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Axial Chiral Liquid Crystals – Synthesis of Trisubstituted Allenyl Ethers

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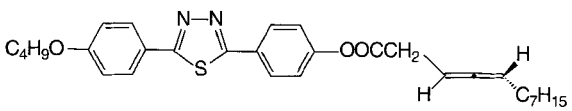
Abstract. The synthesis of racemic and enantiomerical enriched axial chiral liquid crystalline compounds incorporating a trisubstituted allene unit is described. All compounds **16–28** display the smectic C-phase and mostly also a nematic mesophase. All investigated enantiomerically enriched compounds have a ferroelectrically switchable chiral smectic S_C*-phase.

Chiral liquid crystals have grown to a central topic in liquid crystal research owing to their unique physical properties and potential technical applications [1]. Optically active materials forming liquid crystalline phases consisting of layer structures with a tilted arrangement of the molecules in the layers (smectic C-phase) are of particular interest because of their ferroelectric properties [2]. Such materials can be applied for fast-switching bistable electrooptical displays and light shutter devices as well as for NLO-applications [3]. Furthermore the discovery of new chiral mesophases, such as antiferroelectric, ferrielectric phases, twisted grain boundary phases and other frustrated phases has additionally stimulated the research in this field [4, 5]. Most chiral liquid crystals incorporate a center of chirality, usually an asymmetric carbon atom, but also a few mesogenic chiral sulfinates [6] have been reported. In the recent years interest in new molecular structures has grown and one of the questions which arose was, which special properties can be found if molecular chirality is not based on a stereogenic center, but on a stereogenic axis. Therefore attempts have been made to obtain liquid crystals incorporating an axis of chirality (twistane derivatives [7], atropisomeric biphenyl [8], binaphthyl [9], and biphenanthryl derivatives [10], methylenecyclohexanes [11]) or a plane of chirality [12, 13]. However, many of these molecules are not mesogenic themselves, because of the unfavourable shape of these molecules which disturbs their molecular self organization. Especially mesophases with a tilted arrangement of the molecules in layers (S_C-phases) for which ferroelectric properties can be expected are difficult to obtain with these materials. The first ferroelectric S_C*-phase of an axial chiral compound was reported for alkylidenecyclohexanes appended to a polymer backbone [11c,d].

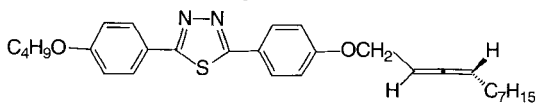
We have recently shown that the axial chiral allene unit is an appropriate structural unit to obtain ferroelectric low molecular mass liquid crystals. When appended to a rod-like structural unit, axial chiral liquid crystalline materials with broad regions of the S_C*-phase have been realized [14–18]. So we reported on the synthesis and investigation of allenylacetates [15]. However, these molecules have only a limited thermal stability. The allenylethers however, represent stable materials. Allenylethers incorporating a 1,3-disubstituted allene unit have recently been described [16]. In this contribution we report the synthesis of trisubstituted allenylethers [14] and selected aspects of their liquid crystalline behaviour [19].

Allenyl acetate:



cr 56 S_C* 152 N* 163 BP 164 is [15]

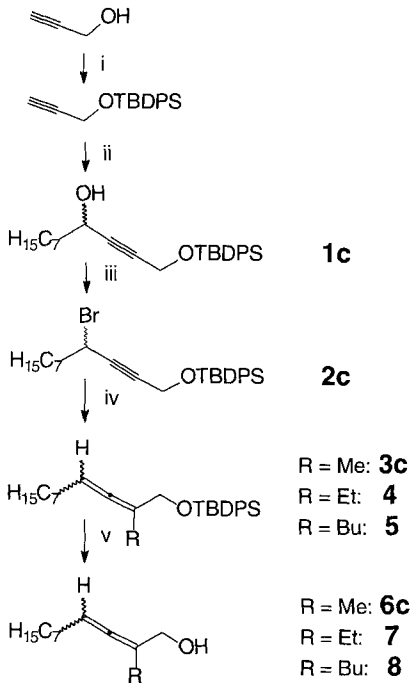
Allenyl ether:



cr 47 S_C* 114 N* 130 BP 131 is [16]

Synthesis

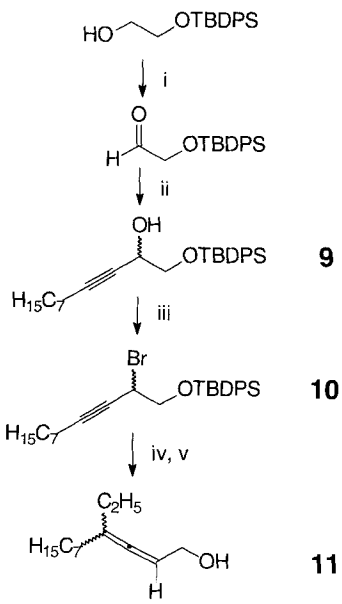
Our strategy was to prepare in a first step liquid crystalline derivatives of racemic trisubstituted allenylalcohols. The aim was to study the influence of the size and the position of branching at the allenic moiety on their liquid crystalline properties. In a second step selected compounds were prepared as enantiomerically enriched samples by enantioselective synthesis.



Scheme 1 Synthesis of the racemic 2-substituted 2,3-undecadiene-1-ols **6c**, **7** and **8**. *Reagents and conditions* - i) TBDPSCl, imidazole, DMF, 0–20 °C, 2 h, 85% [20], ii) *n*-BuLi, THF, 0.5h, –78 °C, followed by $C_7H_{15}CHO$, –78 to 20 °C, 2h, 65–85% [21], iii) CBr_4, PPh_3, pyridine, THF, 20 °C, 3h, 80–90% [22], iv) LiBr, Cu_2I_2, RMgBr, THF, 0 °C, 1h, 67–83% [23], v) Bu_4NF, THF, 20 °C, 20h, 60–90% [24].

