Synthesis of a Novel Series of 6,6′-Disubstituted 4,4′-Bipyrimidines by Radical Anion Coupling: New π-Accepting Ligands for Coordination Chemistry

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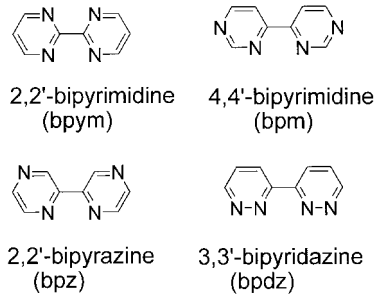
A new family of 6,6′-disubstituted 4,4′-bipyrimidine ligands has been prepared and characterized. The reduction potentials of the new ligands, as determined by cyclic voltammetry, indicate that these new ligands are considerably better π-acceptors than the ubiquitous 2,2′-bipyridine ligand, and are even superior to the parent unsubstituted 4,4′-bipyrimidine ligand. The substituents in 6,6′ positions of the 4,4′-bipyrimidine also cause a red-shift in the π→π* and n→π* absorptions throughout the UV region. The X-ray crystal structure of one member of the family of bipyrimidines demonstrates that the aryl substituents may lie coplanar with the pyrimidine rings in the solid state. The additional electron delocalization afforded by the aryl substituents on the pyrimidine rings contribute to the better π-accepting ability of these compounds.

Introduction

The biheterocyclic ligand 2,2′-bipyridine (bpy) has found extensive applications in the photochemistry of coordination compounds, e.g. for the conversion of solar energy into chemical energy.[1–3] Recent interest in coordination compounds that have attractive redox and photocatalytic properties, such as $[Ru(bpy)_3]^{2+}$, has resulted in numerous attempts to purposefully modify this system.[4] One avenue of modification is by ring substitution of the classical bpy ligand and its incorporation into a larger π-system.[5,6] Another option is the replacement of one CH group in each pyridine ring by a more electronegative nitrogen atom, which leads to a series of more π-electron-deficient bidiazine compounds (Scheme 1), of which the 4,4′-bipyrimidine (bpm) isomer has the lowest π*-level of the set of diazine ligands.[7] This fact figures prominently for successful modification of the photophysical properties of its ruthenium(II) complexes since the lowest energy absorption and longest-lived excited state are the metal-to-ligand charge transfer singlet and triplet states, respectively, which are based on the lowest energy π* orbital of the ligand coordinated to the Ru^{II} metal ion. Thus, efficient syntheses of substituted and unsubstituted 4,4′-bipyrimidines would afford a route to an interesting class of π-accepting ligands.

A number of syntheses of substituted and unsubstituted 4,4′-bipyrimidines were described previously, mainly based on two strategies. The first strategy consisted in the formation of pyrimidine rings from acyclic precursors, although this method required several steps with only poor to moderate yields of the bipyrimidines.[8] The other approach consisted in the homocoupling of smaller pyrimidine units, which were synthesized in previous steps. An Ni-catalyzed homocoupling reaction was shown to be a useful synthetic methodology for the formation of 4,4′-bipyrimidines,[9,10] although substituted heterocycles were required in order to bring two moieties together. A metallation/addition mechanism has also been employed in order to bring together two substituted[11] or unsubstituted[12] pyrimidine rings. Even though direct metallation of azaheterocycles is usually aided by *ortho*-directing metallation groups,[13] pyrimidine can be lithiated directly in the 4-position using lithium 2,2,6,6-tetramethylpiperidine (LTMP) and its addition to another pyrimidine molecule to give 4,4′-bpm in low yield was possible.[12] The electrochemical synthesis of 4,4′-bipyrimidine was also reported, but the yield was modest, and no substituted compounds were prepared.[14]



Scheme 1. Potential bidiazine ligands for coordination chemistry.

A convenient route to synthesize 6,6′-bis(2-pyridyl)-4,4′-bipyrimidine (**3f**) was previously proposed,[11] and in this work we expand this class of compound to various aryl-substituted R-groups. Considering the desirable properties

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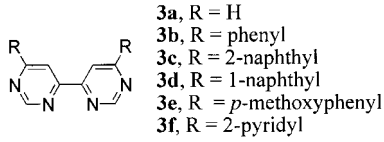
of 4,4′-bipyrimidines, we were surprised to learn that only one other 6,6′-disubstituted 4,4′-bipyrimidine existed, and that no systematic synthetic procedure or analysis of their properties had been presented. In this work we report the preparation of a series of 6,6′-disubstituted 4,4′-bipyrimidine ligands as well as their electrochemical and spectroscopic properties (Scheme 2).



