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The synthesis and high optical birefringence of nematogens incorporating 2,6-disubstituted naphthalenes and terminal cyano-substituents

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A range of nematogenic materials which incorporate a 2,6-disubstituted naphthyl moiety and a terminal cyano-substituent have been synthesized by using palladium-catalysed cross-coupling procedures involving arylboronic acids and alkynylzinc reagents with aryl iodides, bromides and trifluoromethanesulphonates (triflates). The compounds have very high nematic phase stability, but their melting points are also quite high. The birefringences were measured using an extrapolation technique and the values were found to be between 0·26 and 0·42.

1. Introduction

The commercial success of liquid crystals is, in the main, due to their suitability for use in display devices [1] which arises because of their ability to switch between orientations which have different optical properties (optical birefringence). Fascinating optical properties of another kind are also responsible for the use of cholesteric (chiral nematic) materials in thermography.

For incident light normal to the cell surface, the value of the birefringence is zero when the molecules are homeotropically aligned and is at its maximum when they are homogeneously aligned (the quoted value). The birefringence value is dependent on the polarizability of the molecules and their order parameter within the nematic phase [2]. Therefore, molecules which consist of high polarizability groups with high electron density (e.g. benzene rings, polyaromatic systems, ethylene and acetylene (ethynyl) linking groups and terminal cyano-substituents) will have a high optical anisotropy. Conversely, a low Δn is obtained for molecules which are deficient in these types of moieties and consist mainly of alicyclic rings.

The optical anisotropy of a liquid crystal mixture is important when considering its use in display devices. In the twisted nematic display, the plane of polarized light entering the nematic cell will be guided through 90° by the twist of the nematic material if the optical path difference (product of the birefringence (Δn) and the cell spacing (d)) is

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large compared with half the wavelength of the incident light. This condition is known as the Mauguin limit [3] and for optical path differences of $>1\,\mu$m, the light guiding properties of the cell are almost independent of cell thickness. However, when considering displays intended for wider angles of view (e.g. TFT active matrix twisted nematic displays), the cells are constructed with an optical path difference ($d \times \Delta\mathbf{n}$) of $\sim 0{\cdot}48\,\mu$m which is referred to as a first minimum device [4, 5].

The optical path difference is of particular importance for supertwisted nematic devices [6, 7] because the contrast results from an interference between the ordinary and the extraordinary rays and it is usually adjusted to be between 0·8 and 1·0 μm. However, in the OMI device [8], the optical path difference is reduced to between 0·4 and 0·6 μm so that the small wavelength dependence on transmission gives a neutral black and white appearance, but the low optical path difference results in poor brightness.

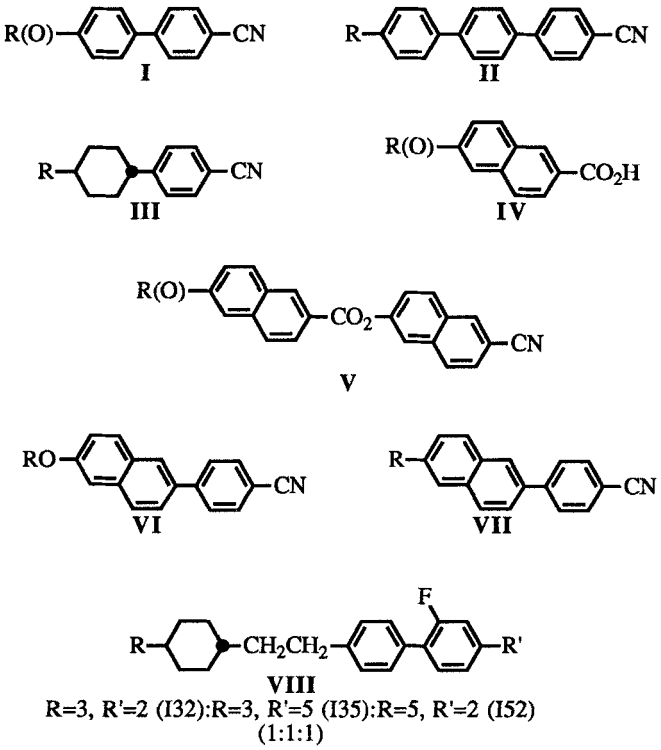
Electrically controlled birefringence (ECB) devices [9] require materials of high optical anisotropy with negative dielectric anisotropy. This device, given the recent availability of suitable negative dielectric anisotropy materials, offers much potential for large area multiplexed addressed displays. The optical path difference has to be large for good brightness, and since the cell spacing should be minimized for a fast response time, the optical anisotropy should be high.

The ferroelectric display device [10] uses a chiral smectic C (S_C^*) mixture and its bistable nature offers high multiplexability. The nature of the device also gives very fast (sub-microsecond) switching speeds. However, in order to maximize the contrast, a tilt angle of 22·5° is required and the optical path difference ($d \times \Delta\mathbf{n}$) must be close to 0·28 μm. If very thin cells are to be avoided, the optical anisotropy ($\Delta\mathbf{n}$) of the ferroelectric mixture, in contrast to ECB mixtures, must be very low; however, improvements in manufacturing now allow cells of 1·5 μm to be obtained.

This introduction outlines the importance of controlling the birefringence ($\Delta\mathbf{n}$) in various display devices in order to optimize the cell parameters such as response time, contrast ratio, brightness, viewing angle, suitable addressing methods, suitability for colour displays and ease of manufacturing. In typical cases, birefringence values range from $\sim 0{\cdot}06$ (low) to $\sim 0{\cdot}2$ (high). Here we discuss the synthesis and transition temperatures of materials which were designed to have extremely high values of birefringence with the intention of assessing their suitability either for devices requiring high birefringence or as additives for achieving specific birefringence values in mixtures.

Terminal cyano-substituted compounds are widely used in display devices because of their positive dielectric anisotropy. Compounds **I-III** [11–13] are of commercial importance and are ideally suited for nematic based display devices because of low melting points, moderate T_{NI} values, relatively low viscosities and suitably high dielectric anisotropies. The 2,6-disubstituted naphthalene unit has previously been used to produce nematic liquid crystals (see, for example, compounds **IV–VII**) [14–18] but this unit produces higher viscosity materials and such compounds offer no advantages for display devices. However, the compact, highly conjugated naphthyl moiety was expected to confer a high optical anisotropy upon the compounds and would therefore be a good unit for the synthesis of materials which have very high values of optical anisotropy.

Our initial work has been based around materials of a similar structure to compounds **VI** [16] and **VII** [17, 18], but some of these compounds also include ethynyl linking groups and ethynyl groups in the terminal chains to increase the polarizability along the molecular long axis.

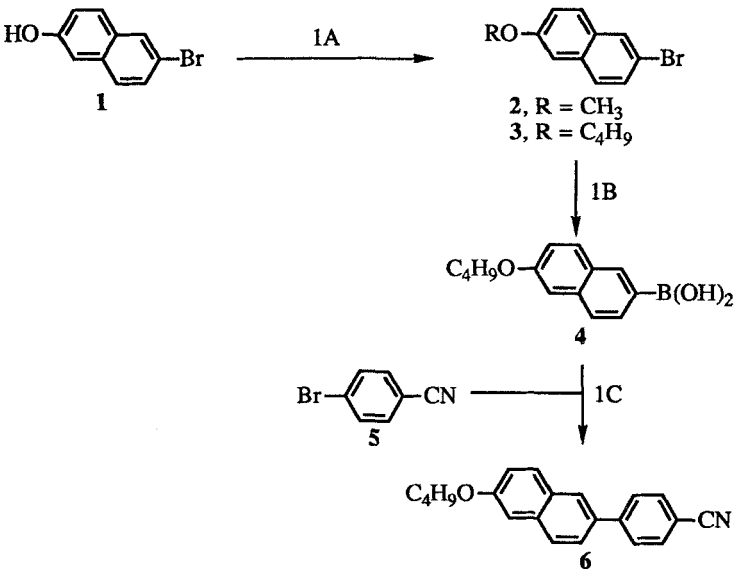


R=3, R'=2 (I32):R=3, R'=5 (I35):R=5, R'=2 (I52) (1:1:1)

2. Discussion of synthetic methods

The synthesis of such a wide range of materials with functional groups in a specified relationship, in order to produce the required physical properties, needed careful consideration [19, 20]. The majority of the syntheses involved the use of metallation techniques [19–24] to prepare arylboronic acids (which can be isolated and stored) and alkynylzinc chlorides (which must be used *in situ*) and the use of existing, and the developments of novel, palladium-catalysed cross-coupling procedures [19–29].

One difficulty in the synthesis of a general range of 2,6-disubstituted naphthalene compounds is the ready availability of only one suitable starting material (6-bromonaphth-2-ol, compound **1**). A good starting point in the synthesis of liquid crystal materials of high optical anisotropy which are based on 2,6-disubstituted naphthalenes is shown in scheme 1. *O*-Alkylation of compound **1** was followed by the conversion into a boronic acid derivative by the low temperature metallation of compound **3** followed by treatment with tri-isopropyl borate (or trimethyl borate) and the subsequent hydrolysis of the borate ester (*in situ*). It was found that a low temperature (−78°C) was required for the lithiation of compound **3** with *n*-butyllithium, to prevent the formation of 2-butoxy-6-butylnaphthalene, because the naphthyl anion appears to react readily with 1-bromobutane formed in the transmetallation. This boronic acid was subsequently coupled to 4-bromobenzonitrile (**5**) by an efficient palladium-catalysed cross-coupling reaction (which we have successfully used in the past to provide some interesting liquid crystal materials) [19–24] to give a good yield (79 per cent) of compound **6**. Compound **6** has previously been prepared, in 32 per cent yield, by Zollinger and co-workers [16] by using an arylzinc chloride palladium-catalysed cross-coupling procedure.



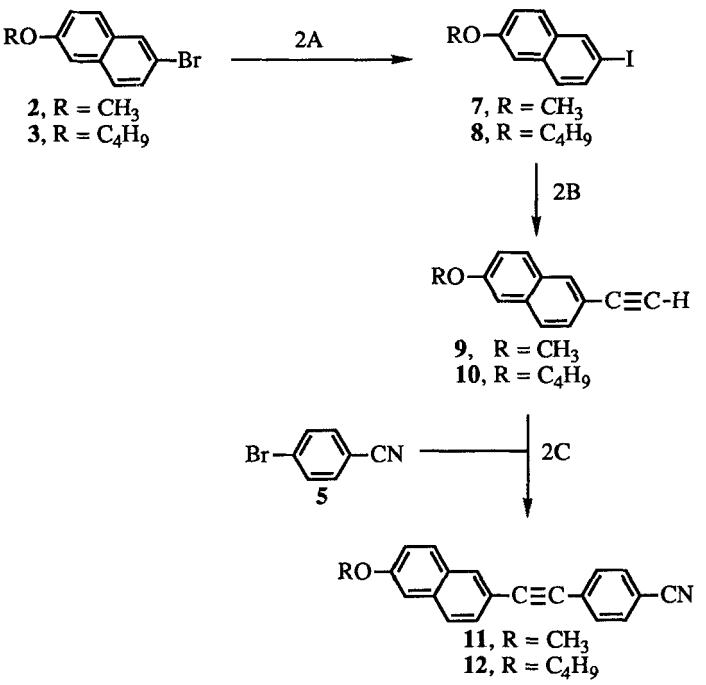
1A, Dimethyl sulphate, KOH, water (for $R = CH_3$) or C_4H_9Br, butanone, K_2CO_3 (for $R = C_4H_9$). 1B, (*i*) *n*BuLi, THF; (*ii*) $(^iPrO)_3B$, THF; (*iii*) 10 per cent HCl. 1C, $Pd(PPh_3)_4$, dimethoxyethane, $2MNa_2CO_3$.

Scheme 1.

The incorporation of an ethynyl linking group into 2,6-disubstituted naphthalenes was particularly desirable in our quest for nematogens of high optical anisotropy. Scheme 2 shows the synthesis of compounds **11** and **12** by a combination of two palladium-catalysed cross-coupling reactions.

