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Synthesis and mesomorphic behaviour of new 5-substituted 4-(thien-2-yl)phenyl benzoates

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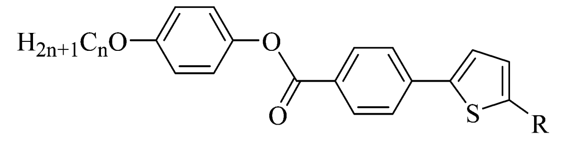
4-(5-Alkylthien-2-yl)phenyl 4-alkoxybenzoates and 4-(5-cyanothien-2-yl)phenyl 4-alkoxbenzoates are synthesised by using Pd (0) catalysed coupling reactions as key steps. The thermotropic liquid crystalline behaviour of these compounds is investigated using polarised optical microscopy (POM) and differential scanning calorimetry (DSC). Broad temperature ranges of nematic and/or smectic A mesophases are found in these compounds. The influence of the length of the alkoxy chains and molecular polarisability on the mesophase behaviours is discussed.

Keywords: thiophene; Pd (0)-catalysed coupling reaction; calamitic, liquid crystals

1. Introduction

Shape anisotropy, dipole–dipole interaction, microphase segregation and non-covalent interactions are considered as the most fundamental factors in designing liquid crystalline molecules (*1*). Thiophene-based calamitic liquid crystals are currently the subject of intensive study (*2–8*). Their application as ferroelectric materials as well as potential materials for molecular electronic devices, such as organic field effect transistors (OFETs), are of special interest. Metal catalysed coupling reactions are nowadays used to construct the heterocyclic rigid cores (2,5-diphenylthienyl (*3, 4*) or phenylthienyl (*3, 4, 9–12*)) of these molecules. However, often, the yield of the coupling reaction is low and in some cases the more expensive aryl iodides are required for successful coupling (*2–4*, *9–13*). Chiral and achiral phenyl 4-(5-alkyl-2-thienyl)benzoates (**I**) (*13*):



Ia : R=C_4H_9, *n*=5: Cr 96 N 154 Iso
Ib : R=C_4H_9, *n*=7: Cr 97 N 150 Iso
Ic: R=C_8H_{17}, *n*=7: Cr92 SmB 98 SmC 126 SmA 139 N 146 Iso
Id: R=C_8H_{17}, *n*=5: Cr 89 SmB 100 SmA 138 N 147 Iso

belong to the most intensively studied thiophene-based calamitic liquid crystals (*3, 4, 14–17*), owing to their structural similarity to MHPOBC and related ferroelectric and antiferroelectric materials (*18*). To the best of the author's knowledge, there are however no reports regarding 4-(5-alkylthienylphenyl) benzoates, which are related to compounds **I** and differ from these compounds by a reversed direction of the COO linkage. Herein an efficient synthesis of these compounds (**8/*n***) is reported.

Recently, we have systematically studied Suzuki coupling reactions between 2,5-dibromo thiophene and 4-methoxyphenylboronic acid. Either mono- or double-coupling products were obtained as major products, depending on the conditions used for the coupling reaction (*19*). The mono-coupling product (**2**) was obtained in 65% yield if $NaHCO_3$ was used as the base (*19*). In this compound both, bromo and methoxy groups can be used for further functionalisation. The bromo substituent can either be exchanged by lithium in a halogen–metal-exchange reaction, followed by a coupling reaction with bromoalkanes, or replaced in a Cu-catalysed substitution by polar groups such as cyano. The methoxy group at the benzene ring can be demethylated and the resulting phenols **5** (compounds of type **5** were previously synthesised by Suzuki coupling of 5-alkyl-2-bromothiophenes with 4-methoxybenzene boronic acid, followed by demethylation (*3, 4*), but this synthetic route requires the complete synthesis to be performed for each homologue) and **6** (reported methods to obtain compound **6** use a Suzuki coupling reaction between 5-bromothiophene-2-carbonitrile and 4-methoxybenzene boronic acid, followed by demethylation (*3*))

