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Preliminary communication

A novel class of heterocyclic liquid crystals with broad smectic C phase

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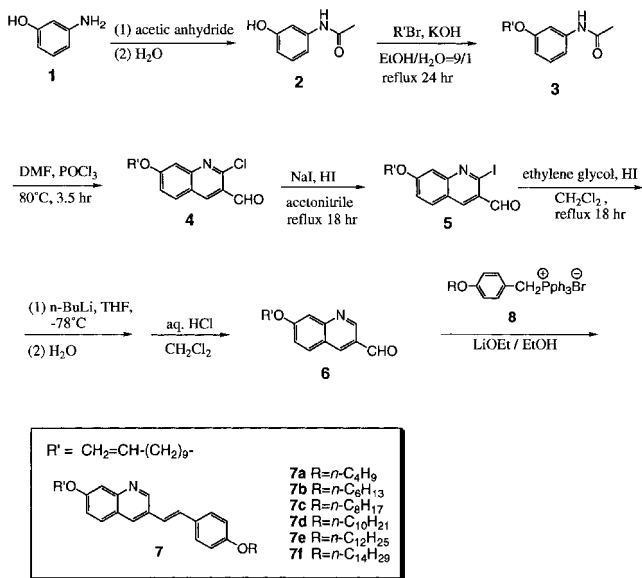
A successful approach in molecular design through fusing aromatic/heterocyclic rings for broadening the smectic C (SmC) phase and the synthesis of the first heterocyclic liquid crystalline (LC) molecules containing 3,7-disubstituted quinoline with one of the widest SmC phases are reported. Their naphthalene analogues are compared. The nitrogen atom in quinoline system introduces attractive forces to aid the formation of the tilted SmC phase and the flexible chain length also influences the tilted SmC phase effectively.

Recently ferroelectric liquid crystals (FLCs) have attracted considerable attention and interest since the invention of fast switching, bistable and electro-optic devices [1]. Generally, the FLC materials were made from achiral host liquid crystal mixtures, which have low viscosities and a wide range SmC phase (tilted layer structure), and a chiral dopant having a large spontaneous polarization. Importantly, a single component of the SmC achiral host LC possessing a wide range SmC phase has been sought as a good candidate in FLC mixtures [2]. Most researches have elaborated on attaching lateral substituents [3] or branching the terminal chain [4] on molecules to broaden the range of the SmC* phase. In order to obtain broad range SmC host materials, there are presently few systematic ways to design and synthesize [5]. For instance, two alkoxy terminal chains in a molecule are more likely to promote the SmC phase [6], which is adopted in our molecular design. From the structural point of view, the fused-ring system possessing a long and polarizable core structure, such as naphthalene, has a positive influence on the formation of the SmC phase [7]. Furthermore, the lone pair of electrons of the heterocyclic structure may introduce a transverse dipole moment and thus possess a high negative dielectric anisotropy, and can avoid the disadvantage of broadening the system by lateral polar substituents [8]. Some heterocyclic compounds, such as pyridines and pyrimidines incorporating the nitrogen hetero-atom, have been reported to favour the tilted

layer structure as expected on the basis of current theories of the SmC phase [9]. Based on these concerns, the heterocyclization of naphthalene, i.e. quinoline, has become a suitable candidate for the goal of broadening the SmC phase. Hence, this work is concentrated on broadening the SmC phase by tuning the rigid core through the fused (naphthalene) and heterocyclic (quinoline) design. A few LCs containing 2,6-disubstituted quinoline [10] have been synthesized to study their mesogenic properties; however, they only show a narrow SmC phase (ranging 40°C at most) [10(c)]. Herein, we wish to report the successful synthesis of the first heterocyclic LCs containing 3,7-disubstituted quinoline with a broad SmC phase (ranging 90°C) at moderately elevated temperatures [11].

Two series of 7-*n*-alkenyloxy-3-(4'-*n*-alkoxystyryl)quinolines and 7-*n*-alkenyloxy-3-(4'-*n*-alkoxystyryl)naphthalenes were synthesized and systematically compared. The synthetic approach of the quinoline derivatives (fixing terminal chain *R'* and altering the length of the alkoxy chain *R*) is summarized in scheme 1. Compounds 4 and 5 were prepared according to the literature method [12]. Compounds 6 were obtained by the protection of aldehyde group of 5 using ethylene glycol in the presence of HI, followed by removing the iodide and then the deprotection; the overall yield was 28 per cent. Quinoline derivatives 7 [13] were prepared by the Wittig reaction in 60–70 per cent yield from the precursors 6 and the phosphonium salts 8. Compounds 8 were obtained from the reactions of triphenylphosphine with the alkoxy benzyl bromides in boiling xylene for

