Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron 64 (2008) 4619–4626
Tetrahedron
www.elsevier.com/locate/tet

Buchwald protocol applied to the synthesis of *N*-heterotolan liquid crystals

Ursula B. Vasconcelos, Abel Schrader, Guilherme D. Vilela, Antonio C.A. Borges, Aloir A. Merlo*

Chemistry Institute, Federal University of Rio Grande do Sul, Bento Gonçalves Avenue, 9500, Campus do Vale, 91501 970 Porto Alegre, RS, Brazil

Received 27 April 2007; received in revised form 27 February 2008; accepted 3 March 2008
Available online 7 March 2008

Abstract

A homologous series of the new *N*-heterotolans **8a–d** were synthesized using two cross-coupling reactions mediated by copper and palladium/copper. The final compounds present the phenyl-pyridyl framework connected by the acetylene group. The evaluation of thermal properties for this series is described. All compounds exhibit the smectic A and X mesophase. For comparison were also synthesized compounds **10**, **12**, and **14**. Their LC properties are reported.

Keywords: Liquid crystal; *N*-Heterotolan; Phenylpyridyl framework; Buchwald protocol; Sonogashira coupling

1. Introduction

Liquid crystal displays (LCDs) have become essential as information displays in our technological society. Since highly birefringent liquid crystal materials are required,[1,2] many display parameters such as response time, contrast ratio, brightness, and viewing angle are important parameters to be considered.[1b] High birefringence liquid crystals are useful materials for application in reflective-type LCDs, spatial light modulators, compensation film reflectors, and polarizers.

A number of calamitic nematic liquid crystals showing high birefringence of relevance to LCDs such as cyanobiphenyls,[3] phenylpyrimidines,[4] phenylcyclohexanes,[5] and cyanopyridines[6] have been synthesized.

Tolan (diphenylacetylene) and its *N*-hetero version (pyridylphenylacetylene) play a prominent role in the field of liquid crystals science. From academic and technological research point of view, the planning and construction of new molecular materials containing such connectivity mentioned above have recently received much effort since they exhibit interesting electrical and optical properties.[7]

N-Heterotolan represents an interesting class of materials considering that the nitrogen atom in pyridine alters the optical, electrical, and thermal properties. Pyridine derivatives are aimed to provide a satisfactory selection of the best components of liquid crystals materials for TN and STN applications.[8] They also can be used as a template for high performance LC materials when substituted adequately by polar groups or alkyl/alkoxy tails.

Aromatic nucleophilic substitution using π-electron deficient systems such as halopyridines is sometimes used for the synthesis of pyridine derivatives. The major limitations of this methodology are related to the substrate availability and reactivity.[9]

The copper-mediated Ullmann-type condition[10] is an alternative method to synthesize aromatic and heteroaromatic derivatives. The nucleophilic aromatic substitution mediated by copper between nucleophiles (e.g., substituted phenoxides and amines) with aryl or heteroaryl halides allows the synthesis of the corresponding aryl/heteroaryl ethers and amines. However, the harsh reaction (125–220 °C in neat phenol or solvents such as pyridine, collidine, or DMF), which requires

* Corresponding author. Tel.: +55 51 3308 7316; fax: +55 51 3308 9304.
E-mail address: aloir@iq.ufrgs.br (A.A. Merlo).

0040-4020/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2008.03.005

stoichiometric (or greater) quantities of the copper complex, and the fact that inactivated aryl halides usually react in low yields have limited the utility of this reaction. These drawbacks commonly result in low functional group tolerance and low and/or irreproducible yields.

Buchwald[11] and Hartwig[12] were pioneers in developing interesting and practical protocols to construct aryl carbon and aryl–heteroatom bond mediated by metals, affording many compounds that have important biological, pharmaceutical, and materials properties.

For the synthesis of diaryl ethers, Buchwald et al. established a general procedure using aryl bromides and iodides with a variety of phenols catalyzed by copper complex, cesium carbonate as a base, and 1,10-phenanthroline as a bidentate nitrogenous ligand. The reaction conditions were compatible with a wide range of functionalized substrates.[13] Starting from their initial reports concerning on the Ullmann diaryl ether synthesis and the observation that the yields of N-arylation of imidazoles could be better when carried out in nonpolar solvents,[14] Buchwald's group were able to demonstrated in 2002 that the copper-based protocols could be used to synthesize alkyl aryl ethers by Ullmann type reaction.[15a]

The authors reported a mild, practical, and efficient Cu-catalyzed arylation of aryl halides with alcohols. The method exhibit large substrate and reagent scope and it is extremely selective. Both primary and secondary alcohols can be used, which clearly distinguish this method from Pd-catalyzed reaction, in which secondary alcohols give side products due to ready PdH elimination.[15b] Allylic alcohols give the ethers without allylic rearrangement, even for alcohols with a terminal double bond, which are extremely liable to rearrangements. For chiral alcohols, full retention of configuration is observed.

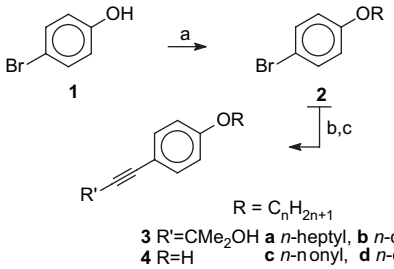
As part of our ongoing studies dealing with the synthesis of pyridine liquid crystals, we had previously reported that 2,5-disubstituted pyridine could easily be prepared[16] using the powerful protocol developed by Buchwald followed by Sonogashira reaction. We now wish to present an extension of application of this protocol to the other *N*-heterotolan compounds.

2. Results and discussion

2.1. Synthesis

The synthesis of the title compounds was carried out according to the synthetic methods outlined in Schemes 1–3. In order to establish the relationship between molecular structure and mesomorphic properties, we have introduced a pyridine moiety to produce *N*-heterotolans using Buchwald protocol[15] and the alkynylation coupling through Sonogashira reaction.[17]

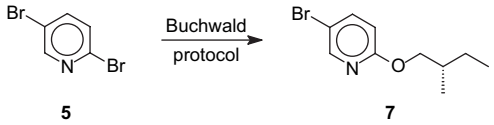
The first step was the synthesis of the intermediates **4a–d** according to Scheme 1. The alkylation of *p*-bromophenol with *n*-alkylbromide gave the products **2a–d** in 65–75% yields. Installation of the acetylene unit was accomplished by Sonogashira alkynylation of **2a–d** with 2-methyl-3-butyn-2-ol



Scheme 1. Alkynylation reaction by Sonogashira coupling. Conditions: (a) RBr, KOH, DMF/C_6H_6 (65–75%); (b) mebynol, PPh_3, $PdCl_2(PPh_3)_2$, CuI, Et_3N (75–90%); (c) KOH, isopropanol (85–90%).

(mebynol) followed by de-protection with KOH and isopropanol.[18] The final compounds **4a–d** were obtained in 70–80% yield from **2**.

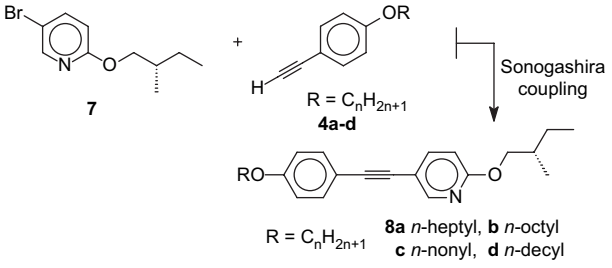
With compounds **4a–d** in hands, the synthesis of chiral key intermediate **7**[16a] was achieved by using the Buchwald protocol. This method was particularly suitable for the conversion of **5** to the chiral precursor **7** in acceptable yields according to Scheme 2.



