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Synthesis of Thermotropic Liquid Crystals Derived from Phenylpiperazine Containing an Enyne Unit

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Thermotropic liquid crystals are of great technological importance. Much research is devoted to the development of stable compounds with transition temperatures close to room temperature. The interest of this work is the synthesis of thermotropic liquid crystal precursor units containing phenylpiperazine and/or phenylacetylenic units. Homologues of a Schiff base series and an enyne series have been synthesized, allowing comparisons of their mesomorphic and thermodynamic properties. The Schiff bases showed smectogenic behavior and the enynes a smectic dimorphism and/or a nematic phase. The synthetic methodology was efficient for the synthesis of the desired precursor, 4-[4′-(prop-1-yn-3-al)phenyl]-piperazine-1-carboxylic acid ethyl ester.

Keywords: phenylpiperazine, enyne, Schiff base

INTRODUCTION

The interest in the synthesis of thermotropic liquid crystals has experienced growth owing to its technological applications. Intensive studies have been done in order to verify the correlations between chemical constitution and mesomorphic behavior [1,2]. Synthesis of chemical compounds having a long extended rodlike molecular shape is still the fundamental premise and guarantee for the occurrence of thermotropic liquid crystalline phases.

Many times aromatic rings have been substituted by heterocyclics and the effect of heteroatoms studied. Changes of polarity, polarizability, and sometimes the geometry of a molecule can be achieved by the introduction of heterocyclic ring [3]. Such changes have a strong influence on the type of

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mesomorphic phase, phase transition temperatures, dielectric constants, and other properties of the mesomorphic compound.

This paper describes the preparation and the thermal properties of some new mesogenic compounds containing phenylpiperazine and enyne units. The phenylpiperazine unit is isogeometric with phenylcyclohexane and should possess a thermal flexibility similar to phenylcyclohexane. However, due to the nitrogen electron lone pair of phenylpiperazine, one should expect changes in mesomorphic behavior. The enyne unit, if conveniently substituted, produces a highly conjugated structural unit with high optical polarizability, which is required for some liquid crystal displays [4,5].

The *N*,*N*-disubstituted piperazine conformations were reported [5] and the system exists preferably in the chair conformation with substituents being arranged on equatorial positions. It is also expected that the mutual conjugation between the lone pair of nitrogen electrons and the substituent groups increase the polarity and polarizability of the skeleton [6]. It is known that these characteristics tend to favor smectic properties.

Smectic behavior is necessary for the occurrence of ferroelectricity, which is observed in smectic C* or other tilted chiral phases F* or I*. Cooray et al. reported new liquid crystals containing phenylpiperazine connected to the chiral group through an ester unit. The compounds show ferroelectric and antiferroelectric mesophases [7].

The carbonyl group, as in esters or ketones, has also proved to be of great importance for the appearance of mesomorphic properties. This group introduces a permanent dipole moment required to increase intermolecular attractions which are necessary for smectogenic behavior.

A conjugated enyne linkage has been incorporated in some liquid crystal compounds, and these materials show low viscosity and high birefringence [8]. It is known that liquid crystalline compounds with a highly conjugated unit (as in tolanes and enynes) show high birefringence, which is of interest for liquid crystal displays.

Liquid crystals containing imine linkage have been extensively studied [1,9] because of a large number of *p*,*p*′-disubstituted benzylideneanilines, which are nematic and/or smectic.

Here we focus on synthesis of compounds containing a piperazine and an enyne (or imine) group in order to evaluate their potential for inducing mesomorphism. The intention was to obtain smectic C phases and if observed, to introduce chiral groups to produce ferroelectric compounds.

