DOI: 10.1002/ejoc.200600059

2-Arylthienyl-Substituted 1,3-Benzothiazoles as New Nonlinear Optical Chromophores

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Keywords: Aldehydes / Benzothiazoles / UV/Vis spectroscopy / Nonlinear optics

A series of nonlinear optical chromophores **6** containing a substituted benzothiazole ring have been synthesized and characterized. 1,3-Benzothiazoles **6** were prepared by treating various formyl derivatives of thienyl compounds with *ortho*-aminobenzenethiol in fair to excellent yields. These in turn were prepared by Suzuki coupling between aryl and thienyl precursors. The electronic interactions between donor and acceptor end groups in the conjugated 1,3-benzothiazoles **6** are revealed by the intense and markedly solvatochromic CT transitions. The solvatochromic behaviour of compounds **6** was determined by linear regression analyses of absorption maxima in several solvents, where benzothiazole **6f** was found to be a very appropriate indicator dye whose absorption wavenumbers ($\Delta\tilde{\nu}_{max}$ = 1590 cm^{-1}) in aliphatic and dipolar aprotic and in aromatic and chlorinated solvents correlated excellently with the π^* values defined by Kamlet and Taft. Hyper-Rayleigh scattering was used to measure the first hyperpolarizabilities β of the aforementioned compounds. Thermogravimetric analysis (TGA) was used to evaluate their thermal stability. The experimental results indicate that good nonlinearity and thermal stability are well balanced for chromophores **6**, making them good candidates for device applications.

Introduction

Dipolar chromophores of the form D–π–A, where D (A) is an electron donor (acceptor) group and π is a conjugated bridge possessing large molecular second-order nonlinear optical (NLO) response and good thermal stability are currently of interest because of their applicability to electrooptic devices. In such molecules, the donor and acceptor substituents provide the requisite ground-state charge asymmetry, whereas the π-conjugated system provides a pathway for the redistribution conjugation of electric charges under the influence of electric fields.[1]

Synthetic studies have demonstrated that replacing the benzene ring of a chromophore's π-bridge with an easily delocalizable five-membered heteroaromatic ring, such as thiazole and thiophene, results in enhanced molecular hyperpolarizability. Selected thiazole, imidazole, oxazole and phenyl analogues have been prepared and characterized for comparison of the nonlinear optical properties. These studies showed that the order of decreasing nonlinearity is thiazoles > oxazoles > imidazoles. For electrooptical poled polymer applications, the substituted thiazoles are viewed as somewhat superior by virtue of the combination of their substantial dipole moments, red-shifted absorption maxima and to some extent enhanced nonlinearities suggesting that thiazole derivatives are good candidates as NLO chromophores.[2] Recently, computational studies have suggested that heteroaromatic rings play a subtle role in influencing the second-order NLO response properties of donor acceptor compounds.[3] While the aromaticity of heteroaromatic rings affects electronic transmissions between donor and acceptor substituents, the electron-rich or -deficient nature of the heterocyclic ring system also plays a major role in determining the overall electron-donating and -accepting ability of the substituents: electron-rich heterocycles act as auxiliary donors and electron-deficient heterocycles act as auxiliary acceptors.[4]

Our research on new organic and organometallic materials (oligothiophenes, benzothiazoles, thienylpyrroles, thienylphthalazines, thienyl- and bithienylmolybdenum complexes) includes an interest in new molecules with applications in optical and electronic devices.[5] Recently, 2-heteroaryl-substituted benzothiazoles have been investigated by us and due to their solvatochromic and fluorescence properties, benzothiazole derivatives could be used for the manufacture of organic light-emitting diodes (OLEDs) or materials with good NLO properties.[5e–5h]

A number of factors prompted us to synthesize and study the properties of 2-arylthienyl-substituted 1,3-benzothiazoles **6**: (i) our experience in the chemistry of benzothiazoles,[5e–5h] (ii) the scarce mention in the literature of re-

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lated systems[2,3,6] and (iii) the high thermal stabilities of systems derived from benzothiazole,[6c,6g–6i] a very adequate characteristic for possible technological applications of these molecules. Accordingly and as part of our continuing interest in developing chromophores with NLO properties, we describe here the synthesis, UV/Vis absorption and the solvatochromic and nonlinear optical properties of a series of heterocyclic chromophores of the benzothiazole type containing an arylthienyl moiety substituted with various groups such as alkoxy, halogen, hydroxy and dialkylamino.

Results and Discussion

Synthesis of Aldehydes 5

Formyl derivatives **5** were synthesized with several groups (fluoro, alkoxy, hydroxy and dialkylamino) linked to the π-conjugating bridge in order to evaluate the effect of the donating and accepting strength of these groups on the solvatochromic and nonlinear optical properties of benzothiazoles **6**. The formyl derivatives **5a**–**k** were synthesized by $Pd(PPh_3)_4$ catalyzed cross-coupling reaction of thienyl- or arylboronic acids **3a**–**b** and **4a**–**b**, with bromoaryl or bromothienyl compounds **1a**–**i** and **2a** (Figure 1).

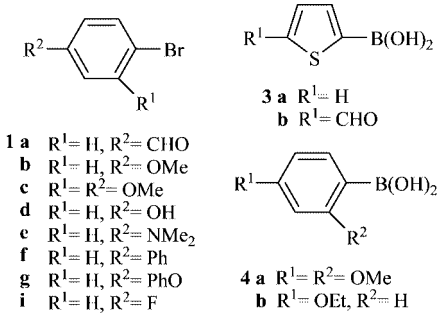
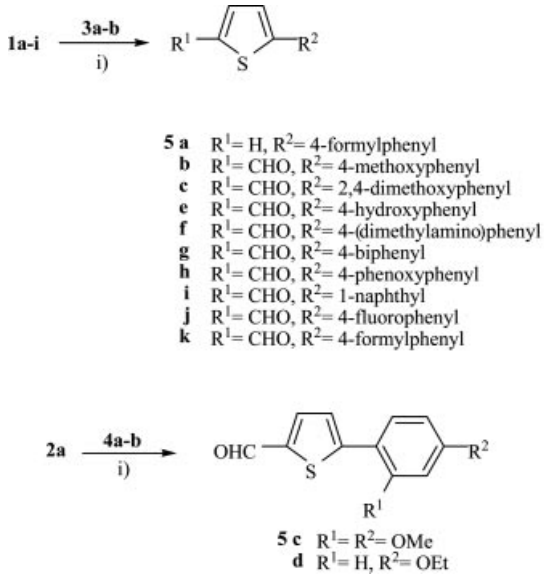


Figure 1. Structures of compounds **1** and **3**–**4**.

The bromo derivatives **1a**–**g**, **i**, 1-bromonaphthalene (**1h**) and 2-bromo-5-formylthiophene (**2a**) were coupled under Suzuki conditions with the thienyl- or arylboronic acids **3a**–**b** and **4a**–**b** to give the formyl derivatives **5**. The Suzuki coupling reactions were performed in 1,2-dimethoxyethane (DME) and aqueous 2 M Na_2CO_3 (2 equiv.) under argon, and $Pd(PPh_3)_4$ (6 mol-%) was used as the palladium catalyst at 80 °C for 18–47 h (Scheme 1).



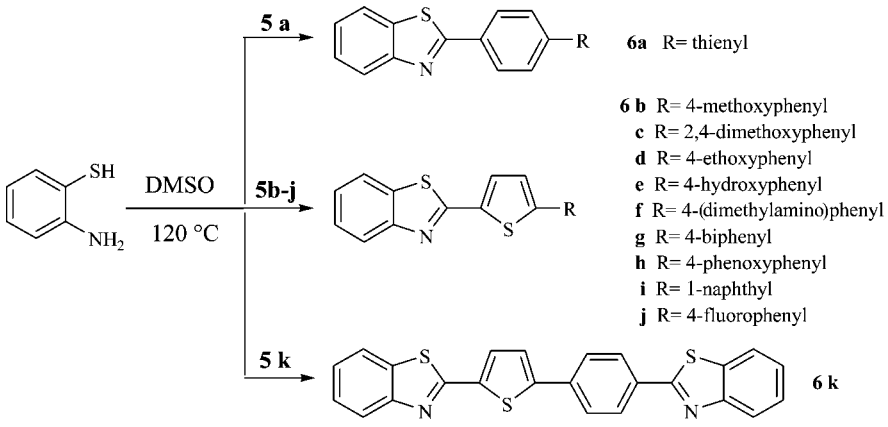
Scheme 1. Synthesis of formyl derivatives **5a**–**k** by Suzuki coupling. Reagents and conditions: (i) DME, $Pd(PPh_3)_4$ (6 mol-%), Na_2CO_3 (2 M), 80 °C, Ar.