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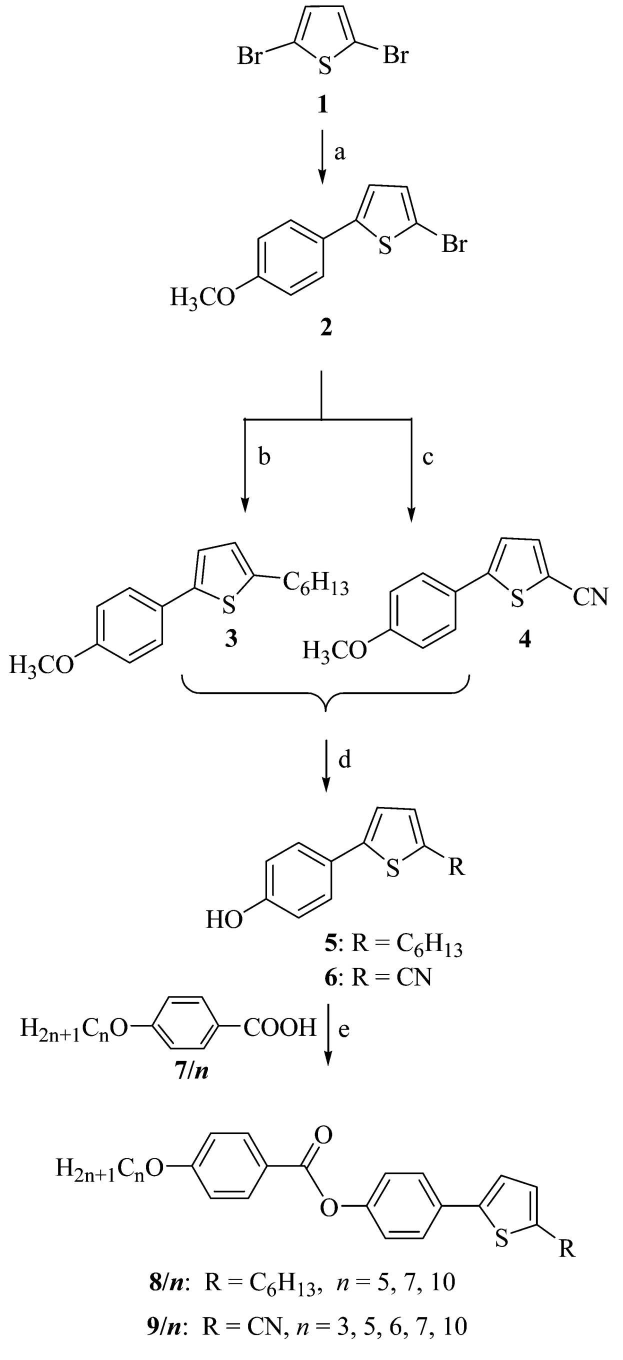
represent valuable intermediates which can be easily etherified or esterified (e.g. with 4-alkoxybenzoic acids) to yield different types of liquid crystalline materials. In this report attention is focused on a series of 4-(5-*n*-alkylthien-2-yl)phenyl benzoates **8/*n*** and 4-(5-cyanothien-2-yl)phenyl benzoates **9/*n***. The thermotropic liquid crystalline behaviour of these compounds was investigated using polarised optical microscopy (POM) and differential scanning calorimetry (DSC). The influence of the type of substituent and the length of the alkoxy chains of these derivatives on the mesomorphic properties is studied. All compounds are mesogens and most of them exhibit enantiotropic nematic and/or smectic A phases.