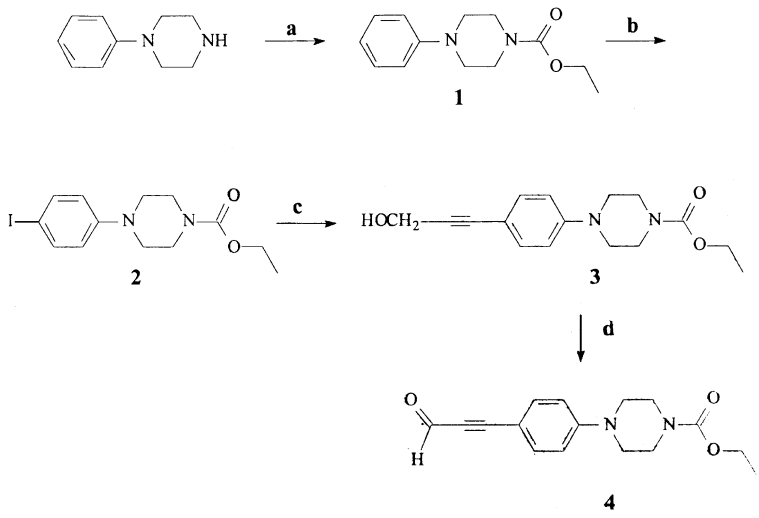
We have investigated the synthesis and mesomorphic behavior of four homologues of the series 1-[4-(N-ethoxycarbonylpiperazinyl)phenyl]-3-(4-n-

alkoxyphenyl)-(prop-1-yn-3-imine), **5**, and two homologues of the series 1-[4-(N-ethoxycarbonylpiperazinyl)phenyl]-4-(4-n-alkoxyphenyl)but-3-en-1-yne, **6**.

SYNTHESIS

The first objective was to obtain the intermediate 4-[4′-(prop-1-yn-3-al)-phenyl]-piperazine-1-carboxylic acid ethyl ester **4** (see Scheme 1) in order to synthesize series **5** and **6**.

The intermediate **4** was synthesized in four steps, starting with *N*-phenylpiperazine. The synthesis begins with the preparation of the carbamate **1**, obtained by acylation with ethyl chloroformate in the presence of potassium carbonate. The following step was the iodination of protected *N*-phenylpiperazine with iodine in a biphasic mixture of aqueous sodium bicarbonate and dicloromethane, leading to the desired Sonogashira [10] reagent **2**. After purification by recrystallization, iodide **2** was cross coupled in the presence of a palladium catalyst to yield 4-[4′-(prop-1-yn-3-ol)phenyl]-piperazine-1-carboxylic acid ethyl ester **3**. The propargyl alcohol was



a) $ClCO_2Et$, K_2CO_3, MEK (62.2%); b) I_2, $NaHCO_3$, CH_2Cl_2, H_2O (86.0%); c) $PdCl_2(PPh_3)_2$, CuI Et_3N, THF, $HOCH_2CCH$, (70.4%) d) MnO_2, CH_2Cl_2 (89.5%)

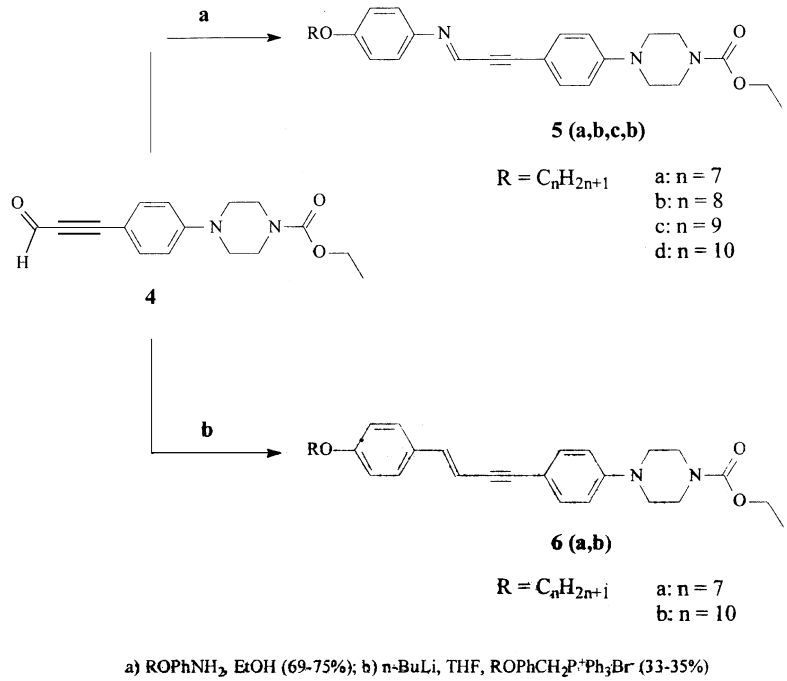
SCHEME 1 Synthetic route of intermediate **4**.

then oxidized to the intermidiate aldehyde **4**, with manganese dioxide. Dry dichloromethane and an inert atmosphere are essential for a good yield in this step.