Scheme 2. Arylation reaction under copper-mediated Buchwald protocol. Buchwald conditions: $CsCO_3$, CuI, 1,10-phenanthroline, toluene, (*S*)-**6**.

Thus, the arylation reaction using 2,5-dibromopyridine (**5**) with (*S*)-(−)-2-methyl-1-butanol (**6**) in the presence of cesium carbonate as a mild base, as well as 1,10-phenanthroline as a bidentate nitrogenous ligand and catalytic amount of copper iodide furnished the chiral intermediate **7** in 60% yield.

The synthesis of the *N*-heterotolan homologues **8a–d** was achieved using a second Sonogashira coupling between **7** and **4a–d**, according to Scheme 3 (45–60%).

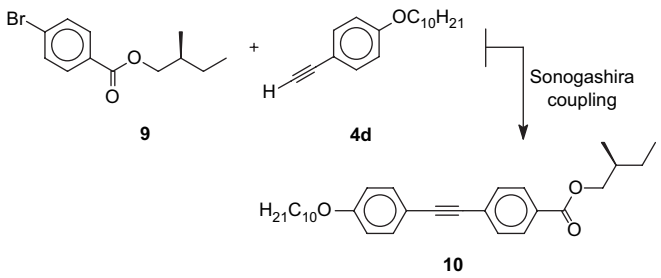


Scheme 3. Synthesis of **8a–d** using Sonogashira coupling. Sonogashira conditions: $PdCl_2(PPh_3)_2$, CuI, PPh_3, Et_3N (45–60%).

Attempting to compare the influence on liquid-crystalline behavior of the carboxylate group and the relative position of the nitrogen atom on the pyridine ring, we also synthesized compounds **10** and **12**. The liquid crystals properties were compared with the series **8a–d**.

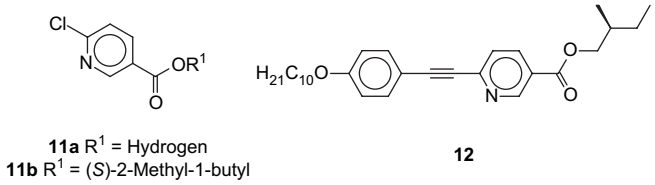
The synthesis of compound **10** was accomplished by alkynylation reaction between the chiral ester **9** and the selected

alkyne **4d**. The intermediate **9** was synthesized by exposure of 4-bromobenzoic acid to $SOCl_2$ solution and then a solution of (*S*)-(−)-2-methyl-1-butanol (**6**) in triethylamine. The final compound **10** was obtained in 75% yield (Scheme 4).



Scheme 4. Synthesis of **10**.

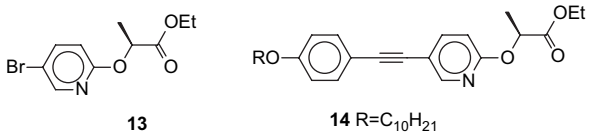
Compound **12** was selected for the synthesis due to the nitrogen atom in the pyridine ring. The chiral chloro-nicotinate ester **11b** was prepared by reaction of the acid **11a** and alcohol **6** in 89% yield mediated by DCC and DMAP. Compound **12** was obtained through the Pd–Cu-mediated reaction between 6-chloronicotinate ester **11b** and the alkyne **4d** with 65% yield.



11a R^1 = Hydrogen
11b R^1 = (*S*)-2-Methyl-1-butyl

12

The Buchwald protocol opens the possibility of accessing a great variety of new products, which would be very difficult to be made by a non-copper-mediated nucleophilic aromatic substitution reaction. The protocol can be successfully applied to the alkyl aryl ethers' synthesis from secondary substrates such as allylic and chiral *sec*-phenyl ethyl alcohol. To our expectation the reaction conditions in the protocol could be extended to more hindered substrates such as chiral ethyl lactate[19] to give **13**, which is recognized as an attractive precursor for the synthesis of chiral liquid crystals. We explore the O-arylation coupling to prepare compound **14** in a good yield, which is a potential dopant with polar conformational bias.[20]



3. Liquid crystal properties

Thermal analysis of all compounds synthesized was done by differential scanning calorimetry (DSC) and the data are compiled in Table 1. The transition temperatures and enthalpy values were collected from second heating scans. The texture of the mesophase[21] was identified by microscopic studies. When the sample was cooled from its isotropic phase, the smectic A phase appeared and exhibited focal-conic texture. The stable enantiotropic smectic A phase was found. For example, on heating the sample **8a** enters into the smectic A phase at 40.0 °C and finally melts to an isotropic liquid at 49.0 °C. The range of temperature for the mesophase is 9.0 °C. The two peaks observed at 40.0 °C and 49.0 °C were associated with $\mathbf{K \rightarrow S_A}$ and $\mathbf{S_A \rightarrow I}$ transitions, respectively, during the microscopy studies. The other members of this series exhibited smectic A phase along with smectic X phase. Tolan **10** shows only SmA* phase. The first change is associated with crystal–crystals transition. On heating the sample **10**, it enters into the crystal phase at 53 °C followed by an SmA phase at 55 °C and finally melts to an isotropic liquid at 59 °C. However, on cooling the sample did not show the crystal–crystals transition. The texture that emerges on cooling remains unchanged down to 50 °C. Below this temperature, the sample crystallizes.

For compounds **12** and **14**, the DSC and POM analyses reveal that samples are stable under heating. The melting point temperatures and enthalpy values were collected from second heating scans. However, the new compounds synthesized didn't show mesomorphic behavior. The absence of liquid-crystalline properties makes them good candidates for dopants for liquid crystals mixture studies. This study is in progress and will be presented in due course.

Compounds **10** and **12** are similar in the chemical structure. The difference between them is the nitrogen atom at 3-position

Table 1
Transition temperatures (°C) for series **8a–d**, **10**, **12**, and **14** and enthalpy values (ΔH, kcal mol^{-1})

Entry	Phase transition temperatures (°C)		Enthalpy values	
	Heating	Cooling	Melt[a]	Iso[b]
8a	K_1 32 K_2 40 SmA* 49 I	K 35 SmA* 43 I	0.7	0.8
8b	K 22 SmX 46 SmA* 55 I	K_1 1.5 K_2 9.0 SmX 41 SmA* 49 I	1.4	1.5
8c	K 25 SmX 39 SmA* 54 I	K -2.2 SmX 34 SmA* 48 I	4.6	1.4
8d	K 45 SmA* 56 I	K 16 SmX 38 SmA* 52 I	6.6	1.9
10	K_1 53 K_2 55 SmA* 59 I	K 30 SmA* 58 I	[c]	—
12	K1 69 K2 72 I	K 52 I	[c]	—
14	K 25 I	K 18 I	6.3	—

Scan rate: 10 °C min^{-1} for all samples; K_1 and K_2=crystal phase, SmA*=Chiral smectic A phase.
[a] Enthalpy values were determined from crystal phase to smectic A* phase for **8a** and **8d** and smectic X phase for **8b** and **8c**.
[b] Enthalpy values were determined from isotropic phase to a liquid-crystalline SmA* phase at second heating stage.
[c] Value not determined.

on the nicotinate ester ring. However, by changing carbon to nitrogen, the liquid crystals properties disappear for **12**. The non-liquid crystalline behavior of **12** may be associated with the dipolar moment of the nitrogen atom on the nicotinate ring, according to Refs. 16a and b.