There are several methods available for the preparation of aryl-substituted terminal ethynes (e.g. compounds **9**, **10**, **15** and **18**) and the one chosen will depend on the available starting materials; typically, methods from aryl methyl ketones (chlorination followed by dehydrochlorination) and aryl aldehydes (via the debromination of a β,β-dibromostyrene derivative) are used [30]. Palladium-catalysed cross-coupling methods, in the preparation of terminal ethynes, can be particularly efficient and are essential if starting from aryl halides or phenols (from which aryl triflates can be prepared). A popular method which we have used successfully several times for other work involves a palladium-catalysed cross-coupling procedure with trimethylsilylacetylene, a rather expensive reagent, which provides a protected terminal ethyne; deprotection is achieved in a quantitative yield using potassium hydroxide in methanol at room temperature [31]. Palladium-catalysed cross-coupling methods involving other protected acetylenes are also available using propargyl alcohol (prop-2-yn-1-ol) [32] and 2-methylbut-3-yn-2-ol [33, 34].

For this work, however, we decided to use a palladium-catalysed cross-coupling reaction which directly provided the desired terminal ethyne [25]. This involved the coupling of the zinc chloride derivative of lithium acetylide ethylenediamine complex to an appropriate aryl iodide or activated aryl bromide. Normal aryl bromides cannot be used (nor can normal triflate derivatives) since elevated temperatures are required in the reaction and this leads to the starting material coupling to the product as it is

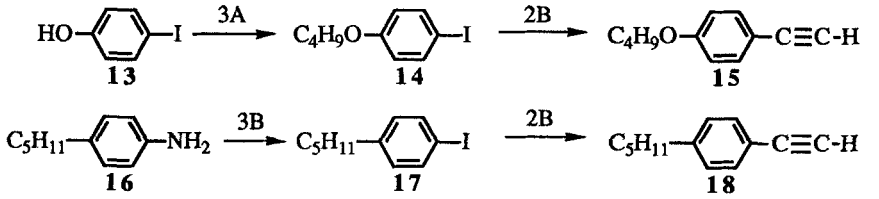


2A, KI, CuI, HMPA. 2B, (*i*) Lithium acetylide ethylenediamine complex, $ZnCl_2$, THF; (*ii*) $Pd(PPh_3)_4$. 2C, (*i*) *n*BuLi, THF; (*ii*) $ZnCl_2$, THF; (*iii*) $Pd(PPh_3)_4$, THF.

Scheme 2.

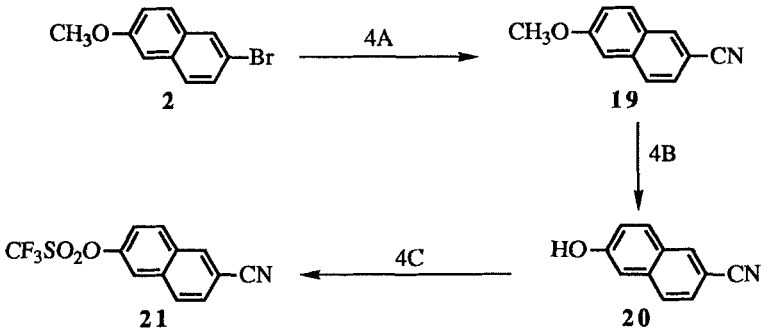
formed [19]. In the reactions of scheme 2, this may have been a problem because only aryl bromides were available, but an excellent method was found for the quantitative conversion of naphthyl bromides into naphthyl iodides [35, 36]. The main conclusion to be drawn from our work with this direct method of preparation of terminal ethynes is that purification by column chromatography (compounds **9** and **10**) is preferable to distillation (compounds **15** and **18**) which leads to partial polymerization resulting in low (~50 per cent) yields. Higher yields are guaranteed for those methods involving protecting groups [31–34] since the protected compound can be purified without such losses and the deprotected product can be used without the need for further purification. Palladium-catalysed cross-coupling reactions were then carried out involving the zinc chloride derivative of the terminal alkyne (**9** and **10**) with an appropriate aryl halide [25] or triflate [27] (for example, 4-bromobenzonitrile (**5**) in scheme 2). This method produced excellent yields of materials which were quite easily purified. We find this method preferable to the direct coupling procedure (palladium catalyst and copper (I) iodide in triethylamine) [37] which, although circumventing the need for the alkynylzinc chloride derivative, gives products which can be difficult to purify [38].

Scheme 3 shows the preparation of two simple phenyl-substituted terminal alkynes (compounds **15** and **18**). The appropriate aryl iodides were more easily obtained than for the naphthyl analogues and the palladium-catalysed cross-coupling reactions were as used previously (see scheme 2) [25].



3A, C_4H_9Br, butanone, K_2CO_3. 3B, (*i*) $NaNO_2$, 36 per cent HCl; (*ii*) KI.

Scheme 3.



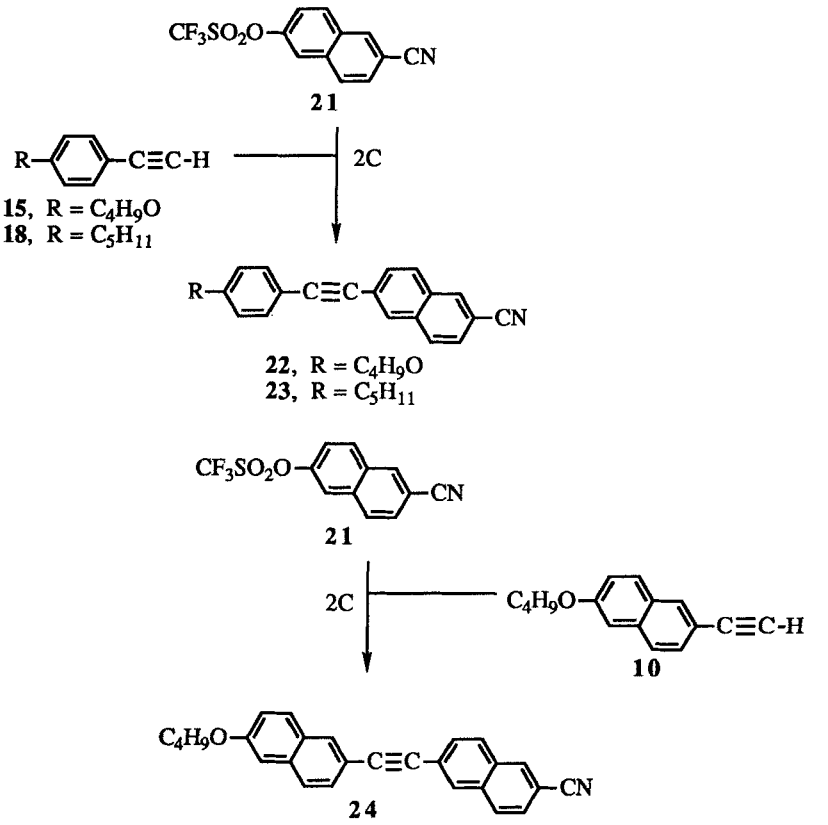
4A, CuCN, DMF. 4B, BBr_3, CH_2Cl_2. 4C, *N*-Phenyltriflamide, Et_3N, CH_2Cl_2.

Scheme 4.

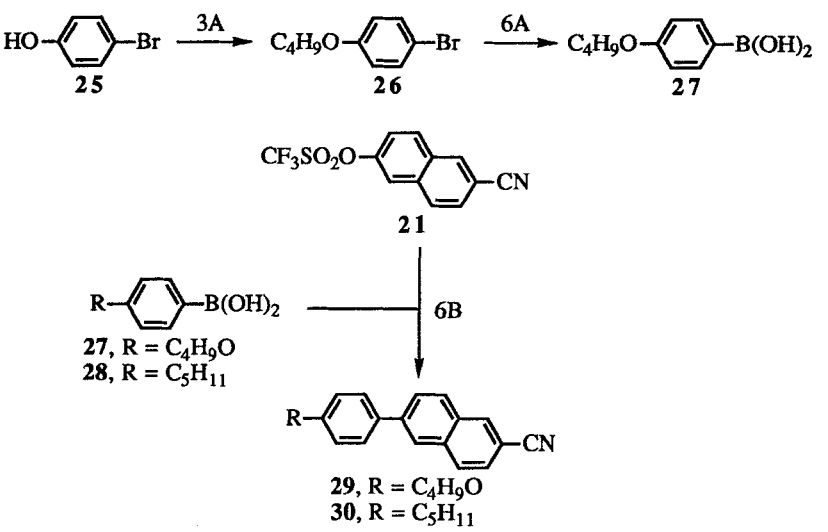
In order to place the cyano-substituent in the naphthyl ring and still use 6-bromonaphth-2-ol (compound **1**) as the basic starting material (scheme 4), we investigated the use of aryl trifluoromethanesulphonates (triflates) in palladium-catalysed cross-coupling reactions to alkynylzinc chlorides (scheme 5). Compound **1** was methylated (see scheme 1) and the bromo-substituent was converted into a cyano-substituent in good yield by a common procedure (copper (I) cyanide in DMF) followed by a quantitative demethylation (boron tribromide in dry dichloromethane) [39] to give compound **20**. This was converted into the triflate derivative (compound **21**) in excellent yield using *N*-phenyl triflamide (scheme 4) [40]. However, this reagent is rather expensive and equally good results have been obtained using trifluoromethanesulphonic acid anhydride in pyridine at 0°C [41].

Scheme 5 shows how 6-cyanonaphth-2-yl triflate (compound **21**) has been used in palladium-catalysed cross-coupling reactions [27] with the alkynylzinc chloride derivatives of some terminal alkynes. The usual conditions are used (heated under reflux), except that lithium chloride is added to facilitate the transmetallation step of the mechanism (not strictly necessary since lithium chloride is formed in the preparation of the alkynylzinc chloride derivative) and excellent yields of compounds **22**, **23** and **24** were obtained.

In view of the success of the alkynylzinc chloride couplings [27] to aryl triflate **21** in scheme 5, It was expected that aryl triflates (e.g. compound **21**) would also couple to arylboronic acids and this was found to be the case (see scheme 6). Again the usual conditions for boronic acid couplings were used, except that lithium chloride was

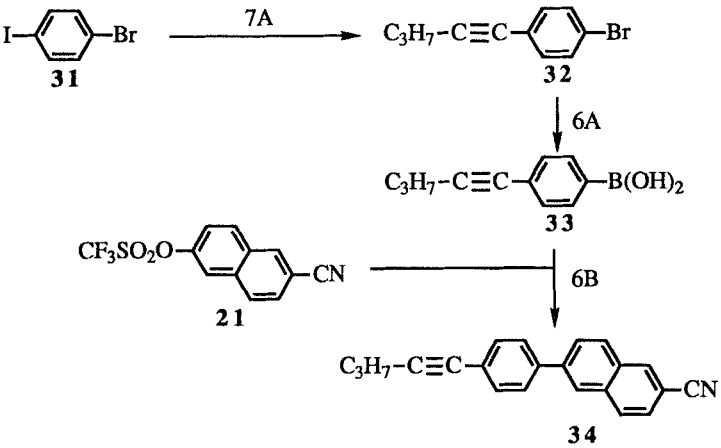


Scheme 5.



6A, (*i*) Mg, THF; (*ii*) $(^{i}PrO)_3B$, THF; (*iii*) 10 per cent HCl. 6B, $Pd(PPh_3)_4$, LiCl, dimethoxyethane, Na_2CO_3.

Scheme 6.



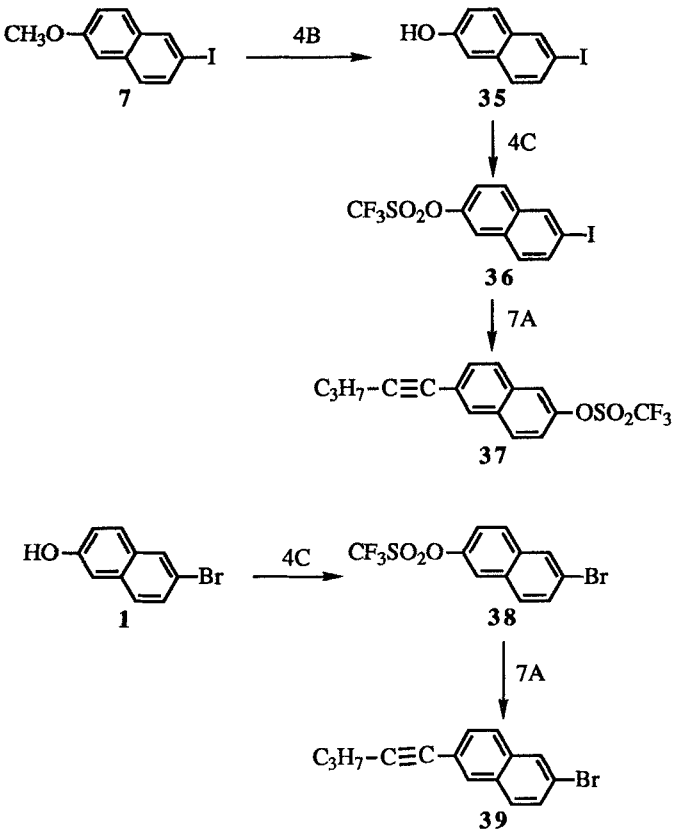
7A, (*i*) Pent-1-yne, *n*BuLi, THF; (*ii*) $ZnCl_2$, THF; (*iii*) $Pd(PPh_3)_4$.

