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The effect on mesomorphic properties of a triple bond in a terminal chain of 4,4'-disubstituted phenyl benzoates and phenyl thiobenzoates

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The effect on mesomorphic properties of a triple bond in a terminal chain of 4,4′-disubstituted phenyl benzoates and phenyl thiobenzoates

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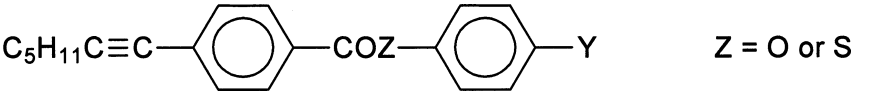
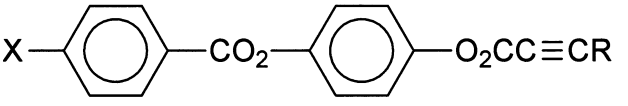
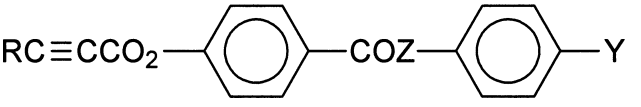
The effect of a triple bond in a terminal chain on the mesomorphic properties of rod-like mesogens was studied by replacing a straight alkyl chain with a terminal 1,2-alkynyl chain in some esters and thioesters of the type:



or by incorporating the triple bond into an alkyl ester chain in esters and thioesters of the types:





The triple bond should provide increased rigidity to the triple bond region but increased flexibility at the adjacent single bond. These should have opposite effects on the mesomorphic properties. The first compounds were synthesized by esterification of the appropriate alkynylbenzoic acids with various phenols or thiols using the carbodiimide method. Detailed syntheses are provided for the alkynylbenzoic acids. Preparation of the alkynyl ester compounds was by acylation of the precursor hydroxyl esters or thioesters using either the acid chloride or carbodiimide method. The synthesis of the phenolic or thiolic ester intermediates, usually using a protection group, is described. Mesomorphic properties of these new esters and thioesters were determined using hot stage polarizing microscopy and DSC and compared with those for the known parent compounds. Fewer mesophases having shorter temperature ranges and lower transition temperatures were usually observed. Some of the intermediate phenols or benzyl ethers were also studied. Long chain benzyloxy esters showed a nematic phase as did some of the hydroxy thioesters but no mesophases were observed in the hydroxy esters.

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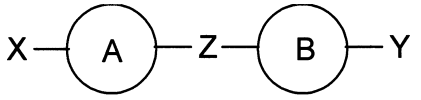
1. Introduction

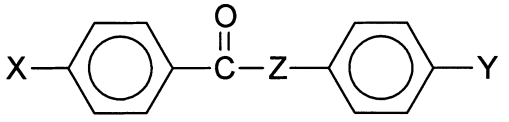
A variety of structural features influence the mesomorphic properties in rod-like molecules of the type **1**:



1

Structure–property relationship studies have shown that the core part of these structures consisting of the two ring systems *A* and *B* (usually aromatic) plus the connecting group *Z* determines the types of mesophase that can occur for these structures; it also influences the temperature and range of these phases. The two terminal chains *X* and *Y* help to modify the properties set by the core.

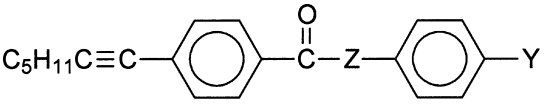
In previous structure–property relationship studies of the mesomorphic properties in the esters **2** and the thioesters **3**,



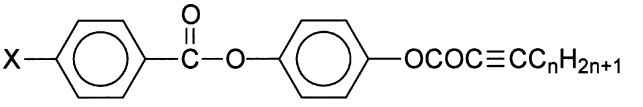
2 Z = O

3 Z = S

we found that increasing the flexibility of the terminal chain by inserting carbonyl-containing groups in different positions of the terminal chain tended to produce fewer mesophases, having shorter ranges and lower transition temperatures [1–7]. We also found that no additive effect occurred using different *X* and *Y* substituents [8]. From these studies arose the obvious question: would a more rigid chain improve the mesomorphic properties? A cinnamate chain (Y=CH=CHCO$_2R$) is known to yield wider range mesophases but with higher transition temperatures in the anils [9]. Studies of the effect of 1-alkenyl chains on a variety of mesogens suggest that these chains also yield better mesophases [10]. Our recent work with 1-alkenyl diphenyldiacetylenes showed that these compounds had wider range nematic phases [11]. We considered two more chain modifications that could yield more rigid terminal chains: perfluorinated chains and alkynyl chains. Our work with perfluorinated chains in esters will be reported elsewhere. In this paper, we discuss the effect of alkynyl chains on the mesomorphic properties of esters and thioesters. Although a 1-alkynyl chain increases the rigidity of the terminal chain at the C_1 and C_2 positions, flexibility would increase at the C_3 position with the absence of C_2 hydrogens to hinder rotation around the C_2–C_3 bond. However, there is also less hindrance around this bond in the 1-alkenyl compounds, although rather more than with the triple bond. Thus, we chose to synthesize examples of the following esters and thioesters:



4 Z = O **5** Z = S



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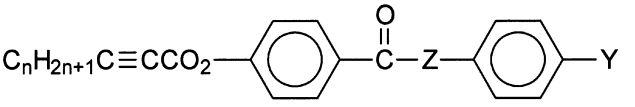
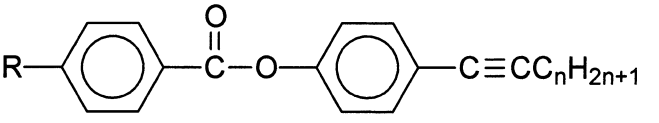


7 Z = O **8** Z = S

Synthesis of the alkynyl esters **9**



9

was reported earlier [12] but no transition temperatures were given. Introducing the triple bond as part of an ester chain is an easy way to add it to the terminal chain without it being conjugated to the benzene ring. The ester-ring linkage through the ether side of the ester is sterically hindered to rotation around the ring-O bond due to steric hindrance between the carbonyl group and the ring *ortho* protons. The triple bond attached directly to the ring (**4**, **5**) does not have this restricted

rotation. Conjugation of the triple bond with the benzene ring would make the chain rigid in the first two carbon atoms, effectively extending the core length. Flexibility, however, would increase at the C_2–C_3 bond.

2. Synthesis

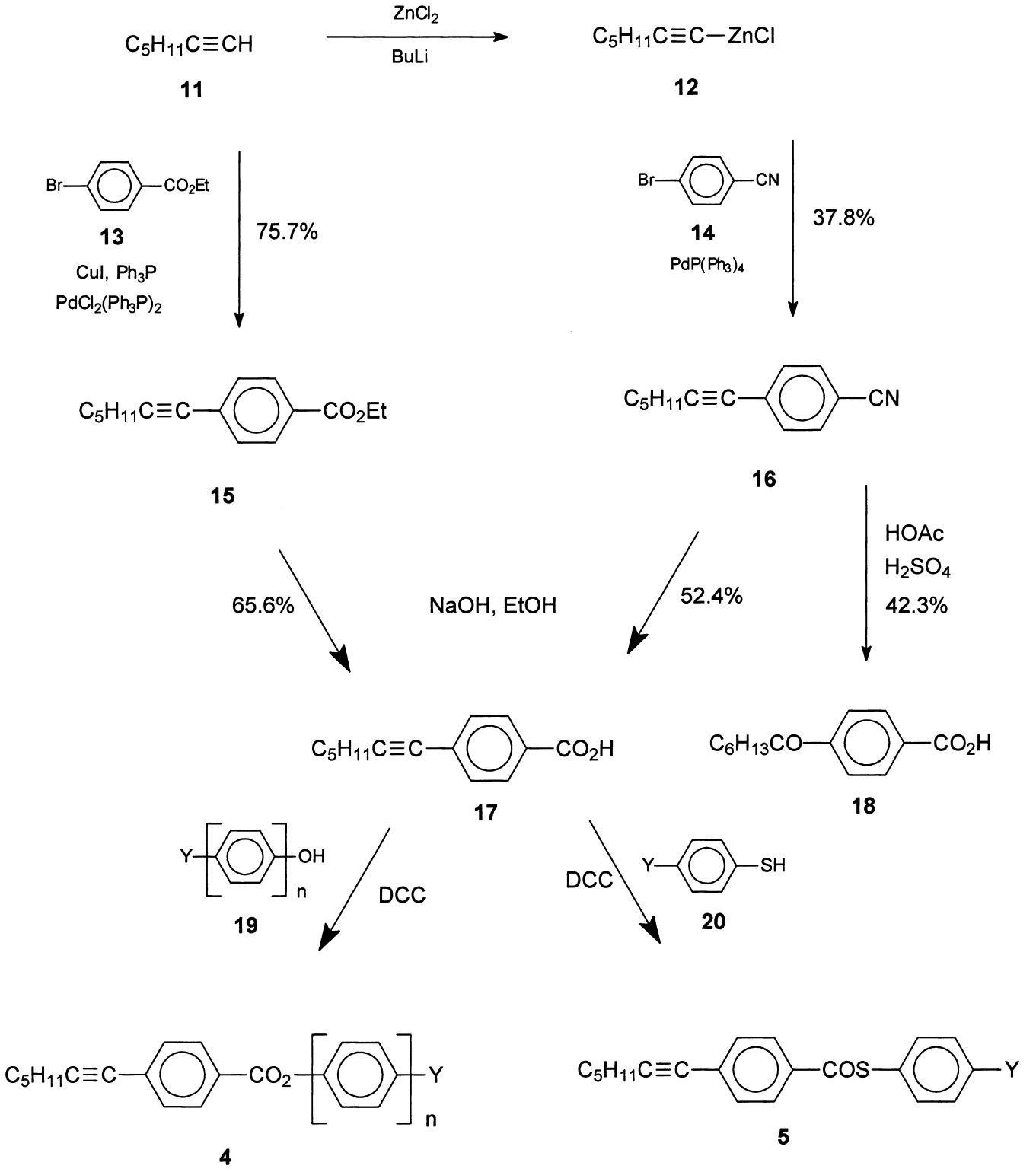
Synthesis of the esters **4** and thioesters **5** is shown in scheme 1 An attempt at a direct coupling of 1-heptyne (**11**) with 4-bromobenzoic acid gave a mixture of compounds, but a coupling with the ester **13** gave the alkynyl ester **15** in a good yield [13, 14]. Hydrolysis of this ester gave the desired acid **17**. Converting the acetylene **11** to the zinc couple **12** and then coupling this to the bromonitrile **14** gave the alkynyl nitrile **16** but in a lower yield than the ester **15**. Treatment of the nitrile **16** with acid led to the addition of water to the triple bond as well as hydrolysis of the nitrile group providing an improved synthesis of the α-keto acid **18** than that reported earlier [7]. Basic hydrolysis of the nitrile **16** gave the desired alkynyl acid **17**. Since the ester **15** is easier to hydrolyse than the nitrile, the route through the ester became the method of choice. Esterification of the alkynyl acid **17** with the phenols **19** using the carbodiimide procedure gave the esters **4**; reaction with the thiols **20** gave the thioester **5** (Y=R, OR'). The 4-substituted phenols **19** were available from our earlier work but we had only a few of the alkyl/alkoxy (Y=R, branched chain, OR) thiols **20** so only a few thioesters were prepared. We chose to prepare the ester/thioesters **24** with n=3 and 9 using the method shown in scheme 2[15]. Esterification of 4-hydroxythiophenol with the acid chlorides **21** gave primarily the desired thioesters **22** with X=C_7H_{15} and $C_5H_{11}C{\equiv}C$. With X=C_7H_{15}, some of the ester thioester **23** was also isolated (*c* 10.4%). Esterification of these phenols **22** with the appropriate acid chlorides or acid gave the thioesters **24**.

The synthesis for the esters **6** is presented in scheme 3 Obviously, the easiest approach to the desired phenol **36** would be a simple acylation of hydroquinone with one equivalent of the alkynyl acid chloride which was widely used earlier [16–18] More recent results indicate that acylation of a monoprotected hydroquinone is more effective [19]. In our experience, using only one equivalent of a reactant to obtain reaction on only one of two equally (or nearly so) reactive functional groups produces primarily the mono-product, but it is contaminated with small amounts of byproduct, starting material and some unknown higher molecular mass (polymer?) material making it very difficult to obtain a high purity monosubstituted product (see, for example, [2]). Although we were able to obtain some of the phenol **36** in this manner, the yields were too low to be practical for large quantities.