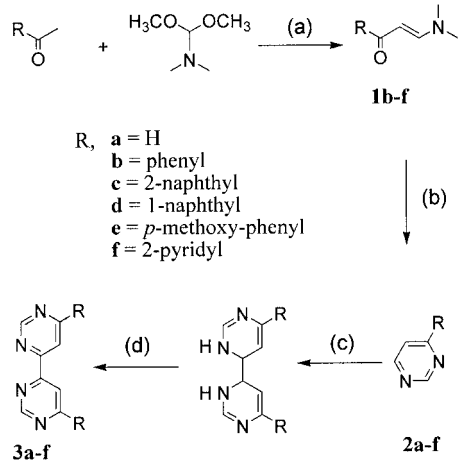
Scheme 2. 4,4′-Bipyrimidine (**3a**) and the 6,6′-disubstituted 4,4′-bipyrimidines **3b**–**3f** presented in this work.

Results and Discussion

The synthesis of the ligands **3a**–**f** consists of three steps, as outlined in Scheme 3. In step (a), enaminones **1b**–**f** were synthesized from their corresponding methyl ketones with a small excess of dimethylformamide dimethylacetal according to a previously established method.[15] All of the enaminones were recrystallized from hexane and their purity was confirmed by elemental analysis.

The condensation of the enaminones **1b**–**f** (step b) with 3 equiv. of formamidine acetate in the presence of 3 equiv. of sodium ethoxide resulted in the formation of the corresponding 4-substituted pyrimidines **2b**–**f** with moderate to high yields. The Michael addition of the free amidine on the enaminone followed by the intramolecular cyclisation and subsequent elimination of a water molecule led to the formation of the 4-R-pyrimidines.[16] All of the pyrimidines were purified by column chromatography (alumina; ethyl acetate/hexane, 1:3) and their purity was confirmed by elemental analysis.

The desired 4,4′-bipyrimidine (**3a**) and the 6,6′-disubstituted 4,4′-bipyrimidines **3b**–**f** were obtained through the radical anion coupling of two molecules of the corresponding pyrimidine **2a** and 4-substituted pyrimidines **2b**–**f**, respectively. The R-substituted pyrimidines dimerize upon treatment with 3 equiv. of sodium in anhydrous THF. As



Scheme 3. Synthesis of 6,6′-disubstituted 4,4′-bipyrimidines **3a**–**f**. Reagents and conditions: (a) EtOH, reflux, 6 h, yield 50–78%; (b) 3 equiv. formamidine acetate, 3 equiv. NaOEt, EtOH, reflux, 24 h, yield 49–69%; (c) 3 equiv. Na(s), THF, 36 h, room temp.; d) air, 1 h, yield 56–93%.

the initial radical anion is generated, the solution turns dark purple, then yellow with the formation of dihydrobipyrimidine. The nature of the solvent and the amount of sodium have an important effect on the ratio monomer/dimer, with 3 equiv. of sodium being the best. Of the various ether-based solvents tested for the reaction, such as diethyl ether, DME, and THF, the latter proved to be the best solvent for the dimerization reaction. The reaction mixture was quenched with ethanol and air was bubbled through the solution for 1 h in order to assure the oxidation of the dihydrobipyrimidines formed during the reaction (Scheme 3). The products were then purified by recrystallization from methanol. A radical anion mechanism is supported by the significantly lower yields of the product after the addition of $CuCl_2$,[11] a known radical reaction quencher.[12]

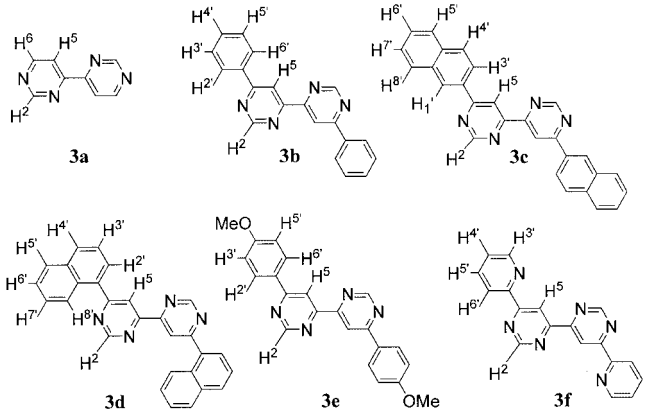
The 400 MHz ^{1}H NMR spectroscopic data for the R-pyrimidines **2a**–**f** and R_2-4,4′-bpm **3a**–**f** are compiled in Table 1 and the numbering scheme for ligands **3a**–**f** is presented in Scheme 4. On going from the pyrimidines **2** to the bipyrimidines **3**, the H^2 proton is deshielded only slightly, whereas a larger deshielding effect is noticed for the H^5 pro-

Table 1. ^{1}H NMR resonances for compounds **2a**–**f** and **3a**–**f**.[a,b]

