Nonlinear optical chromophores with isoquinolines, thieno[2,3-*c*]-pyridines and 2-(2′-thienyl)pyridines as inherently polarized π-electron bridges

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The synthesis and first hyperpolarizabilities of a series of isoquinolines and isoquinolinium salts, and also thienopyridines, thienylpyridines, and the corresponding pyridinium salts, determined by hyper-Rayleigh scattering in solution at 1064 and 1300 nm, are reported. These chromophores exhibit markedly high *β* values. Some of them show absorption maxima well below 400 nm, enabling their use in blue transparent frequency doubling devices. We have performed X-ray structure analyses for thienopyridines 13a,c.

Introduction

In the past 30 years, organic materials have attracted much interest for nonlinear optical (NLO) applications because of their potentially large and fast second- and third-order polarizabilities, β and γ.[1] Applications for molecules with high β values involve the linear electrooptic effect,[2] the photorefractive effect,[3] and second harmonic generation.[4] The most common NLO chromophores contain donor (D)–acceptor (A) substituted π-conjugated systems, such as *p*-nitroaniline (*p*NA), which can potentially exhibit intramolecular charge transfer (CT). According to the two-state model,[5] the magnitude of the molecular second-order optical nonlinearity β is proportional to the oscillator strength of the electronic transition, the difference in dipole moments of ground and excited states, and the square of the reciprocal transition energy. This last factor is responsible for the so-called 'transparency–nonlinearity trade-off'.[6]

In general, in NLO-phores the π-bridge is polarized by externally attached donors and acceptors, as are the nitro- and amino-group in *p*NA. An inherently polarized π-bridge can be generated by fusing or linearly connecting heteroaromatics of different electron densities, *e.g.* the electron poor pyridine and the electron rich thiophene. The use of heteroaromatics in NLO chromophores[7] has two main advantages: (*i*) the improved transparency–nonlinearity trade-off and (*ii*) the higher thermal stability, which is important if the chromophores are embedded in long-term stable thin films of polymers with a high glass transition temperature. The electron-accepting ability of the pyridine moiety can be greatly improved by alkylation of the N atom, as was demonstrated by the remarkably high β values of pyridinium salts[8] and stilbazolium salts.[9]

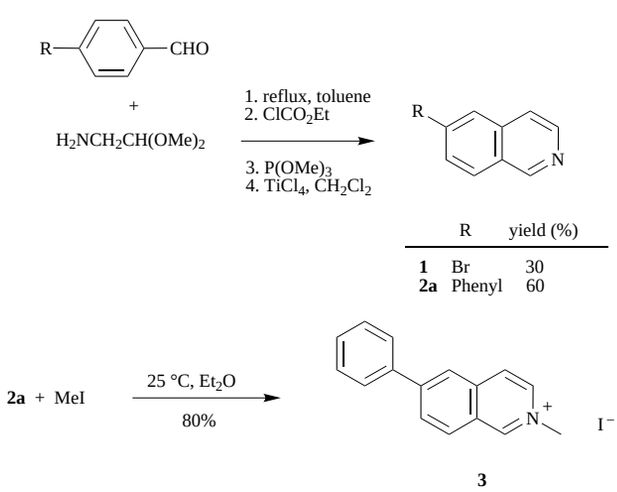
The heteroaromatics investigated in this work are isoquinolines, thieno[2,3-*c*]pyridines or 2-(2′-thienyl)pyridines. The parent compounds of these heteronaphthalenes or heterobiphenyls are inherently polarized push–pull systems with moderate dipole moments (2–3 D).[10] The polarization of these π-systems can be enhanced by introduction of donors into the benzene or thiophene and by introduction of acceptors into, or *N*-alkylation of, the pyridine. The resonance stabilization of these three classes of heteroaromatics is expected to be lower than those of the corresponding carbocycles since the resonance energies per electron (REPE) and aromatic energies of the thiophene (REPE: 0.032)[11] and pyridine (REPE: 0.058)[11] are smaller than that of benzene (REPE: 0.065).[11] Charge transfer (CT) between donor and acceptor group, therefore, should occur more easily in these heteroaromatics than in the corresponding carbocycles.

In order to test this concept we have synthesized and characterized a number of isoquinolines **1**, **2**, **4**–**7**, thieno[2,3-*c*]-pyridines **10**–**14** and 2-(2′-thienyl)pyridines **18**–**21**, and the corresponding salts **3**, **8**, **15** and **22**. The molecular first hyperpolarizabilities β have been measured by hyper-Rayleigh scattering (HRS) in solution at 1064 and 1300 nm.

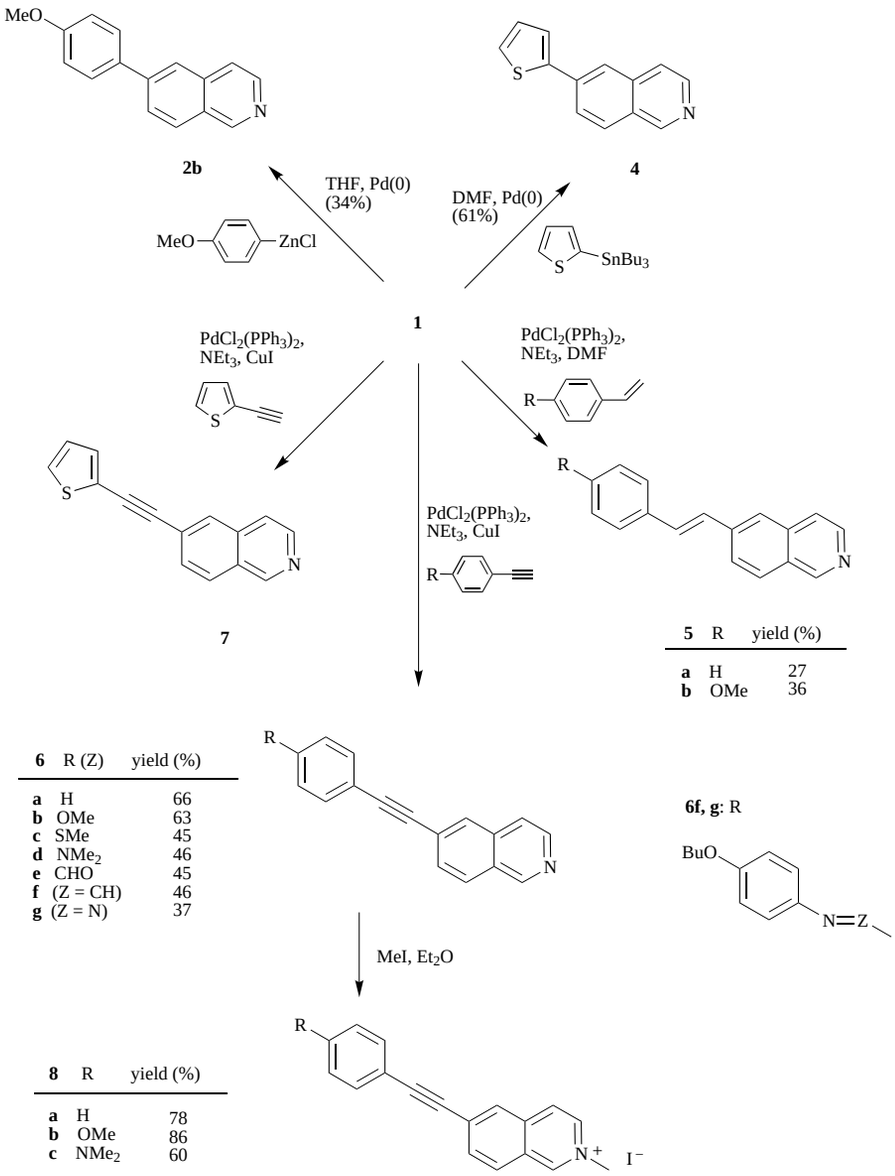
Results and discussion

Syntheses

The 6-phenylisoquinoline **2a** was prepared in 60% yield by a Pomeranz–Fritsch reaction of 4-phenylbenzaldehyde and aminoacetaldehyde dimethyl acetal, analogous to a protocol for the 6-bromoisoquinoline **1** (Scheme 1). The compound **1** is



Scheme 1



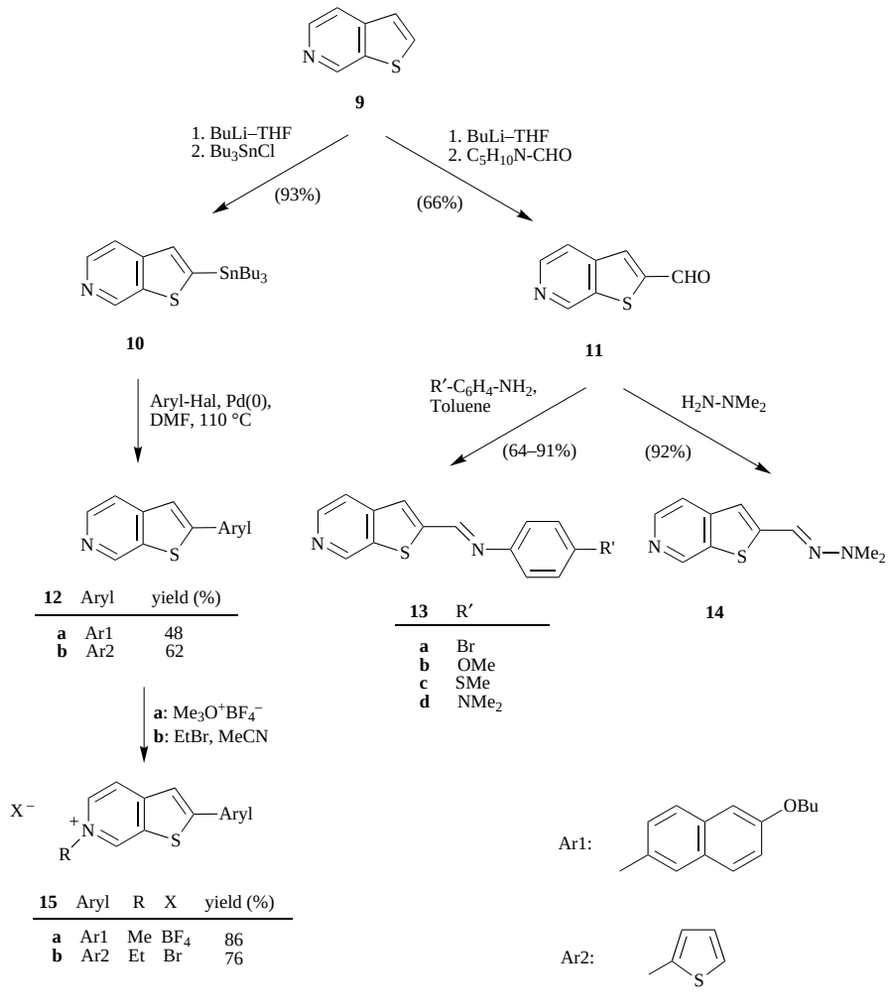
Scheme 2

an important starting material for the 6-substituted isoquinolines **2b**, **4**–**8** (Scheme 2) and was made by a known method. The yield of **1** was greatly improved from 4–30% by optimizing the described procedure.[12] Treatment of **2a** with iodomethane in diethyl ether gave the salt **3** in 80% yield.

The preparation of the isoquinoline derivatives **2b**, **4**–**8** was carried out according to Scheme 2. The cross-coupling of **1** with 4-methoxyphenylzinc chloride gave the 6-arylisoquinoline **2b** in 34% yield. The 6-thienylisoquinoline **4** was obtained by a Stille coupling between **1** and 2-tributylstannylthiophene in 60% yield. The stilbenes **5a**,**b** were synthesized by Heck coupling of **1** and styrene or 4-methoxystyrene in moderate yields. The tolanes **6a**–**e** and **6g** were formed by Hagihara reaction of **1** and the appropriate arylethynes in yields of 45–66%. The aldehyde **6e** was condensed with 4-butoxyaniline to give the azomethine **6f**. 2-Thienylethyne reacted with **1** to produce the 6-(2-thienylethynyl)isoquinoline **7** in 55% yield. The tolanes **6a**,**b**,**d** were easily converted to the corresponding isoquinolinium salts **8a**–**c** in good yields by treatment with iodomethane in diethyl ether.

The isoquinoline analogue thieno[2,3-*c*]pyridine **9** was easily accessible as previously described[13] (Scheme 3). (Hetero)arylation of **9** was achieved by Stille coupling of the key compound **10** leading to (hetero)arylthieno[2,3-*c*]pyridines **12a**,**b**, which could be further *N*-alkylated to enhance the acceptor strength of the pyridine moiety. The compounds **15a**,**b** can be regarded as rigidized stilbazolium salts without free double bonds. Therefore no *E*/*Z*-isomers can occur, and **15a** and **b** do not suffer from hydrolysis as do the normal stilbazolium salts.[14] A disadvantage is the possibility of strong fluorescence, which was observed in the case of **15a** with a high PM3 calculated β value.