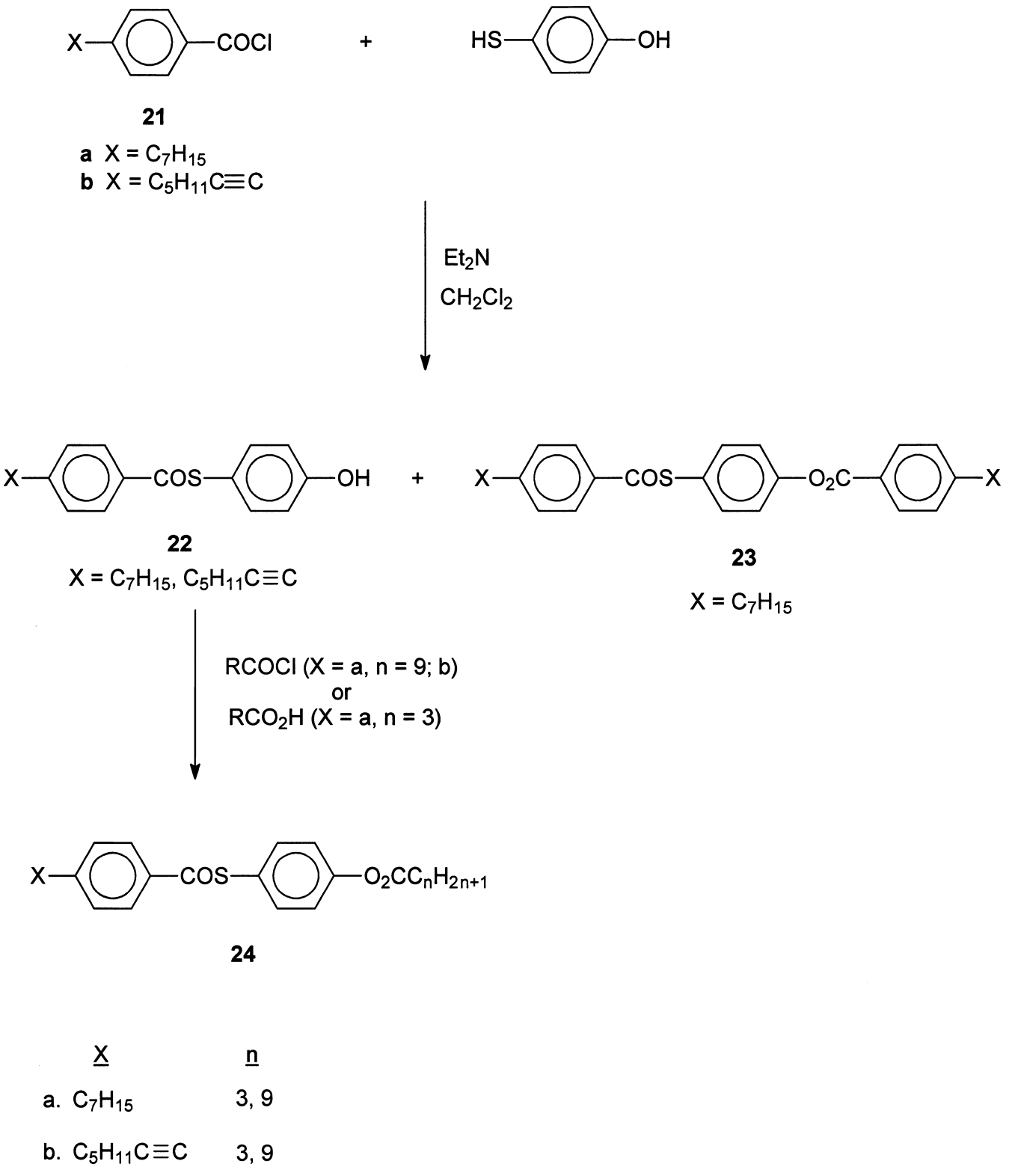
We previously prepared the acyloxy esters **34** by esterifying benzyloxy phenol **25** to obtain the protected acyloxyphenol **27**, removing the benzyl group by hydrogenolysis to obtain the phenol **30** and then esterifying using the carbodiimide method [2]. The triple bond in the alkynyl analogues would, however, not survive the hydrogenolysis. This is not a problem with the *t*-butyldimethyl silyl protecting group since it can be removed by using *p*-toluene sulphonic acid [21]. This protecting group was used successfully to prepare the desired benzyloxy compound **28**. Removal of the benzyl group, acylation of the phenol **31** with the acid **33** and removal of the silyl group from the ether **35** gave the desired phenol **36**. However, this material was difficult to purify. This also was true of the previously prepared alkyl analogues **30**. Perhaps some transesterification occurs.

We found that the best approach was first to esterify benzyloxyphenol **25** with the appropriate acid **26** to obtain the benzyloxyesters **29** (R'=Bn). The silyl-protected ester **29** (R=$SiMe_2t$-Bu) could also be prepared from the phenol **31** although this was a longer route via the protected diether **28**. Removal of the protecting groups from the ether esters **29** gave the hydroxyesters **32**. These could be easily and cleanly esterified with the appropriate alkynyl acid (DCC) or acid chloride to give the desired acyloxy esters **6**. These esters were more soluble than the typical alkyl/alkoxy esters making them more difficult to purify by recrystallization and providing a good reason for using intermediates having high purities. Thus, the synthesis route through the phenol **32** for preparing a large number of esters having various R groups is preferred even though this approach is more time consuming.

We previously reported the synthesis of esters with an acyloxy group on the acid end, **2** and **3**, from the acyloxybenzoic acid [3]. As with the synthesis of the acyloxyphenols, this route also gives materials contaminated with transesterification products. Therefore, we chose a route through the phenols **41** (scheme 4) to prepare the alkynyl acyloxy esters/thioesters **2**, **3**, **7** and **8**. The commercially available hydroxy esters **37**, with R=Me or Et, were used to prepare the benzyl-protected phenol **38a** which was then hydrolyzed to the acid **39a**; this was esterified with the appropriate phenols **40** (Z=O) to give the protected esters **42a** (Z=O). Hydrogenolysis of these esters gave the phenol esters **41a**. Esterification of these phenols with an alkynyl acid using either the carbodiimide (X=OH) or the acid chloride (X=Cl) method gave the desired esters **7**. Data

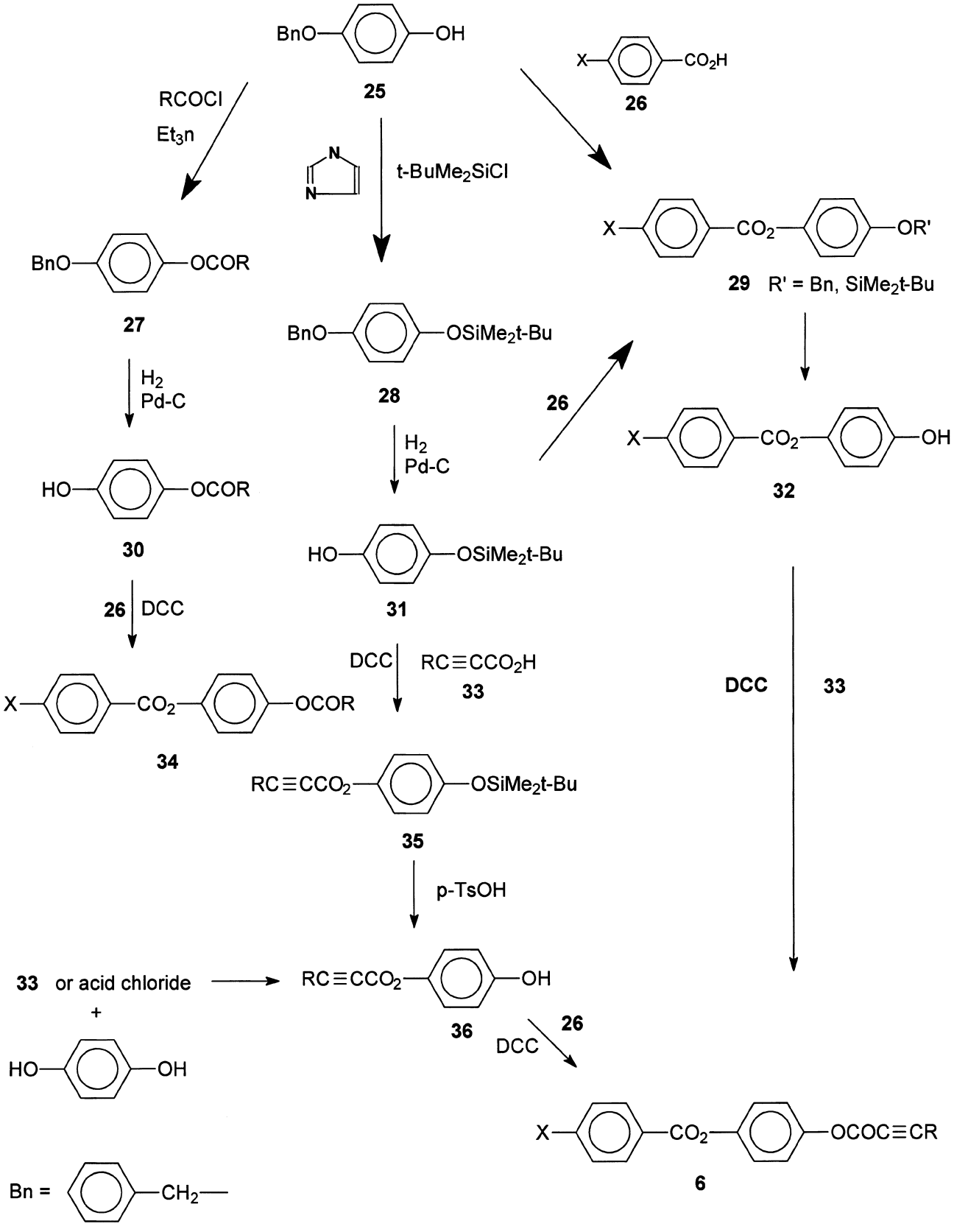


Scheme 1.

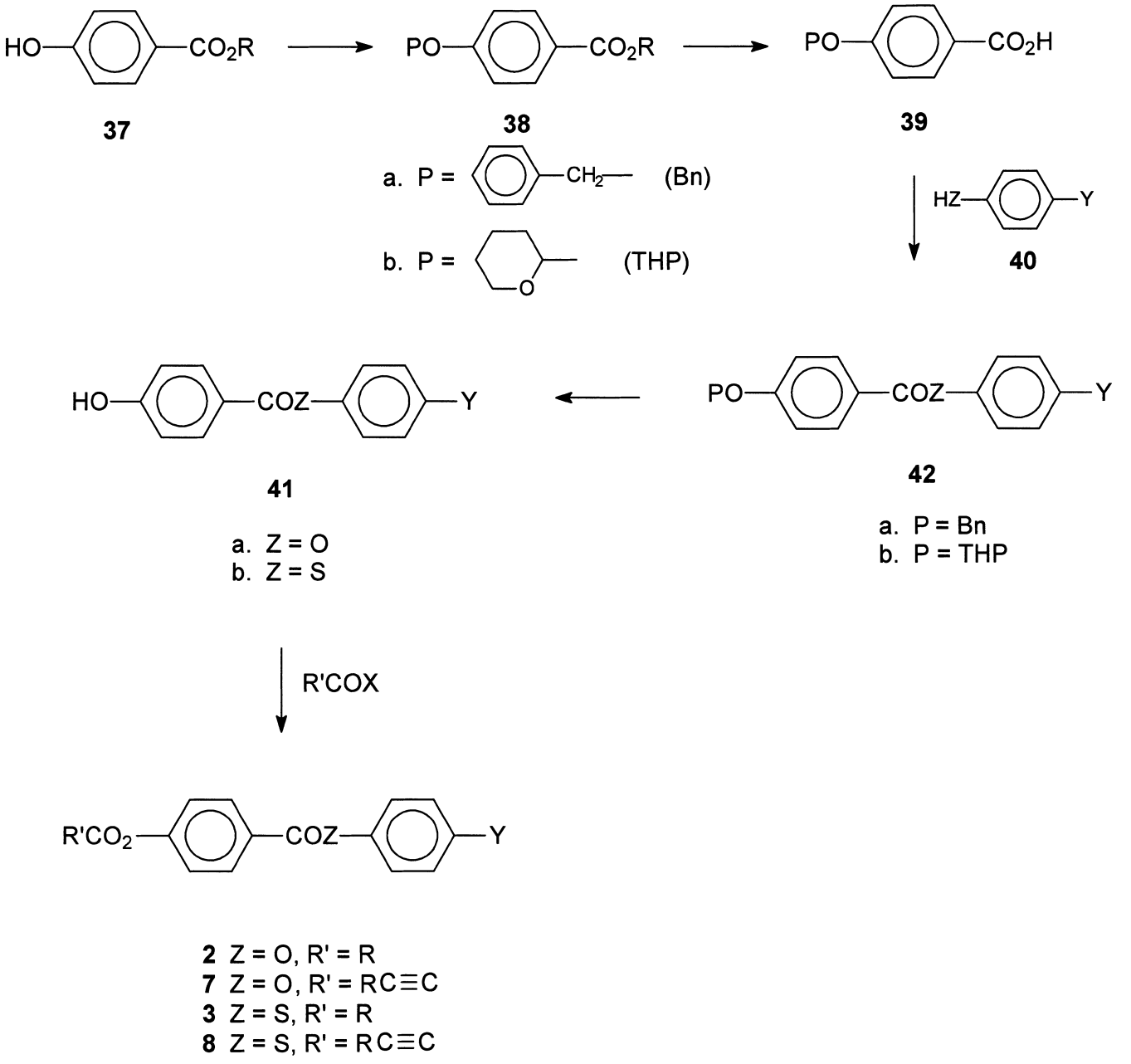


X	n
a. C_7H_{15}	3, 9
b. $C_5H_{11}C\equiv C$	3, 9

Scheme 2.