Compound	Pyrimidine 2	5	6	Substituent R 1′	2′	3′	4′	5′	6′	7′	8′
2a	9.26	7.37	8.77								
2b	9.29	7.733	8.78		8.11	7.53	7.53	7.53	8.11		
2c	9.33	8.00	8.80	8.65		8.30	7.90	7.90	7.60	7.60	8.00
2d	9.44	7.63	8.91		7.98	7.56	8.03	7.72	7.56	7.58	8.22
2e	9.22	7.73	8.73		8.13	7.02		7.02	8.13		
2f	9.29	8.43	8.87			8.51	7.46	7.92	8.73		
3a	9.35	8.46	8.97								
3b	9.42	8.93			8.27	7.588	7.58	7.58	8.27		
3c	9.51	9.10		8.82		8.38	7.98	7.98	7.59	7.59	8.04
3d	9.51	8.87			7.97	7.60	8.05	7.84	7.60	7.69	8.32
3e	9.353	8.89			8.25	7.19		7.19	8.25		
3f	9.48	9.46				8.55	7.47	7.92	8.81		

[a] $CDCl_3$ at 400 MHz, referenced to residual $CHCl_3$. [b] See Scheme 4 for ^{1}H labels.

ton due to the presence of the N-lone pair from the adjacent pyrimidine. This suggests a *trans* orientation of the two pyrimidine rings in solution, which has previously been exploited in alternating pyridine–pyrimidine heterocycles for the formation of helical molecules in solution and the solid state.[17,18] This effect is also observed for the protons adjacent to the interannular bond on the R groups. The $H^{2'}$ and $H^{6'}$ protons of **3b** and **3e** are deshielded more than their corresponding protons in **2b** and **2e**, as are the $H^{1'}$ and $H^{3'}$ protons of 2-naphthyl-substituted ligand **3c**, which follows the same trend. A signal upfield shift for protons $H^{3'}$ and $H^{5'}$ is noted when the phenyl ring is substituted with a methoxy group in the *para* position due to the donor effect of this group.



Scheme 4. 6,6′-Disubstituted 4,4′-bipyrimidines and their ^{1}H NMR labels.

The solid-state structure of **3e** was determined by X-ray crystallography and is presented with its atom labeling scheme in Figure 1.[19] Details of data collection and refinement are given in Table 2. Selected bond lengths for the molecule are listed in Table 3. The two halves of the molecule are related by an inversion center and are in close contact with another bipyrimidine. These contacts are on the order of 3.5–3.7 Å, indicative of π-stacking in the solid state. The nitrogen atoms N(1) and N(2) of the one pyrimidine are *trans* with respect to the nitrogen atoms N(3) and N(4) of the other pyrimidine ring, which minimizes electronic repulsion between lone pairs of nitrogen atoms. The phenyl ring in each half of the molecule is almost coplanar with the pyrimidine ring, just slightly twisted with a dihedral angle of just 2.2°. The two pyrimidine rings are virtually coplanar with the two planes twisted at an angle of just 0.3°. The bond lengths in the pyrimidine ring range from 1.332(2) to 1.3982(19) Å (Table 3) and are similar to those found in unsubstituted 4,4′-bipyrimidine,[14] except for the distances between C(8)–N(1) and C(10)–C(11), which are slightly longer due to the presence of the substituent in 6,6′-positions of the pyrimidine rings. The interannular bond lengths C(10)–C(12) and C(5)–C(8) are 1.492(3) and 1.481(2) Å, respectively, as would be expected for single bonds.

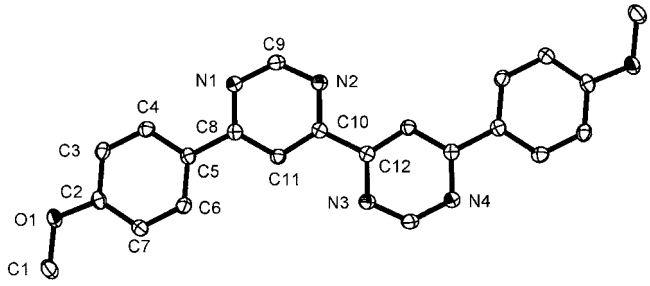


Figure 1. X-ray crystal structure of **3e** as an ORTEP representation. Thermal ellipsoids are set at 50%.

Table 2. Crystallographic data for **3e** recorded at 100 K.

Empirical formula	$C_{22}H_{18}N_4O_2$
M	370.40
Crystal system	monoclinic
Space group	$P2_1/n$
a [Å]	7.1674(1)
b [Å]	8.3271(1)
c [Å]	14.9545(2)
β [°]	98.046(1)
V [Å^3]	883.75
Z	2
R(int)	0.028
R	0.0478
wR_2	0.1479
Goodness of fit	1.091

Table 3. Selected interatomic distances [Å] for **3e**.

