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Synthesis of liquid-crystalline 3,5-diarylisoxazolines

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The synthesis and mesomorphic properties of new liquid-crystalline 3,5-disubstituted isoxazolines are presented and discussed. These isoxazoline derivatives have been synthesised by reacting oximes with the appropriate 4-substituted styrene dipolarophiles in the presence of *N*-chlorosuccinimide and pyridine. The isoxazolines **3a–d** and **7a–g** prepared by this methodology are used as scaffolds for further molecular derivation through a molecular elongation strategy. The selected scaffolds **3a–b** and **7f–g** were transformed into liquid crystals (LCs) by the addition of an arylacetylene group at the C_3 or C_5 carbon atoms on the isoxazoline ring by a Sonogashira reaction. The relevant LC compounds **14a–c**, **15**, **16**, **17** and **18a–c** were synthesised in fair to good yields. The final compounds display both nematic and smectic A liquid-crystalline phases.

Keywords: isoxazoline liquid-crystalline; Sonogashira coupling; nitrile oxide [3+2] cycloaddition; mesomorphic behaviour

1. Introduction

The 1,3-dipolar cycloaddition of nitrile oxides to alkenes and alkynes has proved to be an extremely useful strategy for the preparation of isoxazoline and isoxazole rings [1–7]. These compounds serve as useful building blocks in the synthesis of various compounds, such as α,β-unsaturated ketones, 1,3-amino alcohols, β,γ-dihydroxy ketones and β-hydroxy ketones [6, 7].

Previous studies of isoxazoline derivatives showed that these compounds exhibit a wide spectrum of pharmacological activities [8–10] and are key precursors for different natural products [11, 12]. The isoxazoline was first used as structural molecular element of liquid crystals (LCs) by Daniel Vorlander nearly a century ago [13]. More recently, Bezborodov *et al.* [14] reported mesomorphic behaviour of a series of isoxazolines. Other isoxazoline derivatives exhibiting mesomorphic properties were also developed by a Russian group [15, 16]. We have recently reported that 3,5-disubstituted isoxazolines could easily be prepared using a [3+2] 1,3-dipolar cycloaddition reaction between nitrile oxides and alkenes [17–20]. As part of our continuing interest in the synthesis of new LCs containing the tolane structural unit in the 3- or 5-position of the isoxazoline ring, we explored the synthetic potential of bromoisoxazoline in the preparation of new LC materials. The initial strategy utilised **3a–b** and **7f–g**, advanced intermediates in our research program involving the preparation of novel isoxazoline LCs, as key components for the synthesis of mesogenic 3,5-diarylisoxazolines. By using a Sonogashira reaction, the third benzene ring was installed by connecting a triple bond to both sides of the isoxazoline ring. In this paper we describe the synthesis and the phase behaviour of a series of novel 3,5-disubstituted isoxazoline compounds containing naphthyl and/or phenylacetylene groups attached to the heterocyclic ring. The isoxazolines **14a–c** and **18a–c** are composed of an arylphenylacetylene group linked at the 3- and 5-positions of the isoxazoline ring, respectively. Isoxazolines **15, 16** and **17** are composed of an arylnaphthylacetylene group linked at the 5-position of the isoxazoline ring. Figure 1 shows the general structure of the new 3,5-diarylisoxazolines synthesised in this work.

2. Results and discussion

2.1 Synthesis

The synthesis of 3,5-diarylisoxazolines with non-symmetric phenyl groups was accomplished in a straightforward manner by the 1,3-dipolar cycloaddition of nitrile oxides to alkenes. The synthesis of the first series of 3,5-isoxazolines **3a–d** and **4b** is outlined in Scheme 1. Compound **1** was used as a starting material in the synthesis of some of the final compounds described in this work. The flexible alkyl chain was introduced by an alkylation reaction of **1** following a procedure described by Hsiue and Chen [21]. The oxime derivatives were obtained through a condensation reaction using hydroxylamine salts under basic conditions. The synthesis of cycloadducts **3a–d**

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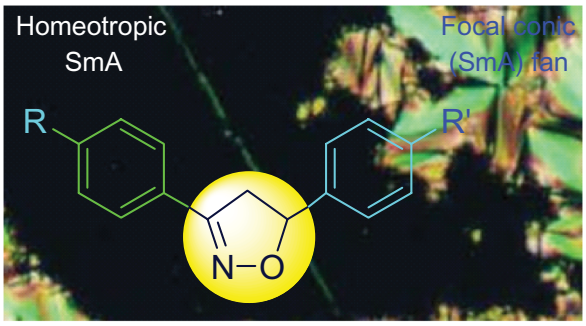
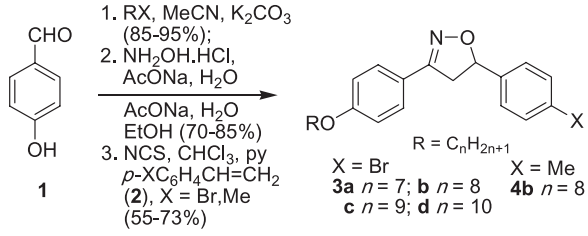


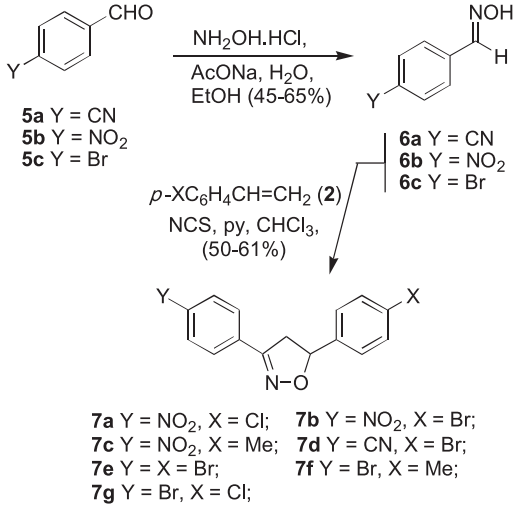
Figure 1. General chemical structure for 3,5-diaryl-isoxazolines.

and **4b** were achieved by the exposure of oximes to 4-substituted styrene **2** (X = Br and CH_3) through the [3+2] 1,3-dipolar cycloaddition reaction shown in Scheme 1.

The second set of cycloadduct 3,5-disubstituted isoxazolines **7a–g** was prepared according to Scheme 2. In this set, we chose the aldehydes **5a–c** containing a more polar group at the *para* position of the benzene ring and three different dipolarophiles **2** (X = Me, Br, Cl).



Scheme 1. Synthesis of the series of 3,5-diarylisoxazolines **3a–d** and **4b**.



Scheme 2. Preparation of cycloadduct isoxazolines **7a–g**.

The final step in Schemes 1 and 2 is a one-pot reaction and was carried out in the following sequence: (i) chlorination reaction of oximes with *N*-chlorosuccinimide (NCS) in chloroform solution to yield the arylhydroximinoyl chloride (**8**); (ii) addition of the dipolarophile; and (iii) dehydrohalogenation reaction by the addition of pyridine as the basic agent for *in situ* generation of the nitrile oxide (**9**) (see [22] for a review, [23] for the isolation of hydroximinoyl chloride in NCS/dimethylformamide (DMF), [24] for hypochlorite oxidation, [25] for oxidation using hypervalent iodine reagents and [26] for oxidising system using sodium bromide/organotin halide).

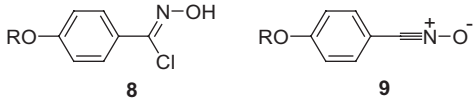


Chart 1 describes the chemical structures of the two acetylene derivatives that are necessary to elongate the isoxazolines **3a–b** and **7f–g** along both phenyl groups. The compounds **11a–d** and **13a–d** were synthesised in three steps by following the previously described method [27, 28] from *p*-bromophenol (**10**) or 6-bromo-2-naphthol (**12**) in three steps – alkylation reaction (85–95%), Sonogashira coupling [29–33] and deprotection reaction (71–81%) [34].