The formyl derivatives **5a**–**k** where obtained in fair to good yields (15–89%) (Table 1). Better yields were achieved when more activated aryl bromides were used in the Suzuki couplings. Compounds **5a**,[7] **5b**,[8] **5c**,[9] **5f**,[10] **5i**[11] and **5j**[12] have been previously synthesized. The synthesis of 2-(4′-formylphenyl)thiophene (**5a**) has been reported by Otha,[7] et al. in a lower yield (63%) through palladium-catalyzed arylation of thiophene with 4-bromo-1-formylbenzene. Compound **5b**[8] was prepared from 2-(4′-methoxyphenyl)-thiophene using a modification of Vilsmeier's formylation reaction ($POCl_3$/DMF/toluene) in 36% yield. Compound **5c** has been reported in a patent[9] but no data about the derivative is given. Mignani,[10] et al. described the synthesis of **5f** (91% yield) by lithiation of 5-[4′-(dimethylamino)-phenyl]thiophene followed by the addition of DMF in THF. No analytical data about the derivative is given. Compound **5i** was described earlier by Stulin[11] et al. by Vilsmeier for-

Table 1. Synthesis and UV/Vis absorption data for formyl derivatives **5a**–**k**.

Bromide	Boronic acid	Aldehyde	Yield [%]	Reaction time [h]	λ_{max} [nm][a] (log ε)
1a	**3a**	**5a**	82	44	324 (4.30)
1b	**3b**	**5b**	15	24	345 (4.26)
1c	**3b**	**5c**	20	18	364 (4.08)
2a	**4a**	**5c**	38	24	
2a	**4b**	**5d**	66	28	345 (4.38)
1d	**3b**	**5e**	30	41	361 (4.14)
1e	**3b**	**5f**	26	44	410 (4.20)
1f	**3b**	**5g**	31	47	332 (4.42)
1g	**3b**	**5h**	26	25	340 (4.36)
1h	**3b**	**5i**	89	24	327 (4.36)
1i	**3b**	**5j**	19	41	329 (4.34)
1a	**3b**	**5k**	85	30	333 (4.47)

[a] Spectra were recorded using degassed absolute ethanol as the solvent.



Scheme 2. Synthesis of benzothiazoles **6a**–**k**.

mylation ($POCl_3$/DMF) of 2-(1-naphthyl)thiophene. Derivative **5j** was synthesized by Bussolari[12] et al. by a modified Suzuki cross-coupling reaction in aqueous medium in 82% yield.

Synthesis of Benzothiazoles 6

A series of benzothiazoles **6** was synthesized with either fluoro, alkoxy, hydroxy or dialkylamino donors on the arylthienyl system. The benzothiazole moiety was obtained by reaction of *o*-aminobenzenethiol with 5-formyl-substituted derivatives **5** in DMSO at 120 °C[13] for 30–60 min (Scheme 2). The reaction is initiated by the formation of the corresponding imine that cyclises spontaneously, yielding the benzothiazoline, which is oxidised to the benzothiazole, aided by the oxidizing character of DMSO. Purification of the crude materials by column chromatography gave the pure benzothiazoles **6** in fair to excellent yields (20–91%) (Table 2).

Table 2. Synthesis and UV/Vis absorption data for benzothiazoles **6a**–**k**.

Aldehyde	Benzothiazole	R	Yield (%)	λ_{max} [nm][a] ($\log\varepsilon$)
5a	**6a**	thien-2-yl	85	340 (4.59)
5b	**6b**	4-$MeOC_6H_4$	86	372 (4.49)
5c	**6c**	2,4-$(MeO)_2C_6H_3$	20	417 (4.26)
5d	**6d**	4-$EtOC_6H_4$	83	372 (4.50)
5e	**6e**	4-HOC_6H_4	40	378 (4.22)
5f	**6f**	4-$Me_2NC_6H_4$	49	406 (4.51)
5g	**6g**	4-PhC_6H_4	89	369 (4.63)
5h	**6h**	4-$PhOC_6H_4$	91	365 (4.55)
5i	**6i**	1-naphthyl	77	339 (4.50)
5j	**6j**	4-FC_6H_4	90	355 (4.51)
5k	**6k**	–	84	386 (4.58)

[a] Spectra were recorded using degassed absolute ethanol as the solvent.

UV/Vis Studies

The interesting photochemical and photophysical properties of compounds such as 2-(arylthienyl)-1,3-benzothiazoles can be attributed to the presence of different chromophores within their structures.

The electronic absorption spectra of all benzothiazole derivatives **6** in absolute ethanol show an intense low-energy charge-transfer absorption band in the UV/Vis region. The position of this band depends on the nature of the substituent at the 2-position of the benzothiazole (Table 2, Figure 2). The reason for the substantial redshift in the investigated compounds **6b**–**f**, (λ_{max} = 372–406 nm) and **6h** (λ_{max} = 365 nm) relative to that of the unsubstituted 2-(5′-phenyl-2′-thienyl)-1,3-benzothiazole[5e] (λ_{max} = 359 nm) and 2-[4′-(2′′-thienyl)-2′-phenyl]-1,3-benzothiazole **6a** (λ_{max} = 340 nm) is the strong inductive and conjugative effect of the hydroxy, alkoxy or dialkylamino substituent in the *para* or in the *ortho*/*para* position of the phenyl ring.

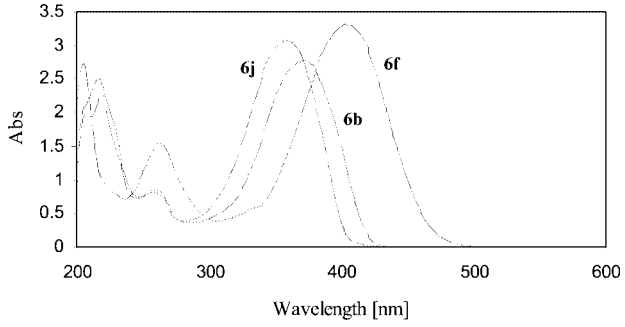


Figure 2. UV/Vis absorption spectra of compounds **6b**, **6f** and **6j** in ethanol.

The greater electron-donating character of the dialkylamino[14] group leads to a bathochromic shift in the absorption maxima, as the longest-wavelength transition is shifted from 340 nm for **6a** to 406 nm for **6f**. The influence of the strength of the donor group is demonstrated by comparison of the absorption maxima of compounds **6b** and **6f** as the longest-wavelength transition is shifted from 372 nm in [(4-methoxyphenyl)thienyl]benzothiazole **6b** to 406 nm in {[4′′-(dimethylamino)phenyl]thienyl}benzothiazole **6f**. The influence of the benzothiazole moiety is demonstrated by comparison of the absorption maxima of compounds **6a** and **6k** as the longest-wavelength transition is shifted from

340 nm in (thienylphenyl)benzothiazole **6a** to 386 nm in the bis(1,3-benzothiazole) **6k**.

The shifts in the absorption maxima are proportional to the intramolecular charge-transfer between the electron-donating and -withdrawing groups. In general, the stronger the donor and/or acceptor group, the smaller the energy difference between the ground and excited states and the longer the absorption wavelength.[15] According to Zyss,[1a] the increase in the β values, which is characteristic of the NLO effects, is accompanied by an increase in λ_{max} in the UV/Vis spectra.

