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Acyloxylactonisations mediated by lead tetracarboxylates

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ABSTRACT

The reaction of lead(IV) tetracarboxylates with carboxylic acids containing unsaturated side chains has been found to give acyloxy lactone products in a diastereoselective process; the reaction can be extended to lead(IV) tetrazolates to give the analogous outcome. Mechanistic implications of these results are discussed.

1. Introduction

The pioneering work of Criegee in the 1960s firmly established the synthetic utility of lead(IV) reagents for a variety of oxidative processes of hydroxy, amino, alkene and carboxylate groups[1–7] and this reagent has found extensive application, for example, in high yielding processes in alkaloid chemistry.[8] The utility of these reagents comes from a potent thermodynamic driving force in the reduction of lead(IV) to lead(II), as indicated by a very high oxidising potential[9] and facile ligand exchange in solution, particularly for carboxylic acids.[10,11] It is perhaps surprising, therefore, that vigorous conditions are required for these oxidative processes, which usually involve refluxing acetic acid or benzene solutions of the substrate with, most commonly, lead tetraacetate; presumably this is a consequence of a kinetically unfavourable rather than an intrinsically thermodynamically difficult process. The synthetic utility of the potent leaving group ability of lead(IV) is illustrated in the well-known oxidative decarboxylation process of carboxylic acids,[12] a reaction which is known to be catalysed by copper(II) and proceeds by a radical mechanism, once again driven by the reduction of lead(IV) to lead(II).[13,14] The ease of lead(IV)-mediated processes and in particular the potent leaving group ability of lead(IV) is further illustrated by the facile Grob fragmentation observed upon treatment of dicarboxylic acids,[15,16] and a more recent variation of this process is the conversion of aminocarboxylic acids to aminophosphonic acids by decarboxylation using lead tetraacetate (LTA).[17] Considerable effort has been expended upon defining the mechanistic course of these lead(IV) mediated reactions, with the most accepted process involving cationic or radical intermediates.[14] More recently, the development of ligand coupling processes,[18] which give synthetically useful carbon–carbon bond forming reactions[19–24] has illustrated a more sophisticated dimension to organolead chemistry, and cyclisation reactions are beginning to emerge, which are driven by this reagent.[25,26] Furthermore, LTA-mediated hetero-domino processes[27] and oxidative cleavage of vicinal diols, [28] have been shown to provide direct and rapid access to high molecular complexity under mild conditions.

Our interest in this area has been in the development of novel reaction processes mediated by lead(IV) and particularly for carbon–carbon bond formation. Lead tetracarboxylates derived from either monocarboxylic acids or dicarboxylic acids by metathesis of lead tetraacetate are readily accessible, and have generally been found to be stable amorphous powders, which can be successfully applied to the Pinhey arylation procedure, and for the transmetallation of allylstannanes leading to the formation of allylic esters.[29] In this earlier work, we examined ligands, principally substituted benzoates, which would be chemically inert to lead(IV), but of interest was examination of carboxylic acids substituted with potentially reactive π-functionality. Reactions of such compounds with LTA are not unknown, and were first reported by Alder and Schneider[30] who indicated that plumbolactonisation of bicyclic dicarboxylic acid **1** could be used to generate bislactone **2** in good (60%) yield. Later, other conformationally restricted dicarboxylic acids (e.g., **3**) were found to be applicable, although yields were not

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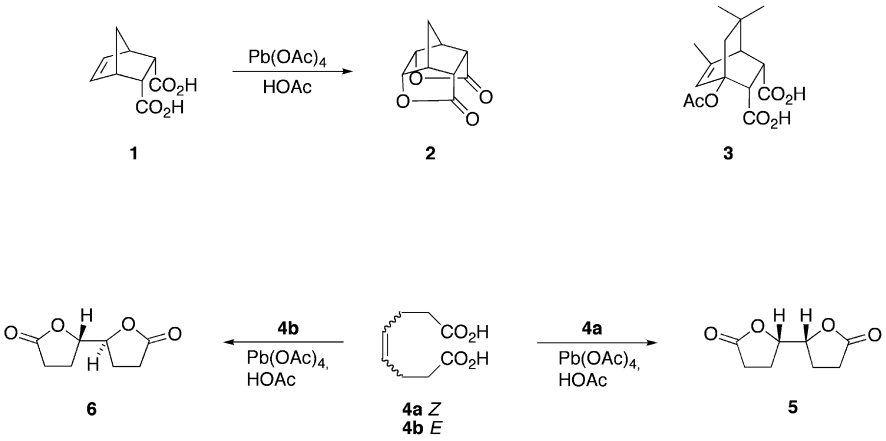
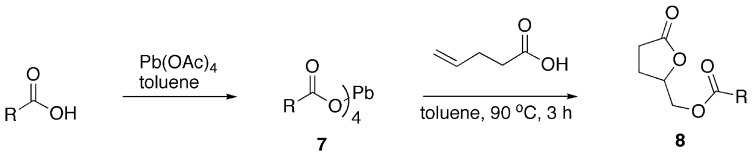


Scheme 1.

always high and the reactions were not developed further.[31–34] Nothing further was done on this reaction until 1980, when Corey reported[35] that the reaction could be applied to a small range of enedioic acid substrates (e.g., **4a**,**b**) to give bislactone products (e.g., **5**, **6**) in a stereospecific manner (Scheme 1), and he suggested that the first step involves plumbolactonisation followed by either S_N1 or S_N2 displacement of the resulting organolead(IV) intermediate, depending on the reaction conditions. Similar processes are of course well known for halo(iodo,bromo)lactonisation[36–39] and halolactamisation,[40–42] mercurilactonisation and selenolactonisation[43,44] as well as other electrophilic cyclisation processes,[37,45,46] which are enjoying a renaissance of interest. The synthetic value of these types of processes has been significantly expanded by recent developments in palladium-catalysed oxygenations,[56] aminations[57,58] and carbocyclisations[59] of alkenes. In order to pursue the reactivity of lead(IV) in this context, we examined lactonisation processes mediated by lead(IV), particularly to establish their generality and stereospecificity; a preliminary report of this work has appeared.[47]

Lead(IV) tetracarboxylates **7a**–**j** were effectively prepared by metathesis of commercially available lead tetraacetate with a range of carboxylic acids, by azeotropic removal of acetic acid in toluene using our published method[48,29] (Scheme 2); these compounds are amorphous colourless or pale yellow powders, freely soluble in chloroform, with the exception of lead tetrathiophenecarboxylate **7i**, which is a bright yellow and very insoluble powder. They were used without further purification. Reaction of lead(IV) tetracarboxylates **7a**–**j** with 4-pentenoic acid gave the lactone products **8a**–**j** in variable but in some cases excellent yield; the formation of butyrolactone ring had been confirmed previously in a closely related system by single crystal X-ray analysis.[49] Notable was that although lead tetraacetate **7a** could give a high yield of product, the reaction was unreliable. On the other hand, lead tetrathiophenecarboxylate **7i** gave a similarly high yield of the lactone product although it was not freely soluble in the reaction mixture; progress of this reaction could be easily monitored visually, beginning as a yellow slurry, and finishing as a white slurry. The 2,6-dimethoxybenzoate **8g** (60%) was formed in substantially better yield than the corresponding benzoate **8b** (45%) and the 2,6-dichlorobenzoate **8h** (22%), consistent with an electronic reactivity correlation, but the lower yields of lactones **8c**,**d**, which lack *ortho*-substitution point to the activating effect of bulk at this position; such reactivity enhancement resulting from the presence of *o*-groups is well known in the reactivity of aryllead triacetates.[22] Purification of products from low yielding reactions (e.g., **8c**) proved to be problematic, principally as a result of the large excess of benzoate by-product generated in the course of the reaction. Of interest is that an attempt to isolate lead tetra(4-pentenoate) by direct metathesis of lead tetraacetate with 4-pentenoic acid gave an unstable product, from which only lactone **9** could be isolated.

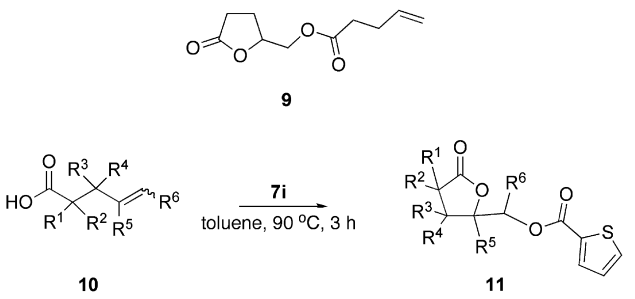
In view of the convenience of handling and the high yielding reaction of lead(IV) tetra(2-thiophenecarboxylate), this reagent was examined with a variety of substituted 4-pentenoic acids **10** to assess the scope of the reaction (Scheme 3 and Table 1); the required acids were available commercially, or were prepared by allylation of methyl isobutyrate followed by ester hydrolysis (entry



R	Yield (%)
a Ph	98
b PhCH=CH	96
c p-BrC_6H_4	99
d p-$MeOC_6H_4$	98
e 3,4-$(MeO)_2C_6H_4$	95
f 2,4-$(MeO)_2C_6H_4$	96
g 2,6-$(MeO)_2C_6H_4$	93
h 2,6-$Cl_2C_6H_4$	98
i C_4H_3S	98
j C_4H_3O	97

R	Yield (%)
a Me	85
b Ph	45
c PhCH=CH	7
d p-$MeOC_6H_4$	39
e 3,4-$(MeO)_2C_6H_3$	30
f 2,4-$(MeO)_2C_6H_3$	48
g 2,6-$(MeO)_2C_6H_3$	60
h 2,6-$Cl_2C_6H_3$	22
i C_4H_3S	84
j C_4H_3O	31

Scheme 2.



Scheme 3.

Table 1
Formation of substituted 4-pentenoic acids **10** and their reaction with lead(IV) tetra(2-thiophenecarboxylate) to give lactones **11** (Scheme 2)

Entry	R^1	R^2	R^3	R^4	R^5	R^6	Method[a]	Acid	Lactone
								Yield (%)	Yield (%)
1	Me	Me	H	H	H	H	A	**10a** (64)	**11a** (58)
2	Ph	Ph	H	H	H	H	B	**10b** (80)	**11b** (69)
3	Me	Ph	H	H	H	H	B	**10c** (94)	**11c** (73)
4	$CH_2CH_2CH_2CH_2CH_2$		H	H	H	H	B	**10d** (78)	**11d** (75)
5	H	H	H	H	H	Ph	C	**10e** (32)	**11e** (0)
6	Me	H	H	H	H	Ph	C	**10f** (73)	**11f** (0)
7	H	H	H	H	Me	H	D	**10g** (48)	**11g** (48)
8	H	H	Me	H	H	H	D	**10h** (37)	**11h** (53[b])
9	H	H	Me	Me	H	H	D	**10i** (6)	**11i** (53)
10	Me	H	H	H	H	H	—	—	**11j** (34)
11	H	H	H	H	H	Me	—	—	**11k** (0)

[a] Method A: allylation of methyl isobutyrate followed by ester hydrolysis; Method B: allylation of substituted acetic acids using 2.5 equiv of LDA; Method C: allylation of malonate followed by ester hydrolysis and decarboxylation; Method D: modification of Johnson orthoester Claisen chemistry.
[b] Mixture of cis/trans diastereomers (1:3.6).

1, Table 1),[50] allylation of substituted acetic acids using 2.5 equiv of LDA (entries 2–4, Table 1),[51] allylation of malonate followed by ester hydrolysis and decarboxylation (entries 5 and 6, Table 1), or a modification of Johnson orthoester Claisen chemistry[52,53] reported by Jäger and Günther (entries 7–9, Table 1).[54] 2-Vinylbenzoic acid **12** was prepared using a method reported by Dale et al.[55] by reaction of the Grignard derived from 2-bromostyrene followed by reaction with crushed dry ice. The substituted 4-pentenoic acids **10a–i** (Scheme 3 and Table 1) were reacted with lead(IV) tetra(2-thiophenecarboxylate) as a solution or suspension in toluene under an argon atmosphere, and heated for 3 h, giving the lactone products **11** of 5-*exo* cyclisation usually in moderate to good yield (Scheme 3, Table 1, entries 1–11), but none of the six-membered ring lactones, formed via 6-*endo* cyclisation, were isolated. Lactones **11c** and **11j** were obtained as single diastereomers, and the five-membered ring structure of all of the products **11** was assigned on the basis of IR spectrometry (1766–1785 cm^{-1}), ^1H NMR spectroscopy as well as X-ray crystallography where possible (lactones **11c**, **11g** and **11j**) (Fig. 1).[56] Noteworthy was that the yield of lactone **8i** derived from 4-pentenoic acid was 60% if the reaction was conducted with microwave irradiation (90 °C, at 150 W and 100 psi), although lactone **9** was also obtained in this case in 20% yield. Good yields of products with substituents α- to the carboxylic acid were obtained (entries 1–4, 10) preferentially giving the cis outcome (entry 10, Table 1) but this contrasted with complete loss of reactivity if substituents were located at the terminus of the double bond (entries 5, 6 and 11, Table 1). Substituents along the length of the chain were tolerated giving good yields of product (entries 7–9, Table 1). Of interest was that 2-vinylbenzoic acid **12** cyclised efficiently to give 3-oxo-1,3-dihydro-isobenzofuran-1-yl methyl 2-thiophenecarboxylate **13** in a 43% yield, and this along with the