The synthesis of the final isoxazolines **14a–c** were reached by a second Sonogashira cross-coupling reaction between the precursor **7f** and three selected alkynes **11a**, **11b** and **11d** following the protocol of

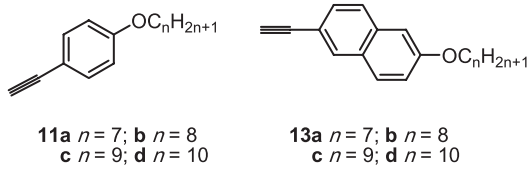
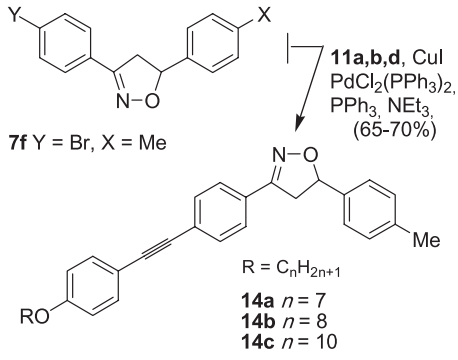


Chart 1. Terminal acetylenes **11a–d** and **13a–d.**

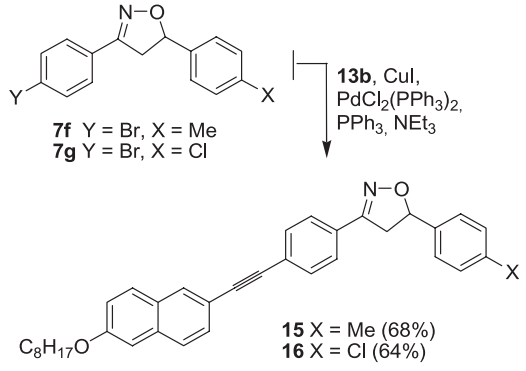


Scheme 3. Synthesis of selected isoxazolines **14a–c**.

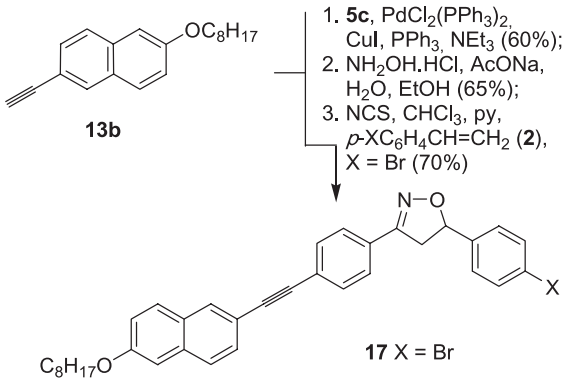
Wong *et al.* [33] according to Scheme 3. Compounds **14a–c** were obtained in moderate yields (65–70%).

Following the procedure described above, isoxazolines **7f** and **7g** were selected and extended by connecting 6-octyloxy-2-ethynylnaphthalene (**13b**) in the Sonogashira step (Scheme 4). As expected for **7g**, the regioselectivity observed in the alkynylation step is in accordance with previous reports as a result of the higher reactivity of the brominated position in relation to the chlorinated position [35–37]. The increase of the length-to-width ratio of the isoxazolines **15**, **16** and **17** favours the formation of stable liquid-crystalline phases [38] .

The synthesis of isoxazoline **17** was accomplished as outlined in Scheme 5. The triple bond inserted between the isoxazoline scaffold and the naphthyl group was added by changing the chemical event sequence. Thus, we perform the second Sonogashira reaction directly after the [3+2] 1,3-dipolar cycloaddition. Firstly, the alkyne **13b** was coupled with aldehyde **5c** under the Sonogashira condition and then the product was reacting with hydroxylamine to yield the corresponding oxime. Finally, ring closure by 1,3-dipolar cycloaddition in the presence of pyridine and NCS yielded the cycloadduct **17**.



Scheme 4. Synthesis of the isoxazolines **15** and **16**.

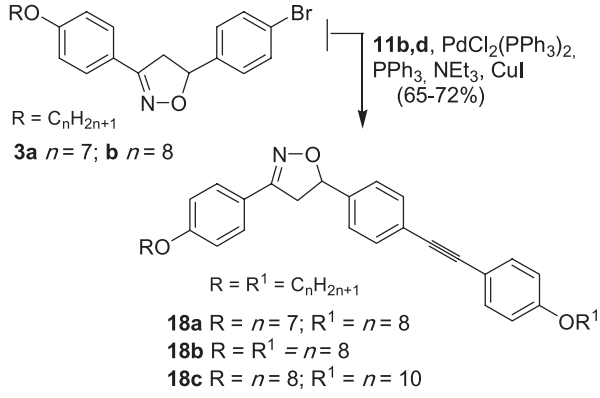


Scheme 5. Synthesis of the cycloadduct **17**.

The construction of the triple bond at the right-hand side of the isoxazoline allows us to prepare an elongated molecular framework with potential LC properties. Scheme 6 outlines the molecular construction of the target materials. The final isoxazolines **18a–c**, containing two flexible chains at the 4-positions in both phenyl rings, were prepared by a cross-coupling reaction of **3a–b** with **11b,d**. The conditions described by Wong *et al.* [33] (lower percentage of palladium(II) catalyst – 0.4 mol%) did not work very well when applied to the Pd-Cu cross-coupling reaction using isoxazolines **3a–b**. Under this condition, the starting material **3a–b** was recovered and no decomposition was detected. However, we have synthesised the final targets **18a–c** in good yield following the procedure described by Price *et al.* [39, 40]. In this case, the key to reaching the compounds is to use the '5,10,20 method' (5 mol% Pd:10 mol% Cu(I):20 mol% PPh_3) as described by the Tour report [39, 40].

2.2 *Thermal analysis of the 3,5-diarylisoxazolines*

The thermal properties of the new isoxazolines prepared in this work were analysed by polarised-light optical microscopy (POM) and differential scanning calorimetry (DSC). The initial 3,5-disubstituted isoxazolines **3a–d, 4b** and **7a–g** are crystalline solids. As expected they are non-mesogenic compounds. The relevant compounds to be considered for LC analysis are **14a–c**, **15**, **16**, **17** and **18a–c**. The observed transition temperatures and enthalpies are tabulated in Table 1. The compounds **14b–c** and **18a–c** exhibit two peaks attributed to solid-to-solid phase transitions. For example, the DSC measurement of **14b** exhibited two endothermic peaks at 100°C and 156°C at a heating rate of 10°C min^{-1}. Compound **14a** did not exhibit this Cr → Cr_1 transition. It seems that the peak at 100°C with small ΔH is due to the first crystal phase (Cr) to the second crystal phase (Cr_1)



Scheme 6. Molecular construction of the isoxazolines **18a–c**.

Table 1. Transition temperatures (°C) for the 3,5-diarylisoxazolines (second heating and cooling, 10°C min^{-1}) and enthalpy (kcal mol^{-1}).

Entry	Behaviour	Enthalpy (heating)
14a	Crystal ⇌ (155 / 134) ⇌ N (b) ⇌ Isotropic	Cr 6.9 N (-[b]) I
14b	Crystal ⇌ (100 / 85) ⇌ Crystal 1 ⇌ (156 / 136) ⇌ N (b) ⇌ Isotropic	Cr 0.3 Cr_1 9.2 N (-[b]) I
14c	Crystal ⇌ (96 / 82) ⇌ Crystal 1 ⇌ (154 / 133) ⇌ N (b) ⇌ Isotropic	Cr 0.4 Cr_1 8.8 N (-[b]) I
15	Crystal ⇌ (168 / 137) ⇌ Nematic ⇌ (194 / 191[a]) ⇌ Isotropic	Cr 4.2 N 0.1 I
16	Crystal ⇌ (176 / 150) ⇌ Smectic A ⇌ (212 / 204) ⇌ Isotropic	Cr 6.8 SmA 0.9 I
17	Crystal ⇌ (170 / 137) ⇌ Smectic A ⇌ (209 / 183) ⇌ Isotropic	Cr 5.9 SmA 1.0 I
18a	Crystal ⇌ (57 / 45) ⇌ Crystal 1 ⇌ (138 / 113) ⇌ N (b) ⇌ Isotropic	Cr 3.2 Cr_1 8.3 N (-[b]) I
18b	Crystal ⇌ (58 / 42) ⇌ Crystal 1 ⇌ (140 / 117) ⇌ N (b) ⇌ Isotropic	Cr 4.0 Cr_1 11. N (-[b]) I
18c	Crystal ⇌ (57 / 44) ⇌ Crystal 1 ⇌ (136 / 110) ⇌ N (b) ⇌ Isotropic	Cr 2.1 Cr_1 6.8 N (-[b]) I

[a] POM data. [b] The transition temperature and the enthalpy value were not measured because of the unstable monotropic nematic phase, see discussion in text. N = nematic phase.

transition, and the other peak at 156°C with a larger ΔH is attributed to the Cr_1 to isotropic phase transition. When the samples were placed between a clean untreated glass slide and a cover slip, and cooled at a rate of 10°C min^{-1}, the POM studies revealed an absence of the mesophase for compounds **14a–c** and **18a–c**. However, the visualisation of the texture is possible when the samples are heated to 10°C above the clearing temperature followed by instantaneous cooling at room temperature. Thus, from the isotropic melt to any temperature below the isotropic temperature (*Ti*), **14a–c** and **18a–c** developed schlieren and homeotropic textures, respectively. The texture inside the region under observation flashed very fast at the border and crystallised quickly. As an example, the nematic flashing micrograph (40×) displayed by compound **18b** on fast cooling (DSC trace inset) is shown in Figure 2. When the analysis was done without a cover slip, the samples developed the droplet texture and crystallised a few seconds later.