Scheme 7.

added to the reaction mixture, and excellent yields of compounds **29** and **30** were obtained. Although an obvious development in palladium-catalysed cross-coupling reactions, at the time of our work this procedure was novel; however, two recent synthetic publications have now reported this type of coupling procedure [42, 43].

Scheme 7 shows how both the alkynylzinc chloride and the arylboronic acid palladium-catalysed cross-coupling reactions can be combined to provide a liquid crystalline material which has an ethynyl moiety as part of the terminal chain. The former method [22, 25, 27] was used to provide a vital intermediate (compound **32**); when carried out at room temperature the pent-1-ynylzinc chloride coupled exclusively at the iodo site. Subsequently the bromo site was lithiated at low temperature (−78°C) and converted into a boronic acid and the latter coupling method [19–24, 26] produced the final compound (**34**) in an excellent yield.

Scheme 8 shows another part of our development work on selective palladium-catalysed cross-coupling reactions which are very important in successful synthetic liquid crystal research. Initially, compounds **36** and **38**, with two suitable leaving groups, were prepared. The synthesis of both compounds was initially from 6-bromonaphth-2-ol (compound **1**) and, although the iodo-substituted triflate required more synthetic steps, the overall yields were high in both cases. The palladium-catalysed cross-coupling reaction of compound **36** with pent-1-ynylzinc chloride was carried out at room temperature and, since triflate derivatives require elevated temperatures for coupling, a 100 per cent selectivity was achieved at the iodo site giving compound **37** in excellent (92 per cent) yield. It had been noticed in some of our work that, in isolation, coupling to aryl triflate derivatives appears to take slightly longer than for similar aryl bromides (reflux conditions being used in each case). It was something of a surprise therefore to find that in the selective coupling of pent-1-ynylzinc chloride with compound **38**, the majority of the coupling occurred at the triflate site (~2 : 1). A complete reaction was obtained and no double-coupled material was observed (GC/MS analysis), and the two products were very easily isolated by column chromatography to give compound **39** in 57 per cent yield. Of course, separation is unnecessary if the next step in a reaction sequence is just another palladium-catalysed cross-coupling reaction, as both sites will react to provide the

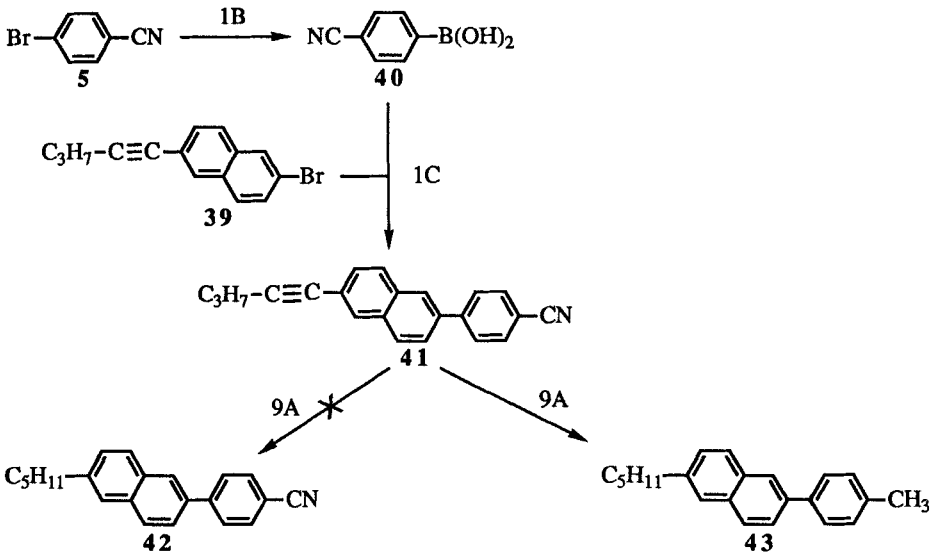


Scheme 8.

same product. However, the isolated bromo-substituted compound (**39**) is valuable because it can, if necessary, be converted into a boronic acid (essential when the other species to be coupled cannot be converted into a boronic acid).

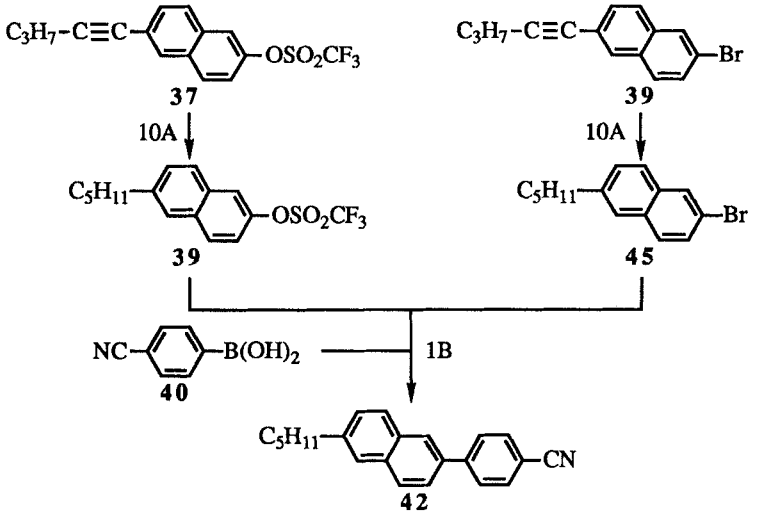
Scheme 9 shows the use of compound **39** (prepared by a selective coupling reaction) in the preparation, in excellent yield, of compound **41**. This involved the preparation of 4-cyanophenylboronic acid (compound **40**) which required the use of a very low temperature ($-100°C$) to prevent the *n*-butyllithium reacting with the nitrile group. It was expected that the known [17, 18] compound **42** could be prepared by hydrogenation of compound **41**. However, this was unsuccessful and reduction of the nitrile group occurred with subsequent hydrogenolysis of the resulting amine to give a good yield of 2-(4-methylphenyl)-6-pentylnaphthalene (compound **43**).

Although the preparation of compound **42** has been reported twice, [17, 18] we wanted to achieve its preparation by selective palladium-catalysed cross-coupling reactions. In order to avoid the problems shown in scheme 9, it was decided to hydrogenate compounds **37** and **39** prior to the coupling reaction. Scheme 10 shows the hydrogenation of the two pent-1-ynylnaphthalenes to give hydrogenated products (compounds **44** and **45**) in poor yields. The poor yields were due to removal of the triflate group (compound **44**) and the bromo-substituent (compound **45**) in the hydrogenations and in both cases a 5:4 ratio of desired product to hydrogenolysed



9A, 5 per cent Pd/C, THF, ethanol.

Scheme 9.



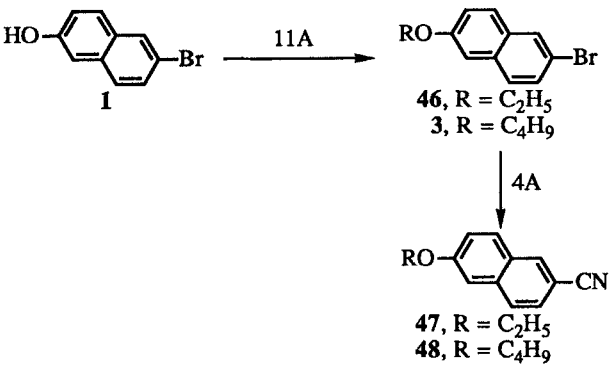
10A, PtO_2, THF, ethanol.

Scheme 10.

material was obtained (GC/MS analysis). This was surprising, especially in the case of compound **45**, because the use of platinum (IV) oxide as a catalyst for hydrogenation in simple phenyl bromide systems ensures the retention of the bromo-substituent [22]. However, the crude mixtures were used in a palladium-catalysed cross-coupling reaction with arylboronic acid **40** without any problems to provide compound **42** in good yield (both compound **44** and **45** were used in the coupling because of the low content of actual starting material in each impure mixture).

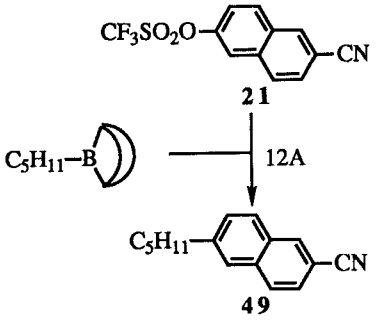
Scheme 11 shows the preparation of two simple 2-cyano-6-alkoxynaphthalenes (compounds **47** and **48**). Although not expected to be liquid crystalline, these materials were thought to be potentially useful dopants for nematic mixtures because of their high electron density structures. The synthetic methods used were similar to those used previously (*O*-alkylations followed by cyanations).

Scheme 12 shows the synthesis of an alkyl analogue (compound **49**) of compounds **47** and **48**, by use of a different type of palladium-catalysed cross-coupling procedure [29]. This method involved the preparation (*in situ*) of 9-pentyl-9-borabicyclo[3.3.1]nonane (9-pentyl-9-BBN) by the interaction of 9-BBN and pent-1-ene. This was followed by the addition of potassium phosphate (K_3PO_4), the triflate (compound **21**) and the palladium catalyst. The palladium catalyst used for this



11A, RBr, K_2CO_3, butanone.

Scheme 11.



12A, (*i*) Pent-1-ene, 9-BBN, THF; (*ii*) $PdCl_2$(dppf), THF.

Scheme 12.

reaction was dichloro[1,1′-*bis*-(diphenylphosphino)ferrocene]palladium(II) [44] and the solvent used was THF. However, tetrakis(triphenylphosphine)palladium(0) [45] can be used in conjunction with a higher boiling solvent (dioxane). Coupling procedures involving organometallic reagents based on alkyl chains are not usually successful because of β-elimination [44]. Although we were able to obtain an excellent yield of compound **49** by this interesting method, 2-cyanonaphthalene was present as an impurity and we were not able to improve the purity beyond 95 per cent (HPLC).

3. Discussion of transition temperatures

The 2,6-disubstituted naphthalene system was shown by Gray and Jones [14] (1954) to be conducive to liquid crystal phase formation for the series of 6-alkoxy-2-naphthoic acids (structure **IV**). 2,6-Disubstituted naphthalene compounds with a terminal cyano-substituent (structure **V**) were reported by Coates and Gray [15] (1976). In 1981, Zollinger and co-workers [16] reported the synthesis and transition temperatures of 2-alkoxy-6-(4-cyanophenyl)naphthalenes (structure **VI**, including compound **6**) and in 1983, Zollinger and co-workers [17], and Gray and Lacey [18] reported the synthesis and transition temperatures of 2-alkyl-6-(4-cyanophenyl)naphthalenes (structure **VII**, including compound **42**).

All of the compounds reported here have a terminal cyano-substituent and include a 2,6-disubstituted naphthalene moiety in their structure. With the exception of the short, single fused ring compounds (**47**–**49**), all of the compounds were expected to exhibit the nematic phase and to have high ($\sim$100–200°C) T_{NI} values. However, as is often the case with liquid crystalline materials, the melting points were less predictable but, based on the evidence of the transition temperatures of the two literature compounds (**6** and **42**), they were expected to be higher than was desired.