Solvatochromic Study

To evaluate the intermolecular forces between the solvents and the solute molecules and in order to determine the best indicator dye, we made a preliminary study of the absorption spectra of compounds **6** in four selected solvents possessing different solvation character (diethyl ether, ethanol, chloroform and DMSO) (Table 3). We found that compound **6f** shows the greatest shift in wavenumber maxima ($\Delta\tilde{\nu}_{max} > 1000\ cm^{-1}$), so a full solvatochromic study involving 14 solvents was carried out. The wavelength maxima λ_{max} and wavenumber maxima $\tilde{\nu}_{max}$ of compound **6f** are listed in Table 4 and are compared with the π* values for each solvent determined by Kamlet and Taft.[16]

For compound **6f** the highest-energy transitions are found in *n*-hexane, a nonpolar solvent. More polar solvents such as DMSO result in lower energy transitions, thus indicating a positive solvatochromic response ($\Delta\tilde{\nu}_{max}$ = 1590 cm^{-1}) that is related to the greater stabilization of the excited state relative to the ground state with increasing polarity of the solvent. Compound **6f** shows excellent correlation between wavenumber maxima and π* values for the 14 solvents tested (Figure 3). Due to the evident solvatochromism and the good correlation with π* values (r = 0.9857), compound **6f** seems to be a very appropriate solvent polarity indicator dye.

Table 4. Solvatochromic data (λ_{max} [nm] and $\tilde{\nu}_{max}$ [cm^{-1}] for the charge-transfer band) for chromophore **6f** in 14 solvents in comparison with π* values by Kamlet and Taft.[16]

Solvent	π*	Compound **6f**	
		λ_{max}	$\tilde{\nu}_{max}$
n-Hexane	–0.08	388.6	25733
Diethyl ether	0.27	394.8	25329
Ethanol	0.54	402.6	24839
Toluene	0.54	400.8	24950
1,4-Dioxane	0.55	402.2	24863
Ethyl acetate	0.55	401.8	24888
THF	0.58	403.8	24765
Methanol	0.60	405.5	24661
Acetone	0.71	405.2	24679
Acetonitrile	0.75	405.6	24655
Chloroform	0.76	406.0	24631
DCM	0.82	408.0	24510
DMF	0.88	411.2	24319
DMSO	1.00	414.2	24143

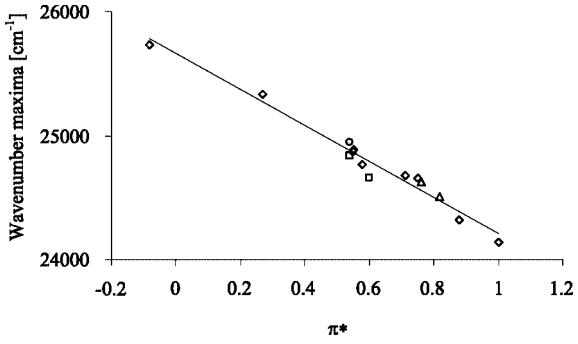


Figure 3. Correlation between absorption wavenumbers $\tilde{\nu}_{max}$ and the π* scale according to Kamlet and Taft for compound **6f**. Solvents: apolar and polar aprotic (◊), protic (□), chlorinated (Δ) and aromatic (○).

Nonlinear Optical Properties and Thermal Stability of Benzothiazoles 6

We have used the hyper-Rayleigh scattering (HRS) technique[17] to measure the first hyperpolarizability (β) value of the chromophores **6** using the 1064 nm fundamental wavelength of a laser beam. 1,4-Dioxane was used as the solvent, and the β values were measured against a reference solution of *p*-nitroaniline (PNA)[18] in the same solvent.

Table 3. Solvatochromic data (λ_{max} [nm] and $\tilde{\nu}_{max}$ [cm^{-1}] for the charge-transfer band) for chromophores **6a**–**k** in selected solvents in comparison with π* values by Kamlet and Taft.[16]

Compound	Solvent (π*)							
	Diethyl ether (0.27)		Ethanol (0.54)		Chloroform (0.76)		DMSO (1.00)	
	λ_{max}	$\tilde{\nu}_{max}$	λ_{max}	$\tilde{\nu}_{max}$	λ_{max}	$\tilde{\nu}_{max}$	λ_{max}	$\tilde{\nu}_{max}$
6a	341.4	29291	342.8	29172	344.0	29070	348.8	28670
6b	366.4	27293	372.0	26882	372.4	26853	378.0	26455
6c	413.6	24178	416.6	24004	418.4	23901	422.8	23652
6d	368.0	27174	372.0	26882	374.0	26738	378.6	26413
6e	369.5	27064	374.0	26738	372.8	26824	379.0	26385
6f	393.8	25394	402.6	24839	406.0	24631	415.2	24085
6g	367.6	27203	372.0	26882	374.5	26702	381.0	26247
6h	364.6	27427	366.5	27285	369.8	27042	373.8	26752
6i	347.4	28785	350.6	28523	353.4	28297	356.8	28027
6j	354.2	28233	359.0	27855	361.5	27663	365.8	27337
6k	384.4	26015	386.5	25873	390.0	25641	393.0	25445

Table 5. UV/Vis absorptions, β values, β_0 values and T_d data for benzothiazoles **6a**–**k**.[a]

Compound	R	λ_{max} [nm]	$\beta \times 10^{-30}$ [esu][b]	$\beta_0 \times 10^{-30}$ [esu][c]	T_d [°C][d]
6a	thien-2-yl	356.0	45	22	318
6b	4-$MeOC_6H_4$	372.0	136	61	350
6c	2,4-$(MeO)_2C_6H_4$	385.0	187	77	346
6d	4-$EtOC_6H_4$	374.0	161	71	342
6e	4-HOC_6H_4	418.0	169	55	270
6f	4-$Me_2NC_6H_4$	405.0	299	108	363
6g	4-PhC_6H_4	376.0	101	44	386
6h	4-$PhOC_6H_4$	369.0	116	53	390
6i	1-naphthyl	352.0	25	13	369
6j	4-FC_6H_4	357.0	48	24	390
6k	–	389.0	170	69	450
PNA	–	352.0	16.9[20]	8	–

[a] Experimental hyperpolarizabilities and spectroscopic data measured using 1,4-dioxane solutions. [b] All the compounds are transparent at the 1064 nm fundamental wavelength. [c] Data corrected for resonance enhancement at 532 nm using the two-level model with $\beta_0 = \beta[1 - (\lambda_{max}/1064)^2][1 - (\lambda_{max}/532)^2]$; damping factors not included 1064 nm.[19] [d] Decomposition temperature (T_d) measured at a heating rate of 20 °C min^{-1} under helium, obtained by TGA.

Table 5 shows the measured values of β together with the lowest-energy absorption maximum of each compound. We have used the two-level model to calculate the static second-order hyperpolarizability value β_0,[19] the results are included in Table 5. These β_0 values are only an estimation and should therefore be treated with caution.

From Table 5 it is clear that the progression of donor substituents from naphthylthienyl, phenylthienyl, (4-fluorophenyl)thienyl, (4-methoxyphenyl)thienyl, (2,4-dimethoxyphenyl)thienyl to [4-(dimethylamino)phenyl]thienyl results in both red-shifted absorption maxima and also enhanced nonlinearities as anticipated from the donor strengths of the substituents. Therefore, the β values of compounds **6a**, **6i**–**j** are virtually identical and 2–3 times of that of PNA, suggesting that the donating properties of these arylthienyl moieties are comparable. However, derivatives **6b**–**e** (having one or two hydroxy or methoxy groups in *ortho* or *ortho*/*para* positions on the aromatic ring) showed higher β values. The β values are 8–11 times that of PNA, whereas the β_0 values are 7–10 times that of PNA. Compound **6f** having a dimethylamino group at the 4-position of the aryl ring exhibits the largest β and β_0 values. The β and β_0 values of **6f** are 18 and 14 times greater, respectively, than those of PNA. Comparison of the β values for hydroxy- or alkoxybenzothiazole derivatives **6b**–**e** with dimethylamino-substituted benzothiazole **6f** shows that the amino donor substitution results in greatly enhanced nonlinearities which are in agreement with the findings of Moylan[2b] et al.