The route for the synthesis of the Schiff bases **5 (a, b, c, d)** and enynes **6 (a, b)** is shown in Scheme 2.

Schiff bases **5** were readily prepared by condensation reaction [11] of aldehyde **4** with the corresponding 4-*n*-alkoxyaniline in ethanol, in good yields (68–75%).

Syntheses of the enynes **6** used a Wittig reaction [12,13], where the ylidium, prepared in situ using n-butyllithium, reacted rapidly with the intermediate aldehyde **4**. The reaction proceeded stereospecifically and gave the desired product with yield of 33–35%. It was concluded that the olefinic product **6** corresponds to the *trans* isomer, as by ^{1}H NMR the characteristic vinyl system AB showed two sets of doublets at 6.93 and 6.22 ppm with $J_{AB} = 16.2$ Hz, which are typical values for *trans* olefins [14].



a) ROPhNH$_2$, EtOH (69-75%); b) n-BuLi, THF, ROPhCH$_2$P$^+$Ph$_3$Br$^-$ (33-35%)

SCHEME 2 Synthetic route of Schiff base **5** and enyne series **6**.

The Wittig reagent (4-*n*-alkoxyphenyl)methyl triphenylphosphonium bromide was prepared as described in the literature [15]. The crude salts were used because purification is difficult [15].

RESULTS AND DISCUSSION

The mesogens were characterized using a polarizing microscope equipped with a hot stage. The transition temperatures for the Schiff base series **5** are listed in Table 1. All the homologues exhibited only smectic phases over a wide temperature range. The high clearing points and phases observed were probably due to conjugation of the nitrogen atom of the piperazine ring with the carbonyl group, thereby increasing the lateral dipole moment and favoring lateral attractions, which stabilize the smectic phase. Formation of the texture was observed through slow cooling of the isotropic liquid, the mesophase separated in the form of colored batonnets, which rapidly coalesce forming a focal-conic texture, typical smectic A. Increasing the number of carbon atoms in the terminal alkyl group did not change the mesomorphism. However, the smectic A temperature range [ΔT (S_A-I)] increased from homologue $n = 7$ to $n = 10$, (43.8°C to 58.7°C).

Differential Scanning Calorimetry (DSC) data for the homologues were very similar and revealed a monotropic smectic phase, as shown in Table 1. For example, on first heating the heptyloxy homologue two endotherms are observed arising from the crystal-smectic A at 137.5°C ($\Delta H = 15.3$ kJ/mol), and smectic A – isotropic transitions are observed at 181.3°C ($\Delta H = 6.0$ kJ/mol). At a cooling rate of 5.0°C/min, three exotherms were observed the isotropic-smectic A transition at 181.3°C, a smectic A–smectic X, and the recrystallization at 99.0°C. The exothermal peak at 123.4°C

TABLE 1 Transition temperatures (°C) and corresponding enthalpies, in brackets [kJ/mol] for the homologous series of Schiff bases **5**

	n	*Cr*		S_X		S_A		*I*	$\Delta T(S_A\text{-}I)$
5a	7	•	137.5 [15.3]	•	(123.4) [6.7]	•	181.3 [6.0]	•	43.8
5b	8	•	134.2 [19.0]	•	(124.5) [8.6]	•	182.5 [4.1]	•	48.3
5c	9	•	132.6 [34.4]	•	(123.3) [12.4]	•	183.6 [9.1]	•	51.0
5d	10	•	125.8 [26.2]	•	(122.2) [12.7]	•	184.5 [9.0]	•	58.7

( ), monotropic transitions.

($\Delta H = 6.7\,kJ/mol$) corresponds to a monotropic smectic phase S_X. The $S_A - S_X$ phase transition could not be detected in microscopic observations, because the optical texture changes were imperceptive. These phases have apparently equal textures, but they were clearly observable with the DSC. In order to identify the smectic phase S_X, conoscopic observations were made with a Leitz 350 heated stage on the homeotropic S_A and uniformly oriented S_X. S_A and S_X were both uniaxial positive. The S_X is most probably a S_B since this is the only known smectic mesophase that can be uniaxial. It would be desirable to try and identify S_X using other methods. X-ray diffraction was tried but due to the fact that S_X is monotropic and therefore metastable it was not possible to maintain the phase for sufficient time to make exposures. Miscibility studies would be the other possible method of identifying S_X, but since the phase is monotropic it does not seem reasonable to expend the effort necessary to do a miscibility study.

