Buchwald-Hartwig reaction applied to synthesis of new luminescent liquid crystal triarylamines derived from isoxazoles.

G. D. Vilela,[1,2] T. H. M. Fernandes,[1] S. M. Kelly,[2] and A. A. Merlo*[1]

1 Chemistry Institute, Univesidade Federal do Rio Grande do Sul, Porto Alegre, Brazil

2 Chemistry Department, University of Hull, Hull, England

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Shortened version of the title for the running head: *LLC triarylamines from Büchwald-Hartwig reaction.*

Abstract

The present work describes the synthesis and characterization of novel series of triarylamines isoxazoles (TAA) addressed to the organic photovoltaic materials. Diarylisoxazoles were synthesized by sequential [3+2] 1,3-dipolar cycloaddition reaction between arylnitrile oxides and selected arylalkenes followed by MnO_2-oxidation. Isoxazoles were coupled to diarylamines by Büchwald-Hartwig reaction to afford desired compounds **6a-k**. Some TAA display liquid-crystalline behaviour and UV-Vis absorption and fluorescence emission were analysed for all samples of TAA **6a-k**.

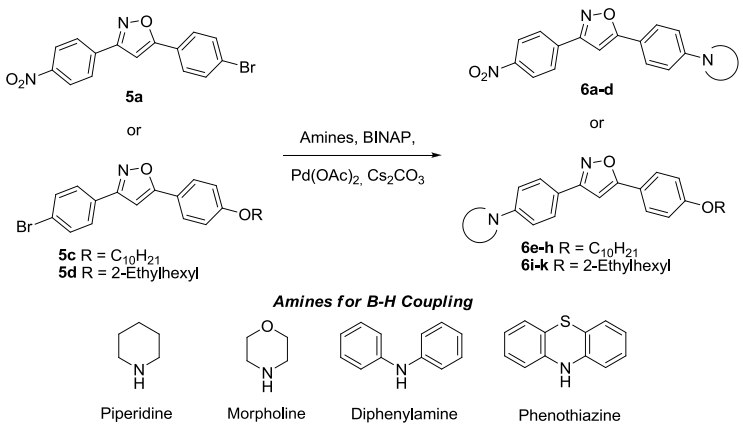
Introduction

Exciton migration and processability are important concepts in the emerging technologies of molecular[1] electronics and optoelectronic devices[2], including photovoltaic cells[3] and organic light-emitting diodes (OLEDs)[4]. The first one is important to optimize the energies of excited states and energy transfer processes, the second one is important to evaluate how this materials will be applied in the devices. Bipolar molecules, which can accept and transport both holes and electrons, are attractive

candidates for optoelectronic studies[5] because the same molecule has both parts of P-N junction; and liquid crystals are widely used because of their physical properties as self-assembling and fluidity[6].

In this field of organic electronics, triarylamines (TAA) have been widely studied to be applied in organic solar cells (OSC) and organic light-emitting diodes (OLED) [7], due to their good electron-donating properties. The triarylamine moieties are known to favour solid-state fluorescence intensity due to their tendency to be amorphous [8]. TAA may be considered a pseudo-3D structure which show strong resistance to crystallization and thus avoid or preventing tight p-stacking interactions. Due to the steric interaction repulsion among phenyl groups, TAA adopts a non-planar propeller shape and, this way, TAA represents an intermediate situation between planar 2D systems and true 3D conjugated systems [9]. Heterocycles, such as isoxazoles, are receiving attention from organic electronic materials (OEM) [10] field because isoxazoles are aromatic heterocycles that behave as electro-acceptor group. To achieve a unique molecular architecture with intramolecular P-N junction, where a hole-transport group (p-type) and an electron-transporting group (n-type) are chemically connected, we chose the Büchwald-Hartwig [11] reaction as final synthetic step to prepare luminescent liquid crystals (LLCs) as bipolar compounds according to Figure 1.

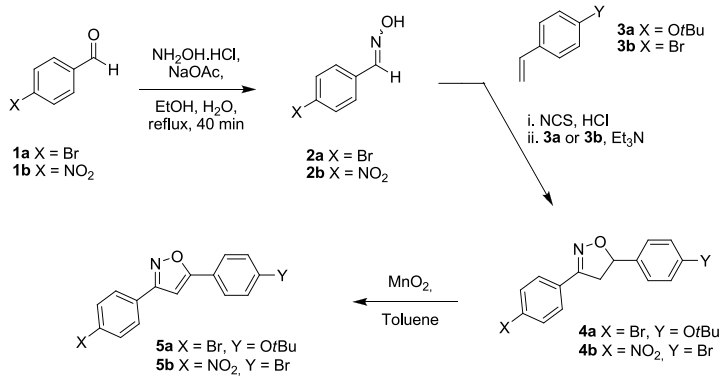
Büchwald-Hartwig reaction is one of the most important methodology to prepare triarylamines by coupling secondary amines and aryl halides, due tolerance to functional groups, giving high yields [8, 12].



Scheme 1: Büchwald-Hartwig reaction between 3,5-isoxazoles and disubstituted amines reported herein.

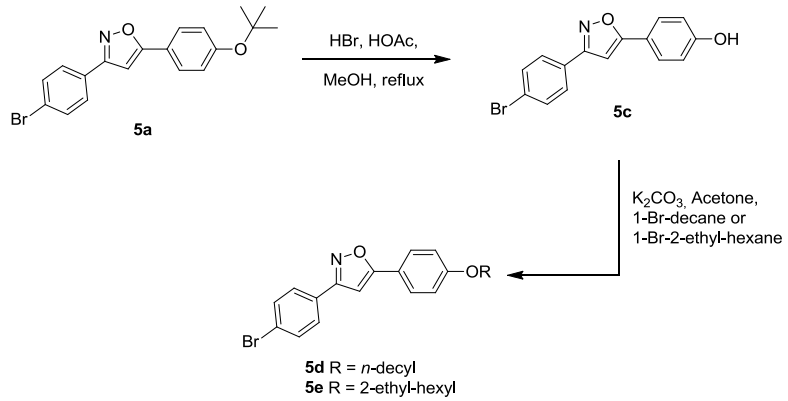
Discussion. Synthesis and Liquid Crystal Behaviour.

The synthesis of key intermediate isoxazoles **5a-b** from isoxazolines **4a-b** is outlined in Scheme 2. To accomplish these transformation a [3+2] 1,3-dipolar cycloaddition between nitrile oxide derived from oxime [13] **2a** and **2b** and styrenes **3a-b** followed by oxidation mediated by MnO_2. The isoxazolines **4a-b**[10] are obtained in medium yields (44 and 27 % respectively) and **5a-b** [14] were obtained in good yields (95 and 87 % respectively) [10, 15]. Products were confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy.



Scheme 2: Synthesis of 3,5-disubstituted isoxazoles.

Isoxazole **5a** containing the labile *tert*-butyl group is the *prime ticket* to enter a precursor phenol which can be transformed into the final key isoxazoles. Thus, *tert*-butyl group from **5a** was removed by acid hydrolysis [16] to give free phenol **5c** and then subjected to the alkylation reaction with linear *n*-decyl and branched 2-ethylhexykl bromide to give **5d-e** [17].



