Synthesis of Oligo(diazaphenyls). Tailor-Made Fluorescent Heteroaromatics and Pathways to Nanostructures

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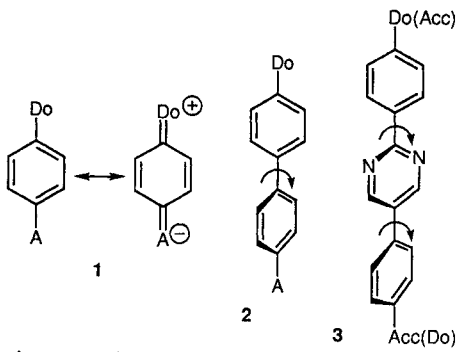
Dedicated to Professor Dieter Seebach on the occasion of his 60th birthday

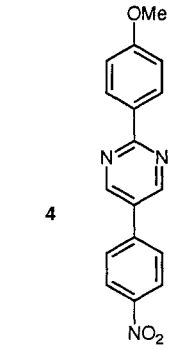
Oligoaza derivatives of biphenyl, terphenyl, quaterphenyl, quinquephenyl, sexiphenyl, septiphenyl, octiphenyl, noviphenyl, deciphenyl and dodeciphenyl and poly(pyrimidinylenephenylene) can be synthesized from readily accessible vinamidinium salts and amidines or *N,N,N'*-tris(trimethylsilyl)amidines. The fluorescence of these systems can be tuned over a wide spectral range by varying number and positions of N atoms. Oligo(diazaphenyls) are thermally and photochemically stable, are easier to reduce than oligophenyls, can be dissolved at any rate in strong acids and show strong blue fluorescence in solution as well as in the solid state.

Dipolar compounds having large hyperpolarizabilities β and second-order nonlinear optical susceptibilities $\chi^{(2)}$, respectively, are interesting materials for second harmonic generation (SHG) (frequency doubling of diode lasers).[1] A typical example is 4-nitroaniline. For SHG it is essential that the absorption is ≤ 415 nm. Unfortunately, β and $\chi^{(2)}$, respectively, of dipolar π-electron systems increase with a red-shift of λ_{max} (transparency-efficiency trade-off).[2] There are a number of possibilities to obtain compounds displaying large β values at $\lambda_{max} \leq 415$ nm.[3] We have previously shown that donor-acceptor substituted 2,5-diarylpyrimidines[4] (diazaterphenyls) and the corresponding octupoles[5] have interesting NLO properties (high β values at $\lambda_{max} < 430$ nm). The general idea for preparing these compounds was to reduce the resonance interaction of acceptor and donor groups in dipolar benzene derivatives **1** or biphenyl derivatives **2** by using instead diazaterphenyl derivatives **3**. As a consequence of the separation of Acc and Do groups and the deviation from coplanarity, λ_{max} is blue-shifted in **3** and at the same time the extended π-electron system gives rise to large β values.



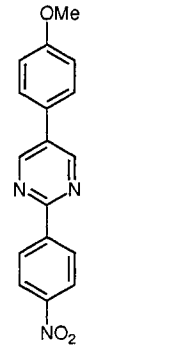
Acc = acceptor group
Do = donor group

The relative positions of the nitrogen atoms as to the substituents Acc and Do in **3** influence the dipole moments of the molecules. This makes it possible to tune the solvatochromism as well as β and $\chi^{(2)}$ of **3**; examples are compounds **4** and **5**.



4

λ_{max} ($CHCl_3$) = 336 nm
λ_{max} (CH_3CN) = 329 nm
$\Delta\nu$($CHCl_3/CH_3CN$) = −630 cm^{-1}



5

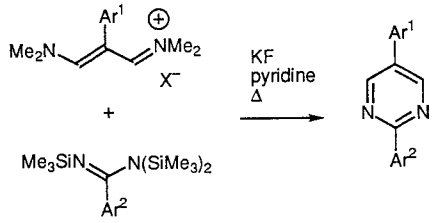
λ_{max} ($CHCl_3$) = 333 nm
λ_{max} (CH_3CN) = 330 nm
$\Delta\nu$($CHCl_3/CH_3CN$) = −270 cm^{-1}

In the course of these studies it turned out that some of the new compounds show blue fluorescence and can be reversibly reduced. Apparently, oligo(diazaphenyls) can be viewed as analogues of oligo(*p*-phenyls). The UV spectrum of pyrimidine[6,7] ($\lambda_{max} = 244$ nm [π-π*], 298 [n-π*]) is different to that of benzene[6,7] ($\lambda_{max} = 184$ nm [π-π*, β-band], 203 [π-π*, p-band], 256 [π-π*, α-band]). In oligo(*p*-phenyls) the α-band is the longest-wavelength absorption.[8] Since substituents in 2 and 5 positions of pyrimidines give rise to a red-shift of the π-π*-band[6] the longest-wavelength absorptions of oligo(diazaphenyls) ought to be π-π*-bands too. Hence oligo(*p*-phenyls) and oligo(diazaphenyls) are expected to be closely related as regards absorption and emission (fluorescence and electroluminescence).

Polyparaphenylene[9] (PPP) and corresponding ladder polymers,[10] polyparaphenylenevinylene[11] (PPV) and polythiophenes (cf.[12]) have been widely investigated as materials for light-emitting diodes (LEDs). They can be readily oxidized but are more difficult to reduce. As compared with benzene, pyrimidine is an electron-poor compound, and poly(pyrimidine-2,5-diyl)[13] (PPym) indeed shows a high electronaffinity. Therefore, oligo(diazaphenyls) should be easier to reduce than oligo(*p*-phenyls) and could possibly form the counterpart of oligothiophenes and polythiophene in two-layer devices. Oligo(diazaphenyls) can be synthesized without any problems and with all substituents required for specific purposes. They are therefore ideal objects for studying a

series of oligomers and well defined polymers. It should be pointed out that investigating homologous series of oligomers is an important method ("The Oligomer Approach")[14] of finding out about the relationship between morphology and function and the change of properties when going from molecules to molecular systems (cf.[15,16]).

The synthesis of oligo(diazaphenyls) (cf. **3**) and related compounds is based on the condensation of amidines with vinamidinium salts in the presence of pyridine[17] (with sodium methoxide in methanol[18] yields were mostly lower and the products impure). Starting materials for amidines are nitriles (Pinner method). Converting compounds with more than one cyano group into amidines proved extremely difficult; inseparable mixtures of amidines were obtained. Moreover, the Pinner method is problematic with nitriles containing donor groups (e.g., *p*-dimethylaminobenzonitrile). The method of choice in these and other cases is the reaction of vinamidinium salts with *N*,*N*,*N*′-tris(trimethylsilyl)amidines (Scheme) which can be synthesized from nitriles by reaction with lithium hexamethyldisilazane, followed by workup with chlorotrimethylsilane (cf.[19–21]) or from *N*,*N*′-bis(trimethylsilyl)carbodiimide by reaction with (sterically hindered) aromatic lithium compounds, followed also by workup with chlorotrimethylsilane (cf.[22,23]). Vinamidinium salts can be readily prepared by reacting arylacetic acids with dimethylformamide–oxalyl chloride or phosphoryl chloride (Vilsmeier–Haack–Arnold reaction).[24–26] Activated methyl groups in heteroaromatics also react with DMF–$POCl_3$. 4-Picoline has been converted to a derivative of dimethylaminoacrolein,[27,28] and the formation of a vinamidinium salt from a 2-methylpyrimidine derivative was mentioned without details.[29]



Scheme

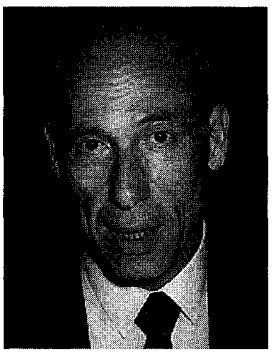
For the "pyrimidine approach" to be applicable for the construction of a homologous series of oligo(diazaphenyls) it is necessary to have a synthesis for a set of vinamidinium salts as building blocks starting from readily accessible precursors. The idea was to use vinamidinium salts and amidines for the sequential linear extension of aromatic systems.

The methodology is demonstrated by the reaction of vinamidinium salt **6b**[25] with acetamidine hydrochloride to form 2-methyl-5-(4′-nitrophenyl)pyrimidine **(7b)**, which on treatment with DMF–$(COCl)_2$ delivered the vinamidinium salt **8b**. Repeating the condensation with acetamidine hydrochloride, 2-methyl-5-[4″-nitrophenyl-(5′-pyrimidin-2′-yl)]pyrimidine **(11b)** was obtained from **8b**. The methyl group of **11b** is less activated than the one of **7b**, and the reaction with DMF–$(COCl)_2$ failed. Compound **11b** was therefore converted by heating with Bredereck's reagent into the enamine **10b**, which then readily reacted with DMF–$(COCl)_2$ to form the vinamidinium salt **9b**. In the same way, from **6a**,[25] **6c**,[46] **6d**,[25] **6g**,[30,31] **6e**,[32] and **6f** the vinamidinium salts **8a**, **8c**, **8d**, **8g**, **8e** and **8f** were synthesized via the methylpyrimidines **7a**,[18] **7c**, **7d**, **7g**, **7e** and **7f** and the enamines **10a**, **10c**, **10g**, **10e** and **10f**.

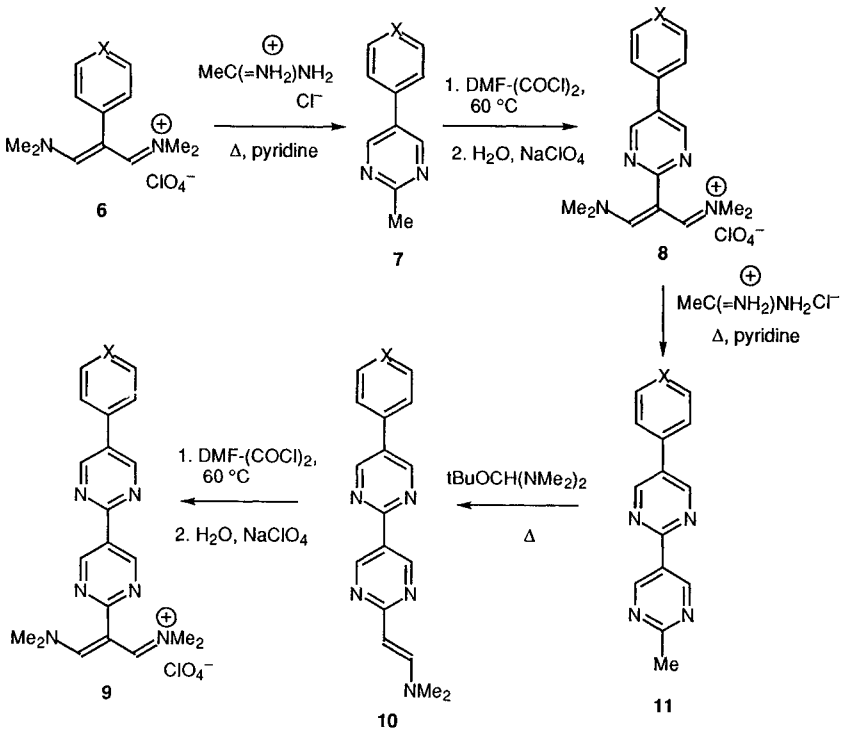
Methylpyrimidines **7** and **11** can be used for condensations with aldehydes as well (diazastilbenes have been prepared from 2-methylpyrimidine and aromatic aldehydes[33–36]). Standard procedures, however, failed. Eventually it was found that activating **7** and **11** firstly with the benzoyl chloride–DMF complex and then reacting the adducts with aromatic aldehydes in the presence of pyridine produced stilbenes **12** in good yields.

Vinamidinium salts **6**, **8** and **9** are the targeted set of building blocks (we have also synthesized the corresponding building blocks containing various other central aromatic moieties). Their condensation and that of other vinamidinium salts with amidines delivered, besides **7** and **11**, diaza derivatives **13–16** of biphenyl **(13)**, terphenyl **(14)**, quaterphenyl **(15)** and quinquephenyl **(16)** in good yields. The variations in the pattern of N atoms and substituents are important for the tuning of the properties (e.g., fluorescence) of oligo(diazaphenyls).