The transition temperatures for the enyne homologues **6** are listed in Table 2. It can be noted that the homologue with $n = 7$ showed a nematic mesophase as well as smectic A. The formation of the nematic mesophase was observed by slow cooling of the isotropic liquid. Small drops rapidly coalesced, generating a *schlieren* texture. Nematic-smectic A transition was at 202.0°C, where the texture changed to focal-conic. The homologue with $n = 10$ showed only a smectic A mesophase with focal-conic texture. Comparison of this behavior with the dialkoxydiphenylenynes was not possible as they are thermally unstable and their physical properties are not available [8].

The mesomorphic behavior of both series, the Schiff bases **5** and the enynes **6**, can be compared by analysis of Tables 1 and 2. The presence of a nitrogen on the Schiff bases (imine linkage) favors smectic polymorphism (S_A and S_B) and increases the mesomorphic range, probably because the lone pair of electrons on the nitrogen increases intermolecular lateral attractions. This does not occur with the enynes, where the homologue with $n = 7$ shows nematic along with smectic behavior. However the thermal stability of the smectic phase in enynes compounds are higher than that of the corresponding Schiff base.

TABLE 2 Transition temperature (°C) and corresponding enthalpies, in brackets [kJ/mol] for the homologous series of enyne **6**

	n	*Cr*		*S*$_A$		*N*		*I*
6a	7	•	175.3 [32.7]	•	202.0 [2.0]	•	210.4 [1.4]	•
6b	10	•	153.9 [17.7]	•	197.8 [4.0]	—	—	•

CONCLUSIONS

The methodology used for the synthesis of the intermediate and final products was appropriate. The enhancement of the alkyl terminal group of the Schiff bases homologous series **5** did not change the mesomorphism. All the homologues showed smectogenic behavior, S_A and most likely S_B. However, there was an increase in thermal stability and transition range, achieving a maximum with the homologue with $n = 10$ (c.p. 184.5°C and $\Delta T = 58.7$°C). The enyne homologous series **6** showed smectic and nematic behavior for $n = 7$ and only smectic for $n = 10$. The increase of the alkyl terminal group inhibits the nematic phase.

EXPERIMENTAL

All reagents were purchased from Aldrich Chemical Company (USA) and solvents from Merck, and all were used as received. The (4-*n*-alkoxyphenyl)methyl triphenylphosphonium bromide and *p*-*n*-alkoxyanilines were prepared as described in the literature [9,13].

Physical Measurements

Infrared spectrums were recorded on a Perkin-Elmer model 781 spectrometer in KBr disk or film. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-200F spectrometer at 200 MHz and 50.4 MHz, respectively. Chemical shifts were reported relative to tetramethylsilane and in units of ppm. Elemental analyses were performed on a Perkin-Elmer model 2400 instrument. The transition temperatures for the mesomorphic compounds were observed by optical microscopy using a Leitz Ortholux polarizing microscope in conjunction with a Mettler FP 52 heating stage. Calorimetric measurements were performed with a Perkin Elmer DSC-2, using indium as a standard calibration.

4-phenyl-piperazine-1-carboxylic acid ethyl ester 1

A solution of N-phenylpiperazine (15.4 g, 94.9 mmol), ethylchoroformate (37 mL, 379.6 mmol), and potassium carbonate (78.8 g, 569.4 mmol) in methyl ethyl ketone (250 mL) was refluxed for 20 h. Then, the solution was cooled to room temperature and filtered. The filtrate was concentrated in a rotatory evaporator, yielding a yellow liquid. Distillation under reduced pressure gave the desired product. Yield = 62.2%, b.p. 147.0–150.0°C (0.5 mmHg). IR

(film): 1702 (C=O), 1600 cm^{-1} (C=C). ^1H NMR (200 MHz, $CDCl_3$): $\delta = 7.31$–6.85 (m, 5H, arom), 4.16 (q, $J = 7.1$ Hz. 2H, OCH_2CH_3), 3.65 (m, 4H, piperazine), 3.11 (m, 4H, piperazine), 1.28 ppm (t, $J = 7.1$ Hz, 3H, CH_3). ^{13}C NMR (50.4 MHz, $CDCl_3$): $\delta = 155.0$ (C=O), 150.8 (C, arom), 128.8, 119.9, 116.3 (CH, arom), 61.0 (CH_2-O), 48.9, 43.2 (C, piperazine), 14.3 ppm (CH_3).