Scheme 3.



Scheme 4.

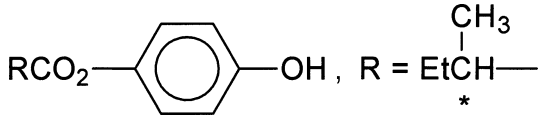
for the parent compounds **2** were available from our earlier work [3].

The benzyl group, however, cannot be used to prepare the thioesters **3** and **8** since the sulphur atom in these compounds poisons the catalyst used in hydrogenolysis. THP groups are commonly used to protect alcohol groups and they can be easily removed by treating with dilute acid. We considered that this group could be used on the methyl/ethyl ester of 4-hydroxybenzoic acid to prepare the thioesters **41b**. This was accomplished via the route from **38** to **41** shown in scheme 4, but several problems were encountered which resulted in low yields. The commonly used method for preparing the THP ethers, using an excess of dihydro-2H-pyran (DHP) in CH_2Cl_2 with *p*-toluenesulphonic acid as the catalyst [22] gave a thick gum-like material that was difficult to purify due to the difficulty in removing the final traces of DHP. Additionally, some of the THP group was cleaved during the hydrolysis of the ester **38**. More recently, different conditions have been used to form the THP-protected benzyl ester **38b** (R=$CH_2C_6H_5$) [23]. In this approach, ethyl acetate

was used as the solvent and HCl as the catalyst; the benzyl ester was cleaved by hydrogenolysis. This could be a better method for preparing the theoesters **42**.

All the alkynyl ester/thioesters were purified by column chromatography followed by recrystallization using a final hot filtration through #50 filter paper. Materials were purified until the mesophase to isotropic transition had a range of $<0.3^\circ$ and the melting range was $<3^\circ$ by microscopy. Structures were confirmed by IR, and ^1H and ^{13}C NMR.

We found that the IR ester carbonyl peak in the intermediate phenols **32** and **41a** was often split into two peaks when the spectra were obtained in Nujol (mineral oil). Initially, this was confusing since it was felt that these materials must be impure, perhaps contaminated with the starting acid. However, repeated purifications did not lead to either the disappearance or a decrease in intensity of one of these peaks. This splitting was not observed in the thioester phenols **22** and **41b** nor in any of the benzyl ether esters. We have observed split carbonyl peaks before in 4-substituted benzoyl chlorides [24] and in the phenol



but not when R is a straight chain. Knowing that these peaks can split in IR spectra can save time in interpreting them correctly.

3. Mesomorphic properties

Mesomorphic properties for the new alkynyl ester/thioesters were determined by hot stage polarizing microscopy and are given in tables 1–4. Data for the analogous alkyl compounds are included for comparison. Some of these have been reported earlier but many are new compounds prepared for this comparison. In some cases, data for nearby homologues that were reported earlier are used. Clearing temperatures decreased in all the alkynyl thioesters **5** (table 2) but often increased in the esters **4** (table 1). Melting temperatures increased or decreased in both the esters and thioesters but increases occurred more often. Mesophases were less favoured in both series. An interesting exception is the thioester with $X=C_5H_{11}C\equiv C$ and $Y=OC_5H_{11}$ which had a wider nematic range than its parent with $X=C_7H_{15}$ along with its lower melting and clearing temperatures. The alkyl esters in some analogues have a smectic A phase as well as a nematic phase but the alkynyl analogues showed only nematic phases. Both the alkyl and alkynyl thioesters showed only nematic phases. Mesophases occurred more often in the alkynyl thioesters and these had wider temperature ranges than did the esters, a trend also observed for the alkyl thioesters.

Likewise, an alkynylacyloxy group on the phenol side of esters **6** (table 3) did not enhance mesomorphic properties. Both clearing and melting temperatures decreased considerably in the few examples studied. Enantiotropic nematic phases were observed only when $X=C_{10}H_{21}O$. The alkyl parents showed monotropic smectic B and C phases as well as the nematic phase, but only monotropic smectic A phases were observed in the alkynyl acyloxy series. We were unable to obtain data for the thioester series to determine the effect in these compounds. Similar results were observed for both the esters and thioesters with an alkynylacyloxy group on the acid side (table 4).

To determine if the thioester **5** ($Y=OC_5H_{11}$) could be useful in a binary mixture of thioesters having a near room temperature nematic phase, a eutectic mixture of this material with the analogue with $Y=C_5H_{11}$ was prepared. To do this, enthalpy values (kJ/mole) were determined by DSC:

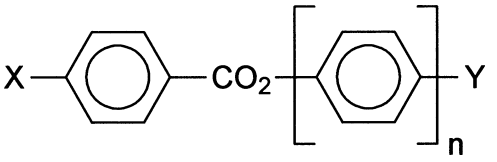
Y	ΔH_m	ΔH_{clp}
C_5H_{11}	10.80	0.75
OC_5H_{11}	31.15	0.86

Using the ΔH_m values in the van Laar equation [29] the eutectic composition was calculated to be 61.5% $Y=C_5H_{11}$ and 38.5% $Y=OC_5H_{11}$ having a melting temperature of 13.8°C, a clearing temperature of 52.6°C and a nematic range of 38.8°C. The observed values were not as promising with 26.2°C (melting), 53.0°C (clearing) and 26.8°C (N range) suggesting that this material would not form a good eutectic mixture.

Although some intermediates used in the synthesis of various mesogens have the potential for forming mesophases, these are often overlooked and not checked for mesophases by microscopy. A typical example is the 4-substituted benzoic acids. Both the 4-alkyl and 4-alkoxy acids show mesophases by forming hydrogen-bonded dimers. We looked for mesophases in the new acids prepared in this work, **17** and **18** but none were observed. Transition temperatures for these are recorded in the experimental section.

The benzyloxy esters **29** ($R'=Bn$), **42a** and the phenol esters/thioesters **32** and **41** also have the potential to form mesophases. Melting temperatures for some of the esters have been reported in the literature. In one benzyl ether, a nematic phase was found; however, most of these compounds were not checked for mesophases. Since we had a variety of these compounds available

Table 1. A comparison of transition temperatures (°C) for:



		X=C_7H_{15}					X=$C_5H_{11}C{\equiv}C$			
Y	n	Cr[a]	SmA	N	I	N range	Cr	N	I	N range
$C_{10}H_{21}$	1	33.1		(36.8–36.9)	40.9–41.3	m	32.0		36-7–38.9	0
COC_4H_9	1	60.3	77.8–78.0		84.0–84.1	0	60.9	77.6–78.0	89.5–89.7	11.7
COC_9H_{19}	1	81.5	92.6–93.1		94.1–94.4	0	83.4(Cr_2)[f]		96.7–97.4(Cr_1) 93.6–94.0(Cr_2)	0
OC_5H_{11}	1	19.9[b]		42.1–44.4	53.0–53.1	11.0	46.9	(43.4)	50.9–53.2	m
$OC_{10}H_{21}$	1	33.2[c]	(43.4–43.5)	47.3–47.9	64.3–64.4	17.1	57.5	(60.4–60.7)	66.0–66.3	m
$OCOC_9H_{19}$	1	68.2		(72.8)	74.1–74.8	m	64.4	(64.5–64.8)	69.0–69.5	m
CN	1	[d]		44	56.3	12.5	42.3	(49.5–49.8)	66.4–68.7	m
CN	2	[e]		92.1	224.4	132.3	62.7	112.7–113.5	248.1–248.4	135.7

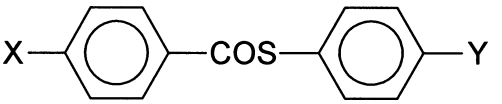
[a]Cr=crystallization obtained on cooling the melt at 2° min^{-1}; phases are designated by SmA=smectic A, N=nematic, I=isotropic liquid. Monotropic phases (those occurring below the melting temperature) are indicated by parentheses and m. Monotropic phase ranges cannot be compared with enantiotropic ones. [b]Two crystal forms were observed. The melt formed Cr_1 on cooling to 19.9°C; further cooling gave Cr_2 which reverted to Cr_1 on reheating to 28.3–34-8°C. Cr_1 melted to the N phase. [c]Two crystal forms were observed. The melt formed Cr_1 at 33.2°C, changing to Cr_2 at 31.2°C with further cooling. Cr_2 melted to N on reheating. [d]Data are from reference [25] [e]Data are from reference [26] [f]Cr_2 converted to Cr_1 at 93.6–94.0°C on heating.

from this and earlier work, we thought it would be worthwhile to study, by microscopy, all of those still available. Our data are collected in tables 5 and 6. When literature data were reported, these are included for comparison. The THP- and silyl-protected phenols were considered too unstable to study. Among the benzyloxy esters **42a** (table 5), the Y=alkyl analogues showed no mesophases but when Y=OR, a monotropic nematic phase was observed for the longer R chains. With a carbonyl group attached to the benzene ring (Y=COC_9H_{19}, $CO_2CH_2C_7F_{15}$), smectic A phases were observed instead of nematic phases. None of the corresponding phenols **41a** showed any mesophases. Among the few benzyl esters **29** (table 6), mesophases were observed only when X=$C_{10}H_{21}O$ which showed an enantiotropic nematic and a monotropic smectic A phase. Again, none of the phenols **32** were found to have mesophases. A monotropic nematic phase was reported in the literature for the X=RO homologous series [25]. Our material did not supercool to the temperature of the nematic phase reported, despite repeated attempts to obtain a lower crystallization temperature. Our higher crystallization temperature could be due to a higher purity. Both of the alkoxy thioester phenols **22** (X=$C_{10}H_{21}O$) and **41b** (Y=OC_8H_{17}) showed monotropic nematic phases (table 6). In some of our earlier work, we found mesophases in phenolic esters that contained more than two benzene rings [30]. A melting point for the phenol **32** (X=NC) was reported earlier [25]. Virgin crystals of our material showed the same melting temperature but this material seemed to change at this temperature. On cooling the melt just a degree below the clearing temperature, a discotic-like texture was observed in some of the melt (see reference [31], plate 117). Reheating this material gave a very broad melting temperature above 200°. A sample that was allowed to cool to room temperature and set overnight gave an even broader melting suggesting that this material was a mixture. We were not interested in studying this further but wish to report that this material seems to undergo a reaction when it melts.