According to scheme 1 the racemic 2-alkyl-2,3-undecadiene-1-ols **6c**, **7** and **8** were synthesized by starting from 2-propyne-1-ol. Protection of the hydroxy group gave the 1-(*tert.*-butyldiphenylsilyloxy)-2-propyne [20] which was deprotonated with *n*-butyllithium to react with *n*-octanal to yield the 1-(*tert*-butyldiphenylsilyloxy)-2-undecyne-4-ol (**1c**) [15, 16, 21]. This propargylic alcohol was transformed into the corresponding bromide **2c** using CBr_4/PPh_3 [22]. S_N2'-Substitution of the halogen with *in situ* prepared organocopper reagents [RCu • LiBr • MgBrI; R = CH_3, C_2H_5 and C_4H_9] [23] afforded the TBDPS-protected alcohols **3c**, **4** and **5** which gave the allenic alcohols **6c**, **7** and **8** after deprotection with Bu_4NF [24].

As shown in scheme 2, the racemic 4-ethyl-2,3-undecadiene-1-ol **11** has been synthesized starting with 2-(*tert*-butyldiphenylsilyloxy)ethanol which was at first oxidized to the corresponding aldehyde (Swern-oxidation [25]). By reaction of the 2-(*tert*-butyldiphenylsilyloxy)acetaldehyde with 1-lithio-1-nonyne the propargylic alcohol **9** was obtained which was used to prepare the 4-branched alcohol **11** by applying the same sequence as described above for the synthesis of **7** from **1c**.

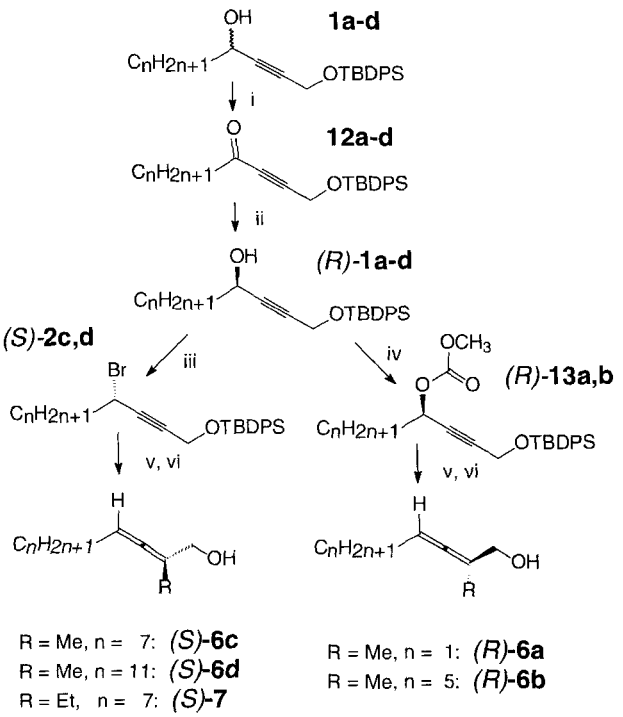


Scheme 2 Synthesis of racemic 4-ethyl-2,3-undecadiene-1-ol **11**. *Reagents and conditions* - i) DMSO, $(COCl)_2$, –78 to 20 °C, 0.5 h, followed by pyridine, NEt_3, –70 to 20 °C, 2h, 55% [25], ii) Li–C≡C–C_7H_{15}, THF, –70 to 20 °C, 2h, 56%, iii) CBr_4, PPh_3, pyridine, THF, 20 °C, 3h, 77% [22], iv) LiBr, Cu_2I_2, EtMgBr, THF, 0 °C, 1h, 80% [23], v) Bu_4NF, THF, 20 °C, 20h, 70% [24].

The synthetic route to the enantiomerically enriched allenic derivatives *(S)*-**6c,d**, *(S)*-**7** and *(R)*-**6a,b** is outlined in scheme 3. The propargylic alcohols **1a–d** (n = 1: **1a**, n = 5: **1b**, n = 7: **1c**, n = 11: **1d**) were oxidized to give the 1-(*tert*-butyldiphenylsilyloxy)-2-alkyne-3-ones **12a–d** using CrO_3 (Jones reagent [26]) or PCC [27] which both gave comparable yields. Reduction with *(R)*-Alpine-Borane® afforded the optically active *(R)*-1-(*tert*-butyldiphenylsilyloxy)-2-undecyne-4-ols *(R)*-**1** in 87–89% *ee* after oxidative work up [28]. The enantiomeric purity of these compounds was determined by analyzing the *(S)*-MTPA-Esters by ^{19}F NMR and ^1H NMR spectroscopy (Mosher's method [29]).

The optically active 1-(*tert*-butyldiphenylsilyloxy)-2-alkyne-4-ols were transformed into the corresponding bromides [22] *(S)*-**2** or carbonates *(R)*-**13** [30] with inversion (bromides) or retention (carbonates) of the configuration at the stereogenic center so that we obtained both the *(S)*- and the *(R)*-propargylic precursors, respectively. The *anti*-S_N2'-substitution with organocopper reagents (RCu • LiBr • MgBrI) [23] afforded the TBDPS-protected chiral alcohols which gave after deprotection with Bu_4NF the optical active allenic alcohols *(S)*-**6c,d**, **7** and *(R)*-**6a,b** respectively with *ee* of 25–52% (Mosher's method).

As shown in table 1 the enantiomeric purity of the allenyl alcohols is independent on the leaving group used, but it strongly depends on the reaction time, because

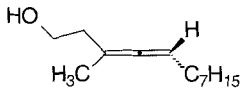


Scheme 3 Synthesis of the enantiomerically enriched 2-substituted 2,3-alkadiene-1-ols *(S)*-**6c,d**, *(S)*-**7** and *(R)*-**6a,b** from **1a–d** (compounds **1**, **2**, **12** and **13**: n = 1: **a**, n = 5: **b**, n = 7: **c**, n = 11: **d**). *Reagents and conditions* - i) CrO_3, H_2SO_4, H_2O, acetone, 20 °C, 2h, 90–95% [26], ii) *(R)*-Alpine Borane (neat), 0 °C, 2h, followed by NaOH, H_2O_2, H_2O, 20–30 °C, 3h, 80% [28b], iii) CBr_4, PPh_3, pyridine, THF 20 °C, 3h, 80–90% [22], iv) $ClCOOCH_3$, pyridine, THF, 0–20 °C, 2h, 45–71% [30], v) LiBr, Cu_2I_2, RMgBr, THF, 0 °C, 1h, 80% [23], vi) Bu_4NF, THF, 20 °C, 20h, 60–90% [24].

