydroxy-α-(2-fluoro-4-nitrophenyl) phenylacetate 4c. White crystals, mp 73–76 °C (hexane/AcOEt). ^{1}H NMR Table 4, ^{13}C NMR, Table 5 MS (EI): *m/z* (%)=333 (M^+, 2), 246 (M^+ − 87, 100), 168 (63), 122 (18). Anal. Calcd for $C_{17}H_{16}FNO_5$: C, 61.26; H, 4.84; N, 4.2. Found: C, 61.09; H, 4.91; N, 4.21.

4.2.19. *iso*-Propyl α-hydroxy-α-(3-chloro-4-nitrophenyl) phenylacetate 4d. White crystals, mp 65–70 °C (hexane/

AcOEt). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.25 (d, 3H, J=6.2 Hz), 1.32 (d, 3H, J=6.4 Hz), 4.43 (s, 1H), 5.2 (m, 1H), 7.3–7.4 (m, 5H), 7.53 (dd, 1H, J=8.6, 2.0 Hz), 7.76 (d, 1H, J=2.0 Hz), 7.83 (d, 1H, J=8.6 Hz). ^{13}C NMR ($CDCl_3$): δ=21.45, 21.48, 72.21, 79.89, 125.01, 126.69, 126.8, 126.97, 128.58, 128.66, 130.87, 141.04, 147.03, 147.64, 172.17. MS (EI): m/z (%)=349 (M^+, 1), 262 (100), 184 (28), 105 (13). Anal. Calcd for $C_{17}H_{16}ClNO_5$: C, 58.38; H, 4.61; N, 4.0; Cl, 10.14. Found: C, 58.38; H, 4.41; N, 3.97; Cl, 9.98.

4.2.20. *iso*-Propyl α-hydroxy-α-(2-chloro-4-nitrophenyl) phenylacetate 4e. White crystals, mp 65–75 °C (heptane). ^{1}H NMR Table 4, ^{13}C NMR, Table 5 MS (EI): m/z (%)=349 (M^+, 2), 262 (100), 184 (41). Anal. Calcd for $C_{17}H_{16}ClNO_5$: C, 58.38; H, 4.61; N, 4.0; Cl, 10.14. Found: C, 58.18; H, 4.81; N, 3.98; Cl, 9.94.

4.2.21. *iso*-Propyl α-hydroxy-α-(3-bromo-4-nitrophenyl) phenylacetate 4f. White crystals, mp 68–75 °C (heptane). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.26 (d, 3H, J=6.3 Hz), 1.32 (d, 3H, J=6.3 Hz), 4.39 (s, 1H), 5.16–5.24 (m, 1H), 7.3–7.44 (m, 5H), 5.58 (dd, 1H, J=8.6, 2 Hz), 7.8 (d, 1H, J=8.6 Hz), 7.96 (d, 1H, J=2 Hz). ^{13}C NMR ($CDCl_3$): δ=21.49, 21.52, 72.24, 79.23, 114.09, 125.01, 126.85, 127.68, 128.6, 128.69, 134.03, 141.09, 147.5, 148.97, 172.24. MS (EI): m/z (%)=393 (M^+, 2), 306 (100), 228 (30), 105 (20), 77 (15), 43 (21). Anal. Calcd for $C_{17}H_{16}BrNO_5$: C, 51.79; H, 4.09; N, 3.55. Found: C, 51.52; H, 4.28; N, 3.49.

4.2.22. *iso*-Propyl α-hydroxy-α-(2-bromo-4-nitrophenyl) phenylacetate 4g. Colourless oil. ^{1}H NMR Table 4, ^{13}C NMR, Table 5 MS (EI): m/z (%)=393 (M^+, 1), 306 (M^+- 87, 100), 262 (42), 228 (43), 184 (25), 105 (27), 77 (21), 43 (27). Anal. Calcd for $C_{17}H_{16}BrNO_5$: C, 51.79; H, 4.09; N, 3.55. Found: C, 51.65; H, 3.91; N, 3.6.

4.2.23. *iso*-Propyl α-hydroxy-α-(2-iodo-4-nitrophenyl) phenylacetate 4h. Colourless oil. ^{1}H NMR Table 4, ^{13}C NMR, Table 5 MS (EI): m/z (%)=441 (M^+, 2), 354 (100), 276 (39). HRMS (ES) calcd for $C_{17}H_{16}INO_5Na$: 463.9965. Found: 463.9986. Anal. Calcd for $C_{17}H_{16}INO_5$: C, 46.28; H, 3.66; N, 3.17. Found: C, 47.83; H, 3.95; N, 2.95.