Compounds **6**, **42**, **29** and **30** (table 1) have directly linked naphthyl-aryl structures and all have high T_{NI} values. The T_{NI} values for the butoxy-substituted compounds (**6** and **29**) are higher than those for their pentyl-substituted analogues (**42** and **30**) by 32·5 and 37·5°C, respectively; such differences are expected and are typical of the differences in the T_{NI} values of alkyl and alkoxy compounds seen in other systems. Melting points too are higher for the butoxy-substituted compounds by similar amounts (41·0 and 30·5°C), but these differences are more difficult to rationalize than T_{NI} values and are often variable. Perhaps more interesting is the effect of the cyano-substituent being in the naphthyl moiety (compounds **29** and **30**) rather than the phenyl ring (compounds **6** and **42**). The T_{NI} values for those compounds with the cyano-substituent in the naphthyl moiety (compounds **29** and **30**) are slightly higher (8·5 and 3·5°C) than those of compounds **6** and **42** (cyano-substituent in the phenyl ring), respectively. This rather modest difference in T_{NI} values is probably because of the higher degree of polarizability created by having the cyano-substituent in conjugation with the compact, fused-ring naphthyl moiety. More significant, from a practical point of view, are the reduced melting points of compounds **29** and **30** (98·5 and 68·0°C) when compared with those for compounds **6** and **42**, the former melting points are at least approaching reasonable levels.

Table 2 shows five compounds which are similar to those shown in table 1, except that the structures include an ethynyl (acetylene) linking group between the naphthyl and phenyl rings. The introduction of this conjugating linking group was expected to increase T_{NI} values and was also expected to increase melting points. The melting point of the methoxy-substituted compound (**11**) is much higher than for the comparable butoxy-substituted homologue (**12**), a typical effect of a methoxy-substituent. The

Table 1. Transition temperatures (°C) for some terminal cyano-substituted phenylnaphthalenes ((Compounds **6, 42, 29** and **30**).

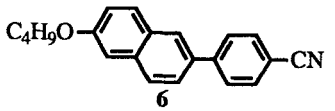
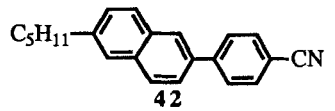
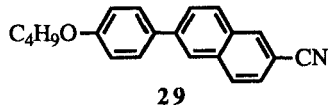
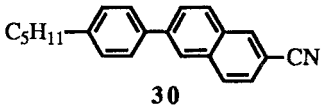
Compound	Transition temperatures/°C					Birefringence
 **6**	C	125·0	N	159·0	I	0·33
	C	125·0	N	159·0	I[16]	
 **42**	C	84·0	N	126·5	I	0·30
	C	85·5	N	128·0	I[17, 18]	
 **29**	C	98·5	N	167·5	I	0·33
 **30**	C	68·0	N	130·0	I	0·30

Table 2. Transition temperatures (°C) for some terminal cyano-substituted naphthylethynes (Compounds **11**, **12**, and **22–24**).

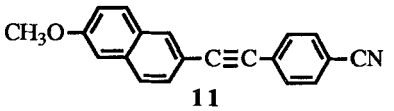
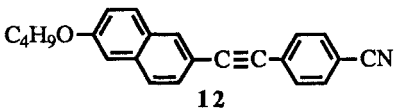
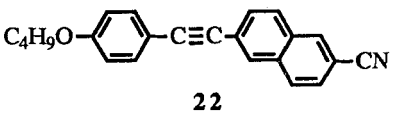
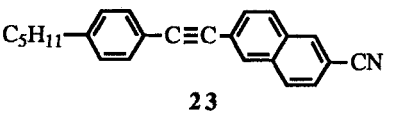
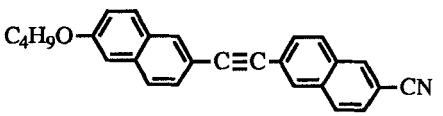
Compound	Transition temperatures/°C					Birefringence
 **11**	C	144·0	N	210·0	I	—
 **12**	C	106·5 111·5	N	186·0	I	0·42
 **22**	C	110·5 120·5	N	186·0	I	0·41
 **23**	C	79·5	N	164·0	I	0·40
 **24**	C	185·0	N	270·5	I	—

Table 3. Transition temperatures (°C) for some terminal cyano-substituted phenylnaphthalenes with terminal ethynyl-substituents (Compounds **41** and **34**).

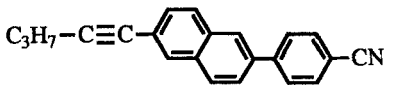
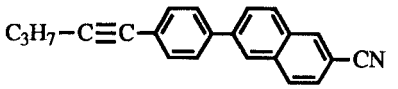
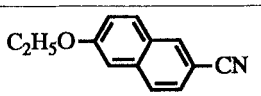
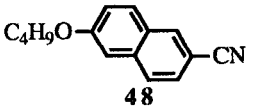
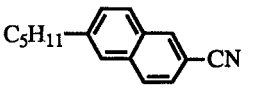
Compound	Transition temperatures/°C					Birefringence
 **41**	C	109·0	N	166·0	I	0·43
 **34**	C	113·0	N	193·0	I	0·41

Table 4. Transition temperatures (°C) for some terminal cyano-substituted naphthalenes (Compounds **47–49**).

Compound	Transition temperatures/°C					Birefringence
 **47**	C	100·5	[N	−11·0]	I	0·29
 **48**	C	73·0	[N	−16·0]	I	0·26
 **49**	C	40·0	[N	−20·0]	I	—

double naphthyl compound (**24**) has a high clearing point, and although it is expected to have a high optical anisotropy, its high melting point is too serious a disadvantage to make it a useful compound. In some of the other examples, melting points are not as high as expected and compound **12** actually has a lower melting point than the directly linked analogue (compound **6**) by 13·5°C. The T_{NI} values of the ethynyl linked compounds are, as expected, all very high and for comparable systems (compounds **12**, **22** and **23**) they are higher (by 27·0, 28·0 and 34·0°C, respectively) than the values for the directly linked compounds (**6**, **29** and **30**). The usual difference (31·5°C) is seen in the T_{NI} value between the butoxy-substituted compound (**22**) and the pentyl-substituted compound (**23**). A higher T_{NI} value (9·5°C) is again seen when the cyano-substituent is in the naphthyl moiety (compound **22**) than for the case where it is in a phenyl ring (compound **12**). Attention is drawn to the dual melting point values for compounds **12** and **22**. In both cases, the compounds melted to the nematic phase at the lower values and when heated slowly the compounds crystallized and then melted to the nematic phase again at the higher values quoted in table 2 (optical microscopy). This behaviour was not revealed when a faster rate of heating was used or when the compounds were subjected to DSC analysis.

Table 3 shows two compounds which contain an ethynyl moiety in the terminal chain (compounds **41** and **34**). Compound **34**, in comparison with compound **23** (the most similar compound with an ethynyl moiety linking the rings), shows an even higher T_{NI} value (by 29·0°C), but the melting point of compound **34** is also higher (by 33·5°C). As seen with similar comparisons for compounds in tables 1 and 2, a higher T_{NI} value arises for compound **34** (cyano-substituent in the naphthyl moiety) than for compound **41**, although in this case the difference (27·0°C) is much greater.

Table 4 shows that the simple non-mesomorphic naphthyl-substituted compounds (**47–49**) have only slightly lower melting points (by ~25°C) than comparable two ring compounds (**29** and **30**). Virtual T_{NI} values have been measured for compounds (**47–49**) by extrapolation of T_{NI} values of mixtures in a commercial nematic host (E7) and these are very low (−11·0, −16·0 and −20·0°C, respectively).

4. Discussion of birefringence values

Generally, the extrapolated values of the birefringence for these cyano-substituted naphthalene compounds are very high, between 0·26 and 0·42. The values can be compared with those of compounds of type **I** and **II**, which are 0·25 and 0·14, respectively (where $R = C_5H_{11}$) measured in the same manner as described in § 6.

Table 1 shows two pairs of isomeric cyano-substituted naphthalene materials (compounds **6**, **29** and **42**, **30**) and the birefringence is identical with either the cyano-substituent in the phenyl or naphthyl moieties. However, the butoxy-substituent confers a higher birefringence (0·33) when compared with the pentyl-substituted analogue (0·30) which is caused by the additional electron density on the ether oxygen. Table 2 shows the effect on birefringence of incorporating a tolane linkage in the centre of the core. Here the results show little difference between the butoxy-substituted materials (**12** and **22**) and the pentyl-substituted material (**23**), but the effect of the tolane has been quite dramatic in raising birefringence to 0·42 for compound **12**. This rise was, of course, expected and is explained by the high density of polarizable electrons associated with the tolane linkage in conjugation with both phenyl and naphthyl moieties. The high melting compound (**24**) was completely insoluble in the nematic host, but would be expected to have a high birefringence.

The effect on birefringence of transferring the tolane linkage to the end of the molecule was investigated by the preparation of compounds **41** and **34** (birefringences of 0·43 and 0·41 respectively). The values (table 3) are nearly identical to those for compounds with the tolane linkage in the centre of the molecule and again, there is little significant difference between the values where the cyano-substituent is in the naphthyl or in the phenyl moieties.

The birefringence of small, compact cyano-substituted naphthalenes (table 4) was investigated (compounds **47** and **48**). As was expected, these materials were non-mesomorphic, but they were expected to be useful dopants for increased birefringence of mixtures. The birefringence values were higher than expected considering the small length to breadth ratio, and the high value (0·29) for the ethoxy-substituted material shows the dilution effect of the longer butoxy chain in reducing birefringence (0·26).

5. Conclusions

(1) Various types of palladium-catalysed cross-coupling reactions have been used in the preparation of some known and novel liquid crystalline materials. These methods proved to be very efficient and offer a high degree of flexibility in all areas of organic synthesis.

(2) Selective palladium-catalysed cross-coupling reactions involving the use of bromo, iodo and triflate leaving groups are particularly useful in the systematic synthesis of multi-component compounds.

(3) As expected from previous work [15–18], the materials were nematic (except for the small, compact, non-mesomorphic materials shown in table 4) with high to very high nematic phase stabilities and moderate to high melting points.

(4) Where the cyano-substituent was in the compact naphthalene moiety, the T_{NI} value was $\sim 10°C$ higher than when in the simple phenyl ring in each case. However, this suspected higher degree of polarizability was not reflected in the birefringence values which were identical in all cases.

(5) Encouragingly, the birefringence values are higher for the tolane materials (0·42), but it is these materials, in general, that have the higher melting points and the lower solubilities than the non-tolane analogues (0·33).

(6) All of the moieties that are conducive to high birefringence, unfortunately, confer high melting points and low solubility.

6. Experimental

Confirmation of the structures of intermediates and products was obtained by ^{1}H NMR spectroscopy (JEOL JNM-GX270 spectrometer), infrared spectroscopy (Perkin–Elmer 457 grating spectrophotometer) and mass spectrometry (Finnigan-MAT 1020 GC/MS spectrometer). The progress of reactions was frequently monitored using a Perkin–Elmer 8320 capillary gas chromatograph fitted with a 12 m QC2/BP1-1·0 SGE column. Transition temperatures were measured using a Mettler FP 5 hot-stage and control unit in conjunction with an Olympus BH 2 polarizing microscope and these were confirmed using differential scanning calorimetry (Perkin–Elmer DSC-7 and IBM data station). The purity of each of the compounds in tables 1,2,3 and 4 was checked by GLC analysis (see above) and by HPLC analysis (Microsorb C18 80-215-C5 RP column) and all compounds were >99 per cent pure, except where indicated otherwise. All of the birefringence values quoted were measured as extrapolated values from mixtures in the I eutectic mixture (commercially available from Merck Ltd., Poole, Dorset) shown under structure **VIII**. An Abbé refractometer (Bellingham and Stanley) was used to measure the refractive indices of several mixture compositions at 10°C intervals (on a cooling cycle from 65°C to −5°C for each compound) from the critical angle of reflection. A sodium lamp and filter were used to provide the light source at 598 nm. The birefringence values, at the same reduced temperature ($T/T_{NI}=0·781$), for all of the mixtures for each compound are then extrapolated to give an estimate of the birefringence of the pure compound and these values are shown in tables 1–4.

6.1. *Preparation of dichloro[1,1′-bis-(diphenylphosphino)ferrocene]palladium (II) and tetrakis (triphenylphosphine)palladium(0)*

Dichloro[1,1′-bis-(diphenylphosphino)ferrocene]palladium(II) [44] and tetrakis (triphenylphosphine)palladium(0) [45] were prepared according to literature procedures. Compound **28** was prepared as described in [22].