The mesophase range in Table 1 is very short for all of the compounds **14a–c** and **18a–c**. These values were not estimated due to their extremely short transition time (only enough to take a picture). This mesophase

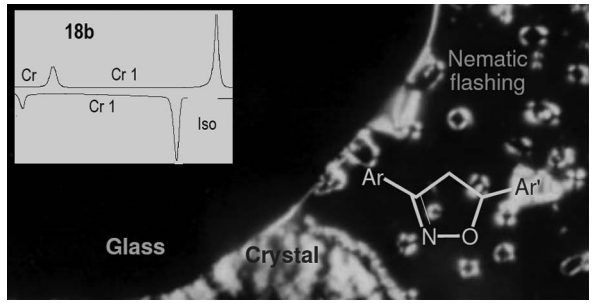


Figure 2. Nematic flashing micrograph (40×) displayed for compound **18b** on instantaneous cooling at room temperature (DSC trace inset).

was assigned as a nematic phase [41, 42]. Enantiotropic liquid-crystalline behaviour was found for compounds **15**, **16** and **17**. The LC **15** showed a nematic phase, while both **16** and **17** exhibited smectic A (SmA) phases. For instance, the DSC trace of **17** shows two endothermic peaks at 170°C and 209°C at a heating rate of 10°C min^{-1}. The two peaks were associated with Cr → SmA and SmA → I transitions, respectively, during the microscopy studies. On slow cooling of the sample

from the isotropic liquid it enters into the smectic phase with the formation of focal conic fans, which is typical of a smectic phase A. The thermal range of the mesophase, on heating, increases in the sequence **17** > **16** > **15** ($\Delta T = 39°C$ for **17;** $\Delta T = 36°C$ for **16**, $\Delta T = 26°C$ for **15**). This behaviour is a consequence of the efficiency of the terminal group in stabilising the LC phase. Thus, the order Br > Cl > CH_3 found in this work is in agreement with what is typically observed in low molecular mass LCs [17–20, 43, 44].

The mesomorphic behaviour of **14a–c**, **15**, **16**, **17** and **18a–c** can be understood in terms of the non-linearity of the isoxazoline ring coupled with the non-coplanarity of the two aryl groups located at C_3 and C_5 on the heterocyclic ring. To minimise this unfavourable disposition of the groups, the final central core must be as long as possible and possess high polarisability. In this way, the potential LC materials are reached through a molecular elongation strategy from the isoxazoline intermediates. This elongation builds off the rigid isoxazoline core to form a more polarisable and mesogenic one.

Specifically, the mesomorphic behaviour found in this work is due to the presence of the extended aromatic group adjacent to the isoxazoline ring. However, in some cases the molecular dimensions (length-to-breadth ratio) of the aromatic group are not sufficient to overcome the non-coplanarity of the aryl group connected on the isoxazoline ring. In this situation no mesophase or an unstable mesophase, i.e. monotropic behaviour, appears. By changing the phenyl group to a more polarisable naphthyl group at the C_3 carbon atom of the isoxazolinic system, a stable liquid-crystalline state becomes apparent. The appearance of a stable mesophase in **15**, **16** and **17** is due to the increased length-to-breadth ratio of the group bonded on the isoxazoline ring. The length-to-breadth ratio of the arylnaphthylacetylene group is bigger than the arylphenylacetylene group in **14a–c** and **18a–c**.

3. Conclusions

We have synthesised a set of 3,5-disubstituted isoxazoline derivatives by [3+2] 1,3-dipolar cycloaddition. These intermediates can be used in the preparation of liquid-crystalline materials. We selected some appropriated isoxazolines containing a halogen group at the *para* position of the aryl group to connect the triple bond through a Pd/Cu-catalysed coupling reaction. Under these conditions, series of LCs have been successfully synthesised in fair to good yields. The final LC compounds **14a–c** and **18a–c**, containing the phenylacetylene group at the C_3 or C_5 atom on the isoxazoline ring, exhibited a monotropic nematic phase. By changing from a phenyl to a naphthylacetylene group at the C_3 atom on the isoxazolinic system, the LC behaviour of the **15**, **16** and **17** changed to an enantiotropic phase. Compound **15** presented a nematic phase, whereas **16** and **17** exhibited SmA phases.

4. Experimental section

4.1 General

Nuclear magnetic resonance (NMR) spectra were obtained on Varian 200 and Varian Inova VNMRs 300 MHz instruments. Chemical shift values are given in parts per million (δ) and are referenced from tetramethylsilane (TMS). Infrared spectra were recorded on a Perkin-Elmer Spectrum One Fourier transform infrared (FTIR) Spectrometer Instrument, using NaCl plates in the case of solids and thin film supported between KBr plates in the case of liquids, and are reported as wavenumbers (cm^{-1}). Electron Ionization Mass Espectrometry (EI-MS) were measured at 70 eV on Gas chromatography-mass spectroscopy (CG-MS). The low-resolution mass spectra were obtained using a varisan Saturn 2100T CG-MS equipped with a 100 meter CP Sil Pona CB (0.25 mm) column. The initial column temperature was 50°C and was gradually ramped to 230°C (15°C min^{-1}). CHN analyses were performed on a Perkin-Elmer 2400 CHN Elemental Analyser. DSC analyses were performed on a DSC 2910 TA. The melting points and textures of the samples were evaluated on a Mettler Toledo FP82HT Hot Stage with an FP90 central processor in conjunction with an Olympus BX43 polarising microscope. 4-Hydroxybenzaldehyde, 1-bromoalkanes, hydroxylamine hydrochloride, 4-bromostyrene, 4-chlorostyrene, 4-methylstyrene, chloroform, ethanol, NCS, potassium hydroxide, 4-bromobenzaldehyde, sodium acetate, acetonitrile and toluene were used without further purification from Aldrich Co. Pyridine was distilled under reduced pressure. All other commercial solvents and reagents were used without further purification. All reactions involving Sonogashira couplings were performed in a one-neck round-bottom flask equipped with septum stoppers and charged with triethylamine (Et_3N), aromatic iodide and alkyne under an argon atmosphere for 30 min. Copper(I) iodide (CuI), triphenylphosphine (PPh_3) and *bis*-(triphenylphosphine)palladium(II) chloride [$PdCl_2(PPh_3)_2$] were then added.

4.1.1 Synthesis

4-*n*-Alkyloxybenzadehyde and the corresponding oximes were prepared from 4-hydroxybenzaldehyde (**1**) according to [17–20, 45, 46]. The general procedure for the preparation of 5-(4-bromophenyl)-3-[(4-*n*-alkyloxy)phenyl]-4,5-dihydroisoxazole **(3a-d)** is as follows.

To a solution of the *p*-X-bromostyrene (**2**) (2 mmol), chloroform (4 mL), *N*-bromosuccinimide (2 mmol) and pyridine (3 mmol) at 0°C under an argon atmosphere was added dropwise to the solution of oxime (1.7 mmol) in chloroform. The solution was heated to room temperature for 4 hours. The mixture was washed with HCl 1 M (3 × 20 mL), $NaHCO_3$ 10% (15 mL), water (15 mL) and brine (15 mL) and then dried with Na_2SO_4. After solvent evaporation the product was recrystallised from ethanol. Data for *n*-heptyl **3a.** Yield 0.61g, 73%; white solid; mp 119–120°C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.9 (t, 3H, CH_3, $J = 6.4$ Hz), 1.3 (m, 8H, $(CH_2)_4$), 1.8 (quint, 2H, C<u>H</u>$_2$CH$_2$O, $J = 6.6$ Hz), 3.2 (dd, 1H, C<u>H</u>HCH, $^2J_{gem} = 16,6$ Hz, $^3J_{trans} = 8.0$ Hz), 3.7 (dd,1H, CH<u>H</u>CH, $^2J_{gem} = 16.6$ Hz, $^3J_{cis} = 10.8$ Hz), 4.0 (t, 2H, CH_2O, $J = 6.6$ Hz), 5.6 (dd, 1H, CHHC<u>H</u>, $^3J_{cis} = 10.8$ Hz, $^3J_{trans} = 8$ Hz), 6.9 (d, 2H, Ar, $J = 8.8$ Hz), 7.2 (d, 2H, Ar, $J = 8.2$ Hz), 7.5 (d, 2H, Ar, $J = 8.4$ Hz), 7.6 (d, 2H, Ar, $J = 9.0$ Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.0, 22.6, 25.9, 29.0, 29.1, 31.7, 43.4, 68.1, 81.4, 114.6, 121.4, 121.9, 127.5, 128.2, 131.7, 140.1, 155.6, 160.7. IR ν_{max} (cm^{-1}): 2923, 1610, 1598 (C=N), 1249, 1013, 813 (nujol).

