Supplementary Material

All mps were determined on a Dr Tottoli melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer FTIR 1600 spectrophotometer. NMR spectra: Bruker AM 300 (300 MHz: FT ^{1}H NMR; 75 MHz: ^{13}C NMR); Bruker AC 200 (200 MHz: FT ^{1}H NMR; 50 MHz: ^{13}C NMR); internally referenced on Me_4Si ($CDCl_3$ or [$^{2}H_6$]DMSO). UV spectra: Zeiss DMR 10 spectrophotometer; mass spectra: Finnigan MAT 8230 mass spectrometer by using 70 eV ionization potential (EI) or chemical ionization (CI) (isobutane) method.

Terephthalaldehyde diethylacetal
A suspension of 25.0 g (186 mmol) terephthalaldehyde in 50 ml ethanol was heated until complete dissolution. 3 drops of concd. sulfuric acid and afterwards 34 ml (200 mmol) of triethylorthoformiate were added under vigorous stirring. After 12 h at room temp. the solvent was destilled off, the residue solved in a small amount of diethylether and treated with an excess of *n*-pentane. After cooling for 1 h the solid starting material was filtered off, washed with a small amount of ethanol and the procedure repeated once. The filtrate was destilled in vacuo and yields 22.1 g (57%) of monoacetal and 8.40 g (16%) of bisacetal as colourless oils.

IR (Film): $\tilde{\nu}$ = 2975 (s), 2928 (m), 1705 (C=O), 1611 (m), 1580 (w), 1444 (w), 1335 (w), 1299(w), 1207 (m), 1113 (s), 1055 (s), 920 (w), 798 (w).

^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.23 (t, 6H, CH_3), 3.57 (q, 4H, CH_2), 5.54 (s, 1H, CH), 7.46-8.03 (m, 4H, aromatic H), 10.03 (s, 1H, CHO).

4-(Diethoxymethyl)-*N*-methylthiobenzamide (2)
A mixture of 48.0 g (231 mmol) terephthaldialdehyde diethylacetal, 9.57 g (300 mmol) sulphur and 120 ml of methylamine (33proz. in ethanol) in 120 ml abs. ethanol was heated under stirring to 110 °C in an autoclave for 4 h. After standing overnight, the solution was heated with 1 g of charcoal for 10 min, filtered and concentrated to 150 ml. 400 ml of water and 200 ml of dichloromethane were added, the layers separated and the aqueous layer extracted four times with 90 ml of dichloromethane. The combined organic phases were washed twice with water, dried over sodium sulfate and purified by column chromatography on silica gel (eluent: cyclohexane/ethyl acetate = 1/1) to yield **2** (brownred oil, 44.3 g, 69%).

IR (Film): $\tilde{\nu}$ = 3266 (b), 2974 (s), 2929 (m), 2881 (m), 1533 (s, C=S), 1503 (m), 1440 (m), 1401 (m), 1350 (s), 1259 (m), 1209 (m), 1097 (s), 1052 (s), 945 (m), 921 (w), 849 (m), 704 (m).

^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.23 (t, 6H, CH_3), 3.33 (d, 3H, N-CH_3), 3.57 (q, 4H, CH_2), 5.50 (s, 1H, CH), 7.48 (d, 2H, aromatic H), 7.72 (d, 2H, aromatic H), 7.78 (s, 1H, NH).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 15.09 (q, CH_3), 33.57 (q, N-CH_3), 61.18 (t, CH_2), 100.87 (d, CH), 126.48 (d, C-2*, C-6*), 126.70 (d, C-3*, C-5*), 141.42 (s, C-1**), 141.98 (s, C-4**), 199.59 (s, CHO). Signals with * or ** are possibly interchanged.

MS (EI, 70 eV), *m/z* (%): 253 (13) [M^+], 237 (100), 208 (24), 207 (31), 179 (30), 135 (80), 133 (21), 111 (28), 107 (27), 105 (27), 97 (44), 95 (30), 83 (44), 79 (65), 71 (65), 69 (53).

