J. prakt. Chem. 338 (1996) 451–459

Journal für praktische Chemie
Chemiker-Zeitung

An Efficient New Pyrimidine Synthesis – A Pathway to Octupoles [1])

Stefan Brandl, Rudolf Gompper, and Kurt Polborn

München, Institut für Organische Chemie der Ludwig-Maximilians-Universität

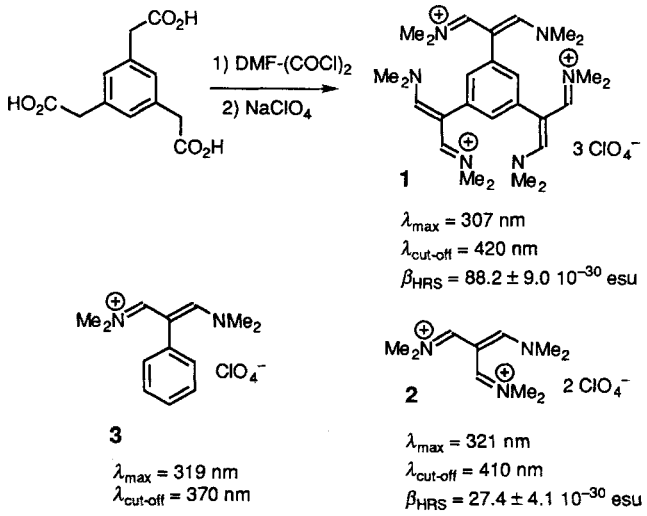
Received January 17th, 1996

Abstract. The condensation of *N,N,N'*-tris(trimethylsilyl)-amidines (**6**, **11**, **22**) with vinamidinium salts (**1**, **7**) in the presence of potassium fluoride is the method of choice for the synthesis of pyrimidines (**8**, **12**, **20**, **23**). Octupoles comprising 1,3,5-benzene (**8**) and triphenylamine (**12**, **20**) derivatives can be prepared in high yields.

Donor–acceptor substituted benzene derivatives such as 4-nitroaniline are solvatochromic and have nonlinear optical (NLO) properties, cf. [1]. For second harmonic generation (SHG) it is essential that the long-wavelength absorption of the compounds in question is ≤ 415 nm. Unfortunately, the hyperpolarizability β and the second-order nonlinear optical susceptibility $\chi^{(2)}$, respectively, of dipolar π-electron systems increases with a red-shift of λ_{max} [2] (transparency-efficiency trade-off). An interesting possibility to escape the consequences of the transparency-efficiency trade-off, i.e., to obtain materials with λ_{max} and $\lambda_{cut\text{-}off} \leq 415$ nm, having at same time high ß values, are octupolar systems [3]. 1,3,5-Triamino-2,4,6-trinitrobenzene is one of the compounds studied in this regard [4, 5]. It absorbs at shorter wavelengths than 4-nitroaniline (PNA) and its ß value is twice as high as that of PNA.

We have shown previously [7] that donor–acceptor substituted 2,5-diarylpyrimidines (diazaterphenyls) having interesting NLO properties (high ß values at $\lambda_{max} <$ 430 nm) can readily be prepared by the condensation of amidines with vinamidinium salts. We wanted now to apply this method for the synthesis of octupoles. To this end, the trisvinamidinium salt **1** was prepared by reaction of 1,3,5-benzene triacetic acid [8] with the dimethylformamide–oxalyl chloride reagent (Scheme 1).

The X-ray analysis of **1** shows (Figure 1), that the planes formed by the dimethylamino groups of the vinamidinium moieties are twisted against one another by 18.18°. The plane formed by the carbon atoms of the vinamidinium moieties are twisted against the plane of the benzene ring by 70.77°. The strong steric interference of the vinamidinium groups of **1**, an indication of which is the blue-shifted λ_{max}, as compared to that of **2**, reduces the resonance interaction in the vinamidinium moeties and this implies that **1** is more reactive than **2**. This is born out by the reaction of **1** with 4-methoxybenzamidine to form 1,3,5-benzene-tris[2-(4-methoxyphenyl)-5-pyrimidine] **4** in 63% yield (Scheme 2). Besides being a novel type of octupole, **1** belongs to the class of star-shaped compounds that can be used as core-groups of dendrimers.



Scheme 1

The hyperpolarizability ß of **1** was measured [9] using the Hyper-Raleigh scattering (HRS) technique [10]. **1** can be viewed as a derivative of the trimethylenemeth-

[1]) Presented in part at the 2nd Iminiumsalz-Tagung in Stimpfach–Rechenberg, Germany (September 20–22, 1995)

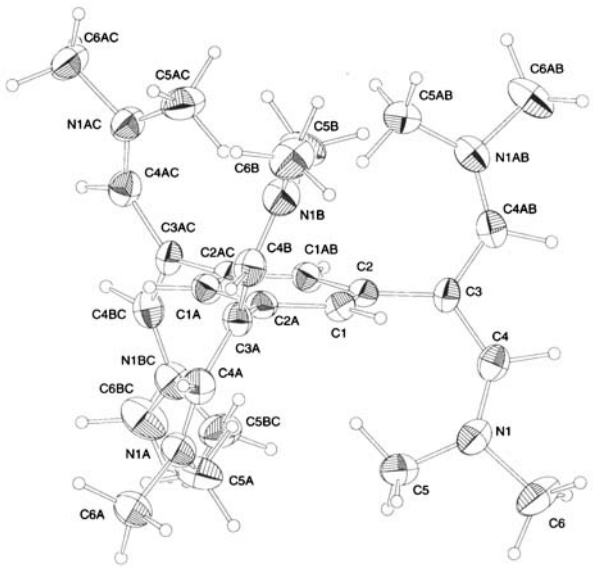
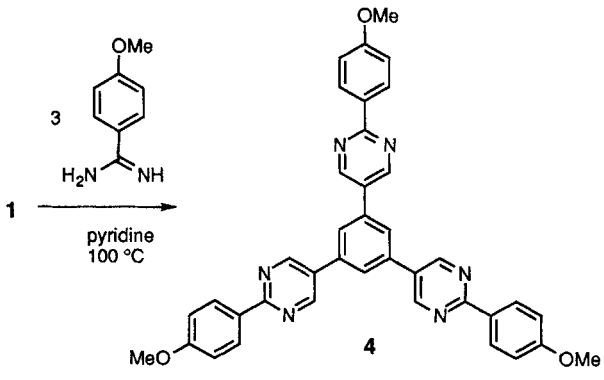


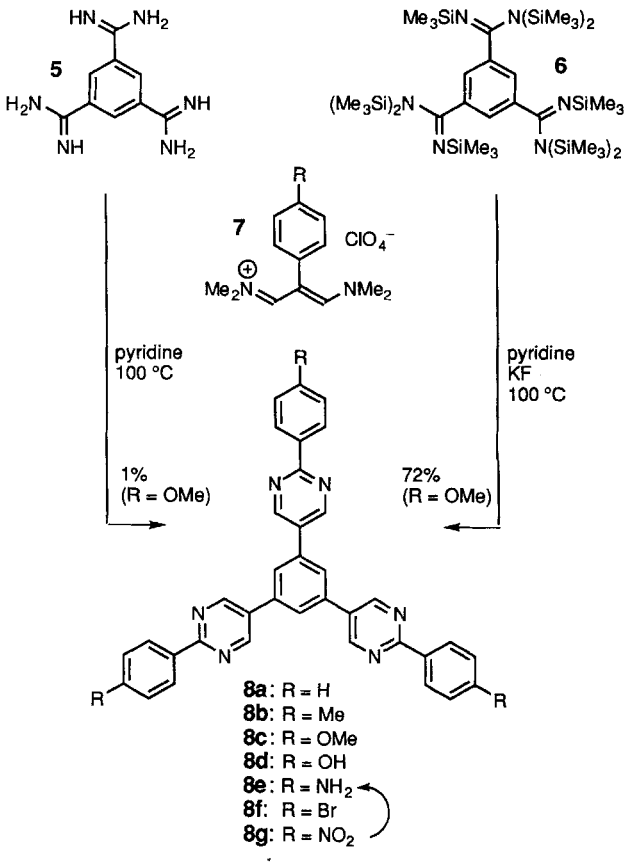
Fig. 1 Structure of **1** in the crystal (Ortep)



Scheme 2

ane dication salt **3** and as a derivative of the mesitylene trianion as well. Accordingly, the ß value of **1** is roughly three times that of **3**.