Scheme 3: Hydrolysis of isoxazole **5a** and follow alkylation of phenol **5c**.

Finally, the Buchwald-Hartwig (B-H) [12] cross-coupling reaction was performed using 1 % mol of $Pd(OAc)_2$, 1 % mol of BINAP, a large excess of Cs_2CO_3, diarylisoxazoles **5b**, **5d** and **5e** and secondary amines, as describe in Scheme 1. Four amines such as piperidine, morpholine, diphenylamine and phenothiazine were selected to participate to the B-H reaction. The final products containing the isoxazoles and tertiary amines moieties **6a-k,** as outlined in Figure 1, were obtained in good yields giving the desired compounds, as showed in Table 1.

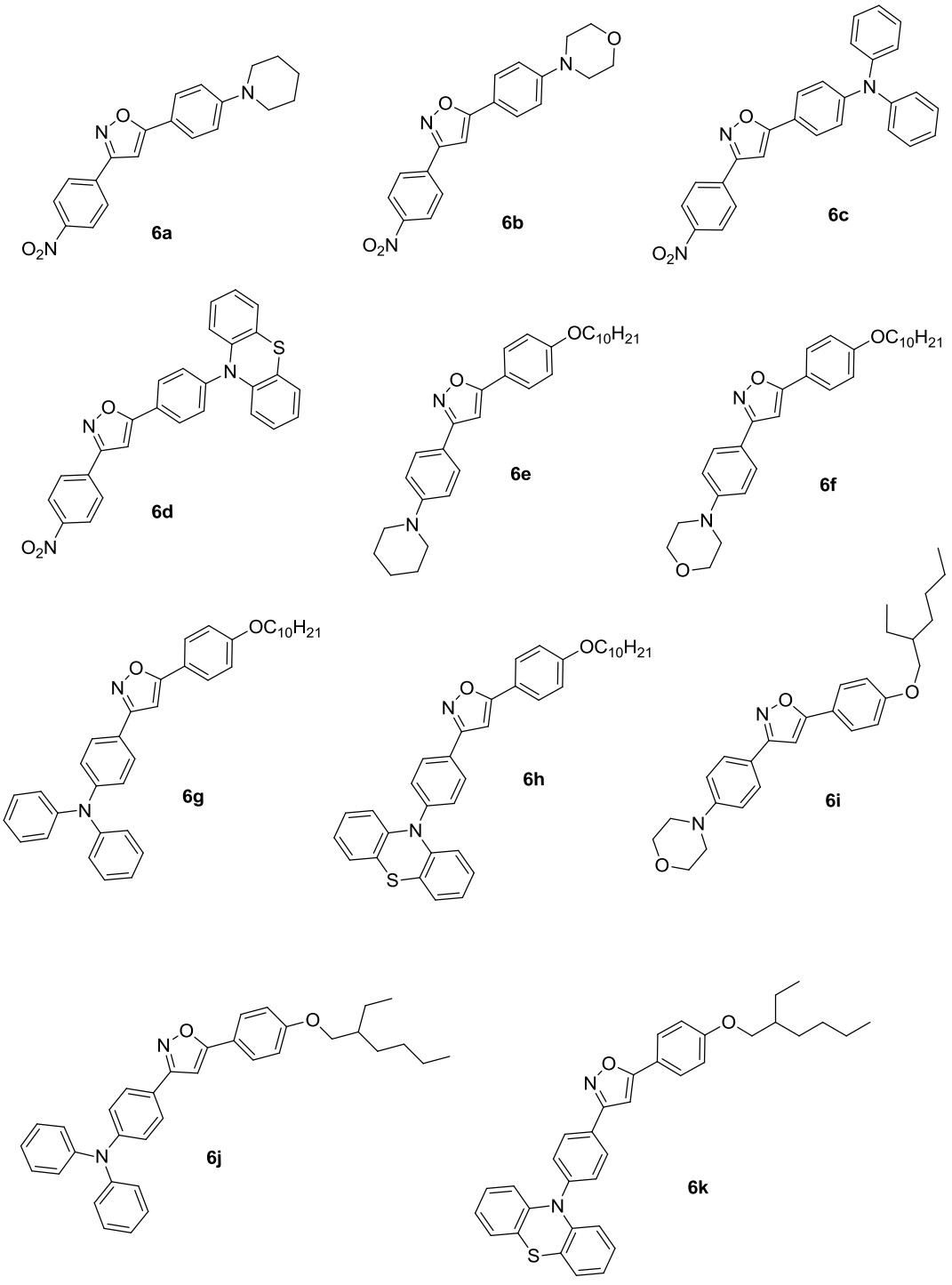


Figure 1: Structure of isoxazoles **6a-k**.

The thermal data for all trisubstituted amines is presented in Table 1. As we can see compounds having linear alkyl chain displayed mesomorphic behaviour while for branched amines no mesophase was observed. Among triarylamines synthesized, compounds **6e-g** have shown mesomorphic behaviour

whereas **6h** did not. Precursor **5d** also have displayed smectogenic behaviour, as reported previously [15]. Only nematic mesophase was found for the piperidine derivative **6e** (Figure 2a). However, as we expected, linear alkyl chain favours the appearance of smectic mesophase as exemplified by **5d** and **6f-g**. These compounds exhibit typical focal-conic texture, as depicted in Figure 2b-d. Compound **6g** also exhibited a second strucutured smectic phase, CrE phase above 78 ºC. The crystallization process to this sample occurs slowly after a long period of time where the CrE texture freeze into the crystal phase.