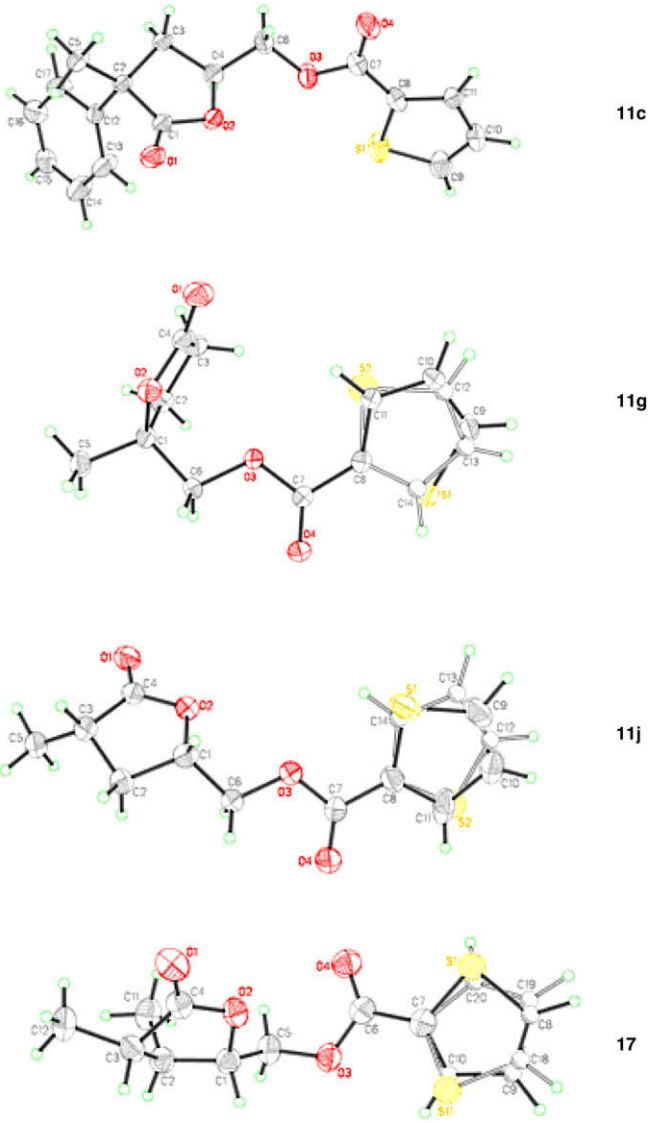
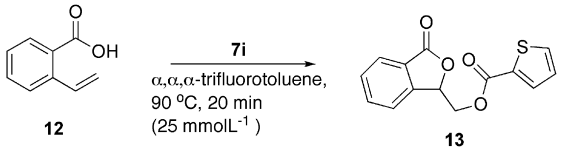


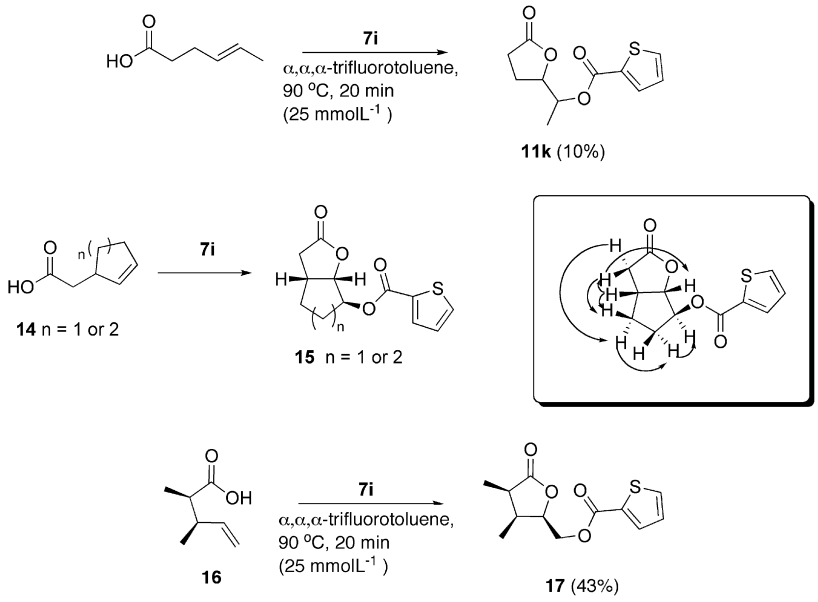
Figure 1. Thermal ellipsoid plots (ORTEP-3) at 40% probability level for compounds **11c**, **11g**, **11j** and **17**.

formation of spirocyclic lactones (entry 4, Table 1), demonstrated that the methodology can be used to generate fused and spirocyclic ring systems (Scheme 4). However, 2-cyclopenten-1-acetic acid **14** (n=1) and 2-cyclohex-2-enylacetic acid **14** (n=2)[57–59] failed to react with lead(IV) tetra(2-thiophenecarboxylate) to give the expected products **15** (n=1 and 2) (Scheme 5). These results show that substitution in positions 2-, 3- and 4- can all be tolerated under the general reaction conditions, but that substitution at the terminal position is not, and this may be a result of unfavourable steric interactions with the eight-coordinate tetaracarboxylate lead(IV) cation, shown by X-ray crystallography of LTA[60] and lead(IV) tetra(*o*-benzoylbenzoate).[61,62]

It became apparent that the yields of the lactones in these reactions were compromised by the formation of benzaldehyde by oxidation of the solvent, toluene, which was readily detected in the



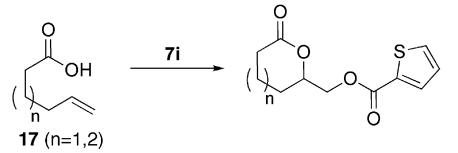
Scheme 4.



Scheme 5.

NMR spectra of crude reaction products, and by formation of lactone **9** in variable amounts; for example, in the reaction of 4-pentenoic acid, this amounted to 15%. When the reaction of 4-pentenoic acid and lead(IV) tetra(2-thiophenecarboxylate) was performed in the non-oxidisable solvents, α,α,α-trifluorotoluene, chlorobenzene, dimethoxymethane, the yields of corresponding lactone **8i** were 62, 67, and 53%, respectively; the convenient removal of α,α,α-trifluorotoluene made this the reagent of choice. Similar efficacy of trifluorotoluene in lead tetraacetate-mediated diol cleavages, which induce subsequent domino reactions has been reported.[63] Reduction of the concentration of the reaction improved yields further; for example, in the reaction of 2-methyl-4-pentenoic acid with lead(IV) tetra(2-thiophenecarboxylate) at 90 °C for 20 min, at 50 and 25 mmol L^{-1}, the yield of lactone **8i** amounted to 77 and 75% and lactone **9** to 17 and 13%, respectively. Thus, dilute reaction conditions improved yields, and the optimal reaction conditions were 25 mmol L^{-1} in α,α,α-trifluorotoluene solvent at 90 °C for 20 min, and the reaction was stopped once all the Pb(IV) had been reduced to Pb(II), indicated by the change in colour of the reaction mixture from bright yellow to white. Similarly, acid **16** was readily converted to lactone **17** in 43% yield, whose stereochemistry was unequivocally established by X-ray crystallographic analysis.[54] Using these optimised conditions at 135–145 °C, even previously unreactive substrates could be converted to the lactones, albeit in low yield; thus, 4-hexenoic acid gave lactone **11k** in 10% yield. Similarly, by reacting 2-cyclopenten-1-acetic acid with lead(IV) tetra(2-thiophenecarboxylate) at 135 °C, a 9% yield of the bicyclic lactone **15** (n=1) was isolated. The stereochemistry of the fused ring system of this compound was established by NOE studies (irradiation of (H-8_{endo}) gives enhancement at (H-3_{endo}); of (H-3_{exo}) gives enhancement at (H-4) (H-5) and (H-8_{exo}); of (H-4) gives enhancement at (H-3_{exo}) and (H-5); of δ 4.93 (H-5) gives enhancement at δ 2.78 (H-3_{exo}), δ 3.13 (H-4); of δ 5.45 (H-6) gives enhancement at (H-8_{endo}), δ 2.00 (H-7_{exo}), δ 2.16 (H-7_{endo})), confirming the reaction had given the cis-fused rings and the 2-thiophenecarboxylate resides in an *exo*-position to the ring junction.

Other higher homologous unsaturated acids were found to be applicable to this sequence; both 5-hexenoic acid and 6-heptenoic acid successfully underwent plumbolactonisation with lead(IV) tetra(2-thiophenecarboxylate) to give six- and seven-membered

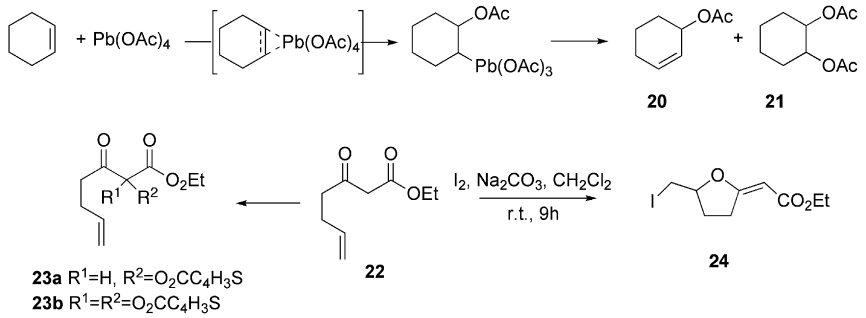


Solvent	18 (n=1)	19 (n=2)
Toluene	48%	26%
Trifluorotoluene	43%	23%

Scheme 6.

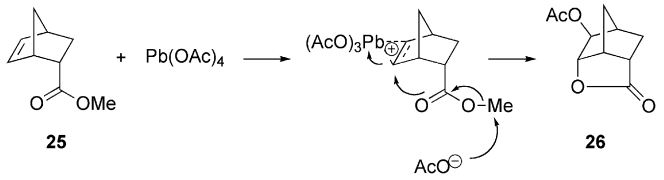
lactones, respectively, **18** and **19** (Scheme 6), assigned on the basis of the carbonyl stretch in their IR spectra (1734 and 1728 cm^{-1}, respectively), in agreement with the reported absorption frequencies for six-membered and larger ring lactones.[64]

The mechanism of these reactions deserves some comment: oxidative decarboxylation of carboxylic acids by lead tetraacetate is well known,[14] and the available evidence supports a free-radical chain mechanism.[13,65–67] However, in the plumbolactonisation process reported here, no products of decarboxylation derived from either the unsaturated ester or thiophenecarboxylic acid were observed, and neither were any products from radical trapping when the reaction between lead(IV) tetra(2-thiophenecarboxylate) and 4-pentenoic acid was carried out in the presence of 1,1-diphenylethylene; this approach has been successfully applied to demonstrate radical intermediacy in related processes.[68,13] Although yields of lactone **8i** were lower in these experiments (20%), 54% of the 1,1-diphenyethylene was recovered and no other products were isolated. Furthermore, if the reaction was conducted in the presence of radical inhibitors (galvinoxyl and benzoquinone), lactone formation was not prevented.[47] Even if the reaction was carried out under an oxygen atmosphere, lactone formation was still achieved in a 53% yield, and when reaction of lead(IV) tetra(2-thiophenecarboxylate) with 4-pentenoic acid in α,α,α-trifluorotoluene at 90 °C in the dark was attempted, lactone **8i** was obtained in a 74% yield. All this evidence together strongly suggests that these reactions of 4-pentenoic acids with lead(IV) tetra(2-thiophenecarboxylate) does not occur via a radical pathway. On the other hand, direct interaction of the lead(IV) species with the π-system does not appear to be operating either; thus, although the reaction of lead tetraacetate with cyclohexene in α,α,α-trifluorotoluene



Scheme 7.

at 90 °C under argon (normally carried out in refluxing benzene or acetic acid[69]) gave products **20** and **21** as detected by GC–MS analysis (Scheme 7), when the analogous reaction was carried out using lead(IV) tetra(2-thiophenecarboxylate), no substitution or addition products were formed, and after 3 h, only starting materials were present. The lack of Pb–π interaction was further demonstrated because no cyclisation of lead(IV) tetra(2-thiophenecarboxylate) with ethyl-3-oxohept-6-enoate **22** occurred, and the only products, which could be isolated were the mono- and di-(2-thiophenecarboxylate) esters **23a** and **23b** (Scheme 7), arising from a reaction analogous to the well known α-acetoxylation of β-dicarbonyl compounds by lead tetracarboxylates.[70] This contrasts with the work of Ferraz et al.[71] who found that substrate **22** could be readily cyclised with iodine to give enol ether **25** in good yield (Scheme 7). Furthermore, reaction of methyl 4-pentenoate with lead(IV) tetra(2-thiophenecarboxylate) in α,α,α-trifluorotoluene at 90 °C for 3 h gave no colour change and only unreacted methyl ester was detected by GC–MS analysis of the crude reaction mixture; no other products were detected. This contrasts with the work of Moriarty, who showed that the reaction of methyl *endo*-5-carboxybicyclo[2.2.1]hept-2-ene **25** gave acetoxy lactone **26** (Scheme 8), while the saturated analogue, methyl *endo*-5-carboxy bicycle[2.2.1]heptane, was completely unreactive under the oxidation conditions.[72,73] For these results, Moriarty concluded



Scheme 8.

that addition to the double bond followed by intramolecular opening by the carbomethoxy group is strongly indicated for the norbornene system. Taken together, the evidence suggests initial carboxylate exchange in the reactions of 4-pentenoic acids, rather than an initial Pb^{IV}–π interaction. Direct evidence for rapid carboxylate ligand exchange at lead(IV) came from an examination of the 104.4 MHz ^{207}Pb spectra for the metathesis of lead tetrabenzoate (PbB_4) with 4-pentenoic acid (P); at 298 K, there was only a broad resonance, but at 225 K, this resolved into a pentet of signals approximately in a ratio of 0.3:2.8:6:4.7:1.32, indicative of a free ligand exchange equilibrium (Fig. 2) but weighted in favour of the benzoate containing species $PbPB_3$ and PbB_4, with lead tetrabenzoate located at one extremity (δ −1896.8 ppm) and lead tetra(4-pentenoate) at the other (δ −1877.0).