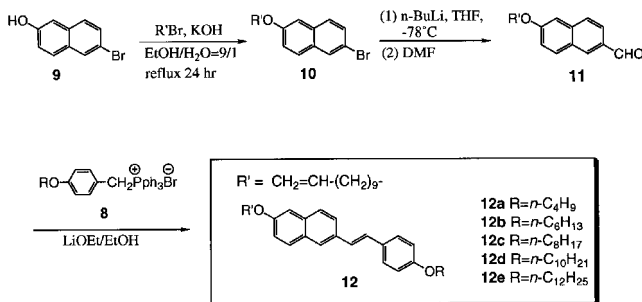
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Scheme 1.

2–3 h and the yields were generally greater than 80 per cent. Similarly, the naphthalene analogues **12** [13] were prepared in 60–70 per cent yield from the reaction of **11** with the phosphonium salts **8** under similar conditions (see scheme 2).

The mesogenic behaviour and phase transitions characterized by polarizing optical microscopy and differential scanning calorimetry (Perkin–Elmer DSC-7) are summarized in table 1, figure 1 (system **7**) and table 2, figure 2 (system **12**). Powder X-ray diffraction (XRD) patterns were obtained from a Siemens D-5000 X-ray diffractometer equipped with a TTK450 temperature controller. The tables show that all compounds possess polymorphism, such as SmA, SmC, SmI and CrG. The orthogonal smectic A phase was characterized by the focal-conic fan texture coexisting with homeotropic alignment, and the tilted smectic C phase was characterized by the broken focal-conic fan texture coexisting with the schlieren texture through optical microscopy and was also confirmed by XRD. The X-ray pattern in the SmC range showed only a sharp reflection in the



Scheme 2.

small-angle region, suggesting a smectic layer structure without order in the layers. The layer thickness of the SmC phase increased gradually with increasing temperature and finally reached an upper limit *d*-spacing (for example, 33.61 Å at 145°C, 33.84 Å at 150°C, 34.52 Å at 155°C, 36.07 Å at 160°C, and 37.62 Å at 165°C for the naphthalene system where *n*=10; 33.28 Å at 80°C, 33.31 Å at 100°C, 33.70 Å at 120°C, 36.12 Å at 140°C, and 35.06 Å at 160°C for the quinoline system where *n*=8) on entering the orthogonal layer structure of SmA region. The tilted layer phases (determined by XRD) below the SmC phase of the quinoline system were tentatively assigned as smectic I (by the frozen fan and frozen schlieren textures) and SmX₁ phase, and those of the naphthalene derivatives were tentatively assigned as CrG (by the arced-fan and mosaic textures) and SmX₂ phase (possibly CrH by the arced-fan and fine cross hatching in mosaic textures). The SmX₁, SmX₂ and SmX₃ phases are all tilted smectic phases which were primarily confirmed by XRD. Further X-ray diffraction studies will be investigated and the detail will be reported in the future. In general, the quinoline derivatives exhibit lower isotropization temperatures than the analogous naphthalene series. Furthermore, the isotropization temperatures decrease with increasing the flexible alkoxy chain length as *n* ≥ 8 in each (quinoline and naphthalene) homologues due to the higher chain flexibility. Surprisingly, the widest SmC phase range (**7d** ranging 90°C) of the quinoline system is much broader than that (**12d** ranging 22°C) of the naphthalene system. Therefore, the most important result shows that compared with their naphthalene analogues the tilted SmC phase is much favoured in the quinoline series. In addition, a distinct variation in the span of the SmC phase with increasing flexible length from *n*=6 to *n*=8 is observed (from 0°C to 22.1°C in the naphthalene system and from 22.7°C to 87.6°C in the quinoline system), and the SmC phase is much more favoured than the SmA phase as *n* ≥ 8. Also, the naphthalene series exhibits the SmC phase at only *n* ≥ 8, so the length of the flexible chain (*n*) plays a very important role in the formation of the tilted SmC phase. Therefore, the huge change of the orthogonal SmA phase to the tilted SmC phase (from *n*=6 to *n*=8) is related to the flexible alkoxy chain length which controls the shape of the molecule in the stacking form, and this phenomenon is known as SmC phase injection as the flexible chain length increases up to a certain length. Nevertheless, as *n* ≥ 12 in the quinoline system, the range of the SmC phase starts to decrease with increasing the alkoxy flexible chain length (*n*). From table 1, at *n*=8, 10, 12, and 14 the ranges of SmC phase are 87.6°C, 90°C, 77.2°C and 74.7°C, respectively. Hence, the SmC phase is most favoured at *n*=8 and 10 in which the alkoxy chain *R* has the most close carbon numbers

Table 1. Phase transition temperatures^a and corresponding enthalpies (J g⁻¹) of the quinoline system 7.