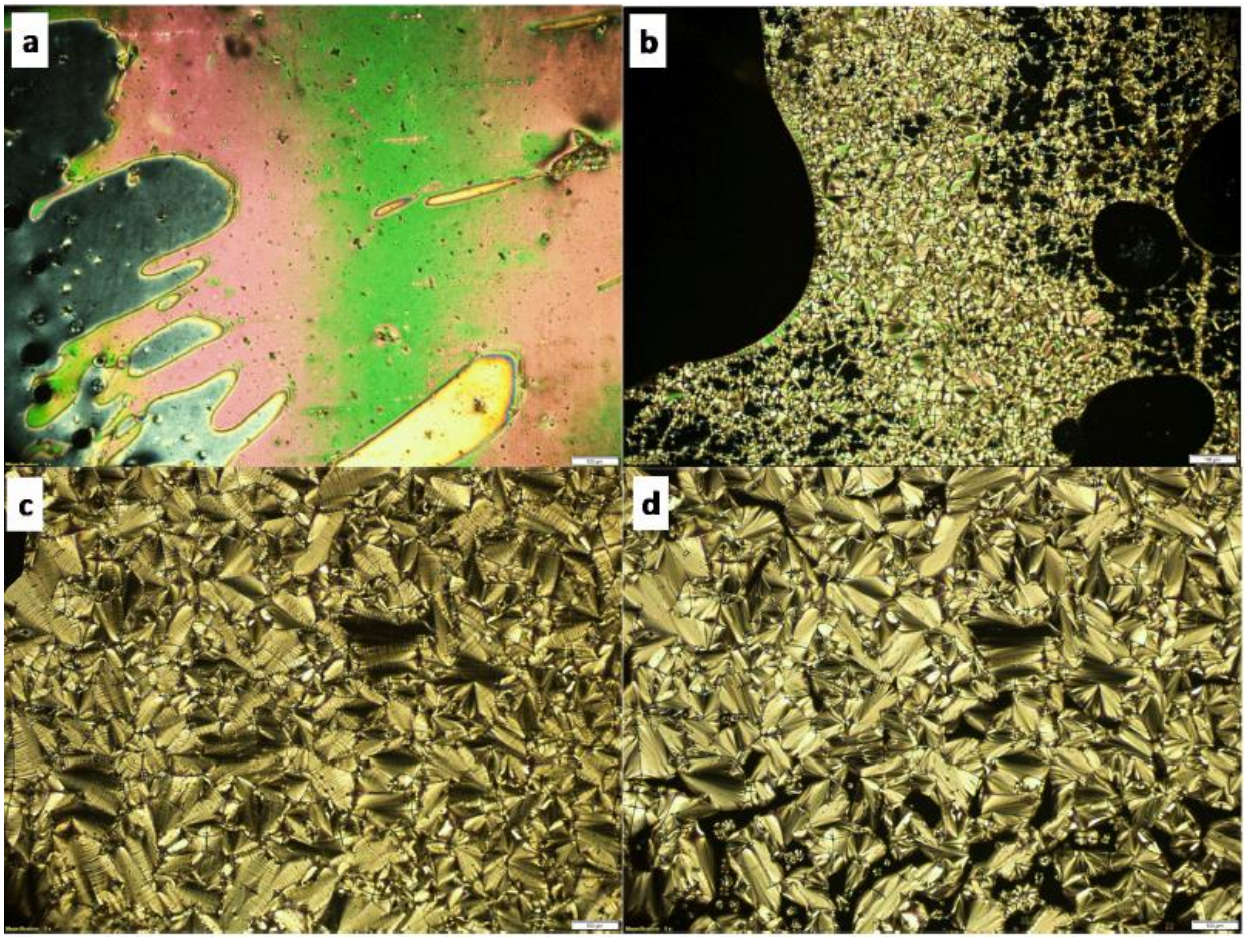


Figure 2: (a) Nematic textures observed by POM at cooling of compound **6e** at 130 ºC, (b) SmA texture for compound **6f** at 147 ºC, (c) CrE texture for compound **6g** at 75 ºC and (d) SmA texture for compound **6g** at 135 ºC.

Nematic phase observed to **6e** may be attributed to the flexibility of non-aromatic piperidine group. Compound **6h** did not show mesophase due to steric hindrance of phenothiazine group that prevents orientational or lamellar arrangement. In general, the results in Table 1 provide the idea that

mesomorphic behaviour is balance between flexibility afforded by alkyl chain and segregation effects between two regions - the rigid core and the less polar alkyl chain. For non liquid crystals TAA listed on Table 1 the melting point tendency observed for **6a-d** and **6i-k** depends on the nature of terminal groups X and Y. TAA from morpholine **6b** and **6i** have the highest melting point n which group of molecules. Of course nature of X and Y group has a great impact on melting point. π-Stacking interaction is strong for derivatives having the nitro group and less efficient for derivatives containing branched alkyl group.

Table 1: Thermal data and yield for the Isoxazoles **5a** and **6a-k.**

LC	X	Y	Thermal Behaviour	Yield (%)
5d	Br	*n*-Decyloxy	Cr 90 CrE 115 SmA 191 I	95
6a	NO_2	Piperidine	207	87
6b	NO_2	Morpholine	259	61
6c	NO_2	Diphenylamine	216	63
6d	NO_2	Phenotiazine	218	60
6e	Piperidine	*n*-Decyloxy	Cr 127 N 134 I	55
6f	Morpholine	*n*-Decyloxy	Cr 142 SmA 156 I	64
6g	Diphenylamine	*n*-Decyloxy	CrE 78 SmA 145 I	56
6h	Phenotiazine	*n*-Decyloxy	121	84
6i	Morpholine	2-Ethyl-1-hexyloxy	136	42
6j	Diphenylamine	2-Ethyl-1-hexyloxy	87	43
6k	Phenotiazine	2-Ethyl-1-hexyloxy	97	42

Photophysical properties

A photophysical study of TAA amines **6a-k** was performed to evaluate their absorption and emission spectrum in solution of dichloromethane. A preliminary analysis of absorption and emission data of these TAA was evaluated from dichloromethane solutions of compounds **6a-k** under UV irradiation at 365 nm. Sample solutions of compounds **6a-d** which bear the NO_2 group did not show fluorescence emission. Fluorescence emission of derivatives containing dipolar nitro group is deeply

influenced by different decay ways present in this group [18]. Generally the main pathway for polar groups with formal charge is associated with charge transfer in the excited state. On the other hand, compounds **6e-k** have shown interesting fluorescence behaviour while under UV irradiation, the effect of coupled amines in the fluorescence behaviour is remarkable, compounds **6h** and **6k** which have phenothiazine group exhibit a red-shifted emission compared to the others, as seen in Figure 1. Another remarkable observation was the intense shine of compounds bearing diphenylamine group.

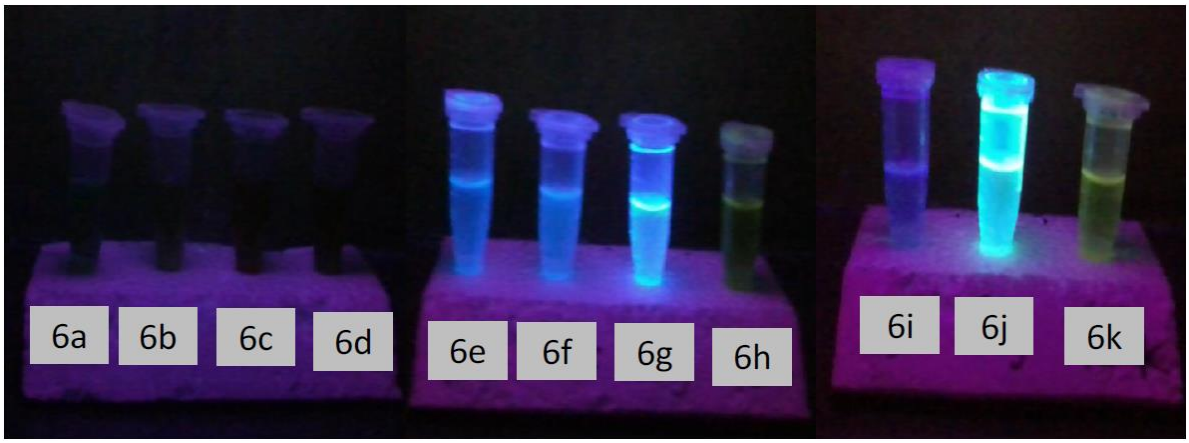


Figure 3: Compounds **6a-k** excited under UV light at 365 nm.