Biographical Sketch



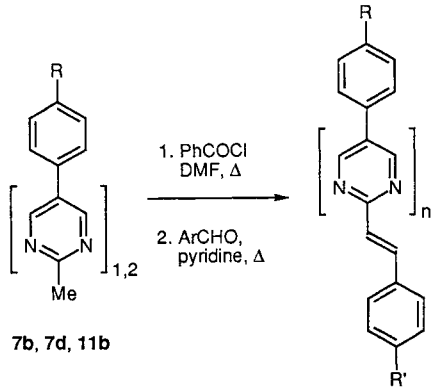
Rudolf Gompper is Professor emeritus of organic chemistry at the University of München. He studied chemistry at the Technische Hochschule of Stuttgart and received his doctoral degree under the supervision of Hellmut Bredereck in Stuttgart in 1953. He then habilitated in Stuttgart (1958) and became apl. Professor in 1964. He joined the University of München in 1965 as an a.o. Professor and advanced in 1968 to full professor of organic chemistry. The general themes of his research are reactivity and selectivity of ambident anions and cations, donor-acceptor effects in π-electron systems, stabilization of intermediates in electrocyclic reactions, cycloadditions and sigmatropic rearrangements, novel chromophores, twisted ethylene derivatives, and the synthesis of novel aromatic, quinoid, and "aromatic antiaromatic" systems. At the center of his materials-oriented research are molecule-based organic ferromagnets, molecular metals, and materials for nonlinear optics, LEDs and fluorescence liquid light guides.



a: X = CH, **b**: X = C-NO_2, **c**: X = C-OH, **d**: X = C-OMe, **e**: X = C-Br, **f**: X = C-Ph, **g**: X = N

Compounds **15c** (X = C–NO_2, A = C–OMe) and **15e** (X = C–OH, A = C–NO_2) are tetraazaquaterphenyl derivatives in which donor and acceptor substituents are exchanged and consequently UV spectra are therefore different (**15c**: λ_{max} = 352 nm, **15e**: λ_{max} = 335 nm). The situation is similar with **16b** (λ_{max} = 387 nm) and **16c** (λ_{max} = 321 nm).

Having powerful donor and acceptor substituents some of the compounds **10** and **13–16** are suited as materials for nonlinear optics (cf. **3**). Hyperpolarizabilities β as measured by hyper-Raleigh scattering and second-order nonlinear optical susceptibilities $\chi^{(2)}$ of **17**, prepared in the same way as **10b**, in a poly(methyl methacrylate) [PMMA] matrix are listed in Table 1. The values of β and $\chi^{(2)}$ are in the same order of magnitude as those of **18** (DANS) but λ_{max} of **17** is significantly blue-shifted (408 vs 427 nm).



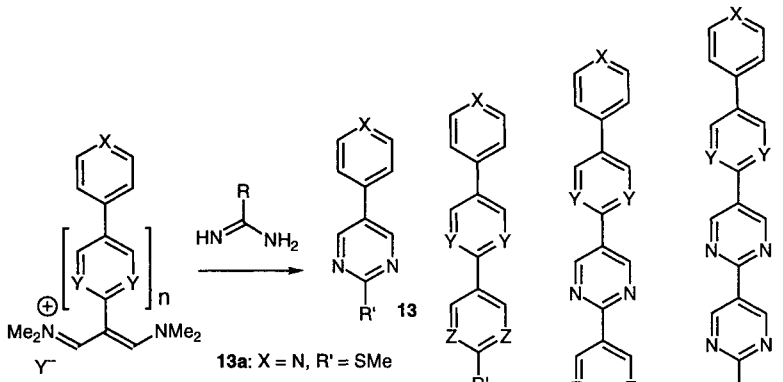
7b, 7d, 11b

12a: n = 1, R = NO_2, R' = OMe
12b: n = 2, R = NO_2, R' = OMe
12c: n = 1, R = NO_2, R = NMe_2
12d: n = 2, R = NO_2, R = NMe_2
12e: n = 1, R = OMe, R' = NO_2
12f: n = 1, R = OMe, R' = CN

An important extension of the scope of the "pyrimidine method" is the condensation of vinamidinium salts such as **6,8** and **9** with bifunctional amidines **21** such as *p*-phenylene-bis[*N*,*N*,*N'*-tris(trimethylsilyl)carboxamidine] (this reaction does not work with simple amidines). The symmetrical terphenyl, quaterphenyl, quinquephenyl, sexiphenyl, septiphenyl, octiphenyl, and noviphenyl derivatives **22–27** were formed in excellent yields and high purities. It should be mentioned at this point that sexi- and quinquephenyl have already been tested in LEDs,[40] and **22–27** and related oligo(diazaphenyls) offer the possibility to tune the properties of these systems through chain length, substituents, and the degree of deviation from coplanarity.

Compound **25**, X = CNO_2, can be reduced to the diaminooctaazaseptiphenyl **28**. It gave upon heating with triphenylpyrylium tetrafluoroborate the bis-pyridinium salt **29** that actually is an undeciphenyl derivative.

Instead of bifunctional amidines, bifunctional vinamidinium salts can be employed as well. Thus, bis(vinamidinium salts) **30** and **33**, respectively, reacted with benzamidine to form the quaterphenyl and quinquephenyl derivatives **31** and **32**. The condensation of **33** with formamidine gave rise to the terphenyl derivative **37**. The polarity of the pyrimidine rings as determined by the positions of the N atoms referring to the central benzene ring (e.g. **25**) can be reversed by the following reaction



6, 8, 9, etc.
n = 0, 1, 2

13a: X = N, R' = SMe
13b: X = N, R' = NMe_2
13c: X = C-NO_2, R' = NMe_2

14a: X = Y = CH, Z = N, R' = H
14b: X = CH, Y = Z = N, R' = H
14c: X = Z = CH, Y = N, R' = H
14d: X = C-NO_2, Y = Z = N, R' = NMe_2, NH_2, OMe, OH, SMe, SC_8H_{17}
14e: X = C-NO_2, Y = N, Z = CH, R' = NMe_2
14f: X = C-OH, Y = Z = N, R' = NH_2
14g: X = Y = N, Z = CH, R' = NMe_2
14h: X = Y = Z = N, R' = NMe_2, OH, SMe
14i: X = C-Br, Y = N, Z = CH, R' = H

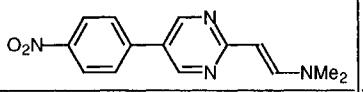
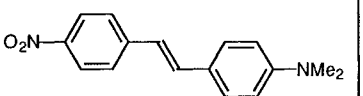
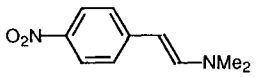
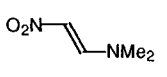
15a: X = Y = Z = CH, A = CH
15b: X = Z = CH, Y = N, A = CH
15c: X = C-NO_2, Y = N, Z = CH, A = C-NMe_2, C-OMe, C-NO_2, N
15d: X = C-NO_2, Y = Z = N, A = C-OMe, C-Me
15e: X = C-OH, Y = N, Z = CH, A = C-NO_2, N, $N^+Me\ BF_4^-$
15f: X = Y = N, Z = CH, A = C-NMe_2, C-OMe, N
15g: X = C-Br, Y = N, Z = CH, A' = CH

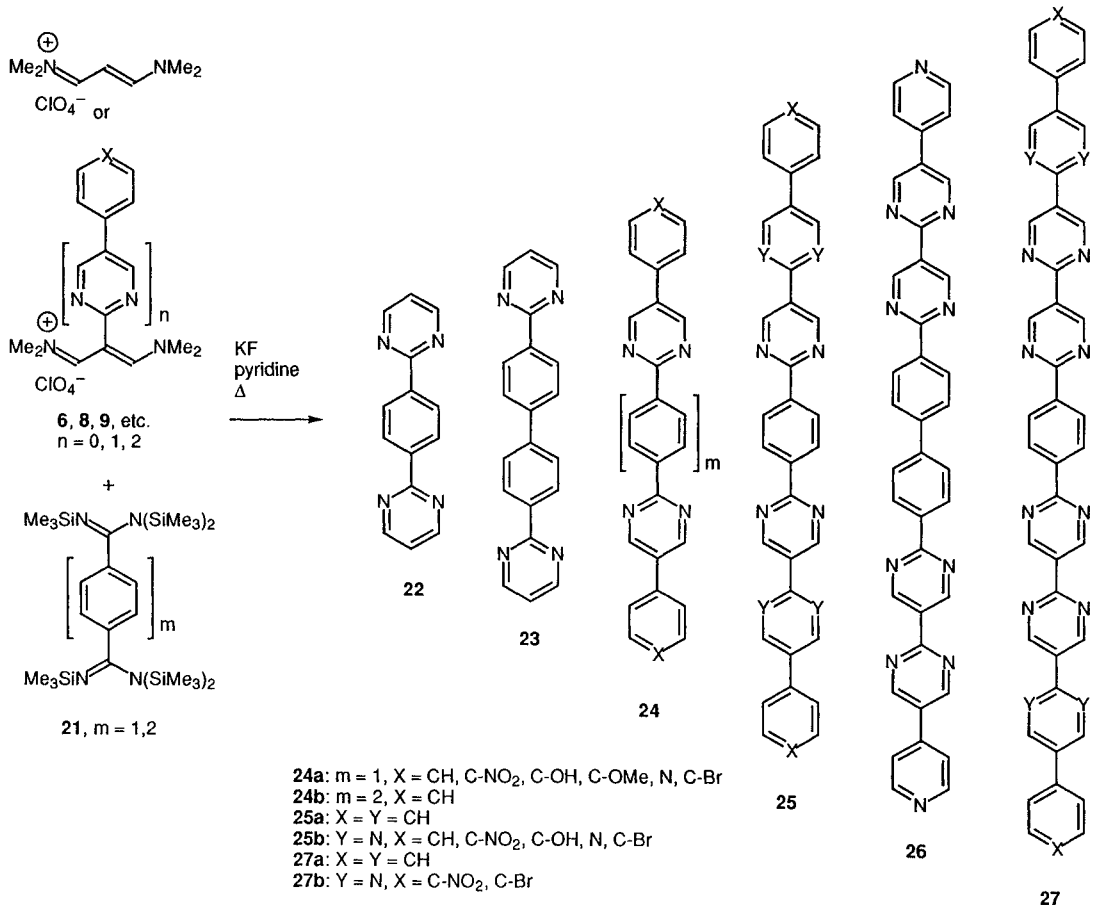
16a: X = Y = Z = CH, A = CH
16b: X = C-NO_2, Y = N, Z = CH, A = C-NMe, C-OMe, C-NO_2
16c: X = C-OH, Y = N, Z = CH, A = C-NO_2, N

sequence. The *p*-phenylene bis(vinamidinium salt) **33** reacted with acetamidine to form 2,2′-dimethyl-5,5′-(*p*-phenylene)dipyrimidine **(34)**. Via the bis-enamine **35** obtained from **34** by heating with Bredereck's reagent the new bis(vinamidinium salt) **36** was obtained using the DMF–oxalyl chloride complex. Compound **36** in turn reacted with benzamidine and γ-pyridinecarboxamidine, respectively, to produce the octa/decaazaseptiphenyl derivatives **38a** and **38b**, respectively.

The scope of the "pyrimidine method" is further demonstrated by the synthesis of the dodecaazadeciphenyl **39a**

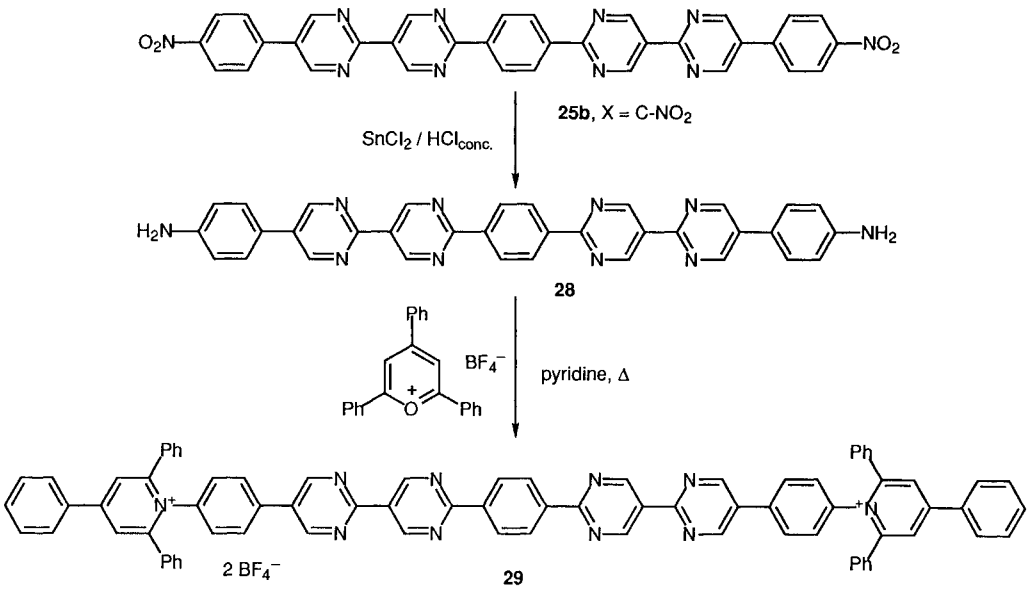
Table 1. β-Values as Determined by Hyper-Raleigh Scattering at 1064 nm, $\chi^{(2)}$ Values (in PMMA) and UV Data of **17** and Related Compounds **18–20**[37] (cf.[38,39]).