4.2.24. *iso*-Propyl α-hydroxy-α-(2-methoxy-4-nitrophenyl)phenylacetate 4j. White crystals, mp 104–112 °C (heptane). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.19–1.3 (m, 6H), 3.97 (s, 3H), 4.44 (s, 1H), 5.14, (m, 1H), 6.91 (d, 1H, J=8.6 Hz), 7.37–7.47 (m, 3H), 7.68 (dd, 1H, J=8.6, 2.2 Hz), 7.69–7.72 (m, 2H), 7.77 (d, 1H, J=2.2 Hz). ^{13}C NMR ($CDCl_3$): δ=21.39, 21.42, 55.92, 70.63, 77.92, 105.71, 115.36, 127.04, 128.2, 128.47, 130.04, 138.21, 138.64, 148.66, 157.59, 173.27. MS (EI): m/z (%)=345 (M^+, 1), 258 (100), 180 (62). Anal. Calcd for $C_{18}H_{19}NO_6$: C, 62.6; H, 5.55; N, 4.06. Found: C, 62.51; H, 5.68; N, 4.11.

4.2.25. *iso*-Propyl α-hydroxy-α-(3-cyano-4-nitrophenyl) phenylacetate 4k. Colourless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.25 (d, 3H, J=6.2 Hz), 1.35 (d, 3H, J=6.3 Hz), 4.41 (s, 1H), 5.16–5.24 (m, 1H), 7.3–7.37 (m, 2H), 7.37–7.42 (m, 3H), 7.97 (dd, 1H, J=8.8, 2.1 Hz), 8.09 (dd, 1H, J=2.1, 0.3 Hz), 8.27 (dd, 1H, J=8.8, 0.4 Hz). ^{13}C NMR ($CDCl_3$): δ=21.5, 21.54, 72.62, 79.88, 107.55, 114.96, 124.99, 126.55, 128.9, 129.06, 132.77, 134.73, 144.77, 147.64, 149.05, 171.5. MS (EI): m/z (%)=340 (M^+, 1), 253 (M^+- 87, 100), 175 (47). Anal. Calcd for $C_{18}H_{16}N_2O_5$: C, 63.52; H, 4.74; N, 8.23. Found: C, 63.43; H, 4.96; N, 8.14.

4.2.26. *iso*-Propyl α-hydroxy-α-[2-(5-nitrothiophen)] phenylacetate 4l. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.19 (d, 3H, J=6.2 Hz), 1.28 (d, 3H, J=6.2 Hz), 4.65 (s, 1H), 5.14, (m, 1H), 6.38 (d, 1H, J=5.6 Hz), 7.3 (d, 1H, J=5.6 Hz), 7.38–7.45 (m, 3H), 7.66–7.69 (m, 2H). ^{13}C NMR ($CDCl_3$): δ=21.47, 21.52, 70.92, 126.09, 128.45, 128.77, 129.48, 131.32, 139.29, 145.56, 147.94, 171.11. MS (EI): m/z (%)=321 (M^+, 1), 234 (M^+- 87, 100), 200 (25), 156 (95), 105 (20), 77 (17), 43 (22). Anal. Calcd for $C_{15}H_{15}NO_5S$: C, 56.07; H, 4.7; N, 4.36. Found: C, 55.84; H, 4.81; N, 4.23.

4.2.27. *iso*-Propyl α-hydroxy-α-[2-(1-nitronaphthyl)]-phenylacetate 4m. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.23 (d, 3H, J=6.4 Hz), 1.36 (d, 3H, J=6.2 Hz), 4.21 (s, 1H), 5.27 (m, 1H), 7.03 (d, 1H, J=8.8 Hz), 7.4–7.46 (m, 3H), 7.51–7.55 (m, 2H), 7.56–7.66 (m, 2H), 7.78 (m, 2H), 7.86 (m, 1H). ^{13}C NMR ($CDCl_3$): δ=21.41, 21.59, 71.78, 80.62, 122.06, 124.7, 126.85, 127.05, 127.71, 127.75, 128.59, 128.66, 128.74, 129.34, 130.81, 133.34, 141.23, 146.16, 171.82. MS (EI): m/z (%)=365 (M^+, 2), 278 (M^+- 87, 100), 200 (32), 105 (11). Anal. Calcd for $C_{21}H_{19}NO_5$: C, 69.03; H, 5.24; N, 3.83. Found: C, 69.18; H, 5.44; N, 3.63.