In fluorescence phenomenon, the molecule is excited to a singlet state of higher energy, after this the molecule can return to its ground state by different pathways, charge transfer, fluorescence, phosphorescence or vibrational relaxation, as described in the well known Jablonski's diagram. Stokes shift and quantum efficiency are mainly determined by the way of that molecules return to ground state.

The absorption and emission behavior of TAA structures in dichloromethane (DCM) solution were analyzed by UV-vis and photoluminescence (PL) measurements as shown in Figure 2, Figure 3 and Table 2. These materials exhibited absorption bands of 250–340 nm assigned to π–π* transitions of the diarylisoxazole moiety.

Absorption spectra of compounds **6e-k** showed in Figure 3 are divided in three groups when analysing their absorption spectra. First group is formed by compounds **6e**, **6f** and **6i**, which were coupled with non aromatic piperidine and morpholine (Figure 3a). They show λ_{max} of absorption near

290 nm. Second group is formed by compounds **6g** ad **6j**, which were coupled with diphenylamine (Figure 3b) show λ_{max} at 336 nm and another intense absorption band at 290 nm. Finally, a third group is formed by compounds **6h** and **6k**, which were coupled with phenothiazine (Figure 3c) with λ_{max} of absorption is also near 290 nm accompanied by another higher intense transition at 257 nm. For comparison of the absorption spectra behaviour **6i**, **6j** and **6k** were grouped in Figure 3d. They have the same linear *n*-decyl chain and morpholine for **6i**, diphenylamine for **6j** and phenothiazine for **6k**. Absorption λ_{max} at 337 nm of **6j** containing the diphenyl group is red-shifted whereas **6k** is blue-shifted with λ_{max} at 289 nm.

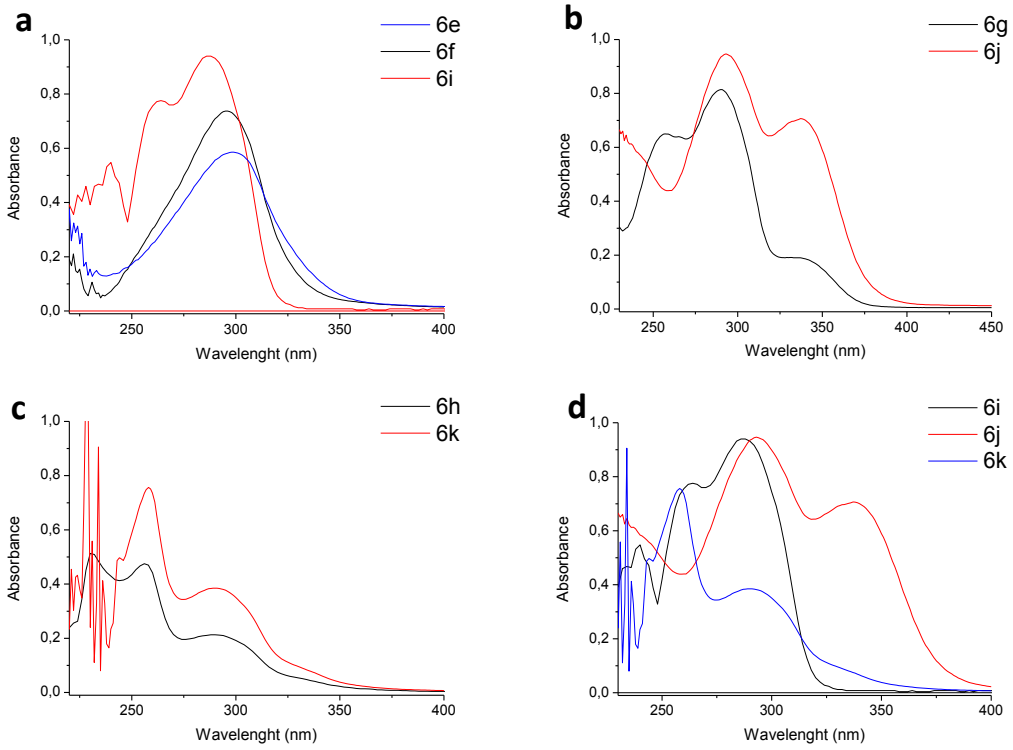


Figure 4: UV-Vis absorption spectra of compounds **6e-k.** (a) Spectra of compounds bearing piperidine and morpholine groups. (b) Spectra of compounds bearing diphenylamine group. (c) Spectra of compounds bearing phenothiazine group. (d) Comparison among compounds bearing the same branched alkyl chain, but with different coupled amines.

Absorption band at 290 nm can be associated to the excitation of the basic rigid core, because this value appears in all samples and 3,5-diphenyl-isoxazole shows absorption maxima (λ_{max}) at 263 mn [19], slightly red-shifted by the electro-donating alkyl groups [18], as seen in Figure 3**d**. Compounds **6e**, **6f** and **6l** have only the absorption maxima (λ_{max}) at 290 nm because piperidine and morpholine are non aromatic and they do not affect the π−conjugation. Compounds **6h** and **6k** showed absorption maxima (λ_{max}) at 289 nm as less intense transition, suggesting that the main excitation way do not include the phenothiazine core. It is possible if the nitrogen turns to a sp^3 configuration, breaking both, conjugation and planarity. The absence of planarity can also explain the absence of mesomorphic behaviour in compound **6h** (Table 1). On the other hand, compounds **6g** and **6j** show as less energetic absorption band λ_{max} at 337 nm, indicating that two phenyl rings of coupled amine are taking place in conjugation promoting a decreasing in the gap between HOMO and LUMO, as expected to an interaction between a donator group and an acceptor group.

Figure 4 displays the fluorescence emission spectra that were acquire in dichromethane solution. Two different groups of chromophores can be seen with blue-shifted and red-shifted of λ_{max} of emission. Emission at λ_{max} at 408-425 nm belongs to chromophores **6e**, **6f**, **6g**, **6i** and **6j**. TAA with emission at λ_{max} 513 and 524 nm belong to chromophores **6h** and **6k** containing the phenothiazine group. Red-shifted behaviour for **6h** and **6k** can be attributed to influence of internal conversions of different configurations of phenothiazine group leading to non-radiative relaxation of molecules in the excited state.

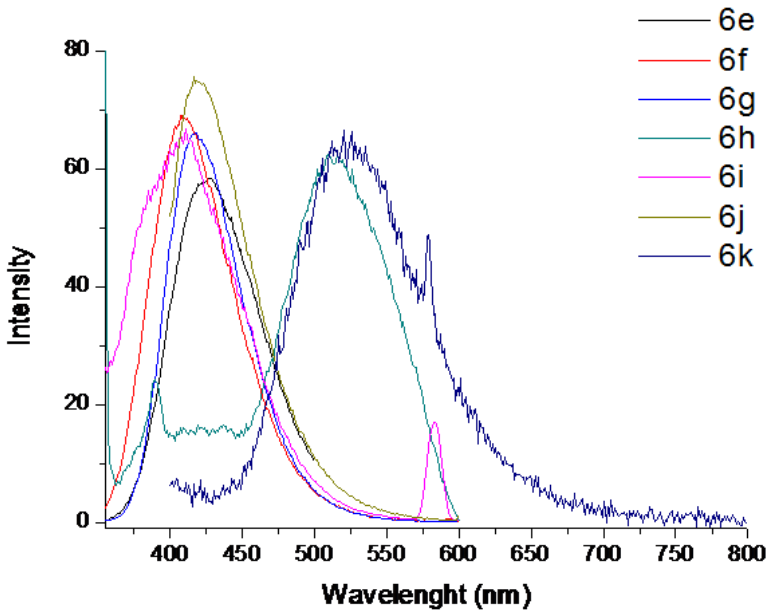


Figure 5: Fluorescence emission spectra of compounds **6e-k** in dichloromethane solution. Signal in 582 nm is due to re-absorption of sample.