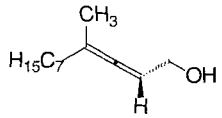
Table 1 Enantiomeric purity of the propargylic alcohols *(R)*-**1** and the allenyl alcohols **6** in dependence on the reaction conditions.

Comp.	n	*ee* (%)	Bromide/ carbonate	*t* (h)	Comp.	*ee* (%)
(R)-**1b**	5	91	*(R)*-**13b**	1	*(R)*-**6b**	51
(R)-**1c**	7	88	*(S)*-**2c**	1	*(S)*-**6c**	51
(R)-**1c**	7	88	*(S)*-**2c**	3	*(S)*-**6c**	24
(R)-**1d**	11	89	*(S)*-**2d**	1	*(S)*-**6d**	44

the allenes racemize in the presence of the organocopper species [31].



(R)-**14**



(S)-**15**

The *(R)*-3-methyl-3,4-dodecadiene-1-ol *(R)*-**14** was obtained using the same sequence (see scheme 3, *via* the carbonate), however starting with 4-butyne-1-ol. *(S)*-4-methyl-2,3-undecadiene-1-ol [compound *(S)*-**15**] was synthesized in an analogous manner starting with 1-(*tert*-butyldiphenylsilyloxy)-3-undecyne-2-ol (compound **9**) *via* the propargylic bromide **10**.

Finally, the racemic allenic alcohols **6c**, **7**,**8** and **11** and the optical active allenic alcohols *(R)*-**6a,b**, *(S)*-**6c,d**, *(S)*-**7**, *(R)*-**14** and *(S)*-**15** were appended to promesogenic phenols by the Mitsunobu etherification reaction [32] and/or to promesogenic carboxylic acids by esterification with carbodiimide/DMAP [33].

Mesomorphic Properties

The transition temperatures, transition enthalpy values and selected analytical data of the synthesized final compounds are summarized in tables 2–5. All compounds display the smectic C-phase and mostly also a nematic mesophase. Enlarging the substituent at C-2 of the allene moiety leads to a decrease of the mesophase stability (see figure 1 and table 1; *rac*-**16c**, *rac*-**18**, *rac*-**19**). However the influence on the S_C–N-transition temperature is less pronounced than on the clearing temperature (N-is-transition). Even for the butyl substituted compound **19** the smectic C-phase can be observed. It seems however, that an alkyl substituent at C-3 of the allene moiety more strongly disturbs the liquid crystalline properties (compare compounds **16c** and **17** or **18** and **20** in table 2).

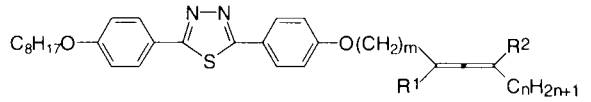
All enantiomerically enriched compounds display the chiral smectic S_C*-phase. Furthermore, in some cases the S_C*-phase was accompanied by the cholesteric (N*) and a Blue Phase (BP).

We have found out that all investigated enantiomerically enriched compounds show a typical bistable (ferroelectric) switching process by applying an electric field. Details of the ferroelectric properties [17, 18] and also the influence of donor-acceptor interactions on the mesomorphic properties [34] are reported in separate papers.

Experimental

^1H NMR and ^{13}C NMR spectra: VARIAN Gemini (200 MHz), VARIAN Gemini 2000 (400 MHz) or VARIAN Unity (500 MHz). IR spectra: Perkin Elmer FT-IR 1000 spectrometer. Mass spectra: AMD 402 mass spectrometer (70 eV). Microanalyses: Carlo-Erba 1102 and Leco CHNS-932 elemental analyzer. Thin layer chromatography: MERCK TLC aluminum sheets (silica gel 60 F_{254}). Column chromatography: silica gel 0.040 mm – 0.063 mm or 0.063 mm – 0.20 mm (MERCK). A METTLER FP 82 HT hot stage and control unit in conjunction with a NIKON Optiphot-2 polarizing microscope was used to determine the

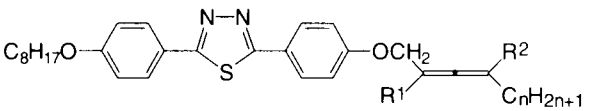
Table 2 Phase transition temperatures and analytical data of the thiadiazole derivatives **16**–**21**. Abbreviations: cr = crystalline solid, S_C = smectic C-phase, S_C* = chiral smectic C-phase, N, nematic phase, N* = cholesteric phase, BP = blue phase, is = isotropic liquid