C(1)–O(1)	1.4346(18)	C(6)–C(7)	1.391(2)
O(1)–C(2)	1.3605(17)	C(8)–N(1)	1.3492(18)
C(2)–C(3)	1.392(2)	C(8)–C(11)	1.3982(19)
C(2)–C(7)	1.393(2)	N(1)–C(9)	1.332(2)
C(3)–C(4)	1.381(2)	C(9)–N(2)	1.3323(19)
C(4)–C(5)	1.405(2)	N(2)–C(10)	1.3346(18)
C(5)–C(6)	1.395(2)	C(10)–C(11)	1.3831(19)
C(5)–C(8)	1.481(2)	C(10)–C(12)	1.492(3)

The reduction potentials of bipyrimidines **3a**–**f** are given in Table 4. All 6,6′-disubstituted 4,4′-bipyrimidines, as well as the unsubstituted bpm ligand, exhibit reversible first reduction waves in their cyclic voltammograms. The compounds with phenyl and 2-naphthyl substituents, **3b** and **3c**, respectively, are easier to reduce than unsubstituted bipyrimidine due to the extension of the delocalization of the π-electronic system, which in turn leads to the better π-acceptor properties of the ligands. The reduction potential of the bipyrimidine with the 1-naphthyl substituent is more negative than those of the other substituted bipyrimidines due to the non-planarity of the 1-naphthyl and the pyrimidine rings, which diminishes the extent of π-electron delocalization. As a consequence, the ligand is less π-accepting, which makes the reduction of the ligand more difficult. The reduction potential of the bipyrimidine with *p*-methoxyphenyl as substituent in 6,6′ positions, **3e**, is intermediate between those of **3b**–**c** and **3d**. The donor effect of the methoxy group has less influence when it is in the *para* position of the phenyl ring than if it were linked directly to the pyrimidine ring. The withdrawing ability of the 2-pyridyl

substituent in **3f** stabilizes the π*-accepting orbitals and facilitates the reduction of the **3f** ligand. The second reduction waves are all quasi-reversible and close to the solvent potential limit.

Table 4. Reduction potentials for compounds **3a**–**f** in DMF.[a]

Compound	E_{red} [V]	
3a	–1.44 (73)	–2.27 (118)
3b	–1.36 (68)	–2.08 (114)
3c	–1.33 (60)	–1.93 (91)
3d	–1.43 (70)	–2.22 (97)
3e	–1.39 (100)	–2.11 (125)
3f	–1.35 (61)[b]	_[c]

[a] Potentials are in Volts vs. SCE for DMF solutions, 0.1 M in Bu_4NPF_6, recorded at 25±1 °C at a sweep rate of 200 mV/s, vs. ferrocene in DMF; ΔE_p values in mV given in parentheses. [b] In acetonitrile.[11] [c] Reduction peak at the potential limit of the solvent.

The absorption data for all compounds are summarized in Table 5. The absorption spectra of compounds **3a**, **3b**, **3d** and **3e** in dichloromethane solution are presented in Figure 2. The UV spectra are dominated by π→π* transitions at higher energy, with additional bands characteristic for the phenyl or naphthyl rings, as compared to the unsubstituted bpm. All of the absorption bands are red-shifted for the substituted bipyrimidines, due to the better stabilization of the π*-orbitals with the aromatic substituents. The band at longer wavelength (350–369 nm) is attributed to an n→π* transition originating on the nitrogen atoms. This band is also red-shifted with respect to unsubstituted bipyrimidine **3a**.

Table 5. Absorption maxima for **3a**–**f** in dichloromethane at room temperature.

Compound	λ [nm] (ε×10^{-3} [mol^{-1} cm^{-1}])		
3a	272 (12.4)	282 (10.2)	
3b	252 (26.4)	295 (19.5)	306 (18.8)
3c	241 (10.6)	258 (13.3)	289 (6.8)
	317 (5.8)		
3d	241 (22.2)	261 (20.9)	271 (21.3)
	281 (20.0)	326 (12.3)	
3e	263 (25.4)	272 (24.6)	292 (23.6)
3f	225 (12.6)	236 (11.5)	297 (15.4)

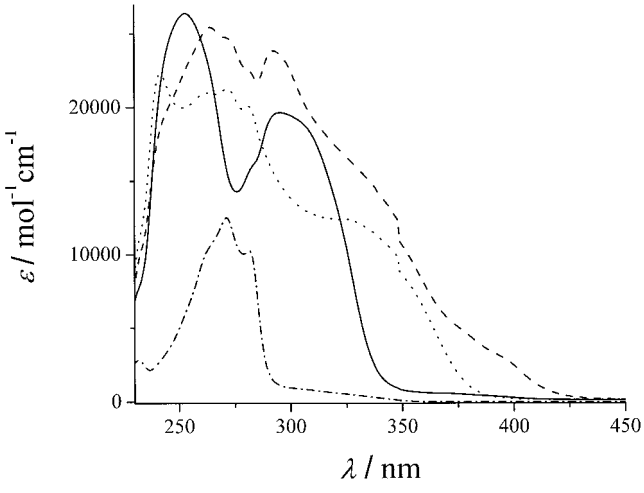


Figure 2. Absorption spectra of **3a** (-·-·-), **3b** (——), **3d** (·····) and **3e** (---) in dichloromethane.