4. Conclusions

Inserting a triple bond into the 1,2-position of a terminal chain on the phenyl benzoates and phenyl thiobenzoates or through a chain ester linkage did not improve liquid crystalline properties. Mesophase temperature ranges were usually smaller, and mesophases were less likely to occur, than those for the parents. Often transition temperatures were lower but

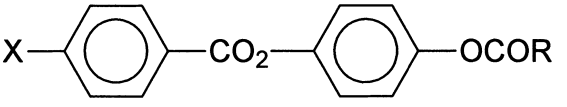
Table 2. A comparison of transition temperatures (°C) for:



	X=C_7H_{15}				X=$C_5H_{11}C{\equiv}C$			
Y	Cr[a]	N	I	N range	Cr	N	I	N range
C_4H_9		34.6[b]	42.1	8.0	9.3(Cr_2)[c]	(26.5–26.9)	35.2–36.7(Cr_1) 33.7–34.6(Cr_2)	m
C_5H_{11}	14.3	28.0–28.4	55.4–55.5	27.1	1.5	33.8–34.1	45.6–45.9	11.8
C_7H_{15}	22.2[d]	39.4	56.1	16.7	18.2	44.9–45.5	48.4–48.7	3.2
$C_{10}H_{21}$	20.2[e]	34.5–35.0	48.3–48.7	13.7	20.3(Cr_1)[f]	40.9–41.4(K_2)	49.5–49.6	8.2
OCH_3	24.0(Cr_2)[g]	53.8–54.9(Cr_1)	69.0–69.1	14.2	15.3	(55.3)	60.2–60.8	m
OC_5H_{11}	19.3	57.3–58.2	71.4–71.5	13.3	6.8	37.0–37.4	64.4–64.6	27.2
OC_8H_{17}	18.4	38.4–39.0	72.2–72.6	33.6	28.9	54.5–55.5	72.2–72.5	17.0
$OCOC_3H_7$	53.0	62.2–63.1	89.4–89.6	26.7	53.7	70.1–71.0	84.1–84.4	13.3
$OCOC_9H_{19}$	72.5	76.8–78.5	85.6	7.1	60.2	68.2–69.4	81.6–81.7	12.8
$CH_2CH(Me)Et$	3.8[h]	(25.4–25.5)	27.8–30.1	m	−20(Cr_2)[i]	(9.5–11.0)	25.2–27.0(Cr_1)	m

[a]Cr=crystallization temperature obtained on cooling the melt at 2° min^{-1}. Types of mesophases are indicated by SmA=smectic A, N=nematic, I=isotropic liquid. Parentheses around a temperature indicate a monotropic phase which are those that occur below the melting temperature on cooling the melt. Phase ranges for these cannot be compared with those for enantiotropic mesophases. [b]Data are from reference [26]. [c]This compound showed two crystal forms with two different melting temperatures. The crystals formed on cooling (Cr_2) had a lower melting temperature than the virgin crystals (Cr_1) but converted to Cr_1 on standing at room temperature for several days. [d]Data are from reference [27]. [e]The first crystals formed at 20.2°C and then changed to another form on cooling to 17.4°C; on reheating these crystals (Cr_2) melted to the N phase. [f]Two crystal forms were observed. Cr_2 formed on cooling the melt to 20.3°C changing to Cr_1 at about 19.1°C. On reheating Cr_1 melted to the N phase. [g]Two crystal forms were observed. Cr_2 formed on cooling the melt to 24.0°C, converting to Cr_1 at 50.7–53.8°C on heating. These melted to the N phase. [h]These data are for X=C_8H_{17} obtained from reference [28]. [i]When heated to 8.6°C, Cr_2 changed to Cr_1 which melted to the isotropic liquid.

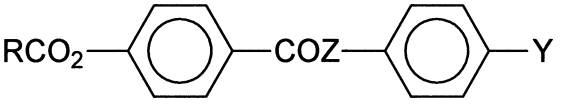
Table 3. A comparison of transition temperatures (°C) for



		R=C_nH_{2n+1}[a]				R=$C{\equiv}CC_nH_{2n+1}$					
X	n	Sm[b]	N	I	M range	n	Cr	A	N	I	M range
C_4H_9	6					4	33.5			50.5–51.8	0
C_4H_9	7					5	29.2			45.8–47.9	0
$C_{10}H_{21}$	5		(66.7)	68.9	m	4	0.6	(3.5)	(19.4–20.4)	27.5	m
	7	(61.7)C	69.0	70.4	m, 1.4						
$C_{10}H_{21}O$	6	(68.7) B 70.0 C 80.5		92.3	m, 22.3	4	33.4	(42.8)	53.8–56.2	66.2–66.4	10.2
$C_{10}H_{21}O$	7	(64.1) B 73.6 C 85.0		94.9	m, 21.3	5	19.4	(32.7–33.0)	51.2–53.0	66.4–66.9	15.7

[a]Data are from reference [2]; M range=mesophase temperature range. [b]Phases are identified by the abbreviations Cr=crystallization obtained on cooling the melt at 2° min^{-1}, Sm=smectic with the type identified by C or B, N=nematic, I=isotropic liquid and m=monotropic. Parentheses around a temperature indicate a monotropic phase.

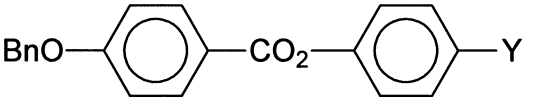
Table 4. A comparison of transition temperatures (°C) for:

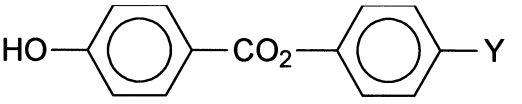


		$R=C_7H_{15}$						$R=C_5H_{11}C\equiv C$		
Y	*Z*	Cr[a]	B	C	N	I	Ref.	Cr	N	I
$C_{10}H_{21}$	O	46		56.7	58.6	67.9	[3]	4.1	(26.0–26.1)	35.0–35.3
OC_5H_{11}	O				55	84	[24]	1.5	(52.6–52.7)	54.1–54.4
$OC_{10}H_{21}$	O			72	75	89	[24]	11.7	43.4–44.8	57.3–57.5
C_8H_{17}	S	30.4[b]	(45.7	54.9	75.5	96.1	[3]	23.8	59.3–59.7	69.3–69.4

[a]Phases are identified by the abbreviations Cr=crystallization obtained on cooling the melt at 2° min^{-1}. Parentheses around a temperature indicate a monotropic phase. [b]Data are for the $R=C_9H_{19}$ homologue.

Table 5. Transition temperatures (°C) for:





Y	Cr[a]	SmA	N	I	Lit. m.p.[b]	Cr	I	Lit. m.p.
C_5H_{11}	102.9			125.7[c]	124	136.7	143.0	142, 148
C_6H_{13}	108.7			119.0	115	139.4	146.1	136
C_9H_{19}	99.2			116.3[c]		122.7	125.5[c]	
$C_{10}H_{21}$	86.9			115.3		113.4	117.5	
OC_5H_{11}	122.8			132.7	131	152.7	160.1	158
OC_8H_{17}	86.6		(105.2)	127.0	126	151.9	160.0	156
$OC_{10}H_{21}$	103.9[d]		(104.2)	123.8	122	142.4	147.0	148[e]
COC_9H_{19}	108.6(Cr_2)	141.1(Cr_1)[f]		141.9		116.8	123.3	
$CO_2CH_2C_7F_{15}$[g]	125.7	143.9		183.0		158.2	168.5	

[a]Phases are indentified as Cr=crystallization on cooling the melt at 2° min^{-1}; SmA=smectic A, N=nemtic and I=isotropic liquid. Bn=benzyl group ($C_6H_5CH_2$). [b]Data are from reference [25] [c]Data are from reference [30] [d]The monotropic nematic was not always seen; often crystallization occurred at a higher temperature. The crystals formed on cooling the nematic phases (Cr_2) converted to another form (Cr_1) on heating at 109.3–111.9°C. A DSC scan showed a split crystallization peak at 78.9°C and melting at 115.4°C ($\Delta H=23.51\,kJ\,mol^{-1}$). [e]Data are from reference [32] [f]Two crystal forms were observed. Crystals (Cr_2) formed at 108.6° on cooling the melt; on reheating, Cr_2 converted to Cr_1 at 129.3–127.7°C. Further heating caused Cr_1 to melt to the smectic A phase. [g]Synthesis described in reference [20].

as usual some variation occurred in the melting temperatures. The thioesters showed better mesomorphic properties than did the esters as has been observed in similar ester–thioester comparisons. Nematic phases were favoured over smectics; if a smectic occurred it was a smectic A rather than a C or B.

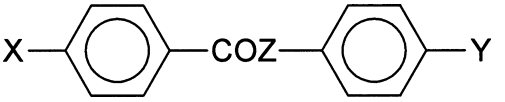
Some mesophases (N and SmA) were found in the intermediate benzyloxy-protected esters but none were seen in the corresponding phenols. Monotropic nematic phases were, however, seen in two of the hydroxy thioesters.

5. Experimental

5.1. *Characterization*

TLC data were collected using Anal-Tech silica gel GHLF Uniplates with UV light and I_2 as detectors unless otherwise indicated. Silica gel (230–400 mesh) was used for all flash chromatography. Capillary GC

Table 6. Transition temperatures (°C) for:



X	Z	Y	Cr[a]	SmA	N	I	Lit. m.p.[b]
C_4H_9	O	OBn[c]	71.5			97.2	
C_4H_9	O	OH	81.0			106.9	
$C_{10}H_{21}$	O	OH	105.3			109.7	109
$C_{10}H_{21}O$	O	OBn	81.0	(82.3)	98.4	99.3	97
$C_{10}H_{21}O$	O	OH	106.5			110.5	107[d]
NC	O	OH				186.8[e]	186
C_7H_{15}	S	OH	130.8			145.1	
$C_5H_{11}C{\equiv}C$	S	OH	94.6(Cr_2)			149.6(Cr_1)[f]	
$C_{10}H_{21}O$	S	OH	109.3		(116.2)	131.1	131.3[g]
HO	S	C_5H_{11}	94.5			113.4	
HO	S	OC_8H_{17}	92.1		(109.4)	112.5	

[a]Phases are indicated by Cr=crystallization obtained on cooling the melt at 2° min^{-1}, SmA=smectic A, N=nematic and I=isotropic liquid. [b]Literature values are from reference [25] unless otherwise indicated [c]Bn=benzyl group ($CH_2C_6H_5$). [d]A monotropic N at 96° was also reported; see the text for a discussion. [e]This is the melting temperature for virgin crystals. However, this material changed at this temperature as discussed in the text. [f]Two crystal forms were observed: the virgin crystals (Cr_1) and those formed on cooling the melt (Cr_2). Cr_2 converted to Cr_1 on heating at 105.4–109.9°C. [g]Data are from reference [15].

analyses were obtained using a Hewlett Packard (HP) model 5890 instrument having a HP integrator, FID detector and HP 5 m or 10 m methylsilicone gum column. Temperature programming was from 100° (0) at 20° min^{-1} to 250–270° (0 to 15) with detector and injector temperatures at 270–290° using a split valve rate of 182 ml min^{-1} and a column head pressure=16.22 ml min^{-1} unless otherwise noted. Retention times (t_R) are given in minutes.

Melting points were determined using a Thomas–Hoover melting point apparatus and are corrected. These were not determined for materials for which transition temperatures were obtained. Structural characterizations were determined using a Nicolet Magna FTIR 55 spectrometer and NaCl plates (absorptions are given cm^{-1}), and a Varian Gemini instrument 200 MHz (^{1}H NMR) and 50 MHz (^{13}C NMR) equipped with a VXR 400 data system. Spectra were obtained in $CDCl_3$ solutions containing TMS as the internal standard with chemical shifts given in δ(ppm) and coupling constants in Hz.

Transition temperatures (°C) were determined using a Leitz Laborlux 12 POL polarizing microscope fitted with a Bertrand lens for conoscopic studies and a modified, calibrated Mettler FP-2 heating stage at a heating rate of 2° min^{-1}. Crystallization temperatures were obtained by cooling the melt at 2° min^{-1} until crystals formed, to ensure that all mesophases above this temperature were observed. Mesophases are described by their characteristic textures as provided earlier [33]. Mesogens were purified by recrystallization and/or chromatography until the clearing temperature was constant within 0.3° for nematics and 0.4° for smectic A phases and no unmelted solids remained in the isotropic liquid. DSC data were collected using a Perkin-Elmer DSC 7 instrument equipped with a TAC 7/PC instrument controller at a rate of 5° min^{-1}.

5.2. *Synthesis*

The phenols **19** (n=1, Y=R) [34], RO [35], CO_2R[4], COR[1], OCO_2R[2]; thiols **20** (Y=R) [33], RO [36] and acids **26** (n=1, X=R) [24] were prepared using previously published methods. All other starting materials were commercially available and used without purification. Organic extracts were dried over anhydrous Na_2SO_4. All temperatures are in °C.