The thermal stabilities of chromophores **6** were estimated by thermogravimetric analysis. All samples had very high decomposition temperatures (T_d = 270–450 °C), measured at a heating rate of 20 °C min^{-1}. Experimental results for compounds **6c**–**d**, **6f** and **6k** indicate that good nonlinearity/thermal stability is well balanced for these chromophores which possess β values from 161×10^{-30} to 299×10^{-30} esu and higher decomposition temperatures (T_d = 343–450 °C). Bearing in mind these properties and also the structure of the compounds, we suggest that these chromophores will be good candidates for device applications in host–guest systems.

Conclusions

Starting from the easily available formyl derivatives **5a**–**k**, as well as by using simple and convenient procedures, several (arylthienyl)-1,3-benzothiazoles **6** were obtained in fair to excellent yields by reaction of the formyl derivatives with *ortho*-aminobenzenethiol in DMSO.

The solvatochromic behaviour of benzothiazoles **6** was evaluated by linear regression analyses of their absorption maxima in several solvents. Due to their pronounced solvatochromic properties benzothiazoles **6**, especially compound **6f**, were found to be suitable for the investigation of the solvent polarity by means of their absorption wavenumbers.

Hyper-Rayleigh scattering was used to determine the first hyperpolarisability value, β, of (arylthienyl)benzothiazoles **6**, the data showing that β is dependent upon the substituent(s) on the arylthienyl moiety. It also shows that some of the compounds have high molecular nonlinearities as their values are 10–18 times greater than that of the well-known PNA. All the compounds exhibit excellent thermal stability as evaluated by TGA.

In agreement with the UV/Vis absorption, solvatochromic and nonlinear optical studies, some of the new 2-(arylthienyl)-1,3-benzothiazoles **6** synthesized could be used for the manufacture of new materials with good nonlinear optical properties.

Experimental Section

General: Thin layer chromatography was carried using 0.25 mm thick precoated silica plates (Merck Fertigplatten Kieselgel $60F_{254}$). Preparative chromatography was carried using Merck Kieselgel 60 (230–400 mesh). All melting points were measured using a Gallenkamp melting point apparatus and are uncorrected. ^1H NMR spectra were recorded at 25 °C with a Varian 300 Unity Plus spectrometer at 300 MHz; chemical shifts are given in δ (ppm) using TMS as standard and J values are given in Hz. Assignments were made by comparison of chemical shifts, peak multiplicity and J values. ^{13}C NMR spectra were recorded with the same instrument at 75.4 MHz and using the solvent peak as internal reference; peak assignments were carried out by the DEPT 135, HMQC and HMBC techniques.

IR spectra were recorded with an FTIR Perkin–Elmer 1600 spectrophotometer. Elemental analyses were carried out using a Leco CHNS 932 instrument. Mass spectrometry was performed at the C.A.C.T.I. – Unidad de Espectrometria de Masas of the University of Vigo, Spain, using a Hewlett Packard 5989 A spectrometer for low-resolution spectra and a VG Autospec M spectrometer for high-resolution mass spectra. Toluene and DME were dried by standard procedures. All Suzuki couplings were carried out under argon. The phenyl and thienyl bromides **1a**–**i** and **2a** and the phenyl- and thienylboronic acids **3a**–**b** and **4a**–**b**, respectively, were purchased from Aldrich and used as received. The experimental setup for hyper-Rayleigh measurements is very similar to the one presented by Clays et al.[17] The incident beam came from a Q-switched Nd:YAG laser (10 Hz, ca. 20 mJ, ca. 10 ns) at a fundamental wavelength of 1064 nm and was focused on the solution (beam diameter ca. 0.5 mm). The hyper-Rayleigh signal was normalized by a second harmonic signal from a quartz plate to compensate for laser power fluctuations. The concentrations of the solutions under study were chosen so that the corresponding relative hyper-Rayleigh signals all fell within the dynamic range of the apparatus. All solutions were previously filtered (0.2 μm porosity) to avoid spurious signals from suspended dust and other impurities. The first hyperpolarizability values β of the molecules in dioxane solutions were measured using the external reference method.[18] For two dilute solutions of chromophores with dominant hyperpolarizabilities along the charge transfer axis, in the same solvent, the relative hyperpolarizability is given by $\beta/\beta_{ref} = m/m_{ref}$, where m is the coefficient of variation of the HRS signal with chromophore concentration. The reference chosen was a 1×10^{-2} M solution of PNA in dioxane since its β is known to be $\beta_{PNA/1,4\text{-dioxane}} = 16.9\pm0.4\ 10^{-30}$ esu from EFISH measurements for the same wavelength.[20] For each solution, we estimated the linear coefficients m using two experimental points: the HRS signal for the solvent and the HRS signal for the solution. The error associated with the HRS-measured β values is typically 10%. We were careful to test if the hyper-Rayleigh signal was artificially increased by possible molecular fluorescence near 532 nm. To do so, we carried out measurements using two different interference filters in front of the photomultiplier, each with slightly different transmission characteristics. The transmission of both filters were centered near the second harmonic at 532 nm, but the transmission band of the narrower filter was 1.66 nm (full width at half maximum), while that of the wider filter was 3.31 nm. The transmission of each filter at the second harmonic wavelength was carefully determined using a crystalline quartz sample. By assuming that any fluorescence from the solutions was essentially constant over the transmission of both interference filters, a comparison of the signals obtained from the two different filters allowed the estimatation of the relative strengths of the hyper-Rayleigh and possible fluorescence signals to be carried out. We were unable to detect the presence of any fluorescence using this method. Thermogravimetric analysis of the samples was carried out using a TGA 50 Shimadzu instrument under high-purity helium supplied at a constant 50 mL min^{-1} flow rate. All samples were subjected to a 20 °C min^{-1} heating rate and were characterized between 25 and 500 °C.

Experimental Procedures for the Synthesis of Aldehydes 5 through Suzuki Cross-Coupling: The bromo compounds **1a**–**i** or **2a** (1.2 mmol) were coupled with the boronic acids **3a**–**b** or **4a**–**b** (1.6 mmol) in a mixture of DME (15 mL), aqueous 2 M Na_2CO_3 (1 mL) and $Pd(PPh_3)_4$ (6 mol%) at 80 °C under argon. The reactions were monitored by TLC which determined the different reaction times (Table 1). After cooling, the mixture was filtered. Ethyl acetate and a saturated solution of NaCl were added and the phases were separated. The organic phase was washed with water (3 × 50 mL) and with a solution of NaOH (10%) (1 × 50 mL). The organic phase obtained was dried ($MgSO_4$), filtered and solvent removed to give a crude mixture which was chromatographed to afford the coupled products **5**.

2-(4′-Formylphenyl)thiophene (5a): Yellow solid (185 mg, 82%). M.p. 69.0–69.5 °C [ref.[7] 67–68 °C (*i*PrOH)]. ^{1}H NMR ($CDCl_3$): δ = 7.15 (m, 1 H, 4-H), 7.41 (dd, J = 5.1, 1.2 Hz, 1 H, 5-H), 7.48 (dd, J = 3.6, 1.2 Hz, 1 H, 3-H), 7.76–7.81 (m, 2 H, 2′- and 6′-H), 7.88–7.93 (m, 2 H, 3′- and 5′-H), 10.01 (s, 1 H, CHO) ppm. ^{13}C NMR ($CDCl_3$): δ = 125.01, 126.00, 126.90, 128.45, 135.05, 140.06, 142.68, 191.45 ppm. IR (nujol): $\tilde{\nu}$ = 1692 (s) cm^{-1}. $C_{11}H_8OS$ (188.25): calcd. C 70.19, H 4.25, S 17.05; found C 70.39, H 4.46, S 17.06.

2-Formyl-5-(4′-methoxyphenyl)thiophene (5b): Beige solid (39 mg, 15%). M.p. 114.4–115.8 °C (ref.[8] 119–120 °C). ^{1}H NMR ($CDCl_3$): δ = 3.85 (s, 3 H, OCH_3), 6.95 (d, J = 9.0 Hz, 2 H, 3′- and 5′-H), 7.30 (d, J = 3.9 Hz, 1 H, 4-H), 7.61 (d, J = 9.0 Hz, 2 H, 2′- and 6′-H), 7.71 (d, J = 3.9 Hz, 1 H, 3-H), 9.86 (s, 1 H, CHO) ppm. ^{13}C NMR ($CDCl_3$): δ = 55.37, 114.53, 122.95, 125.70, 127.75, 137.68, 141.44, 154.47, 160.66, 182.62 ppm. IR (nujol): $\tilde{\nu}$ = 1650 (s) cm^{-1}. $C_{12}H_{10}O_2S$ (218.28): calcd. C 66.03, H 4.58, S 14.71; found C 66.03, H 4.63, S 14.50.

