Axial chiral allenylacetates as novel ferroelectric liquid crystals

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Liquid crystalline alkane-3,4-dienoates (allenylacetates) have been synthesized. Most compounds incorporate a heterocyclic 1,3,4-thiadiazole ring or a pyrimidine ring as a constituent of the rigid core. These axial chiral allene derivatives were at first obtained as racemic mixtures. Some of them were also synthesized in enantiomerically enriched form by enantioselective synthesis. The compounds were investigated by polarizing microscopy and by differential scanning calorimetry. The three-ring compounds exhibit broad regions of smectic C-phases. The optically active three-ring compounds show broad S_c*-phases with moderate values of spontaneous polarization.

Due to their special physical properties and potential technical applications,[1] chiral mesophases have grown to be a central topic in liquid crystal research. Materials exhibiting a chiral smectic C-phase are of particular interest because of their ferroelectric properties and their use for displays and light shutter devices.[2,3] Until now most liquid crystals with chiral mesophases have incorporated a centre of chirality. Only a few examples of mesogenic compounds and dopants that possess an axis[4–7] or a plane[8,9] of chirality have been reported (Fig. 1).

A major drawback of these compounds is the fact that the rigid rod-like molecular shape is significantly disturbed by the structural units necessary to realize an axis or a plane of chirality. Thus, none of the binaphthyl derivatives exhibits liquid crystalline properties[6] and only one axial chiral biphenyl derivative has been reported to form an enantiotropic cholesteric phase.[5c] Only cholesteric and non-tilted smectic phases have been described for some low molecular mass alkylidenecyclohexanes,[4a,b,e] but by appending alkylidenecyclohexanes to a polymeric backbone S_c*-phases can be obtained.[4c,d]

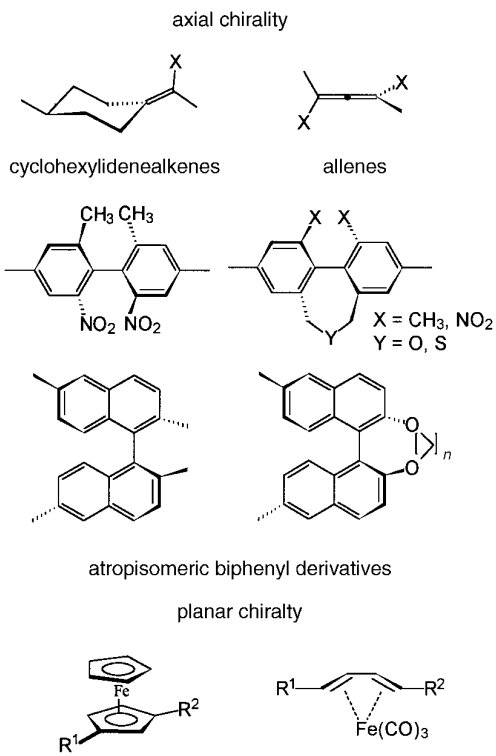
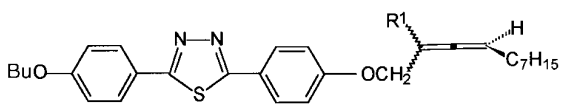


Fig. 1 Structural units of axial chiral and planar chiral mesogens and dopants

In a project aimed at the synthesis of novel mesogenic compounds with ferroelectric properties, the first liquid crystalline allene derivatives displaying broad S_c*-phases have recently been synthesized[10,11] (*e.g.* compounds **1** and **2**).



1 $R^1 = H$,
2 $R^1 = CH_3$

These are the first axial chiral low molecular mass liquid crystals with broad S_c-phase ranges. It was found that enantiomerically enriched allene derivatives can exhibit ferroelectric switchable S_c*-phases with surprisingly large values of spontaneous polarization.

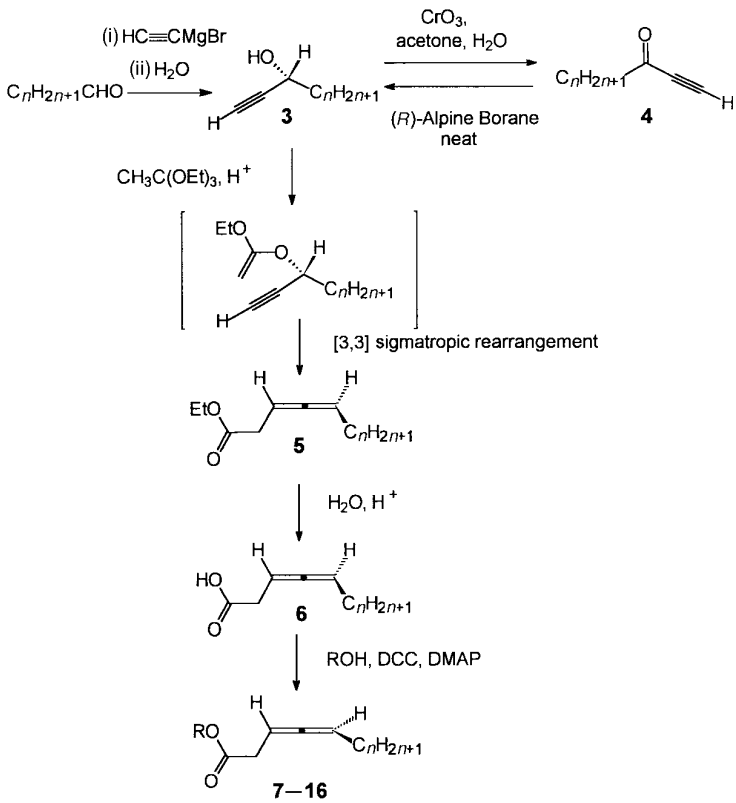
To make ferroelectric materials, it is also important to tailor other properties, such as tilt angle, optical anisotropy, smectic C-range and response time. This can be done by mixing the ferroelectric liquid crystals with other liquid crystals. Therefore it is useful to have materials with high values of the spontaneous polarization which can tolerate the presence of rather large amounts of non-chiral additives. In order to further increase the magnitude of the spontaneous polarization, we set out to synthesize liquid crystalline allene derivatives with increased dipole moments[2] within the substituents attached to the axis of chirality.

Herein we report on the synthesis and on preliminary investigations of chiral alka-3,4-dienoates incorporating phenylpyrimidine and phenyl-1,3,4-thiadiazole mesogens. In order to find suitable systems exhibiting broad S_c-phases and in order to investigate the influence of changes in the substitution pattern of the allene moiety on the mesogenic behaviour we first synthesized several types of chiral allene derivatives as racemates. After checking the liquid crystalline properties of the racemic derivatives, selected compounds were synthesized in their enantiomerically enriched form.

Results and Discussion

Synthesis

According to Scheme 1, the alka-3,4-dienoic acids have been synthesized starting from substituted prop-2-ynylic alcohols.



Scheme 1 Synthesis of the racemic and the enantiomerically enriched alka-3,4-dienoates **7a**, **8a**, **11a** ($n=1$), **8b**–**10b**, **12b**, **13**–**16** ($n=5$) and **8c**–**10c**, **12c** ($n=7$)

For the synthesis of the heptyl substituted derivatives **8c**–**10c** and **12c**, *n*-octanal ($n=7$) was treated with ethynylmagnesium bromide to yield racemic dec-1-yn-3-ol (*rac*-**3c**).[12] Oxidation with CrO_3 (Jones' reagent[13]) provided the prochiral dec-1-yn-3-one **4c**, which was treated with (*R*)-Alpine borane[14] to give the optically active prop-2-ynylic alcohol **3c** in 87% ee after oxidative work-up.[15–17] By comparison with models for the diastereomeric transition states of (*R*)-Alpine borane reduction of dec-1-yn-3-one, the absolute configuration (*R*) was assigned to the major enantiomer.[15] The enantiomeric purity of this compound was determined by derivation with (*S*)-α-methoxy-α-trifluoromethylphenylacetyl chloride [(*S*)-MTPACl] and analysing the resulting (*R*)-MTPA-esters by ^{19}F NMR spectroscopy (Mosher's method).[18]

To obtain the allenic moiety (*R*)-dec-1-yn-3-ol [(*R*)-**3c**] was transformed to the appropriate propynyl vinyl ether by heating with triethyl orthoacetate. This immediately undergoes the stereospecific Claisen-type [3,3] sigmatropic rearrangement.[19] Thereby chirality from the asymmetric centre is transferred to the stereogenic axis of the allene moiety formed. The ester (*R*)-**5c** was easily purified by distillation and transformed into the appropriate (*R*)-dodeca-3,4-dienoic acid (*R*)-**6c** by acid-catalysed aqueous hydrolysis.† In the final step the enantiomerically enriched (*R*)-dodeca-3,4-dienoic acid (*R*)-**6c** was appended to the appropriate phenols[20–23] by carbodiimide esterification.[24] Although we were not able to directly determine the enantiomeric purity of the allenylacetic acid or its esters by chromatographic methods or by NMR investigations in the presence of chiral shift reagents, the success of chirality transfer was revealed by comparison of the molar optical rotation of the ethyl ester (*R*)-**5c** ($[\alpha]^{22}_D=-90.4$) with the molar optical rotation of the homologous compound ethyl 3,4-tridecadienoate ($[\alpha]^{22}_D=-112$; ee = 90%).[25] Therefrom we calculated that the enantiomeric purity should be *ca.* 73% ee.