5.2.1. Ethyl 4-heptynylbenzoate 15. A mixture of the bromoester **13** (25.4 g, 0.11 mol), 1-heptyne (12.7 g, 0.13 mol), Ph_3P (3.16 g, 0.012 mol), CuI (0.54 g, 2.86 mmol), $PdCl_2(Ph_3P)_2$ (900 mg, 1.28 mmol) and Et_3N (165 ml) in pyridine (65 ml) was heated under reflux for 48 h under N_2, cooled to r.t. and the solvent removed *in vacuo*. Et_2O was added to the remaining material and the insoluble solid removed by filtration. The filtrate was washed with H_2O (300 ml), 3M HCl (300 ml), H_2O (2 × 300 ml); then dried, filtered and the solvent removed from the filtrate

to give the crude product (30.0 g). This material was chromatographed on silica gel using 40% CH_2Cl_2 in hexane to give 20.5 g (75.7%) of the ester **15** as a yellow liquid. TLC ($CHCl_3$) R_f=0.72; GC t_R=2.63 and 7.45 (99.6%). IR (film) 2240, 2216 (wk, alkyne) 1718 (str, ester), 1602 (str, Ar) and 1286 (str, ether). ^{1}H NMR 7.96 (d, 2, J=8.54, ArH *ortho* to ester), 7.44 (d, 2, J=8.59, ArH *ortho* to alkyne), 4.37 (q, 2, J=7.14, ethyl CH_2), 2.43 (t, 2, J=7.03, α-CH_2), 1.62–1.58 (m, 2, β-CH_2), 1.40 (t, 3, J=7.13, ethyl Me), 1.46–1.34 (m, 4, 2 CH_2), and 0.93 (t, 3, J=6.76, pentyl Me).

5.2.2. 4-Heptynylbenzonitrile 16. To a stirred solution of 1-heptyne **11** (20.2 g, 210 mmol) in THF (105 ml) at 0° under N_2 was added dropwse a solution of *n*-BuLi (1.6M) in hexane (131.2 ml) and this mixture was stirred for 15 min. A solution of $ZnCl_2$ (28.6 g, 210 mmol) in THF (205 ml) was added dropwise and stirring continued at 0° for 10 min. The reaction mixture was allowed to warm to r.t., stirred for 30 min and then cooled to 0°. A solution of the nitrile **14** (38.2 g, 2.10 mmol) in THF (205 ml) was added dropwise followed by a solution of $Pd(PPh_3)_2$ (12.1 g, 0.10 mmol) in THF (205 ml). The reaction mixture was allowed to warm to r.t. and stirred for 24 h. The solvent was removed *in vacuo* and the residue acidified with 2M HCl (500 ml). This material was extracted with Et_2O (3×) and the Et_2O extract washed with H_2O, dried and filtered. The filtrate was passed through silica gel to remove traces of the catalyst and the solvent removed *in vacuo* to give 43.1 g (104%) of the crude nitrile **16**. Distillation of this liquid at atmospheric pressure yielded a forerun fraction at 62° shown by TLC to be 1-heptyne followed by two intermediate fractions below 140° (9.69 g) which TLC and IR indicated contained a small amount of product. The final several fractions boiling at 175–180° (yellow liquid) were indicated by TLC and IR to be primarily the product **16**. These latter fractions were combined (15.8 g) and chromatgraphed on silica gel using 1/1 CH_2Cl_2/hexane to give 15.6 g (37.8%) of the purified nitrile **16**. TLC (1/1 CH_2Cl_2/hexane) R_f=0.40. IR (film) 2115 (str, CN and alkyne) and 1505 (str, Ar). ^{1}H NMR : 7.55 (d, 2, J=8.71, ArH *ortho* to CN), 7.43 (d, 2, J=8.62, ArH *ortho* to alkyne), 2.41 (t, 2, J=7.02, α-CH_2), 1.59 (m, 2, β-CH_2), 1.46–1.33 (m, 4, 2 CH_2) and 0.92 (t, 3, J=7.10, CH_3). ^{13}C NMR 133.3, 132.6, 132.0, 131.8, 129.1, 128.5, 118.6, 110.7 and 95.7.

5.2.3. 4-Heptynylbenzoic Acid 17. From the nitrile **16**: A mixture of the nitrile **16** (14.2 g, 0.072 mol) in a solution of NaOH (85.2 g, 2.13 mol) in H_2O (100 ml) containing abs EtOH (166 ml) was heated under reflux for 66 h, cooled to r.t. and the solvent removed *in vacuo*. The remaining solid was dissolved in a minimum of H_2O and the solution acidified with concd HCl (*c*. 177 ml). The resulting precipitate was removed by filtration, washed thoroughly with H_2O and dried to give 11.6 g (74.5%) of the crude product. TLC (1/1 CH_2Cl_2/hexane) showed several spots with R_f=0.04, 0.33, 0.64 and 0.91. This material was dissolved in toluene, hot filtered to remove some insoluble solid (2.2 g) and the solvent removed *in vacuo*. The remaining solid was recrystallized by dissolving in EtOH, adding H_2O to nearly the cloud point and cooling to give the purified acid **17** (8.95 g, 57.4%).

From the ester **15**: A mixture of the ester **15** (20.5 g, 84.0 mmol) in a solution of NaOH (10.8 g, 0.27 mol) in abs EtOH (53.4 ml) containing H_2O (57.5 ml) was heated under reflux for 17 h, cooled to r.t. and the EtOH removed (carefully to avoid bumping) *in vacuo*. The remaining mixture was diluted with H_2O (300 ml), extracted with Et_2O (4×200 ml), cooled and acidified with dil HCl. The resulting precipitate was removed by filtration, washed with H_2O, air dried for 36 h and then vacuum dried to give the crude product. An attempt to purify this solid by recrystallizing from hexane yielded a slightly yellow material. It was then dissolved in abs EtOH, treated with Norite, filtered through Celite and the solvent removed *in vacuo*. The residue was recrystallized from hexane to give 11.9 g (65.6%) of the purified acid **17** as a colourless solid. IR (Nujol) 3500–2700 (br, acid OH), 2243, 2211 (wk, alkyne), 1697 (str, C=O and Ar) and 1608 (str, Ar). ^{1}H NMR 8.04 (d, 2, J=8.63, ArH *ortho* to CO_2H), 7.50 (d, 2, J=8.50, ArH *ortho* to alkyne), 2.46 (t, 2, J=7.04, α-CH_2), 1.63–1.59 (m, 2, β-CH_2), 1.42–1.38 (m, 4, 2 CH_2) and 0.95 (t, 3, J=6.92, CH_3). ^{13}C NMR 172.0, 131.6, 130.0, 129.7, 127.9, 94.7, 80.1, 31.1, 28.3, 22.2, 19.5 and 14.0. Transition temperatures: 145.1–146.1° (Cr–I) and 142.5° (I–Cr).

5.2.4. 4-Heptanoylbenzoic Acid 18. A mixture of the nitrile **16** (4.17 g, 0.20 mol) in glac. HOAc (48 ml) containing 3M H_2SO_4 (48 ml) was heated under reflux for 22 h, cooled to 0°, ice added (300 ml) and extracted with CH_2Cl_2 (4×). The organic layer was washed with H_2O (4×), dried, filtered and the solvent removed *in vacuo* to give the crude product (4.10 g, 87.6%). This material was recrystallized twice from $CHCl_3$/hexane to give 1.98 g (42.3%) of the purified keto acid **18** as a colourless solid, m.p. 134–143°, TLC ($CHCl_3$) R_f=0.04. IR (Nujol) 3250–3050 (br, str acid OH) and 1680 (str, CO and CO_2H). ^{1}H NMR 8.21 (d, 2, J=8.46, ArH *ortho*

to ketone) 8.04 (d, 2, J=8.67, ArH *ortho* to acid), 3.01 (t, 2, J=7.33, α-CH_2), 1.76 (quint, 2, J=7.04, β-CH_2), 1.55–1.20 (m, 6, 3 CH_2) and 0.90 (t, 3, J=6.45, CH_3). ^{13}C NMR 200.1, 166.9, 140.0, 134.7, 129.8, 128.2, 38.5, 31.4, 28.5, 23.8, 22.3 and 14.2.

5.2.5. Preparation of the esters 4 and thioesters 5. All these compounds were synthesized using the carbodiimide method described earlier [2]. A reflux time of 2 h was sufficient to obtain a complete reaction for the esters **4** (n=1) and **5** but the esters **4** with n=2 required at least 6.5 h as determined by TLC monitoring of the reaction. Purification was usually by recrystallization from 95% or abs EtOH; or column chromatography was used with approximately 50% CH_2Cl_2 in hexane followed by recrystallization. Yields varied from 20–66%; typical IR and NMR data are as follows:

Esters **4** (n=1). *Y*=$C_{10}H_{21}$: IR (Nujol) 1750 (str, ester) and 1650 (med, Ar). ^{1}H NMR 8.11 (d, 2, J=8.42, ArH *ortho* to CO_2Ar), 7.50 (d, 2, J=8.47, ArH *ortho* to alkyne), 7.22 (d, 2, J=8.51, ArH *ortho* to OCOAr), 7.10 (d, 2, J=8.62, ArH *ortho* to $C_{10}H_{21}$), 2.62 (t, 2, J=7.65, pentyl α-CH_2), 2.44 (t, 2, J=7.06, alkyne CH_2), 1.64–1.57 (d, 6, 2 β-CH_2), 1.45–1.26 (m, 18, 9 CH_2), 0.94 (t, 3, J=6.88, alkyne CH_3) and 0.88 (t, 3, J=6.96, alkyl CH_3). *Y*=COC_4H_9: IR (Nujol) 2360 and 2341 (wk, alkyne), 1750 (str, ester), 1680 (str, ketone), 1597 (wk, Ar) and 1281 (med, ether). ^{1}H NMR 8.07 (d, 2, J=8.10, ArH *ortho* to CO_2Ar), 7.98 (d, 2, J=8.79, ArH *ortho* to CO), 7.45 (d, 2, J=8.14, ArH *ortho* to alkyne), 7.24 (d, 2, J=8.59, ArH *ortho* to OCOAr), 2.90 (t, 2, J=7.37, $COCH_2$), 2.38 (t, 2, J=7.00, alkyne CH_2), 1.68–1.56 (m, 4, 2 β-CH_2), 1.40–1.13 (m, 16, 8 CH_2), 0.87 (t, 3, J=7.03, alkyne CH_3) and 0.82 (t, 3, J=7.80, keto CH_3). *Y*=$OC_{10}H_{21}$: IR (Nujol) 2241, 2223 (vwk, alkyne), 1743 (str d, ester) and 1609 (str, Ar). ^{1}H NMR 8.10 (d, 2, J=8.18, ArH *ortho* to CO_2Ar), 7.50 (d, 2, J=8.14, ArH *ortho* to alkyne), 7.10 (d, 2, J=8.91, ArH *ortho* to OCOAr), 6.92 (d, 2, J=8.92, ArH *ortho* to O*R*), 3.95 (t, 2, J=6.41, OCH_2), 2.44 (t, 2, J=7.10, alkyne CH_2), 1.77 (quint, 2, J=7.41, alkyne β-CH_2), 1.62 (q, 2, J=7.16, alkoxy β-CH_2), 1.49–1.35 (m, 18, 9 CH_2), 0.94 (t, 3, J=6.96, alkyne CH_3) and 0.89 (t, 3, J=6.30, alkoxy CH_3). ^{13}C NMR 157.4, 144.7, 132.1, 130.4, 130.0, 128.8, 122.8, 115.6, 95.0, 80.6, 68.9, 32.4, 31.6, 30.1, 30.0, 29.9, 29.8, 28.8, 26.5, 23.2, 22.7, 20.0, 14.6 and 14.5. *Y*=$OCOC_9H_{19}$: IR (Nujol) 2361, 2344 (wk, alkyne), 1755 (med, OCOR), 1743 and 1729 (str, CO_2Ar), 1605 (wk, Ar) and 1512 (str, Ar). ^{1}H NMR 8.10 (d, 2, J=8.43, ArH *ortho* to CO_2Ar), 7.51 (d, 2, J=8.42, ArH *ortho* to alkyne), 7.22 (d, 2, J=8.87, ArH *ortho* to OCOAr), 7.13 (d, 2, J=8.95, ArH *ortho* to OCO*R*), 2.56 (t, 2, J=7.51, $COCH_2$), 2.44 (t, 2, J=7.02, alkyne CH_2), 1.80–1.72 (quint, 2, J=7.47, alkyne β-CH_2), 1.68–1.60 (quint, 2, J=7.04, ester β-CH_2), 1.49–1.28 (m, 16, 8 CH_2), 0.94 (t, 3, J=6.80, alkyne CH_3) and 0.89 (t, 3, J=6.59, ester CH_3). *Y*=*CN*: IR (Nujol) 2230 (med, CN), 1750 (str, ester) and 1602 (str, Ar). ^{1}H NMR 8.09 (d, 2, J=8.10, ArH *ortho* to CO_2Ar) 7.74 (d, 2, J=8.79, ArH *ortho* to CN), 7.52 (d, 2, J=8.34, ArH *ortho* to alkyne), 7.36 (d, 2, J=8.43, ArH *ortho* to OCOAr), 2.45 (t, 2, J=7.10, α-CH_2), 1.70–1.55 (m, 2, β-CH_2), 1.52–1.25 (m, 4, 2 CH_2) and 0.94 (t, 3, J=6.96, CH_3).