2. Results and discussion

2.1. *Synthesis*

The synthesis of compounds **8/*n*** and **9/*n*** is shown in Scheme 1. Palladium-catalysed Suzuki cross-coupling between commercially available 2,5-dibromothiophene and 4-methoxyphenylboronic acid gave mono-coupling product **2** (*19*), whose bromo substituent was at first exchanged with Li and then coupled with bromoalkanes, or substituted by CN through refluxing with CuCN in DMF (*20*). It should be emphasised that, for the halogen–metal-exchange reaction, two equivalent units of *t*-BuLi were used: the *t*-BuBr which was the byproduct of the halogen–metal-exchange reaction was eliminated by the second equivalent of *t*-BuLi to form isobutane, isobutene and LiBr (*21*). Cleavage of the methyl group using BBr_3 (*22*) yielded phenols **5** and **6** which were esterified with 4-*n*-alkoxybenzoic acids **7/*n*** with DCC/DMAP (*23*) as condensation reagents yielding the target compounds **8/*n*** and **9/*n***. The advantage of this procedure compared with previously reported procedures (*2–4*) is that different terminal alkyl chain or a cyano group can be introduced after the coupling reaction, which allows an easy variation of the alkyl chains and substitution pattern as required for the systematic studies of the dependence of mesomorphic properties on the molecular structure. Purification of these products was performed by crystallisation or column chromatography, the structure and purity of all compounds are confirmed by proton nuclear magnetic resonance (^{1}H-NMR) and high-resolution mass spectrometry (HRMS) spectra.

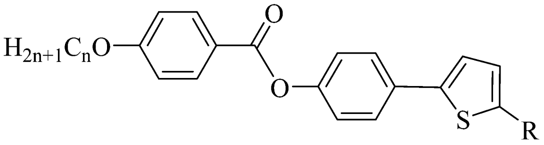


Scheme 1. Synthesis of compounds **8/n** and **9/n**. Reagents and conditions: (a) 4-methoxyphenylboronic acid, $Pd(PPh_3)_4$, $NaHCO_3$, DME, reflux 6 h (65%); (b) *t*-BuLi, −60°C, THF, *n*-$C_6H_{13}Br$, room temperature, 24 h (70%); (c) CuCN, Pyridine, DMF, reflux, 24 h (68%); (d) BBr_3, −78°C CH_2Cl_2, room temperature, 24 h (90%); (e) DCC, DMAP, CH_2Cl_2, 20°C, 72 h (20–90%).

2.2. *Mesophase behaviour*

The liquid crystalline properties of compounds **8/*n*** and **9/*n*** were investigated using POM and DSC. The transition temperatures and corresponding enthalpy values are collected in Table 1. Except the shortest alkyl substituted compound **8/5**, all synthesised compounds exhibit broad temperature ranges of enantiotropic nematic and/or smectic A mesophases. Under POM, the nematic phase is characterised by its

Table 1. Transition temperatures T (°C; determined by DSC, peak temperature, first heating scan, 5°C min^{-1}) and associated enthalpy values ΔH (kJ mol^{-1}) of compounds **8/*n*** and **9/*n***. (Cr=crystal; N=nematic; SmA=smectic A ; Iso=isotropic liquid.)



Compound	*R*	*n*	T (°C) [ΔH (kJ mol^{-1})]
8/5	C_6H_{13}	5	Cr 110 [19.3] Iso
8/7	C_6H_{13}	7	Cr 110 [26.9] N 136 [0.9] Iso
8/10	C_6H_{13}	10	Cr 101 [31.2] SmA 119 [1.2] N 139 [1.5] Iso
9/3	CN	3	Cr 136 [16.4] N>210[a] Iso
9/5	CN	5	Cr 122 [38.9] N 208 [0.5] Iso
9/6	CN	6	Cr 122 [24.1] SmA 141 [1.1] N 196 [1.2] Iso
9/7	CN	7	Cr 117 [33.4] SmA 165 [0.1] N 195[a] Iso
9/10	CN	10	Cr 124 [41.4] SmA 190 [2.4] Iso

[a] The transition from N to isotropic was too weak to be recognised in the DSC thermogram, and the temperature was determined by POM.

typical marble or Schlieren texture. The smectic A phase is characterised by texture consisting of both focal-conic and pseudo isotropic regions. The occurrence of focal-conic fans suggests a layered structure, whereas the pseudo isotropic region indicates an on average orthogonal organisation of the molecules with respect to the layer planes (*24*).