Attempts to synthesize the isomer **8c** of **4** by condensation of 1,3,5-benzenetriscarboxamidine **5** with the corresponding vinamidinium salt **7c**, resulted in a frustratingly low yield of 1% (Scheme 3). Obviously, the vinamidinium salt **7c** is much less reactive than **1**. In order to overcome this problem we decided to use *N,N,N'*-tris(trimethylsilyl)amidines [11] for the condensation with vinamidinium salts. Thus, the reaction of **6** [IIb] with **7c** in the presence of potassium fluoride provided **8** in 72% yield. This very good result demonstrates quite clearly, that the condensation of vinamidinium salts with *N,N,N'*-tris(trimethylsilyl)amidines is the method of choice for the synthesis of pyrimidines. Further compounds **8** could be prepared in the same way with 2-arylvinamidinium salts **7** as well as compounds **9** using 2-cyano- and 2-nitro-vinamidinium salts.



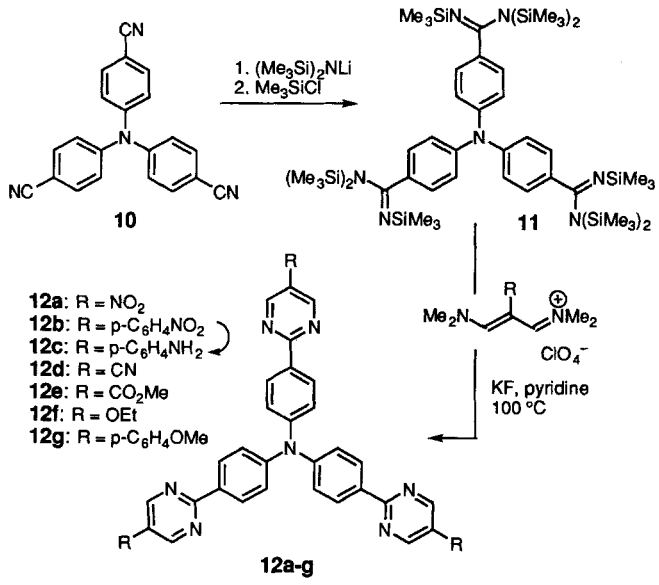
Scheme 3

Reduction of **8g** delivers the triamine **8e** which can be treated with triphenylpyrylium tetrafluororborate to give rise to the tripyridinium salt **8h**.

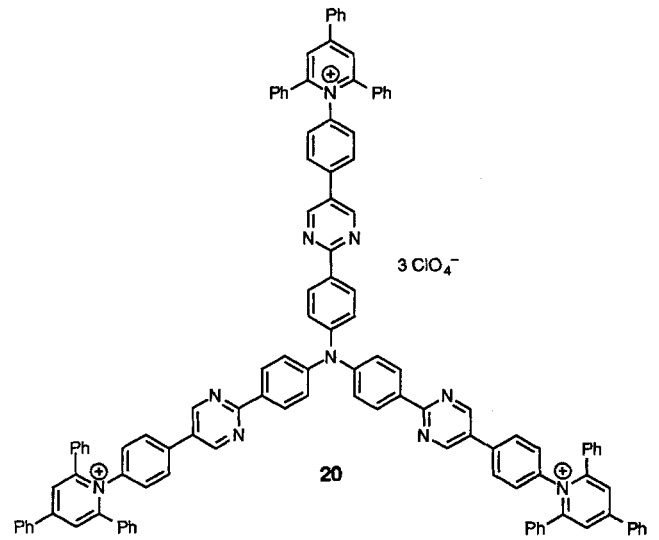
Starting from tricyanotriphenylamine **10** [12] (when prepared from triiodotriphenylamine [13] instead of tribromotriphenylamine with CuCN in DMF, there is no need to purify the compound through sublimation and chromatography) the per(trimethylsilyl)amidine **11** was prepared using the standard procedure. Its condensation with vinamidinium salts in the presence of potassium fluoride gave rise to 4,4',4"-tris(pyrimid-2-yl)triphenylamines **12** in good yields (Scheme 4).

12b can be reduced with stannous dichloride to provide the corresponding triamino derivative **12c** which in turn can be treated with 2,4,6-triphenylpyrylium tetrafluoroborate to produce the tripyridinium salt **20**.

The dipolar diazaterphenyl derivative **14** absorbs at shorter wavelengths than the phenylpyrimidine derivative **13** ($\Delta\lambda$ = 46 nm) and the same is true for the corresponding octupoles **12c** and **12a** (cf. Table 1). With related terphenyl and biphenyl derivatives the hypsochromic shift is much smaller ($\Delta\lambda$ = 12 nm [2]. The fact that the octupolar compounds **12a**, **12b**, **12d** and **12e** have roughly the same λ_{max} as their dipolar analogues **13–16** but higher hyperpolarizabilities ß shows that octupoles are promising candidates for SHG.

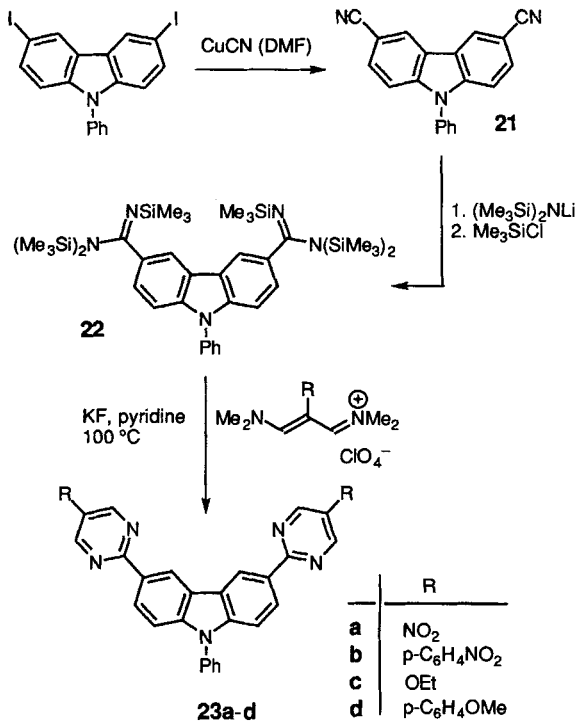


Scheme 4



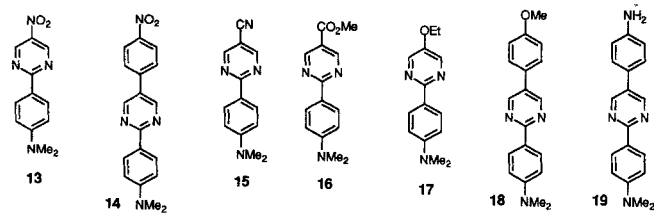
In contrast to the situation with dipolar systems the donor substituted diazaterphenylderivative **18** absorbs at longer wavelengths than the phenylpyrimidine derivative **17**.

Another application of the new pyrimidine synthesis is the preparation of new carbazole derivatives. Starting material is 3,6-dicyano-*N*-phenylcarbazol **21**, prepared from 3,6-diiodo-*N*-phenylcarbazol [14] with CuCN in DMF, that can be transformed into *N*-phenylcarbazolyl-3,6-bis[*N*,*N*,*N'*-tris(trimethylsilyl)-carboxamidine] **22** the in situ condensation of which with vinamidinium salts in the presence of KF gives rise to the carbazole derivatives **23** (Scheme 5).