4. Conclusions

In conclusion, we have synthesized new *N*-heterotolan liquid crystals using two powerful methodologies. Using the Buchwald protocol, we prepared a chiral intermediate **7** and **13** as a promising candidate for a variety of 2,5-disubstituted pyridine liquid crystals. All final compounds were synthesized through a double Sonogashira reaction. The series **8a–d** and **14** contains a nitrogen atom at 2-position on the aromatic ring. For compounds **10** and **12**, a carboxylate group was inserted between the benzene ring and the chiral tail. The final compounds **8a–d** and **10** showed chiral smectic A* phase. Compounds **12** and **14** did not show liquid-crystalline properties. These results suggest that the relative position of the nitrogen atom on pyridine ring and the nature of the polar group linking the mesogenic core with alkyl chain are important structural parameters to be considered in the design and synthesis of potential technological molecular materials.

5. Experimental

5.1. General

^{1}H and ^{13}C NMR spectra in $CDCl_3$ were obtained using Varian-200 and 300 MHz spectrometers using TMS as the internal standard. Optical rotations were recorded on a Perkin–Elmer 341 polarimeter at the sodium D line. The thermal transitions and the mesomorphic textures were determined using an Olympus BX43 polarizing microscope in conjunction with Mettler FP90 controller and HT84 heating stage and Perkin–Elmer 141 differential scanning calorimeter. The rate of heating or cooling was 10 °C min^{-1}. ESI-MS data were collected on a Waters® Micromass® Q-Tof micro™ mass spectrometer with Z-spray electrospray source. Samples were infused from a 100 μL gas-tight syringe at 5 μL min^{-1}, via a syringe pump. Instrument settings were unexceptional: capillary voltage 4500 V, cone voltage 50 V, source temperature 100 °C, desolvation gas temperature 100 °C. Nitrogen was used as the desolvation gas. Elemental analyses were conducted at the central analitica/IQ-UFRGS using a Perkin–Elmer 2400 CHN Analyser. Purification by column chromatography was carried out on 70–230 mesh Merck silica gel 60. 4-Bromobenzoic acid, 6-chloro-nicotinic acid, 4-(*N*,*N*-dimethylamino) pyridine, 2,5-di-bromopyridine, (*S*)-(−)-2-methyl-1-butanol (~95%), 1,3-dicyclohexylcarbodiimide, triphenylphosphine, palladium(II) chloride, 2-methyl-3-butyn-2-ol, and copper(I) iodide were purchased from Aldrich, and used as-received unless otherwise specified. Chemicals were used without further purification. Dichloromethane (CH_2Cl_2) was distilled over calcium hydride (CaH_2) under argon immediately before use. Triethylamine (Et_3N) was distilled over potassium hydroxide (KOH) under argon immediately before use. The reactions were monitored by analytical thin-layer chromatography (TLC) with Merck aluminum plates with 0.2 mm of silica gel 60 F_{254} and Shimadzu GC 17 A Series. Anhydrous sodium sulfate was used to dry all organic extracts. Toluene was first heated at reflux over sodium and then distilled under argon. All reactions involving Sonogashira coupling were performed in one-neck round-bottom flask equipped with septum stoppers and charged with triethylamine (Et_3N), aromatic iodide, and alkyne under argon atmosphere for 20 min. Copper(I) iodide (CuI), triphenylphosphine (PPh_3), and bis-(triphenylphosphine)palladium(II) chloride ($PdCl_2(PPh_3)_2$) were then added.

5.2. Representative procedure for homologues **2a**

5.2.1. 1-Bromo-4-heptyloxybenzene (**2a**)

p-Bromophenol (5.5 g, 34.8 mmol) and potassium hydroxide (2.2 g, 38.3 mmol) were added to benzene/DMF (1:1 v/v, 40 mL) solution and heated at 50 °C for 20 min. Then, *n*-heptylbromide (6.0 mL, 38.4 mmol) was added dropwise and the mixture heated under reflux for 6 h. The solid formed was filtered and the filtrate concentrated. The residue was dissolved in diethyl ether (75 mL), washed with solution of 10% sodium bicarbonate (2×75 mL) and water (75 mL), and dried over anhydrous sodium sulfate. The solvent was removed and a pale yellow oil was distilled at reduced pressure yielding 95% of colorless oil. Bp 115 °C at 1 mmHg. ^{1}H NMR ($CDCl_3$/TMS, 200 MHz) δ (ppm): 0.9 (t, 3H, J=6.4 Hz, CH_3), 1.0 (m, 8H, CH_2), 1.2 (m, 2H, CH_2), 3.9 (t, 2H, J=6.6 Hz, OCH_2), 6.7 (d, 2H, J=9.0 Hz, Ar), 7.3 (d, 2H, J=9.2 Hz, Ar).

5.2.2. Data for 1-bromo-4-octyloxybenzene (**2b**)

Bp 117 °C at 1 mmHg. Yield: 90%. ^{1}H NMR ($CDCl_3$/TMS, 200 MHz) δ (ppm): 0.9 (t, 3H, J=6.4 Hz, CH_3), 1.0 (m, 10H, CH_2), 1.3 (m, 2H, CH_2), 3.9 (t, 2H, J=6.6 Hz, OCH_2), 6.8 (d, 2H, J=9.0 Hz, Ar), 7.4 (d, 2H, J=9.2 Hz, Ar).

5.2.3. Data for 1-bromo-4-nonyloxybenzene (**2c**)

Bp 115 °C at 1 mmHg. Yield: 95%. ^{1}H NMR ($CDCl_3$/TMS, 200 MHz) δ (ppm): 0.9 (t, 3H, J=6.4 Hz, CH_3), 1.0 (m, 12H, CH_2), 1.2 (m, 2H, CH_2), 3.9 (t, 2H, J=6.6 Hz, OCH_2), 6.7 (d, 2H, J=9.0 Hz, Ar), 7.3 (d, 2H, J=9.2 Hz, Ar).

5.2.4. Data for 1-bromo-4-decyloxybenzene (**2d**)

Bp 143 °C at 1 mmHg. Yield: 96%. ^{1}H NMR ($CDCl_3$/TMS, 200 MHz) δ (ppm): 0.9 (t, 3H, J=6.4 Hz, CH_3), 1.0 (m, 14H, CH_2), 1.2 (m, 2H, CH_2), 3.9 (t, 2H, J=6.6 Hz, OCH_2), 6.7 (d, 2H, J=9.0 Hz, Ar), 7.3 (d, 2H, J=9.2 Hz, Ar).