A ligand coupling mechanism[74,18] has been proposed for vinylations, phenylations and alkynylations mediated by organolead(IV) tricarboxylates[22] by reductive elimination at the lead(IV) centre, and the possibility of the existence of radicals under the reaction conditions appears to be excluded. Since the available evidence indicates that reaction of lead(IV) tetra(2-thiophenecarboxylate) is with the carboxylic acid functionality rather than the double bond of pentenoic acids, it seems likely that the first step of the reaction with 4-pentenoic acid is ligand exchange to give a mixed lead tetracarboxylate **27** (Scheme 9). Rather than decarboxylation of the carboxylic acid via a radical pathway, the lead(IV) centre directs cyclisation, possibly by the formation of a π-complex **28**. A rearrangement could then occur to give a transient Pb–σ complex **29**, which then undergoes ligand coupling to give the observed product. Attempts to trap the putative Pb–σ complex **29** using an external nucleophile, such as methyl Meldrum's acid or sodium azide, have not been successful, and no products other than the lactone ester **8i** was isolated. This may be due to the fact that such Pb–σ

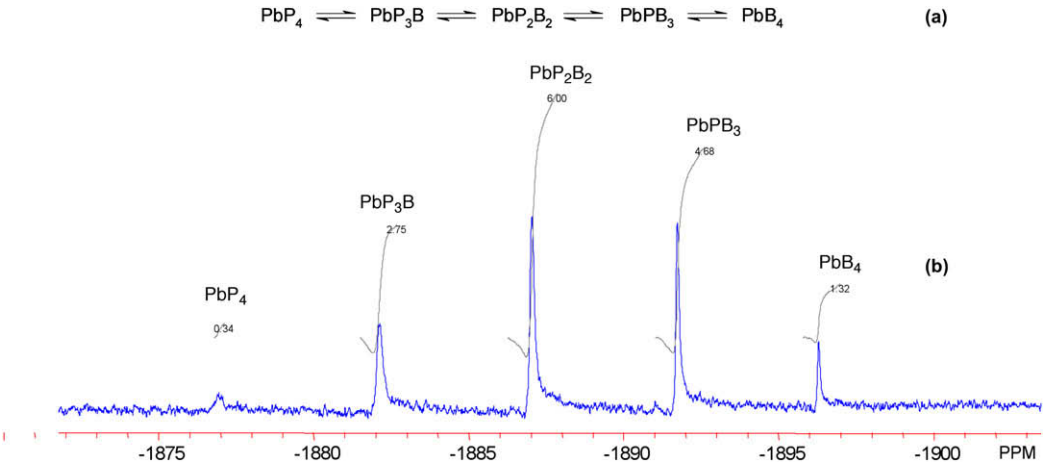
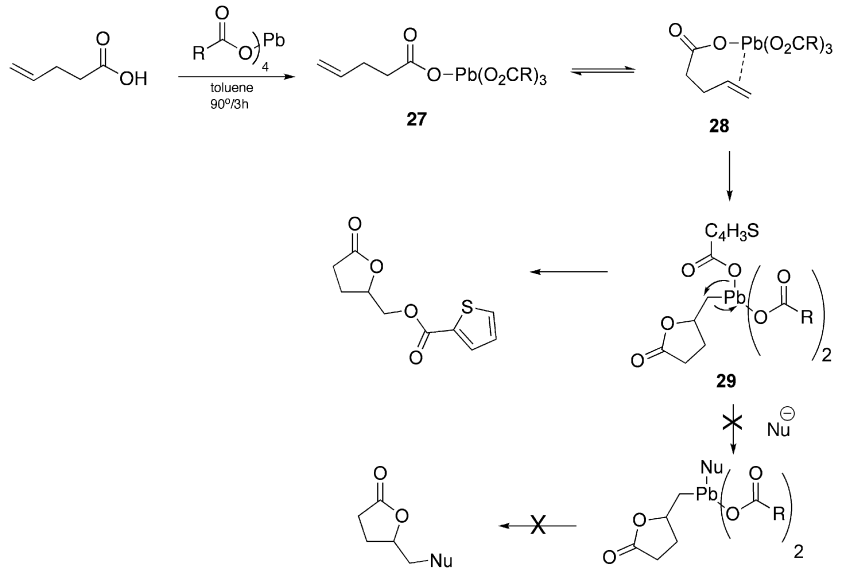
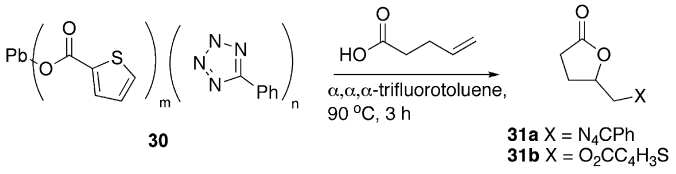


Figure 2. Ligand exchange between lead tetrabenzonate (PbB_4) and 4-pentenoic acid (P).



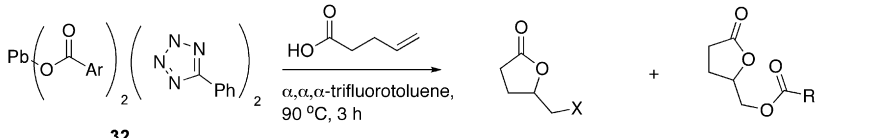
Scheme 9.



Scheme 10.

complexes, if they exist, are very unstable and rapidly undergo reductive elimination to liberate the lead(II) salt and the lactone product before any exchange with external nucleophiles is possible.

In an effort to further extend the scope of the plumbolactonisation process, systems containing tetrazole ligands were examined; the tetrazolyl unit, with a pK_a of 4.5, is of similar acidity to carboxylic acids, but has not been previously examined as a ligand for lead(IV). In the event, preparation of mixed ligand complexes **30** (m+n=4) was readily achieved using the metathesis process described earlier with lead tetraacetate and different stoichiometries of 2-thiophenecarboxylic and 5-phenyl-(1*H*)-tetrazole, although the products were found to be of low solubility in common solvents, and were moisture sensitive, with lead(IV) tetra(5-phenyl-(1*H*)-tetrazolide) **30** (n=4) decomposing to brown lead(II) oxide in a closed container within a week; complexes containing 1 equiv or more of 2-thiophenecarboxylic acid were markedly more stable. Lead tetra(5-phenyltetrazol-1-ide) was found to react effectively with pentenoic acid in α,α,α-trifluorotoluene to give only the tetrazolylmethyl lactone **31a**, which could be isolated in 53% yield, although the mixed ligand complexes returned product mixtures (conversions 34–72%) containing mainly tetrazole **31a** along with ester **31b** (Scheme 10) in a ratio of about 2:1 regardless of the stoichiometry of the starting lead(IV) compound, consistent with a higher migratory aptitude for the tetrazolyl ligand. Of interest was that these reactions were much faster than the analogous processes involving lead tetracarboxylates, consistent with the lower stability of tetrazolyl lead(IV) derivatives. In an effort to fine tune this process further, the reaction of a range of benzoate-tetrazolyl lead(IV) complexes **32** was examined, in which the benzoates were chosen for their variation in steric and electronic modifying substituents. Again, these were readily prepared by the metathesis process described earlier with lead tetraacetate and equal stoichiometries of the benzoate and 5-phenyl-(1*H*)-tetrazole units; of interest was that all *p*-substituted benzoate lead(IV) carboxylates were much more moisture stable than the corresponding *o*-substituted ones, and that all were substantially more stable than lead(IV) tetra(5-phenyl-(1*H*)-tetrazolide) **30** (n=4). These ditetrazole dicarboxylate lead(IV) complexes **32** were reacted with 4-pentenoic acid in α,α,α-trifluorotoluene (Scheme 11) under both thermal conditions and microwave conditions; overall, yields were generally better and the reaction faster in cases in which microwave conditions were used (reaction times reduced to 10 min), and in some cases these conditions gave very good conversions of product (66, 61 and 61%, respectively, entries 2–4, Table 2). Each reaction yielded a mixture of products due to the transferral of the tetrazole ligand **33a**, the benzoate ligand **34a**–**i** or the 4-pentenoic acid **33b** to the lactone product (Scheme 11 and Table 2). In the majority of cases, preference for the transferral of the tetrazole, over the carboxylate, to the

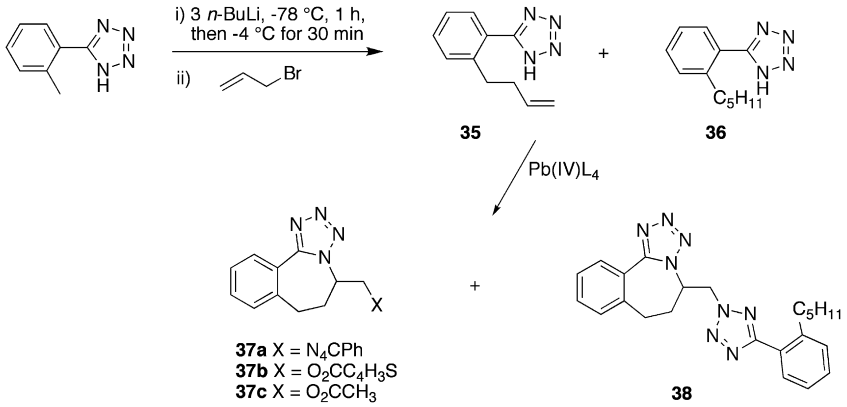


Scheme 11.

Table 2
Reaction times, conversions and product ratios for lactones **33a**, **34a–i** and **33b** for the reactions of lead(IV) ditetrazole complexes **32** with 4-pentenoic acid[a] according to Scheme 11

Entry	Benzoic acid derivative in lead(IV) ditetrazole complex **32**	Lactone product	Time to decolouration under thermal conditions	Conversion (%) (product ratio)	
				Thermal conditions	Microwave conditions
1	Benzoic acid	**34a**	20 min	51 (4:2:1)	55 (3:1:1)
2	*p*-Methoxybenzoic acid	**34b**	3 h	31 (4:1:1)	66 (4:1:1)
3	*o*-Methoxybenzoic acid	**34c**	3 h	41 (5:2:1)	61 (5:1:1)
4	*p*-Methylbenzoic acid	**34d**	30 min	31 (5:2:1)	61 (3:1:1)
5	*o*-Methylbenzoic acid	**34e**	15 min	48 (5:2:1)	37 (3:1:1)
6	*p*-Chlorobenzoic acid	**34f**	15 min	38 (4:1:1)	50 (3:1:1)
7	*o*-Chlorobenzoic acid	**34g**	10 min	50 (6:8:1)	40 (5:4:1)
8	2-Benzoylbenzoic acid	**34g**	5 min	50 (4:7:1)	43 (5:6:1)
9	2,6-Dimethoxybenzoic acid	**34i**	10 min	42 (1:1:1)	52 (4:4:1)

[a] 4-Pentenoic acid (1 equiv) and a lead(IV) complex (1 equiv) were reacted with microwave irradiation (ramp time: 5 min, power: 300 W). All products were identified by ^{1}H NMR and mass spectrometric analysis.



Scheme 12.

lactone product was observed; some exceptions were found for which almost no selectivity of tetrazole over carboxylate transfer was observed (entries 7–9, Table 2). One interesting case is that of lead(IV) di(*o*-methoxybenzoate) di(5-phenyl(1*H*)-tetrazole), which reacts very slowly under thermal conditions, and shows a high conversion of the tetrazole-containing product **33a** compared with the carboxylate-containing product **34c** when the reaction is performed under microwave conditions (entry 3, Table 2). This may be due to coordination between the *o*-methoxy group and the Pb(IV), which has been observed spectroscopically in related systems.[75] However, the addition of a second *o*-methoxy group (entry 9, Table 2) does not benefit from similar selectivity, and a near 1:1 ratio of products **33a**/**34i** is obtained, as it is in the case of *o*-chloro and *o*-benzoyl groups, which also do not benefit from the possibility of coordination (entries 7–9, Table 2).