In order to avoid fluorescence we decided to synthesize slightly twisted molecules. Such a structure was expected for the imines **13a**–**d**, which were easily prepared by condensation of the aldehyde **11** with arylamines. The shorter hydrazone **14** bears the potent dimethylaminohydrazone donor, which shows higher NLO activity than the dimethylamino group.[15] We have performed X-ray structure analyses for compounds **13a**,**c**. As expected for imines with weak donor and acceptor groups[16] the thioether **13c** (Fig. 2) is twisted with an interplanar angle of 38° between the two ring systems. Interestingly the bromo analogue **13a** (Fig. 1) is planar. In contrast to *p*-bromo-*N*-(*p*-dimethylaminobenzylidene)aniline,[17] where a nearly planar geometry results from the contribution of a quinoid structure, strong donor or acceptor groups are not present in **13a**. The X-ray structures of **13a**,**c** are in good agreement with our PM3 calculations,[18] so that crystal packing effects are unlikely to be responsible for the planarity of **13a**. Both compounds crystallize in a centrosymmetric space group and therefore are NLO-inactive in crystalline form.



Scheme 3

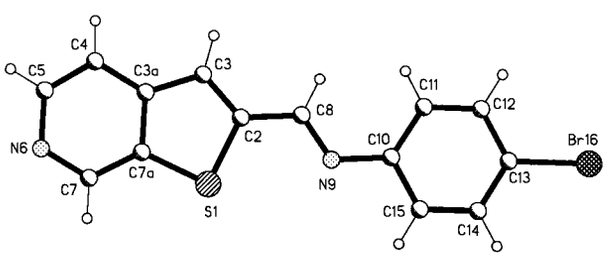


Fig. 1 Structure of **13a** in the crystal. Bond distances C(2)–C(8) 1.444(3), C(8)–N(9) 1.269(3) Å, bond angles C(8)–N(9)–C(10) 121.0(2), C(15)–C(10)–N(9) 115.8(2)°, interplanar angle between ring systems 1.4(1)°.

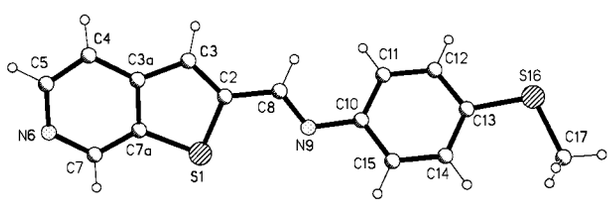
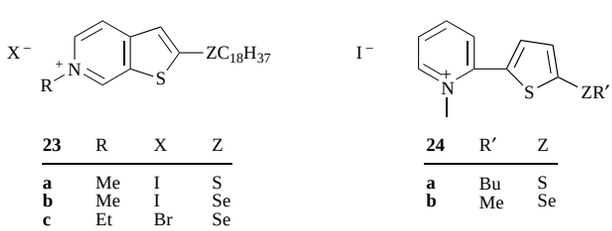


Fig. 2 Structure of **13c** in the crystal. Bond distances C(2)–C(8) 1.447(2), C(8)–N(9) 1.276(2) Å, bond angles C(8)–N(9)–C(10) 118.5(1), C(15)–C(10)–N(9) 117.9(1)°, interplanar angle between ring systems 38.4(1)°, torsion angle C(14)–C(13)–S(16)–C(17) 1.5(1)°.

The commercially available 2-(2′-thienyl)pyridine **16** (Scheme 4) was *N*-alkylated to its quaternary salt **17**, whereby the molar extinction coefficient ε diminishes from 14 400 to 9300 because of a strong twisting of **17**, with a PM3-calculated angle of 75°. Crystalline **16** is nearly planar.[19] Compound **16** can be lithiated in the 5′-position in the thiophene ring[20] (Scheme 4). Reaction of the lithio compound with iodine or *N*-formylpiperidine gave the iodo compound **18** and the aldehyde **19**, respectively. The tolane **20** was prepared by Hagihara coupling of **18** with phenylacetylene in good yield and converted to the corresponding salt **22** by treatment with Meerwein's reagent in good yield. Condensation of the aldehyde **19** with arylamines led to the imines **21a**,**b**. As previously described,[21c] we prepared the thio- and seleno-ethers **23**, **24**, which are mentioned here for comparison.

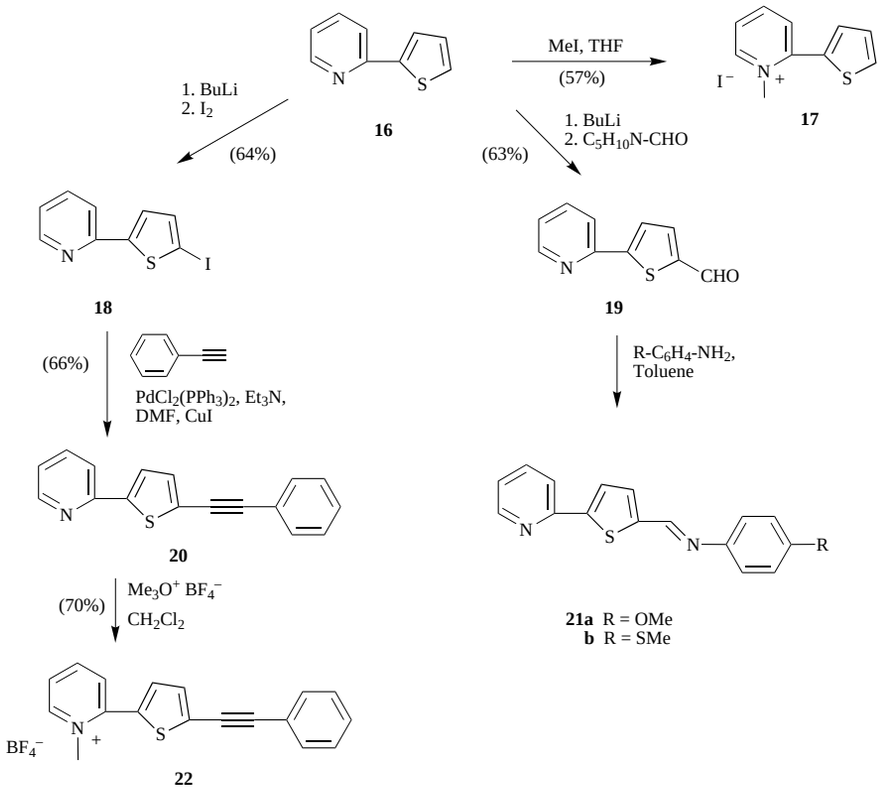


Linear and nonlinear optical properties

Table 1 lists the dynamic (at 1064 and 1300 nm) and static first hyperpolarizabilities (determined using the two-state model) of the compounds studied, along with the UV–VIS data in chloroform and acetonitrile, respectively.

All compounds investigated exhibit negative solvatochromism in the solvent pair chloroform–acetonitrile, which means that the ground state is more polar than the excited state.

The salt **15a** shows a fluorescence maximum of 510 nm (acetonitrile), which is located in the region of the second harmonic (532 nm) so that no correct HRS measurement at 1064 nm was possible.[23] The high Stokes shift of 6430 cm^{-1} is comparable to that of aminonaphthylpyridinium salts.[12]



Scheme 4

Alkylation of the pyridine nitrogen enhances the acceptor strength, which is reflected in the bathochromic shift of the absorption wavelength and the larger hyperpolarizabilities of the isoquinolinium salts compared to the corresponding isoquinolines. This is true for the pairs **2a/3** and **6a/8a**, which lack an electron donor. As expected, this effect is more marked in donor-substituted isoquinoline derivatives, as the comparison of the β values for **6b** and **8b** and for **6d** and **8c** clearly demonstrates. The substitution of the phenyl unit in **2a** by a thiophene moiety (→**4**) leads to a small bathochromic shift and doubling of $\beta(0)$. This is attributable to the donating ability of the thiophene moiety. In the case of the related alkynes **6a** and **7** there is only a small difference of λ_{max} and no difference of the $\beta(0)$ values. This can be explained by the reduced conjugation efficiency of the C≡C triple bond. Extension of the phenyl-substituted **2a** by a C=C double bond (→**5a**) leads to a bathochromic shift and a tripling of $\beta(0)$. Interestingly the alkyne **6a** absorbs at shorter wavelength than **2a** but shows a nearly tripled $\beta(0)$. Also in the case of the corresponding methoxy derivatives **2b**, **5b** and **6b** the superiority of the C=C bond with regard to the $\beta(0)$ value can be seen. Extension of the π-conjugated system in **6b** by a C=N (→**6f**) or an N=N bond (→**6g**) leads to an increase in λ_{max} and $\beta(0)$. The imine **6f** shows a better efficiency–transparency trade-off than the azo compound **6g**.

Comparison of the hyperpolarizabilities of the alkynes **6b** and **6c** reflects the well-known superiority of the thioether group over the methoxy group as an electron donor in NLO chromophores.[21] As expected, the dimethylamino compound **6d** with the strongest donor of the series exhibits the longest absorption wavelength and the largest hyperpolarizability. The latter is undoubtedly dispersion-enhanced, since the cut-off of the absorption band of **6d** is close to the wavelength of the second harmonic.

As with the isoquinolines, the acceptor strength of the pyridine in the thieno- and thienyl-pyridines is increased by alkylation, which is reflected in the linear and nonlinear optical properties. This effect can be observed even without a classical electron-donating group, as the hyperpolarizabilities and absorption maxima of **20** and **22** demonstrate. Comparison with the analogous isoquinolines **6a** and **8a** shows that in the case of the electroneutral ethynes isoquinoline is the more efficient π-bridge than thienylpyridine. The nonlinear optical properties of the salts **8a** and **22** are dominated by the pyridinium moiety so that they exhibit the same $\beta(0)$ value.

The comparison of the thienopyridines **13b** and **13c** again reflects the superiority of the thioether group over the ether group as an electron donor. Interestingly, this tendency cannot be observed with the corresponding thienylpyridines **21a** and **21b**, whose absorption maxima are quite similar and whose first hyperpolarizabilities are equal within the estimated accuracy of the HRS experiment (±15%). This could be due to the worse π-orbital overlap between the tilted rings in the thienylpyridines compared to the planar thienopyridines. The variation of the strength of the electron donor should, therefore, affect the properties of the latter more than those of the former. This is especially obvious for **13a** and **13d** with the weak Br-donor[22] and the strong dimethylamino-donor, respectively. The large β for **13d** is dispersion-enhanced. Reduction of the length of the π-conjugated system in **13d** naturally leads to a strong hypsochromic shift of the absorption wavelength and a strong decrease of the dynamic and static hyperpolarizabilities; the $\beta(0)$ value of **14** is about four times smaller than that of **13d**.

The unsubstituted thienylpyridinium salt **17** exhibits only a very small first hyperpolarizability due to the poor electron-donating ability of the thiophene moiety. Introduction of an electron donor in the thio- and seleno-ethers **24a** and **24b** leads to a strong bathochromic shift and tripling of $\beta(0)$. The small decrease of the hyperpolarizability of selenoethers compared to thioethers has been discussed previously.[21c]

An interesting comparison can be made between the thienylpyridines **21a** and **21b** and the corresponding thienopyridines **13b** and **13c**. The difference in absorption maxima between the methoxy derivatives **21a** and **13b** is twice that of the corresponding thioethers **21b** and **13c**. The same tendency can be observed with the hyperpolarizabilities. The β value of **21a** is almost twice that of **13b** while those of **21b** and **13c** are quite similar.

Table 1 UV–VIS data and β (1064 nm) and $\beta(0)$ values ($CHCl_3$) of compounds **1**–**8**, **12**–**15**, **17**, **18** and **20**–**24**

Isoquinoline	$\lambda_{max}(\lambda_{cut\text{-}off})$ ($CHCl_3$)/nm	$\lambda_{max}(\lambda_{cut\text{-}off})$ (CH_3CN)/nm	$\beta_{HRS,1064}$ (1300[a])/ 10^{-30} esu	$\beta_{HRS,0}$/ 10^{-30} esu
1	320 (350)	—	—	—
2a	322 (350)	—	6	4
2b	306 (385)	—	15	9
3	336 (480)	326 (385)	25[b]	14[b]
4	334 (380)	—	17	10
5a	340 (380)	—	25	14
5b	328 (400)	—	28	15
6a	316 (385)	—	18	11
6b	334 (425)	—	22	13
6c	344 (425)	—	33	18
6d	372 (550)	—	123	56
6f	358 (465)	—	47	23
6g	376 (580)	—	24[a]	19
7	324 (390)	—	18	11
8a	368 (570)	358 (410)	51[b]	26[b]
8b	394 (490)	376 (450)	108[b]	42[b]
8c	478 (600)	444 (600)	271[a,b]	108[b]
Thieno[2,3-*c*]-pyridine	$\lambda_{max}(\lambda_{cut\text{-}off})$ ($CHCl_3$)/nm	$\lambda_{max}(\lambda_{cut\text{-}off})$ (CH_3CN)/nm	$\beta_{HRS,1064}$/ 10^{-30} esu	$\beta_{HRS,0}$/ 10^{-30} esu
12a	336 (410)	330 (384)	—	—
12b	320 (382)	316 (370)	—	—
13a	342 (456)	336 (422)	15	8
13b	352 (460)	348 (440)	22	11
13c	366 (500)	356 (460)	32	15
13d	428 (550)	418 (542)	145	42
14	344 (460)	342 (430)	21	11
15a	402 (474)	384 (464)	—	—
15b	372 (430)	366 (424)	45	20
2-(2′-Thienyl)-pyridine	$\lambda_{max}(\lambda_{cut\text{-}off})$ ($CHCl_3$)/nm	$\lambda_{max}(\lambda_{cut\text{-}off})$ (CH_3CN)/nm	$\beta_{HRS,1064}$/ 10^{-30} esu	$\beta_{HRS,0}$/ 10^{-30} esu
17	328 (530)	322 (374)	8	4
18	318 (358)	314 (360)	—	—
20	348 (396)	342 (392)	11	6
21a	374 (484)	370 (464)	39	18
21b	380 (532)	378 (472)	37	16
22	376 (455)	358 (435)	51[b]	25[b]
23a	362 (480)	352 (400)	36	18
23b	370 (500)	360 (410)	26	12
23c	370 (426)	360 (412)	26	12
24a	368 (560)	358 (450)	26	12
24b	374 (*ca.* 500)	370 (456)	23	10

[a] β is determined at 1300 nm. [b] Solvent is CH_3CN.