With the elongation of the terminal alkoxy chains, a decrease of the melting points is observed in both series of compounds **8/*n*** and **9/*n*** (except compound **9/10**). The clearing points of the alkoxy substituted compounds **8/*n*** increases with elongation of these chains, whereas in the series of CN substituted compounds **9/*n*** a decrease of the clearing points is observed with increasing chain length. Upon elongation of the terminal alkoxy chains, the mesophase type changed from nematic into Smectic A in both series of compounds **8/*n*** and **9/*n***. By comparison, the cyano substituted compounds **9/*n*** exhibit much higher melting and clearing points than those of the analogous alkoxy substituted compounds **8/*n***. The presence of a highly polar and polarisable cyano group with a large permanent dipole moment in compounds **9/*n*** as opposed to the alkyl chains in compounds **8/*n*** in the terminal position should result in compounds **9/*n*** having higher melting points and clearing points than those of alkylated compounds **8/*n***. Also the alkyl substituted compound **8/5** has no mesophase, while its cyano substituted analogue **9/5** exhibits an enantiotropic nematic phase providing further proof that the cyano group stabilises the mesophases (*25, 26*).

A comparison of the influence of the direction of the ester group on the liquid crystalline properties is possible by comparing molecules with the same total alkyl chain length. For example, compound **Id** with n=5 and R=C_8H_{17} (Cr 89 SmB 100 SmA 138 N 147 Iso) can be compared with compound **8/7**. It seems that all melting points of compounds **8/*n*** are slightly higher, whereas the phase transition temperatures are lower compared to related compounds **I** and also a richer polymorphism including SmC and SmB phases is observed for the phenyl thienylbenzoates **Ic** and **Id**.

3. Conclusion

4-(5-Bromothien-2-yl)anisole **2** was prepared in a single step synthesis and this is a useful building block for 2,5-disubstituted thiophene-based mesogens. New 5-cyano and 5-hexylthienyl substituted phenyl benzoates were synthesised starting with this intermediate to demonstrate its versatility. The obtained mesogens exhibit broad ranges of nematic and smectic A phases. Future work will focus on new types of thiophene-based mesogens, such as amphiphilic and polyphilic molecules (*27–31*) incorporating hydrogen-bond-mediated or ionic self-assembly (*32–35*).

4. Experimental details

4.1. General

Reactions requiring an inert gas atmosphere were conducted under argon and the glassware was oven-dried (140°C). Tetrahydrofuran (THF) was distilled from sodium prior to use. Commercially available chemicals were used as received. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker DRX-500 spectrometer. HRMS data were recorded on a Finnigan MAT 90 spectrometer at an ionisation potential of 70 eV. Field-desorption (FD) mass spectra were recorded on a VG ZAB 2-SE-FPD spectrometer. Column chromatography was performed with Merck silica gel 60 (230–400 mesh).

4.2. *Procedures*

*2-Bromo-5-(4-methoxyphenyl)thiophene (**2**) (see (9, 10)).*

A mixture of 2,5-dibromothiophene (2.43 g, 10 mmol), 4-methoxyphenylboronic acid (1.82 g, 12 mmol), Pd(PPh$_3$)$_4$ (0.58 g, 5% mol), ethyleneglycol dimethyl ether (5 ml) and saturated NaHCO$_3$ solution (5 ml) was refluxed for 6 h under an argon atmosphere. After staying overnight at room temperature, the reaction mixture was extracted with chloroform (10 ml × 3). The combined chloroform solution was dried over anhydrous magnesium sulfate, the solvent was evaporated and the product was purified by column chromatography (eluent: petroleum ether/ethyl acetate V:V=15:1). The yield was 65% (1.75 g) of colourless crystals; melting point 110–112°C. ^{1}H-NMR (500 MHz; CDCl$_3$): δ=3.83 (s, 3H, CH$_3$), 6.90 (d, J=8.8Hz, 2H, ArH), 6.93 (d, J=3.8Hz, 1H, ArH), 6.98 (d, J=3.9Hz, 1H, ArH), 7.43 (d, J=8.8Hz, 2H, ArH).