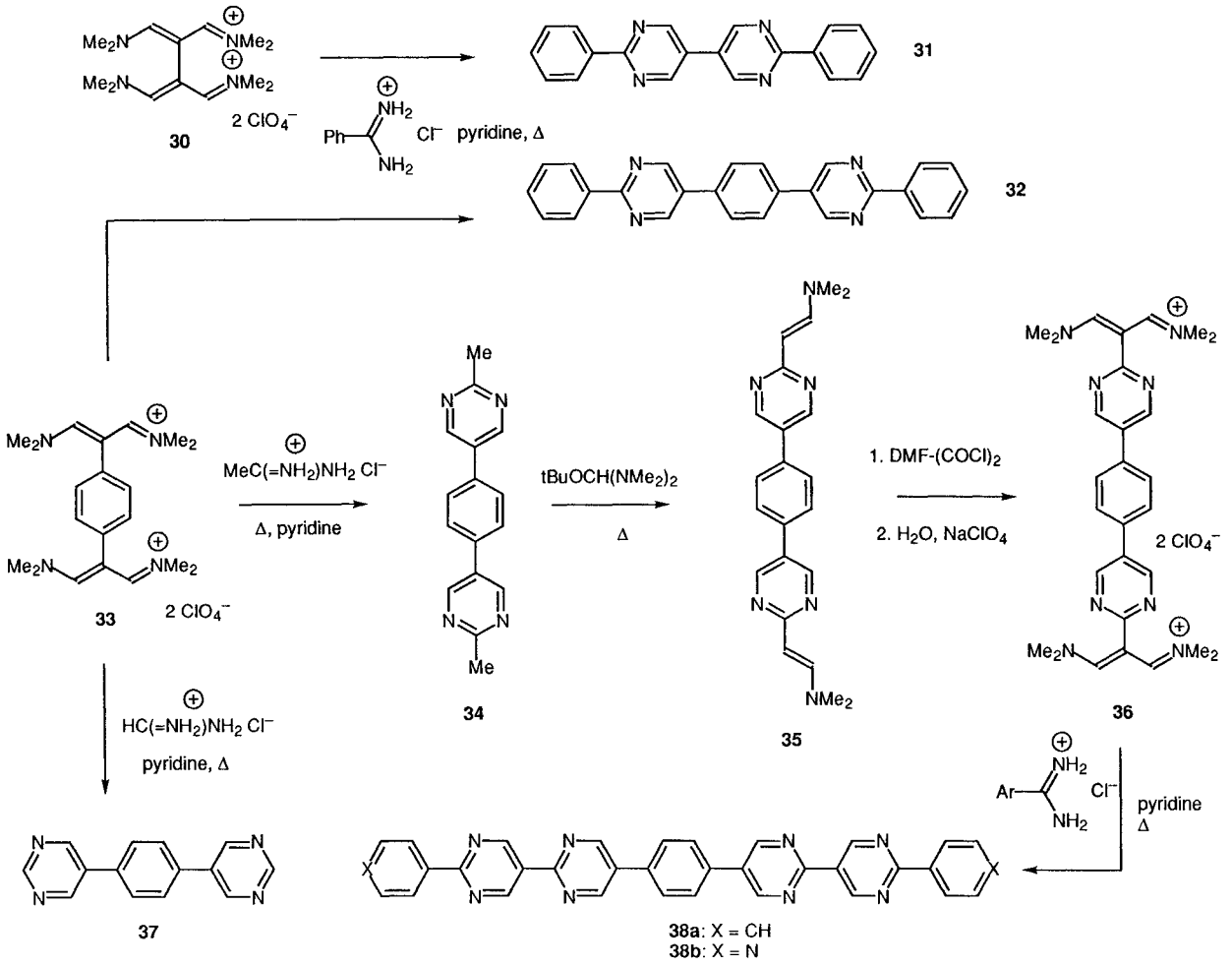
		β [10^{-30} esu] ($CHCl_3$)	$\chi^{(2)}$ [pm / V] (PMMA)	λ_{max} [nm] ($CHCl_3$)
17		77.8 ± 14.0	17.0 ± 3.4	408
18		73.0 ± 9.3	16.7 ± 3.0	427
19		35.0 ± 4.3		438
20		8		348



and the dodecaazadodeciphenyl **39b** (yield 92%!) through condensation of *p*,*p*'-biphenylyl-bis(*N*,*N*,*N*'-tris-(trimethylsilyl)carboxamidine) **(21)**, m = 2, with the vinamidinium salts **9a** and **9f**, respectively. With a calculated length of 4.91 nm **39b** belongs to the class of nanostructures and can be viewed either as an oligomer or as a tailor-made polymer having a defined chain length.

The reaction of a bifunctional amidine (**21**, m = 2) with a bifunctional vinamidinium salt **33** delivered a polymer **40**, which can be dissolved in sulfuric acid without decomposition. The repetition units **A** and **B** represent different types of unsymmetrical tetraazaquaterphenyls.





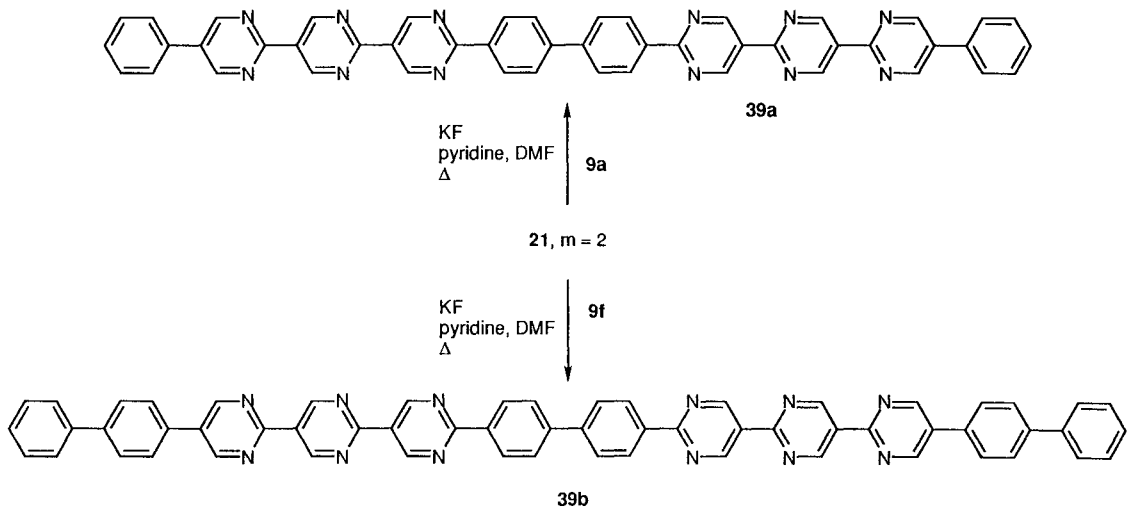
The properties of the oligo(diazaphenyls) described in this paper can be summarized as follows. They are

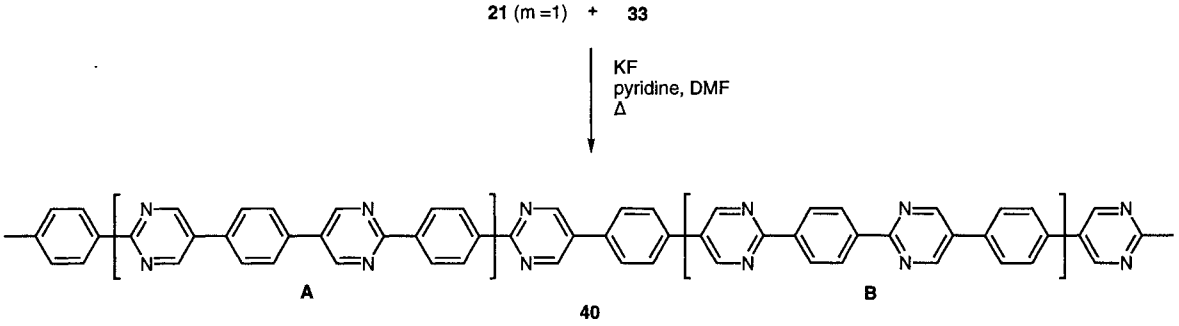
- thermally and photochemically stable,
- soluble (at least) in strong acids (CF_3CO_2H, H_2SO_4 etc.),
- NLO active, if containing A and Do substituents, they show
- (blue) fluorescence and electroluminescence

and their

- electron affinity is higher than that of oligophenyls and PPP.

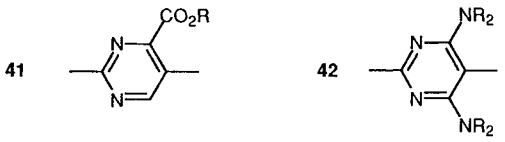
The high thermal stability of oligo(diazaphenyls) is demonstrated, among other things, by the fact that mass spectra of **24**, **26**, **27**, **38**, and **39** could be measured with the EI method. The DTA analysis of **27**, X = CNO_2,





revealed an exothermic signal at 460 °C; a corresponding signal did not appear during cooling. Heating to 1100 °C showed no further signals. A black material was obtained that contained 91.05 % carbon and 0.91 % hydrogen (elemental analysis); nitrogen could not be detected. Apparently, some kind of graphite was formed.

It goes without saying that solubilities of oligo(diazaphenyls) depend on chain lengths. Increasing the chain length decreases the solubility in common solvents. Introducing moieties like **41**[41] and **42**[42] brings about much better solubilities.

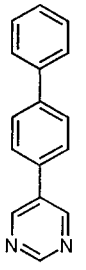
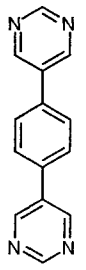
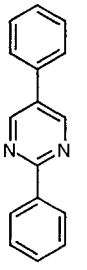
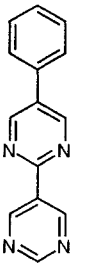
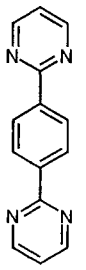
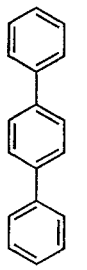


UV spectra of oligo(diazaphenyls) in most cases are similar to those of oligophenyls (cf. Table 2, 3). Terphenyl and diazaterphenyl **14a** have the same λ_{max} (285 nm) whereas **37** absorbs at shorter wavelengths (279 nm) and **14c** (290 nm), **14b** (288 nm), and **22** (294 nm) at longer wavelengths (cf. Table 2). It has to be assumed that as a consequence of a certain deviation from coplanarity through *ortho*-H/*ortho'*H interaction resonance in terphenyl (30° [43]), **14a**, and **37** is weaker than in **14c**, **14b**, and **22** and this explains the variation in λ_{max} (**22** has no *ortho*-H/*ortho'*H interaction at all, the rings are therefore expected to be coplanar, and **22** shows the longest wavelength absorption).

With emission spectra, however, the situation is quite different. Although in terphenyls, **14a** and **37** the *ortho*-H/*ortho'*H interactions are the same, there is a difference of 102/86 nm in λ_{max}(fluorescence). Table 2 shows that N atoms in terphenyl derivatives generally give rise to a red shift in λ_{max}(fluorescence). As a consequence, simply by changing the number and position of N atoms in terphenyl derivatives λ_{max}(fluorescence) can be tuned without changing the length of the π-electron system. A similar situation is observed with quaterphenyl/oligoazaquaterphenyl derivatives (cf. Table 3) and quinquephenyl/oligoazaquinquephenyl derivatives.