The thienopyridinium salts **15b** and **23a** both have sulfur-containing donor groups. The thioether **23a** absorbs at slightly shorter wavelengths compared to **15b** with the additional thiophene moiety. The hyperpolarizabilities of both chromophores are similar. While the thioether group in principle is the better electron donor, the effect of the thiophene moiety is mainly due to the elongation of the π-conjugated system (the thiophene is a poor electron donor, see **17** above). Again, the selenoether **23b** has a smaller first hyperpolarizability than the thioether **23a**. The change of the counterion in **23b** (→**23c**) only affects the linear optical properties (the cut-off wavelength of the iodide is far red-shifted compared to the bromide, due to an interionic charge transfer in **23b**).

The aryl-isoquinolines **2a**,**b**, **4**, the arylethenyl-isoquinolines **5a**,**b** and the alkynes **6a**, **7** and **20** are blue-transparent and, therefore, suitable for SHG of 830 nm laser diodes. The stilbenes **5a**,**b** show the best transparency–nonlinearity trade-off of these blue-transparent compounds and higher NLO activity than *p*NA. The other chromophores examined by hyper-Rayleigh scattering exhibit cut-offs above 415 nm and therefore cannot be used for SHG of 830 nm diodes. Their high β values make them potential candidates for other applications in the field of optical telecommunications (*e.g.* the linear electrooptical effect). Compound **8c** is an especially effective NLO-phore with a $\beta(0)$ of 108×10^{-30} esu in acetonitrile.

Conclusion

In this paper, we have presented the first molecular hyperpolarizabilities β of a series of isoquinolines, thienopyridines, thienylpyridines and the corresponding pyridinium salts as determined *via* hyper-Rayleigh scattering in solution at 1064 and 1300 nm respectively. These heteroaromatics exhibit high β values and some of them additionally have absorption maxima well below 400 nm. The results have been discussed in terms of structure–property relationships. This work indicates that an inherently polarized π-bridge is an important structural aspect for the design of new NLO chromophores with high β values and good transparency.

Experimental

General

^1H and ^{13}C NMR spectra were run on Bruker AM 400 (400.13 MHz) and 400 (100.61 MHz) instruments, using respectively $CDCl_3$ ($SiMe_4$ as internal reference) or [$^2H_6$]DMSO as solvent

and internal reference. *J* Values are given in Hz. The degree of substitution of the carbon atoms was determined by DEPT 135° experiments. Further assignments were made with the help of CH correlation and COLOC spectra (indicated in the ^{13}C NMR assignments by superscript CHC or COL, respectively). Electron impact mass spectra were recorded on a Finnigan MAT 8430 spectrometer operating at 70 eV. FAB MS (+ve) were recorded on a Finnigan MAT 8340 spectrometer. Xenon was used for neutral beam production with a beam energy of 8 kV. 3-Nitrobenzyl alcohol (NBA) was used as liquid matrix. UV–VIS absorption spectra were measured with a Hewlett Packard diode array spectrophotometer 8452 A. Melting points were determined on a Kofler hot stage microscope and all values are uncorrected. Elemental analyses were carried out by the Analytisches Laboratorium des Instituts für Pharmazeutische Chemie, Technical University of Braunschweig. Separations by column chromatography were performed on 70–230 mesh silica gel from Merck, Darmstadt. In all reactions requiring anhydrous conditions, solvents were dried by distillation under nitrogen from the appropriate drying agent, glassware was flame-dried and cooled afterwards under a steady stream of nitrogen.

HRS measurements

The first hyperpolarizabilities of the heteroaromatic compounds studied in this work were determined by hyper-Rayleigh scattering (HRS)[24] in solution at 1064 and 1300 nm. The experimental set up, theory and data evaluation of the HRS-technique have been described in detail previously.[23,25]

X-Ray structure determination and refinements of 13a and 13c

Crystal data for **13a**: $C_{14}H_9BrN_2S$, $M_r = 317.20$, monoclinic, space group $P2_1/c$, $a = 1483.4(3)$, $b = 1403.4(3)$, $c = 582.51(10)$ pm, $\beta = 91.57(3)°$, $V = 1.2122$ nm^3, $Z = 4$, $D_c = 1.738$ Mg m^{-3}, λ(Mo-Kα) = 0.710 73 Å, $\mu = 3.5$ mm^{-1}, $T = 143$ K. Data collection and reduction: a pale yellow tablet, 0.6 × 0.4 × 0.4 mm, was mounted in inert oil. Data were collected to $2\theta_{max}$ 55° on a Stoe STADI-4 diffractometer (scan type ω/θ). Of 3793 data, 2793 were unique (R_{int} 0.019). An absorption correction based on ψ-scans was applied, with transmissions 0.74–0.85. Structure solution and refinement: the structure was solved by direct methods and refined anisotropically on F^2 using all reflections (program SHELXL-93, G. M. Sheldrick, University of Göttingen, Germany). Hydrogen atoms were included using a riding model. The final $wR(F^2)$ was 0.072 for 164 parameters, conventional $R(F)$ 0.032; $S = 1.10$, max. Δ/σ 0.001; max. $\Delta\rho$ 323 e pm^{-3}.

Crystal data for **13c**: $C_{15}H_{12}N_2S_2$, $M_r = 284.39$, monoclinic, space group $P2_1/n$, $a = 1002.3(3)$, $b = 808.6(2)$, $c = 1665.7(4)$ pm, $\beta = 95.24(3)°$, $V = 1.3443$ nm^3, $Z = 4$, $D_c = 1.405$ Mg m^{-3}, $\mu = 0.38$ mm^{-1}, $T = 143$ K. Data collection and reduction: as above, with following differences: yellow cube, 0.6 × 0.6 × 0.6 mm, $2\theta_{max}$ 50°, 4898 data, 2376 unique (R_{int} 0.027), no absorption correction. Structure solution and refinement: as above, with the following differences: rigid methyl group, $wR(F^2)$ 0.075 for 174 parameters, conventional $R(F)$ 0.027; $S = 1.03$, max. Δ/σ 0.001; max. $\Delta\rho$ 224 e pm^{-3}.

Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, available *via* the RSC Web pages (http//www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 188/113.

Syntheses

***N*-Methylation of isoquinolines with iodomethane (procedure *1*).** A solution of the isoquinoline and a large excess of iodomethane (>20 equiv.) in diethyl ether was stirred at 20–25 °C for 3–4 d. The precipitate was filtered off and recrystallized from the given solvent.

(Hetero)arylethynyl-isoquinolines by Hagihara coupling (procedure *2*).[26] A mixture of 3–5 mmol of 6-bromoisoquinoline **1**, 1.5–2.9 equiv. of the (hetero)arylethyne, 5 mol% of bis-(triphenylphosphine)palladium(II) chloride and 3 mol% of copper(I) iodide in 25–40 ml of anhydrous triethylamine was stirred at 40–60 °C for the given time. The triethylamine was distilled off *in vacuo* and the residue was filtered over silica gel with diethyl ether as eluent. The eluate was extracted with 3 M HCl, and the extract was washed with diethyl ether, made alkaline with aqueous NaOH, and extracted with diethyl ether. The organic layer was dried with Na_2SO_4 and the solvent was evaporated.

Condensation of heteroaromatic aldehydes with aryl- and alkyl-amines (procedure *3*). Either (***a***) a toluene solution connected to a Dean–Stark trap or (***b***) an ethanolic solution of equimolar amounts of the heteroaromatic aldehyde and the amine was refluxed for the given time. The precipitate was filtered off, washed with toluene and dried at 0.1 mbar.

6-Bromoisoquinoline 1.[27] A toluene solution of 30.0 g (0.16 mol) of 4-bromobenzaldehyde and 17.0 g (0.16 mol) of aminoacetaldehyde dimethyl acetal was refluxed into a Dean–Stark trap until the theoretical amount of water was evolved. The solution was evaporated *in vacuo*. The residue was dissolved in 250 ml of anhydrous tetrahydrofuran (THF). After cooling to −10 °C 19.3 g (0.18 mol) of ethyl chloroformate were added dropwise. Then the mixture was stirred for 10 min and allowed to warm to 25 °C. Subsequently 22.0 g (0.178 mol) of trimethyl phosphite were added. After stirring the mixture for 10 h at 20–25 °C the solvent was evaporated. The residue was dissolved in 250 ml of anhydrous CH_2Cl_2, 70.0 ml (4 equiv.) of titanium tetrachloride were added dropwise, and the solution was stirred at 45 °C for 7 d. The mixture was poured onto ice and conc. aqueous NaOH was added to pH 8–9. The suspension was stirred with diethyl ether (4 × 250 ml), which was decanted each time. The filtrate was extracted with 3 M HCl, and the extract was washed with diethyl ether, made alkaline with aqueous NaOH, and extracted with diethyl ether. The organic layer was dried with Na_2SO_4 and the solvent was evaporated. Filtration over silica gel–diethyl ether (R_f 0.35) followed by sublimation (0.3 mbar at 90 °C) gave 10.0 g (30%) of **1** as a colorless solid, mp 44 °C (lit.,[12] 43–44 °C). ν_{max}/cm^{-1} 1622s, 947s, 872s, 831s; $\delta_H(CDCl_3)$ 9.14 (1 H, s, 1-H), 8.48 (1 H, d, ^3J 5.8, 3-H), 7.89 (1 H, d, ^4J 1.4, 5-H), 7.73 (1 H, d, ^3J 8.7, 8-H), 7.58 (1 H, dd, ^3J 8.7, ^4J 1.9, 7-H), 7.45 (1 H, d, ^3J 5.8, 4-H); $\delta_C(CDCl_3)$ 152.3 (d, C-1), 144.0 (d, C-3), 136.6 (s, C-4a), 130.8 (d, C-7), 129.1 (d, C-8), 128.6 (d, C-5), 126.8 (s, C-8a), 125.0 (s, C-6), 119.3 (d, C-4); *m*/*z* (EI-MS) 209 (M^+, 98%), 207 (M^+, 100), 128 (68); λ_{max}/nm (log ε) ($CHCl_3$) 274 (3.62), 306 (3.29), 320 (3.40).

6-Phenylisoquinoline 2a. According to the above preparation of **1**, 5.00 g (27.5 mmol) of 4-phenylbenzaldehyde, 3.20 g (30.5 mmol) of aminoacetaldehyde dimethyl acetal, 3.18 g (29.3 mmol) of ethyl chloroformate, 3.41 g (27.5 mmol) of trimethyl phosphite and 15.0 ml (5 equiv.) of titanium tetrachloride yielded 3.38 g (60%) of **2a** as a colorless solid, mp 79 °C (Found: C, 87.79; H, 5.21; N, 6.80. $C_{15}H_{11}N$ requires C, 87.77; H, 5.40; N, 6.83%); ν_{max}/cm^{-1} 1625m, 890m, 832m, 757m, 689m; $\delta_H(CDCl_3)$ 9.27 (1 H, s, 1-H), 8.54 (1 H, d, ^3J 5.8, 3-H), 8.01 (1 H, d, ^3J 8.5, 8-H), 7.98 (1 H, d, ^4J 0.7, 5-H), 7.84 (1 H, dd, ^3J 8.5, ^4J 1.8, 7-H), 7.70 (2 H, m, 10, 14-H), 7.67 (1 H, d, ^3J 5.8, 4-H), 7.50 (2 H, m, 11, 13-H), 7.42 (1 H, m, 12-H); $\delta_C(CDCl_3)$ 152.3 (d, C-1), 143.4 (d, C-3), 143.0 (s, C-6), 140.2 (s, C-9), 136.1 (s, C-4a), 129.0 (d, C-11, 13), 128.2 (d, C-12), 128.1 (d, C-8), 127.7 (s, C-8a), 127.6 (d, C-10, 14), 127.1 (d, C-7), 124.2 (d, C-5), 120.6 (d, C-4); *m*/*z* (EI-MS) 205 (M^+, 100%); λ_{max}/nm (log ε) ($CHCl_3$) 254 (4.64), 286 (4.03), 322 (3.42).