4.2.28. *iso*-Propyl 2-(2-fluoro-4-nitrophenyl)-2{4-[1-(2-fluoro-4-nitrophenyl)-1-hydroxy-2-*iso*-propoxy-2-oxo-ethyl]-phenyl}-2-phenylacetate 5c. ^{1}H NMR Table 6, ^{13}C NMR, Table 7. MS (EI): m/z (%)=561 (M^+- 87, 100), 474 (M^+- 2×87, 32), 306 (10), 43 (67). Anal. Calcd for $C_{34}H_{30}F_2N_2O_9$: C, 62.96; H, 4.66; N, 4.32. Found: C, 63.38; H, 4.68; N, 3.95.

4.2.29. *iso*-Propyl 2-(2-chloro-4-nitrophenyl)-2{4-[1-(2-chloro-4-nitrophenyl)-2-hydroxy-2-*iso*-propoxy-2-oxo-ethyl]-phenyl}-2-phenylacetate 5e. ^{1}H NMR Table 6, ^{13}C NMR, Table 7 MS (LSIMS+): m/z=703 (M^++23). MS (EI): m/z (%)=593 (M^+- 87, 100), 506 (40), 43 (35). HRMS (EI) calcd for (M-87 (COO*i*Pr)) $C_{30}H_{23}^{35}Cl_2N_2O_7$: 593.08823. Found: 593.08804. Anal. Calcd for $C_{34}H_{30}Cl_2N_2O_9$: C, 59.92; H, 4.44; N, 4.11; Cl, 10.4. Found: C, 59.67; H, 4.59; N, 4.27; Cl, 9.51.

4.2.30. *iso*-Propyl 2-(2-bromo-4-nitrophenyl)-2{4-[1-(2-bromo-4-nitrophenyl)-1-hydroxy-2-*iso*-propoxy-2-oxo-ethyl]phenyl}-2-phenylacetate 5g. White crystals. ^{1}H NMR Table 6, ^{13}C NMR, Table 7. MS (ES) ($CHCl_3$): m/z=793. MS (EI): m/z (%)=683 (M^+- 87, 100), 639 (32), 596 (40), 552 (15), 43(85). HRMS (ES) calcd for $C_{34}H_{30}Br_2N_2O_9Na$: 791.0210. Found: 791.0239. Anal. Calcd for $C_{34}H_{30}Br_2N_2O_9$: C, 53.01; H, 3.92; N, 3.64. Found: C, 54.05; H, 4.45; N, 3.48.

4.2.31. *iso*-Propyl 2-(2-iodo-4-nitrophenyl)-2{4-[1-(2-iodo-4-nitrophenyl)-1-hydroxy-2-*iso*-propoxy-2-oxoethyl]-phenyl}-2-phenylacetate 5h. White powder. ^{1}H NMR

Table 6, ^{13}C NMR, Table 7. MS (ES): *m/z* (%)=887 (M^++23).

4.2.32. *iso*-Propyl 2-(2-methoxy-4-nitrophenyl)-2{4-[1-(2-methoxy-4-nitrophenyl)-1-hydroxy-2-*iso*-propoxy-2-oxoethyl]phenyl}-2-phenylacetate 5j. Colourless oil. ^{1}H NMR Table 6, ^{13}C NMR, Table 7. MS (LSIMS+): *m/z* (%)=695 (M^++23), 655, 585 (M^+− 87). HRMS (ES) calcd for $C_{36}H_{36}N_2O_{11}Na$: 695.2211. Found: 695.2231. Anal. Calcd for $C_{36}H_{36}N_2O_{11}$: C, 64.28; H, 5.39; N, 4.16. Found: C, 63.98; H, 5.55; N, 3.98.