Compound	Transition data	
7 a ($n=4$)	Cr $\xleftrightarrow[34.4^{\circ}\text{C}(69.3)]{66.7^{\circ}\text{C}(84.5)}$ SmC $\xleftrightarrow[95.0^{\circ}\text{C}^{\text{b}}]{96.0^{\circ}\text{C}^{\text{b}}}$ SmA $\xleftrightarrow[157.8^{\circ}\text{C}(8.2)]{164.2^{\circ}\text{C}(8.3)}$ I	
7 b ($n=6$)	Cr $\xleftrightarrow[23.2^{\circ}\text{C}(40.7)]{57.3^{\circ}\text{C}(55.9)}$ SmC $\xleftrightarrow[79.0^{\circ}\text{C}^{\text{b}}]{80.0^{\circ}\text{C}^{\text{b}}}$ SmA $\xleftrightarrow[161.1^{\circ}\text{C}(10.1)]{165.4^{\circ}\text{C}(11.0)}$ I	
7 c ($n=8$)	Cr $\xleftrightarrow[41.1^{\circ}\text{C}(60.9)]{58.3^{\circ}\text{C}(55.7)}$ SmX ₁ $\xleftrightarrow[60.0^{\circ}\text{C}^{\text{b}}]{65.1^{\circ}\text{C}(1.3)}$ SmI $\xleftrightarrow[66.5^{\circ}\text{C}(1.2)]{69.6^{\circ}\text{C}(0.7)}$ SmC $\xleftrightarrow[154.9^{\circ}\text{C}(0.2)]{157.2^{\circ}\text{C}(0.4)}$ SmA $\xleftrightarrow[165.2^{\circ}\text{C}(15.3)]{167.9^{\circ}\text{C}(16.6)}$ I	
7 d ($n=10$)	Cr $\xleftrightarrow[61.2^{\circ}\text{C}(74.9)]{71.2^{\circ}\text{C}(76.0)}$ SmI $\xleftrightarrow[71.8^{\circ}\text{C}(3.0)]{72.0^{\circ}\text{C}^{\text{b}}}$ SmC $\xleftrightarrow[158.0^{\circ}\text{C}^{\text{b}}]{162.0^{\circ}\text{C}^{\text{b}}}$ SmA $\xleftrightarrow[162.0^{\circ}\text{C}(18.2)]{164.5^{\circ}\text{C}(18.9)}$ I	
7 e ($n=12$)	Cr $\xleftrightarrow[72.7^{\circ}\text{C}(84.1)]{83.2^{\circ}\text{C}(82.7)}$ SmC $\xleftrightarrow[157.6^{\circ}\text{C}(15.0)]{160.4^{\circ}\text{C}(17.2)}$ I	
7 f ($n=14$)	Cr $\xleftrightarrow[61.0^{\circ}\text{C}(60.3)]{73.5^{\circ}\text{C}(57.8)}$ SmI $\xleftrightarrow[75.1^{\circ}\text{C}(4.3)]{79.3^{\circ}\text{C}(4.1)}$ SmC $\xleftrightarrow[149.7^{\circ}\text{C}(15.4)]{154.0^{\circ}\text{C}(16.0)}$ I	

Cr=crystalline phase, SmX₁=unidentified smectic phase, I=isotropic liquid. ^aPhase transition temperatures and corresponding enthalpies were determined by the 2nd heating and cooling scans (at a heating and cooling rate of 10°C min⁻¹). ^bThe enthalpy was too small to be detected by differential scanning calorimetry and the phase transition temperature was assigned by polarizing optical microscopy.

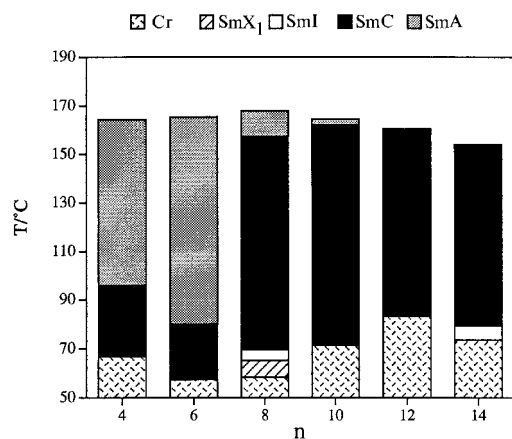


Figure 1. Phase transition temperatures of system 7 (styryl-quinolines) versus the number of carbon atoms (n) in the alkyl chain (R).