Since the synthesis of fused tetrazole and imidazole derivatives of medicinal chemistry relevance by iodocyclisation has been of recent interest,[76] we wondered if the plumbolactonisation sequence might be extended to include the analogous aza one. The required butenylphenyl-1*H*-tetrazole **35** was prepared by a modification of the literature procedure[76] using *n*-BuLi as the base, although the desired product **35** was obtained as a mixture along with butyl derivative **36**. Reaction of the butenylphenyl-1*H*-tetrazole **35**,[76] with lead tetracetate, lead(IV) tetra(2-thiophenecarboxylate), and lead(IV) tetra(5-phenyl-(1*H*)-tetrazolide) gave complex mixtures **37a–c**, in which the expected products could be detected by mass spectrometric analysis, but from which only product **38** could be isolated; noteworthy is that detailed NMR analysis indicated this to be the 2*H*-tetrazolyl system (Scheme 12).

Hydroxy lactonisations are known and have been achieved with hydrogen peroxide catalysed by methyltrioxorhenium,[78] acidic hydrogen peroxide[79] or by asymmetric dihydroxylation.[80] However, direct acyloxy lactonisation processes have been rarely reported previously; such processes have been achieved using ammonium persulfate and trifluoromethanesulfonic acid in acetic acid,[81] or in two-step sequences by selenolactonisations of dienylcarboxylic acids followed by oxidative elimination.[82] The plumbolactonisation process described in this paper represents a one-step method for efficient access to hydroxy lactones. The behaviour of the plumbolactonisation process contrasts with the outcome using hypervalent iodine reagents, in which lactonisation with rearrangement is obtained.[83]

2. Conclusion

We have demonstrated that plumbolactonisations using lead tetracarboxylates, giving acyloxy lactone products, are viable processes, experimentally simple to execute, and which can proceed with high diastereocontrol. Extension to tetrazolyl containing analogues is possible, giving tetrazolyl lactone products, although in these cases the reaction is limited by the stability of the lead(IV) reagent.

3. Experimental

3.1. Formation of lead(IV) carboxylates 19a–j: general method[48]

Lead(IV) tetraacetate (1.0 equiv) and a carboxylic acid (4.0 equiv) were dissolved in dry toluene (150 mL) and stirred at room temperature for 20 min. The solvent was then removed in

vacuo (40 °C, 65 mbar). The resulting solid was then re-dissolved in dry toluene (150 mL), stirred for a further 20 min and the solvent was removed in vacuo. This procedure was repeated for a third time to ensure all acetic acid had been removed.

3.1.1. Lead(IV) tetrabenzoate ***7a***

Lead(IV) tetraacetate (2.00 g, 4.5 mmol) and benzoic acid (2.20 g, 18.0 mmol) were reacted according to the General Method to give carboxylate **7a** as a yellow powder (3.05 g, 98%). Mp 186–189 °C (lit.[70] 176 °C); ν_{max}(Nujol)/cm^{-1} 1599w, 1412s; δ_H(200 MHz; $CDCl_3$) 8.14 (2H, d, *J* 7.2, Ar*H o*- to CO_2), 7.63 (1H, t, *J* 7.6, Ar*H p*- to CO_2), 7.47 (2H, dd, *J* 7.7 and 7.4, Ar*H m*- to CO_2).

3.1.2. Lead(IV) tetracinnamate ***7b***

Lead(IV) tetraacetate (2.97 g, 6.8 mmol) and cinnamic acid (4.01 g, 27.1 mmol) were reacted according to the General Method to give carboxylate **7b** as a yellow/brown powder (5.19 g, 96%). Mp 139–140 °C; ν_{max}(film)/cm^{-1} 2361s, 1718w, 1564w, 1433m; δ_H(200 MHz; $CDCl_3$) 7.93 (1H, d, *J* 15.9, CH=*CH*Ph), 7.41–7.58 (5H, m, Ar*H*), 6.51 (1H, d, *J* 15.9, C*H*=CHPh).

3.1.3. Lead (IV) tetra(4-bromobenzoate) ***7c***

Lead(IV) tetraacetate (4.49 g, 10.13 mmol) and 4-bromobenzoic acid (8.15 g, 40.53 mmol) were reacted according to the General Method to give carboxylate **7c** as a brown powder (10.81 g, 99%). ν_{max}(film)/cm^{-1} 1586s, 1422s; δ_H(200 MHz; $CDCl_3$) 7.95 (2H, d, *o*- to CO_2), 7.65 (2H, d, *m*- to CO_2).

3.1.4. Lead(IV) tetra(4-methoxybenzoate) ***7d***

Lead (IV) tetraacetate (3.55 g, 8.01 mmol) and *p*-anisic acid (4.87 g, 32.03 mmol) were reacted according to the General Method to give carboxylate **7d** as a yellow powder (6.35 g, 98%). ν_{max}(film)/cm^{-1} 2359s, 2339s, 668s; δ_H(200 MHz; $CDCl_3$) 8.07 (2H, d, *J* 5.0, Ar*H o*- to CO_2), 6.92 (2H, d, *J* 5.0, Ar*H m*- to CO_2), 3.86 (3H, s, O*C*H_3).

3.1.5. Lead(IV) tetra(3,4-dimethoxybenzoate) ***7e***

Lead(IV) tetraacetate (4.50 g, 10.0 mmol) and 3,4-dimethoxybenzoic acid (7.397 g, 40.0 mmol) were reacted according to the General Method to give carboxylate **7e** as an orange powder (9.02 g, 95%). ν_{max}(film)/cm^{-1} 2361w, 1684w, 1597m, 1518m, 1456m, 1419s, 1386m, 1275s; δ_H(200 MHz; $CDCl_3$) 7.8 (1H, dd, H-5), 7.6 (1H, s, H-2), 6.90 (1H, d, H-5), 3.95 (3H, s, OMe), 3.91 (3H, s, OMe).

3.1.6. Lead(IV) tetra(2,4-dimethoxybenzoate) ***7f***

Lead(IV) tetraacetate (3.00 g, 6.77 mmol) and 2,4-dimethoxybenzoic acid (4.93 g, 27.07 mmol) were reacted according to the General Method to give carboxylate **7f** as a bright yellow powder (6.05 g, 96%), which was unstable in $CDCl_3$ solution, turning brown immediately preventing a ^{1}H NMR spectrum being obtained. Mp 159 °C; ν_{max}/cm^{-1} 1610s, 1387w.

3.1.7. Lead(IV) tetra(2,6-dimethoxybenzoate) ***7g***

Lead(IV) tetraacetate (3.00 g, 6.77 mmol) and 2,6-dimethoxybenzoic acid (4.93 g, 27.07 mmol) were reacted according to the General Method to give carboxylate **7g** as an orange powder (5.88 g, 93%). Mp 161 °C; ν_{max}(film)/cm^{-1} 1597s, 1434w; δ_H(200 MHz; $CDCl_3$) 7.37 (1H, t, ArH-4), 6.63 (2H, d, ArH-3,-5), 3.91 (6H, s, 2×OMe).

3.1.8. Lead(IV) tetra(2,6-dichlorobenzoate) ***7h***

Lead(IV) tetraacetate (3.50 g, 7.89 mmol) and 2,6-dimethoxybenzoic acid (6.031 g, 31.57 mmol) were reacted according to the General Method to give carboxylate **7h** as an yellow powder (7.50 g, 98.2%). ν_{max}(film)/cm^{-1} 2360s, 1718br, 1564m, 1433m; δ_H(200 MHz; $CDCl_3$) 7.19–7.52 (3H, m, Ar*H*-3,-4,-5).

3.1.9. Lead(IV) tetra(thiophene-2-carboxylate)[48] ***7i***

Lead(IV) tetraacetate (3.11 g, 7.0 mmol) and 2-thiophenecarboxylic acid (3.59 g, 28.0 mmol) were reacted according to the General Method to give carboxylate **7i** as a yellow powder (4.90 g, 98%). Mp 208 °C; [Found: C, 33.35; H, 1.93; S, 17.71. $C_{20}H_{12}O_8S_4Pb$ requires: C, 33.56; H, 1.69; S, 17.92.] ν_{max} ($CDCl_3$)/cm^{-1} 2360s, 2341s, 1525m, 1420m; δ_H(200 MHz; $CDCl_3$) 7.98 (1H, d, *J* 3.4, H-3), 7.69 (1H, d, *J* 4.8, H-5), 7.22 (1H, m, H-4).

3.1.10. Lead(IV) tetrafuroate[48] ***7j***

Lead(IV) tetraacetate (2.00 g, 4.5 mmol) and 2-furoic acid (2.02 g, 18.0 mmol) were reacted according to the General Method 1 to give carboxylate **7j** as a pale brown powder (4.44 g, 97%). Mp 86–87 °C; ν_{max}($CDCl_3$)/cm^{-1} 1764s, 1682s, 1480m, 1304s; δ_H(400 MHz; $CDCl_3$) 7.66 (1H, dd, *J* 0.8 and 1.8, H-3), 7.34 (1H, dd, *J* 0.8 and 3.6, H-5), 6.57 (1H, dd, *J* 1.8 and 3.6, H-4).

3.2. Cyclisation of 4-pentenoic acid by lead(IV) carboxylates: general method

4-Pentenoic acid (1.0 equiv) and a lead(IV) tetracarboxylate (1.0 equiv) were dissolved in dry toluene (15 mL). The reaction mixture was stirred at 90 °C under argon for 3 h. The excess solvent was removed in vacuo at 40 °C (usually 77 mbar). The residue was dissolved/suspended in ethyl acetate (100 mL) and filtered. The filtrate was then washed with 5% sodium carbonate (aq) (150 mL), 5% sodium chloride (aq) (100 mL), dried over magnesium sulfate, filtered and concentrated in vacuo. The residue was purified by flash column chromatography. The eluting solvent is specified in each case.

3.2.1. (5-Oxotetrahydrofuran-2-yl)methyl acetate ***8a***

4-Pentenoic acid (200 mg, 2 mmol) and lead(IV) tetraacetate **7a** (0.87 g, 2.0 mmol) were reacted according to the General Method. The crude product was purified using flash column chromatography, eluting with dichloromethane to give lactone **8a** (269 mg, 85%), a colourless oil. [Found: C, 53.05; H, 6.6. $C_7H_{10}O_4$ requires: C, 53.16; H, 6.37.] ν_{max}(film)/cm^{-1} 1777s, 1742s; δ_H(200 MHz; $CDCl_3$) 4.71–4.77 (1H, m, H-2), 4.10–4.40 (2H, m, CH_2O), 2.11 (3H, s, CH_3), 1.95–2.47 (4H, m, 2×H-3,-4); δ_C(50.3 MHz; $CDCl_3$) 177.0, 170.8, 77.3, 65.2, 28.0, 23.6, 20.5; *m*/*z* (CI, NH_3) 176 (96%, M+NH_4^+), 159 (100, M+H^+), 85 (42).

3.2.2. (5-Oxotetrahydrofuran-2-yl)methyl benzoate ***8b***

4-Pentenoic acid (200 mg, 2 mmol) and lead(IV) tetrabenzoate **7a** (1.38 g, 2 mmol) were reacted according to the General Method. The crude product was purified using flash column chromatography, eluting with 2:1 (40–60) petroleum ether/ethyl acetate to give lactone **8b** (196 mg, 45%), a colourless oil. R_f=0.37 (2:1 (40–60) petroleum ether/ethyl acetate); [Found: C, 65.32; H, 5.66. $C_{12}H_{12}O_4$ requires: C, 65.32; H, 5.66.] ν_{max}(film)/cm^{-1} 1776s, 1719s, 1272s; δ_H(200 MHz; $CDCl_3$) 7.98 (2H, d, *J* 7.2, Ar*H o*- to CO_2), 7.33–7.61 (3H, m, Ar*H*), 4.75–4.89 (1H, m, H-2), 4.30–4.55 (2H, m, CH_2O), 1.95–2.64 (4H, m, 2×H-3,-4); δ_C(50.3 MHz; $CDCl_3$) 177.1, 166.4, 133.6, 129.8, 129.5, 128.7, 77.4, 65.7, 28.1, 23.8; *m*/*z* (CI, NH_3) 238 [M+NH_4]$^+$, 221 [M+H]$^+$. HRMS (ES$^+$) found 221.0815 (MH$^+$), $C_{12}H_{13}O_4$ requires 221.0814.

When this reaction was carried out in the presence of the radical inhibitor benzoquinone (22 mg, 0.2 mmol) a colourless oil (0.131 g, 29%) was obtained; in the presence of the radical inhibitor galvinoxyl (98 mg, 0.23 mmol) resulting in a colourless oil (0.277 g, 67%) was obtained.

3.2.3. (5-Oxotetrahydrofuran-2-yl)methyl 3-phenylacrylate ***8c***

4-Pentenoic acid (200 mg, 2 mmol) and lead(IV) tetracinnamate **7b** (1.62 g, 2 mmol) were reacted according to the General Method.