5.3. Representative procedure for homologues **3a**

5.3.1. 4-(4-Heptyloxyphenyl)-2-methylbut-3-yn-2-ol (**3a**)

A test tube was charged with Et_3N (2 mL), 2-methyl-3-butyn-2-ol (0.2 mL, 1.5 mmol), and **2a** (0.3 g, 1.0 mmol) under argon. To the solution were added CuI (0.7 mg), PPh_3 (4.3 mg), and $PdCl_2(PPh_3)_2$ (2.2 mg). The mixture was heated for 20 h at 90 °C. After cooling, the solid was filtered and washed with

diethyl ether (20 mL). The filtered mixture was evaporated, and the resulting dark yellow oil was dissolved in CH_2Cl_2 (30 mL) and washed with water (3×20 mL), cold 5 N hydrochloric acid (20 mL), and water (20 mL) again. The organic layer was dried over anhydrous sodium sulfate. The solvent was evaporated and the remaining solid was purified by chromatography. A yellow oil was obtained with a yield of 75%. ^{1}H NMR ($CDCl_3$/TMS, 200 MHz) δ (ppm): 0.8 (t, 3H, J=6.4 Hz, CH_3), 1.2 (m, 8H, CH_2), 1.5 (s, 6H, CH_3), 1.6 (m, 2H, CH_2), 2.1 (s, 1H, OH), 3.8 (t, 2H, J=6.5 Hz, OCH_2), 6.7 (d, 2H, J=7.4 Hz, Ar), 7.2 (d, 2H, J=7.6 Hz, Ar). ^{13}C NMR ($CDCl_3$/TMS, 50 MHz) δ (ppm): 159.0, 132.9, 114.5, 114.3, 92.3, 82.0, 68.0, 65.5, 31.8, 31.5, 29.3, 25.9, 22.6, 14.0.

*5.3.2. Data for 4-(4-octyloxyphenyl)-2-methylbut-3-yn-2-ol (**3b**)*

Yield: 83%. ^{1}H NMR ($CDCl_3$/TMS, 200 MHz) δ (ppm): 0.8 (t, 3H, J=6.4 Hz, CH_3), 1.2 (m, 10H, CH_2), 1.5 (s, 6H, CH_3), 1.6 (m, 2H, CH_2), 2.1 (s, 1H, OH), 3.8 (t, 2H, J=6.5 Hz, OCH_2), 6.7 (d, 2H, J=7.4 Hz, Ar), 7.2 (d, 2H, J=7.6 Hz, Ar). ^{13}C NMR ($CDCl_3$/TMS, 50 MHz) δ (ppm): 159.0, 132.9, 114.5, 114.3, 92.3, 82.0, 68.0, 65.5, 31.8, 31.5, 29.5, 29.3, 25.9, 22.6, 14.0.

*5.3.3. Data for 4-(4-nonyloxyphenyl)-2-methylbut-3-yn-2-ol (**3c**)*

Yield: 78%. ^{1}H NMR ($CDCl_3$/TMS, 200 MHz) δ (ppm): 0.8 (t, 3H, J=6.4 Hz, CH_3), 1.2 (m, 12H, CH_2), 1.5 (s, 6H, CH_3), 1.6 (m, 2H, CH_2), 2.1 (s, 1H, OH), 3.8 (t, 2H, J=6.5 Hz, OCH_2), 6.7 (d, 2H, J=7.4 Hz, Ar), 7.2 (d, 2H, J=7.6 Hz, Ar). ^{13}C NMR ($CDCl_3$/TMS, 50 MHz) δ (ppm): 159.0, 132.9, 114.5, 114.3, 92.3, 82.0, 68.0, 65.5, 31.8, 31.5, 29.5, 29.3, 29.1, 25.9, 22.6, 14.0.

*5.3.4. Data for 4-(4-decyloxyphenyl)-2-methylbut-3-yn-2-ol (**3d**)*

Yield: 87%. ^{1}H NMR ($CDCl_3$/TMS, 200 MHz) δ (ppm): 0.8 (t, 3H, J=6.4 Hz, CH_3), 1.2 (m, 14H, CH_2), 1.5 (s, 6H, CH_3), 1.6 (m, 2H, CH_2), 2.1 (s, 1H, OH), 3.8 (t, 2H, J=6.5 Hz, OCH_2), 6.7 (d, 2H, J=7.4 Hz, Ar), 7.2 (d, 2H, J=7.6 Hz, Ar). ^{13}C NMR ($CDCl_3$/TMS, 50 MHz) δ (ppm): 159.0, 132.9, 114.5, 114.3, 92.3, 82.0, 68.0, 65.5, 31.8, 31.5, 29.5, 29.3, 29.2, 29.1, 25.9, 22.6, 14.0.

*5.4. Representative procedure for homologues **4a***

*5.4.1. 1-Ethynyl-4-heptyloxybenzene (**4a**)*

Potassium hydroxide (0.3 g, 5.4 mmol) and isopropanol (4 mL) were added to a round bottomed flask and heated at 50 °C for 10 min. Then, a solution of 4-(4-heptyloxyphenyl)-2-methylbut-3-yn-2-ol (0.5 g, 1.8 mmol) and isopropanol (5 mL) was added at once. The mixture was heated under reflux for 2 h. The solvent was evaporated, the residue was dissolved in diethyl ether (30 mL), and washed with water (3×20 mL). The organic layer was dried over anhydrous sodium sulfate. The solvent was evaporated and a yellow oil was obtained in 76% yield. ^{1}H NMR ($CDCl_3$/TMS, 200 MHz) δ (ppm): 0.9 (t, 3H, J=6.4 Hz, CH_3), 1.3 (m, 8H, CH_2), 1.8 (m, 2H, CH_2), 3.0 (s, 1H, CH), 3.9 (t, 2H, J=6.4 Hz, OCH_2), 6.8 (d, 2H, J=8.8 Hz, Ar), 7.4 (d, 2H, J=8.8 Hz, Ar). ^{13}C NMR ($CDCl_3$/TMS, 50 MHz) δ (ppm): 159.5, 133.5, 114.4, 113.8, 83.7, 75.6, 68.0, 31.9, 29.3, 25.9, 22.6, 14.0.

*5.4.2. Data for 1-ethynyl-4-octyloxybenzene (**4b**)*

Yield: 77%. ^{1}H NMR ($CDCl_3$/TMS, 200 MHz) δ (ppm): 0.9 (t, 3H, J=6.4 Hz, CH_3), 1.3 (m, 10H, CH_2), 1.8 (m, 2H, CH_2), 3.0 (s, 1H, CH), 3.9 (t, 2H, J=6.4 Hz, OCH_2), 6.8 (d, 2H, J=8.8 Hz, Ar), 7.4 (d, 2H, J=8.8 Hz, Ar). ^{13}C NMR ($CDCl_3$/TMS, 50 MHz) δ (ppm): 159.5, 133.5, 114.4, 113.8, 83.7, 75.6, 68.0, 31.9, 29.5, 29.2, 25.9, 22.6, 14.0.

*5.4.3. Data for 1-ethynyl-4-nonyloxybenzene (**4c**)*

Yield: 71%. ^{1}H NMR ($CDCl_3$/TMS, 200 MHz) δ (ppm): 0.9 (t, 3H, J=6.4 Hz, CH_3), 1.3 (m, 12H, CH_2), 1.8 (m, 2H, CH_2), 3.0 (s, 1H, CH), 3.9 (t, 2H, J=6.4 Hz, OCH_2), 6.8 (d, 2H, J=8.8 Hz, Ar), 7.4 (d, 2H, J=8.8 Hz, Ar). ^{13}C NMR ($CDCl_3$/TMS, 50 MHz) δ (ppm): 159.5, 133.5, 114.4, 113.8, 83.7, 75.6, 68.0, 31.9, 29.5, 29.3, 29.1, 25.9, 22.6, 14.0.