Data for *n*-octyl **3b**. Yield 0.94g, 55%; white solid; mp 116–117°C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.9 (t, 3H, CH_3, $J = 6.4$ Hz), 1.3 (m, 10H, $(CH_2)_5$), 1.8 (quint, 2H, C<u>H</u>$_2$CH$_2$O, $J = 6.5$ Hz), 3.2 (dd, 1H, C<u>H</u>HCH, $^2J_{gem} = 16.6$ Hz, $^3J_{trans} = 8.0$ Hz), 3.7 (dd, 1H, CH<u>H</u>CH, $^2J_{gem} = 16.4$ Hz, $^3J_{cis} = 10.8$ Hz), 4.0 (t, 2H, CH_2O, $J = 6.6$ Hz), 5.6 (dd, 1H, CHHC<u>H</u>, $^3J_{cis} = 10.8$ Hz, $^3J_{trans} = 8.0$), 6.9 (d, 2H, Ar, $J = 8.6$ Hz), 7.2 (d, 2H, Ar, $J = 8.4$ Hz), 7.5 (d, 2H, Ar, $J = 8.4$ Hz); 7.6 (d, 2H, Ar, $J = 8.6$ Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.1, 22.6, 25.9, 29.1, 29.2, 29.3, 31.8, 43.4, 68.1, 81.4, 114.6, 121.4, 121.9, 127.5, 128.2, 131.8, 140.2, 155.6, 160.7. IR ν_{max} (cm^{-1}): 2922, 1615, 1590, 1250, 1024), 821, (nujol).

Data for *n*-nonyl **3c**. Yield 0.62g, 70%; white solid; mp 114–115°C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.8 (t, 3H, CH_3, $J = 6.2$ Hz), 1.2 (m, 12H, $(CH_2)_6$), 1.7–1.8 (m, 2H, C<u>H</u>$_2$CH$_2$O), 3.2 (dd, 1H, C<u>H</u>HCH, $^2J_{gem} = 16.6$ Hz, $^3J_{trans} = 7.8$ Hz), 3.6 (dd, 1H, CH<u>H</u>CH, $^2J_{gem} = 16.4$ Hz, $^3J_{cis} = 10.7$ Hz), 4.0 (t, 2H, CH_2O, $J = 6.6$ Hz), 5.5 (dd, 1H, CHHC<u>H</u>, $^3J_{cis} = 10.8$ Hz, $^3J_{trans} = 8.0$ Hz), 6.8 (d, 2H, Ar, $J = 8.8$ Hz), 7.2 (d, 2H, Ar, $J = 8.6$ Hz), 7.4 (d, 2H, Ar, $J = 8.6$ Hz), 7.5 (d, 2H, Ar, $J = 8.8$ Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.1, 22.6, 25.9, 29.1, 29.2, 29.4, 29.5, 31.8, 43.4, 68.1, 81.4, 114.6, 121.4, 121.9, 127.5, 128.2, 131.8, 140.2, 155.6, 160.7. IR ν_{max} (cm^{-1}): 2926, 1610, 1595, 1248, 1025, 825 (nujol).

Data for *n*-decyl **3d**. Yield 0.91g, 66%; white solid; mp 111–112°C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.8 (m, 3H, CH_3), 1.9 (m, 14H, $(CH_2)_7$), 1.7–1.8 (m, 2H, C<u>H</u>$_2$CH$_2$O), 3.2 (m, 1H, C<u>H</u>HCH), 3.8 (m, 1H, CH<u>H</u>CH), 4.0 (t, 2H, CH_2O, $J = 6.6$ Hz), 5.5 (m, 1H, CHHC<u>H</u>), 6.8 (d, 2H, Ar, $J = 8.4$ Hz), 7.2 (d, 2H, Ar, $J = 8.0$ Hz), 7.4 (d, 2H, Ar, $J = 8.4$ Hz), 7.5 (d, 2H, Ar, $J = 8.2$ Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.1, 22.6, 25.1, 29.1, 29.3, 29.4, 29.5, 31.8, 43.4, 68.1, 81.4, 114.6, 121.4, 121.9, 127.5, 128.2, 131.7, 140.1, 155.6, 160.7 (one signal of aliphatic C are missing due to overlap). IR ν_{max} (cm^{-1}): 2925, 1608, 1590, 1248, 1030, 829 (nujol).

Data for 3-(4-*n*-octyloxyphenyl)-5-*p*-tolyl-4,5-dihydroisoxazole (**4b**). Yield 0.44g, 60%; yellow pale solid; mp 94–95°C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.8 (m, 3H, CH_3), 1.3 (m, 10H, $(CH_2)_5$), 1.8 (quint, 2H, C<u>H</u>$_2$CH$_2$O, $J = 6.5$ Hz), 2.3 (s, 3H, CH_3), 3.3 (dd, 1H, C<u>H</u>HCH, $^2J_{gem} = 16.6$ Hz, $^3J_{trans} = 7.8$ Hz), 3.7 (dd, 1H, CH<u>H</u>CH, $^2J_{gem} = 16.4$ Hz, $^3J_{cis} = 10.7$ Hz), 4.0 (t, 2H, CH_2O, $J = 6.4$ Hz), 5.6 (dd, 1H, CHHC<u>H</u>, $^3J_{cis} = 10.8$ Hz, $^3J_{trans} = 8.0$ Hz), 6.9 (d, 2H, Ar, $J = 8.8$ Hz), 7.2 (d, 2H, Ar, $J = 8.4$ Hz), 7.3 (d, 2H, Ar, $J = 8.6$ Hz), 7.6 (d, 2H, Ar, $J = 8.8$ Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.1, 21.1, 22.6, 25.9, 29.1, 29.2, 29.3, 31.8, 43.3, 68.0, 82.2, 114.5, 121.6, 125.8, 128.1, 129.3, 137.8, 137.9, 155.7, 160.6. IR ν_{max} (cm^{-1}): 2922, 1607, 1598, 1249, 907, 829 (nujol).

Data for 4-cyanobenzaldehyde oxime (**6a**). Yield 0.730g, 50%; white solid; mp 174–175°C. [thermal degradation after isotropic temperature – lit. [47] mp 174–176°C].^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.6 (d, 2H, Ar, $J = 8.4$ Hz), 7.7 (d, 2H, Ar, $J = 8.6$ Hz), 8.1 (s, 1H, HC=NOH), 11 (s, 1H, OH).

Data for 4-nitrobenzaldehyde oxime (**6b**). Yield 1.12g, 45%; yellow pale solid; mp 128–129°C [lit. [48] mp 132–133°C. ^{1}H NMR ($CDCl_3$, 200 Hz]: δ 7.7 (d, 2H, Ar, $J = 8.8$ Hz), 8.2 (d, 2H, Ar, $J = 8.8$ Hz), 8.4 (s, 1H, HC=NOH), 9.0 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 123.85, 127.29, 138.96, 146.8, 147.26. IR ν_{max} (cm^{-1}): 3289, 2930, 1640, 1599, 1534, 1456, 1347, 960, 841 (nujol).

Data for 4-bromobenzaldehyde oxime (**6c**). Yield 0.52g, 65%; white solid; mp 112–113°C [lit. [49] mp 110–112°C). ^{1}H NMR ($CDCl_3$, 200 Hz]: δ 7.5 (s, 4H, Ar), 8.0 (s, 1H, HC=NOH), 10.9 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 123.2, 128.0, 131.6, 132.3, 148.0. IR ν_{max} (cm^{-1}): 3290, 1635, 1599, 1534, 1347, 1013, 841 (nujol).

Data for 5-(4-chlorophenyl)-3-(4-nitrophenyl)-4,5-dihydroisoxazole (**7a**). Yield 0.62g, 51%; mp 141–142°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.3 (dd, 1H, C<u>H</u>HCH, $^2J_{gem} = 16.8$ Hz, $^3J_{trans} = 8.4$ Hz); 3.8 (dd, 1H, CH<u>H</u>CH, $^2J_{gem} = 16.8$ Hz, $^3J_{cis} = 11.4$ Hz); 5.7 (dd, 1H, CHHC<u>H</u>, $^3J_{cis} = 11.2$ Hz, $^3J_{trans} = 8.2$ Hz); 7.3 (d, 2H, Ar, $J = 8.7$ Hz); 7.4 (d, 2H, Ar, $J = 8.7$ Hz); 7.8 (d, 2H, Ar, $J = 8.7$ Hz); 8.2 (d, 2H, Ar, $J = 9.3$ Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 42.5, 82.8, 124.0, 127.2, 127.4, 129.0, 134.4, 135.3, 138.6, 148.5, 154.6.