2-Methyl-6-phenylisoquinolinium iodide 3. According to procedure *1*: 0.50 g (2.4 mmol) of **2a** yielded 0.68 g (80%) of **3** as a

pale yellow powder, mp 208 °C (diethyl ether–acetone) (Found: C, 55.28; H, 3.83; N, 3.89. $C_{16}H_{14}NI$ requires C, 55.35; H, 4.07; N, 4.03%); ν_{max}/cm^{-1} 1647s; δ_H([$^2H_6$]DMSO) 10.01 (1 H, s, 1-H), 8.70 (1 H, dd, ^3J 6.8, ^4J 1, 3-H), 8.66 (1 H, s, 5-H), 8.53–8.56 (2 H, m, 4, 8-H), 8.40 (1 H, dd, ^3J 8.7, ^4J 1.6, 7-H), 7.96 (2 H, dd, ^3J 7.2, ^4J 1.5, 10, 14-H), 7.61 (2 H, m, 11, 13-H), 7.55 (1 H, m, 12-H), 4.48 (3 H, s, 15-H); δ_C([$^2H_6$]DMSO) 150.2 (d, C-1), 147.4 (s, C-6), 137.7 (s, C-4a), 137.2 (s, C-9), 136.2 (d, C-3), 130.8 (d, C-8), 130.1 (d, C-7), 129.8 (d, C-12), 129.5 (d, C-11, 13), 127.8 (d, C-10, 14), 126.2 (s, C-8a), 125.4 (d, C-4), 124.2 (d, C-5), 47.9 (q, N*C*H$_3$); *m*/*z* [FAB MS (+ve)] 914 (3 Cat. + 2 I$^-$, 0.5%), 567 (2 Cat. + I$^-$, 4), 220 (Cat., 100); λ_{max}/nm (log ε) ($CHCl_3$) 336 (4.18), 384 (sh, 3.51).

6-(4-Methoxyphenyl)isoquinoline 2b. A solution of 1.7 g (7.3 mmol) of 4-iodoanisole in 20 ml of anhydrous THF was treated at −50 °C with 5.9 ml (9.4 mmol) of butyllithium (1.6 M in hexane). After warming to −15 °C, 1.29 g (9.4 mmol) of $ZnCl_2$ were added and the solution was allowed to warm to 20–25 °C. This solution was added dropwise to a warm (55 °C) solution of 1.0 g (4.8 mmol) of **1** and 0.28 g (0.24 mmol) of tetrakis(triphenylphosphine)palladium(0) in 30 ml of anhydrous THF. After stirring for 1 h at this temperature 1 ml of water was added and the solvent was evaporated under reduced pressure. To the residue 100 ml of water were added. The aqueous layer was extracted with diethyl ether (3 × 100 ml). The combined organic layer was extracted with 3 M HCl as described for **1**. Sublimation at 120 °C and 0.2 mbar afforded 0.38 g (34%) of **2b** as a colorless powder, mp 133 °C (Found: C, 81.75; H, 5.67; N, 5.90. $C_{16}H_{13}NO$ requires C, 81.68; H, 5.57; N, 5.95%); ν_{max}/cm^{-1} 1602s, 1290s, 839s; δ_H($CDCl_3$) 9.24 (1 H, s, 1-H), 8.52 (1 H, d, ^3J 5.9, 3-H), 8.00 (1 H, d, ^3J 8.6, 8-H), 7.93 (1 H, s, 5-H), 7.81 (1 H, dd, ^3J 8.6, ^4J 1.8, 7-H), 7.63–7.68 (3 H, m, 4, 10, 14-H), 7.00–7.08 (2 H, m, 11, 13-H), 3.87 (3 H, s, OC*H*$_3$); δ_C($CDCl_3$) 159.8 (s, C-12), 152.2 (d, C-1), 143.4 (d, C-3), 142.6 (s, C-6), 136.2 (s, C-4a), 132.5 (s, C-9), 128.6 (d, C-10, 14), 128.0 (d, C-8), 127.4 (s, C-8a), 126.8 (d, C-7), 123.5 (d, C-5), 120.5 (d, C-4), 114.4 (d, C-11, 13), 55.4 (q, O*C*H$_3$); *m*/*z* (EI-MS) 235 (M$^+$, 100%), 220 (32); λ_{max}/nm (log ε) ($CHCl_3$) 300 (4.17), 306 (4.18).

6-(2-Thienyl)isoquinoline 4. A solution of 0.60 g (2.9 mmol) of **1**, 1.40 g (3.8 mmol) of 2-tributylstannylthiophene[28] and 0.10 g (0.1 mmol) of tetrakis(triphenylphosphine)palladium(0) in 15 ml of anhydrous dimethylformamide (DMF) was stirred at 95 °C for 2 h. The mixture was poured into water and extracted three times with diethyl ether. Extraction with 3 M HCl as described for **1** followed by sublimation at 95 °C and 0.05 mbar yielded 0.37 g (61%) of **4** as a colorless solid, mp 115 °C (Found: C, 73.68; H, 4.29; N, 6.57. $C_{13}H_9NS$ requires C, 73.90; H, 4.29; N, 6.63%); ν_{max}/cm^{-1} 1623s, 1422m, 1247m, 943m, 887s, 835m, 831m, 719m, 709m; δ_H($CDCl_3$) 9.19 (1 H, s, 1-H), 8.50 (1 H, d, ^3J 5.8, 3-H), 7.97 (1 H, s, 5-H), 7.93 (1 H, d, ^3J 8.4, 8-H), 7.83 (1 H, dd, ^3J 8.4, ^4J 1.7, 7-H), 7.61 (1 H, d, ^3J 5.8, 4-H), 7.48–7.52 (1 H, m, 10-H), 7.38–7.42 (1 H, m, 12-H), 7.11–7.14 (1 H, m, 11-H); δ_C($CDCl_3$) 152.2 (d, C-1), 143.7 (d, C-3), 143.2 (s, C-4a), 136.2 (s, C-6), 136.0 (s, C-8a), 128.4 (d, C-11), 128.3 (d, C-8), 127.7 (s, C-9), 126.4 (d, C-12), 125.7 (d, C-7), 124.7 (d, C-10), 122.2 (d, C-5), 120.4 (d, C-4); *m*/*z* (EI-MS) 211 (M$^+$, 100%); λ_{max}/nm (log ε) ($CHCl_3$) 320 (4.24).

(*E*)-6-(2-Phenylethenyl)isoquinoline 5a. A solution of 0.60 g (2.9 mmol) of **1**, 0.45 g (4.3 mmol) of styrene, 0.06 g (0.3 mmol) of palladium(II) acetate and 0.175 g (0.67 mmol) of triphenylphosphine in 15 ml of anhydrous DMF and 15 ml of anhydrous triethylamine was stirred at 110 °C for 3 d. The mixture was poured into water and was extracted several times with diethyl ether. The organic phase was washed with water and then extracted with 3 M HCl as described for **1**. The yield was 0.18 g (27%) of **5a** as a pale yellow solid, mp 158 °C (Found: C, 88.28; H, 5.66; N, 6.00. $C_{17}H_{13}N$ requires C, 88.28; H, 5.67; N, 6.06%); ν_{max}/cm^{-1} 1619s, 1496m, 969m, 963m, 695s; δ_H($CDCl_3$) 9.20 (1 H, s, 1-H), 8.51 (1 H, d, ^3J 5.7, 3-H), 7.93 (1 H, d, ^3J 8.6, 8-H), 7.83 (1 H, dd, ^3J 8.7, ^4J 1.3, 7-H), 7.80 (1 H, s, 5-H), 7.61 (1 H, d, ^3J 5.7, 4-H), 7.54–7.60 (2 H, m, 12, 16-H), 7.38–7.42 (2 H, m, 13, 15-H), 7.25–7.33 (3 H, m, 9, 10, 14-H); δ_C($CDCl_3$) 152.1 (d, C-1), 143.6 (d, C-3), 139.2 (s, C-6), 136.7 (s, C-11), 136.2 (s, C-4a), 131.4 (d, C-14), 128.8 (d, C-13, 15), 128.3 (d, C-9), 128.0 (s, C-8a), 127.9 (d, C-8), 127.8 (d, C-10), 126.8 (d, C-12, 16), 125.0 (d, C-7), 124.6 (d, C-5), 120.4 (d, C-4); *m*/*z* (EI-MS) 231 (M$^+$, 96%), 230 (100); λ_{max}/nm (log ε) ($CHCl_3$) 324 (4.46), 340 (sh, 4.33).

(*E*)-6-[2-(4-Methoxyphenyl)ethenyl]isoquinoline 5b.† A solution of 1.0 g (4.8 mmol) of **1**, 0.84 g (6.3 mmol) of 4-methoxystyrene, 0.05 g (0.2 mmol) of palladium(II) acetate and 0.10 g of triphenylphosphine in 15 ml of anhydrous DMF and 15 ml of anhydrous triethylamine was stirred at 105 °C for 24 h, then for a further 8 h at 125 °C. Work-up as described for **5a** gave 0.45 g (36%) of **5b** as a pale yellow solid, mp 172 °C (Found: C, 82.83; H, 5.68; N, 5.20. $C_{18}H_{15}NO$ requires C, 82.73; H, 5.79; N, 5.36%); ν_{max}/cm^{-1} 1259s (CO); *m*/*z* (EI-MS) 261 (M$^+$, 100%), 246 (18), 230 (30); λ_{max}/nm (log ε) ($CHCl_3$) 328 (4.25).

6-Phenylethynylisoquinoline 6a. According to procedure ***2*** (t = 11 h): 0.70 g (3.4 mmol) of **1** and 1.0 g (10 mmol) of phenylacetylene yielded 0.512 g (66%) of **6a** as a colorless solid, mp 113 °C (Found: C, 89.13; H, 4.54; N, 5.92. $C_{17}H_{11}N$ requires C, 89.05; H, 4.84; N, 6.11%); ν_{max}/cm^{-1} 2215w, 2200w, 1621s, 1492m; δ_H($CDCl_3$) 9.24 (1 H, s, 1-H), 8.55 (1 H, d, ^3J 5.8, 3-H), 8.01 (1 H, s, 5-H), 7.94 (1 H, d, ^3J 8.5, 8-H), 7.70 (1 H, dd, ^3J 8.4, ^4J 1.5, 7-H), 7.62 (1 H, d, ^3J 5.8, 4-H), 7.57–7.60 (2 H, m, 12, 16-H), 7.36–7.41 (3 H, m, 13, 14, 15-H); δ_C($CDCl_3$) 152.3 (d, C-1), 143.7 (d, C-3), 135.4 (s, C-4a), 131.7 (d, C-12, 16), 129.9 (d, C-7), 129.6 (d, C-5), 128.8 (d, C-14), 128.4 (d, C-13, 15), 127.6 (d, C-8), 127.6 (s, C-8a), 125.4 (s, C-6), 122.6 (s, C-11), 120.0 (d, C-4), 91.9 (s, C-10), 88.8 (s, C-9); *m*/*z* (EI-MS) 229 (M$^+$, 100%); λ_{max}/nm (log ε) ($CHCl_3$) 264 (4.44), 274 (4.49), 308 (4.38), 316 (4.37).

2-Methyl-6-phenylethynylisoquinolinium iodide 8a. According to procedure ***1***: 0.35 g (1.53 mmol) of **6a** yielded 0.44 g (78%) of **8a** as a yellow solid, mp 245 °C (diethyl ether–acetone) (Found: C, 58.27; H, 3.65; N, 3.74. $C_{18}H_{14}NI$ requires C, 58.24; H, 3.80; N, 3.77%); ν_{max}/cm^{-1} 2208m, 1647s; δ_H([$^2H_6$]DMSO) 10.01 (1 H, s, 1-H), 8.72 (1 H, dd, ^3J 6.8, ^4J 1, 3-H), 8.56 (1 H, s, 5-H), 8.49–8.53 (2 H, m, 4, 8-H), 8.13 (1 H, dd, ^3J 8.5, ^4J 1.5, 7-H), 7.66–7.69 (2 H, m, 12, 16-H), 7.48–7.55 (3 H, m, 13, 14, 15-H), 4.47 (3 H, s, NC*H*$_3$); δ_C([$^2H_6$]DMSO) 150.4 (d, C-1), 136.8 (d, C-3), 136.6 (s, C-4a), 133.0 (d, C-7), 131.9 (d, C-12, 16), 130.6 (d, C-8), 130.1 (d, C-14), 130.0 (s, C-6), 129.8 (d, C-5), 129.1 (d, C-13, 15), 126.3 (s, C-8a), 125.0 (d, C-4), 121.0 (s, C-11), 95.7 (s, C-12), 88.2 (s, C-9), 48.0 (q, N*C*H$_3$); *m*/*z* [FAB MS (+ve)] 615 (2 Cat. + I$^-$, 3%), 244 (Cat., 100); λ_{max}/nm (log ε) ($CHCl_3$) 356 (4.38), 368 (4.39), 416 (3.30).