($n=8$ and 10) to that of the other terminal chain R' excluding the vinyl carbons ($n'=9$ at $\text{C}=\text{C}-\text{C}_9-\text{O}$ —excluding $\text{C}=\text{C}$). This result suggests that near symmetrical terminal chains may form the SmC phase more easily in the quinoline system. The terminal double bond in both the quinoline and naphthalene systems will be potential LC materials for polymerization in practical uses. An analogous compound 7- n -undecoxy-3-(4'- n -alkoxystyryl)quinoline (Cr 80°C SmC 160°C SmA 170°C

isotropic) similar to compound 7c without the double bond was synthesized to compare the influence of the terminal double bond on the SmC phase. It exhibits the SmC phase between 80°C–160°C (ranging 80°C) which is narrower and higher than that of compound 7c 69.6°C–157.2°C (ranging 87.6°C). This result agrees with those which have been reported in the literature [14] in that the introduction of double bonds in the flexible part can stabilize the SmC phase. Overall, the existence of the N atom in the quinoline rigid core stabilizes (broaden and lower) the tilted SmC phase accordingly. From our results, it suggests that the N atom might have the potential to break the inversion centre of symmetry and to improve its polarity in these self-ordering mesogenic phases. Moreover, the length of the flexible part, which is related to the molecular stacking shape rather than the dipole moment, is critical to generate the tilted SmC phase, since increasing the alkoxy chain length from $n=6$ to $n=8$ does not change the dipolar property so much as to cause the major preference of the tilted organization. Thus, the formation of tilted smectogens is governed by both the steric shape and dipolar character of the molecule. Theoretical calculations (by MM3) of the conformational and dipolar effects on these molecules are under way. As well as liquid crystalline properties, non-linear optical (NLO) properties of compounds 7c and 12c have been investi-

Table 2. Phase transition temperatures and corresponding enthalpies (J g^{-1}) of the naphthalene system **12**.

Compound	Transition data										
	Cr	Cr'	Cr''	SmX ₃	SmX ₂	CrG	SmA	I	Cr	Cr'	Cr''
12a ($n=4$)	95.6°C(7.8)	106.1°C ^a	113.3°C	142.9°C(1.0)	146.0°C(0.7)	154.9°C(10.5)	180.4°C(15.1)				
	75.8°C(45.4)			137.8°C(1.1)	142.0°C(0.9)	151.4°C(11.3)	177.3°C(13.7)				
12b ($n=6$)	92.9°C(34.8)			143.2°C(1.3)	147.2°C(6.5)	174.1°C(4.9)					
	58.5°C(45.4)			139.9°C(0.7)	143.0°C(5.9)	158.1°C(4.7)					
12c ($n=8$)	51.3°C(0.6)	77.8°C(15.6)		141.5°C(0.8)	145.7°C(4.4)	167.8°C(0.4)					
	46.3°C(45.3)			137.4°C(0.9)	142.1°C(6.7)	165.5°C(0.6)					
12d ($n=10$)	54.5°C(0.6)	91.9°C ^a		141.7°C(19.4)	141.7°C(19.4)	164.0°C ^b					
		77.3°C ^a		138.3°C(19.7)	138.3°C(19.7)	158.1°C ^b					
12e ($n=12$)				93.6°C(36.5)	134.4°C(18.1)	156.0°C ^b					
				89.5°C(34.5)	131.3°C(17.4)	155.0°C ^b					

Cr', Cr'' = crystalline phases, SmX₂, SmX₃ = unidentified smectic phases. ^aOverlapped peaks (enthalpies could not be resolved). ^bThe enthalpy was too small to be detected by DSC and the phase transition temperature was assigned by POM.