Comp.	R^1	R^2	n	m	Formula	Transition temperatures T (°C) Transition enthalpies ΔH (kJ·mol^{-1})	calcd. found %C	%H	%N	%S
(R)-**16a** [a]	CH_3	H	1	1	$C_{24}H_{26}N_2O_2S$ (406.17)	cr 90 S_C* 116 N* 132 is *27.7 1.99 1.03*	70.91 *70.9*	6.4 *6.3*	6.89 *7.0*	7.89 *8.1*
(R)-**16b** [b]	CH_3	H	5	1	$C_{28}H_{34}N_2O_2S$ (462.23)	cr 65 S_C* 95 N* 99.5 BP 100.5 is [c] *27.2 2.04 0.76*	72.69 *72.1*	7.41 *7.8*	6.05 *6.15*	6.93 *7.15*
rac-**16c**	CH_3	H	7	1	$C_{30}H_{38}N_2O_2S$ (490.27)	cr 60 S_C 91 N 101 is *27.4 1.54 0.89*	73.43 *73.15*	7.81 *7.8*	5.71 *5.7*	6.53 *6.72*
(S)-**16d** [d]	CH_3	H	11	1	$C_{34}H_{46}N_2O_2S$ (546.33)	cr 54 S_C* 79 N* 86 BP 86.6 is [e] *30.6 1.3 0.98*	74.68 *74.5*	8.48 *8.3*	5.12 *5.2*	5.86 *6.0*
(S)-**17**	H	CH_3	7	1	$C_{30}H_{38}N_2O_2S$ (490.27)	cr 75 (S_C* 74.5) N* 83 is	[e]			
rac-**18**	C_2H_5	H	7	1	$C_{31}H_{40}N_2O_2S$ (504.28)	cr 87 S_C 91 N 93 is *35.5 1.41 1.02*	73.77 *73.4*	7.99 *7.9*	5.55 *5.6*	6.35 *6.45*
(S)-**18** [f]	C_2H_5	H	7	1	$C_{31}H_{40}N_2O_2S$ (504.28)	cr 84 (S_C* 81) N* 95.5 is *32.1 (1.36) 0.77*	73.77 *72.9*	7.99 *7.7*	5.55 *5.85*	6.35 *6.7*
rac-**19**	C_4H_9	H	7	1	$C_{33}H_{44}N_2O_2S$ (532.31)	cr 68 S_C 74 N 78.5 is *36.4 1.68 0.98*	74.39 *74.3*	8.32 *8.3*	5.26 *5.4*	6.02 *6.2*
rac-**20**	H	C_2H_5	7	1	$C_{31}H_{40}N_2O_2S$ (504.28)	cr 89 (S_C 78 N 85) is *34.5 1.8 0.5*	73.77 *73.35*	7.99 *7.8*	5.55 *5.55*	6.35 *6.6*
(R)-**21**	CH_3	H	7	2	$C_{31}H_{40}N_2O_2S$ (504.28)	cr 48 S_C* 83 N* 104 is *13.6 1.8 0.5*	[g]			

[a] $[a]_D^{20}$ = −5.81 (*c* = 1.18, $CHCl_3$); 33% *ee*. [b] $[a]_D^{20}$ = −19.9 (*c* = 1.71, $CHCl_3$); 51% *ee*. [c] Two additional phase transitions with low enthalpy values occur in the S_C-phase range of these compounds, which presumably correspond to a S_{CA}*-$S_C\gamma$-S_C* phase sequence on increasing temperature (S_{CA}* = antiferroelectric S_C-phase, $S_C\gamma$* = ferrielectric S_C-phase, S_C* = ferroelectric S_C-phase). For details see ref. [18] [d] $[a]_D^{20}$ = 18.66 (*c* = 0.52, $CHCl_3$); 44% *ee*. [e] HRMS: *m/z* calcd. 490.2654, found 490.2676; 24% *ee*.
[f] $[a]_D^{20}$ = 14.45 (*c* = 0.82, $CHCl_3$). [g] HRMS: *m/z* calcd. 504.2810, found 504.2814; $[a]_D^{20}$ = −16.04 (c = 0.7, $CHCl_3$); 45% *ee*.

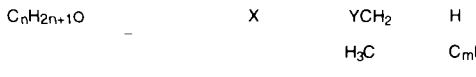
Table 3 Phase transition temperatures and analytical data of the thiadiazole derivatives **22**–**24**. Abbreviations: S_X = smectic low-temperature mesophase with unknown structure, for the other abbreviations see table 2



Comp.	R^1	R^2	n	Formula	Transition temperatures T(°C) Transition enthalpies ΔH (kJ·mol^{-1})	calcd. found %C	%H	%N	%S
(S)-**22a** [a] [14]	CH_3	H	7	$C_{34}H_{46}N_2O_2S$ (546.33)	cr 67 S_C* 99 N* 100 BP 101 is	74.68 *74.5*	8.48 *8.4*	5.12 *5.1*	5.86 *5.95*
rac-**22a** [14]	CH_3	H	7	$C_{34}H_{46}N_2O_2S$ (546.33)	cr 64 S_C 98 N 101 is *29.9 1.9 1.37*	74.68 *74.0*	8.48 *8.3*	5.12 *5.2*	5.86 *6.1*
(S)-**22b**	CH_3	H	11	$C_{38}H_{54}N_2O_2S$ (602.39)	cr 62 S_C* 80 N* 88 is *39.8 0.3 0.82*	[b]			
rac-**23**	C_2H_5	H	7	$C_{35}H_{48}N_2O_2S$ (560.34)	cr 50 S_C 92 N 95 is *27.9 2.24 1.68*	74.96 *74.5*	8.63 *8.5*	4.99 *5.05*	5.72 *5.9*
rac-**24**	H	C_2H_5	7	$C_{35}H_{48}N_2O_2S$ (560.34)	cr 45 S_X 74 S_C 81 N 88 is *25.5 0.1 1.15 0.8*	[c]			

[a] 52% *ee*. [b] HRMS: *m/z* calcd. 602.3906, found 602.3879; $[\alpha]_D^{20}$ = 13.04 (c = 0.59, $CHCl_3$); 44% *ee*.
[c] HRMS: *m/z* calcd. 560.3436, found 560.3452.

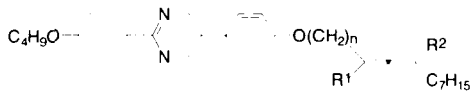
Table 4 Phase transition temperatures and analytical data of the biphenyl derivatives **25** and **26**. Abbreviations: S_A = smectic A-phase, for the other abbreviations see table 2



Comp.	X	Y	n	m	Formula	Transition temperatures T(°C) Transition enthalpies ΔH (kJ·mol^{-1})	calcd. found %C	%H
(R)-**25a** [a]	OOC	O	11	5	$C_{40}H_{52}O_4$ (596.39)	cr 96 S_C* 108 N* 126 is *32.2 0.7 0.2*	80.5; *78.2;*	8.78 *8.6*
rac-**25b**	OOC	O	11	7	$C_{42}H_{56}O_4$ (624.42)	cr 98 (S_C 97) is *37.3 (0.6)*	[b]	
(S)-**26** [c]	COO	COO	10	7	$C_{42}H_{54}O_5$ (638.40)	cr 39 S_C* 76 S_A 128 is *32.8 0.1 3.0*		

[a] $[\alpha]_D^{20} = -3.58$ (c = 0.65, $CHCl_3$); 51% *ee*. [b] HRMS: *m/z* calcd. 624.4178, found 624.4163. [c] $[\alpha]_D^{20} = 5.47$ (c = 0.71, $CHCl_3$); 51% *ee*.