4.2.33. Fluoro trimer 6c. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.2–1.29 (m, 18H), 4.39 (s, 1H), 5.15–5.25 (m, 3H), 6.97–7.06(m, 2H), 7.1–7.17 (m, 1H), 7.17–7.28 (m), 7.30–7.38 (m, 5H), 7.55–7.59 (m, 2H), 7.88–8.0 (m, 6H). ^{13}C NMR ($CDCl_3$): δ=21.21, 21.3, 2121.16, 21.36, 21.42, 63.3, 63.54, 70.31, 70.44, 72.14, 111.12 (d, *J*=29.2 Hz), 111.29 (d, *J*=28 Hz), 111.65 (d, *J*=27.53 Hz), 118.78 (d, *J*=3.4 Hz), 118.85 (d, *J*=3 Hz), 118.94 (d, *J*=3 Hz), 126.68, 126.72, 127.96, 128.4, 129.36, 129.55, 129.77, 130.57, 130.7, 130.73, 130.84, 137.03–137.12 (m), 137.9–137.93 (m), 138.9 (d, *J*=12.8 Hz), 139.12–139.25 (m), 139.76–139.84 (m), 140.4–140.47 (m), 148.03–148.18 (m), 148.73 (d, *J*=9.2 Hz), 159.3, 159.35, 159.37, 161.34, 169.37, 161.39, 170.11, 170.28, 172.3. ^{19}F NMR ($CDCl_3$): δ=−107.6–(−107.8) (m, 1F), −101.2–(−101) (m, 1F), −100.95–(−101) (m, 1F). MS (EI) *m/z* (%)=876 (M^+−87, 24), 789 (5), 149 (68), 43 (100).

4.2.34. Chloro trimer 6e. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.2–1.3 (m, 18H), 4.41 (s, 1H), 5.15–5.3 (m, 3H), 6.98–7.06 (m, 3H), 7.15–7.45 (m), 7.58–7.65 (m, 1H), 7.93–8.08 (m, 3H), 8.25–8.29 (m, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ=21.03, 21.3, 21.36, 21.4, 21.47, 65.32, 65.57, 70.49, 70.63, 72.08, 72.11, 79.55, 79.75, 121.17, 121.24, 121.36, 125.39, 125.41, 125.51, 125.77, 126.73, 126.79, 127.95, 128.43, 129.49, 129.72, 129.99, 130.02, 130.08, 130.14, 131.38, 131.59, 131.73, 135.44, 136.65, 138.18, 139.5, 139.58, 140.02, 140.05, 140.09, 140.18, 140.22, 140.69, 140.75, 146.09, 146.13, 147.19, 147.26, 147.86, 148.78, 148.8, 148.84, 149.05, 149.09, 170.24, 170.37, 170.4, 172.36. MS (ES): *m/z* (%)=1034 $(M+Na)^+$.

General remarks concerning spectra of compounds **6g**, **6h**, **6j** and **6j′**: (a) denotes approximate average for a group of slightly non-equivalent protons or carbons; (b) denotes that no efforts were made to assign chemical shifts to individual ^{1}H or ^{13}C nuclei within this group; H′ (C′), H″ (C″) and H‴ (C‴) denotes that the particular protons (or carbons) belong to subsequent aromatic rings A′(B′), A″ (B″) or A‴ (B‴), for atom numbering see Tables 6 or 7. For additional comments see also the main body of the text.

4.2.35. Bromo trimer 6g. Yellowish, amorphous powder (^{1}H and ^{13}C NMR spectra measured in acetone-d_6).

C(CH_3)$_2$ (1.25, 18 H)[a], OH (5.700, 1H), H2, H2′, H2″ (5.12, 3H)[a], H10′, H10″ (7.152d; 7.150d; 7.143d; 7.140d, 1H, 7.095, 1H)[b], H10 (ca. 7.28, a signal hidden under aromatic signals), Ar (7.30, 7.37, 9H)[a], H13 (7.444, 2H), H12 (7.668, 2H), H9 (8.109dd, 1H), H9′, H9″ (8.179, 2H)[a], H7′, H7″ (8.442, 2H)[a,b], H7 (8.463d, 1H) C1, C1′, C1″ (21.54), C2(71.59; 71.56), C3(172.11; 172.06), C4 (81.93), C5(149.52), C6(124.82), C7(129.70), C8(148.54), C9(122.60), C10 (132.18; 132.16), C11 (140.47), C12 (128.01; 127.98), C13(130.84), C14(141.92), C2′, C2″(71.27, 71.13)[b], C3′, C3″(170.99; 170.97, 170.90)[b], C4′, C4″(67.72; 67.70, 67.53; 67.51)[b], C5′, C5″(151.61, 151.40)[b], C6′, C6″(127.33), C7′, C7″ (129.45, 129.53)[b], C8′, C8″(148.00, 148.05), C9′, C9″(122.74, 122.80), C10′, C10″(133.16, 131.10), C11′, C11″(141.24, 141.65)[b], C12′, C12″(130.53, 130.82)[b], C13′, C13″(130.71, 129.22)[b], C14′, (140.96; 140.91)[b], C14″ (128.64). MS (ES, negative ions: *m/z*=1170. Anal. Calcd for $C_{51}H_{44}N_3Br_3O_{13}$: C, 53.42, H, 3.87; N, 3.66: Br, 20.64. Found: C, 53.2, H, 4.09; N, 3.86: Br, 20.51.