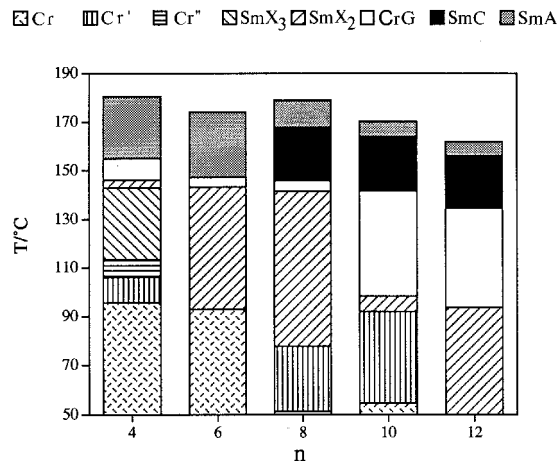


Figure 2. Phase transition temperatures of the system **12** (styryl-naphthalenes) versus the number of carbon atoms (n) in the alkyl chain (R).

gated by the Kurtz powder method published in our previous publication [15]. Compound **7c** has SHG intensity 7 times of quartz and half of **12c**. This NLO result reveals that both systems break the inversion centre of symmetry in their powder forms. However, the N atom does not enhance its powder SHG intensity as much as expected. Further EFISH (electric-field-induced second harmonic generation) measurements will give us more details.

In conclusion, this work presents a successful way in molecular design for generating the tilted SmC phase effectively through fusing benzene and pyridine rings. Compared with the naphthalene analogues the reduced symmetry and central transverse dipoles in the quinoline derivatives result in the stabilization of the SmC phase, and the flexible chain length also plays an important role. Eutectic FLC mixtures with broad range SmC smectogens can reduce phase transition temperatures and widen the range of the SmC phase, hence quinoline derivatives exhibiting one of the widest range of SmC phase are very useful as FLC basic materials.

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Supplementary information

Products **7a–7f** were identified as the required materials and judged to be pure by ^1H and ^{13}C NMR spectroscopy, and mass spectroscopy. Elementary analyses for C, H and N were also satisfactory. Selected data for **7a–7f** are as follows.

7a: ^1H NMR: δ (CDCl_3), 0.99 (t, 3H, Me), 1.25–2.06 (m, 20H, $10 \times \text{CH}_2$), 3.99 (t, 2H, OCH_2), 4.11 (t, 2H, OCH_2), 4.90–5.03 (m, 2H, $=\text{CH}_2$), 5.75–5.86 (m, 1H, $=\text{CH}$), 6.91 (d, 2H, $J=8.72\text{ Hz}$, $2 \times \text{Ar-H}$), 7.01–7.25 (m, 3H, $2 \times =\text{CH} + \text{Qu-H}$), 7.40 (d, 1H, $J=2.18\text{ Hz}$, Qu-H), 7.47 (d, 2H, $J=8.71\text{ Hz}$, $2 \times \text{Ar-H}$), 7.67 (d, 1H, $J=9.11\text{ Hz}$, Qu-H), 8.05 (s, 1H, Qu-H), 8.98 (s, 1H, Qu-H); ^{13}C NMR: δ (CDCl_3), 13.81, 19.22, 26.05, 28.89, 29.03, 29.09, 29.34, 29.40, 29.48, 31.29, 33.77, 67.77, 68.57, 107.66, 114.09, 114.81, 120.56, 122.87, 123.29, 127.79, 128.65, 129.46, 131.77, 139.16, 148.51, 149.15, 159.24, 160.13. Anal. Calc. for $\text{C}_{32}\text{H}_{41}\text{NO}_2$: C, 81.49; H,