IR ν_{max} (cm^{-1}): 2924, 1592, 1422, 1345, 1266, 1090, 1040, 869, 739 (nujol).

Data for 5-(4-bromophenyl)-3-(4-nitrophenyl)-4-5-dihydroisoxazole (**7b**). Yield 0.70g, 50%; mp 150–151°C. ^{1}H NMR ($CDCl_3$, 200 Hz): δ 3.2 (dd, 1H, C<u>H</u>HCH, $^2J_{gem}$ = 16.8 Hz, $^3J_{trans}$ = 8.4 Hz), 3.8 (dd, 1H, CH<u>H</u>CH, $^2J_{gem}$ = 16.8 Hz, $^3J_{cis}$ = 11.2 Hz), 5.7 (dd, 1H, CHHC<u>H</u>, $^3J_{cis}$ = 11.2 Hz, $^3J_{trans}$ = 8.6 Hz), 7.4 (d, 2H, Ar, J = 8.6 Hz), 7.6 (d, 2H, Ar, J = 9.2 Hz), 8.0 (d, 2H, Ar, J = 9.2 Hz), 8.2 (d, 2H, Ar, J = 8.2 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): 42.5, 82.8, 122.5, 124.0, 127.4, 127.5, 132.0, 135.2, 139.2, 148.5, 154.6. IR ν_{max} (cm^{-1}): 2922, 1592, 1422, 1345, 1266, 1072, 1011, 869, 739 (nujol).

Data for 3-(4-nitrophenyl)-5-*p*-tolyl-4,5-dihydroisoxazole (**7c**). Yield 0.69g, 61%; mp 122-–23°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.4 (s, 3H, $PhCH_3$), 3.3 (dd, 1H, C<u>H</u>HCH, $^2J_{gem}$ = 16.8 Hz, $^3J_{trans}$ = 8.4 Hz), 3.8 (dd, 1H, CH<u>H</u>CH, $^2J_{gem}$ = 16.6 Hz, $^3J_{cis}$ = 11.2 Hz), 5.8 (dd, 1H, CHHC<u>H</u>, $^3J_{cis}$ = 11.1 Hz, $^3J_{trans}$ = 8.7 Hz), 7.2 (d, 2H, Ar, J = 7.8 Hz), 7.3 (d, 2H, Ar, J = 8.1 Hz), 7.8 (d, 2H, Ar, J = 9.0 Hz), 8.3 (d, 2H, Ar, J = 8.7 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.1, 42.3, 83.6, 124.0, 125.8, 127.4, 129.5, 135.6, 137.0, 138.4, 148.4, 154.6. IR ν_{max} (cm^{-1}): 1523, 1422, 1346, 1266, 896, 739 (neat).

Data for 4-[5-(4-bromophenyl)-4,5-dihydroisoxazol-3-yl]benzonitrile (**7d**). Yield 0.78g, 60%; mp 115–116°C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 3.4 (dd, 1H, C<u>H</u>HCH, $^2J_{gem}$ = 16.8 Hz, $^3J_{trans}$ = 8.4 Hz), 3.9 (dd, 1H, CH<u>H</u>CH, $^2J_{gem}$ = 16.8 H, $^3J_{cis}$ = 11.2 Hz), 5.8 (dd, 1H, CHHC<u>H</u>, $^3J_{cis}$ = 11.2 Hz, $^3J_{trans}$ = 8.6 Hz), 7.3 (d, 2H, Ar, J = 8.6 Hz), 7.5 (d, 2H, Ar, J = 9.2 Hz), 7.9 (d, 2H, Ar, J = 9.2 Hz), 8.3 (d, 2H, Ar, J = 8.2 Hz). IR ν_{max} (cm^{-1}): 1607, 1516, 1257, 1175, 1039, 1014, 876 (neat).

Data for 3,5-*bis*-(4-bromophenyl)-4,5-dihydroisoxazole (**7e**). Yield 0.86g, 55%; mp 132–133°C. **[1]**H NMR ($CDCl_3$, 200 MHz): δ 3.1 (dd, 1H, C<u>H</u>HCH, $^2J_{gem}$ = 16.6 Hz, $^3J_{trans}$ = 8.3 Hz), 3.7 (dd, 1H, CH<u>H</u>CH, $^2J_{gem}$ = 16.8 Hz, $^3J_{cis}$ = 11 Hz), 5.6 (dd, 1H, CHHC<u>H</u>, $^3J_{cis}$ = 11.0 Hz, $^3J_{trans}$ = 8.3 Hz), 7.2 (d, 2H, Ar, J = 8.6 Hz), 7.4 (d, 2H, Ar, J = 8.6 Hz), 7.8 (d, 2H, Ar, J = 8.4 Hz), 8.3 (d, 2H, Ar, J = 8.6 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): 42.8, 82.0, 122.2, 124.5, 127.5, 128.0, 128.1, 131.9, 132.0, 139.6, 155.2. IR ν_{max} (cm^{-1}): 2923, 1460, 1376, 1070, 1005, 900, 874, 827, 721, 664 (nujol).

Data for 3-(4-bromophenyl)-5-*p*-tolyl-4,5-dihydroisoxazole (**7f**). Yield 0.67g, 53%; mp 142–143°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.3 (s, 3H, CH_3), 3.3 (dd, 1H, C<u>H</u>HCH, $^2J_{gem}$ = 16.5 Hz, $^3J_{trans}$ = 8.7 Hz), 3.7 (dd, 1H, CH<u>H</u>CH, $^2J_{gem}$ = 16.5 Hz, $^3J_{cis}$ = 10.8 Hz), 5.7 (dd, 1H, CHHC<u>H</u>, $^3J_{cis}$ = 10.8 Hz, $^3J_{trans}$ = 8.7 Hz), 7.2 (d, 2H, Ar, J = 8.1 Hz), 7.3 (d, 2H, Ar, J = 8.1 Hz), 7.5 (s, 4H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.1, 42.7, 82.9, 124.3, 125.8, 128.1, 128.5, 129.4, 131.9, 137.5, 138.2, 155.3. IR ν_{max} (cm^{-1}): 2922, 1459, 1397, 1376, 1071, 1006, 909, 830, 813 (nujol).

Data for 3-(4-bromophenyl)-5-(4-chlorophenyl)-4,5-dihydroisoxazole (**7g**). Yield 0.82g, 61%; mp 120–121°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.4 (dd, 1H, <u>CH</u>HCH, $^2J_{gem}$ = 16.6 Hz, $^3J_{trans}$ = 8.2 Hz), 3.8 (dd, 1H, CH<u>H</u>CH, $^2J_{gem}$ = 16.5 Hz, $^3J_{cis}$ = 11.2 Hz); 5.7 (dd, 1H, CHHC<u>H</u>, $^3J_{cis}$ = 11.2 Hz, $^3J_{trans}$ = 8.2 Hz), 7.3 (d, 2H, Ar, J = 8.6 Hz), 7.4 (d, 2H, Ar, J = 8.6 Hz), 7.8 (d, 2H, Ar, J = 8.7 Hz), 8.2 (d, 2H, Ar, J = 9.0 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 43.4, 82.4, 123.0, 127.4, 128.0, 130.0, 131.4, 132.3, 134.6, 143.6, 157.6.

1-Ethynyl-4-alkyloxybenzene. Compounds **11a–d** and **13a–d** were synthesised according to [27, 28].

Data for *n*-heptyl **11a**. Yield 1.64g, 76%; colourless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.9 (t, 3H, J = 6.4 Hz, CH_3), 1.3 (m, 8H, CH_2), 1.8 (quint, 2H, J = 6.9 Hz, CH_2), 3.0 (s, 1H, CH), 3.9 (t, 2H, J = 6.6 Hz, OCH_2), 6.8 (d, 2H, J = 8.8 Hz, Ar), 7.4 (d, 2H, J = 8.8 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.5, 133.5, 114.4, 113.8, 83.7, 75.6, 68.0, 31.9, 29.3, 26.0, 25.9, 22.6, 14.0.

Data for *n*-octyl **11b**. Yield 1.77g, 77%; colourless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.9 (t, 3H, J = 6.4 Hz, CH_3), 1.3 (m, 10H, CH_2), 1.8 (quint, 2H, J = 6.8 Hz, CH_2), 3.0 (s, 1H, CH), 3.9 (t, 2H, J = 6.6 Hz, OCH_2), 6.8 (d, 2H, J = 8.8 Hz, Ar), 7.4 (d, 2H, J = 8.8 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.5, 133.5, 114.4, 113.8, 83.7, 75.6, 68.0, 31.9, 29.5, 29.2, 26.0, 25.9, 22.6, 14.0.