*5.4.4. Data for 1-ethynyl-4-decyloxybenzene (**4d**)*

Yield: 80%. ^{1}H NMR ($CDCl_3$/TMS, 200 MHz) δ (ppm): 0.9 (t, 3H, J=6.4 Hz, CH_3), 1.3 (m, 14H, CH_2), 1.8 (m, 2H, CH_2), 3.0 (s, 1H, CH), 3.9 (t, 2H, J=6.4 Hz, OCH_2), 6.8 (d, 2H, J=8.8 Hz, Ar), 7.4 (d, 2H, J=8.8 Hz, Ar). ^{13}C NMR ($CDCl_3$/TMS, 50 MHz) δ (ppm): 159.5, 133.5, 114.4, 113.8, 83.7, 75.6, 68.0, 31.9, 29.5, 29.3, 29.2, 29.1, 25.9, 22.6, 14.0.

*5.5. (S)-(+)-5-Bromo-2-(methylbutyloxy)pyridine (**7**)*

A one-neck round-bottom flask equipped with septum stoppers was charged with CuI (0.3 g, 1.6 mmol), 1,10-phenanthroline (0.6 g, 3.2 mmol), Cs_2CO_3 (10.4 g, 32.0 mmol), 2,5-dibromopyridine (**5**) (3.8 g, 16.0 mmol), (*S*)-(−)-2-methyl-1-butanol (**6**) (4 mL, 32.0 mmol), and dried toluene (8 mL). The tube was sealed and the mixture was stirred at 110 °C for 26 h. The reaction mixture was cooled to room temperature and filtered through a pad of silica gel, eluting with diethyl ether. The filtrate was concentrated and the residue was purified by chromatography. The colorless oil was obtained with a yield of 60%. $[\alpha]_D^{20}$ +12 (CH_2Cl_2). ^{1}H NMR ($CDCl_3$/TMS, 300 MHz) δ (ppm): 0.9 (t, 3H, J=7.5 Hz, CH_3), 1.0 (d, 3H, J=6.3 Hz, CH_3), 1.2 (m, 1H, C*H*HCH$_3$), 1.4 (m, 1H, CH*H*CH$_3$), 1.8 (m, 1H, CHCH$_3$), 4.0 (dd, 1H, J_{gem}=10.4 Hz, J_{trans}=6.8 Hz, OCH_2), 4.1 (dd, 1H, J_{gem}=10.4 Hz, J_{cis}=6.5 Hz, OCH_2), 6.6 (d, 1H, J=8.1 Hz, Ar), 7.6 (dd, 1H, J=6.3 Hz, 2.6 Hz, Ar), 8.2 (d, 1H, J=2.3 Hz, Ar). ^{13}C NMR ($CDCl_3$/TMS, APT, 75 MHz) δ (ppm): 162.8, 147.3, 140.6, 112.4, 111.1, 70.9, 34.2, 26.0, 16.3, 11.1.

*5.6. Representative procedure for homologues **8a***

*5.6.1. (S)-(+)-5-(4-Heptyloxyphenylethynyl)-2-(2-methylbutyloxy)pyridine (**8a**)*

A test tube was charged with Et_3N (2 mL), 1-ethynyl-4-heptyloxybenzene (**4a**) (0.3 g, 1.4 mmol), and **7** (0.2 g, 0.9 mmol)

under argon. CuI (0.6 mg), PPh_3 (4.0 mg), and $PdCl_2(PPh_3)_2$ (2.1 mg) were added to the stirred solution. The mixture was heated for 20 h at 90 °C. After cooling, the solid was filtered off and washed with diethyl ether (20 mL). The solution was evaporated and the resulting dark yellow oil was dissolved in CH_2Cl_2 (30 mL), and this phase was washed with water (3×20 mL), cold 5 N hydrochloric acid (20 mL), and water (20 mL). The organic phase was dried over anhydrous sodium sulfate. The solvent was evaporated and the remaining solid was purified by chromatography. The yellow oil was obtained with a yield of 54%. $[\alpha]_D^{20}$ +3 (CH_2Cl_2). ^{1}H NMR ($CDCl_3$/TMS, 200 MHz) δ (ppm): 0.8–0.9 (m, 9H, CH_3), 1.1–1.5 (m, 13H, CH, CH_2), 3.9 (t, 2H, J=6.4 Hz, CH_2O), 4.0 (m, 1H, OCH_2), 4.1 (m, 1H, OCH_2), 6.6 (d, 1H, J=8.8 Hz, Ar), 6.8 (d, 2H, J=8.0 Hz, Ar), 7.4 (d, 2H, J=8.6 Hz, Ar), 7.5 (dd, 1H, J=7.8 Hz, 2.2 Hz, Ar), 8.1 (d, 1H, J=2.0 Hz, Ar). ^{13}C NMR ($CDCl_3$/TMS, APT, 50 MHz) δ (ppm): 163.2, 159.2, 149.7, 141.0, 132.9, 114.8, 114.5, 113.2, 110.7, 90.6, 84.8, 71.1, 68.1, 34.5, 31.9, 29.4, 29.2, 26.2, 26.0, 22.7, 16.5, 14.2, 11.4. Anal. Calcd for $C_{25}H_{33}NO_2$: C, 79.11; H, 8.76; N, 3.69. Found: C, 78.96; H, 8.42; N, 3.78. HRMS (ESI): *m/z* calcd for $[M]^+$ 379.2511, found $[M+1]^+$: 380.2585.

5.6.2. Data for (S)-(+)-5-(4-octyloxyphenylethynyl)-2-(2-methylbutyloxy)pyridine (**8b**)

Yield: 60%. ^{1}H NMR ($CDCl_3$/TMS, 200 MHz) δ (ppm): 0.8–0.9 (m, 9H, CH_3), 1.2–1.6 (m, 15H, CH, CH_2), 3.9 (t, 2H, J=6.4 Hz, CH_2O), 4.0 (m, 2H, OCH_2), 6.6 (d, 1H, J=8.8 Hz, Ar), 6.8 (d, 2H, J=8.0 Hz, Ar), 7.4 (d, 2H, J=8.6 Hz, Ar), 7.5 (dd, 1H, J=7.8, 2.2 Hz, Ar), 8.1 (d, 1H, J=1.9 Hz, Ar). ^{13}C NMR ($CDCl_3$/TMS, APT, 50 MHz) δ (ppm): 163.2, 159.2, 149.7, 141.0, 132.9, 114.8, 114.5, 113.2, 110.7, 90.6, 84.8, 71.1, 68.1, 34.5, 31.9, 29.5, 29.3, 29.2, 26.2, 26.0, 22.7, 16.5, 14.2, 11.4. Anal. Calcd for $C_{26}H_{35}NO_2$: C, 79.35; H, 8.96; N, 3.56. Found: C, 79.30; H, 9.04; N, 3.34. HRMS (ESI): *m/z* calcd for $[M]^+$ 393.2667, found $[M+1]^+$: 394.2742.