The assumptions made as to the different twist angles in terphenyl and oligoazaterphenyl derivatives are born out by the X-ray analysis of **24a**, X = CH (cf. Figure 1). The rings of the central tetraazaterphenyl moiety are almost

Table 2. Absorption and Emission Maxima of Terphenyl and Oligoazaterphenyl Derivatives **14a**, **37**, **14c**, **14b**, and **22**

	 **14a**	 **37**	 **14c**	 **14b**	 **22**	
absorption λ_{max} [nm] (DMSO)	285	279	290	288	294	285
emission λ_{max} [nm] (DMSO)	444	428	392	371	367	342

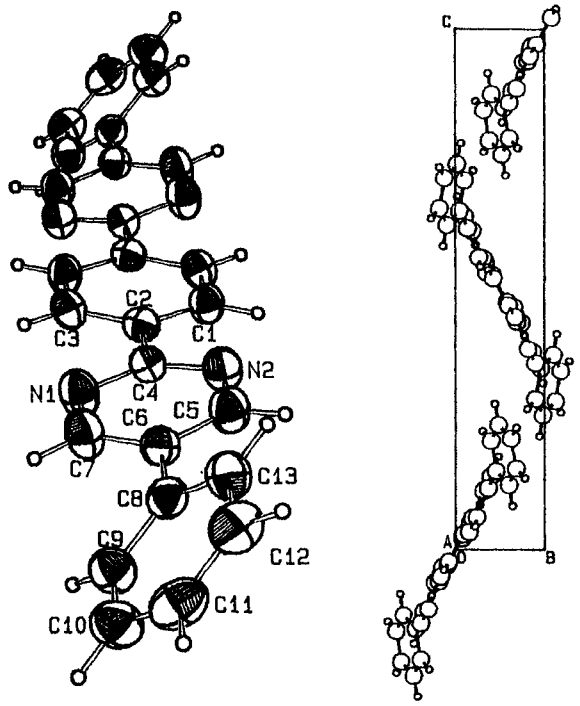
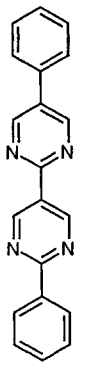
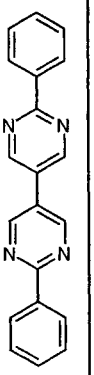
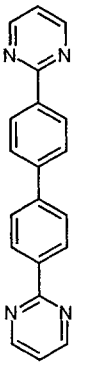
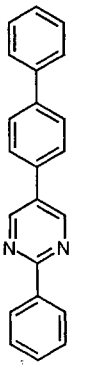
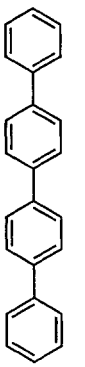


Figure 1. Structure of **24a**, X = CH, in the crystal (ORTEP), and unit cell.[44] Selected bond lengths [pm], bond and torsion angles [°]: C1–C2 1.389(3), C2–C3 1.400(3), C2–C4 1.472(3), C4–N1 1.331(3), C4–N2 1.343(3), N1–C7 1.331(3), C6–C7 1.381(3), C5–C6 1.389(3), C5–N2 1.339(3), C6–C8 1.483(3), C8–C9 1.384(3), C9–C10 1.378(3), C10–C11 1.370(4), C11–C12 1.371(4), C12–C13 1.378(3), C8–C13 1.387(3); C4–N1–C7 116.9(2), C4–N2–C5 116.9(2), C1–C2–C3 117.9(2), C1–C2–C4 121.4(2), C3–C2–C4 120.7(2), N1–C4–N2 124.5(2), N1–C4–C2 117.6(2), N2–C4–C2 119.7(2), N2–C5–C6 123.4(2), C5–C6–C7 114.1(2), C5–C6–C8 123.1(2), C7–C6–C8 122.8(2), N1–C7–C6 124.3(2), C6–C8–C9 120.4(2), C6–C8–C13 121.3(2); C1–C2–C4–N2 8.83(0.63), C3–C2–C4–N1 8.26(0.63), C5–C6–C7–C13 36.25(0.37), C7–C6–C8–C9 34.53(0.37).

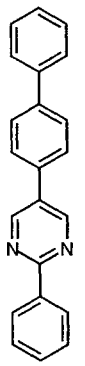
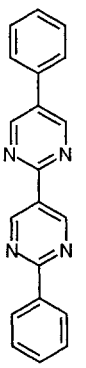
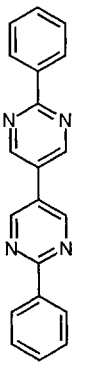
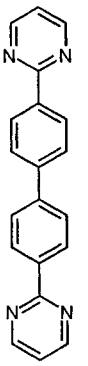
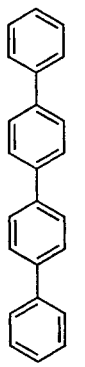
Table 4. Redox potentials (V) of quaterphenyl[45] and oligoazaquaterphenyl derivatives **15a,15b,31**, and **23** (in DMSO+0.1 M Bu_4NPF_6, vs. ferrocene/ferrocene$^+$ = 0.352 V)

	 **15b**	 **31**	 **23**	 **15a**	
E_1	−1.69	−1.74	−1.90	−1.94	−2.24
E_2	−2.14	−2.16	−2.04	−2.33	−2.47
ΔE	0.45	0.42	0.14	0.39	0.23

coplanar (the twist angles of the pyrimidine rings against the central benzene ring are only about 8°). With reference to the central tetraazaterphenyl moiety the terminal benzene rings have, however, a twist angle of about 35°.

The redox properties of oligoazaquaterphenyl derivatives were investigated by means of cyclovoltammetry (cf. Table 4). As expected, all oligoazaquaterphenyl deriva-

Table 3. Absorption and Emission Maxima of Quaterphenyl and Oligoazaquaterphenyl Derivatives **15a,15b,31**, and **23**

	 **15a**	 **15b**	 **31**	 **23**	
absorption λ_{max} [nm] (DMSO)	308	315	308	315	304
emission λ_{max} [nm] (DMSO)	431	408	413	463	373

tives are easier reversibly to reduce than quaterphenyl.[45] In contrast to quaterphenyl, they could not reversibly be oxidized, however, under these conditions. The more pyrimidine rings the molecules contain the lower are the potentials. A symmetrical arrangement of two pyrimidine rings as in **23** has almost the same effect as one pyrimidine ring in **15a**. The influence of the second pyrimidine ring in **23** becomes apparent only in E_2. Two pyrimidine rings connected in 2,5′-bipyrimidine **15b** or 5,5′-bipyrimidine moieties **31** are more effective than two pyrimidine ring separated by a biphenyl moiety **23**. Since the second reduction steps in **15b** and **31** occur at roughly the same potential it can be concluded that the electron in the first formed anion radicals is completely delocalized. It appears that in the cyclovoltammogram of **15b** there is another reversible reduction wave at −2.52 V.

Conclusion

A homologous series of oligo(diazaphenyls), that is, oligoaza derivatives of biphenyl, terphenyl, quaterphenyl, quinquephenyl, sexiphenyl, septiphenyl, octiphenyl, noviphenyl, deciphenyl, and dodeciphenyl – and poly(pyrimidinylenephenylene) can be synthesized in high yields and purities from readily accessible vinamidinium salts and amidines or *N,N,N′*-tris(trimethylsilyl)amidines. Symmetrical as well as unsymmetrical systems with a variety of substituents are available. Their fluorescence can be tuned over a wide spectral range by varying number and positions of N atoms and the deviation from coplanarity of terphenyl moieties that follows from that. In contrast to UV spectra, fluorescence spectra are strongly influenced by the number and relative positions of pyrimidine rings in oligo(diazaphenyls).

Oligo(diazaphenyls) are thermally and photochemically stable, can be dissolved at any rate in strong acids and show strong blue fluorescence in solution as well as in the solid state. Oligo(diazaphenyls) are easier to reduce than oligophenyls. All these properties make them promising candidates for LEDs. Instead of central benzene rings, other ring systems such as thiophene, oxadiazole, thiadiazole, anthracene, pyrene, spirobifluorene, phenothiazine, dihydrophenazine, flavine, porphyrine etc. can be employed, which extends the scope of the "pyrimidine method" even further.

Reagents and solvents were purchased reagent grade and used without purification. ^{1}H NMR spectra were obtained with Bruker WP 80 (80 MHz), Varian VXR 400 S (400 MHz), ^{13}C NMR spectra with Varian VXR 400 S (100.22 MHz) spectrometers. IR spectra were recorded on Perkin–Elmer 125 and Bruker IFS 45 spectrometers, UV/Vis spectra on Zeiss DMR 10 and Perkin–Elmer Lambda 3 spectrometers, fluorescence spectra on a Perkin–Elmer 3000. Mass spectra were determined on a Finnigan MAT 90 spectrometer.

2-Methyl-5-(4-nitrophenyl)pyrimidine (7b); Typical Procedure:
(Similar procedure for methylpyrimidines **7a**, **7c–g**, **11a–c**, **11e–g**, **34**, and pyrimidines **13–16**, **31**, **32**, **37**, **38**). The solution of **6b**[25] (3.50 g, 10.06 mmol) and acetamidine hydrochloride (1.43 g, 15.10 mmol) in pyridine (15 mL) was refluxed for 12 h. The precipitate was collected by filtration, washed with H_2O and acetone. Yield 1.45 g (67%); colourless powder, mp 250 °C (DMSO/MeOH 1:1).

IR (KBr): ν = 3078, 1604, 1549, 1518, 1449, 1354, 1111, 1004, 856, 754, 697, 656 cm^{-1}.

UV (DMSO): λ_{max} (lg ε) = 303 nm (4.184).

^{1}H NMR (CF_3CO_2D): δ = 3.23 (s, 3H, CH_3), AA′BB′ signal centred at 8.03 (^3J = 9 Hz, 2H, $O_2NCCHCH$) and 8.55 (^3J = 9 Hz, 2H, O_2NCCH), 9.62 (s, 2H, pyrimidine-H).

Anal. Calcd for $C_{11}H_9N_3O_2$ (215.2): C, 61.39; H, 4.22; N, 19.53. Found: C, 61.75; H, 4.19; N, 19.31.

2-Methyl-5-phenylpyrimidine **(7a)** (cf[18]):

Compound **6a**[25] (2.50 g, 8.26 mmol), acetamidine hydrochloride (1.56 g, 16.52 mmol) and sodium methylate (2.23 g, 41.29 mmol) in MeOH (20 mL) were refluxed for 13 h. After cooling, aq HCl (2 mL) was added the mixture evaporated and the residue recrystallized from H_2O (270 mL). Yield 1.18 g (84%); colourless crystals, mp 72 °C.

IR (KBr): ν = 1585, 1543, 1448, 1378, 1284, 1006, 919, 771, 766, 701, 654, 522 cm^{-1}.

UV (MeCN): λ_{max} (lg ε) = 245 nm (4.198).

^{1}H NMR ($CDCl_3$): δ = 2.79 (s, 3H, CH_3), 7.39–7.59 (m, 5H, Ph–H), 8.84 (s, 2H, pyrimidine-H).

Anal. Calcd for $C_{11}H_{10}N_2$ (170.2): C, 77.62; H, 5.92; N, 16.46. Found: C, 77.70; H, 6.12; N, 16.34.

5-(4-Hydroxyphenyl)-2-methylpyrimidine **(7c)**:

Compound **6c**[46] (20.00 g, 62.74 mmol), acetamidine hydrochloride (8.90 g, 94.12 mmol); workup with *i*-PrOH. Yield 8.65 g (74%); colourless powder, mp 259 °C (MeOH):

IR (KBr): ν = 3440, 3068, 3027, 2819, 1611, 1589, 1557, 1523, 1453, 1399, 1287, 1239, 1185, 841, 816, 664 cm^{-1}.

UV (DMSO): λ_{max} (lg ε) = 278 nm (4.264).

^{1}H NMR (CF_3CO_2C): δ = 3.18 (s, 3H, CH_3), AA′BB′ signal centred at 7.24 (^3J = 8 Hz, 2H, $HOCCH$) and 7.70 (^3J = 8 Hz, 2H, $HOCCHCH$), 9.47 (s, 2H, pyrimidine-H).

Anal. Calcd for $C_{11}H_{10}N_2O$ (186.2): C, 70.95; H, 5.41; N, 15.04. Found: C, 71.10; H, 5.41; N, 14.94.

5-(4-Methoxyphenyl)-2-methylpyrimidine **(7d)**:

Compound **6d**[25] (23.00 g, 69.11 mmol), acetamidine hydrochloride (9.80 g, 103.67 mmol); workup with *i*-PrOH. Yield 9.13 g (66%); colourless powder, mp 192 °C (*i*-PrOH–H_2O 1:1).

IR (KBr): ν = 1612, 1588, 1545, 1519, 1452, 1444, 1294, 1267, 1251, 1185, 1035, 840, 747, 657 cm^{-1}.

UV (DMSO): λ_{max} (lg ε) = 274 nm (4.233).