*2-Hexyl-5-(4-methoxyphenyl)thiophene (**3**) (see (3, 4)).*

2 (0.27 g, 1 mmol) was dissolved in dry THF (3.5 ml) and cooled to −78°C, *t*-BuLi (1.5 M solution in *n*-hexane, 1.33 ml, 2 mmol) was added and the solution was stirred for 30 min, then 1-bromohexane (0.49 g, 3 mmol) was added, the mixture was stirred at room temperature overnight. The crude product was purified by column chromatrography (eluent: petroleum ether) and then crystallised from ethyl acetate. The yield was 56% (0.15 g) of colourless crystals; melting point 58–59°C; ^{1}H-NMR (500 MHz; CDCl$_3$): δ=0.93 (t, J=7.6 Hz, 3H), 1.31–1.39 (m, 6H), 1.66–1.70 (quintets, 2H), 2.80 (t, J=7.6 Hz, 2H), 3.83 (s, 3H), 6.71 (d, J=3.0 Hz, 1H), 6.90 (d, J=8.6 Hz, 2H), 7.00 (d, J=3.3 Hz, 1H), 7.48 (d, J=8.6 Hz, 2H). IR ν_{max}/cm^{-1}: 2956, 2921, 2854, 1608, 1554, 1515, 1470, 1289, 1254, 1181, 1031, 831, 798.

*5-(4-Methoxyphenyl)thiophene-2-carbonitrile (**4**) (see (11, 12)).*

To a solution of 2-bromo-5-(4-methoxyphenyl)thiophene (0.60 g, 2.23 mmol) and CuCN (0.30 g, 3.35 mmol) in dry DMF (5 ml), several drops of pyridine was added. The mixture was refluxed for 24 h under an argon atmosphere. The cooled mixture was washed with 20% ammonia and extracted with chloroform (10 ml × 3). The combined chloroform solution was dried over anhydrous magnesium sulfate, the solvent was evaporated and the product was purified by column chromatography using silica gel and petroleum ether/ethyl acetate (V:V=10:1) as eluent. The yield was 68% (0.33 g) of colourless crystals; melting point 103–105°C; ^{1}H-NMR (500 MHz; CDCl$_3$): δ=3.86 (s, 3H), 6.95 (d, J=8.6 Hz, 2H), 7.16 (d, J=3.9 Hz, 1H), 7.53 (d, J=8.6 Hz, 2H), 7.56 (d, J=3.7 Hz, 1H). IR ν_{max}/cm^{-1}: 2968, 2915, 2850, 2202, 1605, 1561, 1507, 1439, 1390, 1289,1260, 1183, 1113, 1058, 1026, 809.

*5-Hexyl-2-(4-hydroxyphenyl)thiophene (**5**) (see (3, 4)) and 5-cyano-2-(4-hydroxyphenyl)thiophene (**6**) (see (3, 4)).*

Compound **3** (0.14 g, 0.50 mmol) or **4** (0.11 g, 0.50 mmol) was dissolved in CH$_2$Cl$_2$ (15 ml) and cooled to 0°C, BBr$_3$ (0.25 g, 1 mmol) was added and the solution was stirred at room temperature overnight under an argon atmosphere. Water (20 ml) was carefully added, the precipitate was filtered and washed with water (10 ml) and petroleum ether (20 ml) and dried *in vacuo* at 40°C for 4 h. Thus obtained quantitative product was used directly for the next step.

*General procedure for preparation of 4-(5-alkylthien-2-yl)phenyl 4-alkoxybenzoate (**8In**) and 4-(5-cyanothien-2-yl)phenyl 4-alkoxybenzoate (**9In**).*

Compound **5** or **6** (1 eq.) was dissolved in dry CH$_2$Cl$_2$ (10mL), appropriate 4-alkoxybenzoic acid **7/n** (see (*36–38*)) (1.2 eq.), DCC (1.2 eq.) and a catalytic amount of DMAP were added, the mixture was stirred for 72 h at 20°C. The solid was filtered off and washed with CH$_2$Cl$_2$, the combined organic phase was washed with HCl (10%), NaOH (10%) and H$_2$O and dried over anhydrous magnesium sulfate, and the solvent was removed *in vacuo*. The crude product was purified by column chromatography using silica gel and petroleum ether/ethyl acetate (V:V=10:1) as an eluent.