6-(4-Methoxyphenylethynyl)isoquinoline 6b. According to procedure ***2*** (t = 3 h): 0.64 g (3.1 mmol) of **1** and 0.61 g (4.6 mmol) of 4-methoxyphenylacetylene gave 0.50 g (63%) of **6b** as a colorless solid, mp 136 °C (Found: C, 83.41; H, 4.97; N, 5.35. $C_{18}H_{13}NO$ requires C, 83.37; H, 5.05; N, 5.40%); ν_{max}/cm^{-1} 1253s (CO); *m*/*z* (EI-MS) 259 (M$^+$, 100%), 244 (46); λ_{max}/nm (log ε) ($CHCl_3$) 322 (4.44), 334 (4.42).

6-(4-Methoxyphenylethynyl)-2-methylisoquinolinium iodide 8b. According to procedure ***1***: 0.15 g (0.58 mmol) of **6b** yielded 0.20 g (86%) of **8b** as a yellow solid, mp 254 °C (decomp.; acetone–methanol) (Found: C, 57.06; H, 3.89; N, 3.31. $C_{19}H_{16}NOI$ requires C, 56.88; H, 4.02; N, 3.49%); ν_{max}/cm^{-1} 1250s (CO); *m*/*z* [FAB MS (+ve)] 675 (2 Cat. + I$^-$, 2%), 274 (Cat., 100); λ_{max}/nm (log ε) ($CHCl_3$) 394 (4.37).

6-(4-Methylthiophenylethynyl)isoquinoline 6c. According to procedure ***2*** (t = 6 h): 0.75 g (3.6 mmol) of **1** and 0.80 g (5.4

† NMR data of **5b**, **6b**–**d**, **8b**–**c**, **13b**, **13d** and **21a** have been supplied as supplementary data (SUPPL. NO. 57322, 6 pp). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 2*, available *via* the RSC Web pages (http://www.rsc.org/authors).

mmol) of 4-methylthiophenylacetylene yielded 0.45 g (45%) of **6c** as a pale yellow solid, mp 135 °C (Found: C, 78.58; H, 4.70; N, 4.98. $C_{18}H_{13}NS$ requires C, 78.51; H, 4.76; N, 5.09%); ν_{max}/cm^{-1} 1619m, 1494m, 903m, 842m, 817s; *m*/*z* (EI-MS) 275 (M^+, 100%), 260 (48); λ_{max}/nm (log ε) ($CHCl_3$) 332 (4.51), 344 (sh, 4.48).

6-[4-(Dimethylamino)phenylethynyl]isoquinoline 6d. A mixture of 1.0 g (4.8 mmol) of **1**, 1.12 g (7.7 mmol) of 4-dimethylaminophenylacetylene, 0.175 g (0.25 mmol) of bis(triphenylphosphine)palladium(II) chloride, 0.028 g (0.15 mmol) of copper(I) iodide and 40 ml of anhydrous triethylamine was stirred at 40–60 °C for 3.5 h. The solvent was evaporated and 500 ml of diethyl ether were added to the residue. The organic layer was washed with 100 ml of aqueous Na_2CO_3 and dried with $MgSO_4$. Purification by column chromatography over 300 g of silica gel with CH_2Cl_2 as eluent (R_f 0.5) yielded 0.60 g (46%) of **6d** as a yellow solid, mp (decomp.) 165 °C (Found: C, 83.43; H, 5.93; N, 10.15. $C_{19}H_{16}N_2$ requires C. 83.79; H, 5.92; N, 10.29%); ν_{max}/cm^{-1} 2192m; *m*/*z* (EI-MS) 272 (M^+, 100%); λ_{max}/nm (log ε) ($CHCl_3$) 248 (4.51), 288 (4.35), 344 (sh, 4.36), 372 (4.47).

6-(4-Dimethylaminophenylethynyl)-2-methylisoquinolinium iodide 8c. A mixture of 0.22 g (0.8 mmol) of **6d** and 2.5 ml (40 mmol) of iodomethane in 30 ml of CH_2Cl_2 was refluxed for 24 h. After evaporation of the solvent the residue was recrystallized three times from acetone–methanol. The yield was 0.20 g (60%) of **8c** as a red solid, mp (decomp.) 235 °C (Found: C, 57.12; H, 4.69; N, 6.82. $C_{20}H_{19}N_2I$ requires C, 57.82; H, 4.62; N, 6.76%); ν_{max}/cm^{-1} 2189m, 1595s; *m*/*z* [FABMS (+ve)] 287 (Cat., 100); λ_{max}/nm (log ε) ($CHCl_3$) 478 (4.46).

6-(4-Formylphenylethynyl)isoquinoline 6e. According to procedure ***2*** (t = 17 h): 1.40 g (6.7 mmol) of **1** and 1.80 g (13.9 mmol) of 4-ethynylbenzaldehyde yielded 0.75 g (43%) of **6e** as a beige solid, mp 143 °C (Found: C, 83.90; H, 4.29; N, 5.29. $C_{18}H_{11}NO$ requires C, 84.03; H, 4.31; N, 5.44%); ν_{max}/cm^{-1} 1687s (C=O); δ_H($CDCl_3$) 10.04 (1 H, s, C*H*O), 9.16 (1 H, s, 1-H), 8.57 (1 H, d, ^3J 5.6, 3-H), 8.04 (1 H, s, 5-H), 7.96 (1 H, d, ^3J 8.6, 3-H), 7.88–7.93 (2 H, m, 13, 15-H), 7.69–7.76 (3 H, m, 7, 12, 16-H), 7.63 (2 H, d, ^3J 5.8, 4-H); δ_C($CDCl_3$) 191.3 (d, *C*HO), 152.3 (d, C-1), 143.9 (d, C-3), 135.8 and 135.3 (s, C-4a, 14), 132.3 (d, C-12, 16), 130.2 (d, C-5), 129.7 (d, C-7), 129.6 (d, C-13, 15), 128.8 and 127.8 (s, C-8a, 6), 127.8 (d, C-8), 124.5 (s, C-11), 120.0 (d, C-4), 92.5 (s, C-10), 90.7 (s, C-9); *m*/*z* (EI-MS) 257 (M^+, 100%), 256 (60), 228 (28); λ_{max}/nm (log ε) ($CHCl_3$) 286 (4.37), 320 (4.47), 336 (sh, 4.41).

6-[4-(4-Butoxyphenyliminomethyl)phenylethynyl]isoquinoline 6f. A solution of 0.30 g (1.7 mmol) of **6e** and 0.55 g (3.3 mmol) of 4-butoxyaniline in 30 ml of toluene was refluxed into a Dean–Stark trap for 5 h. After cooling to 20–25 °C the yellow precipitate was filtered off and washed with light petroleum (bp 40–60 °C). Further purification was achieved by column chromatography over 300 g of SiO_2 with diethyl ether as eluent. The yield was 0.31 g (46%) of **6f** as a pale yellow solid, mp 162 °C (Found: C, 83.15; H, 6.01; N, 6.87. $C_{28}H_{24}N_2O$ requires C, 83.14; H, 5.98; N, 6.93%); ν_{max}/cm^{-1} 1251s (CO); δ_H($CDCl_3$) 9.17 (1 H, s, 1-H), 8.48 (1 H, d, ^3J 5.8, 3-H), 8.42 (1 H, s, 17-H), 7.95 (1 H, s, 5-H), 7.87 (1 H, d, ^3J 8.6, 8-H), 7.81–7.84 (2 H, m, 13, 15-H), 7.63 (1 H, dd, ^3J 8.4, ^4J 1.5, 7-H), 7.56–7.60 (2 H, m, 12, 16-H), 7.53 (1 H, d, ^3J 5.8, 4-H), 7.15–7.20 (2 H, m, 20, 24-H), 6.83–6.89 (2 H, m, 21, 23-H), 3.91 (2 H, t, ^3J 6.5, 25-H), 1.68–1.78 (2 H, m, 26-H), 1.38–1.49 (2 H, m, 27-H), 0.91 (3 H, t, 28-H); δ_C($CDCl_3$) 158.2 (s, C-22), 156.8 (d, C-17), 152.3 (d, C-1), 144.2 (s, C-19), 143.8 (d, C-3), 136.6 (s, C-14), 135.4 (s, C-4a), 132.1 (d, C-12, 16), 129.8 (d, C-5, 7), 128.5 (d, C-13, 15), 127.7 (d, C-8), 125.1 and 125.0 (s, C-6, 11), 122.3 (d, C-20, 24), 120.0 (d, C-4), 115.0 (d, C-21, 23), 91.7 (s, C-10), 90.9 (s, C-9), 67.9 (t, C-25), 31.3 (t, C-26), 19.2 (t, C-27), 13.8 (q, *C*H_3); *m*/*z* (EI-MS) 404 (M^+, 98%), 348 (100); λ_{max}/nm (log ε) ($CHCl_3$) 336 (sh, 4.56), 358 (4.57), 370 (sh, 4.54).

6-[4-(4-Butoxyphenylazo)phenylethynyl]isoquinoline (6g). A mixture of 0.70 g (3.4 mmol) of bromoisoquinoline **1**, 1.30 g (4.7 mmol) of (4-butoxyphenyl)-(4-ethynylphenyl)diazene, 0.12 g (0.2 mmol) of bis(triphenylphosphine)palladium(II) chloride and 0.02 g (0.11 mmol) of copper(I) iodide in 45 ml of anhydrous triethylamine was stirred at 50 °C for 9 h. After evaporation of the solvent the residue was purified by column chromatography with 250 g of SiO_2 and diethyl ether–CH_2Cl_2 (9 : 1) as eluent, yielding 0.50 g (37%) of **6g** as a yellow solid, mp 167 °C (Found: C, 79.93; H, 5.67; N, 10.34. $C_{27}H_{23}N_3O$ requires C, 79.97; H, 5.72; N, 10.36%); ν_{max}/cm^{-1} 1252s (CO); δ_H($CDCl_3$) 9.27 (1 H, s, 1-H), 8.59 (1 H, s, 3-H), 8.02 (1 H, s, 5-H), 7.87–7.97 (5 H, m, 8, 13, 15, 20, 24-H), 7.68–7.74 (3 H, m, 7, 12, 16-H), 7.64 (1 H, s, 4-H), 6.98–7.03 (2 H, m, 21, 23-H), 4.04 (2 H, t, ^3J 6.5, 25-H), 1.85–1.95 (2 H, m, 26-H), 1.45–1.60 (2 H, m, 27-H), 1.00 (3 H, t, ^3J 7.4, 28-H); δ_C($CDCl_3$) 162.0 (s, C-22), 152.3 (d, C-1), 152.2 (s, C-14), 146.8 (s, C-19), 143.8 (d, C-3), 135.4 (s, C-4a), 132.6 (d, C-12, 16), 129.9 (d, C-5), 129.8 (d, C-7), 127.7 (d, C-8), 125.2 and 124.4 (s, C-6, 8a, 11), 125.0 (d, C-20, 24), 122.7 (d, C-13, 15), 120.4 (d, C-4), 114.7 (d, C-21, 23), 91.8 and 90.8 (s, C-9, 10), 68.0 (t, C-25), 31.2 (t, C-26), 19.2 (d, C-27), 13.8 (q, *C*H_3); *m*/*z* (EI-MS) 405 (M^+, 100%), 228 (50), 177 (38), 149 (98); λ_{max}/nm (log ε) ($CHCl_3$) 322 (sh, 4.35), 342 (4.45), 376 (4.44), 438 (3.74).

6-(2-Thienylethynyl)isoquinoline 7. According to procedure ***2*** (t = 8 h): 1.0 g (4.8 mmol) of **1** and 0.57 g (5.3 mmol) of 2-ethynylthiophene yielded, after sublimation at 100 °C and 0.2 mbar, 0.62 g (55%) of **7** as a colorless powder, mp 119 °C (Found: C, 76.54; H, 3.84; N, 5.92. $C_{15}H_9NS$ requires C, 76.57; H, 3.86; N, 5.95%); ν_{max}/cm^{-1} 2207w, 1623s, 897s, 828s, 716s; δ_H($CDCl_3$) 9.22 (1 H, s, 1-H), 8.53 (1 H, d, ^3J 5.8, 3-H), 7.97 (1 H, s, 5-H), 7.92 (1 H, d, ^3J 8.5, 8-H), 7.66 (1 H, dd, ^3J 8.5, ^4J 1.5, 7-H), 7.59 (1 H, d, ^3J 5.7, 4-H), 7.32–7.38 (2 H, m, 12, 14-H), 7.02–7.07 (1 H, m, 13-H); δ_C($CDCl_3$) 152.3 (d, C-1), 143.8 (d, C-3), 135.4 (s, C-4a), 132.6 (d, C-12), 129.5 (d, C-7), 129.4 (d, C-5), 128.0 (d, C-14), 127.6 (d, C-8), 127.5 (s, C-8a), 127.3 (d, C-13), 125.0 (s, C-6), 122.6 (s, C-11), 120.0 (d, C-4), 92.5 (s, C-9), 85.2 (s, C-10); *m*/*z* (EI-MS) 235 (M^+, 100%); λ_{max}/nm (log ε) ($CHCl_3$) 324 (4.42), 342 (4.39).