Table 5 Phase transition temperatures and analytical data of the pyrimidine derivatives *rac*-**27** and *(R)*-**28**



Comp.	R^1	R^2	n	Formula	Transition temperatures T/°C calcd. *Transition enthalpies* ΔH (kJ·mol^{-1})	found %C	%H	%N
rac-**27**	H	C_2H_5	1	$C_{33}H_{42}N_2O_2$ (498.32)	cr 69 S_C 74 N 78.5 is *28.7 4.8 0.6*	79.48 *79.5*	8.49 *8.35*	5.62 *5.45*
(R)-**28**	CH_3	H	2	$C_{33}H_{42}N_2O_2$ (498.32)	cr 32 S_C* 101 N* 121 is *18.5*	[a]		

[a] HRMS: *m/z* calcd. 498.3246, found 498.3251; $[\alpha]_D^{20} = -18.55$ (c = 0.54, $CHCl_3$); 45% *ee*.

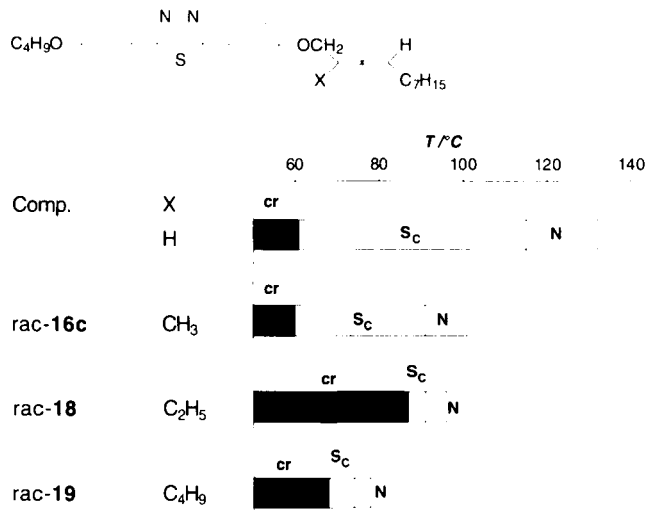


Fig. 1 The influence of the size of the substituent X at the allenic moiety on the phase transition temperatures T (°C)

phase transition temperatures and to analyze the optical textures. DSC measurements: PERKIN ELMER DSC-7 calorimeter. The syntheses of the compounds **16**–**28** are quite similar. Therefore, the synthesis of only one representative [compound *(S)*-**16d**] is described in detail. The complete set of analytical data is provided for this compound and its synthetic intermediates. Selected analytical data (elemental composition or HRMS, specific rotation) of the final compounds **16**–**28** are collected in the tables 2–5.

1-(tert-Butyldiphenylsilyloxy)-2-pentadecyne-4-ol (**1d**)

n-Butyllithium (16.4 ml of a 1.6M in *n*-hexane, 26 mmol) was added at −78°C (ethanol/CO_2) to a solution of 1-(*tert*-butyldiphenylsilyloxy)-2-propyne (7.65 g, 26 mmol) [20] in dry THF (40 ml) placed in a 250 ml three-necked flask, equipped with a thermometer, gas inlet and outlet and a magnetic stirrer. After stirring the reaction mixture at −70 °C for 30 minutes 1-dodecanal (7.4 g, 25 mmol), dissolved in dry THF (20 ml) was added while the temperature was kept below −65 °C. After 3 h the reaction mixture was allowed to warm to room temperature

followed by hydrolysis with hydrochloric acid (80 ml of a 10% w/w solution). Diethyl ether (100 ml) was added, the phases were separated, and the aqueous phase was extracted with diethyl ether (3× 50ml). The combined organic extracts were washed successively with water (2–3× 50 ml) and brine (2–3× 50 ml) and dried over Na_2SO_4. After filtration and evaporation of the solvent a slightly yellow oil was obtained which was purified by column chromatography (eluent: light petroleum/ ethyl acetate; v/v 10:2, 40 cm × 8 cm, R_f: 0.2 – 0.3) to afford **1d** as a colorless oil; Yield: 9 g (84% d. Th.); n_D^{20} : 1.5179. – ^{1}H NMR (400 MHz, $CDCl_3$, *J*/Hz): δ_H/ppm = 7.71–7.69 (m, 4H, Ar-H), 7.44–7.35 (m, 6H, Ar-H), 4.35 (d, 2H, *J* 1.55, OCH_2), 4.26 (t, 1H, *J* 6.5, CHOH), 1.56 (m, 2H, CH_2), 1.38–1.2 (m, 18H, CH_2), 1.04 [s, 9H, $C(CH_3)_3$], 0.87 (t, 3H, *J* 6.7, CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ_C/ppm = 135.8, 133.44, 129.88, 127.75 (Ar–C), 86.43 (C≡C), 83.21 (C≡C), 62.47 (CHOH), 52.66 (OCH_2), 37.54, 31.82, 29.56, 29.52, 29.48, 29.44, 29.24, 29.2 (CH_2), 26.62 [$C(\underline{C}H_3)_3$], 24.97 (CH_2), 22.56 (CH_2), 19.02 (SiC), 13.95 (CH_3).

1-(tert-Butyldiphenylsilyloxy)-2-pentadecyne-4-one (**12d**)

The oxidation of **1d** (20 mmol) was carried out by using CrO_3 (Jones-reagent) according to the standard procedure [26].