4.2.36. Iodo trimer 6h. Yellowish, amorphous powder (^{1}H and ^{13}C NMR measured in $CDCl_3$).

C(CH_3)$_2$ (1.32, 18 H)[a], O*H* (4.336; 4.326; 4.324; 4.322; 1H), H2, H2′, H2″ (5.12, 3H)[a,b], H10, H10′, H10″(6.96, 3H)[a,b], Ar (7.25, 7.37, 11 H)[a], H12 (7.585 2H), H9 (8.055dd, 1H), H9′, H9″ (8.155, 2H)[a,b], H7 (8.808d, 1H), H7′, H7″ (8.782, 2H)[a,b] C1, C1′, C1″ (21.5)[a,b], C2(72.26), C3(172.07), C4 (81.94; 81.91), C5(149.79), C6(96.51), C7(136.56), C8(147.12), C9(122.33), C10(131.70), C11(139.05; 139.03), C12(127.04; 126.98), C13(130.52; 130.48), C14(141.06), C2′, C2″(70.89; 70.86, 71.03; 70.99)[b], C3′, C3″(170.52, 170.48)[b], C4′, C4″(68.92, 68.70)[b], C5′, C5″(153.58; 153.55, 153.31; 153.24; 153.19)[b], C6′, C6″(101.86, 101.80)[b], C7′, C7″ (136.18, 136.04)[b], C8′, C8″(146.36, 146.28)[b], C9′, C9″(122.25, 122.20)[b], C10′, C10″(131.58, 131.02)[b)], C11′, C11″(139.78, 141.06)[b], C12′, C12″(129.93, 130.48)[b], C13′, C13″(129.89, 128.55)[b], C14′, (140.67; 140.63), C14″(128.01). MS (ES) *m/z*=1310.1 ($C_{51}H_{44}N_3I_3O_{13}Na$).

4.2.37. Methoxy trimer 6j. Yellowish, amorphous powder (^{1}H and ^{13}C NMR measured in $CDCl_3$) C(CH_3)$_2$ (1.19, 18H)[a,b], OCH_3′–OCH_3″ (3.74, 6H)[a,b], OCH_3, (3.96, 3H), OH (4.41, 1H), H2, H2′, H2″ (5.12, 3H)[a], H10, H10′, H10″ (6.90, 3H)[a], Ar (7.25, 11 H)[a], H12 (7.58, 2H), H7, H7′, H7″, H9, H9′, H9″ (7.72, 6H)[a,b] C1, C1′, C1″ (21.39), C2(70.71; 70.67), C3(173.13), C4 (77.88), C5(138.40; 138.31), C6(157.62), C7(105.74), C8(148.71), C9(115.51), C10(129.90), C11(137.16), C12(126.49; 126.42), C13(129.90), C14(141.14), O*C*H$_3$ (55.93) C2′, C2″(69.30, 69.21)[b], C3′, C3″(171.15, 171.05)[b], C4′, C4″(63.41, 63.18)[b], C5′, C5″ (140.28, 140.33)[b], C6′, C6″ (157.57, 157.51)[b], C7′, C7″ (105.42,105.35)[b], C8′, C8″(148.16, 148.09)[b], C9′, C9″, (115.44, 115.43)[b], C10′, C10″ (129.90)[b], C11′, C11″(139.83), C12′(129.61), C12″(129.35), C13′ (129.53), C13″ (127.79), C14′ (140.78), C14″ (127.24). MS (LSIMS+) *m/z* (%))=1022(M^++23), 982, 912 (M^+−87). Anal. Calcd for $C_{54}H_{53}N_3O_{16}$: C, 64.68; H, 5.34; N, 4.2. Found C, 64.93; H, 5.52; N, 3.75.