5.6.3. Data for (S)-(+)-5-(4-nonyloxyphenylethynyl)-2-(2-methylbutyloxy)pyridine (**8c**)

Yield: 45%. ^{1}H NMR ($CDCl_3$/TMS, 200 MHz) δ (ppm): 0.8 (d, 3H, J=6.3 Hz, CH_3), 0.9 (t, 6H, J=6.6 Hz, CH_3), 1.2–1.5 (m, 16H, CH_2), 1.7 (m, 1H, CH), 3.9 (t, 2H, J=6.4 Hz, CH_2O), 4.0 (dd, 1H, J_{gem}=10.2 Hz, J_{trans}=6.6 Hz, OCH_2), 4.1 (dd, 1H, J_{gem}=10.2 Hz, J_{cis}=6.0 Hz, OCH_2), 6.6 (d, 1H, J=8.8 Hz, Ar), 6.8 (d, 2H, J=8.0 Hz, Ar), 7.4 (d, 2H, J=8.6 Hz, Ar), 7.5 (dd, 1H, J=7.8, 2.2 Hz, Ar), 8.1 (d, 1H, J=1.9 Hz, Ar). ^{13}C NMR ($CDCl_3$/TMS, APT, 50 MHz) δ (ppm): 163.2, 159.2, 149.7, 141.0, 132.9, 114.8, 114.5, 113.2, 110.7, 90.6, 84.8, 71.1, 68.1, 34.5, 31.9, 29.5, 29.4, 29.3, 29.2, 26.2, 26.0, 22.7, 16.5, 14.2, 11.4. Anal. Calcd for $C_{27}H_{37}NO_2$: C, 79.56; H, 9.15; N, 3.44. Found: C, 79.87; H, 9.27; N, 3.30. HRMS (ESI): *m/z* calcd for $[M]^+$ 407.2824, found $[M+1]^+$: 408.2906.

5.6.4. Data for (S)-(+)-5-(4-decyloxyphenylethynyl)-2-(2-methylbutyloxy)pyridine (**8d**)

Yield: 57%. ^{1}H NMR ($CDCl_3$/TMS, 200 MHz) δ (ppm): 0.8–0.9 (m, 9H, CH_3), 1.2–1.7 (m, 19H, CH, CH_2), 3.9 (t, 2H, J=6.4 Hz, CH_2O), 4.0 (m, 1H, OC*H*H), 4.1 (m, 1H, OCH*H*), 6.6 (d, 1H, J=8.8 Hz, Ar), 6.8 (d, 2H, J=8.0 Hz, Ar), 7.4 (d, 2H, J=8.6 Hz, Ar), 7.5 (dd, 1H, J=7.8 Hz, 2.2 Hz, Ar), 8.1 (d, 1H, J=2.0 Hz, Ar). ^{13}C NMR ($CDCl_3$/TMS, APT, 50 MHz) δ (ppm): 163.2, 159.2, 149.7, 141.0, 132.9, 114.8, 114.5, 113.2, 110.7, 90.6, 84.8, 71.1, 68.1, 34.5, 31.9, 29.5, 29.4, 29.3, 29.2, 29.1, 26.2, 26.0, 22.7, 16.5, 14.2, 11.4. Anal. Calcd for $C_{28}H_{39}NO_2$: C, 79.77; H, 9.32; N, 3.32. Found: C, 79.71; H, 9.30; N, 3.70. HRMS (ESI): *m/z* calcd for $[M]^+$ 421.2980, found $[M+1]^+$: 422.3038.

5.7. (S)-(+)-(2-Methyl)butyloxy-4-bromobenzoate (**9**)

4-Bromobenzoic acid (4.0 g, 20.0 mmol) and distilled $SOCl_2$ (7.3 mL, 92.5 mmol) were added to 20 mL of benzene under argon atmosphere. The mixture was heated under refluxed for 3 h. The reaction mixture was cooled and the solvent and excess of $SOCl_2$ were removed. The viscous oil was dissolved in dried pyridine (10 mL, 71.0 mmol) under argon atmosphere. The mixture was cooled in an ice bath and a solution of (*S*)-(−)-2-methyl-1-butanol (**6**) (2 mL, 20 mmol) in dried CH_2Cl_2 (15 mL) was added dropwise. The mixture was heated under reflux for 6 h and at room temperature for additional 12 h. The solid residue was filtered and the organic layer was dissolved in diethyl ether (100 mL). The organic phase was washed with a saturated solution of NaCl (20 mL), $NaHCO_3$ (2×20 mL), and NaCl (20 mL). The organic phase was dried over anhydrous sodium sulfate and the solvent was evaporated. The remaining solid was obtained with a yield of 50%. ^{1}H NMR ($CDCl_3$/TMS, 200 MHz) δ (ppm): 0.9 (t, 3H, J=7.4 Hz, CH_3), 1.0 (d, 3H, J=6.8 Hz, CH_3), 1.2 (m, 1H, C*H*HCH_3), 1.5 (m, 1H, CH*H*CH_3), 1.8 (m, 1H, $CHCH_3$), 4.1 (dd, 1H, J_{gem}=10.8 Hz, J_{trans}=6.6 Hz, OCH_2), 4.2 (dd, 1H, J_{gem}=10.8 Hz, J_{cis}=6.0 Hz, OCH_2), 7.6 (d, 2H, J=8.6 Hz, Ar), 7.9 (d, 2H, J=8.6 Hz, Ar). ^{13}C NMR ($CDCl_3$/TMS, APT, 50 MHz) δ (ppm): 165.8, 149.3, 132.2, 131.5, 127.8, 69.8, 34.2, 26.1, 16.5, 11.4.

5.8. (S)-2-(2-Methyl)butyloxy-4-(4-decyloxyphenylethynyl)benzoate (**10**)

A test tube was charged with Et_3N (6 mL), **4d** (0.2 g, 0.75 mmol), and **9** (0.1 g, 0.5 mmol) under argon. CuI (0.2 mg), PPh_3 (1.3 mg), and $PdCl_2(PPh_3)_2$ (0.7 mg) were added to the stirred solution. The mixture was heated for 20 h at 90 °C. After cooling, the solid was filtered off and washed with diethyl ether (20 mL). The filtered mixture was evaporated and the resulting dark yellow oil was dissolved in diethyl ether (20 mL) and washed with water (3×20 mL), cold 1 N hydrochloric acid (20 mL), and water (20 mL). The organic phase was dried over anhydrous sodium sulfate and the solvent was evaporated. The remaining solid was purified by chromatography affording a yellow solid with a yield of 75%. ^{1}H NMR ($CDCl_3$/TMS, 200 MHz) (ppm): 0.8–0.9 (m, 9H, CH_3), 1.2–1.8 (m, 19H, CH_2, CH), 3.9 (t, 2H, J=6.6 Hz, OCH_2), 4.1 (m, 2H, $COOCH_2$), 6.3 (d, 2H, Ar), 7.4 (d, 2H, Ar), 7.5 (d, 2H, Ar), 7.9 (d, 2H, Ar). ^{13}C NMR

($CDCl_3$/TMS, APT, 50 MHz) δ (ppm): 166.1, 159.5, 133.2, 131.2, 129.4, 128.3, 114.5, 114.4, 92.6, 87.4, 69.6, 68.0, 34.3, 31.9, 29.5, 29.4, 29.3, 29.2, 26.2, 26.0, 22.7, 16.5, 14.2, 11.3. Anal. Calcd for $C_{30}H_{40}O_3$: C, 80.32; H, 8.99. Found: C, 79.87; H, 9.24. HRMS (ESI): *m/z* calcd for $[M]^+$ 448.2977, found $[M+1]^+$: 449.3065.