Conclusions

A new family of 6,6′-disubstituted 4,4′-bipyrimidines was synthesized and characterized. All of the compounds, except **3d**, are more easily reduced than the parent 4,4′-bipyrimidine, due to the increased π-electron delocalization that the aryl substituents afford. Thus, these ligands offer interesting possibilities as π-accepting chelate agents. In the case of the 1-naphthyl-substituted compound **3d**, the *peri* substitution on the naphthyl ring does not favour a coplanar alignment of the naphthyl and pyrimidyl rings, which limits the extent of π-electron delocalization. This feature could be advantageous when the lowering of naphthyl groups' absorption energy is not desirable, for example, when higher energy light absorption is needed in a light-harvesting complex. In the case of **3d**, the bipyrimidine core does not interact well with the naphthyl groups and the latter's absorption bands remain relatively high in energy. This effect would be more pronounced in substituted anthracenes and pyrenes, and the extension of this synthetic approach is currently being applied to these synthetic targets. The application of this series of ligands to the coordination chemistry of transition metal ions is also currently underway and will be reported in due course.[20]

Experimental Section

General: Nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ at room temperature (room temp.) with a Bruker AV400 spectrometer at 400 MHz for ^{1}H NMR and at 100 MHz for ^{13}C NMR spectroscopy. Chemical shifts are reported in parts per million (ppm) relative to residual solvent protons (δ =7.26 ppm for [D]chloroform) and carbon resonance of the solvent. Melting points were collected using a Meltemp™ 200 apparatus and are reported uncorrected. Accurate mass measurements were performed with an LC-MSD-TOF instrument from Agilent technologies in electrospray positive ionization mode. Fast-atom bombardment (FAB, positive mode) spectra were recorded with a ZAB-HF-VB analytical apparatus in an *m*-nitrobenzyl alcohol (*m*-NBA) matrix and Ar atoms were used for the bombardment (8 keV). Routine absorption spectra were measured in deaerated dichloromethane at room temp. with a Cary 500i UV/Vis/NIR spectrophotometer. Electrochemistry data were collected in deaerated DMF with 0.1 M Bu_4NPF_6 with a BAS CV-50W Voltammetric Analyzer. Redox potentials were corrected by internal reference ferrocene. All 4-substituted pyrimidines were purified by column chromatography on alumina. Tetrabutylammonium hexafluorophosphate was purchased from Aldrich and purified by recrystallization from toluene/methanol (20:1). DMF for electrochemical experiments and dichloromethane for photophysical experiments were of spectroscopic grade. Elemental analyses were performed by Laboratoire d'Analyse Elementaire de l'Université de Montréal. The starting reagents were obtained from commercial sources.

General Procedure for the Synthesis of the Enaminones 1b–f

3-(Dimethylamino)-1-phenylprop-2-en-1-one (1b):[21] Dimethylformamide dimethyl acetal (8.85 g, 0.074 mol) was added dropwise to a

stirred solution of acetophenone (6 g, 0.05 mol) in boiling absolute EtOH (20 mL) and the stirring was continued for 6 h, at which time hexane was added. A yellow solid precipitated which was isolated by filtration. Yield 73%. M.p. 92–95 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.89 (d, J = 7.9 Hz, 2 H, 2′-H, 6′-H), 7.78 (d, J = 12.3 Hz, 1 H, 1-H), 7.40 (t, J = 7.9 Hz, 2 H, 3′-H, 5′-H), 7.38 (t, J = 9.9 Hz, 1 H, 4′-H), 5.67 (d, J = 12.3 Hz, 1 H, 2-H), 3.09 (s, 3 H, NMe1), 2.87 (s, 3 H, NMe2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 189.0, 154.6, 140.9, 131.2, 128.5, 127.8, 93.1, 45.5, 38.0 ppm. LR-FAB: m/z = 205.3 $[M + H]^+$. $C_{13}H_{18}NO$ (204.29): calcd. C 76.43, H 8.88, N 6.86; found C 75.98, H 8.43, N 6.69.