4.2.38. Methoxy tetramer 6j′. Yellowish, amorphous powder (^{1}H and ^{13}C NMR measured in $CDCl_3$) C(CH_3)$_2$ (1.19, 24 H)[a,b], OCH_3′–OCH_3‴ (3.74, 9H)[a], OCH_3, (3.95, 3H), OH (4.396; 4.390; 4.378; 4.376, 1H), H2, H2′, H2″, H2‴ (5.12, 4H)[a], H10-10‴ (6.90, 4H)[a], Ar (7.17, 10 H)[a], Ar

(7.28 5H)[a], H12 (7.58, 2H), H7-7‴ and H9-9‴ (7.72, 8H)[a] C1, C1′, C1″, C1‴ (21.39)[a,b], C2(70.70; 70.66), C3(173.10), C4 (77.94), C5(138.49; 138.40), C6 (157.68), C7 (105.83; 105.81), C8(148.77), C9(115.51), C10(130 vs, broad), C11(137.28), C12 (126.54; 126.46), C13(129.5), C14(141.22; 141.17; 141.12), OCH_3 (55.96) C2′, C2″, C2‴ (69.31, 69.24; 69.20)[b], C3′, C3″, C3‴ (171.14, 171.11, 171.03 broad)[b], C4′, C4″, C4‴(63.46, 63.24; 63.23, 63.11)[b], C5′, C5″, C5‴(a group of the signals at 140.3)[b], C6′, C6″, C6‴(157.63, 157.59, 157.57)[b], C7′, C7″, C7‴ (105.52; 105.49, 105.43; 105.40)[b], C8′, C8″, C8‴(148.23, 148.17, 148.16)[b], C9′, C9″, C9‴(115.45 vs, broad signal), C10′, C10″, C10‴(130, vs, broad), C11′, C11″, C11‴(a group of the signals at about 140)[b], C12′, C12″, C12‴, C13′, C13″ (129.55, 129.38; 129.34, vs, broad signals)[b], C13‴(127.80), C14′, C14″ (140.86,140.41)[b], C14‴(127.26). MS (ES) m/z=1349.4 ($C_{72}H_{70}N_4O_{21}Na$).

4.2.39. *iso*-Propyl α-(3-chloro-2-hydroxyphenyl)phenylacetate 8d. Colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.21 (d, 3H, J=6.3 Hz), 1.23 (d, 3H, J=6.3 Hz), 4.87 (s, 1H), 5.07 (m, 1H), 5.66 (s, 1H), 6.94 (d, 1H, J=8.4 Hz), 7.11 (dd, 1H, J=8.4, 2.2 Hz), 7.25–7.35 (m, 6H). ^{13}C NMR ($CDCl_3$): δ=21.59, 21.64, 56.11, 68.82, 116.16, 119.86, 127.3, 128.35, 128.64, 128.69, 129.08, 132.07, 138.48, 150.51, 171.78, MS (EI): m/z (%)=304 (M^+, 13), 217 (100), 182 (20), 136 (20), 107 (22). HRMS (EI) calcd for $C_{17}H_{17}^{35}ClO_3$: 304.08662. Found: 304.08594.

4.2.40. *iso*-Propyl α-(3-chloro-4-hydroxyphenyl)phenylacetate 9d. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.22 (d, 3H, J=6.3 Hz), 1.25 (d, 3H, J=6.2 Hz), 5.1 (m, 1H), 5.24 (s, 1H), 6.37 (s, 1H), 6.78–6.83 (m, 1H), 6.99–7.03 (m, 1H), 7.25 (dd, 1H, J=8.3, 1.7 Hz), 7.27–7.35 (m, 5H). ^{13}C NMR ($CDCl_3$): δ=21.58, 21.64, 52.2, 69, 120.48, 120.76, 126.91, 127.36, 128.11, 128.53, 128.61, 137.16, 149.4, 172.37. MS (EI): m/z (%)=304 (M^+, 18), 244 (29), 217 (100), 182 (32). Anal. Calcd for $C_{17}H_{17}ClO_3$: C, 67; H, 5.62; Cl, 11.63. Found: C, 66.86; H, 5.79; Cl, 11.33.

4.2.41. *iso*-Propyl α-(2-chloro-4-hydroxyphenyl)phenylacetate 8e. White crystals, mp 133–134 °C (heptane). ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.2 (d, 3H, J=6.3 Hz), 1.27 (d, 3H, J=6.3 Hz), 5.12 (sep, 1H, J=6.3 Hz), 5.31 (s, 1H), 6.18 (s, 1H), 6.82 (d, 1H, J=8.6 Hz), 6.48 (dd, 1H, J=8.6, 2.6 Hz), 6.82 (d, 1H, J=2.6 Hz), 7.20–7.36 (m, 5H). ^{13}C NMR ($CDCl_3$): δ=21.48, 21.64, 53.74, 69.34, 114.29, 116.59, 127.42, 128.33, 128.76, 128.84, 130.74, 134.37, 137.2, 155.7, 172.99. MS (EI): m/z (%)=304 (M^+, 14), 244 (25), 217 (100), 182 (19). Anal. Calcd for $C_{17}H_{17}ClO_3$: C, 67; H, 5.62; Cl, 11.63. Found: C, 66.96; H, 5.7; Cl, 11.66.