The crude reaction mixture was purified by flash column chromatography eluting with dichloromethane to give lactone **8c** (26 mg, 7%) as a yellow oil. R_f=0.28 (dichloromethane); [Found: C, 68.56; H, 5.93. $C_{14}H_{14}O_4$ requires: C, 68.28; H, 5.73.] ν_{max}(film)/cm^{-1} 1631s, 1409s; δ_H(200 MHz; $CDCl_3$) 7.75 (1H, dd, *J* 16.0, CH=C*H*Ph), 7.32–7.61 (5H, m, Ar*H*), 6.44 (1H, d, *J* 16.0, C*H*=CHPh), 4.70–4.89 (1H, m, H-2), 4.21–4.46 (2H, m, CH_2O), 1.96–2.72 (4H, m, 2×H-3,-4); δ_C(50.3 MHz; $CDCl_3$) 176.7, 166.5, 145.9, 134.0, 130.7, 128.9, 128.3, 115.7, 77.5, 65.3, 28.5, 23.9; *m*/*z* (CI, NH_3) 247 ([M+H]$^+$, 10%), 131 (100); HRMS (ES$^+$) found 246.0894 (M$^+$), $C_{14}H_{14}O_4$ requires 246.0892.

3.2.4. (5-Oxotetrahydrofuran-2-yl)methyl 4-methoxybenzoate **8d**

4-Pentenoic acid (167 mg, 1.66 mmol) and lead(IV) tetra(4-methoxybenzoate) **7d** (1.35 g, 1.66 mmol) were reacted according to the General Method except that acetonitrile was used as the solvent. The crude product was purified using flash column chromatography eluting with 1:1 (30–40) petroleum ether/ethyl acetate. The product crystallised out to give lactone **8d** as white needles (0.21 g, 39%). Mp 76 °C; R_f=0.44 (1:1 (30–40) petroleum ether/ethyl acetate); [Found: C, 62.07; H, 5.64. $C_{13}H_{14}O_5$ requires: C, 62.39; H, 5.64.] δ_H(200 MHz; $CDCl_3$) 7.98 (2H, dd, *J* 4.8 and 2.1, ArH-2,-6), 6.90 (2H, dd, *J* 4.8 and 2.1, ArH-3,-5), 4.80–4.92 (1H, m, H-2), 4.36–4.58 (2H, m, CH_2O), 3.85 (3H, s, OMe), 2.04–2.73 (4H, m, 2×H-3, 2×H-4); HRMS (ES$^+$) found 251.0921 ([M+H]$^+$) $C_{13}H_{14}O_5$, requires 251.0919; *m*/*z* (CI, NH_3) 251 [M+H]$^+$, 153 (12%), 136 (15), 135 (100).

3.2.5. (5-Oxotetrahydrofuran-2-yl)methyl 3,4-dimethoxybenzoate **8e**

4-Pentenoic acid (200 mg, 2.00 mmol) and lead(IV) tetra(3,4-dimethoxybenzoate) **7e** (1.86 g, 2.00 mmol) were reacted according to the General Method. The crude product was purified by flash column chromatography eluting with dichloromethane followed by 10% methanol/dichloromethane to give lactone **8e** (170 mg, 45%), a yellow oil. R_f=0.11 (10% methanol/dichloromethane); δ_H(200 MHz; $CDCl_3$) 7.67 (1H, dd, *J* 2.0 and 8.4, ArH-6), 7.52 (1H, d, *J* 2.0, ArH-2), 6.90 (1H, d, *J* 8.5, ArH-5), 4.86–4.91 (1H, m, H-2), 4.4–4.6 (2H, m, CH_2O), 3.94 (6H, s, 2×OMe), 1.92–2.67 (4H, m, 2×H-3,-4); *m*/*z* (APCI) 281 ([M+H]$^+$). HRMS (EI) found 280.0952 (M$^+$), $C_{14}H_{16}O_6$ requires 280.0947.

3.2.6. (5-Oxotetrahydrofuran-2-yl)methyl 2,4-dimethoxybenzoate **8f**

4-Pentenoic acid (200 mg, 2.00 mmol) and lead(IV) tetra(2,4-dimethoxybenzoate) **7f** (1.86 g, 2.00 mmol) were reacted according to the General Method. The crude product was purified by flash column chromatography eluting with 1:1 (30–40) petroleum ether/ethyl acetate, to give lactone **8f** (267 mg, 48%), a yellow oil. R_f=0.13 (1:1 (30–40) petroleum ether/ethyl acetate); ν_{max}(film)/cm^{-1} 1777s, 1733s, 1269s; δ_H(200 MHz; $CDCl_3$) 7.85 (1H, d, *J* 7.3, ArH-6), 6.5–6.6 (2H, m, ArH), 4.1–4.5 (3H, m, CH_2O and H-2), 3.84 and 3.86 (6H, 2×s, 2×OMe), 2.0–2.8 (4H, m, 2×H-3,-4); δ_C(50.3 MHz; $CDCl_3$) 136.3, 134.2. 115.8, 104.7, 98.9, 77.6, 65.4, 55.8. 55.5, 28.2, 24.0; *m*/*z* (APCI) 281 ([M+H]$^+$). HRMS (EI) found 298.1292 (M+NH_4^+), $C_{14}H_{16}O_6$ requires 298.1291.

3.2.7. (5-Oxotetrahydrofuran-2-yl)methyl 2,6-dimethoxybenzoate **8g**

4-Pentenoic acid (200 mg, 2.00 mmol) and lead(IV) tetra(2,6-dimethoxybenzoate) **7g** (1.86 g, 2.00 mmol) were reacted according to the General Method. The crude product was purified by flash column chromatography eluting with dichloromethane to give a yellow oil **8g** (0.36 g, 60%). R_f=0.1 (dichloromethane); ν_{max}(film)/cm^{-1} 1773m, 1734m, 1257w, 1112m; δ_H(200 MHz; $CDCl_3$) 7.32 (1H, d, *J* 8.5, ArH-4), 6.57 (2H, d, *J* 8.4, ArH-3,-5), 4.87 (1H, m, H-2), 4.56 (2H, m, CH_2O), 3.83 (6H, s, 2×OMe), 2.20–2.71 (4H, m, 2×H-3,-4); δ_C(50.3 MHz; $CDCl_3$) 131.5, 77.4, 65.6, 56.0, 28.1, 23.8; *m*/*z* (CI, NH_3) 281 ([M+H]$^+$, 7%), 166 (10), 165 (100); HRMS (ES$^+$) found 281.1026 (M+H), $C_{14}H_{16}O_6$ requires 281.1025.

3.2.8. (5-Oxotetrahydrofuran-2-yl)methyl 2,6-chlorobenzoate **8h**

4-Pentenoic acid (197 mg, 1.97 mmol) and lead(IV) tetra(2,6-dichlorobenzoate) **7h** (1.91 g, 1.97 mmol) were reacted according to the General Method. The crude product was purified by flash column chromatography eluting with 1:1 ethyl acetate:(40–60) petroleum ether to give the product (126 mg, 22%), a pale yellow oil. R_f=0.33 (1:1 (30–40) petroleum ether/ethyl acetate); ν_{max}-(film)/cm^{-1} 1780m, 1742m, 1274m, 1143m; δ_H(200 MHz; $CDCl_3$) 7.26–7.40 (3H, m, ArH-3,-4,-5), 4.83–4.92 (1H, m, H-2), 4.44–4.68 (2H, m, CH_2O), 2.04–2.64 (4H, m, 2×H-3, 2×H-4); δ_C(50.3 MHz; $CDCl_3$) 131.5, 128.0, 76.8, 66.5, 28.1, 23.9; *m*/*z* (APCI) 289, 291, 292 [M+H]$^+$, 177 (12%), 175 (65) 173 (100); HRMS (ES$^+$) found 306.0297 (M+NH_4), $C_{12}H_{10}Cl_2O_4$, requires 306.0300.

3.2.9. (5-Oxo-tetrahydrofuran-2-yl)methyl thiophene-2-carboxylate **8i**

4-Pentenoic acid (200 mg, 2.00 mmol) and lead(IV) tetra(thiophene-2-carboxylate) **7i** (1.43 g, 2.00 mmol) were reacted according to the General Method. After work-up, the crude product was purified by flash column chromatography eluting with dichloromethane to give lactone **8i** (0.38 g, 84%). R_f=0.14 (dichloromethane); mp 42–45 °C; ν_{max}(film)/cm^{-1} 1777s, 1711s, 1261s, 1163m; δ_H(200 MHz; $CDCl_3$) 7.83–7.86 (1H, dd, *J* 1.3 and 3.8, thiophene H-2), 7.61–7.63 (1H, dd, *J* 1.3 and 5.0, thiophene H-5), 7.12–7.16 (1H, m, thiophene H-4), 4.85–4.89 (1H, m, H-2), 4.45 (H, m, CH_2O), 2.20–2.71 (4H, m, 2×H-3 and 2×H-4); δ_C(50.3 MHz; $CDCl_3$) 134.2, 133.2. 128.0, 77.3, 65.9. 28.2, 24.0; HRMS (ES$^+$) found 227.0378 (M$^+$), $C_{10}H_{11}O_4S$ requires 227.0378.

3.2.10. (5-Oxo-tetrahydrofuran-2-yl)methyl furan-2-carboxylate **8j**

4-Pentenoic acid (200 mg, 2.0 mmol) and lead(IV) tetrafuroate **7j** (1.30 g, 2.0 mmol) were reacted according to General Method 3. A brown precipitate was seen to form during the 3 h of heating under argon. After the general work-up the crude product (a yellow oil) was purified by flash column chromatography eluting with 8:1 (40–60) petroleum ether/ethyl acetate to give lactone **8j** as a colourless oil (0.13 g, 31%). R_f=0.1 (8:1 (30–40) petroleum ether/ethyl acetate); ν_{max}(film)/cm^{-1} 1810s, 1739s, 1291m, 1041s; δ_H(400 MHz; $CDCl_3$) 7.68 (1H, m, furan H-2), 7.33 (1H, m, furan H-5), 5.59 (1H, m, furan H-4), 5.76–5.92 (1H, m, H-2), 5.03–5.18 (2H, m, CH_2O), 2.36–2.62 (4H, m, 2×H-3 and 2×H-4); δ_C(100.6 MHz; $CDCl_3$) 168.1, 153.4, 143.2, 135.7, 121.4, 112.6. 34.4, 28.1.

3.2.11. Carboxylate ligands exchange in lead(IV) complexes by ^{207}Pb NMR spectroscopy

Lead(IV) tetrabenzoate (0.034 g, 0.05 mmol) was dissolved in $CDCl_3$ and transferred to an NMR tube. 4-Pentenoic acid (20 μL, 0.20 mmol) was then added to the NMR tube directly. A spectrum was taken at 295 K on the Amx500 NMR spectrometer to give a 104.4 MHz ^{207}Pb NMR spectrum showing five sharp peaks representing PbP_4, PbP_3B, PbP_2B_2, $PbPB_3$ and PbB_4 in a ratio of 0.3:2.8:6:4.7:1.32.

3.3. Cyclisation of substituted 4-pentenoic acid by lead(IV) carboxylates

3.3.1. (4,4-Dimethyl-5-oxo-tetrahydrofuran-2-yl)methyl thiophene-2-carboxylate **11a**

2,2-Dimethyl-4-pentenoic acid (210 mg, 1.6 mmol) and lead(IV) tetra(thiophene-2-carboxylate) (1.17 g, 1.6 mmol) were reacted according to the General Method. After work-up, the crude product

was obtained as a yellow oil, which was then recrystallised from (40–60) petroleum ether and ethyl acetate to give lactone **11a** as a white needles (242 mg, 58%). Mp 95–97 °C; ν_{max}(film)/cm^{-1} 1772s, 1712s, 1260s; δ_H(200 MHz; $CDCl_3$) 7.84 (1H, dd, *J* 1.2 and 3.7, thiophene H-3), 7.59 (1H, dd, *J* 1.2 and 5.0, thiophene H-5), 7.10 (1H, dd, *J* 3.7 and 5.0, thiophene H-4), 4.77 (1H, m, H-2), 4.45 (2H, m, CH_2O), 2.20 (1H, dd, *J* 12.8 and 6.5, H-3 *trans*- to CH_2), 1.95 (1H, dd, *J* 9.8 and 12.8, H-3 *cis*- to CH_2), 1.33 (3H, s, Me), 1.31 (3H, s, Me); δ_C(50.3 MHz; $CDCl_3$) 181.2, 161.8, 134.1, 133.1, 127.9, 74.0, 65.6, 40.0, 39.0, 25.1, 24.7; HRMS (ES$^+$) found 255.0687, $C_{12}H_{15}O_4S$ requires 255.0691.

3.3.2. (5-Oxo-4,4-diphenyl-tetrahydrofuran-2-yl)methyl thiophene-2-carboxylate **11b**

2,2-Diphenyl 4-pentenoic acid (495 mg, 2.0 mmol) and lead(IV) tetra(thiophene-2-carboxylate) (1.43 g, 2.0 mmol) were reacted according to the General Method. After work-up, the crude product (a yellow oil) was purified by flash column chromatography eluting with dichloromethane to give lactone **11b** as a pale yellow oil, which crystallised on standing (504 mg, 69%). Mp 125–127 °C; R_f=0.3 (dichloromethane); ν_{max}(film)/cm^{-1} 1769s, 1712s; δ_H(400 MHz; $CDCl_3$) 7.83 (1H, dd, *J* 1.2 and 3.8, thiophene H-3), 7.60 (1H, dd, *J* 1.2 and 5.0, thiophene H-5), 7.24–7.44 (10H, m, ArH), 7.11 (1H, dd, *J* 3.8 and 5.0, thiophene H-4), 4.65 (1H, dd, *J* 3.1 and 12.2, C*H*$_2$O), 4.71 (1H, m, H-2), 4.43 (1H, dd, *J* 5.9 and 12.2, C*H*$_2$O), 3.09 (1H, dd, *J* 5.3 and 13.1, H-3), 2.87 (1H, dd, *J* 10.5 and 13.1, H-3); δ_C(100.6 MHz; $CDCl_3$) 176.5, 161.7, 141.6, 139.2, 127.3, 74.4, 64.9, 57.8, 39.4; *m*/*z* (APCI) 378.5 (M$^+$, 100%); HRMS (ES$^+$) found 396.1268, $C_{22}H_{17}O_4S$ [M+NH$_4$]$^+$ requires 396.1270.