6.2. *Preparation of 2-bromo-6-methoxynaphthalene* (**2**)

Dimethyl sulphate (33·8 g, 0·268 mol) was added to a stirred solution of compound **1** (50·0 g, 0·224 mol) and potassium hydroxide (15·0 g, 0·268 mol) in water (220 ml) at room temperature. The stirred mixture was heated at 70°C for 1 h and stirred at room

temperature overnight (TLC and GLC analysis revealed a complete reaction). The product was filtered off, washed with 10 per cent sodium hydroxide, water and dried well, and then extracted into dichloromethane. The organic extract was washed with 10 per cent sodium hydroxide, water and dried ($MgSO_4$). The solvent was removed *in vacuo* to give a colourless solid.

Yield 50·9 g (96 per cent); mp 108–110°C; ^{1}H NMR ($CDCl_3$) δ 3·90(3 H, s), 7·09(1 H, d), 7·16(1 H, q), 7·49(1 H, q), 7·60(1 H, d), 7·64(1 H, d), 7·91(1 H, d); IR (KCl) ν_{max} 1630, 1595, 1500, 1390, 1265, 1215, 1170, 1070, 1035, 905, 855, 820 cm^{-1}; MS *m/z* 238(M^+), 236(M^+), 223, 221, 208, 206, 195, 193.

6.3. *Preparation of 2-bromo-6-butoxynaphthalene* (3)

Quantities: compound **1** (40·0 g, 0·18 mol), 1-bromobutane (50·0 g, 0·36 mol), potassium carbonate (51·0 g, 0·37 mol). The experimental procedure was as described in a previous publication [21]. The crude product was recrystallized from ethanol to yield an off-white powder.

Yield 32·2 g (64 per cent); mp 52–53°C; ^{1}H NMR ($CDCl_3$) δ 1·00(3 H, t), 1·55(2 H, sext), 2·85(2 H, quint), 4·05(2 H, t), 7·08(1 H, d), 7·15(1 H, q), 7·48(1 H, q), 7·58(1 H, d), 7·63(1 H, d), 7·90(1 H, q); IR (KCl) ν_{max} 2960, 2950, 2880, 1630, 1590, 1500, 1390, 1260, 1210, 1175, 1070, 920, 890, 850, 830 cm^{-1}; MS *m/z* 280(M^+), 278(M^+), 224, 222, 195, 193.

6.4. *Preparation of 6-butoxynaphth-2-ylboronic acid* (4)

Quantities: compound **3** (8·60 g, 0·031 mol), *n*-butyllithium (12·40 ml, 2·5 M in hexanes, 0·031 mol), tri-isopropyl borate (12·0 g, 0·064 mol). The experimental procedure was as described in a previous publication [23].

Yield 8·50 g (100 per cent); ^{1}H NMR ($CDCl_3$) δ 1·05(3 H, t), 1·55(2 H, sext), 1·85(2 H, quint), 4·10(2 H, t), 7·14(1 H, d), 7·22(1 H, q), 7·82(1 H, d), 7·96(1 H, d), 8·24(1 H, q), 8·72(1 H, d) no obvious OH absorption; IR (KCl) ν_{max}3600–3100, 2960, 2940, 2860, 1630, 1485, 1470, 1385, 1350, 1325, 1205, 805 cm^{-1}; MS *m/z* 590, 579, 565, 552, 536, 522, 509, 496, 480, 465, 255, 200, 144.

6.5. *Preparation of 2-butoxy-6-(4-cyanophenyl)naphthalene* (6)

Quantities: compound **5** (1·25 g, 6·87 mmol), compound **4** (2·01 g, 8·24 mmol), tetrakis(triphenylphosphine)palladium(0) (0·2917 g, 0·25 mmol). The experimental procedure was as described in a previous publication [21] except that dimethoxyethane replaced ethanol and benzene as solvent and GLC analysis revealed a complete reaction after 4 h. The crude product was purified by column chromatography (silica gel/petroleum fraction (bp 40–60°C)–dichloromethane, 3 : 1) to give a colourless solid which was recrystallized from ethanol–ethyl acetate (8 : 1) to yield colourless crystals.

Yield 1·63 g (79 per cent); transitions (°C) C 125·0 N 159·0 I (as lit. values) [16]; ^{1}H NMR ($CDCl_3$) δ 1·00(3 H, t) 1·55(2 H, sext), 1·85(2 H, quint), 4·00(2 H, t), 7·15(1 H, d), 7·20(1 H, q), 7·65(1 H, q), 7·72(2 H, d), 7·76(2 H, d, 7·78(1 H, d), 7·82(1 H, d), 7·97(1 H, d); IR (KCl) ν_{max} 2960, 2940, 2860, 2230, 1630, 1605, 1500, 1470, 1395, 1255, 1205, 1195, 1135, 1030, 1010, 845, 805 cm^{-1}; MS *m/z* 301(M^+), 273, 245, 227, 216.

6.6. *Preparation of 2-iodo-6-methoxynaphthalene* (7)

A mixture of compound **2** (15·0 g, 0·063 mol), potassium iodide (158·0 g, 0·95 mol) and copper (I) iodide (60·5 g, 0·32 mol) in hexamethylphosphoramide (HMPA) (180 ml)

was stirred at 160°C under dry nitrogen for 18 h (GLC analysis revealed a complete reaction). The cooled mixture was poured into 10 per cent hydrochloric acid (300 ml) and the product was extracted into ether, and left at room temperature overnight. The insoluble copper salts were filtered off and washed well with ether and the separated aqueous layer was washed with ether. The combined ethereal extracts were washed with water, aqueous sodium sulphite, water and dried ($MgSO_4$). The solvent was removed *in vacuo* to yield a pale-yellow solid.

Yield 17·5 g (98 per cent); mp 138–140°C; ^{1}H NMR ($CDCl_3$) δ 3·95(3 H, s), 7·07(1 H, d), 7·13(1 H, q), 7·46(1 H, d), 7·60(1 H, d), 7·65(1 H, q), 8·14(1 H, d); IR (KCl) ν_{max} 2960, 2940, 2840, 1625, 1580, 1500, 1390, 1265, 1215, 1035, 900, 855, 820 cm^{-1}; MS *m/z* 284(M^+), 269, 241.

6.7. *Preparation of 2-butoxy-6-iodonaphthalene* (**8**)

Quantities: compound **3** (20·0 g, 0·072 mol), potassium iodide (180·0 g, 1·08 mol), copper (I) iodide (68·6 g, 0·36 mol), HMPA (220 ml). The experimental procedure was as described for the preparation of compound **7**.

Yield 22·75 g (97 per cent); mp 66–67°C; ^{1}H NMR ($CDCl_3$) δ 1·00(3 H, t), 1·50(2 H, sext), 1·80(2 H, quint), 4·05(2 H, t), 7·05(1 H, d), 7·13(1 H, q), 7·45(1 H, d), 7·60(1 H, d), 7·64(1 H, q), 8·12(1 H, d); IR (KCl) ν_{max} 2960, 2940, 2860, 1625, 1585, 1500, 1460, 1390, 1260, 1215, 1170, 915, 890, 855, 825 cm^{-1}; MS *m/z* 326(M^+), 270, 200, 143.

6.8. *Preparation of 6-methoxynaphth-2-ylethyne* (**9**)

A solution of zinc chloride (13·35 g, 0·098 mol) in dry THF (100 ml) was added dropwise to a stirred, cooled (−5 to 0°C) solution of lithium acetylide ethylenediamine complex (9·00 g, 0·098 mol) in dry THF (100 ml) under dry nitrogen. The mixture was stirred at 10°C for 30 min and a solution of compound **7** (10·0 g, 0·035 mol) in dry THF (50 ml) was added dropwise at −5 to 0°C followed by the addition of tetrakis (triphenylphosphine)palladium(0) (1·62 g, 1·40 mmol). The mixture was stirred at room temperature overnight (GLC analysis revealed a complete reaction). The mixture was poured into 10 per cent hydrochloric acid and the product was extracted into ether (× 2). The combined ethereal extracts were washed with aqueous sodium hydrogen carbonate and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue was purified by column chromatography (silica gel/petroleum fraction (bp 40–60°C)–dichloromethane, 10 : 1) to give a colourless solid.

Yield 4·18 g (66 per cent); mp 97–98°C; ^{1}H NMR ($CDCl_3$) δ 3·10(1 H, s), 3·90(3 H, s), 7·09(1 H, d), 7·15(1 H, q), 7·48(1 H, q), 7·67(1 H, d), 7·69(1 H, d), 7·95(1 H, d); IR (KCl) ν_{max} 3280, 2110, 1630, 1605, 1505, 1485, 1390, 1260, 1230, 1170, 1035, 905, 860, 820 cm^{-1}; MS *m/z* 182(M^+), 167, 139.

6.9. *Preparation of 6-butoxynaphth-2-ylethyne* (**10**)

Quantities: lithium acetylide ethylenediamine complex (8·50 g, 0·092 mol), zinc chloride (12·60 g, 0·093 mol), compound **8** (12·00 g, 0·037 mol), tetrakis (triphenylphosphine)palladium(0) (2·15 g, 1·86 mmol). The experimental procedure was as described for the preparation of compound **9**. The crude product was purified by column chromatography (silica gel/petroleum fraction (bp 40–60°C)–dichloromethane, 10 : 1) to yield a colourless solid.

Yield 6·76 g (82 per cent); mp 35–36°C; ^{1}H NMR ($CDCl_3$) δ 1·00(3 H, t), 1·50(2 H, sext), 1·80(2 H, quint), 3·10(1 H, s), 4·05(2 H, t), 7·08(1 H, d), 7·15(1 H, q), 7·47(1 H, q), 7·64(1 H, d), 7·68(1 H, d), 7·93(1 H, d); IR (KCl) ν_{max} 3320, 2960, 2940, 2880,

2120, 1635, 1605, 1505, 1470, 1395, 1270, 1230, 1175, 1125, 895, 855, 815 cm^{-1}; MS *m/z* 224(M^+), 168, 150, 139.

6.10. *Preparation of 1-(4-cyanophenyl)-2-(6-methoxynaphth-2-yl)ethyne* (**11**)

A solution of *n*-butyllithium (8·50 ml, 2·5 M in hexanes, 0·021 mol) was added dropwise to a stirred, cooled (−5 to 0°C) solution of compound **9** (3·86 g, 0·021 mol) in dry THF (50 ml) under dry nitrogen. This mixture was stirred for 10 min and a solution of zinc chloride (2·86 g, 0·021 mol) in dry THF (30 ml) was added dropwise at −5 to 0°C. This mixture was stirred at room temperature for 15 min and a solution of compound **5** (3·86 g, 0·021 mol) in dry THF (20 ml) was added at −5 to 0°C followed by the addition of tetrakis(triphenylphosphine)palladium(0) (0·97 g, 0·84 mmol). The mixture was heated under reflux for 18 h (GLC and TLC analysis revealed a complete reaction). The crude product was purified by column chromatography (silica gel/petroleum fraction (bp40–60°C)–dichloromethane, 1 : 1) to give a pale yellow solid which was recrystallized from ethanol–ethyl acetate (10 : 1) to yield colourless, fluorescent crystals.

Yield 4·68 g (79 per cent); transitions (°C) C 144·0 N 210·0 I; ^{1}H NMR ($CDCl_3$) δ 3·95(3 H, s), 7·13(1 H, d), 7·18(1 H, q), 7·53(1 H, q), 7·61(2 H, d), 7·66(2 H, d), 7·71(1 H, d), 7·73(1 H, d), 8·00(1 H, d); IR (KCl) ν_{max} 2240, 1610, 1480, 1390, 1260, 1215, 1170, 1140, 1025, 860, 835 cm^{-1}; MS *m/z* 283(M^+), 268.

6.11. *Preparation of 1-(6-butoxynaphth-2-yl)-2-(4-cyanophenyl)ethyne* (**12**)

Quantities: compound **10** (1·80 g, 8·04 mmol), *n*-butyllithium (3·30 ml, 2·5 M in hexanes, 8·25 mmol), zinc chloride (1·15 g, 8·46 mmol), compound **5** (1·42 g, 7·80 mmol), tetrakis(triphenylphosphine)palladium(0) (0·4691 g, 0·41 mmol). The experimental procedure was as described for the preparation of compound **11** except that the mixture was stirred at room temperature overnight. The crude product was purified by column chromatography (silica gel/petroleum fraction (bp 40–60°C)–dichloromethane, 2 : 1) to give a colourless solid which was recrystallized from ethanol–ethyl acetate (20 : 1) to yield colourless, fluorescent crystals.