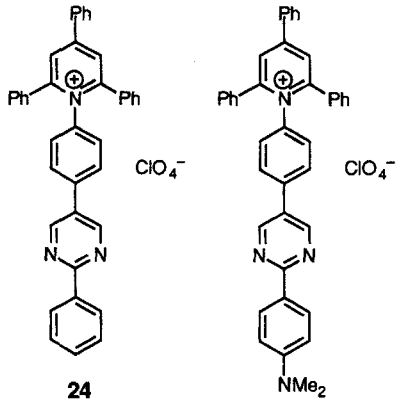
Scheme 5

Table 1 UV/VIS spectra ($\lambda_{max}/\lambda_{cutoff}$ [nm], in DMSO) of dipolar (**13–19**) *vers.* corresponding octupolar compounds (**12a–g**)



13	**14**	**15**	**16**	**17**	**18**	**19**
448/595	402/495	394/484	388/458	335/380	362/415	429/435
12a	**12b**	**12d**	**12e**	**12f**	**12g**	**12c**
450/610	417/530	417/485	407/480	372/420	392/470	399/475

Cyclovoltammetric studies showed that **8h** can be irreversibly reduced at –0.81 V and reversibly/irreversibly oxidized at 4.48/0.91V. Since the reference compound **24** behaves similar (0.37_{rev}/0.66_{irrev} V; -0.78_{irrev} V) it has to be assumed that in **8h** the 3 substructures are electronically independent.



12g can be quasireversibly reduced at –0.51V and **12d** reversibly oxidized at 1.29 V. With **20** three irreversible reduction waves (–0.81, –1.02 V) and one quasireversible oxidation wave (1.04 V) are detected. In contrast to **20**, **25** displays one quasi-reversible reduction wave (–1.33 V), two quasireversible oxidation waves (0.53, 1.17 V) and one irreversible oxidation wave (0.98 V). Obviously, with **20** the 3 substructures interact electronically by way of the central nitrogen atom.

Acknowledgment: This work has been supported by the Volkswagen-Stiftung, the Deutsche Forschungsgemeinschaft and the Fonds der chemischen Industrie.

Experimental

NMR spectra were recorded on a Bruker WP 80 (80MHz) and a Varian VXR 400 S (400 MHz); IR spectra on a Perkin-Elmer 125 and a Bruker IFS 45; UV/VIS spectra on a Zeiss DMR 10 and a Perkin-Elmer model Lambda 3; mass spectra on a AEJ, MS 902, and a MAT 95Q, Cs-Gun). Cyclovoltammetric measurement were performed with a Bioanalytical Systems CV-1B, using a Pt working electrode and an Ag/AgCl reference electrode (Bu_4NPF_6). Melting points were obtained on a Büchi SMP-20 and a Reichert Thermovar BHT apparatus.

Crystal data for 1

$C_{27}H_{45}N_6 \times 3\ ClO_4$, M = 752.05, rhomboedric, space group $R3_C$ (167), a = 1224.8(3) pm, α= 19.16(2)(2)°, V = 1.8373 nm^3, Z = 2, D_c = 1.259 g cm^{-3}, μ = 3.100 cm^{-1}, F (000)= 792.00, $2\Theta_{max}$ = 4-46°, ω-scan, crystal dimensions 7/30 x 20/30x24/30 mm, maximum measuring time 180 s, graphite monochromated Mo-K_α radiation. 2829 measured (h, k, ± l), 838 independent reflections, 762 classed as observed [I > 3σ (I])1; refined parameters: 75. Solution of structure: SHELXS-76, SIR. R = 0.1255, R_w = 0.1115; largest residual electron density ρ = +0.575/–0.679 e pm^{-3} 10^6. Supplementary material on the X-ray structure determination may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD ....., the names of the authors and the journal citation.

2,2',2''-(1,3,5-Benzene)-tris-(3-dimethylamino-N,N-dimethylpropene-2-eneiminium) triperchlorate (**1**)

1,3,5-benzenetriacetic acid (2.0 g, 7.9 mmol) was added to the reagent prepared from dimethylformamide (4.4. ml, 57.2 mmol) and oxalyl chloride (5 ml, 56.3 mmol) and the mixture refluxed for 2 days. After cooling, a solution of sodium perchlorate monohydrate (4.0 g, 28.5 mmol) in water (20 ml) was added dropwise (cooling with ice). The precipitate was collected by filtration, washed with water, stirred with a little methanol and dried in vacuo.
Colorless powder, m.p. 208 °C, yield 2.0 g (34%). –
IR (KBr): ν = 3020 cm^{-1}, 2990, 2942, 2810, 1597, 1490 1443, 1400, 1293, 1286, 1216, 1088, 825, 775, 625. – UV (DMSO): λ_{max} = 307 nm. – ^{1}H NMR ([D_6]DMSO): δ = 7.76 (s, 6 H, vinyl-H), 7.29 (s, 3 H, benzene-H), 3.32 (d, 36 H, NMe_2).

$C_{27}H_{45}C_{13}N_6O_{12}$	Calcd.	C 43.12	H 6.03	N 11.17
(752.1)	Found	C 43.30	H 6.05	N 11.00

1,3,5-Benzene-tris[2-(4-methoxyphenyl)-5-pyrimidine (**4**)

A suspension of **1** (2.0 g, 2.66 mmol) and 4-methoxybenzamidinium chloride [x] in 50 ml of pyridine was heated to 100 °C for 10 h. After cooling, the mixture was poured into water, the precipitate collected by filtration, dissolved in acetonitrile and deposited again by addition of water.
Colorless powder, m.p. 158 °C, yield 1.06 g (63%). –
IR (KBr): ν = 3010 cm^{-1}, 2965, 2940, 2840, 1606, 1582, 1539, 1515, 1456, 1423, 1384, 1334, 1255, 1168, 1028, 878, 846, 798, 709, 653. – UV (DMSO): λ_{max} = 318 nm. – ^{1}H NMR ([D_6]DMSO): δ = 9.20 (s, 6 H, pyrimidine-H), 8.28 (d, 6 H, phenylene-H), 8.13 (s, 3 H, benzene-H), 6.95 (d, 6 H, phenylene-H), 3.76 (s, 9 H, OCH_3). – MS (70 eV): *m/z* (%) = 630.3 (100) [M^+].

$C_{39}H_{30}N_6O_{33}$x0.33H_20	Calcd.	C 73.57	H 4.85	N 13.20
(636.7)	Found	C 73.67	H 5.00	N 13.17

1,3,5-Benzene-tris-(5-phenyl-2-pyrimidine) (**8a**)
General procedure for 8a–8d. 8f. 8g. 9a. 9b. 12a. 12b. 12d–12g. 23a–23d

7a [15] (2.4 g, 7.9 mmol) and potassium fluoride (1.5 g, 25.8 mmol) were added to a suspension of **6** (2.2 g, 2.6 mmol) in pyridine (50 ml) and the mixture stirred at 100 °C for 6 h. After cooling, the product was poured into water (100 ml), the precipitate collected by filtration, washed with water and methanol and recrystallized from *N,N*-dimethylformamide.
Colorless powder, m.p. >300 °C, yield 0.98 g (70%). –
IR (KBr): ν = 3033 cm^{-1}, 1581, 1563, 1443, 1417, 797 747, 697.– V (DMSO): λ_{max} = 296.5 nm. – ^{1}H NMR ([D_6]DMSO): δ = 9.60 (s, 3 H, benzene-H), 9.15 (s, 6 H, pyrimidine-H), 7.76

(m, 6 H, phenyl-H), 7.43 (m, 9 H, phenyl-H). – MS (70 eV): *m/z* (%)= 540 (100) [M+].

$C_{36}H_{24}N_6 \times H_2O$	Calcd.	C 77.40	H 4.69	N 15.04
(558.6)	Found	C 77.09	H 4.60	N 14.92

1,3,5-Benzene-tris-[5-(4-tolyl)-2-pyrimidine] (**8b**)

With **7b** [15] (2.5 g, 7.9 mmol).
Colorless powder, m.p. 260 °C, yield 1.06 g (70%). – IR (KBr): ν = 3019 cm^{-1}, 2920, 1579, 1452, 1420, 1281, 817, 794. – UV (DMSO): λ_{max}= 303 nm. – ^1H NMR ([D$_6$]MSO): δ = 9.55 (s, 3 H, benzene-H), 9.10 (s, 6 H, pyrimidine-H), 7.55 (d, 6 H, phenylene-H), 7.30 (d, 6 H, phenylene-H), 2.38 (s, 9 H, CH_3).