$C_{13}H_{19}NO_2S$ Calcd. 253.1137 Found 253.1134 (MS)

4-(Diethoxymethyl)-N,N‘-dimethylbenzamidine (3)

5.0 ml (80 mmol) of methyl iodide were added to a solution of 10.8 g (43 mmol) 4-(diethoxymethyl)-*N*-methylthiobenzamide in 70 ml of dry diethylether and the mixture was stirred for 70 h at room temp. The solvent was decanted from the resulting brownish oil which was dried in vacuo, redissolved in 100 ml abs. ethanol and treated with 50 ml of methylamine (10proz. in ethanol). After stirring for 7 h, another 20 ml of methylamine-solution was added, and the mixture was stirred for further 30 min. Then the solvent was removed, the residue treated with 100 ml of dichloromethane and 140 ml of 2N sodium hydroxide and the aqueous layer extracted for four times with 50 ml of dichloromethane. The combined organic phases were dried over potassium carbonate and the solvent removed in vacuo to yield 8.87 g (83%, over two steps) of nearly colourless crystals of mp 74 °C.

IR (KBr): $\tilde{\nu}$ = 3421 (b, m), 3201 (b, m), 2976 (m), 2866 (m), 1630 (s, C=N), 1610 (m), 1545 (m), 1403 (m), 1338 (m), 1117 (m), 1093 (m), 1050 (s, C-O-C), 1000 (m), 847 (Ar), 817 (Ar).

^{1}H-NMR (200 MHz, $CDCl_3$): δ = 1.24 (t, 6H, CH_3) 2.90 (s, 6H, N-CH_3), 3.59,3.62 (dq, 4H, CH_2), 4.57 (s, br, 1H, N-H), 5.52 (s, 1H, CH), 7.29 (m, 2H, aromatic H), 7.56 (m, 2H, aromatic H).

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 15.20 (q, CH_3), 33.49 (q, N-CH_3), 61.27 (t, CH_2), 101.11 (d, CH), 126.92 (m, C-3, C-5), 127.47 (C-2, C-6), 134.40 (s, C-1), 140.49 (s, C-4), 161.36 (s, C=N).

MS (EI, 70 eV), *m/z* (%): 250 (32) [M^+], 249 (100), 220 (30), 206 (12), 205 (21), 188 (13), 177 (12), 175 (27), 159 (12), 146 (48), 132 (12), 118 (32), 104 (11), 77 (17).

$C_{14}H_{22}N_2O_2$ Calcd. 250.1681 Found 250.1665 (MS)

5-[4-(Diethoxymethyl)phenyl]-1,3-dimethyl-2-phenyl-6-oxo-6*H*-1-pyrimidinium-4-olate (4)

A solution of 0.480 g (1.9 mmol) of *N*,*N*’-dimethyl-4-(diethoxymethyl)benzamidine in 3 ml of anisole was treated with 1.03 g (1.9 mmol) of phenylbis(2,4,6-trichlorophenyl) malonate and heated to reflux. After 3 min 20 ml of diethylether was added and the crystals sucked off, washed with diethylether and recrystallized from abs. ethanol. Yield: 0.516 g (69%) of nearly colourless plates with mp 274 °C.

IR (KBr): $\tilde{\nu}$ = 1705 (s, HC=O), 1647 (ss, C=O), 1550 (m), 1375 (m), 1256 (m), 1200 (m), 780 (Ar).

UV (CH_3CN): λ_{max} (log ε) = 200 (4.611), 243 (4.294), 354 (3.567).

^{1}H-NMR (300 MHz, [D_6]DMSO): 1.31 (t, 6H, CH_3), 3.19 (s, 6H, N-CH_3), 3.62, 3.67 (dq, 4H, CH_2), 5.58 (s, 1H, CH), 7.19 (m, 3H, aromatic H), 7.37 (m, 2H, aromatic H), 7.70 (m, 2H, aromatic H), 7.81 (m, 2H, aromatic H).