4-(4′-iodophenyl)-piperazine-1-carboxylic acid ethyl ester 2

A solution of **1** (2.43 g, 10.4 mmol), sodium bicarbonate (1.31 g, 15.6 mmol) in dichloromethane (40 mL), and water (30 mL) was kept between 12–15°C while iodine (2.5 g, 9.8 mmol) was added during 45 min. After addition, the mixture was warmed to room temperature and stirred for 1 h. The mixture was then diluted with dichloromethane (200 mL) and water (50 mL). The organic phase was collected and consecutively washed with a saturated solution of sodium thiosulfate, water saturated solution of sodium chloride, and finally water (3×50 mL). The solution was dried with sodium sulphate, concentrated in a rotary evaporator. The resulting solid was recrystallized from n-hexane. Yield = 86.0%, m.p. 77.3–77.6°C. IR (KBr): 1710 (C=O), 1584 (C=C), 816 cm^{-1} (Ar 1, 4-disubstituted). ^1H NMR (200 MHz, $CDCl_3$): $\delta = 7.53$ (d, $J = 8.8$ Hz, 2H), 6.69 (d, $J = 8.8$ Hz, 2H), 4.17 (q, $J = 7.1$ Hz, 2H, $OC\underline{H}_2CH_3$), 3.62 (m, 4H, piperazine), 3.12 (m, 4H, piperazine), 1.28 ppm (t, $J = 7.1$ Hz, 3H, CH_3). ^{13}C NMR (50.4 MHz, $CDCl_3$): $\delta = 156.0$ (C=O), 151.4, 82.8 (C, arom), 138.5, 119.2 (CH, arom), 62.2 (CH_2-O), 49.5, 44.0 (C, piperazine), 15.3 ppm (CH_3).

4-[4′-(prop-1-yn-3-ol)-phenyl]-piperazine-1-carboxylic acid ethyl ester 3

A mixture of **2** (1.09 g, 3.0 mmol), $PdCl_2(PPh_3)_2$ (21.2 mg, 0.03 mmol), and CuI (5.7 mg, 0.03 mmol) in THF (2 mL) and triethylamine (5 mL) was degassed at room temperature under nitrogen for 30 min. Propargyl alcohol (0.2 mL, 3.4 mmol) was added to this mixture. After 20 h, the solution was filtered through silica gel and washed with ethyl acetate/n-hexane 2:3. Column chromatography (SiO_2, ethyl acetate/n-hexane 1:3) gave the pure product. Yield = 70.4%, m.p. 143.4–144.7°C. IR (KBr): 3440 (O-H), 2192 (C≡C), 1676 (C=O), 1606 (C=C), 828 cm^{-1} (Ar 1,4-disubstituted). ^1H NMR (200 MHz, $CDCl_3$): $\delta = 7.33$ (d, $J = 8.6$ Hz, 2H), 6.79 (d, $J = 8.6$ Hz, 2H), 4.47 (d, $J = 5.8$ Hz, 2H, $HOC\underline{H}_2$), 4.17 (q, $J = 7.1$ Hz, 2H, $OC\underline{H}_2CH_3$), 3.62 (m, 4H, piperazine), 3.26 (m, 4H, piperazine), 2.40 (br s, OH), 1.28 ppm

(t, $J = 7.1$ Hz, 3H, CH_3). ^{13}C NMR (50.4 MHz, $CDCI_3$): $\delta = 155.4$ (C=O), 150.7, 113.3 (C, arom), 132.7, 115.5 (CH, arom), 86.0, 85.6 (C≡C), 61.6 (CH_2-O), 51.5 (CH_2-OH), 48.3, 43.3 (C, piperazine), 14.6 ppm (CH_3).