The crude product was purified by column chromatography (eluent: light petroleum/ethyl acetate; v/v 10:1, R_f: 0.4 – 0.5) to afford a colorless oil in 80% yield; n_D^{20} 1.5228. – ^{1}H NMR (400 MHz, $CDCl_3$, *J*/Hz): δ_H/ppm = 7.71–7.67 (m, 4H, Ar-H), 7.46–7.36 (m, 6H, Ar-H), 4.45 (s, 2H, OCH_2), 2.43 (t, 2H, *J* 6.5, $COCH_2$), 1.59 (m, 2H, CH_2), 1.3–1.2 (m, 16H, CH_2), 1.05 [s, 9H, $C(CH_3)_3$], 0.86 (t, 3H, *J* 6.8, CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ_C/ppm = 187.91 (C=O), 135.73, 132.75, 129.74, 127.94 (Ar–C), 89.92 (C≡C), 84.2 (C≡C), 52.41, 45.23, 31.81, 29.5, 29.34, 29.22, 28.88, 26.56, 26.55, (CH_2), 26.48 [$C(\underline{C}H_3)_3$], 23.84 (CH_2), 22.56 (CH_2), 19.06 (SiC), 13.94 (CH_3).

*(R)-1-(tert-Butyldiphenylsilyloxy)-2-pentadecyne-4-ol [(R)-**1d**]*

Synthesized from **12d** (7.1 g, 15 mmol) by enantioselective reduction using *(R)*-Alpine-borane [28b]. The spectroscopic data correspond to those given for the racemic compound; Yield 5.42 g (76% d.Th.); $[\alpha]_D^{20}$: –1.09 (c = 1.52 in $CHCl_3$), 89% *ee* (Mosher's method).

*(S)-4-Bromo-1-(tert.-Butyldiphenylsilyloxy)-2-pentadecyne [(S)-**2d**]*

***(R)*-1d** (5.2g, 10.9 mmol), triphenylphosphine (5.78 g, 22 mmol), THF (30 ml) and dry pyridine (1.0 ml) were placed in a 250 ml three-necked flask, equipped with a dropping funnel, gas-inlet and -outlet and a magnetic stirrer. To this vigorously stirred solution tetrabromomethane (6.3 g, 19 mmol) and dry pyridine (0.1 ml) dissolved in dry THF (10 ml) were added at 20 °C. After 3 h the reaction mixture was diluted with *n*-pentane (150 ml) and filtered. The filtrate was washed successively with aqueous HCl (2× 30 ml), saturated aqueous $NaHCO_3$-solution (2× 30 ml) and brine (2× 30 ml) and was dried with Na_2SO_4. Filtration and evaporation of the solvent under reduced pressure afforded a yellow oil which was purified by column chromatography on silica gel (eluent: light petroleum/ethyl acetate, v/v 10:1, R_f: 0.5–0.55); Yield 91%; n_D^{20} : 1.5320; $[\alpha]_D^{20}$: –5.7 (c = 3.44, $CHCl_3$), ^{1}H NMR (500 MHz, $CDCl_3$, *J*/Hz): δ_H/ppm = 7.71–7.69 (m, 4H, Ar-H), 7.44–7.36 (m, 6H, Ar-H), 4.47 (dt, 1H, ^3J 6.75, ^5J 1.8, CHBr), 4.37 (d, 2H, *J* 2.1, OCH_2), 1.92 (m, 2H, CH_2), 1.46 (m, 2H, CH_2), 1.26–1.2 (m, 16H, CH_2), 1.05 [s, 9H, $C(CH_3)_3$], 0.87 (t, 3H, *J* 7.0, CH_3). – ^{13}C NMR (126 MHz, $CDCl_3$): δ_C/ppm = 135.6, 133.1, 129.8, 127.7 (Ar–C), 85.3 (C≡C), 84.1 (C≡C), 52.8 (CHBr), 39.6, 37.3, 31.9, 29.62, 29.60, 29.53, 29.41, 29.33, 28.7, 27.3 (CH_2), 26.7 [$C(\underline{C}H_3)_3$], 22.7 (CH_2), 19.2 (SiC), 14.1 (CH_3).

(S)-1-(tert-Butyldiphenylsilyloxy)-2-methyl-2,3-pentadecadiene

Methylmagnesiumbromide (6.0 ml of a 3.0M solution in diethyl ether, 18 mmol) was added dropwise at 0 °C to a vigorously stirred suspension of LiBr (1.6 g, 18 mmol) and CuI (3.42 g, 18 mmol) in dry THF (80 ml). After 15 minutes *(S)*-**2d** (5 g, 9.24 mmol) dissolved in dry THF (10 ml) was added at 0 °C. The reaction mixture was stirred for additional 1 h at 0 °C, thereby the color changes from yellow/orange to dark green. Then the reaction was quenched by addition of saturated NH_4Cl-solution (20 ml). After filtration the organic phase was separated, and the solvent was removed under reduced pressure. The residue was dissolved in diethyl ether (100 ml), washed three times with water (3× 50 ml) and dried with Na_2SO_4. The solvent was distilled off under reduced pressure, and the crude product was purified by column chromatography (eluent: light petroleum/ ethyl acetate, v/v 10: 1, R_f: 0.5) to yield *(S)*-1-(*tert.*-butyldiphenylsilyloxy)-2-methyl-2,3-pentadecadiene as colourless oil; Yield 3.6 g (82%); n_D^{20} : 1.5175; $[\alpha]_D^{20}$: 15.79 (c = 2.05 in $CHCl_3$). – ^{1}H NMR (200 MHz, $CDCl_3$, *J*/Hz): δ_H/ppm = 7.73–7.67 (m, 4H, Ar-H), 7.46–7.32 (m, 6H, Ar-H), 5.06 (m, 1H, HC=C=C), 4.12 (d, 2H, ^5J 2.55, OCH_2), 2.0–1.9 (m, 2H, CH_2), 1.72 (d, 3H, ^5J 2.95, C=C=C–$C\underline{H}_3$), 1.4–1.2 (m, 18H, CH_2), 1.06 [s, 9H, $C(CH_3)_3$], 0.88 (m, 6H, *J* 6.3, CH_3). – ^{13}C NMR (50 MHz, $CDCl_3$): δ_C/ppm = 201.03 (C=$\underline{C}$=C), 135.6, 133.93, 129.52, 127.57 (Ar–C), 99.13 (C=C=$\underline{C}$), 91.4 ($\underline{C}$=C=C), 65.97 (OCH_2), 31.93, 29.69, 29.65, 29.51, 29.35, 29.60, 29.26, 29.12, 29.08 (CH_2), 26.81 [$C(CH_3)_3$], 22.69 (CH_2), 19.3 (SiC), 15.9 (CH_3), 14.11 (CH_3).