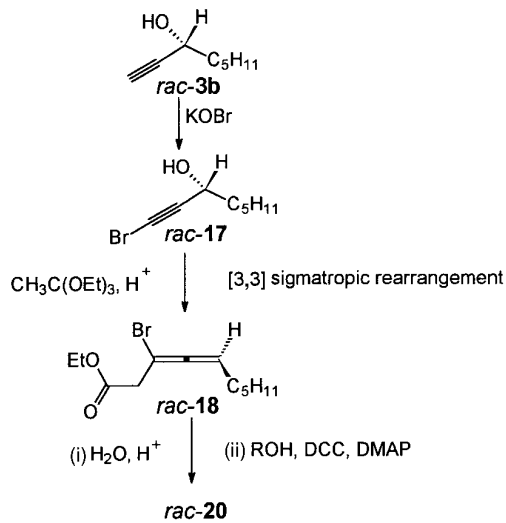
† Alkaline hydrolysis gave the dodeca-3,5-dienoic acid, see ref. 26.

The racemic allenylacetates were synthesized according to Scheme 1 starting with the racemic prop-2-ynylic alcohols.[26] Compound **20**, in which one of the hydrogen atoms of the allene moiety is replaced by a bromine atom, was synthesized in its racemic form according to Scheme 2.[27]

Liquid-crystalline properties of the racemic compounds

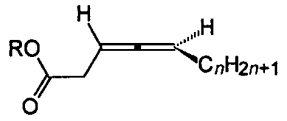
Phase transition temperatures were determined by microscopy between crossed polarizers and were checked by differential scanning calorimetry. The results of these investigations are summarized in Tables 1 and 3.

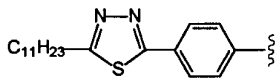
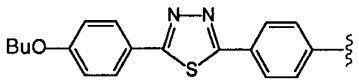
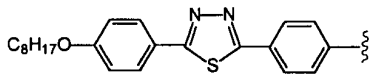
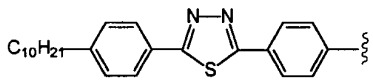
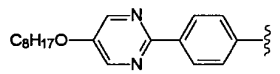
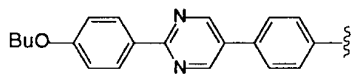
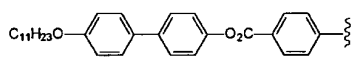
All racemic three-ring pyrimidine and thiadiazole derivatives display broad smectic C-phases with the difference that the



Scheme 2 Synthesis of the racemic 3-bromododeca-3,4-dienoate *rac*-**20**

Table 1 Transition temperatures and corresponding enthalpy values (italicised) of the racemic allenylacetates *rac*-**7**–*rac*-**13**



R	*n*	comp.	phase transitions T/°C enthalpy values ΔH/kJ mol^{-1}
	1	*rac*-**7a**	C 68 Iso
	1	*rac*-**8a**	C 102 S_C 161 N 224 Iso *20.1 1.9 0.7*
	5	*rac*-**8b**	C 61 S_C 147 N 167 Iso *27.6 1.8 0.5*
	7	*rac*-**8c**	C 76 S_C 149 N 164 Iso *25.9 2.1 1.2*
	5	*rac*-**9b**	C 82 S_C 166 Iso *27.6 7.8*
	7	*rac*-**9c**	C 83 S_C 158 Iso *26.7 6.6*
	5	*rac*-**10b**	C 58 S_C 149 Iso
	7	*rac*-**10c**	C 65 S_C 137 Iso *42.6 8.3*
	1	*rac*-**11a**	C 78 (S_A 75) Iso
	5	*rac*-**12b**	C 144 S_C 176 Iso
	7	*rac*-**12c**	C 143 S_C 174 Iso *23.8 7.1*
	5	*rac*-**13**	C 106 S_C 153 N 155 Iso

melting points of the thiadiazole derivatives are mostly shifted to lower temperatures in comparison to the pyrimidine derivatives. Thus, the S_c-ranges of the thiadiazole derivatives are increased. The S_c-phases of the butoxy derivatives *rac*-**8** are accompanied by a nematic phase in contrast to the long chain derivatives *rac*-**9** and *rac*-**10**, which show only S_c-phases. As evident in comparing compounds *rac*-**8a**, *rac*-**8b** and *rac*-**8c**, the nematic and also the S_c-phases are stabilized by cutting the alkyl chain attached to the allene moiety. Stabilization of a smectic phase by decreasing the length of a terminal chain is a remarkable observation.

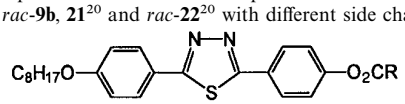
In Table 2 the mesomorphic properties of structurally related thiadiazole derivatives having the same number of carbon atoms, but differing in the structure of one side chain are compared.

By replacing the *n*-nonyl chain of compound **21** by the nona-3,4-dienyl group (*rac*-**9b**) a mesophase destabilization of *ca.* 30 °C is observed. However, the mesophase destabilizing influence of the branching of the alkyl chain in compound *rac*-**22** is even more pronounced ($\Delta T = ca.$ 60 °C). This means, that the disturbance necessary to obtain a centre of chirality by branching an alkyl chain is more severe than that one caused by the bent structure (Fig. 2) of the 1,3-disubstituted allene unit necessary to obtain an axis of chirality.

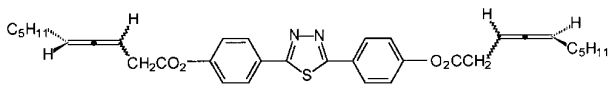
It was also possible to get smectic C compounds incorporating two axes of chirality at each end of a rigid 2,5-diphenyl-1,3,4-thiadiazole mesogen (compound **14**)‡. However, the *p*-terphenyl derivative **15**‡ is only a nematic compound.

‡ Compounds *rac*-**14** and *rac*-**15** are mixtures of two diastereomers.

Table 2 Comparison of transition temperatures of the thiadiazole derivatives *rac*-**9b**, **21**[20] and *rac*-**22**[20] with different side chains R



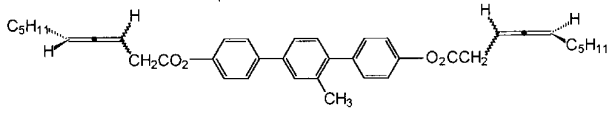
comp.	R	phase transitions T/°C
21	$-C_9H_{19}$	C 90 S_C 194 Iso
rac-**22**	$-CH(CH_3)-C_8H_{17}$	C 65 (S_X 64) S_C 135 Iso
rac-**9b**	$-CH_2-CH=C=CH-C_5H_{11}$	C 82 S_C 166 Iso



14

transition temperatures T/°C: C_1 80 C_2 92 S_C 149 Iso

transition enthalpies ΔH/kJ mol^{-1}: 14.9 10.9 3.5



15

transition temperatures T/°C: C 59 N 64 Iso

transition enthalpies ΔH/kJ mol^{-1}: 37.3 0.9

In order to further investigate the potential of the allene moiety a laterally substituted terphenyl derivative (compound *rac*-**16**) has also been synthesized.