4.2.42. *iso*-Propyl α-(4-chloro-2-hydroxyphenyl)phenylacetate 9e. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.29 (d, 3H, J=6.2 Hz), 1.31 (d, 3H, J=6.2 Hz), 5 (s, 1H), 5.14 (sep, 1H, J=6.2 Hz), 6.86 (dd, 1H, J=8.2, 2.2 Hz), 6.93 (d, 1H, J=2.2 Hz), 7.03 (d, 1H, J=8.2 Hz), 7.16–7.22 (m, 2H), 7.25–7.35 (m, 3H), 8.17 (s, 1H). ^{13}C NMR ($CDCl_3$): δ=21.59, 21.63, 55.1, 70.42, 118.5, 120.74, 122.41, 127.51, 127.56, 128.76, 132.16, 134.65, 136.46, 155.94, 174.85. MS (EI): m/z (%)=304 (M^+, 18), 244 (32), 217 (100), 182 (22). HRMS (EI) calcd for $C_{17}H_{17}^{35}ClO_3$: 304.08662. Found: 304.08801. Anal. Calcd for $C_{17}H_{17}ClO_3$: C, 67; H, 5.62; Cl, 11.63. Found: C, 66.77; H, 5.91; Cl, 11.14.

4.2.43. *iso*-Propyl α-(3-bromo-2-hydroxyphenyl)phenylacetate 8f. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.2–1.25 (m, 6H), 4.87 (s, 1H), 5.01–5.13 (m, 1H), 6.94 (d, 1H, J=8.4 Hz), 7.16 (dd, 1H, J=8.4, 2.2 Hz), 7.26–7.36 (m, 5H), 7.42 (d, 1H, J=2.2 Hz). ^{13}C NMR ($CDCl_3$): δ=21.6, 21.65, 56.01, 68.82, 110.16, 115.98, 126.4, 127.3, 128.33, 128.65, 129.45, 132, 132.48, 138.5, 151.44, 171.76. MS (EI): m/z (%)=348 (M^+, 13), 263 (100), 261 (99),182 (34), 152 (14), 43 (17). HRMS (EI) calcd for $C_{17}H_{17}^{79}NO_3$: 348.03611. Found: 348.03671.

4.2.44. *iso*-Propyl α-(3-bromo-4-hydroxyphenyl)phenylacetate 9f. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.22 (d, 3H, J=6.2 Hz), 1.25 (d, 3H, J=6.3 Hz), 5.04–5.16 (m, 1H), 5.24 (s, 1H), 6.39 (s, 1H), 6.75 (m, 1H), 7.04 (dd, 1H, J=7.8, 1.3 Hz), 7.26–7.36 (m, 5H), 7.39 (dd, 1H, J=8, 1.3 Hz). ^{13}C NMR ($CDCl_3$): δ=21.58, 21.64, 52.5, 69.02, 110.91, 121.35, 126.84, 127.36, 128.32, 128.59, 128.63, 129.33, 131.17, 137.15, 150.24, 172.42. MS (EI): m/z (%)=348 (M^+, 16), 288 (36), 261 (100), 182 (47), 152 (21), 43 (28). HRMS (EI) calcd for $C_{17}H_{17}^{79}BrO_3$: 348.03611. Found: 348.03571.

4.2.45. *iso*-Propyl α-(2-bromo-4-hydroxyphenyl)phenylacetate 8g. White crystals, mp 127–128 °C (heptane). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.2 (d, 3H, J=6.4 Hz), 1.28 (d, 3H, J=6.3 Hz), 5.13 (m, 1H), 5.31 (s, 1H), 6.15, (s, 1H), 6.54 (dd, 1H, J=8.5, 2.6 Hz), 6.84 (d, 1H, J=8.5 Hz), 6.95 (d, 1H, J=2.6 Hz), 7.21–7.4 (m, 5H). ^{13}C NMR ($CDCl_3$): δ=215, 21.66, 56.06, 69.28, 114.85, 119.77, 124.9, 127.39, 128.76, 128.8, 129.97, 130.86, 137.86, 137.44, 155.62, 172.83. MS (EI): m/z (%)=348 (M^+, 11), 306 (5), 288 (25), 261 (100), 182 (74), 181 (55). Anal. Calcd for $C_{17}H_{17}BrO_3$: C, 58.47; H, 4.91. Found: C, 58.6; H, 5.01.