Yield 1·45 g (57 per cent); transitions (°C) C 106·5/111·5 N 186·0 I; ^{1}H NMR ($CDCl_3$) δ 1·00(3 H, t), 1·55(2 H, sext), 1·85(2 H, quint), 4·10(2 H, t), 7·12(1 H, d), 7·18(1 H, q), 7·52(1 H, q), 7·61(2 H, d), 7·66(2 H, d), 7·70(1 H, d), 7·73(1 H, d), 7·99(1 H, d); IR (KCl) ν_{max} 2980, 2880, 2220, 1610, 1475, 1395, 1260, 1215, 1175, 1140, 1040, 1010, 840, 835 cm^{-1}; MS *m/z* 325(M^+), 269, 240.

6.12. *Preparation of 1-butoxy-4-iodobenzene* (**14**)

Quantities: compound **13** (44·0 g, 0·20 mol), 1-bromobutane (45·0 g, 0·33 mol), potassium carbonate (56·0 g, 0·41 mol). The experimental procedure was as described in a previous publication [21] and the crude product was distilled.

Yield 51·81 g (94 per cent); bp 108–110°C at 0·1 mmHg; ^{1}H NMR ($CDCl_3$) δ 0·95(3 H, t), 1·45(2 H, sext), 1·75(2 H, quint), 3·90(2 H, t), 6·65(2 H, d), 7·60(2 H, d); IR (film) ν_{max} 2960, 2940, 2860, 1590, 1575, 1485, 1475, 1285, 1245, 1175, 1000, 820 cm^{-1}; MS *m/z* 276(M^+), 220, 143.

6.13. *Preparation of 4-butoxyphenylethyne* (**15**)

Quantities: Lithium acetylide ethylenediamine complex (21·00 g, 0·228 mol), zinc chloride (31·1 g, 0·23 mol), compound **14** (24·00 g, 0·087 mol), tetrakis (triphenylphosphine)palladium(0) (3·17 g, 2·74 mmol). The experimental procedure was similar to that described for the preparation of compound **9** except that the crude

product was filtered through a short alumina column to remove some of the catalyst and then distilled.

Yield 7·60 g (50 per cent); bp 80–82°C at 0·1 mmHg; ^{1}H NMR ($CDCl_3$) δ 0·95(3 H, t), 1·45(2 H, sext), 1·75(2 H, quint), 3·00(1 H, s), 3·95(2 H, t), 6·80(2 H, d), 7·40(2 H, d); IR (film) ν_{max} 3300, 2960, 2940, 2880, 2120, 1610, 1510, 1475, 1295, 1250, 1175, 835 cm^{-1}; MS *m/z* 174(M^+), 118, 89.

6.14. *Preparation of 1-iodo-4-pentylbenzene* (**17**)

Quantities: compound **16** (20·0 g, 0·12 mol), 36 per cent hydrochloric acid (110 ml), sodium nitrite (10·50 g, 0·15 mol), potassium iodide (43·5 g, 0·26 mol). The experimental procedure was as described in a previous publication [24] and the crude product was distilled.

Yield 29·0 g (88 per cent); bp 90–95°C at 0·1 mmHg; ^{1}H NMR ($CDCl_3$) δ 0·90(3 H, t), 1·25(4 H, m), 1·55(2 H, quint), 2·50(2 H, t), 6·90(2 H, d), 7·55(2 H, d); IR (film) ν_{max} 2960, 2940, 2860, 1490, 1405, 1065, 1010, 795 cm^{-1}; MS *m/z* 274(M^+), 217.

6.15. *Preparation of 4-pentylphenylethyne* (**18**)

Quantities: lithium acetylide ethylenediamine complex (20·25 g, 0·22 mol), zinc chloride (30·0 g, 0·22 mol), compound **17** (24·0 g, 0·088 mol), tetrakis (triphenylphosphine)palladium(0) (3·12 g, 2·70 mmol). The experimental procedure was as described for the preparation of compound **15**.

Yield 7·80 g (52 per cent); bp 122–123°C at 15 mmHg; ^{1}H NMR ($CDCl_3$) δ 0·90(3 H, t), 1·30(4 H, m), 1·55(2 H, quint), 2·55(2 H, t), 3·00(1 H, s), 7·10(2 H, d), 7·40(2 H, d); IR (film) ν_{max} 3320, 2960, 2880, 2130, 1620, 1520, 1480, 1125, 1030, 850, 830, 660, 655, 620, 565 cm^{-1}; MS *m/z* 172(M^+), 115.

6.16. *Preparation of 2-cyano-6-methoxynaphthalene* (**19**)

A mixture of compound **2** (12·0 g, 0·051 mol) and copper (I) cyanide (5·26 g, 0·059 mol) in dry DMF (75 ml) was heated at 185°C for 5 h (GLC analysis revealed a complete reaction). The cooled mixture was poured into 10 per cent hydrochloric acid and the product was extracted into ether. The insoluble salts were filtered off and the separated aqueous layer was washed with ether. The combined ethereal extracts were washed with brine and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue was purified by column chromatography (silica gel/petroleum fraction (bp 40–60°C)–dichloromethane, 1 : 2) to give a pale yellow solid.

Yield 7·60 g (81 per cent); mp 103–104°C; ^{1}H NMR ($CDCl_3$) δ 3·95(3 H, s), 7·15(1 H, d), 7·24(1 H, q), 7·58(1 H, q), 7·80(2 H, d), 8·15(1 H, d); IR (KCl) ν_{max} 3080, 3010, 2940, 2850 (all weak), 2220, 1625, 1605, 1480, 1390, 1270, 1230, 1175, 1030, 895, 875, 815, 665, 550, 475 cm^{-1}; MS *m/z* 183(M^+), 168, 153, 140.

6.17. *Preparation of 6-cyanonaphth-2-ol* (**20**)

Quantities: compound **19** (6·90 g, 0·0377 mol), boron tribromide (24·00 g, 10·0 ml, 0·0956 mol). The experimental procedure was as described in a previous publication [46] and yielded a colourless solid.

Yield 6·40 g (100 per cent); mp 156–157°C; ^{1}H NMR ($CDCl_3$) δ 7·19(1 H, d), 7·24(1 H, q), 7·50(1 H, q), 7·70(1 H, d), 7·76(1 H, d), 8·11(1 H, d), 9·65(1 H, s); IR (KCl) ν_{max} 3400–3100, 2240, 1625, 1485, 1395, 910, 870 cm^{-1}; MS *m/z* 169(M^+).

6.18. *Preparation of 6-cyanonaphth-2-yl triflate* (**21**)

A solution of *N*-phenyltriflamide (9·00 g, 0·025 mol) in dry dichloromethane (50 ml) was added dropwise to a stirred, cooled (−78°C) solution of compound **20** (4·00 g, 0·024 mol) in dry dichloromethane (80 ml) and dry triethylamine (4·90 g, 0·049 mol) under dry nitrogen. The stirred mixture was allowed to warm to room temperature overnight (GLC and TLC analysis revealed a complete reaction). The mixture was washed with aqueous sodium carbonate and the separated aqueous layer was washed with dichloromethane. The combined organic extracts were washed with water and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue was purified by column chromatography (silica gel/dichloromethane) to give a colourless solid.

Yield 7·20 g (99 per cent); mp 93–94°C; ^{1}H NMR ($CDCl_3$) δ 7·52(1 H, q), 7·73(1 H, q), 7·83(1 H, d), 7·99(1 H, d), 8·03(1 H, d), 8·30(1 H, d); IR (KCl) ν_{max} 3080, 2240, 1425, 1250, 1235, 1210, 1140, 1120, 940, 880, 825, 665, 625, 610 cm^{-1}; MS *m/z* 301(M^+), 276, 237, 168, 140.

6.19. *Preparation of 1-(4-butoxyphenyl)-2-(6-cyanonaphth-2-yl)ethyne* (**22**)

Quantities: compound **15** (1·28 g, 7·36 mmol), *n*-butyllithium (2·95 ml, 2·5 M in hexane, 7·38 mmol), zinc chloride (1·05 g, 7·72 mmol), compound **21** (2·10 g, 6·98 mmol), tetrakis(triphenylphosphine)palladium(0) (0·4267 g, 0·37 mmol), lithium chloride (0·6171 g, 0·015 mol). The experimental procedure was similar to that described for the preparation of compound **11** except that lithium chloride was added with the tetrakis(triphenylphosphine)palladium(0) and the mixture was heated under reflux for 16 h. The crude product was purified by column chromatography (silica gel/petroleum fraction (bp 40–60°C)–dichloromethane, 1 : 1) to give a pale-yellow solid which was recrystallized from ethanol–ethyl acetate (10 : 1) to yield colourless fluorescent, crystals.

Yield 1·64 g (72 per cent); transitions (°C) C 110·5/120·5 N 195·5 I; ^{1}H NMR ($CDCl_3$) δ 1·00(3 H, t), 1·50(2 H, sext), 1·80(2 H, quint), 4·00(2 H, t), 6·90(2 H, d), 7·50(2 H, d), 7·61(1 H, q), 7·67(1 H, q), 7·84(1 H, d), 7·87(1 H, d), 8·03(1 H, d), 8·19(1 H, d); IR (KCl) ν_{max} 2960, 2950, 2880, 2240, 2210, 1610, 1600, 1520, 1475, 1290, 1260, 900, 850, 830 cm^{-1}; MS *m/z* 325(M^+), 269, 240.

6.20. *Preparation of 1-(6-cyanonaphth-2-yl)-2-(4-pentylphenyl)ethyne* (**23**)

Quantities: compound **18** (1·29 g, 7·50 mmol), *n*-butyllithium (3·00 ml, 2·5 M in hexanes, 7·50 mmol), zinc chloride (1·05 g, 7·72 mmol), compound **21** (2·12 g, 7·04 mmol), tetrakis(triphenylphosphine)palladium(0) (0·4361 g, 0·38 mmol), lithium chloride (0·6269 g, 0·015 mmol). The experimental procedure was as described for the preparation of compound **22**. The crude product was purified by column chromatography (silica gel/petroleum fraction (bp 40–60°C)–dichloromethane, 2 : 1) to give a colourless solid which was recrystallized from ethanol–ethyl acetate (10 : 1) to yield colourless crystals.

Yield 1·42 g (62 per cent); transitions (°C) C 79·5 N 164·0 I; ^{1}H NMR ($CDCl_3$) δ 0·90(3 H, t), 1·30(4 H, m), 1·60(2 H, quint), 2·60(2 H, t), 7·20(2 H, d), 7·49(2 H, d), 7·62(1 H, q), 7·68(1 H, q), 7·86(1 H, d), 7·89(1 H, d), 8·06(1 H, d), 8·20(1 H, d); IR (KCl) ν_{max} 2960, 2940, 2860, 2240, 2210, 1625, 1510, 900, 890, 840, 815 cm^{-1}; MS *m/z* 323(M^+), 266.

6.21. *Preparation of 1-(6-butoxynaphth-2-yl)-2-(6-cyanonaphth-2-yl)ethyne* (**24**)

Quantities: compound **10** (1·60 g, 7·14 mmol), *n*-butyllithium (2·90 ml, 2·5 M in hexane, 7·25 mmol), zinc chloride (1·00 g, 7·35 mmol), compound **21** (2·00 g, 6·64 mmol), tetrakis(triphenylphosphine)palladium(0) (0·2621 g, 0·23 mmol), lithium chloride

(0·5812 g, 0·014 mol). The experimental procedure was as described for the preparation of compound **22**. The crude product was purified by column chromatography (silica gel/petroleum fraction (bp 40–60°C)–dichloromethane, 1 : 1) to give a yellow solid which was recrystallized from ethyl acetate to yield pale-yellow crystals.