4-[4′-(prop-1-yn-3-al)-phenyl]-piperazine-1-carboxylic acid ethyl ester 4

To a solution of alcohol **3** (0, 10 g, 0.35 mmol) in dry dichloromethane (15 mL) activated dioxide manganese (0.09 g, 1.0 mmol) was added. The reaction was completed after 24 h. Filtration through silica gel with ethyl acetate/n-hexane 1:1 and evaporation of the solvent led to the product. Recrystallization from ethanol gave the pure product. Yield = 89.5%, m.p. 91.5–92.9°C. IR (KBr): 2828-2720 (C-H aldehyde), 2176 (C≡C), 1718 (C=C), 1642 (C=O aldehyde), 1608 (C=C), 818 cm^{-1} (Ar 1, 4-di-substituted). ^1H NMR (200 MHz, $CDCI_3$): $\delta = 9.38$ (s, H aldehyde), 7.52 (d, $J = 8.9$ Hz, 2H), 6.85 (d, $J = 8.9$ Hz, 2H), 4.18 (q, $J = 7.1$ Hz, 2H, CH_2), 3.64 (m, 4H, piperazine), 3.32 (m, 4H, piperazine), 1.29 ppm (t, $J = 7.1$ Hz, 3H, CH_3). ^{13}C NMR (50.4 MHz, $CDCI_3$): $\delta = 176.4$ (C=O, aldehyde), 155.2 (C=O, ester), 152.3, 108.0 (C, arom), 135.1, 114.4 (CH, arom), 97.8, 89.2 (C≡O), 61.4 (CH_2-O), 47.0, 42.9 (C, piperazine), 14.5 ppm (CH_3).

1-[4-(N-ethoxycarbonylpiperazinyl)phenyl]-3-(4-n-alkoxyphenyl)-(1-propargyl-3-imine) 5

p-n-alkoxyaniline (300 mg, 0.1 mmol) was added to a solution of **4** (200 mg, 0.07 mmol) in ethanol. The mixture was refluxed gently for 30 min. After cooling to room temperature a solid was obtained, which was filtered and recrystallized in ethanol.

5a: Yield = 69%, $C_{29}H_{37}N_3O_3$. Obeserved: C 73.21, H 7.83, N 8.86. Required: C 73.23, H 7.84, N 8.83. IR (KBr): 2184 (C≡C), 1700 (C=O), 1628 (C=N), 836 (Ar 1, 4-disubstituted), 720 cm^{-1} ($(CH_2)_n$, n>7). ^1H NMR (200 MHz, $CDCI_3$): $\delta = 7.93$ (s, N=C<u>H</u>), 7.49 (d, $J = 8.7$ Hz, 2H), 6.89 (d, $J = 8.7$ Hz, 2H), 7.21 (d, $J = 8.7$ Hz, 2H), 6.85 (d $J = 8.7$ Hz, 2H), 4.18 (q, $J = 7.1$ Hz, 2H, O<u>C</u>H_2CH_3), 3.96 (t, $J = 6.5$ Hz, 2H, R<u>C</u>H_2O), 3.63 (m, 4H, piperazine), 3.26 (m, 4H, piperazine), 1.70, 1.29, 0.88 ppm (m, aliphatic chain). ^{13}C NMR (50.4 MHz, $CDCI_3$): $\delta = 159.4$ (C=N), 156.1 (C=O), 152.2, 144.6, 141.8, 134.5, 122.9, 115.8, 115.7, 112.3, 96.3, 88.2 (C≡C); 69.0 (R-CH_2-O), 62.3 (CH_3<u>C</u>H_2-O), 48.6, 44.0 (C, piperazine), 34.6, 32.6, 30.2, 30.1, 30.0, 29.9, 26.7, 25.6, 23.4, 15.4 (C, aliphatic chain), 14.8 ppm (CH_3).