3-(Dimethylamino)-1-(naphth-2-yl)prop-2-en-1-one (1c):[22] Yield 67%. M.p. 115–117 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.40 (s, 1 H, 1′-H), 8.0 (d, J = 8.5 Hz, 1 H, 3′-H), 7.94 (d, J = 8.2 Hz, 1 H, 8′-H), 7.87 (m, 3 H, 4′-H, 5′-H, 1-H), 7.54 (t, J = 6.6 Hz, 2 H, 6′-H, 7′-H), 5.91 (d, J = 12.3 Hz, 1 H, 2-H), 2.95 (s, 3 H, NMe1), 2.75 (s, 3 H, NMe2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 188.8, 154.7, 138.2, 135.1, 133.1, 130.0, 129.5, 128.2, 128.0, 127.61, 126.6, 125.0, 92.7, 45.9, 36.4ppm. LR-FAB: m/z = 226.2 $[M + H]^+$. $C_{15}H_{15}NO$ (225.29): calcd. C 79.97, H 6.71, N 6.22; found C 79.66, H 6.57, N 5.93.

3-(Dimethylamino)-1-(naphth-1-yl)prop-2-en-1-one (1d):[23] Yield 78%. M.p. 50–52 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.26 (d, J = 6.2 Hz, 1 H, 8′-H), 8.03 (d, J = 8.4 Hz, 1 H, 4′-H), 7.89 (d, J = 6.8 Hz, 1 H, 2′-H), 7.87 (d, J = 13.66 Hz, 1 H, 1-H), 7.57 (d, J = 6.8 Hz, 1 H, 5′-H), 7.50 (t, J = 5.7 Hz, 1 H, 7′-H), 7.49 (t, J = 10.1 Hz, 2 H, 3′-H, 6′-H), 5.60 (d, J = 12.7 Hz, 1 H, 2-H), 2.95 (s, 3 H, NMe1), 2.79 (s, 3 H, NMe2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 187.7, 152.7, 134.3, 134.1, 130.7, 129.7, 128.5, 127.5, 126.7, 126.5, 125.3, 125.2, 97.54, 46.3, 37.5 ppm. LR-FAB: m/z = 226.2 $[M + H]^+$. $C_{15}H_{15}NO$ (225.29): calcd. C 79.97, H 6.71, N 6.22; found C 79.76, H 6.26, N 6.09.

3-(Dimethylamino)-1-(*p*-methoxyphenyl)prop-2-en-1-one (1e):[24] Yield 57%. M.p. 84–87 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.91 (d, J = 8.8 Hz, 2 H, 2′-H, 6′-H), 7.79 (d, J = 12.3 Hz, 1 H, 1-H), 6.91 (d, J = 8.8 Hz, 2 H, 3′-H, 5′-H), 5.71 (d, J = 12.3 Hz, 1 H, 2-H), 3.84 (s, 3 H, OMe), 3.11 (s, 3 H, NMe1), 2.92 (s, 3 H, Me2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 187.7, 162.3, 154.3, 133.4, 129.8, 113.6, 92.0, 5.76, 37.0, 26.9 ppm. MS LR-FAB: m/z = 206 $[M + H]^+$. $C_{12}H_{15}NO_2$ (205.25): calcd. C 70.22, H 7.37, N 6.82; found C 70.54, H 7.39, N 6.49.

3-(Dimethylamino)-1-(pyrid-2-yl)prop-2-en-1-one (1f): Yield 50%. M.p. 77–80 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.66 (d, J = 4.64 Hz, 1 H, 6′-H), 8.19 (d, J = 8.19 Hz, 1 H, 3′-H), 7.95 (d, J = 12.56 Hz, 1 H, 1-H), 7.88 (t, J = 16.82, Hz 1 H, 5′-H), 7.41 (t, J = 12.19 Hz, 1 H, 4′-H), 6.51 (d, J = 12.98 Hz, 1 H, 2-H), 3.24 (s, 3 H, NMe1), 3.17 (s, 3 H, NMe2) ppm. LR-FAB: m/z = 177.1 $[M + H]^+$. $C_{10}H_{12}N_2O$ (176.22): calcd. C 68.16, H 6.86, N 15.90; found 67.93, H 6.89, N 15.86.

General Procedure for the Synthesis of the 4-R-Pyrimidines 2b–f

4-Phenylpyrimidine (2b):[25] To a stirred solution of **1b** (1.50 g, 0.0085 mol) in absolute ethanol (10 mL) at reflux was added formamidine acetate (2.67 g, 0.025 mol) and stirring was continued for 10 min. A solution of Na (0.59 g, 0.025 mol) in absolute EtOH (20 mL) was added to the reaction mixture and the reflux was maintained for 16 h, after which time the reaction mixture was allowed to cool to room temp. The solution was concentrated under vacuum and the solid residue dissolved in CH_2Cl_2 (50 mL). The precipitate was filtered and the filtrate concentrated. The desired compound was purified by column chromatography on alumina (EtOAc/hexane, 1:5) to give **2b** as a white crystalline powder. Yield 69%. M.p. 60–62 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.29 (s, 1 H, 2-H), 8.78 (d, J = 5.2 Hz, 1 H, 6-H), 8.11 (d, J = 3.6 Hz, 2 H, 2′-H, 6′-H), 7.73 (d, J = 9.0 Hz, 1 H, 5-H), 7.5–7.6 (m, 3 H, 3′-H, 4′-H, 5′-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 163.8, 159.0, 157.4, 136.4, 131.0, 129.0, 127.1, 116.9 ppm. LR-FAB: m/z = 157.07 $[M + H]^+$. $C_{10}H_8N_2$ (156.18): calcd. C 76.90, H 5.16, N 17.94; found C 76.22, H 5.02, N 17.62.