^{13}C-NMR (75 MHz, $CDCl_3$): 15.19 (q, CH_3), 34.91 (q, NCH_3), 61.56 (t, CH_2), 97.66 (d, dipolar C), 100.50 (d, CH), 125.83 (d, aromatic C), 126.01 (d, aromatic C), 127.41 (d,

aromatic C), 128.62 (d, aromatic C), 129.02 (s, aromatic C), 130.53 (d, aromatic C), 134.54 (s, aromatic C), 143.10 (s, aromatic C), 157.63 (s, dipolar C), 158.64 (s, CHO).

MS (EI, 70 eV), *m/z* (%): 394 (100) [M^+], 366 (95), 292 (56), 220 (28), 169 (30), 146 (89), 118 (51), 97 (81), 69 (25).

$C_{23}H_{26}N_2O_4$ Calcd. 394.1893 Found 394.1892 (MS)

1,3-Dimethyl-2-(4-formylphenyl)-5-phenyl-6-oxo-6*H*-1-pyrimidinium-4-olate
A solution of 0.931 g (2.4 mmol) of 5-[4-(diethoxymethyl)phenyl]-1,3-dimethyl-2-phenyl-6-oxo-6*H*-1-pyrimidinium-4-olate in 50 ml of acetonitrile was treated with 100 mg of Lewatit® S 100 (activated by 5N hydrochloric acid) and heated under reflux for 1 h. The crystalline product was sucked off and dried in vacuo to yield yellowish crystals (mp 330 °C, 0.688 g, 88%).

IR (KBr): $\tilde{\nu}$ = 1705 (s, HC=O), 1647 (ss, C=O), 1550 (m), 1375 (m), 1256 (m), 1200 (m), 780 (Ar).

UV (CH_3CN): λ_{max} (log ε) = 200 (4.611), 243 (4.294), 354 (3.567).

^{1}H-NMR (300 MHz, [D_6]DMSO): 3.10 (s, 3H, N-CH_3), 7.14 (m, 1H, aromatic H), 7.29 (m, 2H, aromatic H), 7.70 (m, 2H, aromatic H), 8.03 (m, 2H, aromatic H), 8.22 (m, 2H, aromatic H), 10.15 (s, 1H, CHO).

^{13}C-NMR (125 MHz, [D_6]DMSO): δ = 34.31 (q, N-CH_3), 96.14 (s, dipolar C), 125.03 (d, aromatic C), 126.90 (d, aromatic C), 127.99 (d, aromatic C), 130.34 (d, aromatic C) 130.72 (d, aromatic C), 134.49 (s, aromatic C), 135.47 (s, aromatic C), 137.77 (s, aromatic C), 157.49 (s, dipolar C), 158.21 (s, C-4, CO), 192.77 (d, CHO).

MS (EI, 70 eV), *m/z* (%): 320 (52) [M^+], 292 (47), 146 (80), 118 (22), 98 (56), 83 (100).

HRMS: Found 320.1179 Calcd. 320.1161 $C_{19}H_{16}N_2O_3$

EA: Found C 70.89, H 4.96, N 9.04 Calcd. C 71.24, H 5.03, N 8.74 $C_{19}H_{16}N_2O_3$ (320.1)

2-[4-(1,3-Dihydroxy-4,4,5,5-tetramethyl-1,3-imidazolidin-2-yl)phenyl]-1,3-dimethyl-5-phenyl-6-oxo-6*H*-1-pyrimidinium-4-olate (5)
A suspenion of 0.406 g (1.27 mmol) of 1,3-dimethyl-2-(4-formylphenyl)-5-phenyl-6-oxo-6*H*-1-pyrimidinium-4-olate in 8 ml of methanol and 18 ml of chloroform was treated with 0.274 g (1.85 mmol) 2,3-bis(hydroxylamino)-2,3-dimethylbutane and stirred at 60 °C for 18 h. After cooling the crystals were sucked off and washed with warm methanol to yield **5** (nearly colourless crystals, mp 222 °C, 0.300 g, 52%).