*4-(5-Hexylthien-2-yl)phenyl 4-pentyloxybenzoate (**8I 5**).*

The yield was 90% of colourless crystals. ^{1}H-NMR (500 MHz, CDCl$_3$): δ=0.90 (t, J=7.2 Hz, 3 H), 0.96 (t, J=7.1 Hz, 3 H), 1.28–1.50 (m, 10 H), 1.60–1.71 (quintets, 2 H), 1.81–1.86 (quintets, 2H), 2.83 (t, J=7.8 Hz, 2H), 4.06 (t, J=6.4 Hz, 2H), 6.76 (d, J=3.5 Hz, 1H), 6.98 (d, J=8.9 Hz, 2H), 7.11 (d, J=3.5 Hz, 1H), 7.20 (d, J=8.6, 2H), 7.60 (d,

$J=8.6$ Hz, 2H), 8.15 (d, $J=8.9$ Hz, 2H); ^{13}C-NMR (500 MHz, CDCl$_3$): $\delta=14.00$, 14.08, 22.45, 22.59, 22.71, 28.16, 28.82, 29.72, 30.27, 31.61, 68.34, 114.32, 121.55, 122.13, 122.84, 125.02, 126.50, 132.30, 132.52, 140.83, 145.87, 150.11, 163.59, 164.91; HRMS(ES+): [M+H]$^+$ calculated for $C_{28}H_{34}O_3S$, 451.2229; found, 451.2233. IR ν_{max}/cm^{-1}: 2956, 2926, 2854, 1726, 1605, 1578, 1512, 1467, 1421, 1259, 1215, 1170, 1104, 1073, 1007, 950, 877, 844, 803, 763.

4-(5-Hexylthien-2-yl)pheny 4-heptyloxybenzoate (**8/7**).

The yield was 70% of colourless crystals. ^{1}H-NMR (500 MHz, CDCl$_3$): $\delta=0.90$ (t, $J=7.0$ Hz, 3 H), 0.95 (t, $J=7.5$ Hz, 3H), 1.32–1.49 (m, 14 H), 1.67–1.73 (quintets, 2H), 1.79–1.85 (quintets, 2H), 2.81 (t, $J=7.7$ Hz, 2H), 4.04 (t, $J=6.6$ Hz, 2H), 6.74 (d, $J=3.4$ Hz, 1H), 6.97 (d, $J=8.9$ Hz, 2H), 7.10 (d, $J=3.5$ Hz, 1H), 7.18 (d, $J=8.6$ Hz, 2H), 7.58 (d, $J=8.6$ Hz, 2H), 8.14 (d, $J=8.9$ Hz, 2H); ^{13}C-NMR (500 MHz, CDCl$_3$): $\delta=14.09$, 22.62, 25.98, 28.82–31.78(9C), 68.36, 114.33, 121.54, 122.14, 122.85, 125.03, 126.51, 132.31, 132.52, 140.83, 145.88, 150.11, 163.60, 164.92; HRMS (ES+): [M+H]$^+$ calculated for $C_{30}H_{38}O_3S$, 479.2542; found, 479.2545. IR ν_{max}/cm^{-1}: 2956, 2926, 2854, 1726, 1605, 1578, 1512, 1467, 1421, 1259, 1215, 1170, 1072, 1105, 1007, 950, 877, 844, 803, 764.

4-(5-Hexylthien-2-yl)phenyl 4-decyloxybenzoate (**8/10**).