^{1}H NMR (CF_3CO_2D): δ = 3.18 (s, 3H, CH_3), 4.06 (s, 3H, OCH_3), AA′BB′ signal centred at 7.29 (^3J = 8 Hz, 2H, $MeOCCH$) and 7.76 (^3J = 8 Hz, 2H, $MeOCCHCH$), 9.48 (s, 2H, pyrimidine-H).

Anal. Calcd for $C_{12}H_{12}N_2O$ (200.2): C, 71.98; H, 6.04; N, 13.99. Found: C, 72.27; H, 5.89; N, 13.71.

5-(4-Bromophenyl)-2-methylpyrimidine **(7e)**:

Compound **6e**[32] (20.00 g, 52.40 mmol), acetamidine hydrochloride (6.44 g, 68.13 mmol); workup with *i*-PrOH. Yield 9.27 g (71%); colourless powder, mp 151 °C (*i*-PrOH).

IR (KBr): ν = 1587, 1571, 1446, 1375, 1275, 1077, 1001, 826, 822, 748, 656 cm^{-1}.

UV (DMSO): λ_{max} (lg ε) = 253 nm (4.325).

^{1}H NMR (CF_3CO_2D): δ = 2.79 (s, 3H, CH_3), AA′BB′ signal centred at 7.43 (^3J = 8 Hz, 2H, $BrCCH$) and 7.63 (^3J = 8 Hz, 2H, $BrCCHCH$), 8.82 (s, 2H, pyrimidine-H).

Anal. Calcd for $C_{11}H_9BrN_2$ (249.1): C, 53.04; H, 3.64; N, 11.25. Found: C, 52.91; H, 3.77; N, 11.26.

5-(4-Biphenylyl)-2-methylpyrimidine **(7f)**:

Compound **6f** (2.00 g, 5.22 mmol), acetamidine hydrochloride (0.74 g, 7.83 mmol); workup with MeOH. Yield 1.02 g (79%); colourless powder, mp 206 °C (MeOH).

IR (KBr): ν = 1588, 1539, 1452, 1376, 1277, 1005, 845, 771, 727, 692, 655 cm^{-1}.

UV (DMSO): λ_{max} (lg ε) = 285 nm (4.476).

^{1}H NMR (CF_3CO_2D): δ = 3.18 (s, 3 H, CH_3), AA'BB'C signal centred at 7.41 (^3J = 8 Hz, 1 H, Ph-4-H), 7.48 (^3J = 8 Hz, 2 H, Ph-3-H, Ph-5-H) and 7.66 (^3J = 8 Hz, 2 H, Ph-2-H, Ph-6-H), AA'BB' signal centred at 7.79 (^3J = 8 Hz, 2 H, PhCC*H*) and 7.88 (^3J = 8 Hz, 2 H, PhCCHC*H*), 9.51 (s, 2 H, pyrimidine-H).

Anal. Calcd for $C_{17}H_{14}N_2$ (246.3): C, 82.90; H, 5.73; N, 11.37. Found: C, 83.02; H, 5.66; N, 11.11.

2-Methyl-5-(γ-pyridyl)pyrimidine (**7g**):

Compound **6g**, X = N^+H, Y = HCl_2,[31] (5.76 g, 20.86 mmol), acetamidine hydrochloride (2.37 g, 25.03 mmol) in pyridine (10 mL) and HOAc (2 mL); after cooling, the dark-red mixture was evaporated, the residue triturated in H_2O (20 mL), and undissolved material removed by filtration. Yield 2.43 g (68 %); colourless powder, mp 135 °C (H_2O).

IR (KBr): ν = 3027, 1603, 1562, 1454, 1418, 1386, 1331, 1275, 1225, 989, 824, 750, 725, 650, 595 cm^{-1}.

UV (MeCN): λ_{max} (lg ε) = 272 nm (4.300).

^{1}H NMR (CF_3CO_2D): δ = 3.30 (s, 3 H, CH_3), AA'BB' signal centred at 8.71 (^3J = 5 Hz, 2 H, py-3-H, py-5-H) and 9.21 (^3J = 5 Hz, 2 H, py-2-H, py-6-H), 9.92 (s, 2 H, pyrimidine-H).

Anal. Calcd for $C_{10}H_9N_3$ (171.2): C, 70.16; H, 5.30; N, 24.54. Found: C, 69.54; H, 5.32; N, 24.59.

2'-Methyl-5-phenyl-2,5'bipyrimidine (**11a**):

Compound **8a** (1.47 g, 3.86 mmol), acetamidine hydrochloride (0.55 g, 5.79 mmol); workup with *i*-PrOH. Yield 0.70 g (73 %); pale red powder, mp 287 °C (MeOH).

IR (KBr): ν = 3051, 2928, 1582, 1560, 1430, 1394, 1252, 1034, 804, 747, 690, 645 cm^{-1}.

UV (DMSO): λ_{max} (lg ε) = 288 nm (4.416), 426 nm (3.246).

^{1}H NMR (CF_3CO_2D): δ = 2.99 (s, 3 H, CH_3), 7.65–7.71 (m, 3 H, Ph-3-H, Ph-4-H, Ph-5-H), 7.78–7.84 (m, 2 H, Ph-2-H, Ph-6-H), 9.56 (s, 2 H, pyrimidine-H), 10.22 (s, 2 H, pyrimidine'-H).

Anal. Calcd for $C_{15}H_{12}N_4$ (248.3): C, 72.56; H, 4.87; N, 22.57. Found: C, 72.48; H, 4.94; N, 22.57.

2'-Methyl-5-(4-nitrophenyl)-2,5'-bipyrimidine (**11b**):

Compound **8b** (1.79 g, 4.20 mmol), acetamidine hydrochloride (0.60 g, 6.31 mmol). Yield 1.00 g (81 %); colourless powder, mp > 330 °C (DMF).

IR (KBr): ν = 1601, 1583, 1565, 1517, 1432, 1354, 1338, 1252, 1109, 1033, 856, 804, 751, 697, 646 cm^{-1}.

UV (CF_3CO_2H): λ_{max} (lg ε) = 296 nm (4.433); UV (DMSO): λ_{max} = 313 nm.

^{1}H NMR (CF_3CO_2D): δ = 3.27 (s, 3 H, CH_3), AA'BB' signal centred at 8.02 (^3J = 9 Hz, 2 H, $O_2NCCHCH$) and 8.56 (^3J = 9 Hz, 2 H, O_2NCCH), 9.46 (s, 2 H, pyrimidine-H), 10.24 (s, 2 H, pyrimidine'-H).

Anal. Calcd for $C_{15}H_{11}N_5O_2$ (293.3): C, 61.43; H, 3.78; N, 23.88. Found: C, 61.20; H, 3.77; N, 24.05.

5-(4-Hydroxyphenyl)-2'-methyl-2,5'-bipyrimidine (**11c**):

Compound **8c** (1.12 g, 2.70 mmol), acetamidine hydrochloride (0.38 g, 4.05 mmol); workup with *i*-PrOH. Yield 0.51 g (71 %); pale red powder, mp 303 °C (MeOH).

IR (KBr): ν = 3407, 2816, 1611, 1596, 1569, 1523, 1423, 1281, 1187, 1033, 836, 800, 744, 650 cm^{-1}.

UV (DMSO): λ_{max} (lg ε) = 316 nm (4.360), 423 nm (2.737).

^{1}H NMR (CF_3CO_2D): δ = 3.24 (s, 3 H, CH_3), AA'BB' signal centred at 7.25 (^3J = 8 Hz, 2 H, HOCC*H*) and 7.77 (^3J = 8 Hz, 2 H, HOCCHC*H*), 9.51 (s, 2 H, pyrimidine-H), 10.19 (s, 2 H, pyrimidine'-H).

Anal. Calcd for $C_{15}H_{12}N_4O$ (264.3): C, 68.17; H, 4.58; N, 21.20. Found: C, 68.15; H, 4.54; N, 21.06.

2'-Methyl-5-(γ-pyridyl)-2,5'-bipyrimidine (**11g**):

Compound **8g** (1.12 g, 3.16 mmol), acetamidine hydrochloride (0.45 g, 4.74 mmol); workup with MeOH. Yield 0.61 g (78 %); cream-coloured powder, mp 295 °C (MeOH).

IR (KBr): ν = 3034, 1596, 1567, 1430, 1381, 1254, 1226, 1034, 820, 800, 744, 642 cm^{-1}.

UV (DMSO): λ_{max} (lg ε) = 281 (4.244), 386 nm (2.832).

^{1}H NMR (CF_3CO_2D): δ = 3.26 (s, 3 H, CH_3); AA'BB' signal centred at 8.57 (^3J = 6 Hz, 2 H, py-2-H, py-5-H) and 9.08 (^3J = 6 Hz, 2 H, py-2-H, py-6-H), 9.56 (s, 2 H, pyrimidine-H), 10.29 (s, 2 H, pyrimidine'-H).

Anal. Calcd for $C_{14}H_{11}N_5$ (249.3): C, 67.46; H, 4.45; N, 28.09. Found: C, 67.47; H, 4.03; N, 28.08.

5-(4-Bromophenyl)-2'-methyl-2,5'-bipyrimidine (**11e**):

Compound **8e** (3.14 g, 6.84 mmol), acetamidine hydrochloride (0.97 g, 10.25 mmol); workup with *i*-PrOH. Yield 1.81 g (81 %); cream-coloured powder, mp 308 °C (MeOH).

IR (KBr): ν = 1580, 1572, 1497, 1430, 1374, 1076, 1034, 1015, 1000, 824, 745, 646 cm^{-1}.

UV (DMSO): λ_{max} (lg ε) = 293 nm (4.432).

^{1}H NMR (CF_3CO_2D): δ = 3.25 (s, 3 H, CH_3), AA'BB' signal centred at 7.66 (^3J = 8 Hz, 2 H, BrCC*H*) and 7.81 (^3J = 8 Hz, 2 H, BrCCHC*H*), 9.47 (s, 2 H, pyrimidine-H), 10.20 (s, 2 H, pyrimidine'-H).

Anal. Calcd for $C_{15}H_{11}BrN_4$ (327.2): C, 55.07; H, 3.39; N, 17.12. Found: C, 55.15; H, 3.30; N, 16.93.

5-(4-Biphenylyl)-2'-methyl-2,5'-bipyrimidine (**11f**):

Compound **8f** (1.34 g, 2.93 mmol), acetamidine hydrochloride (0.42 g, 4.40 mmol); workup with MeOH. Yield 0.79 g (83 %); pale red powder, mp 250 °C (DMSO).

IR (KBr): ν = 3031, 1609, 1592, 1578, 1570, 1490, 1425, 1374, 1262, 1034, 836, 803, 764, 725, 690, 646 cm^{-1}.

UV (DMSO): λ_{max} (lg ε) = 311 (4.437), 424 nm (3.239).

^{1}H NMR (CF_3CO_2D): δ = 3.26 (s, 3 H, CH_3), AA'BB'C signal centred at 7.42 (^3J = 8 Hz, 1 H, Ph-4-H), 7.49 (^3J = 8 Hz, 2 H, Ph-3-H, Ph-5-H) and 7.70 (^3J = 8 Hz, 2 H, Ph-2-H, Ph-6-H), AA'BB' signal centred at 7.88 (^3J = 8 Hz, 2 H, PhCC*H*) and 7.92 (^3J = 8 Hz, 2 H, PhCCHC*H*), 9.57 (s, 2 H, pyrimidine-H), 10.20 (s, 2 H, pyrimidine'-H).

Anal. Calcd for $C_{21}H_{16}N_4$ (324.4): C, 77.76; H, 4.97; N, 17.27. Found: C, 77.64; H, 4.89; N, 17.12.

2-Methylsulfanyl-5-(γ-pyridyl)pyrimidine (**13a**):

Compound **6g**, X = N^+H, Y = HCl_2,[31] (0.78 g, 2.82 mmol), *S*-methylisothiourea sulfate (0.59 g, 2.12 mmol). Yield: 0.41 g (72 %); colourless powder, mp 125 °C (MeOH).

IR (KBr): ν = 3044, 2965, 1603, 1585, 1560, 1421, 1415, 1380, 1334, 1200, 1178, 1006, 823, 804, 769, 671, 642, 593 cm^{-1}.

UV (DMSO): λ_{max} (lg ε) = 287 nm (4.382); UV ($CHCl_3$): λ_{max} (lg δ) = 285 nm (4.424).

^{1}H NMR ($CDCl_3$): δ = 2.63 (s, 3 H, SCH_3), AA'BB' signal centred at 7.48 (^3J = 6 Hz, 2 H, py-3-H, py-5-H) and 8.73 (^3J = 6 Hz, 2 H, py-2-H, py-6-H), 8.79 (s, 2 H, pyrimidine-H).