Table 2 displays the photophysical data for compounds **6e-k**. Absorption and emission data were acquired in dichloromethane solutions. Quinine sulphate in 0.5 M H_2SO_4 solution [20] was used as standard to obtain the fluorescence quantum yield calculation.

Table 2: Photophysical data for TAA **6e-k.**

Compound	X	Y	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	$\Delta\lambda_{ST}$ (nm)	$\Delta E_{HOMO-LUMO}$[a] (eV)	Φ_{PL}, (%)
6e	Piperidine	*n*-Decyloxy	298	425	127	2,93	1,2
6f	Morpholine	*n*-Decyloxy	294	409	115	2,97	0,3
6g	Diphenylamine	*n*-Decyloxy	336	419	83	2,60	24,5
6h	Phenothiazine	*n*-Decyloxy	289	513	224	3,02	0,2
6i	Morpholine	2-Ethyl-1-hexyloxy	289	408	119	3,02	0,3
6j	Diphenylamine	2-Ethyl-1-hexyloxy	337	421	84	2,59	50
6k	Phenothiazine	2-Ethyl-1-hexyloxy	289	524	235	3,02	0,1

(a) Calculated by λ_{max}^{abs}.

Spectral UV-vis and fluorescence data can explained by analyzing chemical structure of TAA synthesized in this work. Compounds with piperidine and morpholine groups (**6e**, **6f** and **6i**) have some vibrational freedom that allow relaxation of excited state before emission, this relaxation causes significant decreasing on quantum yield, however absence of internal conversions lead to a narrow Stokes shift. Compounds bearing diphenylamine group **6g** and **6j** have a rigid and conjugated aromatic core and display a shorter energy gap between HOMO and LUMO. The high quantum yields and small Stokes shift for **6g** and **6j** can be explained by the absence of other preferential ways to decay from excited state of fluorescence. In compounds containing phenothiazine group **6h** and **6k**, the resonance between two forms is necessary to allow aromaticity in phenothiazine; according Hückel's law, an aromatic core has 4n+2 electrons π involved in the conjugated core, phenothiazine receives twelve electrons from both benzene rings, allowing just more two electrons to be inserted into the conjugation, these two electrons are from sulphur or nitrogen, never from both at same time, as seen in Figure 5. Interconversion between two different excited states generates a large energetic relaxation and probably causes a large Stokes shifts and low quantum yields.

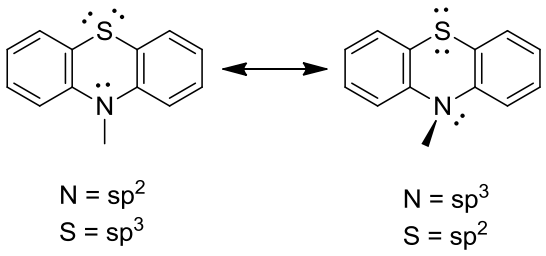


Figure 6: Equilibria between the two forms of phenothiazine.

Conclusions

A collection of eleven TAA **6a-k** derived from 3,5-diaryl-isoxazole core were synthesized using the Büchwald-Hartwig cross-coupling reaction. Compounds **6a-d** did not show fluorescence, because of nitro group. TAA **6e-k** have shown distinct liquid crystals and fluorescence behaviour. Comparison

between two alkyl chains showed that linear alkyl chain induced mesomorphic behaviour in compounds **6e-g**, however branched alkyl chain inhibited mesophase. Effect of branch enhances solubility for compounds **6i-k**. UV-vis and emission data for amines having non-aromatic amines (piperidine and morpholine) are unaffected by these group. However, changes in their absorption and emission spectra were observed for diphenilamine **6g/6j** and phenothiazine **6h**/**6k**.

TAA with diphenilamine group displayed a short Stokes shift (between 83-84 nm) and an good quantum yield (24 % in **6g**, and 50 % in **6j**), probably related to their rigidity and larger conjugation over all rigid core which allow photon emission as low energetic path from excited state to return to the ground state. On the other hand, phenothiazine group decays from excited state by interconversion of two different aromatic conformers, this energy loss induce large Stokes shift (between 224-235 nm) and low quantum yields (0.1 % in **6h** and 0.2 % in **6k**).

Experimental Section

^{1}H NMR and ^{13}C NMR spectra in $CDCl_3$ were obtained using Bruker-400 MHz spectrometer using TMS as an internal standard. The thermal transitions and the textures were determined using an Olympus BX43 polarizing microscope in conjunction with a Mettler FP90 controller and HT84 heating stage and TA Instruments Q20 Serie differential scanning calorimeter. The rate of heating or cooling was 10 °C min^{-1}.

The reagents hydroxylamine chloridrate, 4-hydroxybenzaldehyde, pyridine, 11-bromoundecan-1-ol, methacrylic acid, acrylic acid, N-chlorosuccinimide (NCS) were used as received from Aldrich Co. Analytical thin layer chromatography (TLC) was conducted on Merck aluminium plates with 0.2mm of sílica gel 60F-254. Anhydrous sodium sulfate was used to dry all organic extracts. Toluene and THF were first heated at reflux over sodium and then distilled under argon. AIBN was freshly recrystallised from methanol. Purification by column chromatography was carried out on 70-230 mesh Merck silica gel 60. All other solvents and reagents were used without previous purification.

Syntheses

Synthesis of oximes 2a-b.

Representative procedure for compound **2a**. In a round bottom flask p-bromobenzaldehyde (0.9 g, 25.0 mmol) and hydroxylamine hydrocloride (4.9 g, 62.5 mmol) were dissolved in ethanol (100 mL), then was added sodium acetate (8.2 g, 100 mmol) dissolved in water (50.0 mL). The reaction mixture was stirred at reflux (78 °C) for an hour; after this time part of the solvent was removed under reduced pressure and cooled down to precipitate the crude product. The crude material was recrystallized in ethanol. Data for **2a**: White solid, yield 95 %, m.p. 112 ˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.29 (s, 1H, C<u>H</u>NOH, *Z* isomer), 7.47 (d, 2H, Ar, *J* = 8.4 Hz), 7.57 (m, 4H, Ar, *Z* and *E* isomers), 7.85 (d, 2H, Ar, *Z* isomer, *J* = 8.4 Hz), 8.12 (s, 1H, C<u>H</u>NOH, *E* isomer).