IR (KBr): $\tilde{\nu}$ = 3376 (m), 2968 (w), 1636 (ss) (C=O), 1544 (m), 1445(m), 1380 (m), 1259 (m), 782 (w, Ar).

UV (CH_3CN): λ_{max} (log ε) = 220 (4.539), 257 (3.983), 347 (3.802)

^{1}H-NMR (300 MHz, [D$_6$]DMSO): δ = 1.07 (s, 6H, 18-H, 20-H*), 1.10 (s, 6H, 19-H, 21-H*), 3.11 (s, 6H, N-CH_3), 4.61 (s, 1H, 13-H), 7.12 (m, 1H, 25-H), 7.28 (m, 2H, 24-H, 26-H), 7.69-7.72 (m, 4H, 8-H, 12-H, 23-H, 27-H), 7.77 (m, 2H, 9-H, 11-H), 7.92 (s, 2H, N-OH).

^{13}C-NMR (75 MHz, [D$_6$]DMSO): 17.59 (q, CH_3), 24.83 (q, CH_3), 34.95 (q, N-CH_3), 66.79 [s, C-15, $\underline{C}(CH_3)_2$], 90.22 (d, CH), 96.44 (s, dipolar C), 125.37 (d, aromatic C),126.63 (d, aromatic C), 127.27 (d, aromatic C), 129.06 (s, aromatic C), 130.03 (d, aromatic C), 130.75 (d, aromatic C), 135.96 (s, aromatic C), 145.85 (s, aromatic C), 158.68 (s, dipolar C), 158.99 (s, CO).

MS (EI, 70 eV), *m/z* (%): 450 (47) [M^+], 432 (32), 146 (83), 388 (63), 359 (54), 331 (28), 317 (33), 289 (47), 185 (25), 146 (35), 143 (77), 118 (53), 69 (100).

$C_{25}H_{30}N_4O_4$ Calcd. 450.2267 Found 450.2282 (MS)

2-[4-(1,3-Dimethyl-4-oxido-5-phenyl-6-oxo-6*H*-1-pyrimidinium-4-oxido)phenyl]-4,5-dihydro-4,4,5,5-tetramethyl-3-oxido-3-imidazolio-1-oxyl (6)

0.111 g (0.25 mmol) of 1,3-dimethyl-2-[4-(1,3-dihydroxy-4,4,5,5-tetramethyl-1,3-imidazolidin-2-yl)phenyl]-5-phenyl-6-oxo-6*H*-1-pyrimidinium-4-olate were dissolved in 25 ml of *N*,*N*-dimethylformamide in the heat and treated with 0.540 g (2.30 mmol) of lead dioxide. The suspension was stirred for 3 d at rt., filtered over alumina (neutral) and the solvent removed in vacuo to yield **6** (fine, dark blue-green crystals, mp 238 °C (dec.), 60 mg, 54%).

IR (KBr): ῖ = 3446 (m), 2980 (w), 1655 (ss, C=O), 1546 (w), 1496 (w), 1387 (w), 1368 (m), 1257 (m), 1143 (w), 780 (w, Ar-H).

UV (CH_3CN): λ_{max} (log ε) = 224 (4.603), 267 (4.268), 292 (4.167), 355 (4.107), 371 (4.237), 590 (2.402), 624 (2.344).

MS (EI, 70 eV), *m/z* (%): 447 (5) [M^+], 417 (100), 389 (73), 358 (22), 289 (27), 202 (20), 143 (50), 129 (28), 84 (52).

$C_{25}H_{27}N_4O_4$ Calcd. 447.2032 Found 447.2032 (MS)