2-Formyl-5-(2′,4′-dimethoxyphenyl)thiophene (5c): Yellow solid (41 mg, 14%). M.p. 196.2–196.9 °C (ref.[9] no value quoted). ^{1}H NMR ($CDCl_3$): δ = 3.85 (s, 3 H, OCH_3), 3.95 (s, 3 H, OCH_3), 6.52–6.62 (m, 2 H, 3′- and 5′-H), 7.48 (d, J = 3.6 Hz, 1 H, 4-H), 7.64 (d, J = 8.4 Hz, 1 H, 6′-H), 7.70 (d, J = 3.6 Hz, 1 H, 3-H), 9.88 (s, 1 H, CHO) ppm. ^{13}C NMR ($CDCl_3$): δ = 55.01, 55.54, 98.81, 105.59, 115.05, 124.50, 129.43, 136.46, 141.33, 150.09, 157.47, 161.71, 183.17 ppm. IR (nujol): $\tilde{\nu}$ = 1650 (s) cm^{-1}. MS (EI): m/z (%) = 248 (100) [M^+]. $C_{13}H_{12}O_3S$ (248.30): calcd. C 62.88, H 4.84, S 12.93; found C 62.99, H 5.08, S 12.79.

2-Formyl-5-(4′-ethoxyphenyl)thiophene (5d): Yellow solid (184 mg, 66%). M.p. 104.6–105.4 °C. ^{1}H NMR ($CDCl_3$): δ = 1.45 (t, J = 4.3 Hz, 3 H, OCH_2CH_3), 4.00–4.20 (m, 2 H, OCH_2CH_3), 6.92–6.98 (m, 2 H, 3′- and 5′-H), 7.31 (d, J = 3.9 Hz, 1 H, 4-H), 7.58–7.64 (m, 2 H, 2′- and 6′-H), 7.23 (d, J = 3.9 Hz, 1 H, 3-H), 9.87 (s, 1 H, CHO) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.71, 63.63, 115.00, 122.88, 125.51, 127.76, 137.78, 141.34, 154.63, 160.06, 182.69 ppm. IR (nujol): $\tilde{\nu}$ = 1650 (s) cm^{-1}. $C_{13}H_{12}O_2S$ (232.30): calcd. C 67.22, H 5.17, S 13.82; found C 67.41, H 5.33, S 13.83.

2-Formyl-5-(4′-hydroxyphenyl)thiophene (5e): Pale yellow solid (73 mg, 30%). M.p. 205.6–206.2 °C. ^{1}H NMR ([D_6]acetone): δ = 7.37–7.41 (m, 2 H, 3′- and 5′-H), 7.55 (d, J = 3.9 Hz, 1 H, 4-H), 7.53–7.54 (m, 2 H, 2′- and 6′-H), 7.96 (d, J = 3.9 Hz, 1 H, 3-H), 9.01 (br. s, 1 H, OH), 9.94 (s, 1 H, CHO) ppm. ^{13}C NMR ([D_6]-acetone): δ = 116.94, 123.89, 125.47, 128.69, 139.29, 142.27, 154.81, 159.77, 183.51 ppm. IR (nujol): $\tilde{\nu}$ = 1624 (s) cm^{-1}. MS (EI): m/z (%) = 204 (100) [M^+]. EI HRMS: calcd. for $C_{11}H_8O_2S$ 204.0245, found 204.0245.

2-Formyl-5-[4′-(dimethylamino)phenyl]thiophene (5f): Yellow solid (72 mg, 26%). M.p. 188.9–190.1 °C (ref.[10] no value quoted). ^{1}H NMR ($CDCl_3$): δ = 3.03 [s, 6 H, $N(CH_3)_2$], 6.72 (d, J = 8.7 Hz, 2 H, 3′- and 5′-H), 7.24 (d, J = 4.2 Hz, 1 H, 4-H), 7.56 (d, J = 8.7 Hz, 2 H, 2′- and 6′-H), 7.68 (d, J = 4.2 Hz, 1 H, 3-H), 9.82 (s, 1 H, CHO) ppm. ^{13}C NMR ($CDCl_3$): δ = 29.67, 40.25, 112.20, 121.51, 12147, 138.06, 140.09, 151.03, 155.97, 182.43 ppm. IR (nujol): $\tilde{\nu}$ = 1644 (s) cm^{-1}. MS (EI): m/z (%) = 231 (100) [M^+]. EI HRMS: calcd. for $C_{13}H_{13}NOS$ 231.0718, found 231.0719.

5-(4′-Biphenylyl)-2-formylthiophene (5g): Yellow solid (98 mg, 31%). M.p. 192.9–193.8 °C. ^{1}H NMR ($CDCl_3$): δ = 7.34–7.84 (m,

11 H, 3, 4-H and 9×Ar-H), 9.90 (s, 1 H, CHO) ppm. ^{13}C NMR ($CDCl_3$): δ = 124.03, 126.78, 126.93, 127.76, 127.83, 128.91, 131.89, 137.48, 139.93, 142.19, 142.35, 153.89, 182.75 ppm. IR (nujol): $\tilde{\nu}$ = 1658 cm^{-1} (s) cm^{-1}. MS (EI): *m/z* (%) = 264 [M$^+$, 67], 207 (100). EI-HRMS: calcd. for $C_{17}H_{12}OS$ 264.0609, found 264.0598.

2-Formyl-5-(4′-phenoxyphenyl)thiophene (5h): Yellow solid (87 mg, 26%). M.p. 82.6–83.7 °C. ^{1}H NMR ($CDCl_3$): δ = 7.02–7.10 (m, 4 H, 4×Ar-H), 7.13–7.20 (br. t, *J* = 7.5 Hz, 1 H, Ar-H), 7.33 (d, *J* = 4.2 Hz, 1 H, 4-H), 7.35 (br. t, *J* = 7.5 Hz, 2 H, 2×Ar-H), 7.64 (d, *J* = 8.7 Hz, 2 H, 2×Ar-H), 7.73 (d, *J* = 4.2 Hz, 1 H, 3-H), 9.88 (s, 1 H, CHO) ppm. ^{13}C NMR ($CDCl_3$): δ = 118.81, 119.53, 123.54, 124.07, 127.84, 127.96, 129.94, 137.62, 141.96, 153.87, 156.18, 158.76, 182.74 ppm. IR (nujol): $\tilde{\nu}$ = 1653 (s) cm^{-1}. $C_{17}H_{12}O_2S$ (280.35): calcd. C 72.84, H 4.28, S 11.45; found C 72.86, H 4.33, S 11.40.

2-Formyl-5-(1′-naphthyl)thiophene (5i): Yellow oil (254 mg, 89%). [ref.[11] 72–73 °C (EtOH and benzene)]. ^{1}H NMR ($CDCl_3$): δ = 7.36 (d, *J* = 3.9 Hz, 1 H, 4-H), 7.50–7.64 (m, 4 H, 4×Ar-H), 7.85 (d, *J* = 3.9 Hz, 1 H, 3-H), 7.90–8.00 (m, 2 H, 2×Ar-H), 8.14–8.20 (m, 1 H, Ar-H), 9.97 (s, 1 H, CHO) ppm. ^{13}C NMR ($CDCl_3$): δ = 125.01, 125.16, 126.34, 126.99, 128.27, 128.52, 128.58, 129.72, 130.99, 131.04, 133.73, 136.62, 143.44, 152.24, 182.91 ppm. IR (nujol): $\tilde{\nu}$ = 1666 (s) cm^{-1}. MS (EI): *m/z* (%) = 238 (100) [M$^+$]. EI HRMS: calcd. for $C_{15}H_{10}OS$ 238.0452, found 238.0444.