Anal. Calcd for $C_{10}H_9N_3S$ (203.3): C, 59.09; H, 4.46; N, 20.67; S, 15.78. Found: C, 58.89; H, 4.40; N, 20.37; S, 15.74.

2-Dimethylamino-5-(γ-pyridyl)pyrimidine (**13b**):

Compound **6g**, X = N^+H, Y = HCl_2,[31] (0.78 g, 2.82 mmol), 1,1-dimethylguanidine sulfate (0.58 g, 2.12 mmol) and sodium methanolate (1.53 g, 28.24 mmol) were refluxed for 17 h in MeOH (15 mL). The solution was evaporated, the residue triturated in H_2O and collected by filtration. Yield 0.37 g (66 %); colourless powder, mp 145 °C (EtOH).

IR (KBr): ν = 3042, 2969, 1608, 1580, 1557, 1419, 1382, 1330, 1211, 1179, 831, 807, 764, 671, 640 cm^{-1}.

UV (DMSO): λ_{max} (lg ε) = 303 nm (4.334); UV ($CHCl_3$): λ_{max} (lg ε) = 300 nm (4.430).

^{1}H NMR (CF_3CO_2D): δ = 3.60 (s, 6 H, $N(CH_3)_2$), AA'BB' signal

centred at 8.45 (^3J = 6 Hz, 2H, py-3-H, py-5-H) and 8.96 (^3J = 6 Hz, 2H, py-2-H, py-6-H), 9.19 (s, 2H, pyrimidine-H).

Anal. Calcd for $C_{11}H_{12}N_4$ (200.2): C, 65.98; H, 6.04; N, 27.98. Found: C, 65.81; H, 6.00; N, 27.74.

2-Dimethylamino-5-(4-nitrophenyl)pyrimidine (**13c**):

Compound **6b**[25] (2.00 g, 5.75 mmol), 1,1-dimethylguanidine sulfate (2.35 g, 8.63 mmol); workup with *i*-PrOH. Yield 0.83 g (59%); yellow powder, mp 228°C (MeOH).

IR (KBr): ν = 3069, 2902, 1608, 1589, 1549, 1510, 1415, 1342, 1303, 1114, 856, 796, 752, 694, 539 cm^{-1}.

UV (DMSO): λ_{max} (lg ε) = 375 nm (4.248); UV (toluene): λ_{max} (lg ε) = 363 nm (4.292).

^{1}H NMR (CF_3CO_2D): δ = 3.55 (s, 6H, $N(CH_3)_2$), AA'BB' signal centred at 7.83 (^3J = 9 Hz, 2H, $O_2NCCHCH$) and 8.46 (^3J = 9 Hz, 2H, O_2NCCH), 8.92 (s, 2H, pyrimidine-H).

Anal. Calcd for $C_{12}H_{12}N_4O_2$ (244.3): C, 59.01; H, 4.95; N, 22.94. Found: C, 58.74; H, 5.03; N, 22.69.

5-(4-Biphenylyl)pyrimidine (**14a**):

Compound **6f** (0.81 g, 2.11 mmol), formamidine hydrochloride (0.33 g, 3.17 mmol). Yield 0.33 g (68%); colourless powder, mp 131°C (MeOH).

IR (KBr): ν = 3036, 1583, 1565, 1549, 1488, 1417, 1190, 1123, 1002, 839, 771, 725, 696, 631 cm^{-1}.

UV (DMSO): λ_{max} (lg ε) = 285 nm (4.423); fluorescence (DMSO): λ_{max} = 444 nm.

^{1}H NMR (CF_3CO_2D): δ = AA'BB'C signal centred at 7.43 (^3J = 8 Hz, 1H, Ph-4-H), 7.49 (^3J = 8 Hz, 2H, Ph-3-H, Ph-5-H) and 7.68 (^3J = 6 Hz, 2H, Ph-2-H, Ph-6-H), AA'BB' signal centred at 7.86 (^3J = 8 Hz, 2H, PhCC*H*) and 7.93 (^3J = 8 Hz, 2H, PhC CHC*H*), 9.72 (s, 2H, pyrimidine-H).

Anal. Calcd for $C_{16}H_{12}N_2$ (232.3): C, 82.73; H, 5.21; N, 12.06. Found: C, 82.98; H, 5.26; N, 12.11.

5-Phenyl-2,5'-bipyrimidine (**14b**):

Compound **8a** (1.35 g, 3.54 mmol), formamidine hydrochloride (0.43 g, 5.32 mmol). Yield 0.65 g (78%); colorless powder, mp 278°C (MeOH).

IR (KBr): ν = 3051, 1580, 1563, 1428, 1397, 1248, 1032, 812, 744, 695, 645 cm^{-1}.

UV (DMSO): λ_{max} (lg ε) = 288 nm (4.424); fluorescence (DMSO): λ_{max} = 371 nm.

^{1}H NMR (CF_3CO_2D): δ = 7.66–7.70 (m, 3H, Ph-3-H, Ph-4-H, Ph-5-H), 7.78–7.85 (m, 2H, Ph-2-H, Ph-6-H), 9.56 (s, 2H, pyrimidine-H), 10.24 (s, 2H, pyrimidine'-4-H, pyrimidine'-6-H), 10.04 (s, 2H, pyrimidine'-2-H).

Anal. Calcd for $C_{14}H_{10}N_4$ (234.3): C, 71.78; H, 4.30; N, 23.92. Found: C, 72.01; H, 4.49; N, 23.83.

2,5-Diphenylpyrimidine[47] (**14c**):

Compound **6a**[25] (1.00 g, 3.30 mmol), benzamidine hydrochloride hydrate (0.78 g, 4.95 mmol). Yield 0.66 g (86%); colourless platelets.

UV (DMSO): λ_{max} (lg ε) = 290 nm (4.362); fluorescence (DMSO): λ_{max} = 392 nm.

2'-Dimethylamino-5-(4-nitrophenyl)-2,5'-bipyrimidine (**14d**, R' = NMe_2):

Compound **8a** (0.50 g, 1.17 mmol), 1,1-dimethylguanidine sulfate (0.48 g, 1.76 mmol). Yield 0.29 g (76%); yellow powder, mp >300°C (DMF).

IR (KBr): ν = 2936, 1605, 1580, 1550, 1524, 1454, 1408, 1338, 1301, 1205, 1111, 969, 855, 810, 752, 695, 647, 541 cm^{-1}.

UV (DMSO): λ_{max} (lg ε) = 296, 361 nm; UV (toluene): λ_{max} = 364 nm.

^{1}H NMR (CF_3CO_2D): δ = 3.64 (s, 6H, $N(CH_3)_2$), AA'BB' signal centred at 8.05 (^3J = 9 Hz, 2H, $O_2NCCHCH$) and 8.56 (^3J = 9 Hz, 2H, O_2NCCH), 9.60 (s, 2H, pyrimidine-H), 9.69 (s, 2H, pyrimidine'-H).

Anal. Calcd for $C_{16}H_{14}N_6O_2$ (322.3): C, 59.62; H, 4.38; N, 26.07. Found: C, 59.33; H, 4.39; N, 25.89.

2'-Amino-5-(4-nitrophenyl)-2,5'-bipyrimidine (**14d**, R' = NH_2):

Compound **8a** (0.50 g, 1.17 mmol), guanidine hydrochloride (0.17 g, 1.76 mmol). Yield 0.24 g (69%); yellow powder, mp >330°C.

IR (KBr): ν = 3416, 1612, 1598, 1562, 1505, 1444, 1350, 1338, 1110, 855, 811, 752, 698, 648 cm^{-1}.

UV (DMSO): λ_{max} (lg ε) = 283 (4.221), 349 nm (4.495); UV (toluene): λ_{max} = 338 nm.

^{1}H NMR (CF_3CO_2D): δ = AA'BB' signal centred at 8.04 (^3J = 9 Hz, 2H, $O_2NCCHCH$) and 8.56 (^3J = 9 Hz, 2H, O_2NCCH), 9.56 (s, 2H, pyrimidine-H), 9.75 (s, 2H, pyrimidine'-H).

Anal. Calcd for $C_{14}H_{10}N_6O_2$ (294.3): C, 57.14; H, 3.43; N, 28.56. Found: C, 57.11; H, 3.37; N, 28.50.

2'-Methoxy-5-(4-nitrophenyl)-2,5'-bipyrimidine (**14d**, R' = OMe):

Compound **8a** (0.50 g, 1.17 mmol), *O*-methylisourea hydrogensulfate (0.22 g, 0.88 mmol). Yield 0.22 g (61%); colourless powder, mp >330°C (DMF).

IR (KBr): ν = 1600, 1583, 1567, 1516, 1480, 1449, 1414, 1354, 1335, 1109, 1037, 857, 811, 752, 696, 651 cm^{-1}.

UV (DMSO): λ_{max} (lg ε) = 272 (4.248), 319 nm (4.459); UV (toluene): λ_{max} = 315 nm).

^{1}H NMR (CF_3CO_2D): δ = 4.60 (s, 3H, OCH_3), AA'BB' signal centred at 8.04 (^3J = 9 Hz, 2H, $O_2NCCHCH$) and 8.55 (^3J = 9 Hz, 2H, O_2NCCH), 9.51 (s, 2H, pyrimidine-H), 10.01 (s, 2H, pyrimidine'-H).

Anal. Calcd for $C_{15}H_{11}N_5O_3$ (309.3): C, 58.25; H, 3.58; N, 22.64. Found: C, 58.22; H, 3.58; N, 22.53.

2'-Hydroxy-5-(4-nitrophenyl)-2,5'-bipyrimidine (**14d**, R' = OH):

Compound **8a** (0.50 g, 1.17 mmol), urea (0.11 g, 1.76 mmol). Yield 0.25 g (72%); pale yellow powder, mp >330°C.

IR (KBr): ν = 3416, 1612, 1598, 1582, 1562, 1507, 1433, 1339, 1111, 856, 811, 752, 648 cm^{-1}.

UV (DMSO): λ_{max} (lg ε) = 331 nm (4.498); UV (DMSO + t-BuOK): λ_{max} = 292, 376, 652 nm; UV (toluene): λ_{max} = 315 nm.

^{1}H NMR (CF_3CO_2D): δ = AA'BB' signal centred at 8.00 (^3J = 8 Hz, 2H, $O_2NCCHCH$) and 8.54 (^3J = 8 Hz, 2H, O_2NCCH), 9.39 (s, 2H, pyrimidine-H), 10.00 (s, 2H, pyrimidine'-H).

Anal. Calcd for $C_{14}H_9N_5O_3$ (295.3): C, 56.95; H, 3.07; N, 23.72. Found: C, 57.08; H, 3.17; N, 23.64.

2'-Methylsulfanyl-5-(4-nitrophenyl)-2,5'-bipyrimidine (**14d**, R' = SMe):

Compound **8a** (0.50 g, 1.17 mmol), *S*-methylisothiourea hydrogensulfate (0.25 g, 0.88 mmol). Yield 0.31 g (81%); yellow powder, mp >330°C (DMF).

IR (KBr): ν = 1599, 1576, 1556, 1523, 1452, 1402, 1348, 1204, 1111, 856, 804, 752, 640 cm^{-1}.

UV (DMSO): λ_{max} (lg ε) = 332 nm; UV (toluene): λ_{max} = 337 nm.

^{1}H NMR (CF_3CO_2D): δ = 3.03 (s, 3H, SCH_3), AA'BB' signal centred at 8.04 (^3J = 9 Hz, 2H, $O_2NCCHCH$) and 8.55 (^3J = 9 Hz, 2H, O_2NCCH), 9.52 (s, 2H, pyrimidine-H), 9.98 (s, 2H, pyrimidine'-H).

Anal. Calcd for $C_{15}H_{11}N_5O_2S$ (325.4): C, 55.38; H, 3.41; N, 21.53; S, 9.86. Found: C, 55.11; H, 3.40; N, 21.41; S, 9.87.

2'-Octylsulfanyl-5-(4-nitrophenyl)-2,5'-bipyrimidine (**14d**, R' = SC_8H_{17}):

Compound **8a** (0.50 g, 1.17 mmol), *S*-octylisothiourea picrate (0.74 g, 1.76 mmol). Yield 0.23 g (66%); yellow powder, mp 158°C (DMF).

IR (KBr): ν = 2927, 2855, 1604, 1576, 1556, 1529, 1452, 1401, 1346, 1197, 855, 804, 752, 693, 639 cm^{-1}.

UV (DMSO): λ_{max} (lg ε) = 332 nm (4.458); UV (toluene): λ_{max} (lg ε) = 339 nm (4.593).