8.76; N, 2.97 per cent. Found: C, 81.16; H, 8.69; N, 3.15 per cent. **7b**: ^1H NMR: δ (CDCl_3), 0.92 (t, 3 H, Me), 1.22–2.06 (m, 24 H, $12 \times \text{CH}_2$), 3.99 (t, 2 H, OCH_2), 4.13 (t, 2 H, OCH_2), 4.91–5.03 (m, 2 H, $=\text{CH}_2$), 5.75–5.89 (m, 1 H, $=\text{CH}$), 6.92 (d, 2 H, $J=8.69$ Hz, $2 \times \text{Ar-H}$), 7.02–7.25 (m, 3 H, $2 \times =\text{CH} + \text{Qu-H}$), 7.50–7.51 (m, 3 H, $2 \times \text{Ar-H} + \text{Qu-H}$), 7.71 (d, 1 H, $J=8.96$ Hz, Qu-H), 8.14 (s, 1 H, Qu-H), 8.99 (s, 1 H, Qu-H); ^{13}C NMR: δ (CDCl_3), 14.00, 22.59, 25.72, 26.02, 28.92, 29.04, 29.09, 29.23, 29.34, 29.39, 29.48, 30.87, 31.57, 33.77, 68.16, 68.53, 106.80, 114.09, 114.87, 121.10, 122.38, 123.49, 127.90, 128.76, 128.84, 129.32, 130.02, 132.68, 139.22, 148.09, 160.58. Anal. Calc. for $\text{C}_{34}\text{H}_{45}\text{NO}_2$: C, 81.72; H, 9.08; N, 2.80 per cent. Found: C, 81.65; H, 9.08; N, 3.00 per cent. **7c**: ^1H NMR: δ (CDCl_3), 0.89 (t, 3 H, Me), 1.23–2.08 (m, 28 H, $14 \times \text{CH}_2$), 3.98 (t, 2 H, OCH_2), 4.07 (t, 2 H, OCH_2), 4.91–5.03 (m, 2 H, $=\text{CH}_2$), 5.77–5.88 (m, 1 H, $=\text{CH}$), 6.90 (d, 2 H, $J=8.71$ Hz, $2 \times \text{Ar-H}$), 6.99–7.21 (m, 3 H, $2 \times =\text{CH} + \text{Qu-H}$), 7.39 (s, 1 H, Qu-H), 7.46 (d, 2 H, $J=8.67$ Hz, $2 \times \text{Ar-H}$), 7.65 (d, 1 H, $J=8.92$ Hz, Qu-H), 8.03 (s, 1 H, Qu-H), 8.99 (s, 1 H, Qu-H); ^{13}C NMR: δ (CDCl_3), 14.06, 22.63, 26.04, 28.91, 29.08, 29.25, 29.35, 29.48, 29.67, 31.80, 33.77, 68.10, 68.29, 107.82, 114.09, 114.79, 120.48, 122.93, 127.76, 128.65, 129.37, 129.51, 131.61, 139.16, 148.70, 149.32, 159.22, 160.05. Anal. Calc. for $\text{C}_{36}\text{H}_{49}\text{NO}_2$: C, 81.93; H, 9.36; N, 2.65 per cent. Found: C, 81.79; H, 9.41; N, 2.65 per cent. **7d**: ^1H NMR: δ (CDCl_3), 0.86–2.08 (m, 35 H, $\text{Me} + 16 \times \text{CH}_2$), 3.98 (t, 2 H, OCH_2), 4.07 (t, 2 H, OCH_2), 4.91–5.03 (m, 2 H, $=\text{CH}_2$), 5.73–5.86 (m, 1 H, $=\text{CH}$), 6.91 (d, 2 H, $J=8.72$ Hz, $2 \times \text{Ar-H}$), 7.02–7.26 (m, 3 H, $2 \times =\text{CH} + \text{Qu-H}$), 7.42 (s, 1 H, Qu-H), 7.48 (d, 2 H, $J=8.71$ Hz, $2 \times \text{Ar-H}$), 7.69 (d, 1 H, $J=9.12$ Hz, Qu-H), 8.08 (s, 1 H, Qu-H), 8.99 (s, 1 H, Qu-H); ^{13}C NMR: δ (CDCl_3), 14.08, 20.56, 22.68, 26.05, 28.92, 29.06, 29.12, 29.31, 29.40, 29.51, 29.56, 29.71, 31.91, 68.16, 68.38, 107.53, 114.12, 114.84, 120.71, 122.79, 127.81, 128.71, 129.48, 129.60, 131.96, 159.30. Anal. Calc. for $\text{C}_{38}\text{H}_{53}\text{NO}_2$: C, 82.11; H, 9.61; N, 2.52 per cent. Found: C, 82.03; H, 9.57; N, 2.56 per cent. **7e**: ^1H NMR: δ (CDCl_3), 0.88 (t, 3 H, Me), 1.27–2.08 (m, 36 H, $18 \times \text{CH}_2$), 3.97 (t, 2 H, OCH_2), 4.10 (t, 2 H, OCH_2), 4.91–5.02 (m, 2 H, $=\text{CH}_2$), 5.75–5.88 (m, 1 H, $=\text{CH}$), 6.90 (d, 2 H, $J=8.68$ Hz, $2 \times \text{Ar-H}$), 7.00–7.22 (m, 3 H, $2 \times =\text{CH} + \text{Qu-H}$), 7.46 (d, 2 H, $J=8.65$ Hz, $2 \times \text{Ar-H}$), 7.66 (d, 1 H, $J=9.11$ Hz, Qu-H), 8.04 (s, 1 H, Qu-H), 8.98 (s, 1 H, Qu-H); ^{13}C NMR: δ (CDCl_3), 14.06, 22.635, 26.03, 28.90, 29.07, 29.35, 29.48, 29.57, 31.89, 33.76, 68.10, 68.30, 107.70, 114.09, 114.80, 120.53, 122.87, 123.28, 127.77, 128.65, 129.44, 131.71, 139.16, 148.56, 149.19, 159.24, 160.10. Anal. Calc. for $\text{C}_{40}\text{H}_{57}\text{NO}_2$: C, 82.28; H, 9.84; N, 2.40 per cent. Found: C, 82.53; H, 9.73; N, 2.41 per cent. **7f**: ^1H NMR: δ (CDCl_3), 0.88 (t, 3 H, Me), 1.27–2.09 (m, 38 H, $19 \times \text{CH}_2$), 3.99 (t, 2 H, OCH_2), 4.12