5-(4′-Fluorophenyl)-2-formylthiophene (5j): Yellow solid (47 mg, 19%). M.p. 113.2–114.0 °C (ref.[12] no value quoted). ^{1}H NMR ($CDCl_3$): δ = 7.14 (t, J_{H-F} = 8.4 Hz, 2 H, 3′- and 5′-H), 7.35 (d, *J* = 3.9 Hz, 1 H, 4-H), 7.63–7.68 (m, 2 H, 2′- and 6′-H), 7.75 (d, *J* = 3.9 Hz, 1 H, 3-H), 9.90 (s, 1 H, CHO) ppm. ^{13}C NMR ($CDCl_3$): δ = 116.29 (d, J_{C-F} = 22.1 Hz, C-3′ and -5′), 124.06 (C-4), 128.27 (d, J_{C-F} = 8.4 Hz, C-2′ and -6′), 129.40 (d, J_{C-F} = 3.9 Hz, C-1′), 137.41 (C-3), 142.51 (C-2), 153.03 (C-5), 163.38 (d, J_{C-F} = 250 Hz, C-4′), 182.73 (CHO) ppm. IR (KBr): $\tilde{\nu}$ = 1641 (s) cm^{-1}. MS (EI): *m/z* (%) = 206 [M$^+$, 85], 205 (100). EI HRMS: calcd. for $C_{11}H_7FOS$ 206.0202, found 206.0209.

2-Formyl-5-(4′-formylphenyl)thiophene (5k): Yellow solid (220 mg, 85%). M.p. 145.3–146.1 °C. ^{1}H NMR ($CDCl_3$): δ = 7.54 (d, *J* = 4.2 Hz, 1 H, 4-H), 7.79 (d, *J* = 4.2 Hz, 1 H, 3-H), 7.84 (d, *J* = 8.4 Hz, 2 H, 2′- and 6′-H), 7.96 (d, *J* = 8.4 Hz, 2 H, 3′- and 5′-H), 9.93 (s, 1 H, CHO), 10.05 (s, 1 H, CHO) ppm. ^{13}C NMR ($CDCl_3$): δ = 125.70, 126.78, 130.48, 136.41, 137.13, 138.49, 143.86, 151.78, 182.76, 191.20 ppm. IR (nujol): $\tilde{\nu}$ = 1696 (s), 1654 (s) cm^{-1}. MS (EI): *m/z* (%) = 216 (98) [M$^+$], 215 (100). EI HRMS: calcd. for $C_{12}H_8O_2S$ 216.0245, found 216.0242.

General Procedure for the Syntheses of Benzothiazoles 6: The corresponding formyl derivatives **5** and *o*-aminobenzenethiol (1.1 equiv.) were heated in DMSO (0.5 mL/mmol) at 120 °C with stirring for 30–60 min. The reaction was monitored by TLC using chloroform/hexane (1:1) as eluent. When the reaction was complete, the reaction mixture was cooled and poured into water and extracted with ethyl acetate (3×30 mL). The organic layer was dried with magnesium sulfate and the solvents were evaporated under vacuum. The crude residue was chromatographed using silica gel and mixtures of hexane and chloroform of increasing polarity. The fractions containing the purified product were collected and the solvents evaporated under vacuum.

2-[4′-(Thien-2′′-yl)phenyl]-1,3-benzothiazole (6a): Yellow solid (299 mg, 85%). M.p. 205.5–206.1 °C. ^{1}H NMR ($CDCl_3$): δ = 7.14–7.20 (m, 1 H, 4′′-H), 7.36 (dd, *J* = 5.1, 1.2 Hz, 1 H, 5′′-H), 7.40 (dt, *J* = 7.2, 1.2 Hz, 1 H, 6-H), 7.44 (dd, *J* = 3.6, 1.2 Hz, 1 H, 3′′-H), 7.51 (dt, *J* = 7.2, 1.2 Hz, 1 H, 5-H), 7.74 (d, *J* = 8.8 Hz, 2 H, 3′- and 5′-H), 7.92 (dd, *J* = 7.2, 1.2 Hz, 1 H, 7-H), 8.09 (dd, *J* = 7.2, 1.2 Hz, 1 H, 4-H), 8.11 (d, *J* = 8.8 Hz, 2 H, 2′- and 6′-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 121.61 (C-7), 123.15 (C-4), 124.02 (C-3′′), 125.20 (C-6), 125.85 (C-5′′), 126.17 (C-3′ and -5′), 126.37 (C-5), 128.06 (C-2′ and -6′), 128.28 (C-4′′), 132.40 (C-1′), 134.97 (C-7a), 136.81 (C-4′), 143.26 (C-2′′), 154.15 (C-3a), 167.43 (C-2) ppm. IR (KBr): $\tilde{\nu}$ = 1602, 1479, 1425, 1315, 1250, 1115, 965, 816, 757, 692 cm^{-1}. $C_{17}H_{11}NS_2$ (293.41): calcd. C 69.59, H 3.78, N 4.77, S 21.85; found C 69.53, H 3.91, N 4.84, S 21.54.

2-[5′-(4′′-Methoxyphenyl)thien-2′-yl]-1,3-benzothiazole (6b): Yellow solid (333 mg, 86%). M.p. 154.3–155.7 °C. ^{1}H NMR ($CDCl_3$): δ = 3.86 (s, 3 H, OCH_3), 6.96 (d, *J* = 8.7 Hz, 2 H, 3′′- and 5′′-H), 7.22 (d, *J* = 3.3 Hz, 1 H, 4′-H), 7.37 (dt, *J* = 7.8, 1.2 Hz, 1 H, 6-H), 7.48 (dt, *J* = 7.8, 1.2 Hz, 1 H, 5-H), 7.61 (m, 3 H, 3′-, 2′′- and 6′′-H), 7.84 (dd, *J* = 7.8, 1.2 Hz, 1 H, 7-H), 8.02 (dd, *J* = 7.8, 1.2 Hz, 1 H, 4-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 55.37 (OCH_3), 114.47 (C-3′′ and -5′′), 121.38 (C-7), 122.77 (C-4), 122.79 (C-4′), 125.04 (C-6), 126.31 (C-1′′), 126.39 (C-5), 127.26 (C-2′′ and -6′′), 129.59 (C-3′), 134.57 (C-7a), 135.01 (C-2′), 148.28 (C-5′), 153.71 (C-3a), 159.93 (C-4′′), 161.36 (C-2) ppm. IR (KBr): $\tilde{\nu}$ = 1604, 1544, 1481, 1443, 1431, 1250, 1178, 1023, 904, 830, 794, 735, 724 cm^{-1}. MS (EI): *m/z* (%) = 323 (100) [M$^+$], 308 (55). EI HRMS: calcd. for $C_{18}H_{13}NOS_2$ 323.0439, found 323.0437.

2-[5′-(2′′,4′′-Dimethoxyphenyl)thien-2′-yl]-1,3-benzothiazole (6c): Yellow solid (127 mg, 30%). M.p. 108.0–111.0 °C. ^{1}H NMR ([D$_6$]-DMSO): δ = 3.83 (s, 3 H, OCH_3), 3.98 (s, 3 H, OCH_3), 6.66 (dd, *J* = 8.4, 2.1 Hz, 1 H, 5′′-H), 6.74 (d, *J* = 2.1 Hz, 1 H, 3′′-H), 7.42 (dt, *J* = 8.1, 0.9 Hz, 1 H, 6-H), 7.51 (dt, *J* = 8.1, 0.9 Hz, 1 H, 5-H), 7.62 (d, *J* = 3.9 Hz, 1 H, 4′-H), 7.78 (d, *J* = 3.9 Hz, 1 H, 3′-H), 7.81 (d, *J* = 8.4 Hz, 1 H, 6′′-H), 7.97 (dd, *J* = 8.1, 0.9 Hz, 1 H, 4-H), 8.08 (dd, *J* = 8.1, 0.9 Hz, 1 H, 7-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 55.49 (OCH_3), 55.60 (OCH_3), 98.88 (C-5′′), 105.38 (C-3′′), 115.66 (C-1′′), 121.33 (C-7), 122.69 (C-4), 124.57 (C-4′), 124.84 (C-6), 126.27 (C-5), 128.59 (C-3′), 128.99 (C-6′′), 134.55 (C-7a), 135.07 (C-2′), 143.95 (C-5′), 153.87 (C-3a), 157.05 (C-4′′ or -2′′), 160.95 (C-4′′ or -2′′), 161.96 (C-2) ppm. IR (KBr): $\tilde{\nu}$ = 2961, 2928, 2849, 1605, 1515, 1470, 1447, 1313, 1246, 1021, 835, 740 cm^{-1}. MS (EI): *m/z* (%) = 353 (100) [M$^+$], 338 (42). EI HRMS: calcd. for $C_{19}H_{15}NO_2S_2$ 353.0544, found 353.0530.