$C_{39}H_{30}N_6 \times 0.33\,H_2O$	Calcd.	C 79.57	H 5.15	N 14.28
(588.7)	Found	C 79.81	H 5.36	N 14.41

1,3,5-Benzene-tris-[5-(4-methoxyphenyl)-2-pyrimidine] (**8c**)

With **7c** [15] (2.7 g, 8 mmol).
Colorless powder, m.p. 245 °C, yield 1.18 g (72%). – IR (KBr): ν = 3020 cm^{-1}, 3000, 2935, 2840, 1610, 1579, 1517, 1455, 1425, 1412, 1270, 1181, 1033, 830, 794, 720. – UV (DMSO): λ_{max} = 309 nm. – ^1H NMR ([D$_6$]DMSO): δ = 9.58 (s, 3 H, benzene-H), 9.10 (s, 6 H, pyrimidine-H), 7.70 (d, 6 H, phenylene-H), 7.03 (d, 6 H, phenylene-H), 3.20 (s, 9 H, OCH3). – MS (70 eV): *m/z* (%)= 630.3 (100) [M+].

$C_{39}H_{30}N_6O_3$	Calcd.	C 74.27	H 4.79	N 13.33
(630.7)	Found	C 74.26	H 4.86	N 13.15

1,3,5-Benzene-tris-[5-(4-hydroxyphenyl)-2-pyrimidine] (**8d**)

With **7d** [15] (2.6 g, 8.1 mmol).
Colorless powder, m.p. >300 °C, yield 0.68 g (45%). – IR (KBr): ν = 3424 cm^{-1}, 3020, 1653, 1610, 1589, 1417, 1273, 1177, 833, 792, 730. – UV (DMSO): λ_{max}= 327 nm. – ^1H NMR ([D$_6$]DMSO): δ = 9.50 (s, 3 H, benzene-H), 9.10 (s, 6 H, pyrimidine-H), 7.63 (d, 6 H, phenylene-H), 6.90 (d, 6 H, phenylene-H), 3.70 (s, broad, 3 H, OH). – MS (70 eV): *m/z* (%) = 588 (100) [M+].

$C_{36}H_{24}N_6O_3 \times 1.5\,H_2O$	Calcd.	C 70.23	H 4.42	N 13.65
(615.6)	Found	C 70.38	H 4.63	N 13.48

1,3,5-Benzene-tris-[5-(4-bromophenyl)-2-pyrimidine] (**8f**)

With **7f** [15] (3.0 g, 7.9 mmol).
Colorless powder, m.p. 200 °C, yield 1.43 g (71%). – IR (KBr): ν = 3022 cm^{-1}, 1581, 1534, 1453, 1420, 1281, 1075, 999, 824, 670. – UV (DMSO): λ_{max} = 365 nm. –^1H NMR ([D$_6$]DMSO): δ = 9.74 (s, 3 H, benzene-H), 9.34 (s, 6 H, pyrimidine-H), 7.87 (d, 6 H, phenylene-H), 7.78 (d, 6 H, phenylene-H). – MS (70 eV): *m/z* (%)= 780 (36.89) [M+, 3 ^{81}Br], 778 (99.8) [M+, ^{79}Br, 2 ^{81}Br], 775.9 (100) [M+, 2^{79}Br, ^{81}Br] 774 (31.44) [M+, 3^{79}Br].

$C_{36}H_{21}N_6Br_3$	Calcd.	C 55.62	H 2.72	N 10.81	Br 30.84
(777.3)	Found	C 55.62	H 2.96	N 10.90	Br 30.34

1,3,5-Benzene-tris-[5-(4 -nitrophenyl)-pyrimidine] (**8g**)

With **7g** [15] (2.80 g, 8 mmol).
Colorless powder, m.p. >300 °C, yield 1.40 g (80%). – IR (KBr): ν = 3441 cm^{-1}, 3083, 1601, 1581, 1519, 1455, 1423, 1341, 1280, 850, 797. – UV (DMSO): λ_{max} = 324 nm. – ^1H NMR ([D$_6$]DMSO): δ = 9.77 (s, 3 H, benzene-H), 9.41 (s, 6 H, pyrimidine-H), 8.37 (d, 6 H, phenylene-H), 8.16 (d, 6 H, phenylene-H). – MS (70 eV): *m/z* (%)= 675 (100) [M+].

$C_{36}H_{21}N_9O_6$	Calcd.	C 63.99	H 3.13	N 18.65
(675.6)	Found	C 63.95	H 3.47	N 18.30

1,3,5-Benzene-tris-(5-cyano-2-pyrimidine) (**9a**)

With 2-cyano-3-dimethylamino-*N,N*-dimethyl-prop-2-ene-iminium perchlorate [16] (2.0 g, 7.9 mmol).
Colorless powder, m.p. >300 °C, yield 0.68 9 (68%). – IR (KBr): ν = 2234 cm^{-1}, 1578, 1533, 1452, 1419, 1288, 1215, 925, 796, 762. – UV (DMSO): λ_{max} = 288 nm. –^1H NMR ([D$_6$]DMSO): δ = 9.70 (s, 3 H, benzene-H), 9.40 (s, 6 H, pyrimidine-H).

$C_{21}H_9N_9$	Calcd.	C 65.11	H 2.34	N 32,54
(387.4)	Found	C 65.34	H 2.34	N 32.38

1,3,5-Benzene-tris-(5-nitro-2-pyrimidine) (**9b**)

With 3-dimethylamino-*N,N*-dimethyl-2-nitroprop-2-eneiminium perchlorate [16] (2.17 g, 8 mmol).
Colorless powder, m.p. 325 °C, yield 0.87 g (75%). – IR (KBr): ν = 3080 cm^{-1}, 3040, 1604, 1582, 1563, 1517, 1415, 1347, 1283, 1148, 868, 831, 793. – UV (DMSO): λ_{max} = 314 nm. – ^1H NMR ([D$_6$]DMSO): δ = 9.66 (s, 3 H, benzene-H), 9.63 (s, 6 H, pyrimidine-l-l).

$C_{18}H_9N_9O_6 \times 0.33$ DMF	Calcd.	C 48.38	H 2.42	N 27.72
(471.7)	Found	C 48.64	H 2.69	N 28.06

1,3,5-Benzene-tris-[5-(4-aminophenyl)-2-pyrimidine] (**8e**)

Stannous chloride dihydrate (10.0 g, 44.3 mmol) was added to the suspension of **8g** (2.0 g, 3 mmol) in conc. HCl (50 ml) and the mixture heated to 100 °C for 3 h. After cooling, the precipitate was collected by filtration, dried *in vacuo* and refluxed in DMF for 1 h. After filtration, the solvent was removed in vacuo and the residue recrystallized from acetonitrile.
Pale yellow powder, m.p. >300 °C, yield 1.23 g (70%). IR (KBr): ν = 3356 cm^{-1}, 3242, 3029, 1610, 1536, 1522, 1456, 1417, 1288, 1184, 828, 799. – UV (DMSO): λ_{max}= 365 nm. – ^1H NMR ([D$_6$]DMSO): δ = 9.43 (s, 3 H, benzene-H), 8.98 (s, 6 H, pyrimidine-H), 7.45 (d, 6 H, phenylene-H), 6.65 (d, 6 H, phenylene-H), 5.25 (s, broad, 6 H, NH_2). – MS (70 eV): *m/z* (%) = 585 (100) [M+].