Data for **2b**: Yellow solid, yield 91 %, m.p. 128 ˚C. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.76 (d, 2H, Ar, *J* = 9.0 Hz), 8.11 (s, 1H, OH), 8.21 (s,1H, C<u>H</u>NOH), 8.25 (d, 2H, Ar, *J* = 9.0 Hz).

Synthesis of Isoxazolines 4a-b. (Cicloaddition [3+2] 1,3-Dipolar)

Representative procedure for compound **4a**. In a round bottom flask, were added 4-bromobenzaldehyde oxime (**2a**) (1.0 g, 5.0 mmol), N-chlorossuccinimide (0.8 g, 6.0 mmol), dichloromethane (35.0 mL) and a drop of HCl (conc.), the mixture was stirred for 4 hours to form the oximoyl chloride. After the formation of the intermediate the mixture was cooled in ice bath, and to the solution were added 4-*tert*-butoxystyrene (**3a**) (1.0 g, 5.5 mmol) and triethylamine (2.0 mL, 15.0 mmol) dropwise, then the mixture was stirred at room temperature for 24 hours. After the reaction time the mixture was washed with 1M HCl (2 x 20 mL), water (2 x 20 mL) and brine (30 mL), the organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure giving the crude material. The product was purified by recrystallization in ethanol. Data for **4a**: White solid, yield 44 %, m.p. = 122 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): 1.34 (s, 9H, C(C<u>H</u>$_3$)$_3$), 3.31 (dd, 1H, J_{cis} = 8.4 Hz, J_{gem} = 16.5 Hz), 3.71 (dd, 1H, J_{trans} = 10.8 Hz, J_{gem} = 16.5 Hz), 5.70 (dd, 1H, J_{cis} = 8.7 Hz, J_{trans} = 10.8 Hz), 6.99 (d, 2H, Ar, *J* = 8.4 Hz), 7.27 (d, 2H, Ar, *J* = 8.4 Hz), 7.55 (s, 4H, Ar); ^{13}C RMN ($CDCl_3$, 75.5 MHz): 28.8, 42.7, 78.7, 82.7, 126.6, 126.7, 128.1, 128.5, 131.9, 135.1, 155.4, 155.5.

Data for **4b**: Yellow solid, yield 27 %, m.p. = 132 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): 3.33 (dd, 1H, J_{cis} = 8.1 Hz, J_{gem} = 16.8 Hz), 3.83 (dd, 1H, J_{trans} = 11.1 Hz, J_{gem} = 16.8 Hz), 5.81 (J_{cis} = 8.1 Hz, J_{trans} = 11.1 Hz), 7.27 (d, 2H, Ar, *J* = 8.4 Hz), 7.53 (d, 2H, Ar, *J* = 8.4 Hz), 7.85 (d, 2H, Ar, *J* = 9.0 Hz), 8.27 (d, 2H, Ar, *J* = 9.0 Hz); ^{13}C RMN ($CDCl_3$, 75.5 MHz): 42.5, 82.8, 122.4, 124.0, 127.4, 127.5, 132.0, 135.2, 139.2, 148.5, 154.6.

Synthesis of Isoxazoles 5a-b. (Oxidation Reaction)

Representative procedure for **5a**. In a round bottom flask were added isoxazoline **4a** (2.4 g, 6.4 mmol), benzene (120 mL) and MnO_2 (12.0 g), the reaction was carried under azeotropic reflux for 24 hours. After consumption of starting material (followed by TLC) the mixture was cooled down and filtered over a plug of celite. The solvent was removed under reduced pressure giving the crude product. Data for **5a**: White solid, yield 95 %, m.p. 158 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): 1.40 (s, 9H, $C(C\underline{H}_3)_3$), 6.69 (s, 1H, isoxazole ring), 7.08 (d, 2H, Ar, *J* = 8.7 Hz), 7.59 (d, 2H, Ar, *J* = 8.4 Hz), 7.71 (d, 2H, Ar, *J* = 8.4 Hz), 7.72 (d, 2H, Ar, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): 28.9, 79.4, 96.3, 122.0, 123.9, 124.2, 126.7, 126.8, 128.2, 132.1, 157.6, 161.9, 170.6.

Data for **5b**: Yellow solid, yield 87 %, m.p. 225 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): 7.03 (s, 1H, isoxazole ring), 7.67 (d, 2H, Ar, *J* = 8.4 Hz), 7.75 (d, 2H, Ar, *J* = 8.7 Hz), 8.08 (d, 2H, Ar, *J* = 9.0 Hz), 8.36 (d, 2H, Ar, *J* = 8.7 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): 97.8, 124.1, 124.9, 125.6, 127.1, 127.5, 132.2, 134.8, 148.5, 161.1, 170.1.

Synthesis of Phenol 5c. (Hydrolisis)

A solution of isoxazole **5a** (2.2 g, 5.9 mmol), methanol (180 mL), acetic acid (8.9 mL), HBr (conc.) (4.5 mL) was stirred under reflux for 6 hours. After the consumption of starting material (followed by TLC) the mixture was cooled to room temperature and neutralized to pH 6 with saturated solution of $NaHCO_3$, the product was precipitated and filtered off, giving a white solid. Yield: 95 %, m.p. = 206 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): 2.82 (ws, water), 6.68 (s, 1H, isoxazol ring), 6.95 (d, 2H, Ar, *J* = 8.1 Hz), 7.60 (d, 2H, Ar, *J* = 8.4 Hz), 7.67 (d, 2H, Ar, *J* = 8.4 Hz), 7.73 (d, 2H, Ar, *J* = 8.1 Hz), 9.48 (s, 1H, O<u>H</u>); ^{13}C NMR ($CDCl_3$, 75.5 MHz): 95.0, 115.8, 118.2, 123.6, 127.1, 127.9, 131.7, 158.2, 161.5, 170.7.

Synthesis of Isoxazoles 5d-e. (Alkylation Reaction)

Representative procedure for compound **5d**. In a round bottom flask were added isoxazole **5c** (0.8 g, 2.5 mmol), acetone (30.0 mL), potassium carbonate (0.4 g, 3.0 mmol) and 1-Bromodecane (0.6 mL, 2.8 mmol), the reaction mixture was stirred under reflux for 24 hours (followed by TLC) then mixture was filtered and the solvent was removed under reduced pressure. The crude material was recrystallized in ethanol. Data for **5d**: White solid; yield 95 %; m.p. **K** 90.4 °C **SmE** 115.0 °C **SmA** 190.8 °C **I**; ^{1}H NMR ($CDCl_3$, 300 MHz): 0.88 (t, 3H, $C\underline{H}_3$, J = 6.44 Hz), 1.28 (m, 12H, alkyl chain), 1.47 (ws, 2H), 1.81 (m, 2H, $OCH_2C\underline{H}_2$), 4.00 (t, 2H, $OC\underline{H}_2$, J = 6.59 Hz), 6.66 (s, 1H, isoxazole ring), 6.98 (d, 2H, Ar, J = 8.79 Hz), 7.60 (d, 2H, Ar, J = 8.50 Hz), 7.70 (d, 2H, Ar, J = 8.5 Hz), 7.76 (d, 2H, Ar, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): .