Ester **4** (n=2). *Y*=*CN*: IR (Nujol) 2221 (med, CN), 1741 (str, ester) and 1600 (med, Ar). ^{1}H NMR 8.14 (d, 2, J=8.59, ArH *ortho* to CO_2Ar), 7.75 (d, 2, J=8.62, biphH *ortho* to CN), 7.68 (d, 2, J=8.75, biphH *meta* to CN), 7.65 (d, 2, J=8.75, biphH *meta* to OCOAr), 7.53 (d, 2, J=8.43, ArH *ortho* to alkyne), 7.34 (d, 2, J=8.67, biphH *ortho* to OCOAr), 2.45 (t, 2, J=7.04, α-CH_2), 1.68–1.53 (m, 2, β-CH_2), 1.50–1.32 (m, 4, 2 CH_2) and 0.94 (t, 3, J=6.96, CH_3).

Thioesters **5**. *Y*=C_5H_{11}: IR (Nujol) 2225 (wk d, alkyne), 1684 (str, COS) and 1607 (str, Ar). ^{1}H NMR (2-D COS*Y*) 7.93 (d, 2, J=8.59, ArH *ortho* to COSAr), 7.47 (d, 2, J=8.59, ArH *ortho* to alkyne), 7.40 (d, 2, J 8.22, ArH *ortho* to S), 7.26 (d, 2, J=8.26, ArH *ortho* to C_5), 2.64 (t, 2, J=7.69, alkyl α-CH_2), 2.43 (t, 2, J=6.98, alkyne CH_2), 1.67–1.55 (m, 4, 2 CH_2), 1.45–1.29 (m, 8, 4 CH_2) and 0.92 (t, 6, J=6.96, 2 CH_3). *Y*=OC_8H_{17}: IR (Nujol) 2223 (wk d, alkyne), 1676 (str, COS) and 1593 (str, Ar). ^{1}H NMR 7.94 (d, 2, J=8.63, ArH *ortho* to COS), 7.47 (d, 2, J=8.59, ArH *ortho* to alkyne), 7.39 (d, 2, J=8.83, ArH *ortho* to S), 6.97 (d, 2, J=8.83, ArH *ortho* to O*R*), 3.98 (t, 2, J=6.49, OCH_2), 2.44 (t, 2, J=7.02, CCH_2), 1.90–1.70 (m, 2, ether β-CH_2), 1.70–1.55 (m, 2, alkyne β-CH_2), 1.55–1.20 (m, 14, 7 CH_2), 0.93 (t, J=6.88, alkyne CH_3) and 0.89 (t, 3, J=6.85, alkyne CH_3). *Y*=$CH_2CH(CH_3)C_2H_5$: IR (film) 2223 (wk, alkyne), 1677 (str, COS) and 1603 (str, Ar). ^{1}H NMR 7.94 (d, 2, J=8.06, ArH *ortho* to COSAr), 7.47 (d, 2, J=8.22, ArH *ortho* to alkyne), 7.40 (d, 2, J=7.98, ArH *ortho* to S), 7.23 (d, 2, J=8.06, ArH *ortho* to alkyl chain), 2.68 (dd, 1, J=13.14, 6.37, $ArCH_2$ hydrogen coupled to CH), 2.43 (d, 2, J not determined, $ArCH_2$ proton not coupled with CH), 2.44 (t, 2, J=6.96, alkyne CH_2), 1.80–1.50 (m, 3, alkyne β-CH_2 and CH), 1.55–1.05 (m, 6, branched chain γ-CH_2 and 2 CH_2) and 1.00–0.80 (m, 9, 3 CH_3).

5.2.6. 4-Hydroxyphenyl 4-heptyl thiobenzoate 22a. To a stirred cold (ice bath) solution of the thiophenol (8.0 g, 72.8 mmol) and Et_3N (6.69 g, 66.3 mmol) in CH_2Cl_2 (100 ml) was added dropwise a solution of the acid chloride **21a** (15.8 g, 66.3 mmol) in CH_2Cl_2 (100 ml).

The reaction was stirred at r.t. for 48 h and then washed with H_2O (300 ml) and 5% aq KOH (300 ml). An emulsion formed during the base wash that could only be separated by filtration through glass fibre filter paper. The organic layer was separated, washed with H_2O, dried and filtered. Removal of the solvent from the filtrate gave 19.2 g of a tan solid. Chromatography of this material using 35% CH_2Cl_2 in hexane gave 9.39 g of a material having TLC (CH_2Cl_2), R_f=0.86. Recrystallization of this material twice from abs EtOH (600 ml) gave 2.38 g (53.6% yield, 48.9% of the crude material) of the diester **23** (X=C_7H_{15}). TLC (CH_2Cl_2) R_f=0.88, IR (Nujol) 1742 (str, ester), 1670 (str, thioester) and 1611(wk, Ar). ^{1}H NMR 8.12 (d, 2, J=8.06, ArH *ortho* to COSAr), 7.96 (d, 2, J=7.86, ArH *ortho* to CO_2Ar), 7.57 (d, 2, J=8.34, ArH *ortho* to S), 7.33 (2 d, 4, J=7.33, ArH *ortho* to 2 C_7H_{15}), ~7.30 (d, 2, J=~6.96, ArH *ortho* to O_2CAr), 2.70 (2 q, 4, J=~7.51, 2 α-CH_2), 1.80–1.50 (m, 4, 2 β-CH_2), 1.50–1.20 (m, 16, 8 CH_2), and *c*. 0.91 (2 t, 6, J=~6.37, 2 CH_3). Transition temperatures: 107.1–109.2° (Cr–N). 180.6–180.8° (N–I) and 103.2° (N–Cr).

Further elution of the column with 1/1 CH_2Cl_2/hexane and then with 65% CH_2Cl_2 in hexane gave 5.42 g (24.9% yield, 28.2% of the crude product) of the desired phenol **22a**. A small amount (1.0 g) of this material was recrystallized from benzene (50 ml) to give a sample (colourless solid) for characterization. TLC (CH_2Cl_2) R_f=0.15, IR (Nujol) 3362 (br med, OH), 1651 (str, COS) and 1591 (med, Ar). ^{1}H NMR 7.95 (d, 2, J=7.86, ArH *ortho* to CO_2Ar), 7.32 (d, 2, J not determined, ArH *ortho* to COSAr), 7.29 (d, 2, J=~8.62, ArH *ortho* to C_7), 6.86 (d, 2, J=8.63, ArH *ortho* to OH), 5.58 (s, 1, OH), 2.68 (t, 2, J=7.32, $ArCH_2$), 1.70–1.50 (m, 2, β-CH_2), 1.45–1.15 (m, 8, 4 CH_2) and 0.88 (t, 3, J=6.72, CH_3). Transition temperatures 144.4–145.1 (Cr–I) and 130.8 (I–Cr).

5.2.7. 4-Hydroxyphenyl 4-heptynyl thiobenzoate 22b. A mixture of the acid **17** (2.0 g, 9.2 mmol) and $SOCl_2$ (1.2 g, 10.2 mmol) in anhyd CH_2Cl_2 (25 ml) was heated under reflux for 2 h. The solvent and $SOCl_2$ were removed from the cooled reaction mixture *in vacuo* to give 2.6 g of the crude acid chloride **21** (X=$C_5H_{11}C{\equiv}C$) as shown by IR (film) 1780 and 1748 (COCl). A cooled solution of this material in CH_2Cl_2 (10 ml) was added dropwise to a stirred solution of 4-thiophenol (1.46 g, 11.6 mmol) in CH_2Cl_2 (10 ml) containing Et_3N (0.94 g, 9.29 mmol) at r.t. Stirring was continued for 17 h and then the mixture was diluted to 50 ml with CH_2Cl_2, washed with H_2O (50 ml), satd Na_2CO_3 solution (50 ml) and H_2O (2 × 50 ml). The organic layer was separated, dried and filtered. The filtrate was filtered through a short column of silica gel, the column washed thoroughly with CH_2Cl_2 and the solvent removed *in vacuo* to give 2.49 g (83.0%) of the crude product. TLC (20% EtOAc in hexane) showed two spots with R_f=0.22 and 0.35 (starting thiol). Recrystallization of this material from toluene (30 ml) gave 1.68 g (56.0%) of pale yellow crystals of the desired phenol **22b**. TLC ($CHCl_3$) R_f=0.69. IR (Nujol) 3398 (br str, OH), 2220 (wk d, alkyne), 1650 (str, thioester) and 1599 (str, Ar). ^{1}H NMR 7.95 (d, 2, J=8.46, ArH *ortho* to CO), 7.48 (d, 2, J=8.43, ArH *ortho* to alkyne), 7.34 (d, 2, J=8.66, ArH *ortho* to S), 6.86 (d, 2, J=8.71, ArH *ortho* to OH), 2.44 (t, 2, J=6.98, α-CH_2), 1.70–1.50 (m, 2, β-CH_2), 1.50–1.30 (m, 4, 2 CH_2), and 0.94 (t, 3, J=6.98, CH_3). ^{13}C NMR 192.7, 158.0, 137.3, 135.5, 135.3, 132.3, 130.5, 127.9, 117.3, 95.6, 80.5, 31.6, 28.7, 22.7, 20.0 and 14.5.

5.2.8. Preparation of the thioesters 24. Three of these compounds (**24a**, n=9 and **24b**) were prepared using the acid chloride procedure to esterify the phenol **22** with the appropriate acid [2]. The thioester **24a** (n=3) was prepared using the carbodiimide procedure [2]. Variations from these methods, purifications and characterizations are provided for these compounds as follows

24a (n=3). Reflux time=17 h, purification was by chromatography using EtOAc/hexane (1/10) followed by recrystallization from abs EtOH, yield 33.2% of a coloroless solid: characterization data were similar to those for the C_9 homologue.

24a (n=9). Reaction time=17 h, crude yield=90%, purification was by recrystallization from abs EtOH, chromatography using CH_2Cl_2/hexane (1/1), yield 9.0%. TLC (CH_2Cl_2) R_f=0.88. IR (Nujol) 1756 (str, O_2CR), 1677 (str, COSAr) and 1611 (med, Ar). ^{1}H NMR 7.94 (d, 2, J=8.14, ArH *ortho* to COS), 7.52 (s, 2, J=8.67, ArH *ortho* to S), 7.29 (d, 2, J=8.50, ArH *ortho* to C_7), 7.19 (d, 2, J=8.58, ArH *ortho* to O_2CR), 2.68 (t, 2, J=7.85, O_2CCH_2), 2.58 (t, 2, J=7.51, $ArCH_2$), 1.77 (quint, 2, J=7.32, CH_2 β to O_2C), 1.64 (quint, 2, J=6.92, β-CH_2), 1.50–1.20 (m, 20, 10 CH_2), 0.90 (t, 3, J=6.67, ester chain CH_3) and 0.88 (t, 3, J=6.60, alkyl chain CH_3).

24b (n=9). Recrystallized from abs EtOH containing a small amount of $CHCl_3$ to give 660 mg (60.2%). TLC ($CHCl_3$) R_f=0.82, IR (Nujol) 2225 (str, alkyne), 1756 (str, ester), 1680 (str, thioester) and 1604 (str, Ar). ^{1}H NMR 7.93 (d, 2, J=8.67, ArH *ortho* to COSAr), 7.54 (d, 2, J=8.71, ArH *ortho* to S), 7.50 (d, 2, J=8.67, ArH *ortho* to alkyne), 7.18 (d, 2, J=8.75, ArH *ortho* to $OCOR$), 2.56 (t, 2, J=7.41, $COCH_2$), 2.43 (t, 2, J=7.12, alkyne CH_2), 1.75–1.50 (m, 4, 2 β-CH_2), 1.50–1.20 (m,

18, 9 CH_2), 0.92 (t, 3, J=6.96, alkyne CH_3) and 0.88 (t, 3, J=6.75, ester CH_3).