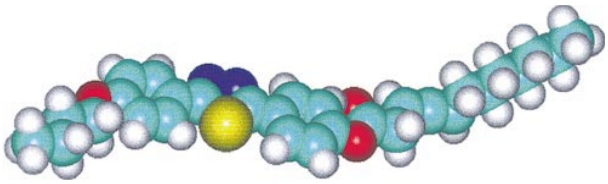
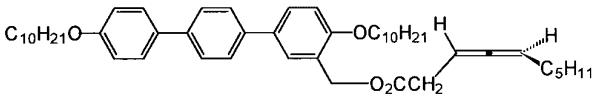


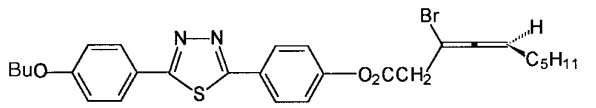
Fig. 2 Molecular model of the allene derivative **8c**



rac-**16**

transition temperatures *T*/°C:	C 60 S_c 66 N 71 Iso
transition enthalpies ΔH/kJ mol^{-1}:	21.1 1.2 0.5

To increase the polarity of the substituents at the allene moiety, compound *rac*-**20** having a bromine atom directly attached to the allene unit was synthesized. Because decomposition occurs at temperatures as low as 100 °C, the synthesis of an optically active compound **20** was not attractive.



rac-**20**

transition temperatures *T*/°C:	C 51 S_c 107 N 135 Iso
transition enthalpies ΔH/kJ mol^{-1}:	12.9 0.6 0.5

The thermal stability of the allene derivatives depends largely on the substitution pattern at the allene moiety and also on the type of rigid core. With the exception of the compounds *rac*-**13** and *rac*-**20** all other allene derivatives synthesized were thermally stable at least up to 100 °C. This was confirmed by annealing samples at this temperature for 1 h. The transition temperatures and the ^{1}H NMR spectra remain unchanged after this time. However at the clearing temperatures (> 150 °C) slow decomposition occurs which can be seen by the slight decrease in the clearing temperature.

Properties of the optically active allene derivatives

After investigating the liquid crystalline properties of the racemic derivatives, some thiadiazole derivatives were synthesized in their enantiomerically enriched forms. The phase transitions of these compounds are summarized and compared to a related allenyl ether [*cf.* (*R*)-**1**[11]] in Table 3.

Compound (*R*)-**8c** not only exhibits a broad chiral smectic C, but also a chiral nematic phase as well as a blue phase (Fig. 3) in a small temperature range.

The spontaneous polarization of this compound was investigated by means of the triangular field method[28] after aligning the sample in a homogeneous bookshelf configuration, using a 4 μm liquid crystal cell (EHC, Tokyo). A plot of the spontaneous polarization P_s *versus* the temperature T is given in Fig. 4. The steep, steplike decrease of P_s at *ca.* 140 °C reflects the first-order S_c*–N* phase transition. The spontaneous polarization of allenylacetate (*R*)-**8c** is significantly lower than for the analogous allenyl ether (*R*)-**1**.§ A gradual shift of phase transition temperatures to lower values was observed for compound (*R*)-**8c** and, even more pronounced, for the bromo derivative **20**. This can be explained by thermal decomposition (Claisen rearrangement) at temperatures close to the clearing point of these compounds.

In conclusion, we have prepared the first axial chiral allenylacetates with broad S_c*-phases. These compounds exhibit ferroelectric properties, but the values obtained for their spontaneous polarization are smaller than those of the corresponding allenyl ethers.

Experimental

General considerations

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Varian Gemini (200 MHz) or a Varian Unity (500 MHz) spectrometer, respectively. IR spectra were recorded on Perkin-Elmer FT-IR 1000 spectrometers. Phase transition temperatures were measured using a Mettler FP 82 HT hot stage and control unit in conjunction with a Nikon Optiphot-2 polarizing microscope, and were confirmed by differential scanning calorimetry on a Perkin-Elmer DSC-7. Mass spectra were recorded on an AMD 402 mass spectrometer (70 eV). Microanalyses were performed using an Carlo-Erba 1104 and Leco CHNS-932 elemental analyser. Refractive indices were measured using a Carl Zeiss Forsina refractometer. Thin layer chromatography was performed on Merck TLC aluminium sheets (silica gel 60 F_{254}) and visualized under UV light by treatment with iodine vapour, or by using a spray-solution of bromothymol blue and developing with gaseous ammonia. Column chromatography was performed with silica gel from Merck [0.040–0.063 mm (flash chromatography) or 0.063–0.20 mm]. Solvents were purified and dried according to standard procedures.[29] But-1-yn-3-ol (Aldrich), oct-1-yn-3-ol (Aldrich), (*R*)-Alpine borane (Aldrich) and *N*-cyclohexyl-*N*′-(2-morpholinoethyl)carbodiimide methotoluene-*p*-sulfonate (Aldrich) were used as obtained. 4-(5-Undecyl-1,3,4-thiadiazol-2-yl)phenol,[20] 4-[5-(4-alkoxyphenyl)-1,3,4-thiadiazol-2-yl]phenols,[20] 4-[5-(4-decylphenyl)-1,3,4-thiadiazol-2-yl]phenol,[20] 4-(5-octyloxypyrimidin-2-yl)phenol,[21] 4-[5-(4-butoxyphenyl)pyrimidin-2-yl]phenol,[21] 4-(4′-undecyloxybiphenyl-4-yloxycarbonyl)phenol,[22] 4-[5-(4-hydroxyphenyl)-1,3,4-thiadiazol-2-yl]phenol,[23] 1,4-bis(4-hydroxyphenyl)-2-methylbenzene[23] and 2-decyloxy-5-[4-(4-decyloxyphenyl)phenyl]benzyl alcohol[30] were synthesized according to the references given.

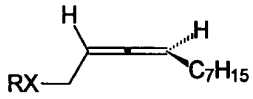
Synthesis of the allenylacetic acids 6a–6c

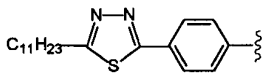
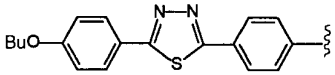
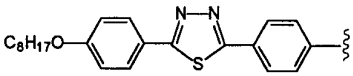
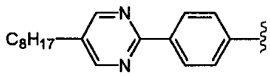
Dec-1-yn-3-ol, *rac*-3c. Compound *rac*-**3c** was obtained as described for the synthesis of *rac*-undec-1-yn-3-ol[12] from ethynylmagnesium bromide (0.2 mol) and octanal (17.9 g, 0.14 mol). Yield 11.9 g (55%); bp 50–53 °C at 0.05 mbar; n_D^{20}: 1.449; δ_H (500 MHz; $CDCl_3$; *J*/Hz): 0.87 (t, 3H, *J* 6.5, CH_3), 1.2–1.52 (m, 10H, CH_2), 1.73 (m, 2H, CH_2), 1.93 (s, 1H, br s, OH), 2.44 (d, 1H, *J* 2.1, C≡C−H), 4.35 (m, 1H, CH_2CH), δ_C(126 MHz; $CDCl_3$): 96.56 (*C*≡C−H), 72.81 (C≡*C*−H), 62.35 (*tert*-*C*H), 37.64, 31.85, 31.73, 29.16, 24.98, 22.61, 14.05 (*C*H$_3$); ν_{max} (neat)/cm^{-1} 3600–3200 (OH), 3580 (OH), 3300 (C≡C−H), 2920, 2850, 2100 (C≡C), 1460, 1380, 1300.

Dec-1-yn-3-one, 4c. A solution of chromium trioxide (6 g, 0.06 mol) and conc. sulfuric acid (5 ml) in water (20 ml) was added during 2 h to a stirred solution of *rac*-**3c** (7.7 g, 0.05 mol) in acetone (20 ml) at 5–10 °C. After stirring for an additional 2 h at room temp., the mixture was diluted with water (200 ml). The reaction mixture was extracted with diethyl ether (3 × 100 ml). After drying the organic solutions (Na_2SO_4), the solvent was removed under reduced pressure and the residue was purified by distillation *in vacuo* to yield a colourless liquid. Yield 5.6 g (73%); bp 72–75 °C at 18–20 mbar; δ_H(200 MHz;

§ It has to be considered that the enantiomeric purity of both compounds is different. Linear extrapolation of the P_s value of (*R*)-**8c** to an ee of 95% [which is the enantiomeric purity of (*R*)-**1**] would give an P_s of *ca.* 15–16 nC cm^{-2}.