(t, 2 H, OCH_2), 4.91–5.02 (m, 2 H, $=\text{CH}_2$), 5.75–5.89 (m, 1 H, $=\text{CH}$), 6.92 (d, 2 H, $J=8.68$ Hz, $2 \times \text{Ar-H}$), 7.00–7.22 (m, 3 H, $2 \times =\text{CH} + \text{Qu-H}$), 7.41 (d, 1 H, $J=2.06$ Hz, Qu-H), 7.46 (d, 2 H, $J=8.65$ Hz, $2 \times \text{Ar-H}$), 7.67 (d, 1 H, $J=9.11$ Hz, Qu-H), 8.04 (s, 1 H, Qu-H), 8.98 (s, 1 H, Qu-H). ^{13}C NMR: δ (CDCl_3), 14.10, 22.67, 26.03, 28.90, 29.07, 29.36, 29.65, 31.91, 33.78, 68.05, 68.22, 107.84, 114.10, 114.73, 120.38, 122.94, 123.20, 127.73, 128.62, 129.48, 131.49, 139.1, 149.20, 149.46, 159.14, 159.95. Anal. Calc. for $\text{C}_{42}\text{H}_{61}\text{NO}_2$: C, 82.43; H, 10.05; N, 2.29 per cent. Found: C, 82.13; H, 10.05; N, 2.31 per cent.

Products 12 a–12 e were identified as the required materials and judged to be pure by ^1H and ^{13}C NMR spectroscopy and mass spectroscopy. Elementary analyses for C, H and N were also satisfactory. Selected data for **12 a–12 e** are as follows.

12 a: ^1H NMR: δ (CDCl_3), 0.98 (t, 3 H, Me), 1.22–2.05 (m, 20 H, $10 \times \text{CH}_2$), 3.97 (t, 2 H, OCH_2), 4.05 (t, 2 H, OCH_2), 4.91–5.02 (m, 2 H, $=\text{CH}_2$), 5.74–5.88 (m, 1 H, $=\text{CH}$), 6.89 (d, 2 H, $J=8.63$ Hz, $2 \times \text{Ar-H}$), 7.04–7.16 (m, 4 H, $2 \times =\text{CH} + 2 \times \text{Ar-H}$), 7.45 (d, 2 H, $J=8.60$ Hz, $2 \times \text{Ar-H}$), 7.66–7.73 (m, 4 H, $4 \times \text{Ar-H}$); ^{13}C NMR: δ (CDCl_3), 13.83, 19.24, 26.10, 28.92, 29.10, 29.25, 29.40, 29.50, 29.68, 31.34, 33.78, 67.77, 68.05, 106.77, 114.10, 114.74, 119.25, 123.99, 125.88, 126.69, 127.03, 127.56, 129.09, 129.32, 130.18, 133.00, 134.03, 139.19, 157.18, 158.81. Anal. Calc. for $\text{C}_{33}\text{H}_{42}\text{O}_2$: 84.21; H, 8.99 per cent. Found: C, 84.01; H, 8.98 per cent. **12 b**: ^1H NMR: δ (CDCl_3), 0.92 (t, 3 H, Me), 1.23–2.06 (m, 24 H, $12 \times \text{CH}_2$), 3.98 (t, 2 H, OCH_2), 4.07 (t, 2 H, OCH_2), 4.91–5.02 (m, 2 H, $=\text{CH}_2$), 5.77–5.86 (m, 1 H, $=\text{CH}$), 6.90 (d, 2 H, $J=8.60$ Hz, $2 \times \text{Ar-H}$), 7.05–7.17 (m, 4 H, $2 \times =\text{CH} + 2 \times \text{Ar-H}$), 7.46 (d, 2 H, $J=8.70$ Hz, $2 \times \text{Ar-H}$), 7.67–7.74 (m, 4 H, $4 \times \text{Ar-H}$); ^{13}C NMR: δ (CDCl_3), 14.03, 22.61, 25.74, 26.12, 28.95, 29.12, 29.28, 29.42, 29.70, 31.61, 33.80, 68.12, 106.80, 114.12, 114.78, 119.28, 124.02, 125.89, 126.70, 127.04, 127.59, 129.33, 130.21, 133.03, 139.21, 157.20, 158.83. Anal. Calc. for $\text{C}_{35}\text{H}_{46}\text{O}_2$: C, 84.29; H, 9.30 per cent. Found: C, 84.03; H, 9.26 per cent. **12 c**: ^1H NMR: δ (CDCl_3), 0.89 (t, 3 H, Me), 1.26–2.08 (m, 28 H, $14 \times \text{CH}_2$), 3.98 (t, 2 H, OCH_2), 4.07 (t, 2 H, OCH_2), 4.91–5.03 (m, 2 H, $=\text{CH}_2$), 5.77–5.89 (m, 1 H, $=\text{CH}$), 6.90 (d, 2 H, $J=8.59$ Hz, $2 \times \text{Ar-H}$), 7.05–7.17 (m, 4 H, $2 \times =\text{CH} + 2 \times \text{Ar-H}$), 7.47 (d, 2 H, $J=8.70$ Hz, $2 \times \text{Ar-H}$), 7.67–7.74 (m, 4 H, $4 \times \text{Ar-H}$); ^{13}C NMR: δ (CDCl_3), 14.08, 22.65, 26.09, 28.93, 29.12, 29.26, 29.39, 29.51, 31.82, 33.79, 68.09, 106.78, 114.11, 114.77, 119.27, 124.01, 125.89, 126.70, 127.03, 127.57, 129.10, 129.32, 130.19, 133.02, 134.04, 139.22, 157.19, 158.82. Anal. Calc. for $\text{C}_{37}\text{H}_{50}\text{O}_2$: C, 84.36; H, 9.57 per cent. Found: C, 84.31; H, 9.58 per cent. **12 d**: ^1H NMR: δ (CDCl_3), 0.89 (t, 3 H, Me), 1.23–2.08 (m, 32 H, $16 \times \text{CH}_2$), 3.98 (t, 2 H, OCH_2), 4.07 (t, 2 H, OCH_2),