The yield was 87% of colourless crystals. ^{1}H-NMR (500 MHz, CDCl$_3$): $\delta=0.89$ (t, $J=7.0$ Hz, 3H), 0.95 (t, $J=7.5$ Hz, 3H), 1.30–1.49 (m, 20H), 1.67–1.73 (quintet, 2H), 1.80–1.85 (quintet, 2H), 2.82 (t, $J=7.7$ Hz, 2H), 4.04 (t, $J=6.5$ Hz, 2H), 6.74 (d, $J=3.4$ Hz, 1H), 6.97 (d, $J=8.8$ Hz, 2H), 7.10 (d, $J=3.5$ Hz, 1H), 7.19 (d, $J=8.5$ Hz, 2H), 7.60 (d, $J=8.5$ Hz, 2H), 8.15 (d, $J=8.8$ Hz, 2H); ^{13}C-NMR (500 MHz, CDCl$_3$): $\delta=14.10$, 22.58, 22.69, 26.00, 28.80–31.91(11C), 68.36, 114.33, 121.54, 122.12, 122.84, 125.02, 126.51, 132.29, 132.52, 140.83, 145.87, 150.11, 163.60, 164.91; HRMS (ES+): [M+H]$^+$ calculated for $C_{33}H_{44}O_3S$, 521.3011; found, 521.3013. IR ν_{max}/cm^{-1}: 2956, 2926, 2854, 1726, 1605, 1577, 1512, 1467, 1425, 1259, 1215, 1172, 1105, 1074, 1007, 950, 877, 844, 803, 763.

4-(5-Cyanothien-2-yl)phenyl 4-propoxybenzoate (**9/3**).

The yield was 48% of white solid; ^{1}H-NMR (500 MHz; CDCl$_3$): $\delta=1.07$ (t, $J=7.0$ Hz, 3H), 1.84–1.87 (sextet, 2H), 4.02 (t, $J=6.3$ Hz, 2H), 6.98 (d, $J=8.1$ Hz, 2H), 7.26 (d, $J=3.8$ Hz, 1H), 7.29 (d, $J=8.0$ Hz, 2H), 7.60 (d, $J=5.1$ Hz, 1H), 7.64 (d, $J=8.0$ Hz, 2H), 8.12 (d, $J=8.1$ Hz, 2H); ^{13}C-NMR (500 MHz, CDCl$_3$): $\delta=10.44$, 22.45, 69.87, 108.46, 114.43, 121.15, 122.81, 123.43, 127.61, 129.89, 132.37, 138.36, 150.95, 152.09, 163.81, 164.63; HRMS (ES+): [M+H]$^+$ calculated for $C_{21}H_{17}NO_3S$, 364.0929; found, 364.0931. IR ν_{max}/cm^{-1}: 2961,2927, 2879, 2212, 1720, 1643, 1603, 1507, 1444, 1260, 1209, 1167, 1068, 966, 837, 754.

4-(5-Cyanothien-2-yl)phenyl 4-pentyloxybenzoate (**9/5**).

The yield was 45% of white solid; ^{1}H-MNR (500 MHz, CDCl$_3$): $\delta=0.95$ (t, $J=7.2$ Hz, 3H), 1.35–1.50 (m, 4H), 1.83–1.85 (quintet, 2H), 4.05 (t, $J=6.9$ Hz, 2H), 6.98 (d, $J=8.9$ Hz, 2H), 7.27 (d, $J=4.3$Hz, 1H), 7.29 (d, $J=8.6$ Hz, 2H), 7.60 (d, $J=5.4$ Hz, 1H), 7.65 (d, $J=8.6$ Hz, 2H), 8.14 (d, $J=8.9$ Hz, 2H); ^{13}C-NMR (500 MHz, CDCl$_3$): $\delta=13.95$, 22.41, 28.13, 28.78, 68.40, 108.47, 114.43, 121.13, 122.80, 123.43, 127.60, 129.87, 132.36, 138.35, 150.94, 152.08, 163.81, 164.62; HRMS (ES+): [M+H]$^+$ calculated for $C_{23}H_{21}NO_3S$, 392.1242; found, 392.1237. IR ν_{max}/cm^{-1}: 2961, 2927, 2879, 2212, 1720, 1643, 1603, 1507, 1444, 1260, 1209, 1167, 1066, 966, 838, 752.

4-(5-Cyanothien-2-yl)phenyl 4-hexyloxybenzoate (**9/6**).