4-(2′-Naphthyl)pyrimidine (2c):[26] Yield: 53%. M.p. 116–120 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.33 (s, 1 H, 2-H), 8.80 (d, J = 5.3 Hz, 1 H, 6-H), 8.65 (s, 1 H, 1′-H), 8.30 (d, J = 8.5 Hz, 1 H, 3′-H), 8.00 (d, J = 8.3 Hz, 2 H, 5-H, 8′-H), 7.90 (d, J = 5.3 Hz, 2 H, 4′-H, 5′-H), 7.60 (t, J = 6.3 Hz, 2 H, 6′-H, 7′-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 165.2, 159.0, 157.4, 135.1, 133.9, 133.6, 129.5, 129.3, 128.3, 128.2, 128.1, 127.2, 121.1, 117.6 ppm. LR-FAB: m/z = 207.1 $[M + H]^+$. $C_{14}H_{10}N_2$ (206.24): calcd. C 81.53, H 4.89, N 13.58; found C 80.07, H 4.68, N 13.26.

4-(1′-Naphthyl)pyrimidine (2d):[26] Yield 58%. M.p. 58–61 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.44 (s, 1 H, 2-H), 8.91 (d, J = 5.2 Hz, 1 H, 6-H), 8.22 (d, J = 6.1 Hz, 1 H, 8′-H), 8.03 (d, J = 8.1 Hz, 1 H, 4′-H), 7.98 (d, J = 6.3 Hz, 1 H, 2′-H), 7.72 (d, J = 6.8 Hz, 1 H, 5′-H), 7.63 (d, J = 8.1 Hz, 1 H, 5-H), 7.58 (t, J = 5.5 Hz, 1 H, 7′-H), 7.56 (t, J = 9.7 Hz, 2 H, 3′-H, 6′-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 166.9, 159.2, 157.5, 130.9, 129.0, 128.5, 126.9, 126.4, 126.4, 125.6, 125.3, 125.2, 122.5, 117.2 ppm. LR-FAB: m/z = 207.8 [M + H]. HRMS: calcd. $[M + H]^+$ for $C_{14}H_{11}N_2$, 207.0911; found 207.0916. $C_{14}H_{10}N_2$ (206.24): calcd. C 81.53, H 4.89, N 13.58; found C 80.96, H 4.52, N 13.43.

4-(*p*-Methoxyphenyl)pyrimidine (2e):[27] Yield 63%. M.p. 76–79 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.22 (s, 1 H, 2-H), 8.73 (d, J = 5.6 Hz, 1 H, 6-H), 8.13 (d, J = 8.9 Hz, 2 H, 2′-H, 6′-H), 7.73 (d, J = 5.6 Hz, 1 H, 5-H), 7.02 (d, J = 8.9 Hz, 2 H, 3′-H, 5′-H), 3.92 (s, 3 H, O–Me) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 164.0, 162.5, 159.1, 157.2, 129.2, 129.1, 116.5, 114.8, 55.2 ppm. LR-FAB: m/z = 187.1 $[M + H]^+$. $C_{11}H_{10}N_2O$ (186.21): calcd. C 70.95, H 5.41, N 15.04; found C 70.62, H 5.42, N 14.88.

4-(2-Pyridyl)pyrimidine (2f):[16] Yield 49%. M.p. 78–80 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.29 (s, 1 H, 2-H), 8.87 (d, J = 5.2 Hz, 1 H, 6-H), 8.73 (d, J = 4.7 Hz, 1 H, 6′-H), 8.51 (d, J = 7.9 Hz, 1 H, 3′-H), 8.43 (d, J = 5.2 Hz, 1 H, 5-H), 7.92 (t, J = 15.5 Hz, 1 H, 5′-H), 7.46 (t, J = 12 Hz, 1 H, 4′-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 162.5, 158.6, 157.9, 153.6, 149.4, 137.1, 125.5, 121.5, 117.3 ppm. LR-FAB: m/z = 158 $[M + H]^+$. $C_9H_7N_3$ (157.17): calcd. C 68.78, H 4.49, N 26.74; found C 68.61, H 4.59, N 25.90.

General Procedure for the Synthesis of the 6,6′-R$_2$-4,4′-Bipyrimidines 3a–f: To a solution of pyrimidine (0.20 g, 0.001 mol) in THF (5 mL) was added sodium metal (0.09 g, 0.003 mol). The solution turned purple and then yellow and was stirred at room temp. overnight. The reaction was quenched with EtOH (4 mL) and triethylamine (0.2 mL) before being oxidized by bubbling air through the solution for 1 h. The reaction mixture was dissolved in CH_2Cl_2 and washed three times with water. The bipyrimidines were purified by recrystallization from methanol.