2-[5′-(4′′-Ethoxyphenyl)thien-2′-yl]-1,3-benzothiazole (6d): Yellow solid (335 mg, 83%). M.p. 147.5–148.9 °C. ^{1}H NMR ($CDCl_3$): δ = 1.45 (t, *J* = 6.9 Hz, 3 H, CH_3), 4.85 (q, *J* = 6.9 Hz, 2 H, CH_2), 6.95 (d, *J* = 8.7 Hz, 2 H, 3′′- and 5′′-H), 7.04 (d, *J* = 3.6 Hz, 1 H, 4′-H), 7.36 (dt, *J* = 7.5, 1.2 Hz, 1 H, 6-H), 7.48 (dt, *J* = 7.5, 1.2 Hz, 1 H, 5-H), 7.60 (m, 3 H, 3′-, 2′′- and 6′′-H), 7.85 (dd, *J* = 7.5, 1.2 Hz, 1 H, 7-H), 8.04 (dd, *J* = 7.5, 1.2 Hz, 1 H, 4-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.76 (CH_3), 63.58 (CH_2), 114.98 (C-3′′ and -5′′), 121.38 (C-7), 122.71 (C-4′), 122.76 (C-4), 125.03 (C-5), 126.13 (C-1′′), 126.38 (C-6), 127.24 (C-2′′ and -6′′), 129.59 (C-3′), 134.56 (C-7a), 134.93 (C-2′), 148.38 (C-5′), 153.72 (C-3a), 159.32 (C-4′′), 161.38 (C-2) ppm. IR (KBr): $\tilde{\nu}$ = 3000, 2990, 1596, 1546, 1483, 1446, 1390, 1251, 1184, 1117, 1081, 1047, 901, 830, 789, 754, 731 cm^{-1}. MS (EI): *m/z* (%) = 337 (100) [M$^+$], 309 (72), 308 (79). EI HRMS: calcd. for $C_{19}H_{15}NOS_2$ 337.0595, found 337.0607.

2-[5′-(4′′-Hydroxyphenyl)thien-2′-yl]-1,3-benzothiazole (6e): Light brown solid (148 mg, 40%). M.p. 212.4–213.5 °C. ^{1}H NMR ($CDCl_3$): δ = 6.82 (d, *J* = 9.0 Hz, 2 H, 3′′- and 5′′-H), 7.11 (d, *J* = 3.9 Hz, 1 H, 4′-H), 7.27 (dt, *J* = 7.8, 1.2 Hz, 1 H, 6-H), 7.38 (dt, *J* = 7.8, 1.2 Hz, 1 H, 5-H), 7.42 (d, *J* = 9.0 Hz, 2 H, 2′′- and 6′′-H), 7.50 (d, *J* = 3.9 Hz, 1 H, 3′-H), 7.76 (dd, *J* = 7.8, 1.2 Hz, 1 H, 7-H), 7.90 (dd, *J* = 7.8, 1.2 Hz, 1 H, 4-H), 9.03 (br. s, 1 H, OH) ppm. ^{13}C NMR ($CDCl_3$): δ = 115.94 (C-3′′ and -5′′), 121.18 (C-

7), 122.10 (C-4′), 122.37 (C-4), 124.63 (C-1′′), 124.78 (C-6), 126.14 (C-5), 127.05 (C-2′′ and -6′′), 129.47 (C-3′), 134.09 (C-7a), 134.25 (C-2′), 148.74 (C-5′), 153.42 (C-3a), 157.87 (C-4′′), 161.20 (C-2) ppm. IR (KBr): $\tilde{\nu}$ = 3500–3000 (OH), 1608, 1587, 1544, 1310, 1260, 1177, 1107, 1020, 910, 830, 799, 755, 730, 518 cm^{-1}. MS (EI): *m/z* (%) = 309 (100) [M$^+$]. EI HRMS: calcd. for $C_{17}H_{11}NOS_2$ 309.0282, found 309.0290.

2-{5′-[4′′-(Dimethylamino)phenyl]thien-2′-yl}-1,3-benzothiazole (6f): Orange solid (197 mg, 49%). M.p. 210.8–211.5 °C. ^{1}H NMR ($CDCl_3$): δ = 3.03 [s, 6 H, $N(CH_3)_2$], 6.74 (d, J = 9 Hz, 2 H, 3′′- and 5′′-H), 7.19 (d, J = 3.9 Hz, 1 H, 4′-H), 7.35 (dt, J = 7.5, 1.2 Hz, 1 H, 6-H), 7.47 (dt, J = 7.5, 1.2 Hz, 1 H, 5-H), 7.56 (d, J = 9 Hz, 2 H, 2′′- and 6′′-H), 7.59 (d, J = 3.9 Hz, 1 H, 3′-H), 7.84 (dd, J = 7.5, 1.2 Hz, 1 H, 7-H), 8.01 (dd, J = 7.5, 1.2 Hz, 1 H, 4-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 40.32 (CH_3), 112.35 (C-3′′ and -5′′), 121.34 (C-7), 121.45 (C-4′), 121.64 (C-1′′), 122.63 (C-4), 124.86 (C-6), 126.31 (C-5), 126.97 (C-2′′ and -6′′), 129.79 (C-3′), 133.59 (C-2′), 134.51 (C-7a), 149.60 (C-5′), 150.55 (C-4′′), 153.79 (C-3a), 161.65 (C-2) ppm. IR (KBr): $\tilde{\nu}$ = 1609, 1543, 1481, 1441, 1363, 1230, 1194, 800 cm^{-1}. MS (EI): *m/z* (%) = 336 (100) [M$^+$]. EI HRMS: calcd. for $C_{19}H_{16}N_2S_2$ 336.0755, found 336.0758.

2-[5′-(4′′-Biphenylyl)thien-2′-yl]-1,3-benzothiazole (6g): Orange solid (394 mg, 89%). M.p. 232.5–233.6 °C. ^{1}H NMR ($CDCl_3$): δ = 7.26–7.34 (m, 3 H, 6-, 4′- and 4′′′-H), 7.34–7.44 (m, 3 H, 5-, 3′′′- and 5′′′-H), 7.52–7.62 (m, 5 H, 3′-, 3′′-, 5′′-, 2′′′- and 6′′′-H), 7.70 (d, J = 8.4 Hz, 2 H, 2′′- and 6′′-H), 7.79 (br. d, J = 8.1 Hz, 1 H, 7-H), 7.94 (br. d, J = 8.1 Hz, 1 H, 4-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 121.26 (C-7), 122.57 (C-4), 123.73 (C-4′), 125.01 (C-6), 126.05 (C-2′′ and -6′′), 126.26 (C-5), 126.64 (C-2′′′ and -6′′′), 127.42 (C-4′′′), 127.46 (C-3′′ and -5′′), 128.66 (C-3′′′ and -5′′′), 129.41 (C-3′), 132.16 (C-1′′), 134.38 (C-7a), 135.81 (C-2′), 139.88 (C-1′′′), 140.93 (C-4′′), 147.47 (C-5′), 153.43 (C-3a), 160.90 (C-2) ppm. IR (KBr): $\tilde{\nu}$ = 1479, 1443, 902, 801, 754 cm^{-1}. MS (EI): *m/z* (%) = 369 (100) [M$^+$]. EI HRMS: calcd. for $C_{23}H_{15}NS_2$ 369.0646, found 369.0648.