^{1}H NMR (CF_3CO_2D): δ = 0.94 (t, J = 7 Hz, 3H, CH_3), 1.35–1.52

(m, 8H, $4CH_2$), 1.62 (quint, $J = 7$ Hz, 2H, $SCH_2CH_2CH_2$), 1.98 (quint, $J = 7$ Hz, 2H, SCH_2CH_2), 3.68 (t, $J = 7$ Hz, 2H, SCH_2), AA'BB' signal centred at 8.03 ($^3J = 9$ Hz, 2H, $O_2NCCHCH$) and 8.56 ($^3J = 9$ Hz, 2H, O_2NCCH), 9.51 (s, 2H, pyrimidine-H), 9.94 (s, 2H, pyrimidine'-H).

Anal. Calcd for $C_{22}H_{25}N_5O_2S$ (423.5): C, 62.39; H, 5.95; N, 16.54; S, 7.57. Found: C, 62.69; H, 5.85; N, 16.27; S, 7.57.

2'-Amino-5-(4-hydroxyphenyl)-2,5'-bipyrimidine (**14f**, R' = NH_2):

Compound **8c** (1.00 g, 2.41 mmol), guanidine hydrochloride (0.35 g, 3.62 mmol). Yield 0.37 g (58%); yellow-brown powder, mp > 330°C (MeOH).

IR (KBr): ν = 3381, 3208, 1611, 1583, 1563, 1517, 1496, 1431, 1329, 1275, 1178, 835, 810 cm^{-1}.

UV (DMSO): λ_{max} (lg ε) = 324 (4.407), 396 nm (3.287).

^1H NMR (CF_3CO_2D): δ = AA'BB' signal centred at 7.26 ($^3J = 8$ Hz, 2H, HOCCH) and 7.76 ($^3J = 8$ Hz, 2H, HOCCHCH), 9.53 (s, 2H, pyrimidine-H), 9.75 (s, 2H, pyrimidine'-H).

Anal. Calcd for $C_{14}H_{11}N_5O \times 0.3\ H_2O$ (265.3): C, 62.12; H, 4.32; N, 25.87. Found: C, 61.86; H, 4.41; N, 25.71.

2'-Dimethylamino-5-(γ-pyridyl)-2,5'-bipyrimidine (**14h**, R' = NMe_2):

Compound **8g**, X = $NH^+HCl_2^-$, (1.00 g, 2.82 mmol), 1,1-dimethylguanidine sulfate (1.15 g, 4.23 mmol); pyridine (9 mL) and acetic acid (3 mL); after refluxing for 14 h, MeOH was added at r.t. Yield 0.65 g (83%); colourless powder, mp 318°C (DMSO).

IR (KBr): ν = 2928, 1600, 1583, 1560, 1453, 1405, 1337, 1307, 1208, 973, 825, 771, 644, 543 cm^{-1}.

UV (DMSO): λ_{max} (lg ε) = 342 nm (4.500); UV (toluene): λ_{max} = 346 nm.

^1H NMR (CF_3CO_2D): δ = 3.62 (s, 6H, $N(CH_3)_2$), AA'BB' signal centred at 8.58 ($^3J = 6$ Hz, 2H, py-3-H, py-5-H) and 9.05 ($^3J = 6$ Hz, 2H, py-2-H, py-6-H), 9.56 (s, 2H, pyrimidine-H), 9.65 (s, 2H, pyrimidine'-H).

Anal. Calcd for $C_{15}H_{14}N_6$ (278.3): C, 64.73; H, 5.07; N, 30.20. Found: C, 64.92; H, 5.08; N, 30.28.

2'-Hydroxy-5-(γ-pyridyl)-2,5'-bipyrimidine (**14h**, R' = OH):

Compound **8g**, X = $NH^+HCl_2^-$, (1.00 g, 2.82 mmol), *O*-methylisourea hydrogensulfate (1.04 g, 4.23 mmol); pyridine (9 mL) and HOAc (3 mL). Yield 0.43 g (59%); colourless powder, mp > 330°C.

IR (KBr): ν = 3357, 3059, 1653, 1631, 1603, 1565, 1450, 1399, 1330, 1238, 1224, 1002, 830, 808, 703 cm^{-1}.

UV (DMSO): λ_{max} (lg ε) = 302 nm (4.444).

^1H NMR (CF_3CO_2D): δ = AA'BB' signal centred at 8.54 ($^3J = 7$ Hz, 2H, py-3-H, py-5-H) and 9.05 ($^3J = 7$ Hz, 2H, py-2-H, py-6-H), 9.46 (s, 2H, pyrimidine-H), 10.01 (s, 2H, pyrimidine'-H).

Anal. Calcd for $C_{13}H_9N_5O \times 0.25\ H_2O$ (251.2): C, 61.05; H, 3.74; N, 27.38. Found: C, 61.16; H, 3.79; N, 27.63.

2'-Methylsulfanyl-5-(γ-pyridyl)-2,5'-bipyrimidine (**14h**, R' = SMe):

Compound **8g**, X = $NH^+HCl_2^-$, (1.00 g, 2.82 mmol), *S*-methylisothiourea hydrogensulfate (1.18 g, 4.23 mmol); pyridine (9 mL) + HOAc (3 mL). Yield 0.63 g (79%); colourless powder, mp 288°C (DMSO).

IR (KBr): ν = 3043, 2934, 1598, 1577, 1565, 1453, 1401, 1336, 1244, 1205, 823, 770, 660, 637 cm^{-1}.

UV (DMSO): λ_{max} (lg ε) = 318 nm (4.584); UV (toluene): λ_{max} = 324 nm.

^1H NMR (CF_3CO_2D): δ = 3.03 (s, 3H, SCH_3), AA'BB' signal centred at 8.57 ($^3J = 7$ Hz, 2H, py-3-H, py-5-H) and 9.06 ($^3J = 7$ Hz, 2H, py-2-H, py-6-H), 9.55 (s, 2H, pyrimidine-H), 10.02 (s, 2H, pyrimidine'-H).

Anal. Calcd for $C_{14}H_{11}N_5S$ (281.3): C, 59.77; H, 3.94; N, 24.89; S, 11.40. Found: C, 59.68; H, 3.97; N, 24.85; S, 11.34.

5-(4-Bromophenyl)-2-phenylpyrimidine (**14i**, R' = Br):

Compound **6**, X = CBr,[32] (4.00 g, 10.48 mmol), benzamidine hydrochloride (2.46 g, 15.72 mmol). Yield 0.2.41 g (74%); colourless platelets, mp 176°C (MeOH).

IR (KBr): ν = 3033, 1582, 1533, 1507, 1489, 1431, 1376, 1328, 1014, 1006, 838, 785, 762, 725, 690, 654 cm^{-1}.

UV (DMSO): λ_{max} (lg ε) = 294 nm (4.411).

^1H NMR (CF_3CO_2D): δ = AA'BB'C signal centred at 7.76 ($^3J = 8$ Hz, 2H, Ph-3-H, Ph-5-H), 7.87 ($^3J = 8$ Hz, 1H, Ph-4-H) and 8.39 ($^3J = 8$ Hz, 2H, Ph-2-H, Ph-6-H), AA'BB' signal centred at 7.67 ($^3J = 8$ Hz, 2H, BrCCH) and 7.82 ($^3J = 8$ Hz, 2H, BrCCHCH), 9.54 (s, 2H, pyrimidine-H).

Anal. Calcd for $C_{16}H_{11}BrN_2$ (311.2): C, 61.76; H, 3.56; N, 9.00. Found: C, 61.98; H, 3.46; N, 9.07.

5-(4-Biphenylyl)-2-phenylpyrimidine (**15a**):

Compound **6f** (1.50 g, 3.91 mmol), benzamidine hydrochloride (0.92 g, 5.87 mmol). Yield 1.00 g (83%); colourless powder, mp 199°C (DMSO).

IR (KBr): ν = 3036, 1606, 1579, 1530, 1489, 1432, 1372, 1334, 1006, 835, 762, 746, 691, 655 cm^{-1}.

UV (DMSO): λ_{max} (lg ε) = 308 nm (4.589); fluorescence (DMSO): λ_{max} = 432 nm.

^1H NMR (CF_3CO_2D): δ = AA'BB'C signal centred at 7.41 ($^3J = 8$ Hz, 1H, phenylene-Ph-4-H), 7.49 ($^3J = 8$ Hz, 2H, phenylene-Ph-3-H, phenylene-Ph-5-H) and 7.69 ($^3J = 8$ Hz, 2H, phenylene-Ph-2-H, phenylene-Ph-6-H), AA'BB' signal centred at 7.84 ($^3J = 8$ Hz, 2H, PhCCH) and 7.91 ($^3J = 8$ Hz, 2H, PhCCHCH), AA'BB'C signal centred at 7.76 ($^3J = 8$ Hz, 2H, pyrimidine-Ph-3-H, pyrimidine-Ph-5-H), 7.88 ($^3J = 8$ Hz, 1H, pyrimidine-Ph-4-H) and 8.36 ($^3J = 8$ Hz, 2H, pyrimidine-Ph-2-H, pyrimidine-6-H), 9.54 (s, 2H, pyrimidine-H).

Anal. Calcd for $C_{22}H_{16}N_2$ (308.4): C, 85.69; H, 5.23; N, 9.08. Found: C, 86.08; H, 5.41; N, 9.11.

2',5-Diphenyl-2,5'-bipyrimidine (**15b**):

Compound **8a** (0.64 g, 1.68 mmol), benzamidine hydrochloride (0.39 g, 2.52 mmol). Yield 0.40 g (77%); colourless powder, mp > 330°C (DMSO).

IR (KBr): ν = 3057, 1577, 1555, 1420, 1374, 1344, 1241, 1029, 1006, 823, 803, 748, 695, 645 cm^{-1}.

UV (DMSO): λ_{max} (lg ε) = 315 nm (4.436); fluorescence (DMSO): λ_{max} = 408 nm.

^1H NMR (CF_3CO_2D): δ = 7.67–7.71 (m, 3H, pyrimidine-Ph-3-H, pyrimidine-Ph-4-H, pyrimidine-Ph-5-H), 7.79–7.85 (m, 2H, pyrimidine-Ph-2-H, pyrimidine-Ph-6-H), AA'BB'C signal centred at 7.79 ($^3J = 8$ Hz, 1H, pyrimidine'-Ph-4-H), 7.95 ($^3J = 8$ Hz, 2H, pyrimidine'-Ph-3-H, pyrimidine'-Ph-5-H) and 8.54 ($^3J = 8$ Hz, 2H, pyrimidine'-Ph-2-H, pyrimidine'-Ph-6-H), 9.60 (s, 2H, pyrimidine-H), 10.31 (s, 2H, pyrimidine'-H).

Anal. Calcd for $C_{20}H_{14}N_4$ (310.4): C, 77.40; H, 4.55; N, 18.05. Found: C, 77.44; H, 4.63; N, 17.84.

2'-(4-Methoxyphenyl)-5-(4-nitrophenyl)-2,5'-bipyrimidine (**15c**, A = C–OMe):

Compound **8b** (0.50 g, 1.17 mmol), 4-methoxybenzamidine hydrochloride[48] (0.28 g, 1.53 mmol). Yield 0.42 g (93%); yellow powder, mp > 330°C (DMSO).

IR (KBr): ν = 1605, 1574, 1517, 1417, 1341, 1257, 1167, 1022, 856, 851, 807, 752, 694, 646 cm^{-1}.

UV (CF_3CO_2H): λ_{max} (lg ε) = 291 (sh, 4.158), 380 nm (4.610); UV (DMSO): λ_{max} = 283 (sh), 348 nm; UV (toluene): λ_{max} = 352 nm.

^1H NMR (CF_3CO_2D): δ = 4.09 (s, 3H, OCH_3), AA'BB' signal centred at 7.32 ($^3J = 9$ Hz, 2H, MeOCCH) and 8.56 ($^3J = 9$ Hz, 2H, MeOCCHCH), AA'BB' signal centred at 8.05 ($^3J = 9$ Hz, 2H, $O_2NCCHCH$) and 8.56 ($^3J = 9$ Hz, 2H, O_2NCCH), 9.53 (s, 2H, pyrimidine-H), 10.16 (s, 2H, pyrimidine'-H).

Anal. Calcd for $C_{21}H_{15}N_5O_3$ (385.4): C, 65.45; H, 3.92; N, 18.17. Found: C, 65.27; H, 3.95; N, 17.93.