Table 3 Transition temperatures and corresponding enthalpy values (italicised) of the enantiomerically enriched allenylacetates (*R*)-**7c**, (*R*)-**8c**, (*R*)-**9c** and (*R*)-**23** and the allenyl ethyl (*R*)-**1**



R	X	comp.	phase transitions T/°C enthalpy values ΔH/kJ mol^{-1}	% ee	P_s/nC cm^{-2}
	OOC	(*R*)-**7c**	C_1 62 C_2 68 Iso *10.5 34.9*	73	
	O	(*R*)-**1**	C 47 S_C* 115 N* 130 BP 131 Iso	95	38
	OOC	(*R*)-**8c**	C 76 S_C* 152 N* 163 BP 164 Iso *37.3 2.2 0.8*	73	12
	OOC	(*R*)-**9c**	C_1 60 C_2 81 S_C* 157 Iso *5.7 23.2 5.4*	73	
	OOC	(*R*)-**23**	C 38 Iso *26.5*	73	

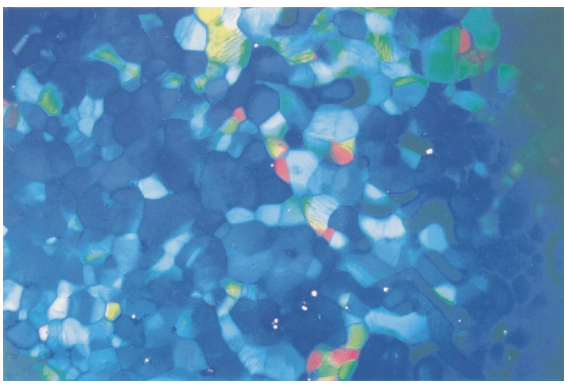


Fig. 3 Optical texture (crossed polarizers) of the blue phase of compound (*R*)-**8c** at 163.5 °C

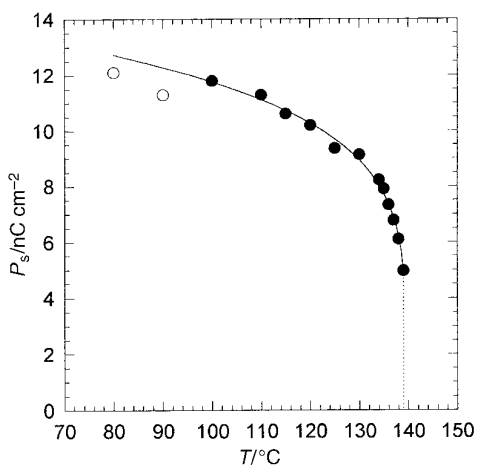


Fig. 4 Spontaneous polarization P_s of compound (*R*)-**8c** *vs.* temperature

$CDCl_3$; *J*/Hz): 0.87 (t, 3H, *J* 6.6, CH_3); 1.2–1.38 (m, 8H, CH_2), 1.56–1.75 (m, 2H, CH_2), 2.58 (t, 2H, *J* 7.6, $COCH_2$), 3.2 (s, 1H, C≡C−H); δ_c(126 MHz, $CDCl_3$): 187.63 (C=O), 81.4 (*C*≡C−H), 78.27 (C≡*C*−H), 45.38, 33.85, 31.52, 28.87, 23.69, 22.49, 13.96 (CH_3).

(*R*)-Dec-1-yn-3-ol, (*R*)-3c. (*R*)-Alpine borane in tetrahydrofuran (108 ml of a 0.5 M solution, 54 mmol) was placed in a 500 ml three-necked flask, equipped with thermometer, magnetic stirrer, argon inlet and outlet. Tetrahydrofuran was removed under reduced pressure (12 mbar, 30 °C) and the vacuum was replaced by argon. The resulting oil was cooled to a temperature between 0 and −5 °C and **4c** (5.5 g, 36 mmol) was added dropwise. During the addition the temperature was kept below 0 °C. After the addition was complete, the cold bath was removed and the mixture was allowed to warm to room temp. The orange mixture was stirred at this temperature until TLC indicated complete consumption of **4c**. To destroy excess Alpine borane, acetaldehyde (3 ml) was added dropwise, whilst the temperature was maintained below 30 °C. The resulting mixture was stirred at room temp. for 1 h. Tetrahydrofuran (50 ml) was added, followed by sodium hydroxide (50 ml of a 3 M aqueous solution). After this, hydrogen peroxide (50 ml of a 30% aqueous solution) was added dropwise (CAUTION! exothermic reaction). During the addition, the temperature was kept below 40 °C. After the addition was complete, the mixture was stirred for 2 h at 40 °C. After the mixture had cooled to room temp., it was poured into diethyl ether (200 ml) and the phases were separated. The aqueous layer was extracted with diethyl ether (3 × 100 ml) and the combined organic layers were washed with brine (100 ml) and dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure (18 mbar, 25 °C) and the resulting oil was fractionated by chromatography on silica gel (light petroleum–ethyl acetate 10 : 2, 40 cm × 8 cm, R_f 0.3) to afford (*R*)-**3c** (3.8 g, 24.7 mmol, 69%) as a colourless oil. $[\alpha]_D^{24}$ 3.48 (*c* 1.61 $CHCl_3$), 87% ee (Mosher's method). The analytical data of (*R*)-**3c** correspond to those given for *rac*-**3c**.

Ethyl dodeca-3,4-dienoate, *rac*-5c. A mixture of *rac*-**3c** (10.9 g, 0.07 mol), propanoic acid (0.4 g, 5 mmol) and triethyl orthoacetate (81 g, 0.5 mol) was heated for 8–10 h at 130 °C under an argon atmosphere. After cooling, the mixture was concentrated *in vacuo*, diluted with diethyl ether (100 ml), washed with aq. $NaHCO_3$ (2 × 40 ml) and brine (2 × 40 ml), and was dried over Na_2SO_4. Distillation under reduced pressure gave pure *rac*-**5c**. Yield 13.3 g (85%); bp 70–74 °C at 0.04 mbar; n_D^{20} 1.4596; δ_H(500 MHz; $CDCl_3$; *J*/Hz): 0.84 (t, 3H, *J* 6.6, CH_3), 1.42–1.44 (m, 13H, CH_2, $COOCH_2CH_3$), 1.9–2.01 (m, 2H, CH_2), 2.99 (dd, 2H, ^3J 2.9, ^5J 6.8,

CH=C=CHCH_2), 4.12 (q, 2H, J 2.96, COOCH_2CH$_3$), 5.09–5.24 (m, 2H, HC=C=CH); δ_c(126 MHz, $CDCl_3$): 205 (C=C=C), 171.6 (C=O), 92.2 (C=C=C), 84.1 (C=C=C), 60.6 (CH_2COOEt), 35.1, 31.8, 29.1, 29.02, 29.03, 28.5, 22.6, 14.21 (CH_3), 14.05 (CH_3); ν_{max}/cm^{-1} (neat) 2960, 2925, 2845, 1960 (C=C=C), 1730 (C=O), 1470, 1400, 1370, 1320.

Ethyl (*R*)-dodeca-3,4-dienoate, (*R*)-5c. Prepared as described for *rac*-**5c** from (*R*)-**3c** (3.4 g, 22 mmol). Yield 3.8 g (77%); $[\alpha]_D^{24}$ −40.35 (*c* 4.5 in $CHCl_3$); the other analytical data of (*R*)-**5c** correspond to those given for *rac*-**5c**.

Ethyl hexa-3,4-dienoate, *rac*-5a. Prepared as described for *rac*-**5c** from *rac*-**3a** (8.6 g, 0.12 mol). Yield 12 g (70%); bp 63–65 °C at 12 mbar; n_D^{20} 1.4548; δ_H(500 MHz; $CDCl_3$; J/Hz): 1.24 (t, 3H, J 6.6, COOCH$_2$CH_3), 1.64 (dd, 3H, ^3J = 6.9, ^5J = 3.3, CH_3CH=C=CH), 2.98 (dd, 2H, ^3J 6.9, ^5J 2.9, CH=C=CHCH_2), 4.13 (q, 2H, J 2.9, COOCH_2CH$_3$), 5.09–5.15 (m, 1H, HC=C=CH), 5.15–5.20 (m, 1H, HC=C=CH).

Ethyl deca-3,4-dienoate, *rac*-5b. Prepared as described for *rac*-**5c** from *rac*-**3b** (22.7 g, 0.18 mol). Yield 23.6 g (67%); bp 63–65 °C at 0.15 mbar; n_D^{20} 1.4563; δ_H(500 MHz; $CDCl_3$; J/Hz): 0.85 (t, 3H, J 6.5, CH_3), 1.24–1.44 (m, 9H, CH_2, COOCH$_2$CH_3), 1.92–2.05 (m, 2H, CH_2), 2.97 (dd, 2H, ^3J 6.9, ^5J 3.1, CH=C=CHCH_2), 4.12 (q, 2H, J 2.9, COOCH_2CH$_3$), 5.10–5.23 (m, 2H, HC=C=CH).