5b: yield = 75%, $C_{30}H_{39}N_3O_3$. Observed: C 73.67, H 8.15, N 8.49. Required: C 73.59, H 8.03, N 8.58. IR (KBr): 2184 (C≡C), 1698 (C=O), 1600 (C=N), 828 (Ar 1, 4-disubstituted), 720 cm^{-1} ($(CH_2)_n$, $n>7$). ^1H NMR (200 MHz, $CDCI_3$): $\delta = 7.93$ (s, N = C<u>H</u>), 7.58 (d, $J = 8.7$ Hz, 2H), 6.98 (d, $J = 8.7$ Hz, 2H), 7.31 (d, $J = 8.7$ Hz, 2H), 6.95 (d, $J = 8.7$ Hz, 2H), 4.32 (q, $J = 7.1$ Hz, O<u>C</u>H_2CH$_3$), 3.96 (t, $J = 6.5$ Hz, C<u>H</u>$_2$O), 3.63 (m, 4H, piperazine), 3.26 (m, H piperazine), 1.72, 1.29, 0.87 ppm (m, aliphatic chain). ^{13}C NMR (50.4 MHz, $CDCI_3$): $\delta = 159.4$ (C=N), 156.1 (C=O), 152.2, 144.6, 141.8, 134.5, 122.9, 115.8, 115.7, 112.3, 96.3, 88.2 (C≡C), 69.0 (R-CH_2-O), 62.3 (CH_3<u>C</u>H_2-O), 48.6, 44.0 (C, piperazine), 34.6, 32.6, 30.2, 30.1, 30.0, 29.9, 26.7, 25.6, 23.4, 15.4 (C, alphatic chain), 14.8 ppm (CH_3).

5C: Yield = 73%, $C_{31}H_{41}N_3O_3$. Observed: C 73.54, H 8.12, N 8.22. Required: C 73.92, H 8.20, N 8.34. IR (KBr): 2184 (C≡C), 1698 (C=O), 1600 (C=N), 830 (Ar 1, 4-disubstituted), 720 cm^{-1} ($(CH_2)_n$, $n>7$). ^1H NMR (200 MHz, $CDCI_3$): $\delta = 7.93$ (s, N=C<u>H</u>), 7.49 (d, $J = 8.7$ Hz, 2 H), 6.89 (d, $J = 8.7$ Hz, 2 H), 7.21 (d, $J = 8.7$ Hz, 2H), 6.85 (d, $J = 8.7$ Hz. 2 H), 4.18 (q, $J = 7.1$ Hz, O<u>C</u>H_2CH$_3$), 3.97 (t, $J = 6.5$ Hz, C<u>H</u>$_2$O), 3.64 (m, 4H, piperazine), 3.26 (m, 4H, piperazine), 1.75, 1.29, 0.88 pmm (m, aliphatic chain). ^{13}C NMR (50.4 MHz, $CDCI_3$): $\delta = 159.4$ (C=N), 156.1 (C=O), 152.2, 144.6, 141.8, 134.5, 122.9, 115.8, 115.7, 112.3, 96.3, 88.2 (C≡C), 69.0 (R-CH_2-O), 62.3 (CH_3<u>C</u>H_2-O), 48.6, 44.0 (C, piperazine), 34.6, 32.6, 30.2, 30.1, 30.0, 29.9, 26.7, 25.6, 23.4, 15.4 (C, aliphatic chain), 14.8 ppm (CH_3).

5d: Yield = 75%, $C_{32}H_{43}N_3O_3$. Observed: C 74.34, H 8.41, N 8.16. Required: C 74.24, H 8.37, N 8.12. IR (KBr): 2186 (C≡C), 1700 (C=O), 1600 (C=N), 836 (Ar 1,4-disubstituted), 722 cm^{-1} ($(CH_2)_n$, n>7). ^1H NMR (200 MHz, $CDCI_3$): $\delta = 7.93$ (s, N=C<u>H</u>), 7.49 (d, $J = 8.7$ Hz, 2H), 6.89 (d, $J = 8.7$ Hz, 2H), 7.21 (d, $J = 8.7$ Hz 2H), 6.85 (d, $J = 8.7$ Hz, 2H), 4.18 (q, $J = 7.1$ Hz O<u>C</u>H_2CH$_3$), 3.96 (t, $J = 6.5$ Hz, C<u>H</u>$_2$O), 3.63 (m, 4H, piperazine), 3.26 (m, 4H, piperazine), 1.60, 1.29, 0.88 ppm (m, aliphatic chain). ^{13}C NMR (50.4 MHz, $CDCI_3$): $\delta = 159.4$ (C=N), 156.1 (C=O), 152.2, 144.6, 141.8, 134.5, 122.9, 115.8, 115.7, 112.3, 96.3, 96.3, 88.2 (C≡C), 69.0 (R-CH_2-O), 62.3 (CH_3<u>C</u>H_2-O), 48.6, 44.0 (C, piperazine), 34.6, 32.6, 30.2, 30.1, 30.0, 29.9, 26.7, 25.6, 23.4, 15.4 (C, aliphatic chain), 14.8 ppm (CH_3).