2',5-Bis(4-nitrophenyl)-2,5'-bipyrimidine (**15c**, A = C–NO_2):

Compound **8b** (0.32 g, 0.75 mmol), 4-nitrobenzamidine hydrochloride[49] (0.20 g, 0.98 mmol). Yield 0.28 g (94%); colourless powder, mp > 330°C (DMSO).

IR (KBr): ν = 3111, 1600, 1562, 1519, 1417, 1344, 1238, 1102, 856, 812, 745, 683, 649 cm^{-1}.

UV (CF_3CO_2H): λ_{max} (lg ε) = 326 nm (4.678).

^1H NMR (CF_3CO_2D): δ = AA'BB' signal centred at 8.05 (^3J = 9 Hz, 2 H, $O_2NCCHCH$-pyrimidine) and 8.57 (^3J = 8 Hz, 2 H, O_2NCCH-pyrimidine') and 8.75 (^3J = 8 Hz, 2 H, $O_2NCCHCH$-pyrimidine'), 9.53 (s, 2 H, pyrimidine-H), 10.38 (s, 2 H, pyrimidine'-H).

Anal. Calcd for $C_{20}H_{12}N_6O_4$ (400.4): C, 60.00; H, 3.02; N, 20.99. Found: C, 59.96; H, 3.12; N, 20.78.

5-(4-Nitrophenyl)-2'-(γ-pyridyl)-2,5'-bipyrimidine (**15c**, A = N):

Compound **8b** (1.00 g, 2.35 mmol), γ-pyridinecarboxamidine hydrochloride[50] (0.48 g, 3.05 mmol). Yield 0.77 g (92 %); colourless powder, mp > 330 °C (DMSO).

IR (KBr): ν = 1601, 1576, 1552, 1517, 1417, 1346, 1108, 856, 805, 785, 725, 708, 697, 641 cm^{-1}.

UV (CF_3CO_2H): λ_{max} (lg ε) = 289 (sh, 4.516), 312 nm (4.574).

^1H NMR (CF_3CO_2D): δ = AA'BB' signal centred at 8.10 (^3J = 9 Hz, 2 H, $O_2NCCHCH$) and 8.60 (^3J = 9 Hz, 2 H, O_2NCCH), AA'BB' signal centred at 9.12 (^3J = 6 Hz, 2 H, py-3-H, py-5-H) and 9.27 (^3J = 6 Hz, 2 H, py-2-H, py-6-H), 9.74 (s, 2 H, pyrimidine-H), 10.10 (s, 2 H, pyrimidine'-H).

Anal. Calcd for $C_{19}H_{12}N_6O_2$ (356.3): C, 64.04; H, 3.39; N, 23.58. Found: C, 64.15; H, 3.38; N, 23.49.

2''-Methoxy-5-(4-nitrophenyl)-2,5';2',5''-terpyrimidine (**15d**, A = C–OMe):

Compound **9b** (0.27 g, 0.54 mmol), *O*-methylisourea hydrogensulfate (0.20 g, 0.80 mmol). Yield 0.16 g (77 %); pale yellow powder, mp > 330 °C (DMSO).

IR (KBr): ν = 1601, 1569, 1516, 1487, 1433, 1405, 1339, 1110, 1032, 856, 816, 752, 669, 637 cm^{-1}.

UV (DMSO): λ_{max} = 270, 328 nm; UV (toluene): λ_{max} = 340 nm.

^1H NMR (CF_3CO_2D): δ = 4.60 (s, 3 H, OCH_3); AA'BB' signal centred at 8.09 (^3J = 9 Hz, 2 H, $O_2NCCHCH$) and 8.58 (^3J = 9 Hz, 2 H, O_2NCCH), 9.73 (s, 2 H, pyrimidine-H), 9.99 (s, 2 H, pyrimidine'-H), 10.08 (s, 2 H, pyrimidine''-H).

Anal. Calcd for $C_{19}H_{13}N_7O_3$ (387.4): C, 58.91; H, 3.38; N, 25.31. Found: C, 58.70; H, 3.42; N, 25.27.

2''-Methyl-5-(4-nitrophenyl)-2,5';2',5''-terpyrimidine (**15d**, A = C–Me):

Compound **9b** (0.73 g, 1.45 mmol), acetamidine hydrochloride (0.21 g, 2.17 mmol). Yield 0.43 g (80 %); yellow powder, mp > 330 °C.

IR (KBr): ν = 1601, 1576, 1567, 1515, 1419, 1362, 1345, 1245, 1110, 1035, 856, 811, 751, 640 cm^{-1}.

UV (CF_3CO_2H): λ_{max} (lg ε) = 310 nm (4.536); UV (DMSO): λ_{max} = 308, 405 (sh) nm.

^1H NMR (CF_3CO_2D): δ = 3.27 (s, 3 H, CH_3), AA'BB' signal centred at 8.10 (^3J = 9 Hz, 2 H, $O_2NCCHCH$) and 8.58 (^3J = 9 Hz, 2 H, O_2NCCH), 9.74 (s, 2 H, pyrimidine-H), 10.01 (s, 2 H, pyrimidine'-H), 10.31 (s, 2 H, pyrimidine''-H).

Anal. Calcd for $C_{19}H_{13}N_7O_2$ (371.4): C, 61.45; H, 3.53; N, 26.40. Found: C, 61.25; H, 3.78; N, 26.22.

5-(4-Hydroxyphenyl)-2'-(4-nitrophenyl)-2,5'-bipyrimidine (**15e**, A = C–NO_2):

Compound **8c** (1.30 g, 3.13 mmol), 4-nitrobenzamidine hydrochloride[49] (0.76 g, 3.76 mmol). Yield 0.95 g (82 %); yellow powder, mp > 330 °C.

IR (KBr): ν = 3477, 1612, 1599, 1556, 1512, 1415, 1339, 1277, 1180, 1102, 1025, 858, 831, 807, 744, 647 cm^{-1}.

UV (CF_3CO_2H): λ_{max} (lg ε) = 303 (4.466), 366 nm (4.364); UV (DMSO): λ_{max} = 288, 354 nm; UV (toluene): λ_{max} = 335 nm.

^1H NMR (CF_3CO_2D): δ = AA'BB' signal centred at 7.26 (^3J = 8 Hz, 2 H, HOCC*H*) and 7.80 (^3J = 8 Hz, 2 H, HOCCHC*H*), AA'BB' signal centred at 8.58 (^3J = 8 Hz, 2 H, O_2NCCH) and 8.69 (^3J = 8 Hz, 2 H, $O_2NCCHCH$), 9.58 (s, 2 H, pyrimidine-H), 10.31 (s, 2 H, pyrimidine'-H).

Anal. Calcd for $C_{20}H_{13}N_5O_3$ (371.4): C, 64.69; H, 3.53; N, 18.86. Found: C, 64.46; H, 3.64; N, 18.58.

5-(4-Hydroxyphenyl)-2'-(γ-pyridyl)-2,5'-bipyrimidine (**15e**, A = N):

Compound **8c** (1.30 g, 3.13 mmol), γ-pyridinecarboxamidine hydrochloride[50] (0.59 g, 3.76 mmol). Yield 0.83 g (81 %); colourless powder, mp > 330 °C.

IR (KBr): ν = 3040, 1606, 1592, 1572, 1521, 1452, 1417, 1287, 1178, 1060, 1008, 833, 801, 783, 637 cm^{-1}.

UV (CF_3CO_2H): λ_{max} (lg ε) = 276 (4.449), 358 nm (4.212); UV (DMSO): λ_{max} (lg ε) = 267 (4.325), 340 nm (4.421); UV (DMSO + *t*-BuOK): λ_{max} = 374, 508 nm; UV (toluene): λ_{max} = 317 nm.

^1H NMR (CF_3CO_2D): δ = AA'BB' signal centred at 7.29 (^3J = 7 Hz, 2 H, HOCC*H*) and 7.83 (^3J = 7 Hz, 2 H, HOCCHC*H*), AA'BB' signal centred at 9.10 (^3J = 5 Hz, 2 H, py-3-H, py-5-H) and 9.28 (^3J = 5 Hz, 2 H, py-2-H, py-6-H), 9.67 (s, 2 H, pyrimidine-H), 10.08 (s, 2 H, pyrimidine'-H).

Anal. Calcd for $C_{19}H_{13}N_5O$ (327.2): C, 69.72; H, 4.00; N, 21.39. Found: C, 69.58; H, 4.10; N, 21.29.

γ-(2'-[5-(p-Hydroxyphenyl)]-2,5'-bipyrimidinyl)-N-methylpyridinium tetrafluoroborate (**15e**, A = N^+–Me BF_4^-):

Compound **15e**, A = N, (0.10 g, 0.31 mmol) and dimethyl sulfate (0.06 mL, 0.64 mmol) in toluene (20 mL) and DMF (5 mL) were refluxed for 48 h. The precipitate was collected by filtration, washed with toluene and then refluxed with $NaBF_4$ (0.34 g, 3.06 mmol) in H_2O (70 mL) for 2 h. The precipitate was collected by filtration from the hot mixture. Yield 0.11 g (79 %); yellow powder, mp > 330 °C.

IR (KBr): ν = 3047, 1643, 1610, 1585, 1556, 1522, 1417, 1286, 1185, 1105, 1084, 847, 803, 788, 644 cm^{-1}.

UV (DMSO): λ_{max} = 278, 368 nm; UV (DMSO + *t*-BuOK): λ_{max} = 390, 465, 560 (sh) nm.

^1H NMR (CF_3CO_2D): δ = 4.64 (s, 3 H, CH_3); AA'BB' signal centred at 7.29 (^3J = 9 Hz, 2 H, HOCC*H*) and 7.83 (^3J = 9 Hz, 2 H, HOCCHC*H*), AA'BB' signal centred at 8.99 (^3J = 6 Hz, 2 H, py-3-H, py-5-H) and 9.18 (^3J = 6 Hz, 2 H, py-2-H, py-6-H), 9.66 (s, 2 H, pyrimidine-H), 10.05 (s, 2 H, pyrimidine'-H).

Anal. Calcd for $C_{20}H_{16}BF_4N_5O \times 1.5\ H_2O$ (429.2): C, 52.66; H, 4.20; N, 15.35. Found: C, 52.85; H, 3.89; N, 15.06.

2'-(4-Methoxyphenyl)-5-(γ-pyridyl)-2,5'-bipyrimidine (**15f**, A = C–OMe):

Compound **8g**, X = N^+H Cl^-, (0.99 g, 2.79 mmol), 4-methoxybenzamidine hydrochloride[48] (0.68 g, 3.63 mmol). Yield 0.86 g (88 %); colourless powder, mp > 330 °C (DMSO).

IR (KBr): ν = 1608, 1579, 1563, 1421, 1332, 1262, 1168, 1022, 829, 808, 796, 643 cm^{-1}.

UV (DMSO): λ_{max} = 338 nm; UV (toluene): λ_{max} = 342 nm.

^1H NMR (CF_3CO_2D): δ = 4.09 (s, 3 H, OCH_3), AA'BB' signal centred at 7.33 (^3J = 8 Hz, 2 H, MeOCC*H*) and 8.56 (^3J = 8 Hz, 2 H, MeOCCHC*H*), AA'BB' signal centred at 8.60 (^3J = 6 Hz, 2 H, py-3-H, py-5-H) and 9.08 (^3J = 6 Hz, 2 H, py-2-H, py-6-H), 9.59 (s, 2 H, pyrimidine-H), 10.19 (s, 2 H, pyrimidine'-H).

MS (70 eV): *m/z* (%): 341 (100) [M^+], 208 (20), 171 (9) [M^{2+}], 133 (16).

Anal. Calcd for $C_{20}H_{15}N_5O \times 0.5\ H_2O$ (341.4): C, 68.56; H, 4.60; N, 19.99. Found: C, 68.43; H, 4.34; N, 20.01.

2',5-Bis-(γ-pyridyl)-2,5'-bipyrimidine (**15f**, A = N):

Compound **8g**, X = N^+H Cl^-, (0.99 g, 2.79 mmol), γ-pyridinecarboxamidine hydrochloride[50] (0.57 g, 3.63 mmol). Yield 0.78 g (89 %); colourless powder, mp > 330 °C.

IR (KBr): ν = 3042, 1597, 1572, 1561, 1419, 1342, 1322, 825, 804, 785, 643, 639 cm^{-1}.

UV (DMSO): λ_{max} = 301 nm.

^1H NMR (CF_3CO_2D): δ = AA'BB' signal centred at 8.65 (^3J = 7 Hz, 2 H, pyrimidine-py-3-H, pyrimidine-py-5-H) and 9.10 (^3J = 7 Hz, 2 H, pyrimidine-py-2-H, pyrimidine-py-6-H), AA'BB'