5.9. (S)-2-(Methyl)butyloxy-6-chloronicotinate (*11b*)

6-Chloronicotinic acid (**11a**) (3.0 g, 19.0 mmol) and (*S*)-(−)-2-methyl-1-butanol (**6**) (2.0 mL, 19.0 mmol) were added to dried CH_2Cl_2 (35 mL) and the mixture was stirred at room temperature for 10 min. DCC (4.7 g, 22.8 mmol) and DMAP (0.03 g, 0.22 mmol) were, then, added and the mixture was stirred for 24 h at room temperature. The resulting solution was filtered over Celite and the solvent evaporated. The remaining solid was recrystallized from ethanol. The white solid was obtained with a yield of 40%. ^{1}H NMR ($CDCl_3$/TMS, 200 MHz) δ (ppm): 0.8−1.0 (m, 6H, CH_3), 1.3 (m, 1H, C*H*HCH$_3$), 1.5 (m, 1H, CH*H*CH$_3$), 1.9 (m, 1H, CHCH$_3$), 4.2 (dd, 1H, J_{gem}=10.8 Hz, J_{trans}=6.6 Hz, OCH_2), 4.3 (dd, 1H, J_{gem}=10.8 Hz, J_{cis}=4.8 Hz, OCH_2), 7.4 (d, 1H, J=8.2 Hz, Ar), 8.2 (dd, 1H, J=6.0, 2.4 Hz, Ar), 9.0 (d, 1H, J=1.6 Hz, Ar). ^{13}C NMR ($CDCl_3$/TMS, APT, 50 MHz) δ (ppm): 164.3, 155.4, 150.9, 139.4, 125.2, 124.1, 70.1, 34.1, 26.0, 16.4, 11.2.

5.10. (S)-2-(2-Methyl)butoxy-6-(4-decyloxyphenylethynyl) nicotinate (*12*)

A test tube was charged with Et_3N (7 mL), **4d** (0.32 g, 1.23 mmol), and **11b** (0.2 g, 0.8 mmol) under argon. CuI (0.5 mg), PPh_3 (3.2 mg), and $PdCl_2(PPh_3)_2$ (1.8 mg) were added to the stirred solution. The mixture was heated for 20 h at 90 °C. After cooling, the solid was filtered off and washed with diethyl ether (20 mL). The filtered mixture was evaporated and the resulting dark yellow oil was dissolved in diethyl ether (20 mL) and washed with water (3×20 mL), cold 1 N hydrochloric acid (20 mL), and water (20 mL). The organic phase was dried over anhydrous sodium sulfate and the solvent was evaporated. The remaining solid was purified by chromatography affording a yellow solid with a yield of 65%. ^{1}H NMR ($CDCl_3$/TMS, 200 MHz) δ (ppm): 0.9−1.1 (m, 9H, CH_3), 1.3−1.9 (m, 19H, CH, CH_2), 4.0 (t, 2H, J=6.6 Hz, OCH_2), 4.2 (m, 2H, $COOCH_2$), 6.9 (d, 2H, J=8.8 Hz, Ar), 7.6 (m, 3H, J=8.6 Hz, Ar), 8.3 (dd, 1H, J=6.0, 2.2 Hz, Ar), 9.2 (d, 1H, J=1.4 Hz, Ar). ^{13}C NMR ($CDCl_3$/TMS, 50 MHz) δ (ppm): 164.9, 160.2, 150.9, 147.3, 137.0, 133.8, 128.2, 124.4, 114.8, 114.5, 113.3, 92.9, 87.4, 70.0, 68.1, 34.2, 31.8, 29.5, 29.4, 29.3, 29.1, 26.1, 26.0, 22.7, 16.5, 14.1, 11.3. Anal. Calcd for $C_{29}H_{39}NO_3$: C, 77.47; H, 8.74; N, 3.12. Found: C, 77.14; H, 9.10; N, 3.17. HRMS (ESI): *m/z* calcd for $[M]^+$ 449.2929, found $[M+1]^+$: 450.3000.

5.11. (S)-Ethyl-2-(5-bromopyridin-2-yl)oxypropionate (*13*)

A one-neck round-bottom flask equipped with septum stopper was charged with CuI (0.3 g, 1.6 mmol), 1,10-phenanthroline (0.6 g, 3.2 mmol), Cs_2CO_3 (10.4 g, 32.0 mmol), 2,5-dibromopyridine (**5**) (3.8 g, 16.0 mmol), (*S*)-(−)-ethyl lactate (3.6 mL, 32.0 mmol), and dried toluene (8 mL). The tube was sealed and the mixture was stirred at 110 °C for 26 h. The reaction mixture was cooled to room temperature and filtered through a pad of silica gel, eluting with diethyl ether. The filtrate was concentrated and the residue was purified by chromatography. The yellow oil was obtained with a yield of 30%. ^{1}H NMR ($CDCl_3$/TMS, 200 MHz) δ (ppm): 1.3 (t, 3H, J=7.2 Hz, CH_3), 1.6 (d, 3H, J=7.0 Hz, $CHCH_3$), 4.2 (q, 2H, J=7.2 Hz, OCH_2CH_3), 5.2 (q, 1H, J=7.0 Hz, $CHCH_3$), 6.8 (d, 1H, J=8.8 Hz, Ar), 7.7 (dd, 1H, J=6.2, 2.6 Hz, Ar), 8.1 (d, 1H, J=2.4 Hz, Ar).

5.12. (S)-(−)-Ethyl-2-{[5-(6-decyloxyphenyl)ethynyl]pyridin-2-yl}oxypropionate (*14*)

A test tube was charged with Et_3N (7 mL), **4d** (0.32 g, 1.23 mmol), and **13** (0.2 g, 0.8 mmol) under argon. CuI (0.5 mg), PPh_3 (3.2 mg), and $PdCl_2(PPh_3)_2$ (1.8 mg) were added to the stirred solution. The mixture was heated for 20 h at 90 °C. After cooling, the solid was filtered off and washed with diethyl ether (20 mL). The filtered mixture was evaporated and the resulting dark yellow oil was dissolved in diethyl ether (20 mL), and washed with water (3×20 mL), cold 1 N hydrochloric acid (20 mL), and water (20 mL). The organic phase was dried over anhydrous sodium sulfate and the solvent evaporated. The remaining solid was purified by chromatography and a yellow solid was obtained with 45% yield. ^{1}H NMR ($CDCl_3$/TMS, 200 MHz) δ (ppm): 0.9 (t, 3H, J=6.6 Hz, CH_3), 1.3 (m, 17H, CH_2 and CH_3), 1.6 (d, 3H, J=7.0 Hz, CHC*H*$_3$), 1.8 (m, 2H, CH_2), 3.9 (t, 2H, J=6.4 Hz, OCH_2), 4.2 (q, 2H, J=7.2 Hz, OCH_2), 5.3 (q, 1H, J=6.8 Hz, C*H*CH$_3$), 6.7 (d, 1H, J=8.4 Hz, Ar), 6.8 (d, 2H, J=8.8 Hz, Ar), 7.4 (d, 2H, J=8.6 Hz, Ar), 7.7 (dd, 1H, J=6.4, 2.2 Hz, Ar), 8.2 (d, 1H, J=2.2 Hz, Ar). ^{13}C NMR ($CDCl_3$/TMS, 50 MHz) δ (ppm): 172.2, 161.4, 159.2, 149.3, 141.2, 132.8, 114.7, 114.5, 114.1, 110.6, 90.9, 84.5, 70.1, 68.0, 61.0, 31.9, 29.5, 29.4, 29.3, 29.2, 26.0, 22.7, 17.6, 14.1. HRMS (ESI): *m/z* calcd for $[M]^+$ 451.2723, found $[M+1]^+$: 452.3101.