Data for *n*-nonyl **11c**. Yield 1.73g, 71%; colourless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.9 (t, 3H, J = 6.4 Hz, CH_3), 1.3 (m, 12H, CH_2), 1.8 (quint, 2H, J = 6.8 Hz, CH_2), 3.0 (s, 1H, CH), 3.9 (t, 2H, J = 6.5 Hz, OCH_2), 6.8 (d, 2H, J = 8.8 Hz, Ar), 7.4 (d, 2H, J = 8.8 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.5, 133.5, 114.4, 113.8, 83.7, 75.6, 68.0, 31.9, 29.5, 29.3, 29.1, 26.0, 25.9, 22.6, 14.0.

Data for *n*-decyl **11d**. Yield 2.10g, 80%; colourless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.9 (t, 3H, J = 6.4 Hz, CH_3), 1.3 (m, 14H, CH_2), 1.8 (quint, 2H, J = 6.9 Hz CH_2), 3.0 (s, 1H, CH), 3.9 (t, 2H, J = 6.6 Hz, OCH_2), 6.8 (d, 2H, J = 8.8 Hz, Ar), 7.4 (d, 2H, J = 8.8 Hz, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.5, 133.5, 114.4, 113.8, 83.7, 75.6, 68.0, 31.9, 29.5, 29.3, 29.2, 29.1, 26.0, 25.9, 22.6, 14.0.

2-Alkyloxy-6-ethynylnaphthalene. Data for *n*-heptyl **13a**. Yield 2.02g, 76%; white solid. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.9 (t, 3H, J = 8.4 Hz, CH_3), 1.3 (m, 8H, CH_2), 1.7–1.8 (m, 2H, CH_2), 3.1 (s, 1H, CH), 4.1 (t, 2H, J = 6.6 Hz, OCH_2), 7.1 (d, 1H, J = 2.2 Hz, Ar), 7.2 (dd, 1H, J = 6.4 Hz, 2.6 Hz, Ar), 7.4 (dd, 1H, J = 6.8 Hz, 2.0 Hz, Ar), 7.6 (d, 1H, J = 9.4 Hz,

Ar), 7.7 (s, 1H, Ar); 7.8 (d, 1H, $J = 1.4$ Hz, Ar). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 158.3, 134.8, 132.4, 129.6, 129.4, 128.5, 127.1, 120.2, 117.1, 106.8, 84.6, 78.0, 76.8, 68.5, 32.3, 29.8, 26.5, 23.1, 14.6. IR ν_{max} (cm^{-1}): 3315, 2924, 2853, 2108, 1601, 1463, 1390, 1225, 1172, 874, 646 (nujol).

Data for *n*-octyl **13b**. Yield 2.27g, 81%; white solid. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.9 (t, 3H, $J = 8.4$ Hz, CH_3), 1.3 (m, 10H, CH_2), 1.7–1.8 (m, 2H, CH_2), 3.1 (s, 1H, CH), 4.1 (t, 2H, $J = 6.6$ Hz, OCH_2), 7.1 (d, 1H, $J =$ 2.2 Hz, Ar), 7.2 (dd, 1H, $J = 6.4$ Hz, 2.6 Hz, Ar), 7.4 (dd, 1H, $J = 6.8$ Hz, 2.0 Hz, Ar), 7.6 (d, 1H, $J = 9.4$ Hz, Ar), 7.7 (s, 1H, Ar), 7.8 (d, 1H, $J = 1.4$ Hz, Ar). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 158.3, 134.8, 132.4, 129.6, 129.4, 128.5, 127.1, 120.2, 117.1, 106.8, 84.6, 78.0, 76.8, 68.5, 32.3, 30.0, 29.7, 26.5, 23.1, 14.6. IR ν_{max} (cm^{-1}): 3315, 2924, 2853, 2108, 1601, 1463, 1390, 1225, 1172, 874, 646 (nujol).

Data for *n*-nonyl **13c**. Yield 2.12g, 72%; white solid. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.9 (t, 3H, $J =$ 8.4 Hz, CH_3), 1.3 (m, 12H, CH_2), 1.7–1.8 (m, 2H, CH_2), 3.1 (s, 1H, CH), 4.1 (t, 2H, $J = 6.6$ Hz, OCH_2), 7.1 (d, 1H, $J = 2.2$ Hz, Ar), 7.2 (dd, 1H, $J =$ 6.4 Hz, 2.6 Hz, Ar), 7.4 (dd, 1H, $J = 6.8$ Hz, 2.0 Hz, Ar), 7.6 (d, 1H, $J = 9.4$ Hz, Ar), 7.7 (s, 1H, Ar), 7.8 (d, 1H, $J = 1.4$ Hz, Ar). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 158.3, 134.8, 132.4, 129.6, 129.4, 128.5, 127.1, 120.2, 117.1, 106.8, 84.6, 78.0, 76.8, 68.5, 32.3, 30.0, 29.8, 29.6, 26.5, 23.1, 14.6. IR ν_{max} (cm^{-1}): 3315, 2924, 2853, 2108, 1601, 1463, 1390, 1225, 1172, 874, 646 (nujol).

Data for *n*-decyl **13d**. Yield 2.30g, 75%; white solid. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.9 (t, 3H, $J = 8.4$ Hz, CH_3), 1.3 (m, 14H, CH_2), 1.7–1.8 (m, 2H, CH_2), 3.1 (s, 1H, CH), 4.1 (t, 2H, $J = 6.6$ Hz, OCH_2), 7.1 (d, 1H, $J =$ 2.2 Hz, Ar), 7.2 (dd, 1H, $J = 6.4$ Hz, 2.6 Hz, Ar), 7.4 (dd, 1H, $J = 6.8$ Hz, 2.0 Hz, Ar), 7.6 (d, 1H, $J = 9.4$ Hz, Ar), 7.7 (s, 1H, Ar), 7.8 (d, 1H, $J = 1.4$ Hz, Ar). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 158.3, 134.8, 132.4, 129.6, 129.4, 128.5, 127.1, 120.2, 117.1, 106.8, 84.6, 78.0, 76.8, 68.5, 32.3, 30.0, 29.8, 29.7, 29.6, 26.5, 23.1, 14.6. IR ν_{max} (cm^{-1}): 3315, 2924, 2853, 2108, 1601, 1463, 1390, 1225, 1172, 874, 646 (nujol).

Data for 3-{4-[(4'-heptyloxyphenyl)ethynyl]phenyl}-5-(*p*-tolyl)-4,5-dihydroisoxazole (**14a**). Yield 0.12g, 65%; white solid; mp 155°C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.9–1.0 (m, 3H, CH_3), 1.4 (m, 8H, $(CH_2)_4$), 1.7–1.8 (m, 2H, C<u>H</u>$_2$CH$_2$O), 2.3 (s, 3H, $PhCH_3$), 3.3 (dd, 1H, C<u>H</u>HCH, $^2J_{gem} = 16.6$ Hz, $^3J_{trans} = 8.4$ Hz), 3.7 (dd, 1H, CH<u>H</u>CH, $^2J_{gem} = 16.6$ Hz, $^3J_{cis} = 11.0$ Hz), 3.9 (t, 2H, CH_2O, $J = 6.6$ Hz), 5.7 (dd, 1H, CHHC<u>H</u>, $^3J_{cis} = 10.8$ Hz, $^3J_{trans} = 8.6$ Hz), 6.8 (d, 2H, Ar, $J = 8.8$ Hz), 7.2 (d, 2H, Ar, $J = 8.2$ Hz), 7.3 (d, 2H, Ar, $J = 8.2$ Hz), 7.4 (d, 2H, Ar, $J = 8.8$ Hz), 7.5 (d, 2H, Ar, $J = 8.2$ Hz), 7.6 (d, 2H, Ar, $J = 8.4$ Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.1, 21.1, 22.6, 25.9, 29.0, 29.2, 31.7, 42.8, 68.0, 82.7, 87.6, 91.6, 114.5, 114.6, 125.3, 125.8, 126.5, 128.7, 129.4, 131.6, 133.6, 137.6, 138.0, 155.7, 159.4. EI-MS: *m*/*z* 452 [M + 1], 225, 119 (100), 91. Anal. calcd. for $C_{31}H_{33}NO_2$: C, 82.45; H, 7.37; N, 3.10. Found: C, 82.55; H, 7.43; N, 3.30. IR ν_{max} (cm^{-1}): 2920, 2851, 1606, 1598, 1519, 1249, 907, 841, 813, 666 (neat).