The yield was 46% of colourless crystals; ^{1}H-MNR (500 MHz, CDCl$_3$): $\delta=0.95$ (t, $J=6.9$ Hz, 3H), 1.38–1.51 (m, 6H), 1.83–1.88 (quintet, 2H), 4.08 (t, $J=6.5$ Hz, 2H), 7.00 (d, J=8.8 Hz, 2H), 7.28 (d, J=2.3 Hz, 1 H), 7.31 (d, $J=8.6$ HZ, 2H), 7.62 (d, $J=4.0$ Hz, 1 H), 7.67 (d, $J=8.6$ Hz, 2H), 8.16 (d, $J=8.8$ Hz, 2H); ^{13}C-NMR (500 MHz, CDCl$_3$): $\delta=11.50$, 20.08, 23.16, 27.19, 29.05, 65.93, 105.97, 111.75, 111.94, 118.63, 120.32, 120.95, 125.12, 127.38, 129.88, 135.88, 148.46, 149.58, 161.32, 162.15; HRMS (ES+): [M+H]$^+$ calculated for $C_{24}H_{23}NO_3S$, 406.1399; found, 406.1401. IR ν_{max}/cm^{-1}: 2961, 2927, 2879, 2212, 1720, 1643, 1603, 1507, 1444, 1260, 1209, 1167, 1068, 966, 837, 755.

4-(5-Cyanothien-2-yl)phenyl 4-heptyloxybenzoate (**9/7**).

The yield was 36% of colourless crystals; ^{1}H-MNR (500 MHz, CDCl$_3$) $\delta=0.90$ (t, $J=7.35$ Hz, 3H), 1.25–1.33 (m, 8H), 1.81–1.84 (quintet, 2H), 4.05 (t, $J=6.5$ Hz, 2H), 6.98 (d, $J=8.6$ Hz, 2H), 7.26 (d,

J=4.3 Hz, 1H), 7.29 (d, J=8.4 Hz, 2H), 7.60 (d, J=3.7 Hz, 1H), 7.65 (d, J=8.4 Hz, 2H), 8.14 (d, J=8.6 Hz, 2H); ^{13}C NMR (500 MHz, $CDCl_3$) δ=14.02, 22.57, 25.94, 29.00, 29.09, 31.74, 68.42, 108.48, 114.21, 114.44, 121.14, 122.79, 123.42, 127.60, 129.87, 132.36, 138.34, 150.94, 152.08, 163.82, 164.63; HRMS (ES+): $[M+H]^+$ calculated for $C_{25}H_{25}NO_3S$, 420.1555; found, 420.1557. IR ν_{max}/cm^{-1}: 2961, 2352, 2211, 1720, 1643, 1601, 1506, 1444, 1260, 1209, 1167, 1068, 966, 837, 756.

4-(5-Cyanothien-2-yl)phenyl 4-decyloxybenzoate (9/10).

The yield was 20% of colourless crystals; ^{1}H-NMR (500 MHz, $CDCl_3$) δ=0.89 (t, J=6.5 Hz, 3H), 1.29–1.48 (m, 14H), 1.81–1.84 (quintet, 2H), 4.05 (t, J=6.4 Hz, 2H), 6.98 (d, J=8.8 Hz, 2H), 7.25 (d, J=4.5 Hz, 1H), 7.29 (d, J=8.6 Hz, 2H), 7.60 (d, J=3.8 Hz, 1H), 7.65 (d, J=8.6 Hz, 2H), 8.14 (d, J=8.8 Hz, 2H); ^{13}C-NMR (500 MHz, $CDCl_3$): δ=14.06, 22.65, 25.97, 29.09, 29.34, 29.53, 31.88, 68.43, 108.47, 114.21, 114.44, 121.13, 122.80, 123.42, 127.60, 129.87, 132.36, 138.34, 150.94, 152.08, 163.82, 164.62; HRMS (ES+): $[M+H]^+$ calculated for $C_{28}H_{31}NO_3S$, 462.2025; found, 462.2026. IR ν_{max}/cm^{-1}: 2961, 2352, 2212, 1720, 1643, 1603, 1507, 1444, 1260, 1209, 1167, 1068, 966, 837, 754.

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