3.3.3. (4-Methyl-5-oxo-4-phenyl-tetrahydrofuran-2-yl)methyl thiophene-2-carboxylate **11c**

2-Methyl 2-phenyl 4-pentenoic acid (380 mg, 2.0 mmol) and lead(IV) tetra(thiophene-2-carboxylate) (1.43 g, 2.0 mmol) were reacted according to the General Method. After work-up, the crude product (a yellow oil) was purified by flash column chromatography eluting with dichloromethane to give lactone **11c** (460 mg, 73%) as colourless blocks (crystal structure details given below). Mp 79–82 °C; R_f=0.23 (dichloromethane); ν_{max}(film)/cm^{-1} 1774s, 1712s, 1260s; δ_H(400 MHz; $CDCl_3$) 7.83 (1H, dd, *J* 1.3 and 3.8, thiophene H-3), 7.60 (1H, dd, *J* 1.3 and 5.0, thiophene H-5), 7.34–7.41 (4H, m, *o*-, *m*- ArH), 7.28–7.34 (1H, m, *p*-ArH), 7.12 (2H, m, thiophene H-4), 4.51–4.61 (2H, m, H-2 and CH_2O), 4.38 (1H, m, CH_2O), 2.24 (1H, m, H-3), 2.80 (1H, m, H-3), 1.63 (3H, s, Me); δ_C(100.6 MHz; $CDCl_3$) 178.7, 161.7, 140.4, 134.1, 133.1, 132.7, 129.1, 127.9, 127.7, 125.8, 74.3, 65.6, 49.5, 39.9, 26.3; *m*/*z* (APCI) 316.6 (M$^+$, 100%); HRMS (ES$^+$) found 334.1109, $C_{17}H_{16}O_4S$ [M+NH$_4$]$^+$ requires 334.1113.

3.3.4. (1-Oxo-2-oxa-spiro[4.5]dec-3-yl)methyl thiophene-2-carboxylate **11d**

2-Cyclohexane 4-pentenoic acid (336 mg, 2.0 mmol) and lead(IV) tetra(thiophene-2-carboxylate) (1.43 g, 2.0 mmol) were reacted according to the General Method. After work-up, the resulting yellow oil crystallised to give lactone **11d** (0.44 g, 75%). Mp 59–62 °C; ν_{max}(film)/cm^{-1} 2933s, 1766s, 1713s, 1261s; δ_H(400 MHz; $CDCl_3$) 7.83 (1H, dd, *J* 1.2 and 5.0, thiophene H-3), 7.60 (1H, dd, *J* 1.2 and 5.0, thiophene H-5), 7.12 (1H, dd, *J* 3.8 and 5.0, thiophene H-4), 4.73 (1H, m, H-2), 4.56 (1H, dd, *J* 3.1 and 12.1, C*H*$_2$O), 4.34 (1H, dd, *J* 6.1 and 12.2, C*H*$_2$O), 2.39 (1H, dd, *J* 6.9 and 13.0, H-3), 1.20–1.89 (11H, m, cyclohexane CH_2 and H-3); δ_C(100.6 MHz; $CDCl_3$) 180.8, 161.8, 134.1, 133.1, 132.7, 127.9, 74.3, 65.7, 44.5, 35.1, 34.1, 31.9, 25.2, 22.0; *m*/*z* (APCI) 294.66 (M$^+$, 100%); HRMS (ES$^+$) found 295.0095, [M+H]$^+$ requires 295.1004; found 312.1261, $C_{15}H_{18}O_4S$ [M+NH$_4$]$^+$ requires 312.1270.

3.3.5. (2-Methyl-5-oxo-tetrahydro-furan-2-yl)methyl thiophene-2-carboxylate **11g**

4-Methyl 4-pentenoic acid (228 mg, 2.0 mmol) and lead(IV) tetra(thiophene-2-carboxylate) (1.43 g, 2.0 mmol) were reacted according to the General Method. After work-up, the crude product (a yellow oil) was purified by flash column chromatography eluting with 2:1 (40–60) petroleum ether/ethyl acetate to give lactone **11g** as colourless plates with crystal structure details given below (231 mg, 48%). R_f=0.23 (2:1 (40–60) petroleum ether/ethyl acetate); ν_{max}(film)/cm^{-1} 1775s, 1712s, 1258m, 1093w; δ_H(400 MHz; $CDCl_3$) 7.82 (1H, dd, *J* 1.2 and 4.9, thiophene H-3), 7.65 (1H, dd, *J* 1.2 and 4.9, thiophene H-5), 7.17 (1H, dd, *J* 3.9 and 4.9, thiophene H-4), 4.39 (2H, s, CH_2O), 2.83 (1H, m, H-4 *trans*- to Me), 2.70 (1H, m, H-4 *cis*- to Me), 2.39 (1H, m, H-3 *trans*- to Me), 2.14 (1H, m, H-3 *cis*- to Me), 1.56 (3H, s, Me); δ_C(100.6 MHz; $CDCl_3$) 176.3, 161.5, 134.1, 133.1, 132.5, 128.0, 83.8, 60.5, 30.6, 29.9, 23.8; HRMS (ES$^+$) found 241.0530, $C_{11}H_{13}O_4S$ requires 241.0535.

3.3.6. (3-Methyl-5-oxo-tetrahydro-furan-2-yl)methyl thiophene-2-carboxylate **11h**

3-Methyl 4-pentenoic acid (301 mg, 2.6 mmol) and lead(IV) tetra(thiophene-2-carboxylate) (1.88 g, 2.6 mmol) were reacted according to the General Method. After work-up, the crude product (a brown oil) was purified by flash column chromatography eluting with 3:1 (40–60) petroleum ether/ethyl acetate to give lactone **11h** as a pale yellow oil (255 mg, 53%). R_f=0.15 (3:1 (40–60) petroleum ether/ethyl acetate); ν_{max}(film)/cm^{-1} 1783s, 1712s, 1260s; δ_H(400 MHz; $CDCl_3$) major diastereomer 7.81 (1H, m, thiophene H-3), 7.58 (1H, m, thiophene H-5), 7.12 (1H, m, thiophene H-4), 4.52 (1H, m, C*H*$_2$O), 4.41 (1H, m, C*H*$_2$O), 4.36 (1H, m, H-2), 2.80 (1H, dd, *J* 8.6 and 17.7, H-4), 2.48 (1H, m, H-3), 2.25 (1H, dd, *J* 8.6 and 17.4, H-4), 1.24 (3H, d, *J* 6.7, Me); minor diastereomer 7.81 (1H, m, thiophene H-3), 7.58 (1H, m, thiophene H-5), 7.12 (1H, m, thiophene H-4), 4.78 (1H, m, H-2), 4.52 (1H, m, C*H*$_2$O), 4.41 (1H, m, C*H*$_2$O), 2.70 (1H, m, H-4), 2.48 (1H, m, H-3), 2.40 (1H, m, H-4), 1.17 (3H, d, *J* 7.1, Me); δ_C(100.6 MHz; $CDCl_3$) major diastereomer 175.8, 134.1, 133.1, 132.6, 127.7, 83.8, 64.5, 36.6, 32.3, 18.1; minor diastereomer 175.8, 134.1, 133.1, 132.6, 127.7, 79.6, 63.5, 36.5, 32.1, 14.0; HRMS (ES$^+$) found 241.0523, $C_{11}H_{12}O_4S$ [M+H]$^+$ requires 241.0535, found 258.0799, [M+NH$_4$]$^+$ requires 258.0800.

3.3.7. (3,3-Dimethyl-5-oxo-tetrahydro-furan-2-yl)methyl thiophene-2-carboxylate **11i**

3,3-Dimethyl 4-pentenoic acid (180 mg, 1.40 mmol) and lead(IV) tetra(thiophene-2-carboxylate) (1.00 g, 1.4 mmol) were reacted according to the General Method. After work-up, the crude product was purified by flash column chromatography eluting with dichloromethane to give lactone **11i** as a yellow oil (190 mg, 53%). R_f=0.33 (dichloromethane); ν_{max}(film)/cm^{-1} 1785s, 1714s, 1260m; δ_H(400 MHz; $CDCl_3$) 7.83 (1H, dd, *J* 1.2 and 3.8, thiophene H-3), 7.60 (1H, dd, *J* 1.2 and 5.0, thiophene H-5), 7.11 (1H, dd, *J* 3.8 and 5.0, thiophene H-4), 4.54 (1H, m, H-2), 4.39 (2H, m, CH_2O), 2.40–2.54 (2H, dd, *J* 17.1 and 32.5, 2×H-4), 1.30 (3H, s, Me), 1.18 (3H, s, Me); δ_C(100.6 MHz; $CDCl_3$) 175.5, 161.7, 84.9, 63.1, 44.0, 38.5, 26.7, 21.6; *m*/*z* (APCI) 254.29 (M$^+$, 100%); HRMS (ES$^+$) found 255.0688, $C_{21}H_{15}O_4S$ requires 255.0691.

3.3.8. cis-(4-Methyl-5-oxo-tetrahydrofuran-2-yl)methyl thiophene-2-carboxylate **11j**

2-Methyl-4-pentenoic acid (287 mg, 2.5 mmol) and lead(IV) tetra(thiophene-2-carboxylate) (1.80 g, 2.5 mmol) were reacted according to the General Method. After work-up, the crude product was purified by flash column chromatography eluting with dichloromethane to give lactone **11j** as colourless plates with crystal structure details given below (203 mg, 30%). R_f=0.39 (dichloromethane); mp 72–76 °C; [Found: C, 54.99; H, 5.03. Calcd

for $C_{11}H_{12}O_4S$: C, 54.99; H, 5.04%.] ν_{max}(film)/cm^{-1} 1773s, 1712s, 1262s; δ_H(400 MHz; $CDCl_3$) 7.83 (1H, dd, *J* 1.2 and 3.7, thiophene H-3), 7.60 (1H, dd, *J* 1.2 and 5.0, thiophene H-5), 7.12 (1H, dd, *J* 3.7 and 5.0, thiophene H-4), 4.70 (1H, m, H-2), 4.55 (1H, dd, *J* 12.2 and 3.1, C*H*$_2$O), 4.35 (1H, dd, *J* 11.4 and 4.2, C*H*$_2$O), 2.78 (1H, m, H-4), 2.25 (1H, m, H-3), 1.71 (1H, dd, *J* 9.8 and 12.8, H-3), 1.35 (1H, d, *J* 3.7, Me); δ_C(50.3 MHz; $CDCl_3$) 178.7, 134.1, 133.1, 127.9, 75.3, 65.4, 35.3, 32.8, 15.3; *m*/*z* (APCI) 240.92 (M^+, 20%), 110.76 (100); HRMS (ES^+) found 258.0795, $C_{11}H_{12}O_4S$ $[M+NH_4]^+$ requires 258.0800. The yield improved to 63% when this reaction was done in α,α,α-trifluorotoluene.

3.3.9. 1-(5-Oxotetrahydrofuran-2-yl)ethyl thiophene-2-carboxylate ***11k***

4-Hexenoic acid (607 mg, 5.3 mmol), lead(IV) tetra(thiophene-2-carboxylate) (3.82 g, 5.3 mmol) were suspended in α,α,α-trifluorotoluene (20 mL) and heated at 145 °C under argon overnight during, which time the colour changed from bright yellow to pale brown. After general work-up the crude product (a brown oil) was purified by flash column chromatography eluting with 5:2 (40–60) petroleum ether/ethyl acetate to give lactone **11k** as a colourless oil (123 mg, 10%). R_f=0.14 (5:2 (40–60) petroleum ether/ethyl acetate); ν_{max}(film)/cm^{-1} 1778s, 1710s, 1260s; δ_H(400 MHz; $CDCl_3$) 7.84 (1H, dd, *J* 1.2 and 3.7, thiophene H-3), 7.60 (1H, dd, *J* 1.2 and 5.0, thiophene H-5), 7.12 (1H, dd, *J* 3.8 and 5.0, thiophene H-4), 5.30 (1H, m, C*H*Me), 4.62 (1H, m, H-2), 2.48 (2H, m, 2×H-4), 2.20–2.42 (2H, m, 2×H-3), 1.38 (3H, d, *J* 6.8, Me); δ_C(100.6 MHz; $CDCl_3$) 133.9, 132.8, 127.9, 80.8, 71.6, 28.0, 22.8, 15.6; *m*/*z* (ESI) 241.18 (M+H, 38%); HRMS (ES^+) found 241. 0529, $C_{11}H_{12}O_4S$ $[M+H]^+$ requires 241.0535; found 258.0807, $[M+NH_4]^+$ requires 258.0800.