$C_{36}H_{27}N_9 \times 2.1\,H_2O$	Calcd.	C 69.34	H 5.04	N 20.21
(623.5)	Found	C 69.04	H 4.57	N 20.10

1,3,5-Benzene-tris-{5-[4-(2,4,6-triphenyl-1-pyridinio)-phenyl]-2-pyrimidine} trisperchlorate (**8h**)

A suspension of **8e** (1.26 g, 2.15 mmol) and triphenylpyrylium tetrafluoroborate (2.6 g, 6.56 mmol) in pyridine (30 ml) was stirred at 100 °C for 2 d. After cooling and filtration a solution of sodium perchlorate monohydrate (0.4 g, 2.8 mmol) in water (10 ml) was added and the solvents removed by destillation *in vacuo* (not to complete dryness!). The residue was triturated in water and the undissolved material removed by filtration. A solution of sodium perchlorate monohydrate (1.0

g, 7.1 mmol) in water(10 ml) was added, the colorless precipitate collected by filtration, washed with water and recrystallized from acetonitrile–methanol. Colorless powder, m.p. 310 °C, yield 2.3 g (61%).
IR (KBr): ν = 3065 cm^{-1}, 1621, 1598, 1577, 1423, 1122, 1096, 850, 775, 771 624. – UV (DMSO): λ_{max} = 315 nm. – ^1H NMR ([D_6]DMSO): δ = 9.63 (s, 3 H, benzene-H), 9.20 (s, 6 H, pyrimidine-H), 8.66 (d, 6 H, pyridinium-H), 8.44–8.25 (m, 6 H), 7.81–7.24 (m, 51 H).

$C_{105}H_{72}C1_3N_9O_{12}$×2 H_2O	Calcd.	C 70.29	H 4.27	N 7.03
(1794.2)	Found	C 70.13	H 4.25	N 7.32

Triphenylamino-4,4,4"-tris-[N,N,N'-tris -(trimethylsilyl)-carboxamidine] (**11**)

Lithium hexamethyidisilazene (2.5 g, 14.9 mmol) was added to a suspension of 1.5 g tricyanotriphenylamine (**10**) (1.5 g, 4.7 mmol) in 50 ml dry ether and the mixture stirred at room temperature for 12 h. The solvent was removed *in vacuo*, toluene (50 ml) and chlorotrimethylsilane (1.9 ml, 15 mmol) added to the residue and the mixture refluxed for 5 h. The solvent was distilled off *in vacuo* and the orange residue (yield 4.8 g) used according to the "general procedure" (cf. **8a**).

Tris-[4-(5-nitro-2-pyrimidinyl)-phenyl]-amine (**12a**)

With **11** (4.8 g, 4.7 mmol) and *N,N*-dimethyl-3-dimethylamino-2-nitroprop-2-eneiminium perchlorate [16] (4.2 g, 15.5 mmol).
Brickred powder, m.p. >300 °C, yield 2.05 g (71%). –
IR (KBr): ν = 1585 cm^{-1}, 1560, 1420, 1342, 1316, 856, 798. – UV (DMSO): λ_{max} = 450 nm; UV (toluene): λ_{max} = 288 nm, 451. – ^1H NMR ([D_6]DMSO): δ = 9.45 (s, 6 H, pyrimidine-H), 8.39 (d, 6 H, phenylene-H), 7.23 (d, 6 H, phenylene-H).

$C_{30}H_{18}N_{10}O_6$	Calcd.	C 58.63	H 2.95	N 22.79
(614.5)	Found	C 59.07	H 3.20	N 22.55

Tris-[4-[5-(4-nitrophenyl)-2-pyrimidinyl]-phenyl]-amine (**12b**)

With **7g** [15] (5.4 g, 15.5 mmol).
Orange powder, m.p. 204 °C, yield 2.81 g (71%). –
IR (KBr): ν = 1597 cm^{-1}, 1578, 1516, 1428, 1342, 1176, 855, 798. – UV (DMSO): λ_{max} = 307 nm, 417; UV (toluene): λ_{max} = 303 nm, 422. – ^1H NMR ([D_6]DMSO): δ = 9.14 (s, 6 H, pyrimidine-H), 8.36 (d, 6 H, phenylene-H), 8.25 (d, 6 H, phenylene-H), 8.00 (d, 6 H, phenylene-H), 7.18 (d, 6 H, phenylene-H).

$C_{48}H_{30}N_{10}O_6$	Calcd.	C 68.40	H 3.59	N 16.62
(842.8)	Found	C 68.20	H 3.73	N 16.41

Tris-[4-(5-cyano-2-pyrimidinyl)-phenyl]-amine (**12d**)

With 2-cyano-*N,N*-dimethyl-3-dimethylaminoprop-2-eneiminium perchlorate [16] (3.7 g, 14.7 mmol). Chromatography on silica gel, eluent $CHC1_3$.
Yellow powder, m.p. 275 °C (from DMF–acetonitrile), yield 1.77 g (68%). –
IR (KBr): ν = 2231 cm^{-1}, 1572, 1424, 1317, 1284, 1176, 798. – UV (DMSO): λ_{max} = 417 nm; UV (acetonitrile): λ_{max} = 410 nm; UV (toluene): λ_{max} = 411 nm. – ^1H NMR ([D_6]DMSO): δ = 9.24 (s, 6 H, pyrimidine-H), 8.36 (d, 6 H, phenylene-H), 7.23 (d, 6 H, phenylene-H). – MS (70 eV): *m/z* (%) = 554 (100) [M^+].

$C_{33}H_{18}N_{10}$	Calcd.	C 71.47	H 3.27	N 25.26
(554.6)	Found	C 71.33	H 3.52	N 24.97

Tris-[4-(5-methoxycarbonyl-2-pyrimidinyl)-phenyl]-amine (**12e**)

With 3-dimethylamino-2-methoxycarbonyl-*N,N*-dimethyl-prop-2-eneiminium perchlorate [17] (4.44 g, 15.6 mmol).
Yellow powder, m.p. 288 °C (from DMF–acetonitrile), yield 2.33 g (76%). –
IR (KBr): ν = 2960 cm^{-1}, 2935, 2865, 1730, 1577, 1422, 1285, 1177, 1133, 802, 756, 728. – UV (DMSO): λ_{max} = 349 nm; UV (acetonitrile): λ_{max} = 401 nm; UV (toluene): λ_{max} = 414 nm. – ^1H NMR ([D_6]DMSO): δ = 9.15 (s, 6 H, pyrimidine-H), 8.36 (d, 6 H, phenylene-H), 3.85 (s, 9 H, CH_3). – MS (70 eV): *m/z* (%) = 653.2 (100) [M^+].

$C_{36}H_{27}N_7O_6$×0.5 H_2O	Calcd.	C 65.25	H 4.26	N 14.80
(662.7)	Found	C 65.51	H 4.34	N 14.67

Tris-[4-(5-ethoxy2-pyrimidinyl)-phenyl]- amine (**12f**)

With 3-dimethylamino-2-ethoxy-*N,N*-dimethyl-prop-2-eneiminium perchlorate [18] (4.20 g, 15.5 mmol). Chromatography on silica gel, eluent $CHC1_3$.
Colorless powder, m.p. 168 °C (from THF), yield 1.15 g (40%). –
IR (KBr): ν = 3050 cm^{-1}, 2981, 2940, 2900, 1599, 1541, 1508, 1433, 1386, 1316, 1272, 1177, 1040, 847, 790, 736. – UV (DMSO): λ_{max} = 265 nrn, 372; UV (acetonitrile): λ_{max} = 366 nm; UV (toluene): λ_{max} = 378 nm.– ^1H NMR ([D_6]DMSO): δ = 8.55 (s, 6 H, pyrimidine-H), 8.23 (d, 6 H, phenylene-H), 7.15 (d, 6 H, phenylene-H), 4.23 (q, 2 H, OCH_2), 1.41 (t, 3 H, CH_3).

$C_{36}H_{33}N_7O_3$×0.5 H_2O	Calcd.	C 69.66	H 5.52	N 15.79
(620.7)	Found	C 69.87	H 5.67	N 15.63

Tris-[4-[5-(4-methoxyphenyl)-2-pyrimidinyl]-phenyl]-amine (**12g**)

With **7c** [15] (5.20 g, 15.6 mmol).
Ochre powder, m.p. 170 °C, yield 2.58 g (69%). –
IR (KBr): ν = 2834 cm^{-1}, 1608, 1579, 1517, 1427, 1251, 1177, 828, 797. – UV (DMSO): λ_{max} = 297 nm, 392; UV (acetonitrile): λ_{max} = 386 nm; UV (toluene): λ_{max} = 292 nm, 400. – ^1H NMR ([D_6]DMSO): δ = 9.16 (s, 6 H, pyrimidine-H), 8.43 (d, 6 H, phenylene-H), 7.80 (d, 6 H, phenylene-H), 7.29 (d, 6 H, phenylene-H), 7.11 (d, 6 H, phenylene-H), 3.84 (s, 9 H, OCH_3).