Acknowledgements

The authors acknowledge Edital Universal-2004-CNPq and CAPES for financial support. Laboratory of Molecular Catalysis-IQ-UFRGS and Prof. Jaïrton. Dupont for ESI-MS facilities. A.S. and G.D.V. are undergraduate students and thank PIBIC-UFRGS and FAPERGS for their fellowship.

Supplementary data

The spectral and analytical data on isolated products, including ^{1}H, ^{13}C NMR spectra, HRMS, DSC thermograms, and mesophase photos are supplied. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.03.005.

References and notes

1. (a) Demus, D.; Goodby, J.; Gray, G. W.; Spiess, H. W.; Vill, V. *Handbook of Liquid Crystals*; VCH: Weinheim, 1998; Vol. 2a; (b) Kelly, S. M.; O'Neill, M. Handbook of Advanced Electronic and Photonic Materials and Devices. *Liquid Crystals, Display and Laser Materials*; Nalwa, H. S., Ed.; Academic: Los Angeles, CA, 2000; Vol. 7.
2. (a) Leroux, N.; Chien, L. C. *Liq. Cryst.* **1996**, *21*, 189; (b) Kirsch, P.; Bremer, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 4216; (c) Karamyshea, L. A.; Kovshev, E. I.; Pavluchenko, A. I.; Roitman, K. V.; Titov, V. V.; Torgova, S. I.; Grebenkin, M. F. *Mol. Cryst. Liq. Cryst.* **1981**, *67*, 241.
3. (a) Finkenzeller, U. *Kontakte* **1988**, *2*, 7; (b) Gray, G. W.; Harrison, K. J.; Nash, J. A. *Electron. Lett.* **1973**, *9*, 130.
4. (a) Boller, A.; Cereghetti, M.; Schadt, M.; Scherrer, H. *Mol. Cryst. Liq. Cryst.* **1977**, *42*, 1225; (b) Bremer, M. *Adv. Mater.* **1995**, *7*, 867; (c) Petrov, V.; Torgova, S. I.; Karamysheva, L. A.; Tanenaka, S. *Liq. Cryst.* **1999**, *26*, 1141.
5. (a) Eidenschink, R.; Erdmann, D.; Krause, J.; Pohl, I. *Angew. Chem., Int. Ed.* **1977**, *89*, 103; (b) Liang, J. C.; Cross, J. O.; Chen, L. *Mol. Cryst. Liq. Cryst.* **1989**, *147*, 199.
6. (a) Reiffenrath, V.; Bremer, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 87; (b) Pavluchenko, A. I.; Smirnova, N. I.; Petrov, V. F.; Grebyonkin, M. F.; Titov, V. V. *Mol. Cryst. Liq. Cryst.* **1991**, *209*, 155.
7. (a) Hird, M.; Toyne, K. J.; Gray, G. W. *Liq. Cryst.* **1993**, *14*, 741; (b) Seto, K.; Shimojitosho, H.; Imazaki, H. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1020; (c) Merlo, A. A.; Vasconcelos, U. B.; Ely, F.; Gallardo, H. *Liq. Cryst.* **2000**, *27*, 657; (d) Merlo, A. A.; Gallardo, H.; Ely, F.; Bortoluzzi, A. J. *Braz. J. Phys.* **2002**, *32*, 548; (e) Gallardo, H.; Ely, F.; Conte, G.; Merlo, A. A. *Liq. Cryst.* **2004**, *31*, 1413; (f) Cross, G. J.; Seed, A. J.; Toyne, K. J.; Goodby, J. W.; Hird, M.; Artal, M. C. *J. Mater. Chem.* **2000**, *10*, 1555; (g) Song, X.; Li, J.; Zhang, S. *Liq. Cryst.* **2003**, *30*, 1123; (h) Song, X.; Li, J.; Liu, G.; Zhang, S.; Ye, C.; Chen, E. *Liq. Cryst.* **2002**, *29*, 1533; (i) Young, D. D.; Scharrer, E.; Yoa, M. V. *Mol. Cryst. Liq. Cryst.* **2003**, *408*, 21; (j) Ribeiro, A. C.; Nguyen, H. T.; Galerne, Y.; Guillon, D. *Liq. Cryst.* **2000**, *27*, 27.
8. Pavluchenko, A. I.; Petrov, V. F.; Smirnova, I. *Liq. Cryst.* **1995**, *19*, 811.
9. Paquette, L. A. *Principles of Modern Heterocyclic Chemistry*; The Benjamin Cummings: Mexico, DF, 1987.
10. (a) Ullmann, F. *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 2382; (b) Goodbrand, H. B.; Hu, N.-X. *J. Org. Chem.* **1999**, *64*, 670; (c) Ullmann, F. *Chem. Ber.* **1904**, *37*, 853; (d) Beletskaya, I. P.; Cheprakov, A. V. *Coord. Chem. Rev.* **2004**, *248*, 2337 and references cited herein.
11. Buchwald, S. L.; Wolfe, J. P.; Wagw, S.; Marcoux, J.-F. *Acc. Chem. Res.* **1998**, *31*, 805.
12. Hartwig, J. *Acc. Chem. Res.* **1998**, *31*, 852.
13. Buchwald, S. L.; Doye, S.; Marcoux, J.-F. *J. Am. Chem. Soc.* **1997**, *119*, 10539.
14. Buchwald, S. L.; Kiyomori, A.; Marcoux, J.-F. *Tetrahedron Lett.* **1999**, *40*, 2657.
15. (a) Buchwald, S. L.; Job, G. E.; Nordmann, G.; Wolfer, M. *Org. Lett.* **2002**, *4*, 973; (b) The Buchwald group has recently reported that bulky biaryl phosphine ligand can help to minimize β-hydride elimination. See: Vorogushin, A. V.; Huang, X.; Buchawald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 8146.
16. (a) Vasconcelos, U. B.; Dalmolin, E.; Merlo, A. A. *Org. Lett.* **2005**, *7*, 1027; (b) Vasconcelos, U. B.; Merlo, A. A. *Synthesis* **2006**, 1141; (c) Barberá, J.; Marcos, M.; Serrano, J. L. *Mol. Cryst. Liq. Cryst.* **1989**, *166*, 61.
17. (a) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *16*, 4467; (b) Sonogashira, K.; Yatake, T.; Tohda, Y.; Takahashi, S.; Hagihara, N. *J. Chem. Soc., Chem. Commun.* **1977**, 291; (c) Takahashi, K.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627; (d) General review, see: Sonogashira, K. *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, 1998; Chapter 5; (e) Negishi, E.-I.; Anastasia, L. *Chem. Rev.* **2003**, *103*, 1979; Verkade, J. G.; Urgaonkar, S. *J. Org. Chem.* **2004**, *69*, 5752.
18. Melissaris, A. P.; Litt, M. H. *Macromolecules* **1994**, *27*, 883.
19. (a) Merlo, A. A.; Gallardo, H. *Synth. Commun.* **1993**, *23*, 2159; (b) Merlo, A. A.; Livotto, P. R.; Gallardo, H.; Taylor, T. R. *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **1998**, *309*, 111.
20. Hartley, C. S.; Lemieux, R. P. *Liq. Cryst.* **2004**, *31*, 1101.
21. Gray, G. W.; Goodby, J. W. G. *Smectic Liquid Crystals. Textures and Structures*; Leonard Hill: London, 1984.