3.4. Microwave-assisted cyclisation of 4-pentenoic acid by lead(IV) tetra(thiophene-2-carboxylate)

4-Pentenoic acid (1 equiv, 0.5 mmol, 0.05 mL) and a lead(IV) tetra(thiophene-2-carboxylate) **3** (1 equiv, 0.5 mmol, 320 mg) were suspended in dry α,α,α-trifluorotoluene (5 mL). The reaction mixture was stirred under argon and irradiated with microwaves in a closed container using the following microwave settings: power (max): 150 W, ramp time (max): 2 min, hold time: 10 min, temperature: 90 °C, pressure (max): 100 psi. The required temperature was obtained within the ramp time. The power supplied reached a maximum of 150 W in the first 100 s then was constant at ~50 W. After 10 min hold time the lead(IV) tetra(thiophene-2-carboxylate) had completely decolourised. The excess solvent was removed in vacuo at 40 °C (usually at 77 mbar) using the rotary evaporator. The resulting residue was then suspended in ethyl acetate (50 mL) and filtered. The filtrate was washed with 10% sodium carbonate (aq) (50 mL), brine (50 mL), dried over magnesium sulfate and filtered. The excess solvent was again removed in vacuo to yield a brown oil (75 mg, 82%) containing a mixture of lactone **11l** and lactone **9**, in the ratio of 3:1.

3.4.1. (3-Oxo-1,3-dihydro-isobenzofuran-1-yl)methyl thiophene-2-carboxylate ***13***

2-Vinylbenzoic acid (296 mg, 2.0 mmol) and lead(IV) tetra-(thiophene-2-carboxylate) (1.43 g, 2.0 mmol) were suspended in α,α,α-trifluorotoluene (15 mL) and heated at 90 °C under argon for 5 h (until the colour had changed from bright yellow to cream). The solvent was removed in vacuo to leave a pale brown solid, which was dissolved in ethyl acetate (100 mL) and filtered. The filtrate was washed with 5% sodium carbonate (aq) (150 mL) then satd brine (2×100 mL). The organic layer was then dried over magnesium sulfate, filtered and concentrated in vacuo to give a yellow oil. Purification by flash column chromatography eluting with 2:1 (40–60) (petroleum ether/ethyl acetate) gave crystalline lactone **13** (257 mg, 43%). Mp 79–82 °C; ν_{max}(film)/cm^{-1} 1765s, 1712s, 1260m; δ_H(400 MHz; $CDCl_3$) 7.97 (1H, m, thiophene H-3), 7.75 (2H, m, ArH), 7.61 (2H, m, ArH, thiophene H-5), 7.10 (1H, dd, *J* 3.9 and 5.0, thiophene H-4), 5.79 (1H, m, H-2), 4.75 (1H, dd, *J* 3.9 and 12.0, C*H*$_2$O), 4.63 (1H, dd, *J* 5.8 and 12.0, C*H*$_2$O); δ_C(100.6 MHz; $CDCl_3$) 183.1, 161.5, 145.9, 132.4, 130.4, 134.3, 134.1, 133.2, 129.9, 127.9, 126.0, 122.4, 78.4, 64.7; HRMS (ES^+) found 292.0642, $C_{14}H_{10}O_4S$ $[M+NH_4]^+$ requires 292.0644.

3.4.2. (2-Oxohexahydro-2H-cyclopenta[b]furan 6-yl)thiophene-2-carboxylate ***15*** *(n=1)*

2-Cyclopenten-1-acetic acid (505 mg, 4.0 mmol) and lead(IV) tetra(thiophene-2-carboxylate) (3.44 g, 4.8 mmol) were suspended in α,α,α-trifluorotoluene (50 mL) and heated at 90 °C under argon for 30 min. The temperature was then increased to 135 °C and after 1 h the reaction mixture had turned from bright yellow to white. The solvent was removed in vacuo to leave a white solid, which was dissolved in ethyl acetate (150 mL) and filtered. The filtrate was washed with 5% sodium carbonate (aq) (2×150 mL) then satd brine (2×100 mL). The aqueous layer was then extracted with ethyl acetate (100 mL) and the combined organic layers were dried over magnesium sulfate, filtered and concentrated in vacuo to give an orange oil. Purification by flash column chromatography eluting with 4:1 (40–60) petroleum ether/ethyl acetate to give lactone **15** (*n*=1) crystals (86 mg, 9%). R_f=0.11 (4:1 (40–60) petroleum ether/ethyl acetate); δ_H(400 MHz; $CDCl_3$) 7.82 (1H, dd, *J* 1.2 and 3.7, thiophene H-4), 7.57 (1H, dd, *J* 1.2 and 5.0, thiophene H-5), 7.12 (1H, dd, *J* 3.7 and 5.0, thiophene H-3), 5.45 (1H, s, H-6), 4.93 (1H, d, *J* 6.9, H-5), 3.13 (1H, m, H-4), 2.78 (1H, dd, *J* 18.6 and 10.3, H-3), 2.40 (1H, dd, *J* 3.0 and 18.6, H-3), 2.31 (1H, m, H-8), 2.16 (1H, m, H-7), 2.00 (1H, m, H-7), 1.68 (1H, m, H-8); δ_C(100.6 MHz; $CDCl_3$) 176.6, 161.0, 133.9, 133.1, 132.9, 127.9, 87.5, 79.0, 36.5, 35.3, 31.0, 29.5; HRMS (ES^+) found 253.0523, $C_{12}H_{12}O_4S$ $[M+H]^+$ requires 253.0535; found 270.0808, $[M+NH_4]^+$ requires 270.0800.

3.4.3. (3,4-Dimethyl-5-oxo-tetrahydrofuran-2-yl)methyl thiophene-2-carboxylate ***17***

2,3-Dimethyl 4-pentenoic acid (256 mg, 2.0 mmol) and lead(IV) tetra(thiophene-2-carboxylate) (1.43 g, 2.0 mmol) were reacted according to General Method 6 in α,α,α-trifluorotoluene (15 mL). After work-up, the crude product was purified by flash column chromatography eluting with 4:1 (40–60) petroleum ether/ethyl acetate to give lactone **17** as colourless blocks with crystal structure details given below (220 mg, 43%). R_f=0.10 (4:1 (40–60) petroleum ether/ethyl acetate); ν_{max}(film)/cm^{-1} 1777s, 1713s, 1261s; δ_H(400 MHz; $CDCl_3$) 7.83 (1H, dd, *J* 1.2 and 3.7, thiophene H-3), 7.61 (1H, dd, *J* 1.2 and 5.0, thiophene H-5), 7.12 (1H, dd, *J* 3.7 and 5.0, thiophene H-4), 4.71 (1H, m, H-2), 4.53 (1H, m, CH_2O), 4.42 (1H, m, CH_2O), 2.85 (1H, m, H-4), 2.72 (1H, m, H-3), 1.20 (3H, d, *J* 7.1, H-4), 0.96 (3H, d, *J* 7.2, Me-3); δ_C(100.6 MHz; $CDCl_3$) 134.09; 133.03, 127.87, 78.19, 63.52, 40.11, 36.13, 9.68, 8.53; HRMS (ES^+) found 255.0690, $C_{12}H_{14}O_4S$ $[M+H]^+$ requires 255.0691; found 272.0957, $[M+NH_4]^+$ requires 272.0957.

3.4.4. (6-Oxo-tetrahydropyran-2-yl)methyl thiophene-2-carboxylate ***18***

5-Hexenoic acid (228 mg, 2.0 mmol) and lead(IV) tetra(thiophene-2-carboxylate) (1.43 g, 2.0 mmol) were reacted according to the General Method. The reaction mixture was seen to change from yellow to white within 1.25 h of heating. After general work-up the crude product (a yellow oil) was purified by flash column chromatography eluting with 1:1 (40–60) petroleum ether/ethyl acetate to give lactone **18** (230 mg, 48%). R_f=0.34 (1:1 (40–60) petroleum ether/ethyl acetate); ν_{max}(film)/cm^{-1} 1734s, 1712s, 1418s, 1262s; δ_H(400 MHz; $CDCl_3$) 7.82 (1H, m, thiophene H-3), 7.58 (1H, dd, *J* 1.2 and 5.0, thiophene H-5), 7.10 (1H, dd, *J*

1.2 and 3.8, thiophene H-4), 4.67 (1H, m, H-2), 4.43 (2H, m, CH_2O), 2.64 (1H, m, H-5), 2.50 (1H, m, H-5), 1.86 (2H, m, 2×H-4), 1.71 (2H, m, 2×H-3); δ_C(100.6 MHz; $CDCl_3$) 161.8, 134.0, 133.0, 132.9, 127.9, 77.6, 66.0, 29.5, 24.4, 18.2; HRMS (ES^+) found 258.0808, $C_{11}H_{12}O_4S$ $[M+NH_4]^+$ requires 258.0800. The same reaction carried out in α,α,α-trifluorotoluene gave the same product in a 43% yield.

*3.4.5. (7-Oxo-oxepan-2-yl)methyl thiophene-2-carboxylate **19***

6-Heptenoic acid (256 mg, 2.0 mmol) and lead(IV) tetra(thiophene-2-carboxylate) (1.43 g, 2.0 mmol) were reacted according to the General Method. The reaction mixture was seen to change from yellow to white within 2 h of heating. After the general work-up the crude product (a yellow oil) was purified by flash column chromatography eluting with 1:1 (40–60) petroleum ether/ethyl acetate to give lactone **19** (130 mg, 26%). R_f=0.45 (1:1 (40–60) petroleum ether/ethyl acetate); ν_{max}(film)/cm^{-1} 1794s, 1728s, 1258s; δ_H(400 MHz; $CDCl_3$) 7.81 (1H, dd, *J* 1.2 and 3.7, thiophene H-4), 7.56 (1H, dd, *J* 1.2 and 5.0, thiophene H-5), 7.10 (1H, dd, *J* 3.7 and 5.0, thiophene H-3), 4.58 (1H, m, H-2), 4.38–4.45 (1H, m, CH_2O), 4.30–4.35 (1H, m, CH_2O), 2.63–2.74 (1H, m, H-6), 2.56–2.63 (1H, m, H-6), 1.90–2.09 (3H, m, H-3, 2×H-5), 1.52–1.71 (3H, m, H-3, 2×H-4); δ_C(100.6 MHz; $CDCl_3$) 134.0, 132.9, 127.8, 77.4, 66.4, 34.8, 31.1, 27.9, 22.8; HRMS (ES^+) found 255.0703, $C_{12}H_{15}O_4S$ requires 255.0691. The same reaction carried out in α,α,α-trifluorotoluene gave the same product in a 23% yield.

3.5. Reaction of ethyl-3-oxohept-6-enoate 22 with lead(IV) tetra(thiophene-2-carboxylate)

Lead(IV) tetra(thiophene-2-carboxylate) (1.57 g, 2.2 mmol) and ethyl-3-oxohept-6-enoate (0.34 g, 2.0 mmol) were suspended in toluene (15 mL) under argon. The reaction mixture was then heated at 90 °C for 3 h, however, after 3 min the reaction had changed from bright yellow to white. Following the general work-up a precipitate formed, which was filtered to give ester **23b** (50.7 mg, 9%). ν_{max}-(film)/cm^{-1} 1782s, 1736s, 1414s, 1262s, 1098s; δ_H(400 MHz; $CDCl_3$) 7.97 (2H, dd, *J* 1.2 and 3.8, thiophene H-3), 7.68 (2H, dd, *J* 1.2 and 4.9, thiophene H-5), 5.89 (1H, m, H-6), 7.15 (2H, dd, *J* 3.3 and 4.9, thiophene H-4), 5.08 (2H, dd, *J* 1.2 and 2.7, 2×H-7), 4.35 (4H, q, *J* 7.1, OCH_2CH_3), 3.21 (2H, m, 2×H-4), 2.49 (2H, m, 2×H-5), 1.34 (6H, t, *J* 7.1, OCH_2CH_3); δ_C(100.6 MHz; $CDCl_3$) 198.7, 162.7, 159.2, 136.7, 135.8, 134.7, 131.0, 128.2, 115.5, 63.4, 37.6, 27.0, 13.8; *m*/*z* (APCI) 423.56 (M+H, 30%), 297.64 (10).

The filtrate gave ester **23a** (0.33 g, 56%). δ_H(400 MHz; $CDCl_3$) 7.97 (2H, dd, *J* 1.2 and 3.8, thiophene H-3), 7.68 (2H, m, thiophene H-5), 7.15 (2H, m, thiophene H-4), (2H, m, thiophene H-3), 5.80 (1H, m, H-6), 5.65 (1H, s, H-2), 4.95–5.11 (2H, m, 2×H-7), 4.12–35 (2H, m, OCH_2CH_3), 2.85 (1H, t, *J* 7.3, H-4), 2.62 (1H, t, *J* 7.3, H-4), 2.30–2.48 (2H, m, 2×H-5), 1.34 (3H, m, OCH_2CH_3); δ_C(100.6 MHz; $CDCl_3$) 199.1, 164.4, 162.6, 160.5, 159.2, 136.7, 135.8, 134.7, 131.0, 128.2, 115.7, 115.5, 89.1, 62.5, 61.3, 42.0, 38.9, 27.4, 27.0, 14.0; *m*/*z* (APCI) 297.62 (M+H, 15%).