$C_{51}H_{39}N_7O_3$	Calcd.	C 76.77	H 4.93	N 12.29
(797.9)	Found	C 76.67	H 5.14	N 12.42

Tris-[4-[5-(4 -aminophenyl)-2-pyrimidinyl]-phenyl]-amine (**12c**)

Same procedure as for **8e** with **12b** (2.0 g, 2.4 mmol). The neutralized and dried precipitate was extracted (Soxhlet) with acetonitrile (200 ml) for 2 d.
Pale yellow powder, m.p. 220 °C, yield 0.9 g (50%). –
IR (KBr): ν = 3439 cm^{-1}, 3390, 3033, 1608, 1579, 1428, 1317, 1285, 1177, 827, 797. – UV (DMSO): λ_{max} = 399 nm. – ^1H

NMR ([D$_6$]DMSO): δ = 8.96 (s, 6 H, pyrimidine-H), 8.33 (d, 6 H, phenylene-H), 7.48 (d, 6 H, phenylene-H), 7.18 (d, 6 H, phenylene-H), 6.68 (d, 6 H, phenylene-H), 4.25 (s, broad, 6 H, NH_2). – MS (70 eV): *m/z* (%)= 752 (12.64) [M^+].

$C_{48}H_{36}N_{10}\times1.5\ H_2O$	Calcd.	C 73.92	H 5.04	N 17.96
(779.9)	Found	C 73.78	H 4.97	N 18.07

Tris-{4-[5-[4-(2,4,6- triphenyl-1-pyridinio)-phenyl]-phenyl}-amine trisperchlorate (**20**)

Same procedure as for **8h** with **12c** (1.0 g, 1.33 mmol).
Yellow powder, m.p. 300 °C, yield 1.79 g (70%).–
IR (KBr): ν = 3070 cm^{-1}, 1621, 1598, 1579, 1429, 1122, 1096, 847, 798. – UV (DMSO): λ_{max} = 308 nm 404. – ^{1}H NMR ([D$_6$]DMSO): δ = 9.14 (s, 6 H, pyrimidine-H), 8.72 (s, 6 H, pyridinium-H), 8.38 (d, 12 H, phenylene-H), 7.80 (d, 6 H, phenylene-H), 7.72–7.38 (m, 51 H), 7.27 (d, 6 H, phenylene-H).

$C_{117}H_{81}C_{13}N_{10}O_{12}\times3\ H_2O$	Calcd.	C 70.99	H 4.43	N 7.08
(1979.4)	Found	C 70.87	H 4.33	N 7.28

2-(4-Dimethylaminophenyl)-5-nitropyrimidine (**13**)

N,N-Dimethyl-3-dimethylamino-2-nitroprop-2-eneiminium perchlorate [16] (1.55 g, 5.7 mmol) was added to a suspension of 4-dimethylaminobenzamidinium chloride [11c] (1.14 g, 5.7 mmol) in pyridine (30 ml) and the mixture heated to 100 °C for 10 h. The solvent was distilled off *in vacuo*, the residue triturated with water, the solid collected by filtration and washed with methanol.
Dark red powder, m.p. 298 °C (from acetonitrile), yield 0.90 g (65%). –
IR (KBr): ν = 3070 cm^{-1}, 2910, 2870, 1606, 1534, 1422, 1367, 1343, 1326, 1188, 1149, 833, 791. – UV (DMSO): λ_{max} = 448 nm;UV (toluene): λ_{max} =435 nm. – ^{1}H NMR ([D$_6$]DMSO): δ = 9.23 (s, 2 H, pyrimidine-H), 8.23 (d, 2 H, phenylene-H), 6.75 (d, 2 H, phenylene-H), 3.00 (s, 6 H, $N(CH_3)_2$).

$C_{12}H_{12}N_4O_2$	Calcd.	C 59.00	H 4.95	N 22.93
(244.3)	Found	C 59.47	H 5.01	N 22.75

2-(4-Dimethylaminophenyl)-5-(4-nitrophenyl)-pyrimidine (**14**)

Lithium hexamethyldisilazene (2.4 g, 14.3 mmol) was added to a suspension of 4-dimethylaminobenzonitrile (2 g, 13.7 mmol) in dry ether (50 ml) and the mixture stirred at room temperature for 10 h. The solvent was removed *in vacuo*, toluene (50 ml) and chlorotrimethylsilane (1.9 ml, 15 mmol) were added and the mixture refluxed for 5 h. The solvent was distilled off *in vacuo* and **7g** [15] (4.76 g, 13.7 mmol), potassium fluoride (2.7 g, 46.5 mmol) and pyridine (50 ml) added to the residue and the mixture stirred at 100 °C for 6 h. After cooling, the product was poured into water (100 ml), the precipitate was collected by filtration and refluxed with DMF for 1 h. The solid material was collected by filtration and washed with methanol.
Red powder, m.p. 322 °C, yield 3.46 g (79%). –
IR (KBr): ν = 3080 cm^{-1}, 2920, 2875, 2830, 1614, 1597, 1583, 1515, 1433, 1372, 1339, 1187, 866, 856, 825, 795. – UV (toluene): λ_{max} = 403 nm. – ^{1}H NMR ([D$_6$]DMSO): δ = 9.05 (s, 2 H, pyrimidine-H), 8.20 (d, 4 H, phenylene-H), 7.93 (d, 2 H, phenylene-H), 6.74 (d, 2 H, phenylene-H), 3.82 (s, 6 H, $N(CH_3)_2$).

$C_{18}H_{16}N_4O_2\times0.25\ H_2O$	Calcd.	C 66.54	H 5.12	N 17.25
(324.9)	Found	C 66.25	H 5.16	N 17.25

5-Cyano-2-(4-dimethylaminophenyl)-pyrimidine (**15**)

Same procedure as for **13** with 2-cyano-*N,N*-dimethyl-3-dimethylaminoprop-2-eneiminium perchlorate [16] (2.2 g, 8.7 mmol).
Yellow powder, m.p. 217 °C, yield 1.22 g (74%). –
IR (KBr): ν = 2920 cm^{-1}, 2875, 2820, 2222, 1808, 1580, 1535, 1515, 1433, 1368, 1183, 833, 793. – UV (DMSO): λ_{max} = 394.5 nm; UV (acetonitrile): λ_{max} = 387 nm; UV (toluene): λ_{max} = 390 nm. – ^{1}H NMR ([D$_6$]DMSO): δ = 9.02 (s, 2 H, pyrimidine-H), 8.21 (d, 2 H, phenylene-H), 6.76 (d, 2 H, phenylene-H), 3.03 (s, 6 H, $N(CH_3)_2$).

$C_{13}H_{12}N_4$	Calcd.	C 69.61	H 5.39	N 24.98
(224.3)	Found	C 69.40	H 5.27	N 25.01

Methyl-2-(4-dimethylaminophenyl)-4-pyrimidinecarboxylate (**16**)

Same procedure as for **14** with 3-dimethylamino-2-methoxycarbonyl-*N,N*-dimethyl-prop-2-eneiminium perchlorate [17] (3.90 g, 13.7 mmol).
Pale yellow powder, m.p. 214 °C, yield 2.82 g (80%). –
IR (KBr): ν = 2910 cm^{-1}, 2820, 1723, 1710, 1611, 1581, 1422, 1366, 1288, 1191, 1134, 798. – UV (DMSO): λ_{max} = 303 nm, 388; UV (acetonitrile): λ_{max} = 380 nm; UV (toluene): λ_{max} = 383 nm. – ^{1}H NMR ([D$_6$]DMSO): δ = 9.00 (s, 2 H, pyrimidine-H), 8.20 (d, 2 H, phenylene-H), 6.70 (d, 2 H, phenylene-H), 3.83 (s, 3 H, OCH_3), 2.98 (s, 6 H, $N(CH_3)_2$).