Yield 1·42 g (57 per cent); transitions (°C) C 185·0 N 270·5 I; ^{1}H NMR ($CDCl_3$) δ 1·00(3 H, t), 1·55(2 H, sext), 1·85(2 H, quint), 4·10(2 H, t), 7·12(1 H, d), 7·18(1 H, q), 7·56(1 H, q), 7·62(1 H, q), 7·70(1 H, d), 7·71(1 H, q), 7·73(1 H, d), 7·87(1 H, d), 7·90(1 H, d), 8·02(1 H, d), 8·10(1 H, d), 8·21(1 H, d); IR (KCl) ν_{max} 2960, 2940, 2860, 2240, 2210, 1620, 1600, 1500, 1470, 1275, 1215, 1160, 910, 900, 880, 820, 660 cm^{-1}; MS *m/z* 375(M^+), 319, 290.

6.22. *Preparation of 1-bromo-4-butoxybenzene* (**26**)

Quantities: compound **25** (70·0 g, 0·405 mol), 1-bromobutane (61·0 g, 0·445 mol), potassium carbonate (130·0 g, 1·25 mol). The experimental procedure was as described in a previous publication [21] and the crude product was distilled.

Yield 74·92 g (82 per cent); bp 90–92°C at 0·1 mmHg; ^{1}H NMR ($CDCl_3$) δ 0·95(3 H, t), 1·45(2 H, sext), 1·65(2 H, quint), 3·90(2 H, t), 6·75(2 H, d), 7·40(2 H, d); IR (film) ν_{max} 2970, 2880, 1580, 1490, 1470, 1280, 1250, 1160, 1060, 1010, 810 cm^{-1}; MS *m/z* 230(M^+), 173, 171.

6.23. *Preparation of 4-butoxyphenylboronic acid* (**27**)

Quantities: compound **26** (30·0 g, 0·131 mol), magnesium (3·66 g, 0·151 mol), triisopropyl borate (50·0 g, 0·266 mol). The experimental procedure was as described in a previous publication [22] to yield a colourless solid.

Yield 21·49 g (85 per cent); ^{1}H NMR ($CDCl_3$) δ 0·95(3 H, t), 1·50(2 H, sext), 1·80(2 H, quint), 4·00(2 H, t), 7·00(2 H, d), 8·15(2 H, d), no obvious OH absorption; IR (KCl) ν_{max} 3600–3100, 2960, 2940, 2880, 1600, 1420–1300, 1250, 1170, 840, 750, 690 cm^{-1}; MS *m/z* 150, 121, 107, 94, 91, 77.

6.24. *Preparation of 2-(4-butoxyphenyl)-6-cyanonaphthalene* (**29**)

Quantities: compound **21** (0·53 g, 1·76 mmol), compound **27** (0·45 g, 2·32 mmol), tetrakis(triphenylphosphine)palladium(0) (0·13 g, 0·11 mmol), lithium chloride (0·22 g, 5·20 mmol). The experimental procedure was similar to that described for the preparation of compound **6** except that lithium chloride was added with the tetrakis(triphenylphosphine)palladium(0). The crude product was purified by column chromatography (silica gel/petroleum fraction (bp 40–60°C)–dichloromethane, 1 : 1) to give a colourless solid which was recrystallized from hexane–dimethoxyethane (1 : 1) to yield colourless crystals.

Yield 0·30 g (58 per cent); transitions (°C) C 98·5 N 167·5 I; ^{1}H NMR ($CDCl_3$) δ 1·00(3 H, t), 1·50(2 H, sext), 1·80(2 H, quint), 4·05(2 H, t), 7·03(2 H, d), 7·61(1 H, q), 7·66(2 H, d), 7·84(1 H, q), 7·93(2 H, d), 8·01(1 H, d), 8·23(1 H, d); IR (KCl) ν_{max} 2960, 2940, 2880, 2230, 1610, 1520, 1470, 1255, 820 cm^{-1}; MS *m/z* 301(M^+), 245, 216.

6.25. *Preparation of 2-cyano-6-(4-pentylphenyl)naphthalene* (**30**)

Quantities: compound **21** (2·00 g, 6·64 mmol), compound **28** (1·55 g, 8·07 mmol), tetrakis(triphenylphosphine)palladium(0) (0·25 g, 0·22 mmol), lithium chloride (0·90 g, 0·021 mol). The experimental procedure was as described for the preparation of compound **29**. The crude product was purified by column chromatography (silica

gel/petroleum fraction (bp 40–60°C)–dichloromethane, 1 : 1) to give a colourless solid which was recrystallized from ethanol to yield colourless crystals.

Yield 1·51 g (76 per cent); transitions (°C) C 68·0 N 130·0 I; ^{1}H NMR ($CDCl_3$) δ 0·90(3 H, t), 1·35(4 H, m), 1·65(2 H, quint), 2·65(2 H, t), 7·32(2 H, d), 7·61(1 H, q), 7·64(2 H, d), 7·86(1 H, q), 7·95(2 H, d), 8·05(1 H, q), 8·24(1 H, d); IR (KBr) ν_{max} 2960, 2940, 2860, 2220, 1630, 1495, 1475, 1405, 910, 810 cm^{-1}; MS *m/z* 299(M^+), 270, 255, 242.

6.26. *Preparation of 1-bromo-4-(pent-1-ynyl)benzene* (**32**)

Quantities: pent-1-yne (5·28 g, 0·078 mol), *n*-butyllithium (7·80 ml, 10·0 M in hexane, 0·078 mol), zinc chloride (10·80 g, 0·079 mol), compound **31** (5·28 g, 0·078 mol), tetrakis(triphenylphosphine)palladium(0) (2·80 g, 2·40 mmol). The experimental procedure was as described for the preparation of compound **12**.

Yield 14·20 g (82 per cent); bp 130–134°C at 15 mmHg; ^{1}H NMR ($CDCl_3$) δ 1·05(3 H, t), 1·60(2 H, sext), 2·35(2 H, t), 7·20(2 H, d), 7·40(2 H, d); IR (film) ν_{max} 2960, 2940, 2860, 1485, 1395, 1340, 1070, 1010, 1000, 820 cm^{-1}; MS *m/z* 224(M^+), 223, 222(M^+), 221, 209, 207, 202, 200, 185, 183.

6.27. *Preparation of 4-(pent-1-ynyl)phenylboronic acid* (**33**)

Quantities: compound **32** (13·45 g, 0·06 mol), magnesium (1·70 g, 0·07 mol), triisopropyl borate (23·00 g, 0·12 mol). The experimental procedure was as described in a previous publication [22] and the crude product was purified by extraction into 10 per cent potassium hydroxide to yield a colourless solid.

Yield 10·21 g (91 per cent); ^{1}H NMR ($CDCl_3$) δ 1·00(3 H, t), 1·55(2 H, sext), 2·40(2 H, t), 7·32 + 7·38(2 H, 2xd), 7·76 + 7·82(2 H, 2xd), 8·12(2 H, s); IR (KCl) ν_{max} 3600–3100, 2960, 2940, 2860, 1605, 1405, 1400–1340, 1310, 1180, 1110, 1020, 840, 750, 695 cm^{-1}; MS *m/z* 444, 428, 415, 405, 384, 375, 362, 349, 336, 325.

6.28. *Preparation of 2-cyano-6-[4-(pent-1-ynyl)phenyl]naphthalene* (**34**)

Quantities: compound **21** (2·25 g, 7·47 mmol), compound **33** (1·69 g, 8·99 mmol), tetrakis(triphenylphosphine)palladium(0) (0·28 g, 0·24 mmol), lithium chloride (1·00 g, 0·024 mol). The experimental procedure was as described for the preparation of compound **29**. The crude product was purified by column chromatography (silica gel/petroleum fraction (bp 40–60°C)–dichloromethane, 1 : 1) to give a colourless solid which was recrystallized from ethanol–ethyl acetate (1 : 1) to yield colourless crystals.

Yield 1·63 g (74 per cent); transitions (°C) C 113·0 N 193·0 I; ^{1}H NMR ($CDCl_3$) δ 1·05(3 H, t), 1·65(2 H, sext), 2·45(2 H, t), 7·52(2 H, d), 7·62(1 H, q), 7·66(2 H, d), 7·85(1 H, q), 7·96(2 H, d), 8·06(1 H, d), 8·25(1 H, d); IR (KCl) ν_{max} 2960, 2940, 2860, 2230, 1495, 900, 850, 810 cm^{-1}; MS *m/z* 295(M^+), 280, 266.

6.29. *Preparation of 6-iodonaphth-2-ol* (**35**)

Quantities: compound **7** (10·0 g, 0·035 mol), boron tribromide (10·0 ml, 22·0 g, 0·088 mol). The experimental procedure was as described for the preparation of compound **20**.

Yield 9·45 g (100 per cent); mp 129–131°C; ^{1}H NMR ($CDCl_3$) δ 5·15(1 H, s), 7·07(1 H, d), 7·09(1 H, q), 7·40(1 H, d), 7·61(1 H, d), 7·63(1 H, q), 8·13(1 H, d); IR (KCl) ν_{max} 3500–3000, 1630, 1585, 1505, 1395, 1350, 1260, 1210, 905, 860, 815 cm^{-1}; MS *m/z* 270(M^+), 182, 143.

6.30. *Preparation of 6-iodonaphth-2-yl triflate* (**36**)

Quantities: compound **35** (6·00 g, 0·022 mol), *N*-phenyltriflamide (8·35 g, 0·023 mol), triethylamine (4·50 g, 0·045 mol). The experimental procedure was as described for the preparation of compound **21**. The crude product was purified by column chromatography (silica gel/dichloromethane) to give a fawn solid.

Yield 8·80 g (100 per cent); mp 65–66°C; ^{1}H NMR ($CDCl_3$) δ 7·38(1 H, q), 7·60(1 H, d), 7·71(1 H, d), 7·80(1 H, d), 7·82(1 H, q), 8·30(1 H, d); IR (KCl) ν_{max} 1500, 1420, 1210, 1200, 1145, 1110, 960, 915, 880, 805, 720, 650, 605 cm^{-1}; MS *m/z* 402(M^+), 269, 241.

6.31. *Preparation of 6-(pent-1-ynyl)naphth-2-yl triflate* (**37**)

Quantities: pent-1-yne (1·60 g, 0·0235 mol), *n*-butyllithium (2·35 ml, 10·0 M in hexane, 0·0235 mol), zinc chloride (3·20 g, 0·0235 mol), compound **36** (8·20 g, 0·020 mol), tetrakis(triphenylphosphine)palladium(0) (1·20 g, 1·0 mmol). The experimental procedure was as described for the preparation of compound **12**. The crude product was purified by column chromatography (silica gel/petroleum fraction (bp 40–60°C)–dichloromethane, 5 : 1) to give a pale yellow oil.

Yield 6·33 g (92 per cent); ^{1}H NMR ($CDCl_3$) δ 1·10(3 H, t), 1·70(2 H, sext), 2·45(2 H, t), 7·34(1 H, q), 7·53(1 H, q), 7·68(1 H, d), 7·75(1 H, d), 7·81(1 H, d), 7·92(1 H, d); IR (film) ν_{max} 2980, 2950, 2880, 2240, 1605, 1505, 1430, 1250, 1220, 1145, 1110, 960, 920, 890, 860, 810 cm^{-1}; MS *m/z* 342(M^+), 313, 209.

6.32. *Preparation of 6-bromonaphth-2-yl triflate* (**38**)

Quantities: compound **1** (2·80 g, 0·0126 mol), *N*-phenyltriflamide (4·93 g, 0·0138 mol), triethylamine (2·55 g, 0·025 mol). The experimental procedure was as described for the preparation of compound **21**. The crude product was purified by column chromatography (silica gel/dichloromethane) to give an off-white solid.

Yield 4·40 g (98 per cent); mp 52–53°C; ^{1}H NMR ($CDCl_3$) δ 7·37(1 H, q), 7·61(1 H, q), 7·69(1 H, d), 7·71(1 H, d), 7·79(1 H, d), 8·01(1 H, d); IR (KCl) ν_{max} 1595, 1505, 1420, 1250, 1210, 1200, 1145, 1110, 920, 890, 880, 805, 720, 660, 610 cm^{-1}; MS *m/z* 356(M^+), 354(M^+), 223, 221, 195, 193.