4.91–5.03 (m, 2 H, =CH₂), 5.77–5.86 (m, 1 H, =CH), 6.90 (d, 2 H, $J=8.72$ Hz, $2 \times$ Ar–H), 7.05–7.17 (m, 4 H, $2 \times$ =CH + $2 \times$ Ar–H), 7.46 (d, 2 H, $J=8.73$ Hz, $2 \times$ Ar–H), 7.64–7.74 (m, 4 H, $4 \times$ Ar–H); ¹³C NMR: δ (CDCl₃), 14.08, 22.68, 26.05, 26.10, 29.12, 29.31, 29.41, 29.57, 31.91, 33.80, 68.08, 68.13, 106.78, 114.12, 114.76, 119.28, 124.02, 125.89, 126.70, 127.03, 127.58, 129.32, 139.22, 158.82. Anal. Calc. for C₃₉H₅₄O₂: C, 84.42; H, 9.81 per cent. Found: C, 84.28; H, 9.66 per cent. **12e**: ¹H NMR: δ (CDCl₃), 0.86 (t, 3 H, Me), 1.11–2.08 (m, 36 H, $18 \times$ CH₂), 3.97 (t, 2 H, OCH₂), 4.06 (t, 2 H, OCH₂),

4.91–5.03 (m, 2 H, =CH₂), 5.75–5.86 (m, 1 H, =CH), 6.89 (d, 2 H, $J=8.62$ Hz, $2 \times$ Ar–H), 7.05–7.17 (m, 4 H, $2 \times$ =CH + $2 \times$ Ar–H), 7.46 (d, 2 H, $J=8.71$ Hz, $2 \times$ Ar–H), 7.66–7.74 (m, 4 H, $4 \times$ Ar–H); ¹³C NMR: δ (CDCl₃) 14.11, 22.70, 26.08, 28.95, 29.14, 29.42, 29.65, 31.93, 33.80, 68.11, 106.79, 114.12, 114.77, 119.27, 124.02, 125.89, 126.14, 126.70, 127.04, 127.36, 127.59, 129.12, 129.34, 130.20, 133.03, 134.06, 139.21, 157.20, 158.60, 158.84. Anal. Calc. for C₄₁H₅₈O₂: C, 84.48; H, 10.03 per cent. Found: C, 84.24; H, 10.20 per cent.