$C_{14}H_{15}N_3O_2$	Calcd.	C 65.35	H 5.88	N 16.33
(257.3)	Found	C 65.01	H 5.92	N 16.24

2-(4-Dimethylaminophenyl)-4-ethoxypyrimidine (**17**)

Same procedure as for **13** with 3-dimethylamino-2-ethoxy-*N,N*-dimethyl-prop-2-eneiminium perchlorate [18] (1.0 g, 3.7 mmol).
Colorless powder, m.p. 157 °C, yield 0.36 g (40%). –
IR (KBr): ν = 2979 cm^{-1}, 2930, 2895, 2820, 1606, 1530, 1479, 1428, 1393, 1367, 1273, 1185, 1046, 829, 789. – UV (DMSO): λ_{max} = 335 nm; UV (acetonitrile): λ_{max} = 321 nm; UV (toluene): λ_{max} = 323 nm. – ^{1}H NMR ([D$_6$]DMSO): δ = 8.44 (s, 2 H, pyrimidine-H), 8.08 (d, 2 H, phenylene-H), 6.74 (d, 2 H, phenylene-H), 4.17 (q, 2 H, OCH_2), 2.95 (s, 6 H, $N(CH_3)_2$).

$C_{14}H_{17}N_3O$	Calcd.	C 69.11	H 7.04	N 17.27
(243.3)	Found	C 69.32	H 7.26	N 17.07

2-(4-Dimethylaminophenyl)-4-(4-methoxyphenyl)-pyrimidine (**18**)

Same procedure as for **14** with **7c** [15] (4.60 g, 13.8 mmol).
Pale yellow powder, m.p. 216 °C, yield 3.50 g (84%). –
IR (KBr): ν = 3040 cm^{-1}, 2910, 2845, 2810, 1608, 1581, 1429, 1364, 1268, 1244, 1168, 1027, 840, 827, 796. – UV (DMSO): λ_{max} = 287 nm, 362; UV (acetonitrile): λ_{max} = 353 nm; UV (toluene): λ_{max} = 357 nm. – ^{1}H NMR ([D$_6$]DMSO): δ = 8.84 (s, 2 H, pyrimidine-H), 8.13 (d, 2 H, phenylene-H), 7.59 (d, 2 H, phenylene-H), 6.95 (d, 2 H, phenylene-H), 6.69 (d, 2 H,

phenylene-H), 3.75 (s, 3 H, OCH_3), 2.94 (s, 6 H, $N(CH_3)_2$).

$C_{19}H_{19}N_3O$	Calcd.	C 74.72	H 6.27	N 13.76
(305.4)	Found	C 74.48	H 6.23	N 13.68

2-(4-Dimethylaminophenyl)-4-(4-aminophenyl)-pyrimidine (**19**)

Stannous chloride dihydrate (7.10 g, 31.5 mmol) was added to the suspension of **14** (2.0 g, 6.24 mmol) in conc. HCl (50 ml) and the mixture heated to 100 °C for 3 h. After cooling, the precipitate was collected by filtration and triturated with 5% aqueous $NaHCO_3$ (50 ml). The remaining solid material was filtered off, dried in vacuo and refluxed in DMF for 1 h. The solution was filtered and the filtrate was evaporated to dryness *in vacuo*.

Pale yellow powder, m.p. 235 °C (from acetonitrile), yield 1.10 g (61%). –

IR (KBr): $\nu = 3458\ cm^{-1}$, 3387, 3040, 2900, 2865, 2815, 1610, 1582, 1530, 1431, 1361, 1191, 827, 794, 657. – UV (DMSO): $\lambda_{max} = 369$ nm. – ^1H NMR ([D_6]DMSO): $\delta = 9.90$ (s, 2 H, pyrimidine-H), 8.19 (d, 2 H, phenylene-H), 7.45 (d, 2 H, phenylene-H), 6.75 (d, 2 H, phenylene-H), 6.63 (d, 2 H, phenylene-H), 5.33 (s, 2 H, NH_2), 2.95 (s, 6 H, $N(CH_3)_2$).

$C_{18}H_{18}N_4 \times 0.33\ H_2O$	Calcd.	C 72.94	H 6.35	N 18.90
(296.4)	Found	C 72.64	H 6.25	N 18.82

N-Phenylcarbazole-3,6-dicarbonitrile (**21**)

A suspension of 3,6-diiodo-*N*-phenylcarbazol [14] (4.0 g, 8.1 mmol) and cuprous cyanide (2.0 g, 22 mmol) in DMF (70 ml) was refluxed under nitrogen for 5 h. After addition of a solution ferric chloride hexahydrate (5.0 g, 18.5 mmol) in ethanol (60 ml) refluxing was continued for 5 min. The solvent was distilled off and the remaining solid material extracted 3 times with dichloromethane (600 ml each time). The combined dichloromethane phases were evaporated to dryness and the residue washed with methanol.

Colorless powder, m.p. 320 °C, yield 1.80 g (76%). –

IR (KBr): $\nu = 3070\ cm^{-1}$, 2219, 1633, 1596, 1502, 1482, 1368, 1294, 1244, 1187, 897, 817, 773, 698. – UV (DMSO): $\lambda_{max} =$ 281 nm, 328, 344; UV (acetonitrile): $\lambda_{max} = 278$ nm, 293, 308, 328; UV (toluene): $\lambda_{max} = 284$ nm, 294, 329, 344. – ^1H NMR ([D_6]DMSO): $\delta = 8.93$ (s, 2 H, 4,5-carbazole-H), 7.89 (d, 2 H, carbazole-H), 7.73 (t, 2 H, phenyl-H), 7.65 (d, 3 H, phenyl-H), 7.43 (d, 2 H, carbazole-H).

$C_{20}H_{11}N_3$	Calcd.	C 81.89	H 3.78	N 14.33
(293.3)	Found	C 81.82	H 3.76	N 14.22

N-Phenylcarbazole-3,6-bis-[N,N,N'-tris-(trimethylsilyl)-carboxamidine] (**22**)

Lithium hexamethyldisilazene (1 .84 g, 11 mmol) was added to a suspension of **21** (1.5 g, 5.1 mmol) in dry ether (50 ml) and the mixture stirred at room temperature for 10 h. The solvent was removed *in vacuo*, toluene (50 ml) and chlorotrimethylsilane (1.5 ml, 12 mmol) were added and the mixture refluxed for 5 h. The solvent was destilled off *in vacuo* and the orange product (3.89 g) used according to the "general procedure" (cf. **8a**).

3,6-Bis-(5-nitro-2-pyrimidinyl)-N-phenylcarbazole (**23a**)

With **22** (3.89 g, 5.1 mmol) and 3-dimethylamino-2-nitro-*N,N*-dimethyl-proeneiminium perchlorate [16] (2.9 g, 10.7 mmol).

Orange powder, m.p. >300 °C, yield 1.60 g (64%). –

IR (KBr): $\nu = 1559\ cm^{-1}$, 1512, 1417, 1338, 1291, 1231, 1132, 856, 798, 772, 699. – UV (DMSO): $\lambda_{max} = 270$ nm, 330, 405; UV (toluene): $\lambda_{max} = 322$ nm, 394. – ^1H NMR ([D_6]DMSO): $\delta = 9.58$ (s, 4 H, pyrimidine-H), 9.50 (s, 2 H, 4,5-carbazole-H), 8.66 (d, 2 H, carbazole-H), 7.80–7.62 (m, 5 H, phenyl-H), 7.53 (d, 2 H, carbazole-H).

$C_{26}H_{15}N_7O_4$	Calcd.	C 63.80	H 3.09	N 20.03
(489.5)	Found	C 63.95	H 3.32	N 20.06

3,6-Bis-[5-(4-nitrophenyl)-2-pyrimidinyl]-N-phenylcarbazole (**23b**)

With **7g** [15] (3.7 g, 10.6 mmol).

Yellow powder, m.p. >300 °C, yield 2.16 g (68%).