4.2.46. *iso*-Propyl α-(4-bromo-2-hydroxyphenyl)phenylacetate 9g. Colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.28 (d, 3H, J=6.2 Hz), 1.31 (d, 3H, J=6.3 Hz), 5 9s, 1H), 5.14 (m, 1H), 6.96 (d, 1H, J=8.3 Hz), 7.01 (dd, 1H, J=8.6, 1.9 Hz), 7.08 (d, 1H, J=1.9 Hz), 7.17–7.22 (m, 2H), 7.26–7.34 (m, 3H), 8.13 (s, 1H). ^{13}C NMR ($CDCl_3$): δ=21.58, 21.61, 55, 70.38, 121.29, 122.46, 123.02, 123.66, 127.56, 128.75, 132.37, 136.39, 155.98, 174.71. MS (EI): m/z (%)=348 (M^+, 22), 306 (8), 288 (26), 261 (100), 181 (22). Anal. Calcd for $C_{17}H_{17}BrO_3$: C, 58.47; H, 4.91. Found: C, 58.6; H, 4.92.

4.2.47. *iso*-Propyl α-(1-4-hydroxynaphthyl)phenylacetate 8m. White crystals. Mp 150–152 °C (hexane/ethyl acetate) ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.28 (d, 3H, J=6.3 Hz), 1.36 (d, 3H, J=6.2 Hz), 5.12 (s, 1H), 5.17 (m, 1H), 7.2–7.3 (m, 6H), 7.38 (d, 1H, J=8.4 Hz), 7.45–7.5 (m, 2H), 7.75–7.79 (m, 1H), 8.31–8.36 (m, 1H), 9.21 (s, 1H). ^{13}C NMR ($CDCl_3$): δ=21.63, 21.73, 56.71, 70.64, 115.93, 120.1, 122.82, 125.31, 126.53, 126.61, 127.18, 127.41, 127.45, 128.72, 129.37, 134.49, 136.91, 151.73, 175.9. MS (EI): m/z (%)=320 (M^+, 24), 260 (43), 231 (100). HRMS (EI) calcd for $C_{21}H_{20}O_3$: 320.14124. Found: 320.14188.

4.2.48. *iso*-Propyl α-(2-1-hydroxynaphthyl)phenylacetate 9m. White crystals, mp 134–135 °C (hexane/ethyl acetate) ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.16$ (d, 3H, $J=6.3$ Hz), 1.30 (d, 3H, $J=6.2$ Hz), 5.03–12 (m, 1H), 5.12 (s, 1H), 6.53 (s, 1H), 7.28–7.43 (m, 6H), 7.72–7.77 (m, 2H), 8.02–8.08 (m, 1H), 8.08–8.14 (m, 1H). ^{13}C NMR ($CDCl_3$): $\delta=21.4$, 21.66, 51.59, 69.24, 126.2, 126.79, 128.15, 129, 129.16, 131.93, 131.99, 133.86, 133.96, 134.51, 136.54, 149, 170.14, 184.44, 185.02. MS (EI): *m/z* (%)=320 (M^+, 18), 260 (47), 231(100). HRMS (EI) calcd for $C_{21}H_{20}O_3$: 320.14124. Found: 320.14076.

4.2.49. *iso*-Propyl α-(5-chloro-2-hydroxy)phenylacetate 9o. White crystals, mp 97–99 °C (heptane), ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=1.29$ (d, 3H, $J=6.2$ Hz), 1.3 (d, 3H, $J=6.3$ Hz), 5.03 (s, 1H), 5.10–5.18 (m, 1H), 6.79, (d, 1H, $J=8.5$ Hz), 7.07 (d, 1H, $J=2.5$ Hz), 7.13 (dd, 1H, $J=8.5$, 2.5 Hz), 7.24–7.35 (m, 5H), 7.8–8.0 (bs, 1H). ^{13}C NMR ($CDCl_3$): $\delta=21.56$, 54.42, 70.1, 118.79, 125.05, 125.84, 127.56, 127.82, 128.75, 128.95, 130.48, 153.57, 174.17. MS (ES, MeOH): *m/z* (%)=327 (M^+ + Na). Anal. Calcd for $C_{17}H_{17}ClO_3$: C, 67.00; H, 5.62; Cl, 11.63. Found: C, 66.81; H, 5.73; Cl, 11.87.

Supplementary data

Supplementary data associated with this article can be found, in the online version at 10.1016/j.tet.2005.09.053

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