Data for **5e**: White solid; yield 92 %; m.p. 134.8 ˚C; ^{1}H NMR ($CDCl_3$, 300 MHz): 0.93 (2 t, 6H, $C\underline{H}_3$, J = 7.5 Hz), 1.33 (m, 4H, $CH_2C\underline{H}_2C\underline{H}_2CH_3$), 1.48 (m, 4H, $OCH_2CH(C\underline{H}_2CH_3)C\underline{H}_2$), 1.75 (m, 1H, $OCH_2C\underline{H}R_2$), 3.90 (d, 2H, $OC\underline{H}_2CH$, J = 5.7 Hz), 6.66 (s, 1H, isoxazole ring), 6.99 (d, 2H, Ar, J = 9.0 Hz), 7.60 (d, 2H, Ar, J = 8.4 Hz), 7.73 (d, 2H, Ar, J = 8.4 Hz), 7.74 (d, 2H, Ar, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): 11.1, 14.1, 23.0, 23.8, 29.1, 30.5, 39.3, 70.7, 95.8, 114.9, 119.7, 124.2, 127.4, 128.3, 129.1, 132.1, 161.1, 162.0, 170.8.

Synthesis of Triarylamines 6a-k. Buchwald-Hartwig Reaction

Representative procedure for compound **6a**. In a Schlenck flask, under inert atmosphere, degassed toluene (15.0 mL), $Pd(OAc)_2$ (4 mg, 1% mol) and BINAP (11 mg, 1% mol) were added and stirred for some minutes to form the complex Pd(BINAP); then the isoxazole **5a** (0.6 g, 1.7 mmol), piperidine (0.2 mL, 2.1 mmol) and Cs_2CO_3 (2.8 g, 8.7 mmol) were added to the flask. The flask was sealed and the reaction mixture was stirred under reflux for 48 hours; after this time the mixture was filtered over celite and the filtrate was washed with 1M HCl, water and brine; the organic layer was dried over Na_2SO_4 and the solvent removed under reduced pressure. General procedure of purification was recrystallization from ethanol, but sometimes column chromatography in hexane/dichloromethane was necessary to purify the products. Data for **6a**: Yield 87 %; m.p. 207 ˚C; ^{1}H NMR ($CDCl_3$, 300 MHz): 1.68 (m, 6H, piperidine ring), 3.32 (t, 4H, piperidine ring, J = 4.5 Hz), 6.71 (s, 1H, isoxazole ring), 6.97

(d, 2H, Ar, *J* = 8.7 Hz), 7.71 (d, 2H, Ar, *J* = 8.4 Hz), 8.04 (d, 2H, Ar, *J* = 8.4 Hz), 8.34 (d, 2H, Ar, *J* = 8.1 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): 8.1, 24.3, 25.5, 49.2, 95.1, 115.0, 115.8, 124.2, 127.2, 127.6, 135.7, 148.6, 151.4, 161.0, 172.0.

Data for **6b**: Yield 61 %; m.p. 259 ˚C; ^{1}H NMR ($CDCl_3$, 300 MHz): 1.53 (ws, water), 3.22 (t, 4H, N(C<u>H</u>$_2$)$_2$, *J* = 4.99 Hz), 3.82 (t, 4H, O(C<u>H</u>$_2$)$_2$, *J* = 4.99 Hz), 6.67 (s, 1H, isoxazole ring), 6.93 (d, 2H, Ar, *J* = 8.8 Hz), 7.69 (d, 2H, Ar, *J* = 8.8 Hz), 7.97 (d, 2H, Ar, *J* = 8.8 Hz), 8.27 (d, 2H, Ar, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): 47.2, 65.6, 94.6, 113.9, 119.5, 123.2, 126.2, 126.6, 134.5, 147.6, 151.4, 160.0, 170.6.

Data for **6c**: Yield 63 %; m.p. 216 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): 6.67 (s, 1H, isoxazole ring), 7.07 (m (3 d), 8H, Ar), 7.24 (t, 4H, Ar, *J* = 7.63 Hz), .58 (d, 2H, Ar, *J* = 8.8 Hz), 7.96 (d, 2H, Ar, *J* = 8.8 Hz), 8,26 (d, 2H, Ar, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): 95.9, 119.6, 121.6, 124.2, 125.5, 126.9, 127.7, 129.6, 135.5, 146.8, 148.6, 150.1, 161.1, 171.5.

Data for **6d**: Yield 60 %; m.p. 218 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): 6.72 (d, 2H, Ar, *J* = 8.4 Hz), 6.89 (s, 1H, isoxazole ring), 7.04 (m, 4H, Ar), 7.22 (d, 2H, Ar, *J* = 7.5 Hz), 7.39 (d, 2H, Ar, *J* = 8.7 Hz), 7.93 (d, 2H, Ar, *J* = 8.7 Hz), 8.06 (d, 2H, Ar, *J* = 8.4 Hz), 8.36 (d, 2H, Ar, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): 97.2, 120.3, 123.9, 124.1, 124.2, 125.5, 125.9, 127.0, 127.6, 27.7, 127.8, 135.2, 142.8, 145.0, 148.7, 161.2, 170.9.

Data for **6e**: Yield 55 %; m.p. K 127 N 134 I; ^{1}H NMR ($CDCl_3$, 300 MHz): 0.80 (t, 3H, C<u>H</u>$_3$, *J* = 6.4 Hz), 1.28 (m, 14H, alkyl chain), 1.47 (m, 2H, OCH$_2$C<u>H</u>$_2$), 1.78 (m, 6H, piperidine ring), 3.26 (t, 4H, N(C<u>H</u>$_2$)$_2$, *J* = 5.3 Hz), 4.00 (t, 2H, OC<u>H</u>$_2$, *J* = 6.4 Hz), 6.63 (s, 1H, isoxazole ring), 6.98 (m, 4H, Ar), 7.74 (m, 4H, Ar); ^{13}C NMR ($CDCl_3$, 75.5 MHz): 14.2, 22.7, 24.3, 25.5, 26.0, 29.2, 29.3, 29.4, 29.5, 29.6, 31.9, 49.8, 68.2, 95.7, 114.8, 115.7, 120.3, 127.3, 127.7, 160.6, 162.7, 165.0, 169.9.

Data for **6f**: Yield 64 %; m.p. K 142 SmA 156 I; ^{1}H NMR ($CDCl_3$, 300 MHz): 0.88 (t, 3H, C<u>H</u>$_3$, *J* = 6.59 Hz), 1.28 (m, 14H, alkyl chain), 1.47 (m, 2H), 1.8 (m, 2H, OCH$_2$C<u>H</u>$_2$), 3.24 (t, 4H, N(C<u>H</u>$_2$)$_2$, *J* = 6.59 Hz), 3.88 (t, 4H, O(C<u>H</u>$_2$)$_2$, *J* = 4.84 Hz), 4.00 (t, 2H, OC<u>H</u>$_2$, *J* = 6.44 Hz), 6.64 (s, 1H, isoxazole ring), 6.97 (d, 4H, Ar, *J* = 8.79 Hz), 7.75 (d, 2H, Ar, *J* = 8.7 Hz), 7.77 (d, 2H, Ar, *J* = 8.7 Hz); ^{13}C NMR

($CDCl_3$, 75.5 MHz): 14.2, 22.7, 26.0, 29.2, 29.3, 29.4, 29.5, 29.6, 31.9, 48.7, 66.7, 68.2, 95.7, 114.9, 115.2, 120.2, 127.4, 127.8, 152.1, 160.7, 162.6, 165.0, 170.1.