4,4′-Bipyrimidine (3a):[14] Yield 67%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.35 (s, H_2), 8.97 (d, J = 5.2 Hz, 2 H, 6-H), 8.46 (d, J = 5.2 Hz, 2 H, 5-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 161.0, 159.4, 159.1, 118.2 ppm. LR-FAB: m/z = 159.2 $[M + H]^+$.

6,6′-Diphenyl-4,4′-bipyrimidine (3b): Yield 93%. M.p. 199–201 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.42 (s, 2 H, 2-H), 8.93 (s, 2 H, 5-H), 8.27 (d, J = 3.5 Hz, 4 H, 2′-H, 6′-H), 7.58 (m, 6 H,

3′-H, 4′-H, 5′-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 166.2, 159.4, 157.3, 136.8, 131.7, 129.4, 127.8, 113.9 ppm. LR-FAB: *m/z* = 311.1 [M + H]$^+$. HRMS: calcd. [M + 1] for $C_{20}H_{15}N_4$, 311.1291; found 311.1302.

6,6′-Bis(2′-naphthyl)-4,4′-bipyrimidine (3c): Yield 82%. M.p. 224–226 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.51 (s, 2 H, 2-H), 9.10 (s, 2 H, 5-H), 8.82 (s, 2 H, 1′-H), 8.38 (d, *J* = 8.6 Hz, 2 H, 3′-H), 8.04 (d, *J* = 8.5 Hz, 2 H, 8′-H), 7.98 (d, *J* = 6.2 Hz, 4 H, 4′-H, 5′-H), 7.59 (t, *J* = 7.2 Hz, 4 H, 6′-H, 7′-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 166.2, 162.0, 159.5, 135.3, 134.1, 133.7, 129.6, 129.3, 128.4, 128.2, 128.1, 127.2, 124.3, 114.1 ppm. LR-FAB: *m/z* = 411.3 [M + H]. HRMS: calcd. [M + H]$^+$ for $C_{28}H_{19}N_4$ 411.1604; found 411.1610.

6,6′-Bis(1′-naphthyl)-4,4′-bipyrimidine (3d): Yield 58%. M.p. 240–243 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.51 (s, 2 H, 2-H), 8.87 (s, 2 H, 5-H), 8.32 (d, *J* = 6.4 Hz, 2 H, 8′-H), 8.05 (d, *J* = 8.1 Hz, 2 H, 4′-H), 7.97 (d, *J* = 6.1 Hz, 2 H, 2′-H), 7.84 (d, *J* = 7.0 Hz, 2 H, 5′-H), 7.69 (t, *J* = 5.5 Hz, 2 H, 7′-H), 7.60 (t, *J* = 9.6 Hz, 4 H, 3′-H, 6′-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 169.0, 161.6, 159.3, 136.1, 134.4, 131.2, 130.9, 129.1, 128.8, 127.7, 126.8, 125.7, 125.3, 119.1 ppm. LR-FAB: *m/z* = 411.1 [M + H]$^+$. HRMS: calcd. [M + 1] for $C_{28}H_{19}N_4$ 411.1604; found 411.1615.

6,6′-Bis(*p*-methoxyphenyl)-4,4′-bipyrimidine (3e): Yield 86%. M.p. 209–211 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.35 (s, 2 H, 2-H), 8.89 (s, 2 H, 5-H_5), 8.25 (d, *J* = 8.8 Hz, 4 H, 2′-H, 6′-H), 7.19 (d, *J* = 8.8 Hz, 4 H, 3′-H, 5′-H), 3.93 (s, 6 H, OMe) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 165.6, 162.8, 161.75, 159.3, 129.4, 129.3, 114.8, 113.0, 55.9 ppm. LR-FAB: *m/z* = 371.2 [M + H]. HRMS: calcd. [M + H]$^+$ for $C_{22}H_{19}N_4O_2$ 371.1502; found 371.1497.

6,6′-Bis(2-pyridyl)-4,4′-bipyrimidine (3f): Yield 56%. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.48 (s, 2 H, 2-H), 9.46 (s, 2 H, 5-H), 8.81 (d, *J* = 4.5 Hz, 2 H, 6′-H), 8.55 (d, *J* = 7.9 Hz, 2 H, 3′-H), 7.92 (t, *J* = 15.5 Hz, 2 H, 5′-H), 7.47(t, *J* = 12.7 Hz, 2 H, 4′-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 164.7, 162.3, 158.9, 153.8, 149.8, 137.1, 125.6, 121.8, 114.4 ppm. LR-FAB: *m/z* = 313.2 [M + H]$^+$.

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