Thieno[2,3-*c*]pyridine-2-carbaldehyde 11. A solution of 0.86 g (6.4 mmol) of thieno[2,3-*c*]pyridine **9** in 30 ml of anhydrous THF was treated with 5.0 ml (8.0 mmol) of butyllithium (1.6 M in hexane) at −78 °C. The solution was warmed to 0 °C, stirred for 15 min and then cooled to −78 °C. Then 0.9 ml (8.0 mmol) of 1-formylpiperidine[29] were added and the mixture was warmed to 20–25 °C within 2.5 h. It was poured into ice–water. After separation of the layers the aqueous layer was extracted three times with diethyl ether. The combined organic layer was dried over $MgSO_4$. After evaporation of the solvent the residue was purified by column chromatography over 25 g of silica gel with diethyl ether as eluent (R_f 0.16) followed by sublimation (0.5 mbar at 90 °C), yielding 0.69 g (66%) of **11** as a colorless solid, mp 115 °C (Found: C, 58.80; H, 3.09; N, 8.59; S, 19.61. C_8H_5NOS requires C, 58.88; H, 3.09; N, 8.59; S, 19.65%); ν_{max}/cm^{-1} 1680vs (C=O); δ_H($CDCl_3$) 10.22 (1 H, s, C*H*O), 9.27 (1 H, s, 7-H), 8.62 (1 H, d, ^3J 5.5, 5-H), 8.07 (1 H, d, J 0.4, 3-H), 7.83 (1 H, dd, ^3J 5.5, J 1.0, 4-H); δ_C($CDCl_3$) 184.7 (d, *C*HO), 147.6 (s, C-2, 8.07^{COL}), 146.1 (d, C-7, 9.27^{CHC}), 143.9 (d, C-5, 8.62^{CHC}), 143.5 (s, C-3a, 8.62^{COL}), 137.9 (s, C-7a, 8.07^{COL}), 132.1 (d, C-3, 8.07^{CHC}), 119.4 (d, C-4, 7.83^{CHC}); *m*/*z* (EI-MS) 163 (M^+, 100%), 162 (77), 135 (15), 134 (36), 108 (10), 107 (13), 63 (35), 62 (10); λ_{max}/nm (log ε) ($CHCl_3$) 280 (4.19), 338 (3.61); (MeCN) 278 (4.17), 336 (3.60).

Thieno[2,3-*c*]pyridine-2-carbaldehyde dimethylhydrazone 14. According to procedure ***3a*** (t = 1.5 h): 0.40 g (2.5 mmol) of **11** and 0.21 ml (2.8 mmol) of *N*,*N*-dimethylhydrazine yielded 0.46 g (92%) of **14** as yellow crystals, mp 159–160 °C (Found: C, 58.54; H, 5.32; N, 20.24; S, 15.40. $C_{10}H_{11}N_3S$ requires C, 58.51; H, 5.40; N, 20.47; S, 15.62%); ν_{max}/cm^{-1} 1552vs, 1351s, 1065s, 868m; δ_H($CDCl_3$) 8.96 (1 H, s, 7-H), 8.39 (1 H, d, ^3J 5.6, 5-H), 7.48 (1 H, dd, ^3J 5.6, J 0.9, 4-H), 7.34 (1 H, s, 8-H), 7.07 (1 H, s, 3-H), 3.06 (6 H, s, CH_3); δ_C($CDCl_3$) 149.4 (s, C-2), 145.7

(s, C-3a), 143.9 (d, C-7, 8.96^{CHC}), 143.2 (d, C-5, 8.39^{CHC}), 135.0 (s, C-7a), 124.0 (d, C-8, 7.34^{CHC}), 118.0 (d, C-3, 7.07^{CHC}), 116.9 (d, C-4, 7.48^{CHC}), 42.5 (q, CH_3); *m*/*z* (EI-MS) 205 (M^+, 100%), 175 (12), 163 (20), 147 (16), 135 (43), 134 (16), 120 (10), 63 (14); λ_{max}/nm (log ε) ($CHCl_3$) 244 (4.24), 344 (4.45); (MeCN) 342 (4.45).

N*-(Thieno[2,3-*c*]pyridin-2-ylmethylene)-4-bromoaniline 13a.** According to procedure ***3b (t = 24 h): 0.33 g (2.0 mmol) at **11** and 0.34 g (2.0 mmol) of 4-bromoaniline yielded 0.41 g (64%) of **13a** as pale yellow crystals, mp 191–193 °C (Found: C, 53.03; H, 2.70; N, 8.61; S, 10.25. $C_{14}H_9BrN_2S$ requires C, 53.01; H, 2.86; N, 8.83; S, 10.11%); ν_{max}/cm^{-1} 1602s, 1477s, 1072s, 857vs; δ_H($CDCl_3$) 9.18 (1 H, s, 7-H), 8.71 (1 H, s, 8-H), 8.54 (1 H, d, ^3J 5.5, 5-H), 7.68–7.71 (2 H, m, 3, 4-H), 7.53, 7.16 (AA′XX′, *N* 8.6, 4 H, 12, 14-H; 11, 15-H); δ_C($CDCl_3$) 153.1 (d, C-8, 8.71^{CHC}), 149.3 (s, C-10, 8.71^{COL}, 7.53^{COL}), 147.9 (s, C-2, 8.71^{COL}, 7.70^{COL}), 145.3 (d, C-7, 9.18^{CHC}), 144.3 (s, C-3a, 8.54^{COL}), 143.7 (d, C-5, 8.54^{CHC}), 137.0 (s, C-7a, 7.70^{COL}), 132.4 (d, C-12, 14, 7.53^{CHC}), 127.8 (d, C-3, 7.70^{CHC}, 7.70^{COL}), 122.9 (d, C-11, 15, 7.16^{CHC}), 120.7 (s, C-13, 7.16^{COL}), 118.4 (d, C-4, 7.70^{CHC}, 8.54^{COL}); *m*/*z* (EI-MS) 318 (M^+, ^{81}Br, 100%), 316 (M^+, ^{79}Br, 97), 237 (31), 157 (19), 155 (20), 135 (11), 76 (13), 75 (11); λ_{max}/nm (log ε) ($CHCl_3$) 242 (4.20), 298 (4.29), 342 (4.33), 352 (sh, 4.30); (MeCN) 228 (4.30), 296 (4.31), 336 (4.34), 344 (sh, 4.31).

N*-(Thieno[2,3-*c*]pyridin-2-ylmethylene)-4-methoxyaniline 13b.** According to procedure ***3a (t = 3 h): 0.34 g (2.1 mmol) of **11** and 0.27 g (2.2 mmol) of *p*-anisidine yielded 0.46 g (81%) of **13b** as yellow crystals, mp 184 °C (Found: C, 67.14; H, 4.43; N, 10.44; S, 12.08. $C_{15}H_{12}N_2OS$ requires C, 67.14; H, 4.51; N, 10.44; S, 11.95%); ν_{max}/cm^{-1} 1249vs (CO); *m*/*z* (EI-MS) 268 (M^+, 100%), 253 (84), 224 (23); λ_{max}/nm (log ε) ($CHCl_3$) 294 (4.16), 352 (4.31), 386 (sh 4.16); (MeCN) 296 (4.25), 348 (4.34), 380 (sh, 4.16).

N*-(Thieno[2,3-*c*]pyridin-2-ylmethylene)-4-methylthioaniline 13c.** According to procedure ***3b (t = 3 h): 0.20 g (1.2 mmol) of **11** and 0.15 ml (1.2 mmol) of 4-methylthioaniline yielded 0.31 g (91%) of **13c** as yellow crystals, mp 179–180 °C (Found: C, 63.19; H, 4.15; N, 9.70; S, 22.58. $C_{15}H_{12}N_2S_2$ requires C, 63.35; H, 4.25; N, 9.85; S, 22.55%); ν_{max}/cm^{-1} 1608s, 1480s, 1405s, 1091s, 857vs; δ_H($CDCl_3$) 9.16 (1 H, s, 7-H), 8.73 (1 H, s, 8-H), 8.53 (1 H, d, ^3J 5.5, 5-H), 7.67 (1 H, dd, ^3J 5.5, J 1.0, 4-H), 7.66 (1 H, s, 3-H), 7.24–7.31 (4 H, m, 11, 12, 14, 15-H), 2.51 (3 H, s, SCH_3); δ_C($CDCl_3$) 151.6 (d, C-8, 8.73^{CHC}), 148.3 (s, C-2, 8.73^{COL}), 147.2 (s, C-10, 8.73^{COL}), 145.2 (d, C-7, 9.16^{CHC}), 144.4 (s, C-3a, 8.53^{COL}), 143.6 (d, C-5, 8.53^{CHC}), 137.9 (s, C-13, 7.26^{COL}), 136.8 (s, C-7a, 7.67^{COL}), 127.20 (d, C-11, 15, 7.28^{CHC}), 127.18 (d, C-3, 7.66^{CHC}), 121.9 (d, C-12, 14, 7.28^{CHC}), 118.3 (d, C-4, 7.67^{CHC}, 8.53^{COL}), 15.9 (q, SCH_3); *m*/*z* (EI-MS) 284 (M^+, 100%), 269 (63), 237 (16), 108 (10), 97 (13), 83 (12), 71 (15), 57 (20); λ_{max}/nm (log ε) ($CHCl_3$) 292 (4.21), 366 (4.26); (MeCN) 292 (4.18), 356 (4.26).

N*-(Thieno[2,3-*c*]pyridin-2-ylmethylene)-4-*N*,*N*-dimethylaminoaniline 13d.** According to procedure ***3a (t = 2 h): 0.39 g (2.4 mmol) of **11** and 0.33 g (2.4 mmol) of 4-amino-*N*,*N*-dimethylaniline yielded 0.51 g (75%) of **13d** as yellow crystals, mp 230 °C (Found: C, 67.99; H, 5.24; N, 14.92; S, 11.43. $C_{16}H_{15}N_3S$ requires C, 68.29; H, 5.37; N, 14.94; S, 11.39%); ν_{max}/cm^{-1} 1614s, 1565vs, 1517m, 1354m, 1173m, 854m, 822m; *m*/*z* (EI-MS) 281 (M^+, 100%), 266 (19), 97 (12), 83 (10), 71 (13), 57 (12); λ_{max}/nm (log ε) ($CHCl_3$) 288 (4.14), 428 (4.36); (MeCN) 284 (4.05), 418 (4.29).

2-Tributylstannylthieno[2,3-*c*]pyridine 10. A solution of 4.19 g (31 mmol) of thieno[2,3-*c*]pyridine **9** in 130 ml of anhydrous THF was treated with 23 ml (37 mmol) of butyllithium (1.6 M in hexane) as described for the preparation of **11**. At −70 °C 11.0 ml (36.5 mmol) of tributyltin chloride were added within 30 min. After stirring for 12 h at 20–25 °C the solvent was evaporated under reduced pressure. Then 50 ml of conc. aqueous $NaHCO_3$ were added and the aqueous layer was extracted with diethyl ether (3 × 40 ml). The combined organic layer was dried with Na_2SO_4. After evaporation of the solvent the residue was purified by column chromatography over 200 g of silica gel with diethyl ether as eluent (R_f 0.44), yielding 12.17 g (93%) of **10** as a pale yellow oil, which was not distillable even at 0.4 mbar and 170 °C (Found: C, 53.81; H, 7.72; N, 3.63. $C_{19}H_{31}NSSn$ requires C, 53.79; H, 7.37; N, 3.30%); δ_H($CDCl_3$) 9.15 (1 H, s, 7-H), 8.44 (1 H, d, ^3J 5.4, 5-H), 7.68 (1 H, dd, ^3J 5.4, ^5J 0.9, 4-H), 7.41 [1 H, t, ^3J(H, Sn) 11.2, 3-H], 1.56–1.63 (6 H, m, 8-H), 1.31–1.41 (6 H, m, 9-H), 1.18–1.23 (6 H, m, 10-H), 0.91 (9 H, t, ^3J 7.3, 11-H); δ_C($CDCl_3$) 147.8 (s, C-2), 145.8 (s, C-3a), 144.0 and 142.5 (d, C-5, 7), 140.9 (s, C-7a), 130.8 (d, C-3), 116.9 (d, C-4), 28.9 (t, C-9), 27.3 (t, C-10), 13.7 (q, C-11), 11.0 (t, C-8); *m*/*z* (EI-MS) 425 (M^+, ^{120}Sn, <1%), 368 ($M^+ - C_4H_9$, ^{120}Sn, 20), 311 ($M^+ - 2\ C_4H_9$, ^{120}Sn, 20), 254 ($M^+ - 3\ C_4H_9$, ^{120}Sn, 25), 135 (100), 108 (20).