Dodeca-3,4-dienoic acid, *rac*-6c. A mixture consisting of hydrochloric acid (20 ml, 20%), dioxane (15 ml), tetrahydrofuran (THF) (6 ml) and *rac*-**5c** (1.12 g, 5 mmol) was vigorously stirred for 24 h at room temp. The reaction mixture was poured into diethyl ether (100 ml), the organic layer was separated, washed with saturated $NaHCO_3$ (2 × 40 ml) and brine (2 × 40 ml), and was dried with Na_2SO_4. After filtration, the solvent was removed under reduced pressure. The residue was purified by column chromatography using $CHCl_3$–MeOH (v/v 10 : 1) as eluent to obtain *rac*-**6c** as a pale-yellow oil. Yield 0.4 g (40%); n_D^{20} 1.4702; δ_H(500 MHz; $CDCl_3$; J/Hz): 0.87 (t, 3H, J 6.45, CH_3), 1.24–1.48 (m, 10H, CH_2), 1.95–2.05 (m, 2H, CH_2), 3.07 (dd, 2H, CH=C=CHCH_2), 5.10–5.25 (m, 2H, HC=C=CH), 8.3 (s, br, 1H, COOH).

(*R*)-Dodeca-3,4-dienoic acid, (*R*)-6c. Prepared as described for *rac*-**6c** from (*R*)-**5c** (0.9 g, 4 mmol). Yield 0.32 g (40%); $[\alpha]_D^{24}$ −30.68 (*c* 0.88 $CHCl_3$); the NMR data correspond to those given for *rac*-**6c**.

Hexa-3,4-dienoic acid, *rac*-6a. Prepared as described for *rac*-**6c** from *rac*-**5a** (1.4 g, 10 mmol). Purification by column chromatography ($CHCl_3$–MeOH; v/v 10 : 1) gave *rac*-**6a** as a colourless oil. Yield 0.4 g (35%); δ_H(200 MHz; $CDCl_3$; J/Hz): 1.65 (m, 3H, CH_3CH=C=CH), 3.05 (m, 2H, CH=C=CHCH_2), 5.13–5.19 (m, 2H, HC=C=CH), 9.5 (s, br, 1H, COOH).

Deca-3,4-dienoic acid, *rac*-6b. Prepared as described for *rac*-**6c** from *rac*-**5b** (1.3 g, 6.6 mmol). Yield 0.5 g (45%); n_D^{20} 1.4741; δ_H(200 MHz; $CDCl_3$; J/Hz): 0.87 (t, 3H, J 7.1, CH_3), 1.24–1.44 (m, 6H, CH_2), 1.98 (m, 2H, CH_2), 3.06 (m, 2H, CH=C=CHCH_2), 5.16–5.23 (m, 2H, HC=C=CH), 9.5 (s, br, 1H COOH).

Synthesis of 3-bromodeca-3,4-dienoic acid, *rac*-19

1-Bromooct-1-yn-3-ol, *rac*-17. Bromine (7 ml, 21.7 g, 0.135 mol) was added slowly to aqueous KOH (4 M, 200 ml) while the temperature was kept below 5 °C. This freshly prepared solution was added within 10 min to *rac*-**3b** (7.25 g, 57 mmol) at 20 °C. After vigorously stirring for 30 min the reaction mixture was quenched by adding water (100 ml). The aqueous phase was twice extracted with diethyl ether (2 × 100 ml). The combined organic phases were washed twice with saturated $NaHCO_3$ (50 ml), brine (50 ml) and finally with water (50 ml). After drying over Na_2SO_4 the solvent was removed under reduced pressure and the residue was purified by distillation *in vacuo* to give a colourless liquid. Yield 10.1 g (68%); n_D^{20} 1.4876; bp 53–55 °C at 0.04 mbar; δ_H(200 MHz; $CDCl_3$; J/Hz): 0.9 (t, 3H, J 6.6, CH_3), 1.22–1.5 (m, 6H, CH_2), 1,82 (s, 1H, OH), 1.86–1.95 (m, 2H, CH_2), 4.39 (dt, J 5.4, 1H, CHOH).

Ethyl 3-bromodeca-3,4-dienoate, *rac*-18. Synthesized according to the procedure given for *rac*-**5c** from *rac*-**17** (10.1 g, 49 mmol). Yield 6.2 g (46%); n_D^{20} 1.4902; bp 105–110 °C at 0.15 mbar; δ_H(200 MHz; $CDCl_3$; J/Hz): 0.88 (t, 3H, J 6.8, CH_3), 1.2–1.8 (m, 9H, COOCH$_2$CH_3, CH_2), 2.04–2.18 (m, 2H, CH_2), 3.41 (d, 2H, ^5J 2.3, HC=C=CBrCH_2), 4.18 (q, 2H, J 7.2, COOCH_2CH$_3$), 5.35–5.45 (m, 1H, HC=C=CBr).

3-Bromodeca-3,4-dienoic acid, rac-19. Synthesized from *rac*-**18** (1.11 g, 4 mmol) according the procedure given for *rac*-**6c**. Purification by column chromatography ($CHCl_3$ MeOH; v/v 10 : 1) gave *rac*-**19** as a colourless oil. Yield 350 mg (35%); δ_H (200 MHz; $CDCl_3$; J/Hz): 0.90 (t, 3H, CH_3), 1.8–1.2 (m, 6H, CH_2), 2.08–2.18 (m, 2H, CH_2), 3.59 (d, 2H, ^5J 1.6, HC=C=CBrCH_2), 5.40 (m, 1H, HC=C=CBr).

General procedure for the esterification of the alka-3,4-dienoic acid

The appropriate phenolic compound (0.8 mmol), *N*-cyclohexyl-*N*′-(2-morpholinoethyl)carbodiimide methotoluene-*p*-sulfonate (1.1 mmol 465 mg) and 4-dimethylaminopyridine (DMAP; 30 mg) were dissolved in dry chloroform (30 ml). The solution was stirred magnetically for 5 min at room temp. The appropriate alka-3,4-dienoic acid (1 mmol), dissolved in dry chloroform (5 ml), was added with a syringe. The mixture was stirred at 20 °C until no starting material could be detected by TLC (*ca.* 20 h). Afterwards, it was poured into water (30 ml) and the phases were separated. The aqueous layer was extracted with chloroform (2 × 50 ml) and the combined organic layer was washed with saturated $NaHCO_3$ (50 ml) and brine (50 ml) and dried (Na_2SO_4). After filtration the solvent was removed under reduced pressure and the resulting crude product was purified by chromatography on silica gel (chloroform–methanol, v/v 20 : 1) and crystallized several times from ethanol.

4-(5-Undecyl-1,3,4-thiadiazol-2-yl)phenyl hexa-3,4-dienoate, *rac*-7a. Synthesized from 4-(5-undecyl-1,3,4-thiadiazol-2-yl)phenol and *rac*-**6a**. Yield 105 mg (46%); mp 68 °C (Found: C, 69.63; H, 8.11; N, 6.67; S, 7.64%; $C_{25}H_{34}O_2N_2S$ requires C, 70.39; H, 8.03; N, 6.57; S, 7.51%); δ_H(200 MHz; $CDCl_3$; J/Hz): 0.85–0.89 (m, 3H, CH_3), 1.2–1.48 (m, 16H, CH_2), 1.68 (dd, 3H, ^3J 6.8, ^5J 2.7, CH_3), 1.78–1.88 (m, 2H, CH_2), 3.1 (t, 2H, J 7.6, ArCH_2), 3.27 (dd, 2H, ^3J 6.9, ^5J 2.8, HC=C=CHCH_2O), 5.20–5.30 (m, 2H, HC=C=CH), 7.20 (d, 2H, J 8.8, ArH), 7.94 (d, 2H, J 8.8, ArH); m/z 426 (M^+, 71%), 398 (4), 383 (5), 355 (4), 333 (100), 299 (11), 286 (25), 274 (22), 261 (10), 245 (24), 219 (4), 205 (37), 192 (83), 137 (17), 95 (24), 67 (44).