3.6. General method for (5-phenyl-(1*H*)-tetrazole) containing complexes

The required stoichiometry (between 0 and 4 equiv) of thiophene-2-carboxylic acid was dissolved in 50 mL of dry toluene. To the resulting solution, the required stoichiometry (between 0 and 4 equiv) of 5-phenyl-(1*H*)-tetrazole in dry THF (20 mL) was added, then 1 equiv of LTA. The mixture was stirred for 20 min, and the solvent was removed in vacuo at 40 °C (usually at 77 mbar). This procedure was repeated twice to remove the acetic acid formed shown by the disappearance of the singlet at δ_H (DMSO-d_6) in the ^{1}H NMR spectrum. Attempts to crystallise these complexes were unsuccessful due to their low solubility and stability in the organic solvents.

*3.6.1. Lead(IV) tri(thiophene-2-carboxylate)mono(5-phenyl-(1H)-tetrazole) **30** (m=3, n=1)*

LTA (2.00 g, 4.5 mmol), thiophene-2-carboxylic acid (1.73 g, 13.5 mmol) and 5-phenyl-(1*H*)-tetrazole (0.60 g, 4.1 mmol) were reacted according to the above general method to give **30** (*m*=3, *n*=1) as a pale yellow powder (2.48 g, 75%): mp 155 °C dec; ν_{max} (KBr disk)/cm^{-1} 1526s, 1423s; δ_H(200 MHz; DMSO-d_6) 8.08 (2H, dd, *J* 4.3 and 8.0, ArH), 7.84 (3H, dd, *J* 1.2 and 4.9, thiophene H-3), 7.68 (3H, dd, *J* 1.2 and 3.7, thiophene H-5), 7.48–7.63 (3H, m, ArH), 7.18 (3H, dd, *J* 3.7 and 4.9, thiophene H-4); δ_C(400 MHz; DMSO-d_6) 165.8, 132.9, 130.3, 129.8, 128.8, 127.3.

*3.6.2. Lead(IV) di(thiophene-2-carboxylate)di(5-phenyl-(1H)-tetrazole) **30** (m=2, n=2)*

LTA (2.00 g, 4.5 mmol), thiophene-2-carboxylic acid (1.15 g, 9.0 mmol) and 5-phenyl-(1*H*)-tetrazole (1.20 g, 8.2 mmol) were reacted according to the above general method to give **30** (*m*=2, *n*=2) as a pale yellow powder (3.13 g, 99%): mp 165 °C dec; ν_{max} (KBr disk)/cm^{-1} 1421s, 1609m, 1164m; δ_H(200 MHz; DMSO-d_6) 8.06 (4H, dd, *J* 4.3 and 8.0, ArH), 7.87 (2H, dd, *J* 1.0 and 4.9, thiophene H-3), 7.68 (2H, dd, *J* 1.0 and 3.8, thiophene H-5), 7.45–7.60 (6H, m, ArH), 7.19 (2H, dd, *J* 3.8 and 4.9, thiophene H-4); δ_C(400 MHz; DMSO-d_6) 127.3, 127.5, 128.7, 129.9, 130.8, 132.3, 132.4, 141.5, 157.8, 166.9.

*3.6.3. Lead(IV) mono(thiophene-2-carboxylate)tri(5-phenyl-(1H)-tetrazole) **30** (m=1, n=3)*

LTA (2.00 g, 4.5 mmol), thiophene-2-carboxylic acid (0.57 g, 4.5 mmol) and 5-phenyl-(1*H*)-tetrazole (1.80 g, 12.3 mmol) were reacted according to the above general method to give **30** (*m*=1, *n*=3) as a pale tan coloured powder (3.00 g, 98%): mp 119 °C dec; ν_{max} (KBr disk)/cm^{-1} 1527s, 1419s, 1609m, 1563s, 1163m; δ_H(400 MHz; DMSO-d_6) 8.06 (6H, dd, *J* 4.3 and 8.0), 7.76 (1H, dd, *J* 1.2 and 4.9, thiophene H-3), 7.62 (1H, dd, *J* 1.2 and 3.7, thiophene H-5), 7.47–7.59 (9H, m), 7.15 (1H, dd, *J* 3.7 and 4.9, thiophene H-4); δ_C(400 MHz; DMSO-d_6) 132.2, 130.4, 129.8, 128.7, 128.1, 127.3.

*3.6.4. Lead(IV) tetra(5-phenyl-(1H)-tetrazole) **30** (m=0, n=4)*

LTA (2.00 g, 4.5 mmol) and 5-phenyl-(1*H*)-tetrazole (2.41 g, 18 mmol) were reacted according to the above general method to give **30** (*m*=0, *n*=4) as a tan coloured powder, which turned deep brown over several days (3.50 g, 97%): mp 114 °C dec; ν_{max} (KBr disk)/cm^{-1} 1609m, 1563s, 1163m; δ_H(400 MHz; DMSO-d_6) 8.03 (8H, dd, *J* 4.3 and 8.0), 7.46–7.64 (12H, m); δ_C(400 MHz; DMSO-d_6) 130.6, 127.4, 128.1, 129.9.

*3.6.5. Reaction of 4-pentenoic acid with lead(IV) tetra-(5-phenyltetrazol-1-ide) **30** (m=0, n=4)*

4-Pentenoic acid (0.2 mL, 2.0 mmol) and lead(IV) tetra(5-phenyltetrazol-1-ide) **30** (*m*=0, *n*=4) (1.56 g, 2.0 mmol) were reacted according to the General Method to yield a brown oil (230 mg, 53%) containing a mixture of products, **33a** and **8b**, in the ratio of 6:1.

5-(5-Phenyltetrazol-1-ylmethyl)dihydrofuran-2-one **33a** (106 mg, 21%) was isolated as a white solid by flash column chromatography eluting with 1:1 ethyl acetate/(40–60) petroleum ether (R_f=0.2 **33a**, 0.45 **8b**). Mp 82–84 °C; ν_{max}(KBr disk)/cm^{-1} 1773s, 1450s, 1182s; δ_H(400 MHz; $CDCl_3$) 8.09–8.18 (2H, m, ArH), 7.46–7.55 (3H, m, ArH), 5.10–5.17 (1H, m, H-2), 4.98 (1H, dd, *J* 3.1 and 14.1, CH_2N), 4.86 (1H, dd, *J* 5.0 and 14.1, CH_2N), 2.14–2.65 (4H, m, H-3, 4); δ_C(400 MHz; $CDCl_3$) 130.6, 128.9, 126.9, 76.3, 55.6, 27.7, 25.0; *m*/*z* (CI, NH_3) 245.11 ($[M+H]^+$, 100%), 262.13 ($[M+Na]^+$, 45); HRMS (ES^+) found 245.1033 $[M+H]^+$, requires 245.1039.

3.7. Reaction of lead(IV) tetraacetate with an excess of 5-(2-(but-3-enyl)phenyl)tetrazole 35

Lead(IV) tetraacetate (0.22 g, 0.5 mmol) was reacted with 5-(2-(but-3-enyl)phenyl)tetrazole **35** (0.40 g, 2 mmol, containing the tetrazole **36**) in dry α,α,α-trifluorotoluene. Work-up in the usual way and attempted purification of the mixture by flash column chromatography on silica gel gave only azepine **38** (10 mg). R_f=0.2 (2:1 heptane/ethyl acetate); δ_H(400 MHz; $CDCl_3$) 8.23 (1H, d, *J* 7.2, ArH), 7.86 (1H, dd, *J* 7.6 and 1.6, ArH), 7.36–7.52 (Ar–H), 7.28–7.34 (Ar–H), 5.49–5.56 (1H, m, CH_2CHN), 5.34–5.39 (1H, m, NCH), 5.16–5.22 (1H, m, NCH), 2.93–3.07 (2H, m, $C_6H_4CH_2$), 2.89 (2H, t, *J* 7.9, $ArCH_2$), 2.51–2.59 (1H, m, CH), 2.20–2.29 (1H, m, CH), 1.47–1.55 (2H, m, CH_2), 1.25–1.33 (4H, m, CH_2CH_2), 0.82–0.91 (3H, m, CH_3); δ_C(100.6 MHz; $CDCl_3$) 166.0, 154.2, 142.4, 139.5, 132.0, 130.6, 130.4, 130.2, 129.9, 129.6, 127.8, 126.0, 125.3, 122.7, 58.4, 55.2, 34.0, 31.7, 30.9, 30.1, 22.5, 14.1; *m*/*z* (ES^+) 473.30 ($[M+MeCN+NH_4]^+$, 100%).

3.8. X-ray crystal structure determination

Crystals of **11c**, **11g**, **11j** and **16** were grown by slow diffusion. Single crystal X-ray diffraction data were collected using graphite monochromated Mo Kα radiation (λ=0.71073 Å) on an Enraf-Nonius KappaCCD diffractometer. The diffractometer was equipped with a Cryostream N2 open-flow cooling device,[84] and the data were collected at 150(2) K. Series of ω-scans were performed in such a way as to cover a sphere of data to a maximum resolution of 0.77 Å. Cell parameters and intensity data were processed using the DENZO-SMN package.[85] The structures were solved by direct methods[86] and refined by full-matrix least squares on F using the CRYSTALS suite.[87] Intensities were corrected for absorption effects by the multi-scan method, based on multiple scans of identical and Laue equivalent reflections. In general, non-hydrogen atoms were refined with anisotropic displacement parameters, however, where there was disorder in the structures for **11g**, **11j** and **17**. For these compounds, examination of the resulting model showed the carbon atoms of the thiophene ring to have large thermal parameters, and a difference Fourier map showed a nearby peak of residuak electron density. These observations were taken to be due to disorder of this group over two orientions related by a 180° rotation about the bond joing it to the remainder of the molecule. Cordinates and site occupancies were refined for the disordered non-hydrogen atoms. For compounds **11g** and **11j** anisotropic thermal parameters of the atoms of the major orientation of the ring and isotropic thermal parameters of the minor orientation were refined, however, for **17** the refinement was unstable, so isotropic thermal parameters were used for both components. For the disordered thiophene rings, geometric restraints were applied (the S–C bond lengths were restrained to 1.71(1) Å, C=C bonds to 1.36(1) Å, C–C bonds to 1.42(1) Å and chemically-equivalent bond angles to their common mean) and the total of the occupancies of the two orientations was constrained to unity. In general, the hydrogen atoms were all visible in a difference map, but were repositioned geometrically, then refined with soft restraints on the bond lengths and angles to regularise their geometry after which the positions were refined with riding constraints. For structure **17** hydrogen atoms were positioned geometrically after each cycle of refinement. In each case, a 3-term Chebychev polynomial weighting scheme was applied.[88,89] Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge from http://www.ccdc.cam.ac.uk/products/csd/request/ (CCDC 693949–693952).

*3.8.1. Single crystal X-ray diffraction data for **11c** (CCDC 693949)*

$C_{17}H_{16}O_4S_1$, M_r=316.38, monoclinic (*P*2(1)/*n*), *a*=6.39800(10) Å, *b*=23.2370(4) Å, *c*=10.3136(2) Å, β=90.3700(7)°, *V*=1533.29(5) $Å^3$, *Z*=4, μ=0.226 mm^{-1} D_{calcd}=1.370 Mg/m^3, *T*=150(2) K, 15,011 reflections collected, 3475 independent [*R*(int)=0.036], R_1=0.0515, wR_2=0.0585 [$I>3\sigma(I)$].

*3.8.2. Single crystal X-ray diffraction data for **11g** (CCDC 693950)*

$C_{11}H_{12}O_4S_1$, M_r=240.28, monoclinic (*P*2(1)/*n*), *a*=11.0732(2) Å, *b*=7.7705(2) Å, *c*=13.4673(3) Å, β=103.9786(11)°, *V*=1124.47(4) $Å^3$, *Z*=4, μ=0.283 mm^{-1} D_{calcd}=1.419 Mg/m^3, *T*=150(2) K, 11,110 reflections collected, 2546 independent [*R*(int)=0.021], R_1=0.0277, wR_2=0.0304 [$I>3\sigma(I)$].

*3.8.3. Single crystal X-ray diffraction data for **11j** (CCDC 693951)*

$C_{11}H_{12}O_4S_1$, M_r=240.28, triclinic (*P*−1), *a*=6.9926(3) Å, *b*=7.4493(4) Å, *c*=11.5072(6) Å, α=97.881(2)°, β=98.856(3)°, γ=103.2016(17)°, *V*=567.29(5) $Å^3$, *Z*=4, μ=0.281 mm^{-1} D_{calcd}=1.407 Mg/m^3, *T*=150(2) K, 7414 reflections collected, 2573 independent [*R*(int)=0.034], R_1=0.0390, wR_2=0.0474 [$I>3\sigma(I)$].

*3.8.4. Single crystal X-ray diffraction data for **17** (CCDC 693952)*

$C_{12}H_{14}O_4S$, M_r=254.31, monoclinic (*P*2(1)/*c*), *a*=7.0552(3) Å, *b*=19.0298(9) Å, *c*=9.4200(4) Å, β=105.478(3)°, *V*=1218.85(9) $Å^3$, *Z*=4, μ=0.265 mm^{-1} D_{calcd}=1.386 Mg/m^3, *T*=150(2) K, 9800 reflections collected, 2748 independent [*R*(int)=0.036], R_1=0.0474, wR_2=0.0593 [$I>3\sigma(I)$].

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.01.042.

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