2-[5′-(4′′-Phenoxyphenyl)thien-2′-yl]-1,3-benzothiazole (6h): Yellow solid (420 mg, 91%). M.p. 170.4–171.8 °C. ^{1}H NMR ($CDCl_3$): δ = 7.02 (m, 4 H, 3′′-, 5′′-, 3′′′- and 5′′′-H), 7.17 (dt, J = 7.8, 1.2 Hz, 1 H, 4′′′-H), 7.26 (d, J = 4.0 Hz, 1 H, 4′-H), 7.34–7.42 (m, 3 H, 6-, 2′′′- and 6′′′-H), 7.48 (dt, J = 7.8, 1.2 Hz, 1 H, 5-H), 7.61 (d, J = 4.0 Hz, 1 H, 3′-H), 7.64 (d, J = 7.8 Hz, 2 H, 2′′- and 6′′-H), 7.86 (dd, J = 7.8, 1.2 Hz, 1 H, 7-H), 8.04 (dd, J = 7.8, 1.2 Hz, 1 H, 4-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 118.97 (C-3′′ and -5′′), 119.32 (C-3′′′ and -5′′′), 121.40 (C-7), 122.82 (C-4), 123.38 (C-4′), 123.78 (C-4′′′), 125.13 (C-6), 126.43 (C-5), 127.40 (C-2′′ and -6′′), 128.51 (C-1′′), 129.55 (C-3′), 129.87 (C-2′′′ and -6′′′), 134.59 (C-7a), 135.61 (C-2′), 147.66 (C-5′), 153.68 (C-3a), 156.54 (C-1′′′), 157.84 (C-4′′), 161.21 (C-2) ppm. IR (KBr): $\tilde{\nu}$ = 3050, 1587, 1547, 1510, 1489, 1481, 1444, 1434, 1312, 1281, 1254, 1174, 1161, 1113, 1073, 1013, 905, 874, 843, 802, 747, 727, 690 cm^{-1}. MS (EI): *m/z* (%) = 385 (100) [M$^+$]. EI HRMS: calcd. for $C_{23}H_{15}NOS_2$ 385.0595, found 385.0590.

2-[5′-(1′′-Naphthyl)thien-2′-yl]-1,3-benzothiazole (6i): Yellow solid (316 mg, 77%). M.p. 157.9–158.8 °C. ^{1}H NMR ($CDCl_3$): δ = 7.31 (d, J = 3.6 Hz, 1 H, 4′-H), 7.39 (dt, J = 7.5, 1.2 Hz, 1 H, 6-H), 7.50 (dt, J = 7.5, 1.2 Hz, 1 H, 5-H), 7.52 (m, 3 H, Ar-H), 7.64 (dd, J = 7.5, 1.2 Hz, 1 H, 2′′-H), 7.75 (d, J = 3.6 Hz, 1 H, 3′-H), 7.87–7.96 (m, 3 H, 7-H and Ar-H), 8.04 (dd, J = 7.5, 1.2 Hz, 1 H, 4-H), 8.30–8.36 (m, 1 H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 121.45 (C-7), 122.93 (C-4), 125.20 (C-6), 125.29, 125.45, 126.23 (naphth), 126.45 (C-5), 126.79, 128.19 (naphth), 128.33 (C-4′), 128.46 (naphth), 128.81 (C-3′), 129.14 (naphth), 131.40 (C-1′′), 131.49 (C-5′′), 133.88 (C-10′′), 134.67 (C-7a), 137.15 (C-2′), 146.05 (C-5′), 153.75 (C-3a), 161.29 (C-2) ppm. IR (KBr): $\tilde{\nu}$ = 1545, 1492, 1432, 1391, 1312, 1231, 900, 796, 761, 729 cm^{-1}. MS (EI): *m/z* (%) = 343 (100) [M$^+$]. EI HRMS: calcd. for $C_{21}H_{13}NS_2$ 343.0489, found 343.0479.

2-[5′-(4′′-Fluorophenyl)thien-2′-yl]-1,3-benzothiazole (6j): Yellow solid (336 mg, 90%). M.p. 165.2–167.9 °C. ^{1}H NMR ($CDCl_3$): δ = 7.12 (t, J_{H-F} = 9.0 Hz, 2 H, 3′′- and 5′′-H), 7.25 (d, J = 3.9 Hz, 1 H, 4′-H), 7.37 (dt, J = 8.0, 1.2 Hz, 1 H, 6-H), 7.50 (dt, J = 8.0, 1.2 Hz, 1 H, 5-H), 7.59 (d, J = 3.9 Hz, 1 H, 3′-H), 7.60–7.65 (m, 2 H, 2′′- and 6′′-H), 7.86 (dd, J = 8.0, 1.2 Hz, 1 H, 7-H), 8.04 (dd, J = 8.0, 1.2 Hz, 1 H, 4-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 116.11 (d, J_{C-F} = 21.9 Hz, C-3′′ and -5′′), 121.42 (C-7), 122.87 (C-4), 123.82 (C-4′), 125.21 (C-6), 126.46 (C-5), 126.67 (d, J_{C-F} = 8.4 Hz, C-2′′ and -6′′), 129.46 (C-3′), 129.80 (d, J_{C-F} = 3.8 Hz, C-1′′), 134.61 (C-7a), 136.13 (C-2′), 146.92 (C-5′), 153.65 (C-3a), 161.06 (C-2), 162.79 (d, J_{C-F} = 250 Hz, C-4′′) ppm. IR (KBr): $\tilde{\nu}$ = 1597, 1547, 1514, 1484, 1446, 1434, 1310, 1258, 1229, 1164, 1015, 905, 801, 755, 729, 703, 622, 604, 533 cm^{-1}. MS (EI): *m/z* (%) = 311 (100) [M$^+$]. EI HRMS: calcd. for $C_{17}H_{10}NS_2F$ 311.0239, found 311.0240.

2-(2′-Benzothiazolyl)-5-[4′′-(2′′′-benzothiazolyl)phenyl]thiophene (6k:) Yellow solid (429 mg, 84%). M.p. 255.9–256.7 °C. ^{1}H NMR ($CDCl_3$): δ = 7.36–7.45 (m, 2 H, 6- and 6′-H), 7.47 (d, J = 3.9 Hz, 1 H, 4′′-H), 7.48–7.56 (m, 2 H, 5- and 5′-H), 7.68 (d, J = 3.9 Hz, 1 H, 3′′-H), 7.81 (dd, J = 8.4, 1.8 Hz, 2 H, 2′′′- and 6′′′-H), 7.88 (dd, J = 8.1, 1.1 Hz, 1 H, 7′-H), 7.93 (dd, J = 8.1, 1.1 Hz, 1 H, 7-H), 8.06 (dd, J = 8.1, 1.1 Hz, 1 H, 4′-H), 8.11 (dd, J = 8.1, 1.1 Hz, 1 H, 4-H), 8.17 (dd, J = 8.4, 1.8 Hz, 2 H, 3′′′- and 5′′′-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 121.5 (C-7′), 121.7 (C-7), 123.1 (C-4′), 123.3 (C-4), 124.8 (C-4′′), 125.4 (C-6 and -6′), 126.3 (C-2′′′ and -6′′′), 126.5 (C-5′), 126.6 (C-5), 128.3 (C-3′′′ and -5′′′), 129.5 (C-3′′), 133.5 (C-4′′′), 134.8 (C-7a′), 135.9 (C-7a), 137.1 (C-2′′), 146.9 (C-5′′), 153.8 (C-3a′), 154.3 (C-3a), 160.9 (C-1′′′), 161.1 (C-2), 167.1 (C-2′) ppm. IR (KBr): $\tilde{\nu}$ = 3049, 1602, 1547, 1484, 1477, 1444, 1313, 1256, 1230, 1185, 1115, 1063, 1015, 961, 904, 833, 802, 755, 728, 701, 619 cm^{-1}. MS (EI): *m/z* (%) = 426 (100) [M$^+$]. EI HRMS: calcd. for $C_{24}H_{14}N_2S_3$ 426.0319, found 426.0334.

Acknowledgments

Thanks are due to the Foundation for Science and Technology (Portugal) for financial support through the Centro de Química (Univ. Minho). The authors are also grateful to Dr. H. Figueiredo and Prof. I. C. Neves of the Department of Chemistry of the University of Minho for the thermogravimetric analyses.

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Received: January 23, 2006
Published Online: July 5, 2006