(*R*)-4-(5-Undecyl-1,3,4-thiadiazol-2-yl)phenyl dodeca-3,4-dienoate (*R*)-7c. Synthesized from 4-(5-undecyl-1,3,4-thiadiazol-2-yl)phenol and (*R*)-**6c**. Yield 60 mg (45%); transitions (°C): C_1 62 C_2 68 Iso; $[\alpha]_D^{24}$ −30.95 (*c* 0.84 $CHCl_3$) (Found: C, 73.06; H, 9.23; N, 5.21; S, 5.18%; $C_{31}H_{46}O_2N_2S$ requires C, 72.90; H, 9.08; N, 5.48; S, 6.28%); δ_H(500 MHz; $CDCl_3$; J/Hz): 0.85–0.88 (m, 6H, CH_3), 1.2–1.44 (m, 26H, CH_2), 1.79–1.85 (m, 2H, CH_2), 2.0–2.05 (m, 2H, CH_2), 3.11 (t, 3H, J 7.6, ArCH_2),

3.27 (dd, 2H, ^3J 7.2, ^5J 3.0, HC=C=CHCH_2O), 5.23–5.33 (m, 2H, HC=C=CH), 7.20 (d, 2H, J 8.5, ArH), 7.94 (d, 2H, J 8.5, ArH); m/z 510 (M^+, 56%), 482 (10), 467 (3), 439 (3), 411 (2), 391 (4), 383 (8), 370 (13), 358 (11), 342 (3), 333 (100), 205 (18), 192 (33), 179 (20), 137 (8).

4-[5-(4-Butoxyphenyl)-1,3,4-thiadiazol-2-yl]phenyl hexa-3,4-dienoate, *rac*-8a. Synthesized from 4-[5-(4-butoxyphenyl)-1,3,4-thiadiazol-2-yl]phenol and *rac*-**6a**. Yield 110 mg (62%); transitions (°C): C 102 S_C 161 N 224 Iso (Found: C, 68.69; H, 5.66; N, 6.37; S, 7.42%; $C_{24}H_{24}O_3N_2S$ requires C, 68.55; H, 5.75; N, 6.66; S, 7,62%; δ_H(500 MHz; $CDCl_3$; J/Hz): 0.98 (t, 3H, J 7.3, CH_3), 1.5 (m, 2H, CH_2), 1.69 (dd, 3H, ^3J 6.9, ^5J 3.4, CH_3), 1.80 (m, 2H, CH_2), 3.28 (dd, 2H, ^3J 6.8, ^5J 3, HC=C=CHCH_2O), 4.02 (t, 3H, J 6.4, OCH_2), 5.19–5.31 (m, 2H, HC=C=CH), 6.97 (d, 2H, J 8.8, ArH), 7.23 (d, 2H, J 8.8, ArH), 7.91 (d, 2H, J 8.9, ArH), 8.00 (d, 2H, J 8.8, ArH).

4-[5-(4-Butoxyphenyl)-1,3,4-thiadiazol-2-yl]phenyl deca-3,4-dienoate, *rac*-8b. Synthesized from 4-[5-(4-butoxyphenyl)-1,3,4-thiadiazol-2-yl]phenol and *rac*-**6b**. Yield 180 mg (67%); transitions (°C): C 61 S_C 147 N 167 Iso (Found: C, 70.42; H, 6.98; N, 5.67; S, 6.56%; $C_{28}H_{32}O_3N_2S$ requires C, 70.56; H, 6.77; N, 5.88; S, 6.73%); δ_H(500 MHz; $CDCl_3$; J/Hz): 0.88 (t, 3H, J 7.1, CH_3), 0.98 (t, 3H, J 7.3, CH_3), 1.24–1.49 (m, 8H, CH_2), 1.79 (m, 2H, CH_2) 2.03 (m, 2H, CH_2), 3.28 (dd, 2H, ^3J 6.8, ^5J 2.8, HC=C=CHCH_2O), 4.02 (t, 3H, J 6.6, OCH_2), 5.25–5.33 (m, 2H, HC=C=CH), 6.97 (d, 2H, J 8.8, ArH), 7.23 (d, 2H, J 8.6, ArH,), 7.92 (d, 2H, J 8.6, ArH), 8.00 (d, 2H, J 8.5, ArH); m/z 476 (M^+, 28%), 448 (1), 424 (1), 326 (100), 270 (37), 193 (2), 151 (19), 137 (10), 81 (3), 67 (8); λ_{max}/nm ($CHCl_3$) 324.7 (0.76).

4-[5-(4-Butoxyphenyl)-1,3,4-thiadiazol-2-yl]phenyl dodeca-3,4-dienoate, *rac*-8c. Synthesized from 4-[5-(4-butoxyphenyl)-1,3,4-thiadiazol-2-yl]phenol and *rac*-**6c**. Yield 50 mg (24%); transitions (°C): C 76 S_C 149 N 164 Iso (Found: C, 71.11; H, 7.15; N, 5.52; S, 6.39%; $C_{30}H_{36}O_3N_2S$ requires C, 71.40; H, 7.19; N, 5.55; S, 6.35%); δ_H(200 MHz; $CDCl_3$; J/Hz): 0.87–0.82 (m, 3H, CH_3), 0.97 (t, 3H, J 7.3, CH_3), 1.2–1.48 (m, 12H, CH_2), 1.74–1.82 (m, 2H, CH_2), 2.0 (m, 2H, CH_2), 3.28 (m, 2H, HC=C=CHCH_2O), 4.01 (t, 3H, J 6.4, OCH_2), 5.23–5.31 (m, 2H, HC=C=CH), 6.97 (d, 2H, J 9.1, ArH), 7.22 (d, 2H, J 8.8, ArH), 7.91 (d, 2H, J 9.1, ArH), 8.00 (d, 2H, J 8.4, ArH); δ_C(126 MHz, $CDCl_3$): 13.82, 14.08, 19.21, 22.64, 28.47, 28.99, 29.05, 29.11, 31.18, 31.84, 35.15, 67.97, 83.36, 92.88, 115.07, 122.35, 128.05, 129.01, 129.49, 152.68, 155.95, 161.63, 165.6, 168.2, 169.7, 205.35; m/z 504 (M^+, 17%), 326 (100), 270 (34), 242 (2), 199 (3), 179 (10), 151 (10), 137 (12), 119 (2).

(*R*)-4-[5-(4-Butoxyphenyl)-1,3,4-thiadiazol-2-yl]phenyl dodeca-3,4-dienoate, (*R*)-8c. Synthesized from 4-[5-(4-butoxyphenyl)-1,3,4-thiadiazol-2-yl]phenol and (*R*)-**6c**. Yield 150 mg (55%); transitions (°C): C 76 S_c* 152 N* 163 BP 164 Iso; $[\alpha]_D^{24}$ −26.96 (*c* 2.3 $CHCl_3$) (Found: C, 71.29; H, 7.33; N, 5.55; S, 6.41%; $C_{30}H_{36}O_3N_2S$ requires C, 71.4; H, 7.19; N, 5.55; S, 6.35%); δ_H(200 MHz; $CDCl_3$; J/Hz): 0.86 (t, 3H, J 6.5, CH_3), 0.97 (t, 3H, J 7.3, CH_3), 1.2–1.48 (m, 12H, CH_2), 1.72–1.84 (m, 2H, CH_2), 1.95–2.08 (m, 2H, CH_2), 3.28 (dd, 2H, ^3J 6.9, ^5J 3.0, HC=C=CHCH_2O), 4.02 (t, 3H, J 6.4, OCH_2), 5.23–5.31 (m, 2H, HC=C=CH), 6.97 (d, 2H, J 8.8, ArH), 7.22 (d, 2H, J 8.7 ArH), 7.91 (d, 2H, J 8.9, ArH), 8.00 (d, 2H, J 8.7, ArH); m/z 504 (M^+, 22%), 326 (100), 270 (35), 193 (4), 179 (12), 151 (11), 137 (11), 119 (3).

4-[5-(4-Octyloxyphenyl)-1,3,4-thiadiazol-2-yl]phenyl deca-3,4-dienoate, *rac*-9b. Synthesized from 4-[5-(4-octyloxyphenyl)-1,3,4-thiadiazol-2-yl]phenol and *rac*-**6b**. Yield 120 mg (57%); transitions (°C): C 82 S_C 166 Iso (Found: C, 71.96; H, 7.54; N, 5.23; S, 6.11%; $C_{32}H_{40}O_3N_2S$ requires C, 72.15; H, 7.57; N, 5.26; S, 6.02%); δ_H(500 MHz; $CDCl_3$; J/Hz): 0.89–0.86 (m, 6H, CH_3), 1.2–1.48 (m, 16H, CH_2), 1.77–1.83 (m, 2H, CH_2), 2.0–2.05 (m, 2H, CH_2), 3.28 (dd, 2H, ^3J 7.1, ^5J 2.7, HC=C=CHCH_2O), 4.01 (t, 3H, J 6.5, OCH_2), 5.23–5.33 (m, 2H, HC=C=CH), 6.97 (d, 2H, J 8.7, ArH), 7.23 (d, 2H, J 8.9, ArH), 7.91 (d, 2H, J 8.9, ArH), 7.99 (d, 2H, J 8.8, ArH); m/z 532 (M^+, 27%), 504 (1), 382 (100), 270 (40), 249 (3), 151 (17), 137 (8).