6.33. *Preparation of 2-bromo-6-(pent-1-ynyl)naphthalene* (**39**)

Quantities: pent-1-yne (1·02 g, 0·015 mol), *n*-butyllithium (6·00 ml, 2·5 M in hexane, 0·015 mol), zinc chloride (2·05 g, 0·015 mol), compound **38** (4·80 g, 0·0135 mol), tetrakis(triphenylphosphine)palladium(0) (0·50 g, 0·43 mmol). The experimental procedure was as described for the preparation of compound **11** except that the mixture was heated under reflux for 4 h (GLC analysis revealed a complete reaction; two product peaks were present but no double-coupled material was detected). The crude product was purified by column chromatography (silica gel/petroleum fraction (bp 40–60°C)) to give a colourless solid.

Yield 2·10 g (57 per cent); mp 80–81°C; ^{1}H NMR ($CDCl_3$) δ 1·05(3 H, t), 1·65(2 H, sext), 2·45(2 H, t), 7·47(1 H, q), 7·52(1 H, q), 7·63(1 H, d), 7·65(1 H, d), 7·85(1 H, d), 7·94(1 H, d); IR (KBr) ν_{max} 2960, 2940, 2860, 1590, 1490, 1465, 1285, 1215, 1140, 1065, 895, 825, 650 cm^{-1}; MS *m/z* 274(M^+), 272(M^+), 259, 257, 245, 243.

6.34. *Preparation of 4-cyanophenylboronic acid* (**40**)

A solution of *n*-butyllithium (8·60 ml, 10·0 M in hexane, 0·082 mol) was added dropwise to a stirred, cooled (−110°C) solution of compound **5** (15·0 g, 0·082 mol) in

dry THF (180 ml) under dry nitrogen. The solution was stirred at below −100°C for 1 h and a solution of tri-isopropyl borate (30·85 g, 0·164 mol) in dry THF (60 ml) was added at below −100°C. The solution was allowed to warm to room temperature overnight, 10 per cent hydrochloric acid was added and the solution was stirred for 1 h at room temperature. The product was extracted into ether (×2) and the combined ethereal extracts were washed with water and dried ($MgSO_4$). The solvent was removed *in vacuo* to give a colourless solid which was dried *in vacuo* (0·05 mmHg) for 2 h.

Yield 11·50 g (95 per cent); ^{1}H NMR (DMSO) δ 7·80(2 H, d), 7·95(2 H, d), 8·20–8·55(2 H, s); IR (KBr) ν_{max} 3600–3100, 2220, 1480–1300, 1160, 1065, 1005, 840 cm^{-1}; MS *m/z* 189, 162, 147(M^+), 120, 105.

6.35. *Preparation of 2-(4-cyanophenyl)-6-(pent-1-ynyl)naphthalene* (**41**)

Quantities: compound **39** (3·20 g, 0·012 mol), compound **40** (2·10 g, 0·014 mol), tetrakis(triphenylphosphine)palladium(0) (0·45 g, 0·39 mmol). The experimental procedure was as described for the preparation of compound **6**. The crude product was purified by column chromatography (silica gel/petroleum fraction (bp 40–60°C)–dichloromethane, 3 : 1) to give a colourless solid which was recrystallized from ethanol–ethyl acetate (50 : 1) to yield colourless crystals.

Yield 2·79 g (79 per cent); transitions (°C) C 109·0 N 166·0 I; ^{1}H NMR ($CDCl_3$) δ 1·10(3 H, t), 1·65(2 H, sext), 2·45(2 H, t), 7·51(1 H, q), 7·69(1 H, q), 7·76(2 H, d), 7·81(2 H, d), 7·84(1 H, d), 7·88(1 H, d), 7·94(1 H, d), 8·00(1 H, d); IR (KBr) ν_{max} 2960, 2220, 1600, 900, 815 cm^{-1}; MS *m/z* 295(M^+), 266.

6.36. *Attempted preparation of 2-(4-cyanophenyl)-6-pentylnaphthalene* (**42**)

5 per cent Palladium-on-charcoal (0·50 g) was added to a stirred solution of compound **41** (1·00 g, 3·39 mmol) in THF (60 ml) and ethanol (60 ml). The mixture was hydrogenated at room temperature and atmospheric pressure for 16 h (GLC analysis revealed a complete reaction). The catalyst was filtered off and the solvent was removed *in vacuo* and the residue was purified by column chromatography (silica gel/petroleum fraction (bp 40–60°C)–dichloromethane, 2 : 1) to give a colourless solid which was recrystallized from ethanol to yield colourless crystals of 2-(4-methylphenyl)-6-pentylnaphthalene (**43**).

Yield 0·64 g (66 per cent); transitions (°C) C 82·5 N 97·5 I; ^{1}H NMR ($CDCl_3$) δ 0·90(3 H, t), 1·40(4 H, m), 1·70(2 H, quint), 2·40(3 H, s), 2·75(2 H, t), 7·28(2 H, d), 7·35(1 H, q), 7·61(2 H, d), 7·63(1 H, d), 7·71(1 H, q), 7·80(1 H, d), 7·83(1 H, d), 7·98(1 H, d); IR (KBr) ν_{max} 2960, 2940, 2860, 890, 815 cm^{-1}; MS *m/z* 288(M^+), 231.

6.37. *Preparation of 6-pentylnaphth-2-yl triflate* (**44**)

A mixture of compound **37** (1·50 g, 4·39 mmol) and platinum (IV) oxide (50 mg) in THF (10 ml) and ethanol (50 ml) was hydrogenated at room temperature and atmospheric pressure for 1·5 h (GLC analysis revealed a complete reaction, but the presence of two products; GC/MS analysis indicated a mixture of the product expected (55 per cent) and 2-pentylnaphthalene (45 per cent)). The catalyst was filtered off and the solvent was removed *in vacuo* to give a colourless oil.

Yield 1·50 g (99 per cent); 55 per cent pure.

6.38. *Preparation of 2-bromo-6-pentylnaphthalene* (**45**)

Quantities: compound **39** (0·80 g, 2·93 mmol), platinum (IV) oxide (30 mg). The experimental procedure was as described for the preparation of compound **44**. GC/MS analysis revealed the same as for compound **44**.

Yield 0·77 g (95 per cent); 55 per cent pure.

6.39. *Preparation of 2-(4-cyanophenyl)-6-pentylnaphthalene* (**42**)

Quantities: compound **44** (1·50 g, 4·34 mmol, 55 per cent pure), compound **45** (0·77 g, 2·78 mmol, 55 per cent pure), compound **40** (1·26 g, 8·57 mmol) tetrakis (triphenylphosphine)palladium(0) (0·25 g, 0·22 mmol), lithium chloride (0·91 g, 0·021 mol). The experimental procedure was as described for the preparation of compound **29**. The crude product was purified by column chromatography (silica gel/petroleum fraction (bp 40–60°C) with the gradual introduction of dichloromethane) to give a colourless solid which was recrystallized from ethanol to yield colourless crystals.

Yield 0·70 g (33 per cent, 60 per cent based on known starting material content); transitions (°C) C 84·0 N 126·5 I (lit. values [17, 18] C 85·5 N 128·0 I); ^{1}H NMR ($CDCl_3$) δ 0·90(3 H, t), 1·35(4 H, m), 1·70(2 H, quint), 2·80(2 H, t), 7·40(1 H, q), 7·64(1 H, d), 7·68(1 H, q), 7·75(2 H, d), 7·81(2 H, d), 7·84(1 H, d), 7·88(1 H, d), 8·02(1 H, d); IR (KBr) ν_{max} 2960, 2940, 2860, 2230, 1605, 1495, 1180, 890, 850, 815, 570, 480 cm^{-1}; MS *m/z* 299(M^+), 284, 256, 242, 227.

6.40. *Preparation of 2-bromo-6-ethoxynaphthalene* (**46**)

Quantities: compound **1** (40·0 g, 0·18 mol), bromoethane (48·9 g, 0·45 mol). The experimental procedure was as described for the preparation of compound **3**.

Yield 30·27 g (67 per cent); mp 83–84°C; ^{1}H NMR ($CDCl_3$) δ 1·45(3 H, t), 4·15(2 H, q), 7·07(1 H, d), 7·15(1 H, q), 7·48(1 H, q), 7·57(1 H, d), 7·64(1 H, d), 7·90(1 H, d); IR (KCl) ν_{max} 2980, 2940, 2860, 1630, 1590, 1500, 1390, 1260, 1210, 1070, 1050, 930, 890, 860, 825 cm^{-1}; MS *m/z* 252(M^+), 250(M^+), 224, 222, 195, 193.

6.41. *Preparation of 2-cyano-6-ethoxynaphthalene* (**47**)

Quantities: compound **46** (3·00 g, 0·012 mol), copper (I) cyanide (1·30 g, 0·015 mol). The experimental procedure was as described for the preparation of compound **19**. The crude product was purified by column chromatography (silica gel/petroleum fraction (bp 40–60°C)–dichloromethane, 1 : 2) to give a colourless solid which was distilled (Kugelrohr, 170°C (maximum) at a 0·1 mmHg) to yield a colourless solid.

Yield 1·75 g (74 per cent); transitions (°C) C 100·5 (N – 11·0) I; ^{1}H NMR ($CDCl_3$) δ 1·50(3 H, t), 4·15(2 H, q), 7·13(1 H, d), 7·23(1 H, q), 7·56(1 H, q), 7·75(1 H, d), 7·77(1 H, d), 8·12(1 H, d); IR (KCl) ν_{max} 2980, 2940, 2220, 1630, 1605, 1505, 1490, 1470, 1390, 1275, 1235, 1180, 1110, 1045, 910, 860, 825, 665 cm^{-1}; MS *m/z* 197(M^+), 169, 140.

6.42. *Preparation of 2-cyano-6-butoxynaphthalene* (**48**)

Quantities: compound **3** (2·95 g, 0·011 mol), copper (I) cyanide (1·14 g, 0·013 mol). The experimental procedure was as described for the preparation of compound **47**.

Yield 1·96 g (79 per cent); transitions (°C) C 73·0 (N – 16·0) I; ^{1}H NMR ($CDCl_3$) δ 1·00(3 H, t), 1·50(2 H, sext), 1·85(2 H, quint), 4·10(2 H, t), 7·14(1 H, d), 7·24(1 H, q), 7·56(1 H, q), 7·78(1 H, q), 8·14(1 H, d); IR (KCl) ν_{max} 2960, 2940, 2860, 2220, 1620, 1605, 1485, 1470, 1395, 1270, 1235, 1175, 1115, 1025, 910, 860, 820, 810 cm^{-1}; MS *m/z* 225(M^+), 169.

6.43. *Preparation of 2-cyano-6-pentylnaphthalene* (**49**)

A solution of 9-borabicyclo[3.3.1]nonane (9-BBN) (18·0 ml, 0·5 M in THF, 9·00 mmol) was added to a stirred, cooled (0°C) solution of pent-1-ene (0·70 g, 0·010 mol) in dry THF (20 ml) under dry nitrogen; the solution was stirred at room temperature for 3 h. Potassium phosphate (2·87 g, 0·014 mol) and dichloro[1,1′-bis-(diphenylphosphino)ferrocene]palladium(II) (0·15 g, 0·20 mmol) were added followed by a solution of compound **21** (2·00 g, 6·64 mmol) in dry THF (30 ml). The stirred mixture was heated under reflux for 18 h (GLC analysis revealed a complete reaction). The mixture was cooled and 3 M sodium acetate (2 ml) and 30 per cent hydrogen peroxide (2 ml) were added and the mixture was stirred for 1 h at room temperature. Water was added, the product was extracted into ether (× 2) and the combined ethereal extracts were washed with brine and dried ($MgSO_4$). The solvent was removed *in vacuo* and the crude product was purified by column chromatography (silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 5 : 1) to give a colourless solid which was recrystallized from ethanol to yield colourless crystals (HPLC analysis revealed 95 per cent purity).

Yield 1·27 g (86 per cent); transitions (°C) C 40·0 (N − 20) I; ^{1}H NMR ($CDCl_3$) δ 0·90(3 H, t), 1·35(4 H, m), 1·70(2 H, quint), 2·80(2 H, t), 7·46(1 H, q), 7·57(1 H, q), 7·65(1 H, d), 7·81(1 H, d), 7·84(1 H, d), 8·18(1 H, d); IR (KBr) ν_{max} 2960, 2940, 2860, 2220, 1630, 1460, 1390, 895, 885, 830 cm^{-1}; MS *m/z* 223(M^+), 180, 167.

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