Data for **6g**: Yield 56 %; m.p. K 78 SmA 145 I; ^{1}H NMR ($CDCl_3$, 300 MHz): 0.88 (t, 3H, C$\underline{H}_3$, *J* = 6.7 Hz), 1.28 (ws, 14H, alkyl chain), 1.47 (m, 2H, alkyl chain), 1.81 (m, 2H, $OCH_2C\underline{H}_2$), 4.01 (t, 2H, O$\underline{CH}_2$, *J* = 6.6 Hz), 6.67 (s, 1H, isoxazole ring), 6.98 (m, 4H, Ar), 7.10 (m, 6H, Ar), 7.27 (d, 2H, Ar, *J* = 8.8 Hz), 7.60 (d, 2H, Ar, *J* = 8.6 Hz), 7.73 (d, 2H, Ar, *J* = 8.6 Hz), 7.75 (d, 2H, ar, *J* = 8.9 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): 14.1, 22.7, 26.0, 29.1, 29.3, 29.4, 29.5, 29.6, 31.9, 68.2, 95.8, 114.9, 119.8, 122.6, 123.5, 124.1, 125.0, 127.4, 127.6, 128.0, 128.2, 129.4, 132.1, 147.2, 160.1, 170.8.

Data for **6h**: Yield 81 %; m.p. 121 ˚C; ^{1}H NMR ($CDCl_3$, 300 MHz): 0.89 (t, 3H, C$\underline{H}_3$, *J* = 5.4 Hz), 1.28 (ws, 12H, alkyl chain), 1.48 (m, 2H, alkyl chain), 1.81 (m, 2H, $OCH_2C\underline{H}_2$), 4.02 (t, 2H, O$\underline{CH}_2$, *J* = 6.6 Hz), 6.42 (d, 2H, Ar, *J* = 7.8 Hz), 6.74 (s, 1H, isoxazole ring), 6.90 (m, 4H, Ar), 7.00 (d, 2H, Ar, *J* = 9.0 Hz), 7.09 (d, 2H, Ar, *J* = 7.2 Hz), 7.46 (d, 2H, Ar, *J* = 8.4 Hz), 7.78 (d, 2H, Ar, *J* = 8.4 Hz), 8.04 (d, 2H, Ar, *J* = 8.1 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): 14.2, 22.7, 26.1, 29.2, 29.3, 29.4, 29.5, 29.6, 31.9, 68.3, 96.0, 115.0, 117.6, 119.9, 122.3, 123.2, 127.0, 127.1, 127.5, 128.3, 129.1, 129.4, 143.2, 143.7, 160.9, 162.2, 170.8.

Data for **6i**: Yield 42 %; m.p. 136 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): 0.94 (2 t, 6H, C$\underline{H}_3$, *J* = 7.2 Hz), 1.33 (m, 4H, alkyl chain), 1.47 (m, 4H, alkyl chain), 1.75 (m, 1H, $OCH_2C\underline{H}R_2$), 3.25 (t, 4H, $N(C\underline{H}_2)_2$, *J* = 4.8 Hz), 3.88 (m, 6H, O$\underline{CH}_2$ + $O(C\underline{H}_2)_2$), 6.65 (s, 1H, isoxazole ring), 6.97 (d, 2H, Ar, *J* = 9.0 Hz), 6.98 (d, 2H, Ar, *J* = 9.0 Hz), 7.75 (d, 2H, Ar, *J* = 8.7 Hz), 7.77 (d, 2H, Ar, *J* = 8.7 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): 11.2, 14.1, 23.1, 23.9, 29.1, 30.5, 39.4, 48.6, 66.8, 70.7, 95.7, 114.9, 115.1, 120.2, 120.4, 127.4, 127.8, 152.3, 160.9, 162.6, 170.1.

Data for **6j**: Yield 93 %; m.p. 87 ºC; ^{1}H NMR ($CDCl_3$, 300 MHz): 0.83 (2 t, 6H, CH_3), 1.24 (m, 4H, alkyl chain), 1.38 (m, 4H, alkyl chain), 1.66 (m, 1H, O$\underline{CH}_2CR_2$), 3.80 (d, 2H, O$\underline{CH}_2$, *J* = 6.0 Hz), 6.54 (s, 1H, isoxazole ring), 6.88 (d, 2H, Ar, *J* = 8.7 Hz), 7.00 (m, 8H, Ar), 7.19 (m, 4H, Ar), 7.61 (d, 2H, Ar, *J* = 8.7 Hz), 7.65 (d, 2H, Ar, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): 11.2, 14.2, 23.1, 23.9, 29.1, 30.5, 39.4, 70.7, 95.8, 115.0, 120.1, 122.6, 122.7, 123.6, 125.0, 127.4, 127.7, 129.5, 147.3, 149.4, 161.0, 162.5, 170.3.

Data for **6k**: Yield 42 %; m.p. 97 ˚C; ^{1}H NMR ($CDCl_3$, 300 MHz): 0.93 (m, 6H, $C\underline{H}_3$), 1.33 (m, 4H, alkyl chain), 1.47 (m, 4H, alkyl chain), 1.76 (m, 1H, $OCH_2C\underline{H}R_2$), 3.91 (d, 2H, $OC\underline{H}_2$, J = 5.7 Hz), 6.42 (d, 2H, Ar, J = 8.1 Hz), 6.74 (s, 1H, isoxazole ring), 6.91 (m, 4H, Ar), 7.01 (d, 2H, Ar, J = 8.8 Hz), 7.09 (d, 2H, Ar, J = 7.3 Hz), 7.46 (d, 2H, Ar, J = 8.4 Hz), 7.78 (d, 2H, Ar, J = 8.8 Hz), 8.04 (d, 2H, Ar, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): 11.1, 14.1, 23.0, 23.8, 29.0, 30.4, 39.3, 70.6, 95.9, 114.9, 117.5, 119.8, 122.2, 123.1, 126.9, 127.4, 128.2, 129.0, 129.6, 143.4, 161.0, 162.2, 170.8.

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Full contact information for authors

Guilherme D. Vilela – e-mail: guilherme.vilela@ufrgs.br, phone: +55 (51) 3308 6293, phone 2: +55 (51) 9227 9820

Thaís H. M. Fernandes – e-mail: thais.hmf@hotmail.com, phone: +55 (51) 9809 2939

Prof. Aloir A. Merlo – e-mail: aloir@iq.ufrgs.br, phone: +55 (51) 3308 7316

Prof. Stephen M. Kelly – e-mail: s.m.kelly@hull.ac.uk, phone: +44 (0) 1482 466347, fax: +44 (0) 1482 466411