4-[5-(4-Octyloxyphenyl)-1,3,4-thiadiazol-2-yl]phenyl dodeca-3,4-dienoate, *rac*-9c. Synthesized from 4-[5-(4-octyloxyphenyl)-1,3,4-thiadiazol-2-yl]phenol and *rac*-**6c**. Yield 100 mg (61%); transitions (°C): C 83 S_C 158 Iso (Found: C, 72.96; H, 7.67; N, 4.87; S, 5.49%; $C_{34}H_{44}O_3N_2S$ requires C, 72.82; H, 7.91; N, 5.00; S, 5.72%); δ_H(200 MHz; $CDCl_3$; J/Hz): 0.87 (m, 6H, CH_3), 1.18–1.48 (m, 20H, CH_2), 1.76–1.84 (m, 2H, CH_2), 2.0 (m, 2H, CH_2), 3.28 (dd, 2H, HC=C=CHCH_2O), 4.00 (t, 3H, J 6.3, OCH_2), 5.26–5.31 (m, 2H, *H*C=C=C*H*), 6.97 (d, 2H, J 8.8, ArH), 7.22 (d, 2H, J 8.8, ArH), 7.92 (d, 2H, J 8.8, ArH), 7.99 (d, 2H, J 8.8, ArH); m/z 560 (M^+, 54%), 532 (2), 382 (100), 270 (65), 249 (5), 242 (3), 199 (4), 179 (10), 151 (13), 137 (17).

(*R*)-4-[5-(4-Octyloxyphenyl)-1,3,4-thiadiazol-2-yl]phenyl dodeca-3,4-dienoate, (*R*)-9c. Synthesized from 4-[5-(4-octyloxyphenyl)-1,3,4-thiadiazol-2-yl]phenol and (*R*)-**6c**. Yield 110 mg (65%); transitions (°C): C_1 60 C_2 81 S_c* 157 Iso; $[\alpha]_D^{24}$ −20 (*c* 1.1 $CHCl_3$) (Found: C, 72.96; H, 7.63; N, 4.87; S, 5.49%; $C_{34}H_{44}O_3N_2S$ requires C, 72.82; H, 7.91; N, 5.00; S, 5.72%); δ_H(500 MHz; $CDCl_3$; J/Hz): 0.87 (m, 6H, $2CH_3$), 1.24–1.49 (m, 20H, CH_2), 1.79 (m, 2H, CH_2), 2.03 (m, 2H, CH_2), 3.28 (dd, 2H, ^3J 7.1, ^5J 2.9, HC=C=CHCH_2O), 4.02 (t, 3H, J 6.6, OCH_2), 5.25–5.33 (m, 2H, HC=C=CH), 6.97 (d, 2H, J 8.8, ArH), 7.23 (d, 2H, J 8.6, ArH), 7.92 (d, 2H, J 8.6, ArH), 8.00 (d, 2H, J 8.5, ArH); m/z 560 (M^+, 38%), 532 (1), 382 (100), 270 (52), 249 (5), 179 (14), 151 (12), 137 (15).

4-[5-(4-Decylphenyl)-1,3,4-thiadiazol-2-yl]phenyl deca-3,4-dienoate, *rac*-10b. Synthesized from 4-[5-(4-decylphenyl)-1,3,4-thiadiazol-2-yl]phenol and *rac*-**6b**. Yield 35 mg (22%); transitions (°C): C 58 S_C 149 Iso (Found: C, 75.05; H, 8.05; N, 5.3; S, 5.1%; $C_{34}H_{44}O_3N_2S$ requires C, 75.0; H, 8.1; N, 5.1; S, 5.9%); δ_H(500 MHz; $CDCl_3$; J/Hz): 0.8–0.97 (m, 6H, CH_3), 1.2–1.72 (m, 22H, CH_2), 1.97–2.08 (m, 2H, CH_2), 2.65 (t, 2H, J 7.7, $ArCH_2$), 3.27 (dd, 2H, ^3J 6.9, ^5J 2.7, HC=C=C*H*H_2O), 5.23–5.28 (m, 1H, *H*C=C=CH), 5.28–5.31 (m, 1H, HC=C=C*H*), 7.23 (d, 2H, J 8.0, ArH), 7.28 (d, 2H, J 8.0, ArH), 7.89 (d, 2H, J 8.9, ArH), 8.01 (d, 2H, J 8.8, ArH).

4-[5-(4-Decylphenyl)-1,3,4-thiadiazol-2-yl]phenyl dodeca-3,4-dienoate, *rac*-10c. Synthesized from 4-[5-(4-decylphenyl)-1,3,4-thiadiazol-2-yl]phenol and *rac*-**6c**. Yield 155 mg (42%); transitions (°C): C 65 S_C 137 Iso (Found: C, 75.45; H, 8.42; N, 4.48; S, 5.5%; $C_{36}H_{48}O_2N_2S$ requires C, 75.48; H, 8.45; N, 4.89; S, 5.6%); δ_H(200 MHz; $CDCl_3$; J/Hz): 0.8–0.97 (m, 6H, CH_3), 1.2–1.72 (m, 26H, CH_2), 1.97–2.08 (m, 2H, CH_2), 2.65 (t, 2H, J 7.5, $ArCH_2$), 3.28 (m, 2H, HC=C=CHCH_2O), 5.23–5.31 (m, 2H, HC=C=CH), 7.21–7.34 (m, 4H, ArH), 7.89 (d, 2H, J 8.9, ArH), 8.01 (d, 2H, J 8.8, ArH); m/z 572 (M^+, 10%), 394 (27), 363 (100), 331 (4), 281 (6), 265 (47), 239 (7), 207 (14), 199 (17), 187 (7), 139 (4).

4-(5-Octyloxypyrimidin-2-yl)phenyl hexa-3,4-dienoate, *rac*-11a. Synthesized from 4-(5-octyloxypyrimidin-2-yl)phenol and *rac*-**6a**. Yield 45 mg (34%); transitions (°C): C 78 (S_A 75) Iso (Found: C, 72.68; H, 7.64; N, 6.63%; $C_{24}H_{30}O_3N_2$ requires C, 73.07; H, 7.66; N, 7.10%); δ_H(200 MHz; $CDCl_3$; J/Hz): 0.85–0.89 (t, 3H, J 6.6, CH_3), 1.18–1.88 (m, 15H, CH_2, H_3CH=C=C), 3.27 (dd, 2H, ^3J 6.9, ^5J 3.3, HC=C=CH−CH_2O), 4.08 (t, 3H, J 6.5, OCH_2), 5.18–5.32

(m, 2H, HC=C=CH), 7.18 (d, 2H, *J* 8.8, ArH), 8.36 (d, 2H, *J* 8.8, ArH), 8.43 (s, 2H, ArH).

(*R*)-4-(5-Octylpyrimidin-2-yl)phenyl dodeca-3,4-dienoate, (*R*)-23. Synthesized from 4-(5-octylpyrimidin-2-yl)phenol and (*R*)-**6c**. Yield 50 mg (35%); mp 38 °C; δ_H(200 MHz; $CDCl_3$; *J*/Hz): 0.82–0.95 (m, 6H, CH_3), 1.2–1.86 (m, 22H, CH_2), 1.95–2.05 (m, 2H, CH_2), 2.6 (t, 2H, *J* 7.2, $ArCH_2$), 3.27 (dd, 2H, ^3J 6.8, ^5J 2.9, HC=C=CHCH_2O), 5.21–5.34 (m, 2H, HC=C=CH), 7.20 (d, 2H, *J* 9.0, ArH), 8.43 (d, 2H, *J* 8.9, ArH), 8.59 (s, 1H, ArH).

4-[5-(4-Butoxyphenyl)pyrimidin-2-yl]phenyl deca-3,4-dienoate, *rac*-12b. Synthesized from 4-[5-(4-butoxyphenyl)pyrimidin-2-yl]phenol and *rac*-**6b**. Yield 45 mg (22%); transitions (°C): C 144 S_C 176 Iso; δ_H(500 MHz; $CDCl_3$; *J*/Hz): 0.85–0.90 (m, 3H, CH_3), 0.98 (t, 3H, *J* 7.3, CH_3), 1.25–1.6 (m, 8H, CH_2), 1.75–1.86 (m, 2H, CH_2), 2.01–2.04 (m, 2H, CH_2), 3.29 (dd, 2H, ^3J 7.1, ^5J 2.7, HC=C=CHCH_2O,), 4.04 (t, 2H, *J* 6.5, OCH_2), 5.24–5.28 (m, 1H, HC=C=CH), 5.30–5.34 (m, 1H, HC=C=CH), 6.99 (d, 2H, *J* 8.8, ArH), 7.25 (d, 2H, *J* 8.7, ArH), 7.60 (d, 2H, *J* 8.5, ArH), 8.41 (d, 2H, *J* 9.0, ArH), 8.93 (s, 1H, ArH); *m*/*z* found: 470.2545 (M^+, 15%); $C_{30}H_{34}N_2O_3$ requires 470.2569.