1-[4-(N-ethoxycarbonylpiperazinyl)phenyl]-4-(4-n-alkoxyphenyl)but-3-en-1-yne 6

n-Butyllithium (1.6M in n-hexane) was added over a solution of (4-*n*-alkoxyphenyl)methyltriphenylphosphonium bromide (0.38 g, 0.64 mmol) in THF (20 mL) until the solution turned red. After 2 h at room temperature,

the compound **4** (0.22 g, 0.76 mmol) was added. The solution was heated for 5 h. The reaction was stirred overnight at room temperature. The mixture, was filtered and the solvent evaporated in a rotatory evaporator. The residue was diluted in ethyl ether and washed with aqueous sodium bicarbonate and water. The organic phase was dried over sodium sulphate. Evaporation of the solvent yielded a yellow solid. Column chromatography (SiO_2, ethyl acetate/n-hexane 1:9) gave the desired product, which was recrystallized in ethanol.

6a: Yield = 33%, $C_{30}H_{38}N_2O_3$. Observed: C 75.83, H 8.14, N 5.89. Required: C 75.92, H 8.07, N 5.90. IR (KBr): 2188 (C≡C), 1694 (C=O), 1602, 1510 (C=C), 822 (Ar 1, 4-disubstituted), 722 cm^{-1} ($(CH_2)_n$, n > 7). ^1H NMR (200 MHz, $CDCI_3$): $\delta = 7.35$–6.85 (m, aromatic, 8H), 6.93 (d, $J = 16.2$ Hz, H, C<u>H</u>=C), 6.22 (d, $J = 16.2$ Hz, H, C=CH), 4.17 (q, $J = 7.1$ Hz, 2H, OC<u>H</u>$_2$CH$_3$), 3.96 (t, $J = 6.5$ Hz, 2H, CH_2O), 3.63 (m, 4H, piperazine), 3.20 (m, 4H, piperazine), 1.78, 0.85 ppm (m, aliphatic chain). ^{13}C NMR (50.4 MHz, $CDCl_3$): $\delta = 159.5$ (C=O), 155.5, 150.4, 139.9, 132.5, 129.2, 127.5, 115.7, 114.6, 114.4, 105.8 (C arom and C=C), 91.3, 88.0 (C≡C), 68.0 (R-CH_2-O), 61.5 (CH_3<u>C</u>H_2-O), 48.5, 43.4 (C, piperazine), 31.9, 29.6, 29.4, 29.3, 29.2, 26.0, 22.7, 14.7 (C, aliphatic chain), 14.1 ppm (CH_3).

6b: Yield = 36%, $C_{33}H_{44}N_2O_3$. Observed: C 76.61, H 8.50, N 5.39. Required: C 76.71, H 8.58, N 5.42. R (KBr): 2188 (C≡C), 1694 (C=O), 1602, 1510 (C=C), 822 (Ar 1,4-disubstituted), 722 cm^{-1} (CH_2 n>7). ^1H NMR (200 MHz, $CDCI_3$): $\delta = 7.35$–6.85 (m, aromatic, 8H), 6.93 (d, $J = 16.2$ Hz, H, C<u>H</u>=C), 6.22 (d, $J = 16.2$ Hz, H, C=C<u>H</u>), 4.17 (q, $J = 7.1$ Hz, 2H, OC<u>H</u>$_2$CH$_3$), 3.96 (t, $J = 6.5$ Hz, 2H, CH_2O), 3.63 (m, 4H, piperazine), 3.20 (m, 4H, piperazine), 1.78, 1.28, 0.85 ppm (m, aliphatic chain). ^{13}C NMR (50.4 MHz, $CDCI_3$): $\delta = 159.5$ (C=O), 155.5, 150.4, 139.9, 132.5, 129.1, 127.5, 115.7, 114.7, 114.4, 105.8 (C arom and C=C), 91.3, 88.0 (C ≡ C), 68.0 (R-CH_2-O), 61.6 (CH_3<u>C</u>H_2-O), 48.5, 43.4 (C, piperazine), 31.9, 29.6, 29.4, 29.3, 29.2, 26.0, 22.7, 14.7 (C aliphatic chain), 14.1 ppm (CH_3).

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