*(S)-2-Methyl-2,3-pentadecadiene-1-ol [(S)-**6d**]*

Tetra-*n*-butylammoniumfluorid solution (15 ml of a 1.0M solution in THF, 15 mmol) was added to a solution of *(S)*-1-(*tert*-butyldiphenylsilyloxy)-2-methyl-2,3-pentadecadiene (3.6 g; 7.55 mmol) dissolved in dry THF (10 ml). The reaction was monitored by TLC and was finished after 5 h at 20 °C. The solvent was evaporated, and the residue was dissolved in methylene chloride (30 ml), washed with water (10 ml) and dried with Na_2SO_4. The solvent was evaporated under reduced pressure, and the residue was purified by column chromatography (eluent: Light petroleum/ethyl acetate, v/v 10:1, R_f: 0.1 – 0.15); Yield 1.48 g (82%); n_D^{20} : 1.4712; $[\alpha]_D^{20}$: 6.41 (c = 2.46 in $CHCl_3$), 44% *ee* (Mosher's method). – ^{1}H NMR (200 MHz, $CDCl_3$, *J*/Hz): δ_H/ppm = 5.29–5.20 (m, 1H, HC=C=C), 3.97 (d, 2H, ^5J 2.55, OCH_2), 2.03–1.93 (m, 2H, CH_2), 1.69 (d, 3H, ^5J 2.75, C=C=C–$C\underline{H}_3$), 1.4–1.2 (m, 18H, CH_2), 0.86 (m, 3H, *J* 6.5, CH_3). – ^{13}C NMR (50 MHz, $CDCl_3$): δ_C/ppm = 199.23 (C=$\underline{C}$=C), 100.39 (C=C=$\underline{C}$), 94.37 ($\underline{C}$=C=C), 63.91 (OCH_2), 31.91, 29.65, 29.61, 29.46, 29.33, 29.21, 29.11, 29.07, 26.56, 22.66, (CH_2), 15.72 (CH_3), 14.2 (CH_3).

*(S)-2-(4-Butoxyphenyl)-5-[4-(2-methyl-2,3-pentadecadienyloxy)phenyl]-1,3,4-thiadiazole [(S)-**16d**]*

The reaction is carried out under inert gas atmosphere. In a 20 ml flask, equipped with a magnetic stirring bar and a rubber septum ***(S)*-6d** (480 mg (2.01 mmol), triphenylphosphine (526 mg, 2 mmol) and 4-[5-(4-butoxyphenyl)-1,3,4-thiadiazol-2-yl]phenol (520 mg (1.6 mmol) were dissolved in dry THF (10 ml). The solution was cooled to 0 °C, and diethylazodicarboxylate (DEAD, 312 µl, 2 mmol) was added afterward dropwise *via* a syringe over a period of 10 minutes. The reaction mixture was allowed to warm to room temperature and stirred at this temperature until reaction was complete (TLC, about 16 h). Then the solvent was removed under reduced pressure (18 mbar, 30 °C), and the residue was dissolved in chloroform (1–2 ml) and purified by column chromatography (eluent: chloroform/methanol, v/v 20:1, R_f: 0.7) and crystallized twice from ethanol (2–3 ml) to give ***(S)*-11d;** yield: 430 mg (49%). – ^{1}H NMR (500 MHz, $CDCl_3$, *J*/Hz): δ_H/ppm = 7.90 (d, 2H, *J* 9.1, Ar-H), 7.88 (d, 2H, *J* 9.1, Ar-H), 6.99 (d, 2H, *J* 8.8, Ar-H), 6.96 (d, 2H, *J* 8.8, Ar-H), 5.15 (m, 1H, HC=C=C), 4.54 (m, 2H, OCH_2), 4.02 (t, 2H, *J* 6.4, OCH_2), 1.98–1.94 (m, 2H, CH_2), 1.83–1.78 (m, 2H, CH_2), 1.76 (d, 3H, ^5J 2.8, CH_3), 1.4–1.16 (m, 20H, CH_2), 0.98 (t, 3H, *J* 7.5, CH_3), 0.85 (t, 3H, CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ_C/ppm = 202.91 (C=C=C), 167.28, 167.21, 161.58, 161.02, 129.43(2C), 129.3(2C), 123.17, 122.95, 115.66(2C), 115.09(2C) (Ar–C), 95.34 (C=C=C), 92.08 (C=C=C), 70.45 (OCH_2), 67.93 (OCH_2), 31.81, 31.1, 29.65, 29.57, 29.56, 29.54, 29.39, 29.23, 29.09, 28.97, 28.65, 22.54, 19.07 (CH_2) 15.93 (CH_3), 13.93 (CH_3), 13.65 (CH_3).