Data for 3-{4-[(4'-octyloxyphenyl)ethynyl]phenyl}-5-(*p*-tolyl)-4,5-dihydroisoxazole (**14b**). Yield 0.12g, 67%; white solid; mp 156°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.9 (t, 3H, CH_3), 1.3 (m, 10H, $(CH_2)_5$), 1.8 (quint, 2H, C<u>H</u>$_2$CH$_2$O, $J = 6.8$ Hz), 2.4 (s, 3H, $PhCH_3$), 3.3 (dd, 1H, C<u>H</u>HCH, $^2J_{gem} = 16.5$ Hz, $^3J_{trans} = 8.7$ Hz), 3.7(dd, 1H, CH<u>H</u>CH, $^2J_{gem} = 16.5$ Hz, $^3J_{cis} = 11.1$ Hz), 4.0 (t, 2H, CH_2O, $J = 6.6$ Hz), 5.7 (dd, 1H, CHHC<u>H</u>, $^3J_{cis} = 10.8$ Hz, $^3J_{trans} = 8.7$ Hz), 6.9 (d, 2H, Ar, $J = 8.7$ Hz), 7.2 (d, 2H, Ar, $J = 7.8$ Hz), 7.3 (d, 2H, Ar, $J = 7.8$ Hz), 7.4 (d, 2H, Ar, $J = 9.0$ Hz), 7.5 (d, 2H, Ar, $J = 8.7$ Hz), 7.7 (d, 2H, Ar, $J = 8.4$ Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1, 21.1, 22.6, 26.0, 29.0, 29.2, 29.3, 31.8, 42.8, 68.0, 82.8, 87.6, 91.6, 114.5, 114.6, 125.3, 125.9, 126.5, 128.7, 129.4, 131.6, 133.1, 137.6, 138.1, 155.7, 159.4. EI-MS: *m*/*z* 465 [M^+], 261, 225, 119 (100), 91. Anal. calcd. for $C_{32}H_{35}NO_2$: C, 82.54; H, 7.58; N, 3.01. Found: C, 82.68; H, 7.62; N, 3.23. IR ν_{max} (cm^{-1}): 2922, 2848, 1610, 1597, 1249, 907, 841, 813, 666 (neat).

Data for 3-{4-[(4'-decyloxyphenyl)ethynyl]phenyl}-5-(*p*-tolyl)-4,5-dihydroisoxazole (**14c**). Yield 0.14g, 70%; white solid; mp 154°C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.8–0.9 (m, 3H, CH_3), 1.8–2.0 (m, 16H, $(CH_2)_8$), 2.3 (s, 3H, $PhCH_3$), 3.3 (dd, 1H, C<u>H</u>HCH, $^2J_{gem} = 16.6$ Hz, $^3J_{trans} = 8.6$ Hz), 3.7 (dd, 1H, CH<u>H</u>CH, $^2J_{gem} = 16.6$ Hz, $^3J_{cis} = 11.0$ Hz), 3.9 (t, 2H, CH_2O, $J = 6.4$ Hz), 5.7 (dd, 1H, CHHC<u>H</u>, $^3J_{cis} =$ 11.0 Hz, $^3J_{trans} = 8.6$ Hz), 6.9 (d, 2H, Ar, $J = 8.8$ Hz), 7.2 (d, 2H, Ar, $J = 8.2$ Hz), 7.3 (d, 2H, Ar, $J = 8.0$ Hz), 7.4 (d, 2H, Ar, $J = 8.6$ Hz), 7.5 (d, 2H, Ar, $J = 8.2$ Hz), 7.6 (d, 2H, Ar, $J = 8.4$ Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.1, 21.1, 22.6, 25.9, 29.1, 29.3, 29.4, 29.5, 30.1, 31.8, 42.8, 68.0, 82.7, 87.6, 91.6, 114.5, 114.6, 125.3, 125.8, 126.5, 128.7, 129.4, 131.0, 133.3, 137.6, 138.0, 155.7, 159.4 (one signal missing due to accidental equivalence). EI-MS: *m*/*z* 493 [M^+], 225, 119 (100), 91. Anal. calcd. for $C_{34}H_{39}NO_2$: C, 82.72; H, 7.96; N, 2.84. Found: C, 82.78; H, 7.97; N, 2.90. IR ν_{max} (cm^{-1}): 2925, 2848, 1604, 1599, 1249, 907, 841, 813, 666 (neat).

Data for 3-{4-[2-(6-octyloxy)naphthalene-2-yl]ethynylphenyl}-5-(*p*-tolyl)-4,5-dihydroisoxazole (**15**). Yield: 0.11g, 68%; brown solid; mp 168°C. ^{1}H NMR ($CDCl_3$, 300 Hz) δ 0.8 (t, 3H, CH_3, $J =$ 7.2 Hz), 1.2–1.8 (m, 12H, $(CH_2)_6$), 2.4 (s, 3H, $PhCH_3$), 3.3 (dd, 1H, C<u>H</u>HCH, $^2J_{gem} = 16.2$ Hz, $^3J_{trans} = 8.2$ Hz), 3.7 (dd, 1H, CH<u>H</u>CH, $^2J_{gem} =$

16.2 Hz, $^3J_{cis}$ = 11.0 Hz), 3.9 (t, 2H, CH_2O, J = 6.4 Hz), 5.7 (dd, 1H, CHHC<u>H</u>, $^3J_{cis}$ = 11.0 Hz, $^3J_{trans}$ = 8.2 Hz), 7.1–7.4 (m, 6H, Ar), 7.7–7.9 (m, 7H, Ar), 8.0 (s, 1H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1, 21.2, 22.6, 26.0, 29.2, 29.3, 29.4, 31.8, 42.8, 68.0, 82.7, 88.6, 92.1, 106.4, 117.5, 119.7, 125.1, 125.8, 126.5, 126.8, 128.3, 128.7, 128.9, 129.3, 129.4, 131.4, 131.7, 134.3, 137.6, 138.0, 155.7, 157.9. EI-MS: *m/z* 516 [M + 1], 424, 402, 397, 386, 355, 129, 119 (100) and 91. Anal. calcd. for $C_{36}H_{37}NO_2$: C, 83.85; H, 7.23; N, 2.72. Found: C, 83.97; H, 7.42; N, 2.80. IR ν_{max} (cm^{-1}): 2920, 2851, 1607, 1599, 1517, 1286, 1250, 1107, 1025, 909, 841, 812, 720, 666 (neat).

Data for 5-(4-chlorophenyl)-3-{4-[2-(6-octyloxynaphthalen-2-yl)ethynyl]phenyl}-4,5-dihydroisoxazole (**16**). Yield 0.10g, 64%; pale yellow solid; mp 176°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.8 (m, 3H, CH_3), 1.2–1.6 (m, 10H, $(CH_2)_5$), 1.8–1.9 (m, 2H, C<u>H</u>$_2$$CH_2O$), 3.3 (dd, 1H, C<u>H</u>HCH, $^2J_{gem}$ = 16.0 Hz, $^3J_{trans}$ = 8.0 Hz), 3.7 (dd, 1H, CH<u>H</u>CH, $^2J_{gem}$ = 16.0 Hz, $^3J_{cis}$ = 10.8 Hz), 3.9 (t, 2H, CH_2O, J = 6.4 Hz), 5.7 (dd, 1H, CHHC<u>H</u>, $^3J_{cis}$ = 10.8 Hz, $^3J_{trans}$ = 8.2 Hz), 7.1–7.4 (m, 6H, Ar,), 7.7–7.9 (m, 7H, Ar), 8.0 (s, 1H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1, 22.7, 26.1, 29.1, 29.2, 29.3, 31.9, 43.0, 68.0, 82.0, 88.6, 92.3, 106.4, 117.5, 119.8, 125.4, 126.6, 126.8, 127.2, 128.3, 128.6, 128.8, 128.9, 129.3, 131.5, 131.8, 134.1, 134.3, 139.2, 155.6, 158.0. EI-MS: *m/z* 538 [M + 2], 536 [M^+], 424, 422, 406, 280, 255, 180, 139 (100), 113 and 111. Anal. calcd. for $C_{35}H_{34}ClNO_2$: C, 78.41; H, 6.39; N, 2.61. Found: C, 78.97; H, 7.37; N, 2.88. IR ν_{max} (cm^{-1}): 2923, 2854, 1625, 1605, 1495, 1469, 1411, 1392, 1259, 1212, 1171, 1095, 898, 858, 840, 824, 721, 666 (neat).