2-(6′-*n*-Butoxynaphthalen-2′-yl)thieno[2,3-*c*]pyridine 12a. A mixture of 6.47 g (15.2 mmol) of stannane **10**, 5.52 g (19.8 mmol) of 2-bromo-6-butoxynaphthalene[30] and 0.170 g (0.15 mmol) of tetrakis(triphenylphosphine)palladium(0) in 50 ml of anhydrous DMF was stirred at 110 °C for 16 h. The mixture was poured onto 100 ml of ice–water and a precipitate **I** was filtered off. The aqueous layer was extracted with diethyl ether (5 × 50 ml). The combined organic layer was washed with 50 ml of conc. aqueous NaCl and dried with $MgSO_4$. After evaporation of the solvent the residue was combined with precipitate **I** and was purified twice by column chromatography over 50 g of silica gel with ethyl acetate as eluent (R_f 0.47). Recrystallization from ethyl acetate afforded 2.44 g (48%) of colorless **12a**, which was further purified by sublimation at 160 °C and 0.2 mbar, mp 185 °C (Found: C, 75.63; H, 5.74; N, 4.15. $C_{21}H_{19}NOS$ requires C, 75.64; H, 5.74; N, 4.20%); ν_{max}/cm^{-1} 1270s (CO); δ_H($CDCl_3$) 9.08 (1 H, s, 7-H), 8.47 (1 H, d, ^3J 5.5, 5-H), 8.08 (1 H, s, 1′-H), 7.74–7.79 (3 H, m, 3′, 4′, 8′-H), 7.61 (1 H, dd, ^3J 5.5, J 0.9, 4-H), 7.56 (1 H, s, 3-H), 7.19 (1 H, dd, ^3J 8.9, ^4J 2.4, 7′-H), 7.12 (1 H, d, ^4J 2.4, 5′-H), 4.08 (2 H, t, ^3J 6.5, OCH_2), 1.80–1.89 (2 H, m, OCH$_2$CH_2), 1.49–1.60 (2 H, m, CH_2CH$_3$), 1.01 (3 H, t, ^3J 7.4, CH$_2$CH_3); δ_C($CDCl_3$) 158.1 (s, C-6′, 7.77^{COL}), 150.7 (s, C-2, 7.56^{COL}, 8.08^{COL}), 146.0 (s, C-3a, 8.47^{COL}), 144.3 (d, C-7, 9.08^{CHC}), 143.5 (d, C-5, 8.47^{CHC}), 135.8 (s, C-7a, 7.56^{COL}), 135.0 (s, 7.77^{COL}, 8.08^{COL}) and 128.3 (s, C-2′, 10′, 7.77^{COL}), 129.8 (d, 7.77^{CHC}, 8.08^{COL}) and 124.7 (d, C-3′, 8′, 7.77^{CHC}, 8.08^{COL}), 128.7 (s, C-9′, 7.19^{COL}), 127.6 (d, C-4′, 7.77^{CHC}, 7.12^{COL}), 126.1 (d, C-1′, 8.08^{CHC}), 120.1 (d, C-7′, 7.19^{CHC}), 117.8 (d, C-3, 7.56^{CHC}), 117.4 (d, C-4, 7.61^{CHC}), 106.5 (d, C-5′, 7.12^{CHC}, 7.77^{COL}), 67.8 (t, OCH_2), 31.3 (t, OCH$_2$CH_2), 19.3 (t, CH_2CH$_3$), 13.9 (q, CH$_2$CH_3); *m*/*z* (EI-MS) 333 (M^+, 50%), 277 (100), 248 (14); λ_{max}/nm (log ε) ($CHCl_3$) 244 (4.54), 286 (4.38), 336 (4.48); (MeCN) 232 (4.59), 282 (4.39), 330 (4.49).

2-(6′-*n*-Butoxynaphthalen-2′-yl)-*N*-methylthieno[2,3-*c*]-pyridinium tetrafluoroborate 15a. A solution of 0.41 g (1.2 mmol) of **12a** and 0.33 g (2.2 mmol) of trimethyloxonium tetrafluoroborate in 30 ml of anhydrous CH_2Cl_2 was stirred for 1.5 h at 20–25 °C. The solvent was distilled off and the residue was recrystallized from methanol–acetone (5:1). The crystals were washed with methanol and dried at 0.1 mbar. The yield was 0.45 g (86%) of light yellow **15a**, mp 213–215 °C (Found: C, 60.98; H, 4.84; N, 3.22. $C_{22}H_{22}BF_4NOS$ requires C, 60.70; H, 5.09; N, 3.05%); ν_{max}/cm^{-1} 2962m, 1623vs, 1189s, 1056vs, 852m; δ_H([$^2H_6$]DMSO) 9.67 (1 H, s, 7-H), 8.63 (1 H, dd, ^3J 6.7, J 1.1, 5-H), 8.43 (1 H, d, J 1.3, 1′-H), 8.29 (1 H, d, ^3J 6.7, 4-H), 8.27 (1 H, s, 3-H), 7.92–7.99 (3 H, m, 3′, 4′, 8′-H), 7.38 (1 H, d, ^4J 2.4, 5′-H), 7.24 (1 H, dd, ^3J 9.0, ^4J 2.4, 7′-H), 4.35 (3 H, s, NCH_3), 4.10 (2 H, t, ^3J 6.6, OCH_2), 1.73–1.79 (2 H, m, OCH$_2$CH_2), 1.45–1.51 (2 H, m, CH_2CH$_3$), 0.96 (3 H, t, ^3J 7.4, CH$_2$CH_3); δ_C([$^2H_6$]DMSO) 160.0 (s, C-2, 8.27^{COL}, 8.43^{COL}), 158.4 (s, C-6′, 7.96^{COL}), 149.5 (s, C-3a, 8.63^{COL}), 141.2 (d, C-7, 9.67^{CHC}), 138.3 (d, C-5, 8.63^{CHC}), 135.7 (s, 7.97^{COL}, 8.43^{COL}) and 128.02 (s) and 126.2 (s, C-2′, 9′, 10′, 7.96^{COL}), 135.4 (s, C-7a, 8.27^{COL}), 130.4 (d, 7.96^{CHC}, 8.43^{COL}) and 128.03 (d, 7.96^{CHC})

and 124.4 (d, C-3′, 4′, 8′, 7.96^{CHC}, 8.43^{COL}), 127.2 (d, C-1′, 8.43^{CHC}, 7.96^{COL}), 120.1 (d, C-7′, 7.24^{CHC}, 7.38^{COL}), 119.8 (d, C-4, 8.29^{CHC}), 118.8 (d, C-3, 8.27^{CHC}), 106.7 (d, C-5′, 7.38^{CHC}), 67.5 (t, O*C*H$_2$), 47.4 (q, N*C*H$_3$), 30.6 (t, OCH$_2$*C*H$_2$), 18.8 (t, *C*H$_2$CH$_3$), 13.7 (q, CH$_2$*C*H$_3$); *m*/*z* [FABMS (+ve)] 348 (Cat., 100); λ_{max}/nm (log ε) ($CHCl_3$) 252 (4.64), 302 (4.05), 402 (4.49); (MeCN) 246 (4.68), 296 (4.11), 384 (4.51).

2-(2′-Thienyl)thieno[2,3-*c*]pyridine 12b. A solution of 6.27 g (14.8 mmol) of **10**, 1.80 ml (18.6 mmol) of 2-bromothiophene and 0.17 g (0.15 mmol) of tetrakis(triphenylphosphine)-palladium(0) in 50 ml of anhydrous DMF was stirred at 105–110 °C for 18 h. The work-up as described for the preparation of **12a** gave a residue that was purified by column chromatography over 200 g of silica gel with diethyl ether as eluent (R_f 0.20). Sublimation at 120–130 °C and 0.2 mbar afforded 1.98 g (62%) of **12b** as a colorless solid, mp 141–143 °C (Found: C, 60.76; H, 3.11; N, 2.23. $C_{11}H_7NS_2$ requires C, 60.80; H, 3.25; N, 2.43%); ν_{max}/cm^{-1} 3062w, 3035w, 1576vs, 1403vs, 842vs, 828vs; δ_H($CDCl_3$) 9.02 (1 H, s, 7-H), 8.46 (1 H, d, ^3J 5.5, 5-H), 7.56 (1 H, dd, ^3J 5.5, *J* 1.0, 4-H), 7.35–7.39 (3 H, m, 3, 3′, 5′-H), 7.06–7.09 (1 H, m, 4′-H); δ_C($CDCl_3$) 145.6 (s, C-3a, 8.47^{COL}), 144.1 (d, C-7, 9.02^{CHC}), 143.7 (d, C-5, 8.46^{CHC}), 143.0 (s, C-2, 7.37^{COL}), 136.2 (s, C-2′, 7.08^{COL}), 135.5 (s, C-7a, 7.37^{COL}, 7.56^{COL}), 128.2 (d, C-4′, 7.08^{CHC}), 127.0 (d, 7.37^{CHC}) and 126.5 (d, C-3′, 5′, 7.37^{CHC}), 118.2 (d, C-3, 7.37^{CHC}), 117.3 (d, C-4, 7.56^{CHC}); *m*/*z* (EI-MS) 217 (M^+, 100%), 172 (11); λ_{max}/nm (log ε) ($CHCl_3$) 242 (3.99), 256 (sh, 3.89), 320 (4.35); (MeCN) 254 (3.88), 316 (4.36).

2-(2′-Thienyl)-*N*-ethylthieno[2,3-*c*]pyridinium bromide 15b. A solution of 0.44 g (2.0 mmol) of **12b** in 10 ml of bromoethane and 30 ml of acetonitrile was refluxed for 6 h. The precipitate was filtered off, washed with diethyl ether and dried at 0.01 mbar. 0.50 g (76%) of **15b** were obtained as pale yellow crystals, mp 206 °C (Found: C, 47.78; H, 3.66; N, 4.30. $C_{13}H_{12}BrNS_2$ requires C, 47.86; H, 3.71; N, 4.29%); ν_{max}/cm^{-1} 1624vs, 1550s, 1449vs, 1191m, 846m; δ_H(D_2O) 8.87 (1 H, s, 7-H), 8.08 (1 H, dd, ^3J 6.7, *J* 1.0, 5-H), 7.60 (1 H, d, ^3J 6.7, 4-H), 7.39 (1 H, dd, ^3J 4.9, ^4J 0.7, 5′-H), 7.04 (1 H, s, 3-H), 6.98 (1 H, dd, ^3J 3.7, ^4J 0.7, 3′-H), 6.77 (1 H, dd, ^3J 4.9, ^3J 3.7, 4′-H), 4,36 (2 H, q, ^3J 7.4, NCH_2), 1.54 (3 H, t, ^3J 7.4, NCH$_2$CH_3); δ_C(D_2O) 153.5 (s, C-2, 7.04^{COL}), 150.4 (s, C-3a, 8.08^{COL}, 8.87^{COL}), 139.0 (d, C-7, 8.87^{CHC}), 137.0 (d, C-5, 8.08^{CHC}), 136.6 (s, C-7a, 7.04^{COL}, 7.60^{COL}), 134.4 (s, C-2′, 6.77^{COL}), 131.8 (d, C-5′, 7.39^{CHC}, 6.98^{COL}), 130.3 (d, C-3′, 6.98^{CHC}, 7.39^{COL}), 129.6 (d, C-4′, 6.77^{CHC}, 6.77^{COL}), 120.8 (d, C-4, 7.60^{CHC}), 118.7 (d, C-3, 7.04^{CHC}), 57.4 (t, N*C*H$_2$), 16.8 (q, NCH$_2$*C*H$_3$); *m*/*z* [FABMS (+ve)] 246 (Cat., 100%); λ_{max}/nm (log ε) ($CHCl_3$) 242 (4.10), 338 (sh, 4.11), 372 (4.44); (MeCN) 336 (sh, 4.15), 366 (4.43).

***N*-Methyl-2-(2′-thienyl)pyridinium iodide 17.** 1.70 g (10.5 mmol) of thienylpyridine **16** and 2.0 ml (32 mmol) of iodomethane in 25 ml of anhydrous THF were refluxed for 57 h. The precipitate was filtered off and dried; yield 1.82 g (57%) of **17** as a pale yellow solid, mp 164–165 °C (lit.,[31] 167–168 °C). ν_{max}/cm^{-1} 3047s, 3024s, 1625s, 1533s, 1271s, 1174s, 774vs; δ_H([$^2H_6$]-DMSO) 9.14 (1 H, 'dd', *J* 6.6, 6-H), 8.59 (1 H, td, *J* 7.9, *J* 1.3, 4-H), 8.23 (1 H, dd, ^3J 8.1, *J* 1.3, 3-H), 8.07–8.16 (2 H, m, 5, 5′-H), 7.83 (1 H, 'dd') and 7.38 (1 H, 'dd', 3′, 4′-H), 4.32 (3 H, s, N*C*H$_3$); δ_C([$^2H_6$]DMSO) 148.7 (s, C-2), 147.3 (d, C-6), 145.1 (d, C-4), 133.6, 133.0, 128.5 (d, C-3′, 4′, 5′), 131.0 (s, C-2′), 130.3 (d, C-3), 126.3 (d, C-5), 47.6 (q, N*C*H$_3$); *m*/*z* [FABMS (+ve)] 782 (3 Cat. + 2 I^-, 0.5%), 479 (2 Cat. + I^-, 9), 176 (Cat., 100); λ_{max}/nm (log ε) ($CHCl_3$) 328 (4.00), 374 (sh, 3.35); (MeCN) 248 (4.28), 322 (3.97).