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References

[1] N. A. Clark, S. T. Lagerwall, Appl. Phys. Lett. **1980**, *36*, 899
[2] S. T. Lagerwall, in Handbook of Liquid Crystals Vol. 2b, Editors D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, V. Vill, Wiley-VCH, Weinheim 1998, p. 515
[3] B. Bahadur, Liquid Crystal – Applications and Uses, Vol. 1–3, World Scientific Publishing Co. Pte. Ltd., Singapore 1990–1992
[4] a) J. W. Goodby, J. Mater. Chem. **1991**, *1*, 307; (b) J. W. Goodby, D. A. Dunmur, P. J. Collings, Liq. Cryst. **1995**, *19*, 703
[5] A. Fukuda, Y. Takanishi, T. Isozaki, K. Ishikawa, H. Takezoe, J. Mater. Chem. **1994**, *4*, 997
[6] a) K. Nishide, A. Nakayama, T. Kusumoto, T. Hiyama, S. Takehara, T. Shoji, M. Osawa, T. Kuriyama, K. Nakamura, T. Fujisawa, Chem. Lett. **1990**, 623; b) M. Z. Cherkaoui, J.-F. Nicoud, D. Guillon, Chem. Mater. **1994**, *6*, 2026
[7] R. C. Geivandov, I. V. Gonscharowa, V. V. Titov, Mol. Cryst. Liq. Cryst. **1989**, *166*, 101
[8] a) G. Solladié, R. Zimmermann, J. Org. Chem. **1985**, *50*, 4062; b) K. Yang, R. F. Lemieux, Mol. Cryst. Liq. Cryst. **1995**, *260*, 247; c) G. Solladié, P. Hugelé, R. Bartsch A. Skoulios, Angew. Chem. **1996**, *108*, 1640, Angew. Chem. Int. Ed. Engl. **1996**, *35*, 1533; d) K. Yang, B. Campbell, G. Birch, V. E. Williams, R. P. Lemieux, J. Am. Chem. Soc. **1996**, *118*, 9557
[9] a) G. Gottarelli, G. P. Spada, Mol. Cryst. Liq. Cryst. **1985**, *123*, 377; b) G. Heppke, D. Lötzsch, F. Oestreicher, Z. Naturforsch. **1986**, *41a*, 1214; c) J. C. Bhatt, S. S. Keast, M. E. Neubert, R. C. Petschek, Liq. Cryst. **1995**, *18*, 367; d) H.-J. Deußen, P.V. Shibaev, R. Vinokur, T. Bjornholm, K. Schaumburg, K. Bechgaard, V.P. Shibaev, Liq. Cryst. **1996**, *21*, 327
[10] K. Yamamura, Y. Okada, S. Ono, M. Watanabe, I. Tabushi, J. Chem. Soc., Chem. Commun. **1988**, 443; K. Yamamura, S. Ono, I. Tabushi, Tetrahedron Lett. **1988**, *29*, 1797
[11] a) G. Solladié, R. Zimmermann, Angew. Chem. **1985**, *97*, 70; Angew. Chem. Int. Ed. Engl. **1985**, *24*, 64; b) J. Org. Chem. **1985**, *50*, 4062; c) H. Poths, R. Zentel, S.U. Vallerien, F. Kremer, Mol. Cryst. Liq. Cryst. **1991**, *203*, 101; d) H. Poths, R. Zentel, F. Kremer, K. Siemensmeyer, Adv. Mater. **1992**, *4*, 351; e) Y. Zhang, G.B. Schuster, J. Org. Chem. **1994**, *59*, 1855
[12] Racemic 1,3-disubstituted ferrocenes: R. Deschenaux, J. Santiago, Tetrahedron Lett. **1994**, *35*, 2169
[13] Butadiene iron-tricarbonyl complexes: a) L. Ziminski, J. Malthête, J. Chem. Soc., Chem. Commun. **1990**, 1495; b) P. Jacq, J. Malthête, Liq. Cryst. **1996**, *21*, 291
[14] Preliminary communication: K. Zab, H. Kruth, C. Tschierske, J. Chem. Soc., Chem. Commun. **1996**, 977
[15] R. Lunkwitz, C. Tschierske, A. Langhoff, F. Gießelmann, P. Zugenmeyer, J. Mater. Chem. **1997**, *7*, 1713
[16] J. Stichler-Bonaparte, H. Kruth, R. Lunkwitz, C. Tschierske, Liebigs Ann. **1996**, 1375
[17] R. Lunkwitz, C. Tschierske, Proc. SPIE **1998**, *3319*, 96
[18] R. Lunkwitz, C. Tschierske, Ferroelectrics **1998**, *212*, 265
[19] Details of the liquid crystalline and ferroelectric properties are reported in ref. [17, 18].
[20] C. L. Branch, M. J. Pearson, J. Chem. Soc., Perkin Trans. 1 **1986**, 1077
[21] M. M. Midland, J. Org. Chem. **1975**, *40*, 2250
[22] O. W. Gooding, C. C. Beard, D. Y. Jackson, D. L. Wren, G. F. Cooper, J. Org. Chem. **1991**, *56*, 1083
[23] a) T. L. Macdonald, D. R. Reagan, R. S. Brinkmeyer, J. Org. Chem. **1980**, *45*, 4740
[24] S. Hanessian, P. Lave, Can. J. Chem. **1975**, *53*, 2975
[25] A.J. Mancuso, D. Swern, Synthesis **1981**, 165.
[26] K. Bowden, J. M. Heilbron, E. R. -H. Jones, B. C. L. Weedon, J. Chem. Soc. **1946**, 39
[27] E. J. Corey, G. Schmidt, Tetrahedron Lett. **1979**, 399
[28] a) M. M. Midland, A. Tramontano, A. Kazubski, R. S. Graham, D. J. S. Tsai, D. B. Cardin, Tetrahedron **1984**, *40*, 1371; b) M. M. Midland, R. S. Graham, Org. Synth. **1984**, *63*, 57
[29] J. A. Dale, H. S. Mosher, J. Am. Chem. Soc. **1973**, *95*, 512
[30] E. J. Corey, J. W. Suggs, J. Org. Chem. **1973**, *38*, 3223
[31] P. Rona, P. Crabbe, J. Am. Chem. Soc. **1969**, *91*, 3289
[32] O. Mitsunobu, Synthesis **1981**, 1
[33] C. Tschierske, H. Zaschke, J. prakt. Chem. **1989**, *331*, 365
[34] R. Lunkwitz, B. Neumann, C. Tschierske, Liq. Cryst. **1998**, *25*, 403

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