24b (n=3). Purification was by recrystallization from abs EtOH, yield was 31.6%, characterization data are similar to those for n=9.

5.2.9. 4-Benzyloxyphenol t-butyldimethyl ether 28. To a stirred solution of 4-benzyloxyphenol **25** (1.0 g, 5.0 mmol), DMF (2.5 ml) and imidazole (820 mg, 12.0 mmol) under N_2 was added dropwise Me_2t-BuSiCl (900 mg, 6.0 mmol); stirring was continued for 20 h and the mixture poured into H_2O (50 ml) and extracted with Et_2O. The Et_2O layer was separated, washed with H_2O (2 × 75 ml), dried, filtered and the solvent removed *in vacuo* to give 1.69 g of the crude product. This material was recrystallized from MeOH to give 901 mg (57.4%) of the purified ether **28**, mp 73–75°. TLC ($CHCl_3$) R_f=0.75. IR (Nujol) 1508 (str, Ar), 1268 (str, SiMe) and 924 (str, SiOAr). ^{1}H NMR 7.41–7.33 (m, 5, C_6H_5), 6.84 (d, 2, J=9.23, ArH *ortho* to benzyl), 6.74 (d, 2, J=9.40, ArH *ortho* to OSi), 4.98 (s, 2, OCH_2), 0.96 (s, 9, *t*-Bu) and 0.15 (s, 6, $SiMe_2$).

5.2.10. 4-t-Butyldimethylsilyloxyphenol 31. A solution of the diether **28** (988 mg, 3.14 mmol) in abs EtOH (75 ml) containing 10% Pd-C (100 mg) was hydrogenated at 60 lbs in^{-2} at r.t. for 22 h and then filtered through Celite. The solvent was removed *in vacuo* to give 940 mg of the crude product. This material was dissolved in CH_2Cl_2, filtered through silica gel and the solvent removed *in vacuo* to give 700 mg (99.3%) of the phenol **31**. TLC ($CHCl_3$) R_f=0.24. IR (Nujol) 3283 (br med, OH), 1511 (str, Ar), 1261 (med, SiMe) and 1018 (wk, ArOSi). ^{1}H NMR 6.71 (s, 4, ArH), 0.98 (s, 9, CMe_3) and 0.17 (s, 6, $SiMe_2$).

5.2.11. 4-t-Butyldimethylsiloxyphenyl 1-hexynylcarboxylate 35. The standard carbodiimide esterification method [2] was used to prepare this ester from the phenol **31** and the acid **33** (R=C_4H_9) in a yield of 64.8% after purification. This was done by chromatography using 1/1 CH_2Cl_2/hexane to give the ester **35** as a colourless liquid. TLC ($CHCl_3$) R_f=0.74. IR (film) 2266, 2234 (med, alkyne), 1741 (str, ester), 1601 (wk, Ar), 1511 (str, Ar), 1261 (str, SiMe), 1236 (str, COC) and 922 (str, ArOSi). ^{1}H NMR 6.96 (d, 2, J=9.08, ArH *ortho* to OCOR, 6.79 (d, 2, J=9.08, ArH *ortho* to OSi), 2.37 (t, 2, J=6.96, α-CH_2), 1.62–1.53 (m, 2, β-CH_2), 1.51–1.41 (m, 2, γ-CH_2), 0.95 (t, 9, J=3.07, CMe_3), 0.92 (t, 3, J=7.25, pentyl CH_3) and 0.17 (t, 6, J=3.14, $SiMe_2$).

5.2.12. 4-Hydroxyphenyl 1-hexynylcarboxylate 34. A mixture of the silyl ether **35** (5.36 g, 16.1 mmol), *p*-toluenesulphonic acid (307 mg, 1.61 mmol), H_2O (5 ml) and THF (100 ml) was stirred at r.t. for 16 h with no obvious change. TLC indicated that the cleavage was incomplete even after 20 h reflux. Glacial HOAc (30 ml) was added and the mixture heated under reflux for 16 h. Additional glacial HOAc (30 ml) and H_2O (10 ml) were added, the mixture heated for an additional hour and then cooled to r.t. The THF was removed *in vacuo* and the remaining material diluted with H_2O (500 ml) and extracted with Et_2O (3 × 100 ml). The organic layer was washed with H_2O (2 × 25 ml), dried, filtered and the solvent removed *in vacuo* to give the crude product (6.34 g). This material was chromatographed on silica gel using 2% EtOAc in CH_2Cl_2, and chromatographed again using $CHCl_3$ to give 2.07 g (58.8%) of the phenol **34** as a liquid. TLC ($CHCl_3$) R_f=0.19. IR (film) 3424 (str, br OH), 2240 (str, alkyne), 1728 (str, ester), 1517 (str, Ar) and 1249 (str, ether). ^{1}H NMR 6.97 (d, 2, J=8.79, ArH *ortho* to OCO*R*), 6.79 (d, 2, J=8.55, ArH *ortho* to OH), 2.39 (t, 2, J=6.92, α-CH_2), 1.56 (quint, 2, J=6.85, β-CH_2), 1.48 (sext, 2, J=6.94, γ-CH_2) and 0.93 (t, 3, J=7.15, CH_3).

5.2.13. 4-Benzyloxyphenyl 4-butylbenzoate 29 (X=n-Bu, R′=Bn). The standard carbodiimide method [2] was used to prepare this ester from the acid **26** and the phenol **25** in a crude yield of 93.3%. This material was recrystallized from abs EtOH to give the purified ester **29** (X=Bu, R'=Bn), yield=53.4%. TLC ($CHCl_3$) R_f=0.68. IR (Nujol) 1736 (str d, ester) and 1607 (med d, Ar). ^{1}H NMR 8.01 (d, 2, J=8.38, ArH *ortho* to ester), 7.50–7.35 (m, 5, C_6H_5), 7.31 (d, 2, J=8.18, ArH *ortho* to Bu), 7.12 (d, 2, J=9.28, ArH *ortho* to OCO), 7.00 (d, 2, J=9.16, ArH *ortho* to OCOAr), 5.07 (s, 2, OCH_2), 2.70 (t, 2, J=7.61, α-CH_2), 1.64 (q, 2, J=7.53, β-CH_2), 1.37 (sext, 2, J=7.28, γ-CH_2) and 0.94 (t, 3, J=7.27, CH_3).

The *X*=$C_{10}H_{21}O$, *R′*=*Bn* analogue was prepared in the same manner in a 47.8% yield after chromatography (40% CH_2Cl_2 in hexane) followed by recrystallization from abs. EtOH. ^{1}H NMR 8.13 (d, 2, J=8.75, ArH *ortho* to CO_2Ar), 7.50–7.29 (m, 5, C_6H_5), 7.12 (d, 2, J=9.03, ArH *ortho* to OCOAr), 7.00 (d, 2, J=8.22, ArH *ortho* to OBn), 6.97 (d, 2, J=8.83, ArH *ortho* to O*R*), 5.07 (s, 2, $PhCH_2$), 4.03 (t, 2, J=6.54, α-CH_2), 1.82 (s, quint, J=6.91, β-CH_2), 1.55–1.15 (m, 14, 7 CH_2) and 0.89 (t, 3, J=6.41, CH_3). Transition temperatures: 97.9–98.4° (Cr–N), 99.2–99.3 (N–I), 82.1–82.3 (A–N) and 81.0 (A–Cr), literature m.p. 96.3° [37].

5.2.14. 4-(t-Butyltrimethyldimethylsiloxy)phenyl 4-n-decylbenzoate 29 (X=$C_{10}H_{21}$, R′=$SiMe_2$t-Bu). This compound was prepared in the same manner, by esterifiying the phenol 31 with the acid 26 (X=$C_{10}H_{21}$)

but using a reflux time of 24 h. The crude product was dissolved in 25% CH_2Cl_2 in hexane, filtered through silica gel and the solvent removed *in vacuo* to give 3.06 g of a liquid which TLC indicated still to contain a trace amount of an impurity. This material was used as the silyl ether **29** (X=$C_{10}H_{21}$, R'=$SiMe_2t$-Bu) without further purification. TLC R_f=0.17, 0.00 (faint). IR (film) 1741 (str, ester), 1620, 1505 (str, Ar), 1274 (str, SiMe) and 929 (str, ArOSi). ^{1}H NMR 8.10 (d, 2, J=8.26, ArH *ortho* to CO_2Ar), 2.69 (t, 2, J=7.65, α-CH_2), 1.65 (quint, 2, J=7.34, β-CH_2), 1.40–1.23 (m, 14, 7 CH_2), 1.00 (t, 9, J=3.01, CMe_3), 0.88 (t, 3, J=6.23, CH_3) and 0.21 (t, 6, J=3.06, $SiMe_2$).

5.2.15. 4-Hydroxyphenyl 4-n-butylbenzoate 32 (X=n-Bu). A solution of the ester **29** (X=Bu, R^1=Bn, 9.5 g, 26.2 mmol) in THF (30 ml) containing 10% Pd-C (940 mg) and abs EtOH (20 ml) was hydrogenated at r.t. for 17 h and then filtered through Celite. The solvent was removed *in vacuo* and the residue dried to give the crude product (7.21 g). This material was recrystallized from hexane to give 5.67 (80.0%) of the purified ester **32** (X=*n*-Bu). TLC ($CHCl_3$) R_f=0.74. IR (Nujol) 3342 (br, str, OH), 1737, 1704 (str, ester) and 1607 (m with sh, Ar) and 1200 (m, ether). ^{1}H NMR 8.10 (d, 2, J=8.22, ArH *ortho* to CO_2Ar), 7.31 (d, 2, J=8.43, ArH *ortho* to *R*), 7.01 (d, 2, J=8.91, ArH *ortho* to OCOAr) and 6.78 (d, 2, J=8.87, Ar H *ortho* to OH), 5.72 (br s, 1, OH), 2.70 (t, 2, J=7.65, α-CH_2), 1.64 (quint, 2, J=7.53, β-CH_2), 1.37 (sext, 2, J=7.28, γ-CH_2) and 0.94 (t, 3, J=7.19, Me). Transition temperatures 104.4–106.9 (Cr–I) and 81.0 (I–Cr).

The analogue with X=$C_{10}H_{21}$ was prepared in the same manner in a 90.3% yield after recrystallization from hexane. IR (Nujol) 3400 (br, OH), 1719 (str, ester) and 1609 (str, Ar). ^{1}H NMR 8.13 (d, 2, J=8.91, ArH *ortho* to CO_2Ar), 7.01 (d, 2, J=8.95, ArH *ortho* to OCOAr), 6.97 (d, 2, J=9.98, ArH *ortho* to O*R*), 6.78 (d, 2, J=8.96, ArH *ortho* to OH), 5.50 (s, 1, OH), 4.04 (t, 2, J=6.56, OCH_2), 1.82 (quint, 2, J=6.89, β-CH_2), 1.60–1.20 (m, 14, 7 CH_2) and 0.89 (t, 3, J=6.45, Me).

5.2.16. 4-Hydroxyphenyl 4-n-decylbenzoate 32 (X=$C_{10}H_{21}$). A solution of the ether **29** (X=$C_{10}H_{21}$, R'=$SiMe_2t$-Bu, 2.76 g, 7.53 mmol) and 1.0M $Bu_4N^+F^-$ (2.95 g) in THF (11.3 ml) was stirred at r.t. for 3 h. This solution was diluted with CH_2Cl_2 (100 ml), washed with H_2O, dried, filtered through silica gel washing thoroughly with CH_2Cl_2, and the solvent removed *in vacuo* to give 2.33 g of a solid. This material was dissolved in CH_2Cl_2 (10 ml), hexane (40 ml) added and the insoluble material removed by filtration. A stream of N_2 was blown through the filtrate until a solid began to crystallize. This solid was removed by filtration, washed thoroughly with ice-cold hexane and dried *in vacuo* to give 1.68 g (88.5%) of the phenol **32** (X=$C_{10}H_{21}$), m.p. 105–108° (lit [25] 109°), TLC ($CHCl_3$) R_f=0.05. IR (film) 3469, 3392 (med, OH), 1722 (str, CO_2R), and 1620, 1607 (wk, Ar). ^{1}H NMR 8.11 (d, 2, J=8.30, ArH *ortho* to CO_2Ar), 7.32 (d, 2, J=7.26, ArH *ortho* to *R*), 7.02 (d, 2, J=8.87, ArH *ortho* to OCOAr), 6.80 (d, 2, J=9.00, ArH *ortho* to OH), 5.60 (s, 1, OH), 2.70 (t, 2, J=7.65, α-CH_2), 1.66 (quint, 2, J=7.04, β-CH_2), 1.35–1.27 (m, 14, 7 CH_2) and 0.89 (t, 3, J=6.41, CH_3).