2-(2′-Thienyl)pyridine-5′-carbaldehyde 19. To a solution of 3.22 g (20.0 mmol) of **16** in 75 ml of anhydrous THF, 14 ml (22 mmol) of butyllithium (1.6 M in hexane) were added at 0 °C. The solution was treated with 2.5 ml (22 mmol) of 1-formylpiperidine[29] and stirred at 20–25 °C for 12 h. The suspension was hydrolysed with 50 ml of water. The mixture was extracted with diethyl ether (3 × 40 ml). The organic layer was washed with conc. NH_4Cl (2 × 30 ml) and was dried with $MgSO_4$. After evaporation of the solvent the residue was purified by column chromatography over 200 g of silica gel with CH_2Cl_2–ethyl acetate (1 : 1) as eluent followed by sublimation at 110 °C and 0.7 mbar, yielding 2.39 g (63%) of **19** as a colorless solid, mp 119–120 °C (Found: C, 63.44; H, 3.73; N, 7.41; S, 17.13. $C_{10}H_7NOS$ requires C, 63.47; H, 3.73; N, 7.40; S, 16.94%); ν_{max}/cm^{-1} 1649vs (C=O); δ_H($CDCl_3$) 9.92 (1 H, s, C*H*O), 8.62 (1 H, dt, 6-H), 7.71–7.78 (3 H, m, 3, 4, 4′-H), 7.66 (1 H, d, ^3J 4.0, 3′-H), 7.25–7.29 (1 H, m, 5-H); δ_C($CDCl_3$) 183.1 (s, *C*HO, 9.92^{CHC}), 153.9 (s, C-2′, 7.77^{COL}), 151.1 (s, C-2, 8.62^{COL}), 149.9 (d, C-6, 8.62^{CHC}), 144.1 (s, C-5′, 7.66^{COL}), 136.8 and 136.9 (d, C-4, 4′, 7.76^{CHC}, 8.62^{COL}), 125.1 (d, C-3′, 7.66^{CHC}), 123.6 (d, C-5, 7.27^{CHC}), 119.7 (d, C-3, 7.73^{CHC}, 7.27^{COL}); *m*/*z* (EI-MS) 189 (M^+, 100%), 188 (90), 160 (48), 116 (30), 89 (13); λ_{max}/nm (log ε) ($CHCl_3$) 330 (4.38), 344 (sh, 4.29); (MeCN) 328 (4.39), 340 (sh, 4.31).

N*-[5-(2-Pyridyl)-2-thienylmethylene]-4-methoxyaniline 21a.** According to procedure ***3a (t = 4 h): 0.51 g (2.7 mmol) of **19** and 0.37 g (3.0 mmol) of *p*-anisidine yielded 0.56 g (70%) of **21a** as fine yellow needles, mp 148–149 °C [ethanol–water–acetone (3 : 1 : 1)] (Found: C, 69.30; H, 4.69; N, 9.40. $C_{17}H_{14}N_2OS$ requires C, 69.36; H, 4.79; N, 9.52%); ν_{max}/cm^{-1} 1250vs (CO); *m*/*z* (EI-MS) 294 (M^+, 100%), 279 (99); λ_{max}/nm (log ε) ($CHCl_3$) 242 (4.03), 302 (sh, 3.90), 374 (4.40); (MeCN) 308 (sh, 4.00), 344 (sh, 4.32), 370 (4.42).

***N*-[5-(2-Pyridyl)-2-thienylmethylene]-4-methylthioaniline 21b.** A solution of 0.47 g (2.5 mmol) of **19** and 0.35 ml (2.8 mmol) of 4-methylthioaniline in 30 ml of toluene was refluxed into a Dean–Stark trap for 4 h. 20 ml of the solvent were distilled off. The precipitate formed at 4 °C was filtered off and dried at 0.2 mbar. **21b**, 0.18 g (23%) was obtained as yellow crystals, mp 150 °C (Found: C, 65.77; H, 4.52; N, 8.95. $C_{17}H_{14}N_2S_2$ requires C, 65.77; H, 4.55; N, 9.03%); ν_{max}/cm^{-1} 1606vs, 1430s, 778s; δ_H($CDCl_3$) 8.60 (1 H, dt, 6-H), 8.55 (1 H, s, C*H*=N), 7.65–7.73 (2 H, m, 3, 4-H), 7.62 (1 H, d, ^3J 3.9, 3′-H), 7.46 (1 H, d, ^3J 3.9, 4′-H), 7.28, 7.20 (4 H, AA′XX′, N = 8.7, 10′, 12′-H; 9′, 13′-H), 7.17–7.22 (1 H, m, 5-H), 2.50 (s, 3 H, SCH_3); δ_C($CDCl_3$) 151.95 (d, *C*H=N, 8.55^{CHC}, 7.46^{COL}), 151.91 (s, C-2, 8.60^{COL}), 149.8 (d, C-6, 8.60^{CHC}), 148.8 (s, C-2′, 7.46^{COL}), 148.5 (s, C-8′, 8.55^{COL}, 7.28^{COL}), 144.0 (s, C-5′, 8.55^{COL}, 7.62^{COL}), 136.7 (d, C-4, 7.70^{CHC}, 8.60^{COL}), 136.2 (s, C-11′, 7.20^{COL}, 2.50^{COL}), 132.6 (d, C-4′, 7.46^{CHC}), 127.5 (d, C-10′, 12′, 7.28^{CHC}), 125.1 (d, C-3′, 7.62^{CHC}), 122.7 (d, C-5, 7.20^{CHC}, 8.60^{COL}, 7.68^{COL}), 121.8 (d, C-9′, 13′, 7.20^{CHC}), 119.4 (d, C-3, 7.68^{CHC}, 7.20^{COL}), 16.3 (q, S*C*H$_3$); *m*/*z* (EI-MS) 310 (M^+, 100%), 295 (75), 277 (57), 132 (11); λ_{max}/nm (log ε) ($CHCl_3$) 242 (4.08), 352 (sh, 4.32), 380 (4.43); (MeCN) 238 (4.04), 284 (sh, 3.92), 346 (sh, 4.34), 378 (4.45).

2-(5′-Iodo-2′-thienyl)pyridine 18. An ice-cooled solution of 3.22 g (20.0 mmol) of thienylpyridine **16** in 100 ml of anhydrous THF was lithiated with 14 ml (22 mmol) of butyllithium (1.6 M in hexane).[20] After 15 min the mixture was cooled to −50 °C and 5.1 g (20 mmol) of iodine were added at once. After stirring for 1 h the cooling bath was removed. The mixture was stirred for 1 h at 20–25 °C and then cooled to 0 °C. A solution of 50 ml of conc. aqueous $NaHCO_3$ was added slowly and the layers were separated. The organic layer was washed with 50 ml of conc. aqueous $Na_2S_2O_3$ and dried with $MgSO_4$. After evaporation of the solvent the brown residue was twice purified by column chromatography over 50 g of silica gel with CH_2Cl_2 as eluent (R_f 0.46). 3.67 g (64%) of **18** as a colorless solid were obtained, mp 105 °C (Found: C, 37.64; H, 2.09; N, 4.71. C_9H_6INS requires C, 37.65; H, 2.11; N, 4.88%); ν_{max}/cm^{-1} 1584s, 1466vs, 1417s, 774s; δ_H($CDCl_3$) 8.53 (1 H, 'dt', 6-H), 7.67 (1 H, td, ^3J 7.8, 4-H), 7.56 (1 H, dt, ^3J 7.8, 3-H), 7.25 (1 H, d, ^3J 3.8) and 7.21 (1 H, d, ^3J 3.8, 3′, 4′-H), 7.12–7.17 (1 H, m, 5-H); δ_C([$^2H_6$]DMSO) 151.0 (s, C-2), 150.2 (s, C-2′), 149.4 (d, C-6), 138.1, 126.8 (d, C-3′, 4′), 137.3 (d, C-4), 122.6 (d, C-5), 118.3 (d, C-3), 79.8 (s, C-5′); *m*/*z* (EI-MS) 287 (M^+, 100%), 160 (57), 116

(17), 80 (10); λ_{max}/nm (log ε) ($CHCl_3$) 274 (sh, 3.79), 318 (4.29); (MeCN) 270 (sh, 3.81), 314 (4.32).

2-(5′-Phenylethynyl-2′-thienyl)pyridine 20. A solution of 1.01 g (3.5 mmol) of **18**, 0.50 ml (4.6 mol) of phenylacetylene, 0.08 g (0.1 mmol) of bis(triphenylphosphine)palladium(II) chloride and 0.02 g (0.1 mmol) of copper(I) iodide in 10 ml of anhydrous triethylamine and 4 ml of anhydrous DMF was stirred at 20–25 °C for 18 h. The solvent was evaporated and the black residue was twice purified by column chromatography over 50 g of silica gel with CH_2Cl_2 as eluent (R_f 0.50). Sublimation at 0.5 mbar and 140 °C gave 0.61 g (66%) of **20** as a colorless solid, mp 137 °C (Found: C, 78.13; H, 4.20; N, 5.20. $C_{17}H_{11}NS$ requires C, 78.13; H, 4.24; N, 5.36%); ν_{max}/cm^{-1} 2201w (C≡C); δ_H($CDCl_3$) 8.56 (1 H, 'dt', 6-H), 7.67 (1 H, td, 4-H), 7.60–7.63 (1 H, m, 3-H), 7.50–7.55 (2 H, m, 9′, 13′-H), 7.46 (1 H, d, ^3J 3.9, 3′-H), 7.32–7.37 (3 H, m, 10′, 11′, 12′-H), 7.26 (1 H, d, ^3J 3.9, 4′-H), 7.13–7.17 (1 H, m, 5-H); δ_C($CDCl_3$) 151.9 (s, C-2, 8.56^{COL}), 149.7 (d, C-6, 8.56^{CHC}), 146.0 (s, C-2′, 7.26^{COL}), 136.7 (d, C-4, 7.67^{CHC}, 8.56^{COL}), 133.0 (d, C-4′, 7.26^{CHC}, 7.46^{COL}), 131.5 (d, C-9′, 13′, 7.53^{CHC}), 128.5 (d, C-11′, 7.35^{CHC}), 128.4 (d, C-10′, 12′, 7.35^{CHC}), 125.0 (s, C-5′, 7.46^{COL}), 124.4 (d, C-3′, 7.46^{CHC}, 7.26^{COL}), 122.8 (s, C-8′, 7.35^{COL}), 122.3 (d, C-5, 7.15^{CHC}, 8.56^{COL}, 7.62^{COL}), 118.8 (d, C-3, 7.62^{CHC}, 7.15^{COL}), 94.4 (s, C-7′, 7.53^{COL}), 83.0 (s, C-6′, 7.26^{COL}); *m*/*z* (EI-MS) 261 (M^+, 100%); λ_{max}/nm (log ε) ($CHCl_3$) 348 (4.56), 364 (sh, 4.40); (MeCN) 342 (4.58), 360 (sh, 4.42).

***N*-Methyl-2-(5′-phenylethynyl-2′-thienyl)pyridinium tetrafluoroborate 22.** 0.25 g (1.0 mmol) of **20** and 0.21 g (1.4 mmol) of trimethyloxonium tetrafluoroborate were refluxed in 20 ml of CH_2Cl_2 for 2 h. Recrystallization of the evaporation residue from ethanol gave 0.25 g (70%) of **22** as pale yellow crystals, mp 188–189 °C (Found: C, 59.29; H, 3.85; N, 3.73. $C_{18}H_{14}BF_4NS$ requires C, 59.53; H, 3.89; N, 3.86%); ν_{max}/cm^{-1} 2203w (C≡C), 1053vs (BF_4^-); δ_H([$^2H_6$]DMSO) 9.13 (1 H, 'd', 6-H), 8.61 (1 H, td, 4-H), 8.26 (1 H, 'dd', 3-H), 8.10–8.16 (1 H, m, 5-H), 7.77 (1 H, d, ^3J 3.9, 3′-H), 7.66 (1 H, d, ^3J 3.9, 4′-H), 7.60–7.64 (2 H, m, 9′, 13′-H), 7.46–7.51 (3 H, m, 10′, 11′, 12′-H), 4.33 (3 H, s, NCH_3); δ_C([$^2H_6$]DMSO) 147.55 (s, C-2, 9.13^{COL}), 147.45 (d, C-6, 9.13^{CHC}), 145.2 (d, C-4, 8.61^{CHC}), 133.9 (d, C-3′, 7.77^{CHC}), 133.3 (d, C-4′, 7.66^{CHC}), 132.1 (s, C-2′, 7.66^{COL}), 131.4 (d, C-9′, 13′, 7.62^{CHC}, 7.49^{COL}), 130.5 (d, C-3, 8.26^{CHC}), 129.7 (d, C-11′, 7.49^{CHC}), 128.9 (d, C-10′, 12′, 7.48^{CHC}), 127.8 (s, C-5′ 7.77^{COL}), 126.8 (d, C-5, 8.13^{CHC}), 121.1 (s, C-8′, 7.48^{COL}), 96.2 (s, C-7′), 81.1 (s, C-6′), 47.6 (q, NCH_3); *m*/*z* [FABMS (+ve)] 276 (Cat., 100); λ_{max}/nm (log ε) ($CHCl_3$) 276 (sh, 4.13), 294 (4.13), 376 (4.25); (MeCN) 272 (sh, 4.13), 302 (4.18), 358 (4.28).

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