Data for 5-(4-bromophenyl)-3-{4-[2-(6-octyloxynaphthalen-2-yl)ethynyl]phenyl}-4,5-dihydroisoxazole (**17**). Yield 85.0 mg, 70%; pale yellow solid; mp 170°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.9 (m, 3H, CH_3), 1.2–1.6 (m, 10H, $(CH_2)_5$), 1.9 (m, 2H C<u>H</u>$_2$$CH_2O$), 3.3 (dd, 1H, C<u>H</u>HCH, $^2J_{gem}$ = 16.3 Hz, $^3J_{trans}$ = 8.2 Hz), 3.7 (dd, 1H, CH<u>H</u>CH, $^2J_{gem}$ = 16.4 Hz, $^3J_{cis}$ = 11.0 Hz), 3.9 (t, 2H, CH_2O, J = 6.4 Hz), 5.7 (dd, 1H, CHHC<u>H</u>, $^3J_{cis}$ = 10.9 Hz, $^3J_{trans}$ = 8.2 Hz), 7.2–7.4 (m, 6H, Ar,), 7.7–7.9 (m, 7H, Ar), 8.0 (s, 1H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.0, 22.6, 26.9, 29.1, 29.3, 29.4, 31.8, 42.9, 68.1, 82.1, 88.5, 92.2, 106.5, 117.4, 119.8, 125.8, 126.6, 126.8, 127.7, 128.3, 128.6, 128.7, 129.2, 129.7, 131.4, 131.8, 131.9, 134.3, 139.8, 155.6, 158.0. EI-MS: *m/z* 582 [M + 2], 580 [M^+], 466, 450, 424, 355, 255, 185 (100), 182, 154, 129 and 113. Anal. calcd. for $C_{35}H_{34}BrNO_2$: C, 72.41; H, 5.90; N, 2.41. Found: C, 73.21; H, 6.03; N, 2.74. IR ν_{max} (cm^{-1}): 2923, 2854, 1623, 1605, 1469, 1259, 1211, 1171, 1075, 1013, 897, 855, 840, 821, 665 (neat).

Data for 3-(4-heptyloxyphenyl)-5-{4-[4-(octyloxyphenyl)ethynylphenyl]}-4,5-dihydroisoxazole (**18a**). Yield 77.0 mg, 70%; pale yellow solid; mp 138°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.9–1.0 (m, 6H, $(CH_3)_2$), 1.4 (m, 18H, $(CH_2)_9$), 1.8 (m, 4H, (C<u>H</u>$_2$$CH_2O)_2$), 3.3 (dd, 1H, C<u>H</u>HCH, $^2J_{gem}$ = 16.5 Hz, $^3J_{trans}$ = 8.1 Hz), 3.7 (dd, 1H, CH<u>H</u>CH, $^2J_{gem}$ = 16.6 Hz, $^3J_{cis}$ = 10.9 Hz), 3.9 (m, 4H, $(CH_2O)_2$), 5.7 (dd, 1H, CHHC<u>H</u>, $^3J_{cis}$ = 10.8 Hz, $^3J_{trans}$ = 8.1 Hz), 6.8 (d, 2H, Ar, J = 8.7 Hz), 6.9 (d, 2H, Ar, J = 9.0 Hz), 7.4 (d, 2H, Ar, J = 8.1 Hz), 7.5 (d, 2H, Ar, J = 8.7 Hz), 7.6 (d, 2H, Ar, J = 8.1 Hz), 7.7 (d, 2H, Ar, J = 9.0 Hz). ^{13}C APT (attached proton test) NMR ($CDCl_3$, 75 MHz): δ 14.1 (2C), 22.5, 22.6, 25.9, 26.0, 28.9, 29.0–29.4 (5C), 31.7, 43.4, 68.0, 68.1, 81.8, 87.6, 89.8, 114.5, 114.6, 114.8, 121.5, 123.5, 125.8, 128.2, 131.7, 133.0, 140.7, 155.6, 159.2, 160.7. EI-MS: *m/z* 565 [M^+], 258, 218 (100). Anal. calcd. for $C_{38}H_{47}NO_3$: C, 80.67; H, 8.37; N, 2.48. Found: C, 80.88; H, 8.30; N, 2.75. IR ν_{max} (cm^{-1}): 2920, 2854, 1608, 1594, 1516, 1468, 1251, 1180, 1107, 898, 829, 719, 666 (neat).

Data for 3-(4-octyloxyphenyl)-5-{4-[4-(octyloxyphenyl)ethynylphenyl]}-4,5-dihydroisoxazole (**18b**). Yield 0.12 g, 65%; pale yellow solid; mp 140°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.9–1.0 (m, 6H, $(CH_3)_2$), 1.3 (m, 20H, $(CH_2)_{10}$), 1.7–1.8 (m, 4H, (C<u>H</u>$_2$$CH_2O)_2$), 3.3 (dd, 1H, C<u>H</u>HCH, $^2J_{gem}$ = 16.5 Hz, $^3J_{trans}$ = 8.1 Hz), 3.7 (dd, 1H, CH<u>H</u>CH, $^2J_{gem}$ = 16.5 Hz, $^3J_{cis}$ = 10.8 Hz), 4.0 (m, 4H, $(CH_2O)_2$), 5.7 (dd, 1H, CHHC<u>H</u>, $^3J_{cis}$ = 10.8 Hz, $^3J_{trans}$ = 8.1 Hz), 6.8 (d, 2H, Ar, J = 8.7 Hz), 6.9 (d, 2H, Ar, J = 8.7 Hz), 7.4 (d, 2H, Ar, J = 8.1 Hz), 7.5 (d, 2H, Ar, J = 9.0 Hz), 7.6 (d, 2H, Ar, J = 8.1 Hz), 7.7 (d, 2H, Ar, J = 8.7 Hz). ^{13}C APT NMR ($CDCl_3$, 75 MHz): δ 14.1 (2C), 22.3, 22.6, 25.9, 26.0, 28.9, 29.0–29.4 (6C), 31.8, 43.4, 68.0, 68.2, 81.9, 87.6, 89.9, 114.5, 114.6, 114.8, 121.6, 123.5, 125.8, 128.2, 131.7, 133.0, 140.7, 155.7, 159.3, 160.7. EI-MS: *m/z* 579 [M^+], 272, 232 (100). Anal. calcd. for $C_{39}H_{49}NO_3$: C, 80.79; H, 8.52; N, 2.42. Found: C, 80.91; H, 8.59; N, 2.50. IR ν_{max} (cm^{-1}): 2925, 2850, 1605, 1592, 1514, 1250, 1181, 1107, 898, 829, 720, 666 (neat).

Data for 3-(4-octyloxyphenyl)-5-{4-[4-(decyloxyphenyl)ethynylphenyl]}-4,5-dihydroisoxazole (**18c**). Yield 87.0mg, 72%; pale yellow solid; mp 136°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.8–0.9 (m, 6H, $(CH_3)_2$), 1.3 (m, 24H, $(CH_2)_{12}$), 1.8 (m, 4H, (C<u>H</u>$_2$$CH_2O)_2$), 3.3 (dd, 1H, C<u>H</u>HCH, $^2J_{gem}$ = 16.5 Hz, $^3J_{trans}$ = 8.1 Hz), 3.7 (dd, 1H, CH<u>H</u>CH, $^2J_{gem}$ = 16.5 Hz, $^3J_{cis}$ = 11.1 Hz), 3.97 (m, 4H, $(CH_2O)_2$), 5.7 (dd, 1H, CHHC<u>H</u>, $^3J_{cis}$ = 10.8 Hz, $^3J_{trans}$ = 8.1 Hz), 6.8 (d, 2H, Ar, J = 6.9 Hz), 6.9 (d, 2H, Ar, J = 6.6 Hz), 7.3 (d, 2H, Ar, J = 8.1 Hz), 7.4 (d, 2H, Ar, J = 8.7 Hz), 7.5 (d, 2H, Ar, J = 8.1 Hz), 7.6 (d, 2H, Ar, J = 8.7 Hz). ^{13}C APT NMR ($CDCl_3$, 75 MHz): δ 14.1 (2C), 22.8, 22.9, 26.2, 26.3, 29.3–29.6 (8C), 32.0, 32.1, 43.7, 68.3, 68.4, 82.2, 87.8, 90.2, 114.7, 114.9, 115.2, 121.8, 123.7, 126.1, 128.5,

132.0, 133.3, 141.0, 156.0, 159.5, 161.0. EI-MS: *m/z* 607 [M^+], 331, 258, 218 (100). Anal. calcd. for $C_{41}H_{53}NO_3$: C, 81.01; H, 8.79; N, 2.30. Found: C, 81.21; H, 8.83; N, 2.45. IR ν_{max} (cm^{-1}): 2922, 2852, 1603, 1591, 1516, 1468, 1251, 1180, 1108, 898, 829, 719, 666 (neat).

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