IR (KBr): $\nu = 1599\ cm^{-1}$, 1581, 1517, 1424, 1345, 1293, 854, 798, 752, 695. – UV (DMSO): $\lambda_{max} = 290$ nm, 353, 379; UV toluene): $\lambda_{max} = 335$ nm, 353, 383. – ^1H NMR ([D_6]DMSO): $\delta = 9.34$ (s, 2 H, 4,5-carbazole-H), 9.19 (s, 4 H, pyrimidine-H), 8.54 (d, 2 H, carbazole-H), 8.25 (d, 4 H, phenylene-H), 8.00 (d, 4 H, phenylene-H), 7.58 (s, 5 H, phenyl-H), 7.35 (d, 2 H, carbazole-H).

$C_{38}H_{23}N_7O_4 \times H_2O$	Calcd.	C 69.19	H 3.82	N 14,86
(659.7)	Found	C 69.15	H 4.16	N 14.76

3,8-Bis-(5-ethoxy-2-pyrimidinyl)-N-phenylcarbarole (**23c**)

With 3-dimethylamino-2-ethoxy-*N,N*-dimethyl-prop-2-eneiminium perchlorate [18] (2.9 g, 10.7 mmol).

Ochre powder, m.p. 242 °C, yield 0.55 g (22%). –

IR (KBr): $\nu = 1598\ cm^{-1}$, 1543, 1502, 1429, 1396, 1274, 918, 899, 789, 698. – UV (DMSO): $\lambda_{max} = 300$ nm, 381, 408; UV (acetonitrile): $\lambda_{max} = 277$ nm, 297, 328; UV (toluene): $\lambda_{max} =$ 300 nm, 335. – ^1H NMR ([D_6]DMSO): $\delta = 9.15$ (s, 2 H, 4,5-carbazole-H), 8.60 (s, 4 H, pyrimidine-H), 8.43 (d, 2 H, carbazole-H), 7.63 (s, 5 H, phenyl-H), 7.40 (d, 2 H, carbazole-H), 4.24 (q, 4 H, CH_2), 1.40 (t, 6 H, CH_3).

$C_{30}H_{25}N_5O_2 \times 0.33\ H_2O$	Calcd.	C 73.00	H 5.24	N 14.19
(493.6)	Found	C 72.99	H 5.20	N 14.25

3,6-Bis-[5-(4-methoxyphenyl)-2-pyrimidinyl]-N-phenylcarbazole (**23d**)

With **7c** [15] (3.5 g, 10.5 mmol).

Ochre powder, m.p. >300 °C, yield 2.16 g (68%). –

IR (KBr): $\nu = 1606\ cm^{-1}$, 1582, 1517, 1502, 1424, 1288, 1251, 1181, 1033, 828, 796. – UV (DMSO): $\lambda_{max} = 321$ nm, 362; UV (acetonitrile): $\lambda_{max} = 315$ nm, 354; UV (toluene): $\lambda_{max} =$ 307 nm, 321, 350, 362. – ^1H NMR ([D_6]DMSO): $\delta = 9.39$ (s, 2 H, 4,5-carbazole-H), 9.20 (s, 4 H, pyrimidine-H), 8.61 (d, 2 H, carbazole-H), 7.83 (d, 4 H, phenylene-H), 7.75 (s, 5 H, phenyl-H), 7.52 (d, 2 H, carbazole-H), 7.13 (d, 4 H, phenylene-H), 3.85 (s, 6 H, OCH_3).

$C_{40}H_{29}N_5O_2$	Calcd.	C 78.54	H 4.78	N 11.45
(611.7)	Found	C 78.27	H 4.76	N 11.49

References

[1] a) D. J. Williams, Angew. Chem. **96** (1984) 637; Angew. Chem. Int. Ed. Engl. **23** (1984) 640; b) D. S. Chem-

la, J. Zyss (Ed.): Nonlinear Optical Properties of Organic Molecules and Crystals, Vol. 1, Academic Press, New York 1987; c) S. R. Marder, J. E. Sohn, G. D. Stucky, Materials for Nonlinear Optics, ACS Symposium Ser. 1991, 455; d) N. Matsuzawa, D. A. Dixon, J. Am. Chem. Sec. **114** (1992) 6232

[2] a) L. T. Cheng, W. Tam, S. H. Stevenson, G. R. Meredith, G. Rikken, S. R. Marder, J. Phys. Chem. **95** (1991) 10631; b) L. T. Cheng, W. Tam, S. R. Marder, A. E. Stiegman, G. Rikken, C. W. Spangler, ibid. **95** (1991)10643

[3] a) J. Jerphagnon, D. Chemla, R. Bonneville, Adv. Phys. **27** (1978) 609; b) J. Jerphagnon, Phys. Rev. B **2** (1970) 1091; c) J. Zyss, B. M. Pierce, J. L. Bredas, F. Meyers, J. Am. Chem. Soc. **114** (1992) 4928; d) M. Joffre, D. Yaron, R. J. Silbey, J. Zyss, J. Chem. Phys. **97** (1992) **XXX**; a) J. Zyss, J. Chem. Phys. **98** (1993) 6583; f) T. Verbiest, K. Clays, C. Samyn, J. Wolff, D. Reinhoudt, A. Persoons, J. Am. Chem. Soc. **116** (1994) 9320

[4] I. Ledoux, J. Zyss, J. S. Siegel, J. Brienne, J.–M. Lehn, Chem. Phys. Lett. **172** (1990) 440

[5] a) J. J. Wolff, S. F. Nelsen, D. R. Powell, J. Org. Chem. **56** (1991) 5908; b) J. J. Wolff, S. F. Nelsen, P. A. Petillo, D. R. Powell, Chem. Ber. **124** (1991) 1719; c) J. J. Wolff, S. F. Nelsen, D. R. Powell, J. M. Desper, ibid. **124** (1991) 1727

[6] a) J. M. Chance, B. Kahr, A. B. Buda, J. S. Siegel, J. Am. Chem. Soc. **111** (1989) 5940; b) K. K. Baldridge, J. S. Siegel, ibid. **115** (1993) 10782

[7] H. Engel, Ph. D. thesis, Universität München 1992

[8] S. Newman, H. S. Lowrie, J. Am. Chem. Soc. **76** (1954) 6196

[9] S. Stadler, F. Feiner, Ch. Bräuchle, S. Brandl, R. Gompper, Chem. Phys. Lett. **245** (1995) 292

[10] a) K. Clays, A. Persoons, Phys. Rev. Lett. **66** (1991) 2980; b) T. Verbiest, K. Clays, A. Persoons, F. Meyers, J. Brédas, Opt. Lett. **18** (1993) 525

[11] a) A. R. Sanger, Inorg. Nucl. Chem. Lett. **9** (1973) 351; b) A. W. Cordes, R. C. Haddon, R. G. Hicks, R. T. Oack-ley, T. T. Palstra, L. F. Schneemeyer, J.V. Waszczak, J. Am. Chem. Soc. **114** (1992) 5000; C) R. T Boere, R. T. Oackley, R. W. Reed, J. Organomet. Chem. **331** (1987)161; d) K. Dehnicke, Chem. Ztg. **10** (1990) 295

[12] G. A. Person, M. Rocek, R. I. Walter, J. Phys. Chem. **82** (1978) 1185

[13] T. N. Baker, W. P. Doherty, W. S. Kelley, W. Newmeyer, J. E. Rogers, R. E. Spalding, R. I. Walter, J. Org. Chem. **30** (1965) 3714

[14] J. Pielichowski, A. Puszynski, Monatsh. Chem. **105** (1974) 772

[15] a) S. N. Balasubrahmanyam, A. S. Radhakrishna, J. Chem. Sec., Perkin Trans. 2 **1977**, 1388; b) D. Lloyd, K. S. Tucker, D. R. Marshall, J. Chem. Sec., Perkin Trans 1 **1981**, 726

[16] J. Kucera, Z. Arnold, Collect. Czech. Chem. Commun. **32** (1967) 1704

[17] K. Hafner, M. Neuenschwander, Angew. Chem. **80** (1968) 443; Angew. Chem. Int. Ed. Engl. **7** (1968) 459

[18] Z. Arnold, Collect. Czech. Chem. Commun. **38** (1973) 1168

Address for correspondence:
Prof. Dr. R. Gompper
Institut für Organische Chemie der Universität München
Karlstraße 23
D-80333 München, Germany