5.2.17. 4-(Alkynyloxycarbonyl)phenyl 4-substituted benzoates 6. Most of these esters were prepared by esterification of the phenols **32** with the acids **33** using the carbodiimide procedure described earlier [2]. The reflux time was usually 17 h. Purified yields were generally low due to difficulty in recrystallizing these very soluble materials. Purification was achieved by chromatography using 1/1 CH_2Cl_2/hexane or EtOAc followed by recrystallization. The best solvent appeared to be hexane. A minimum amount was used to dissolve the ester; the solution was then filtered hot and cooled in an ice/salt bath to obtain crystals. Characterization data for typical esters are as follows.

X=$C_{10}H_{21}$, *R*=C_4H_9: this material was purified by recrystallization from CH_2Cl_2; IR (Nujol) 2267, 2230 (med, alkyne), 1737 (str, esters) and 1611 (str, Ar). ^{1}H NMR 8.10 (d, 2, J=8.22, ArH *ortho* to CO_2Ar), 7.32 (d, 2, J=8.34, ArH *ortho* to alkyl), 7.24 (d, 2, J=8.71, ArH *ortho* to OCOAr), 7.19 (d, 2, J=9.03, ArH *ortho* to OCO*R*), 2.70 (t, 2, J=7.67, alkyne CH_2), 2.42 (t, 2, J=6.92, alkyl α-CH_2), 1.62 (quint, 2, J=6.57, alkyl β-CH_2), 1.49 (quint, 2, J=7.28, alkynyl β-CH_2), 1.32–1.19 (m, 16, 8 CH_2), 0.95 (t, 3, J=7.27, alkyl CH_3) and 0.88 (t, 3, J=6.74, alkynyl CH_3). *X*=$C_{10}H_{21}O$, *R*=C_4H_9: purified by chromatography and recrystallization from EtOH; IR (Nujol) 2229 (med d, alkyne), 1736 (str, esters) and 1608 (str, Ar). ^{1}H NMR 8.12 (d, 2, J=8.91, ArH *ortho* to CO_2Ar), 7.23 (d, 2, J=8.80, ArH *ortho* to OCOAr), 7.18 (d, 2, J=8.80, ArH *ortho* to OCO*R*), 6.96 (d, 2, J=8.92, ArH *ortho* to O*R*), 4.40 (t, 2, J=6.49, CH_2O), 2.41 (t, 2, J=6.94, alkyne CH_2), 1.82 (quint, 2, J=6.91, alkoxy β-CH_2), 1.48 (quint, 2, J=7.24, alkynyl β-CH_2), 1.48–1.20 (m, 16, 8 CH_2), 0.95 (t, 3, J=7.08, alkoxy CH_3) and 0.88 (t, 3, J=6.27, alkynyl CH_3).

One ester was prepared using the acid chloride method. *X*=C_4H_9, *R*=C_4H_9: The acid chloride was

prepared by treating the acid **33** (R=C_4H_9) with $(COCl)_2$ at r.t. for 17 h. An IR spectrum of the crude product after removal of excess $(COCl)_2$ showed peaks at 2226 (str, alkyne) and 1815, 1754 (str d, COCl). Esterification was carried out using the acid chloride method [2]. Hexane was added to the crude product and some insoluble material removed by filtration. The solvent was removed *in vacuo* and the remaining material chromatographed using CH_2Cl_2 in hexane. Yield=25.2%, characterization data were similar to those for X=$C_{10}H_{21}$, R=C_4H_9.

5.2.18. Preparation of esters 41a. These phenol esters were prepared using the method described earlier for preparing the Y=C_5H_{11} and C_9H_{19}[30] homologues. Experimental and characterization data which differ from those reported are given as follows:

42. Y=$C_{10}H_{21}$: yield=36.1%, THF used as the reaction solvent, reflux time=25 h. Y=$OC_{10}H_{21}$: recrystallized from hexane, yield=71.9%. ^{1}H NMR 8.14 (d, 2, J=8.83, ArH *ortho* to carbonyl), 7.41 (m, 5, C_6H_5), 7.07 (t, 4, J=8.83, ArH *ortho* to OCH_2), 6.91 (d, 2, J=9.12, ArH *ortho* to OCO), 5.16 (s, 2, OCH_2Ph), 3.95 (t, 2, J=6.49, OCH_2), 1.75 (q, 2, CH_2), 1.60–1.10 (m, 14, 7 CH_2) and 0.89 (t, 3, J=6.43, CH_3). Y=OC_5H_{11}: the reaction solvent was THF, yield=50.1% after recrystallization from abs EtOH.

41a. Y=$C_{10}H_{21}$: recrystallized from abs EtOH, yield=87.1%. Y=OC_5H_{11}: chromatographed using 25% EtOAc in hexane and then recrystallized from benzene, yield=89.7%. Y=$OC_{10}H_{21}$: recrystallized from benzene, yield=42.3%. IR (Nujol) 3467, 2288 (wk, OH), 1736 (str d, ester) and 1604 (wk d, Ar).

5.2.19. Alkylacyloxy esters 2. The synthesis of these compounds was reported earlier [3]. The method shown in scheme **4** is now considered a better approach. The alkynylacyloxy esters **7** were prepared by esterification of the phenols **41a** (Y=RC≡C) with the acid $C_5H_{11}C{\equiv}C{-}CO_2H$ using the standard carbodiimide method [2]. Deviations in experimental details and characterizations of representative esters are provided here:

R=$C_{10}H_{21}$: reflux time 3.5 h, chromatographed twice using CH_2Cl_2/hexane (3/2) and then recrystallized from hexane in dry ice, yield 28.2%. IR (Nujol) 2249 (wk, alkyne), 1742 (str, ester) and 1610, 1518 (wk, Ar). ^{1}H NMR 8.25 (d, 2, J=8.66, ArH *ortho* to CO_2Ar), 7.30 (d, 2, J=8.71, ArH *ortho* to OCO alkyne), 7.23 (d, 2, J=8.71, ArH *ortho* to $C_{10}H_{21}$), 7.10 (d, 2, J=8.51, ArH *ortho* to OCOAr), 2.63 (t, 2, J=7.67, $ArCH_2$), 2.43 (t, 2, J=7.04, alkyne CH_2), 1.74–1.53 (m, 2, CH_2 β to alkyne), 1.53–1.35 (m, 2, β-CH_2), 1.40–1.20 (m, 18, 9 CH_2), 0.94 (t, 3, J=6.46, alkyne CH_3) and 0.89 (t, 3, J=6.51, alkyl CH_3). R=$OC_{10}H_{21}$: reflux time 24 h, chromatographed using CH_2Cl_2/hexane (2/3) and then recrystallized from hexane, yield 47.7%. IR (Nujol) 2230 (med dl, alkyne), 1736 (str, esters), 1604 (med, Ar) and 1506 (str, Ar). ^{1}H NMR 8.24 (d, 2, J=8.87, ArH *ortho* to CO_2Ar), 7.29 (d, 2, J=9.52, ArH *ortho* to OCOalkyne), 7.10 (d, 2, J=9.07, ArH *ortho* to OCOAr), 6.93 (d, 2, J=9.07, ArH *ortho* to O*R*), 3.96 (t, 2, J=6.55, $ArOCH_2$), 2.42 (t, 2, J=7.00, alkyne CH_2), 1.90–1.70 (m, 2, alkyl β-CH_2), 1.70–1.60 (m, 2, alkyne β-CH_2), 1.60–1.10 (m, 18, 9 CH_2), 0.93 (t, 3, J=5.53, alkyne CH_3) and 0.89 (t, 3, J=6.98, alkyl CH_3).

5.2.20. Preparation of the thioesters 42b. The carbodiimide method described earlier [2] was used to prepare these compounds. Variations from this procedure, purification and characterization are as follows:

Y=C_5H_{11}: reflux time 2 h, crude yield 97.1% of a thick liquid which crystallized after 24 h, purification was by chromatography using increasing amounts of CH_2Cl_2 in hexane, yield 49.7%. TLC ($CHCl_3$) R_f=0.58. IR (Nujol) 1670 (str, COS) and 1597 (str, Ar). ^{1}H NMR 8.00 (d, 2, J=8.79, ArH *ortho* to C=O), 7.41 (d, 2, J=8.14, ArH *ortho* to S), 7.26 (d, 2, J=8.06, ArH *ortho* to CH_2), 7.11 (d, 2, J=8.79, ArH *ortho* to O), 5.53 (s, 1, THPCH), 4.00–3.75 (m, 1, THP-C_6H_{eq}), 3.75–3.55 (m, 1, THP-C_6H_{ax}), 2.64 (t, 2, J=7.70, $ArCH_2$), 2.10–1.80 (m, 2, THP-C_5H), 1.80–1.50 (m, 6, 3 chain CH_2), 1.50–1.20 (m, 4, THP-C_3 and C_4H) and 0.90 (t, 3, J=6.55, CH_3). Y=OC_8H_{17}: stirred at r.t. for 24 h, chromatographed using CH_2Cl_2, yield 70.0%. TLC ($CHCl_3$) R_f=0.51. ^{1}H NMR 8.00 (d, 2, J=8.79, ArH *ortho* to COS), 7.40 (d, 2, J=8.79, ArH *ortho* to S), 7.11 (d, 2, J=9.16, ArH *ortho* to OTHP), 6.97 (d, 2, J=8.79, ArH *ortho* to OCH_2), 5.54 (s, 1, THP-C_1H), 3.99 (t, 2, J=6.41, $ArOCH_2$), 3.95–3.90 (m, 1, THP-C_6H_{eq}), 3.85–3.80 (m, 1, THP-C_6H_{ax}), 2.00–1.80 (m, 8, 3 THP-CH, chain β-CH_2), 1.50–1.30 (m, 10, 5 CH_2) and 0.91 (t, 3, J=~6.96, CH_3).

5.2.21. 4-Pentylphenyl 4-hydroxythiobenzoate 41b (Y=C_5H_{11}). The thioester **42b** (Y=C_5H_{11}), (691 mg, 1.80 mmol) was added to MeOH (7 ml), but THF (7 ml) was needed to obtain a homogeneous solution. The Amberlite ion exchange resin (IR 120-plus, 250 mg) was added and this mixture heated under reflux for 4.5 h. It was then cooled, allowed to stand at r.t. for 48 h and filtered. Removal of the solvent *in vacuo* gave 520 mg of the crude product. This solid was recrystallized with

difficulty from cyclohexane to give 98 mg (18.8%) of the phenol **41b** (Y=C_5H_{11}). TLC ($CHCl_3$) R_f=0.28. IR (Nujol) 3315 (med br, OH), 1650 (str, COS), 1591 (str, Ar). ^{1}H NMR 7.90 (d, 2, J=8.67, ArH *ortho* C=O), 7.40 (d, 2, J=8.06, ArH *ortho* to S), 7.25 (d, 2, J=8.14, ArH *ortho* to CH_2), 6.84 (d, 2, J=8.67, ArH *ortho* to O), 5.78 (s, 1, OH), 2.63 (t, 2, J=7.69, $ArCH_2$), 1.75–1.50 (m, 2, β-CH_2), 1.50–1.20 (m, 4, 2 CH_2) and 0.81 (t, 3, J=6.94, CH_3). The Y=OC_8H_{17} analogue was prepared in the same manner. Reflux time was 3.0 h, r.t. time 20 h. The crude product was chromatographed using CH_2Cl_2 to give 1.66 g (97.7%) of the product as a colourless solid. ^{1}H NMR 7.94 (d, 2, J=8.79, ArH *ortho* to C=O), 7.38 (d, 2, J=9.16, ArH *ortho* to S), 6.91 (d, 2, J=9.16, ArH *ortho* to OCH_2), 6.84 (d, 2, J=9.16, ArH *ortho* to OH), 5.73 (s, 1, OH), 3.96 (t, 2, J=6.41, OCH_2), 1.78 (q, 2, J=7.32, β-CH_2), 1.50–1.10 (m, 10, 5 CH_2) and 0.88 (t, 3, J=~6.59, CH_3).

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