4-[5-(4-Butoxyphenyl)pyrimidin-2-yl]phenyl dodeca-3,4-dienoate, *rac*-12c. Synthesized from 4-[5-(4-butoxyphenyl)pyrimidin-2-yl]phenol and *rac*-**6c**. Yield 95 mg (48%); transitions (°C): C 143 S_C 174 Iso (Found: C, 76.52; H, 7.66; N, 5.49%; $C_{32}H_{38}O_3N_2$ requires C, 77.08; H, 7.68; N, 5.62%); δ_H (200 MHz; $CDCl_3$; *J*/Hz): 0.85–0.9 (m, 3H, CH_3), 1.0 (t, 3H, *J* 7.3, CH_3), 1.25–1.6 (m, 12H, CH_2), 1.75–1.86 (m, 2H, CH_2), 2.0–2.1 (m, 2H, CH_2), 3.32 (m, 2H, HC=C=CHCH_2O), 4.05 (t, 2H, *J* 6.7, OCH_2), 5.23–5.39 (m, 2H, HC=C=CH), 7.01 (d, 2H, *J* 9.0, ArH), 7.26 (d, 2H, *J* 8.7, ArH), 7.62 (d, 2H, *J* 8.6, ArH), 8.42 (d, 2H, *J* 8.9, ArH), 8.95 (s, 1H, ArH); δ_C(126 MHz, $CDCl_3$): 13.83, 14.06, 19.22, 22.64, 28.48, 28.97, 29.03, 29.09, 31.28, 31.82, 35.13, 67.81, 83.44, 92.82, 114.53, 122.55, 127.76, 129.61, 129.76, 130.07, 132.48, 151.14, 155.02, 161.63, 163.55, 169.98, 205; *m*/*z* 490 (M^+, 42%), 320 (100), 264 (42), 235 (1), 179 (3), 118 (5); λ_{max}/nm ($CHCl_3$) 308.2, 306.2.

4-(4′-Undecyloxybiphenyl-4-yloxycarbonyl)phenyl deca-3,4-dienoate, *rac*-13. Synthesized from 4-(4′-undecyloxybiphenyl-4-yloxycarbonyl)phenol and *rac*-**6b**. Yield 125 mg (45%); transitions (°C): C 107 S_C 153 N 155 Iso; δ_H($CDCl_3$, 200 MHz): 0.88 (m, 6H, CH_3), 1.50–1.20 (m, 20H, CH_2), 1.75–1.85 (m, 2H, CH_2), 2.00–2.05 (m, 2H, CH_2), 3.27 (dd, 2H, HC=C=CHCH_2O), 4.0 (t, 2H, *J* 6.45, $ArOCH_2$), 5.23–5.23 (m, 2H, HC=C=CH), 6.91 (d, 2H, *J* 8.8, ArH), 6.95 (d, 2H, *J* 9, ArH), 7.23 (d, 2H, *J* 8.6, ArH), 7.48 (d, 2H, *J* 8.9, ArH), 7.56 (d, 2H, *J* 8.6, ArH), 8.12 (d, 2H, *J* 8.8, ArH); *m*/*z* found: 610.3655 (M^+, 2%); $C_{40}H_{50}O_5$ requires 610.3658.

4-{5-[4-(Nona-2,3-dienylcarbonyloxy)phenyl]-1,3,4-thiadiazol-2-yl}phenyl deca-3,4-dienoate, 14. Synthesized from 4-[5-(4-hydroxyphenyl)-1,3,4-thiadiazol-2-yl]phenol and *rac*-**6b**. Yield 95 mg (40%); transitions (°C): C_1 80 C_2 92 S_C 149 Iso (Found: C, 72.11; H, 7.26; N, 4.53; S, 5.34%; $C_{34}H_{38}O_4N_2S$ requires C, 71.55; H, 6.71; N, 4.91; S, 5.62%); δ_H(500 MHz; $CDCl_3$; *J*/Hz): 0.84–0.91 (m, 6H, CH_3), 1.2–1.48 (m, 12H, CH_2), 1.96–2.08 (m, 4H, CH_2), 3.28 (dd, 4H, HC=C=CHCH_2O), 5.20–5.37 (m, 4H, HC=C=CH), 7.24 (d, 4H, *J* 8.8, ArH), 8.02 (d, 4H, *J* 8.8, ArH); *m*/*z* 570 (M^+, 8%), 421 (23), 270 (100), 151 (66), 137 (44).

1,4-Bis-[4-(nona-2,3-dienylcarbonyloxy)phenyl]-2-methylbenzene, 15. Synthesized from 1,4-bis(4-hydroxyphenyl)-2-methylbenzene and *rac*-**6b**. Yield 95 mg (55%); transitions (°C): C 59 N 64 Iso (Found: C, 81.11; H, 7.69%; $C_{39}H_{44}O_4$ requires C, 81.22; H, 7.69%); δ_H(200 MHz; $CDCl_3$; *J*/Hz): 0.84–0.91 (m, 6H, CH_3), 1.2–1.48 (m, 12H, CH_2), 1.94–2.06 (m, 4H, CH_2), 2.32 (s, 3H, $ArCH_3$), 3.27 (dd, 4H, ^3J 6.7, ^5J 2.5, CH=CHCH_2O), 5.22–5.35 (m, 4H, HC=C=CH), 7.14 (d, 2H, *J* 8.8, ArH), 7.16 (d, 2H, *J* 9.0, ArH), 7.24–7.44 (m, 7H, ArH), 7.60 (d, 2H, *J* 8.6, ArH); *m*/*z* 576 (M^+, 18%), 426 (37), 276 (100), 151 (8).

2-Decyloxy-5-[4-(4-decyloxyphenyl)phenyl]benzyl deca-3,4-dienoate, *rac*-16. Synthesized from 2-decyloxy-5-[4-(4-decyloxyphenyl)phenyl]benzyl alcohol and *rac*-**6b**. Yield 25 mg (34%); transitions (°C): C 60 S_C 66 N 71 Iso; δ_H(500 MHz; $CDCl_3$; *J*/Hz): 0.82–0.92 (m, 9H, CH_3), 1.11–1.48 (m, 32H, CH_2), 1.77–1.83 (m, 4H, CH_2), 1.92–1.98 (m, 2H, CH_2), 3.08 (dd, 2H, HC=C=CHCH_2O), 3.98–4.03 (m, 4H, OCH_2), 5.14–5.26 (m, 2H, HC=C=CH), 5.25 (s, 2H, $ArCH_2OOC$), 6.92–6.95 (m, 4H, ArH), 7.20–7.38 (m, 1H, ArH), 7.54–7.58 (m, 6H, ArH); *m*/*z* found 722.5290 (M^+; 100%), $C_{49}H_{70}O_4$ requires 722.5274.

4-[5-(4-Butoxyphenyl)-1,3,4-thiadiazol-2-yl]phenyl 3-bromodeca-3,4-dienoate, *rac*-20. Synthesized from 4-[5-(4-butoxyphenyl)-1,3,4-thiadiazol-2-yl]phenol and *rac*-**19b**. Yield 25 mg (10%); transitions (°C): C 51 S_C 107 N 135 Iso; δ_H(200 MHz; $CDCl_3$; *J*/Hz): 0.87 (t, 3H, CH_3), 0.98 (t, 3H, *J* 7.6, CH_3), 1.20–1.46 (m, 6H, CH_2), 1.56 (m, 2H, CH_2), 1.82 (m, 2H, CH_2), 2.08 (m, 2H, CH_2), 3.7 (m, 2H, HC=C=CHCH_2O), 4.02 (t, 3H, *J* 6.4, OCH_2), 5.46 (m, 1H, HC=C=CBr), 6.97 (d, 2H, *J* 8.8, ArH), 7.26 (d, 2H, *J* 8.6, ArH,), 7.92 (d, 2H, *J* 8.6, ArH), 8.01 (d, 2H, *J* 9.0, ArH); *m*/*z* found 554.1321 ($M^+ - 1$; 0.33%), $C_{28}H_{31}O_3N_2SBr$ requires 554.1238.

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