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Reactions of 5-amino-1,2-azoles with aromatic and heterocyclic *o*-chloroaldehydes: [1+1] versus [2+1] cyclocondensation

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Abstract—5-Amino-1,2-azoles react with aromatic and heterocyclic aldehydes, having reactive halogen in *ortho*-position, and yield pyrazolo[3,4-*b*;2,3-*b*]quinolines, bispyrazolo[3,4-*b*;4′,3′-*e*]pyridines and their heterocyclic analogs, respectively as [1+1] or [2+1] condensation products. The fluorescent properties of the synthesized compounds are discussed.

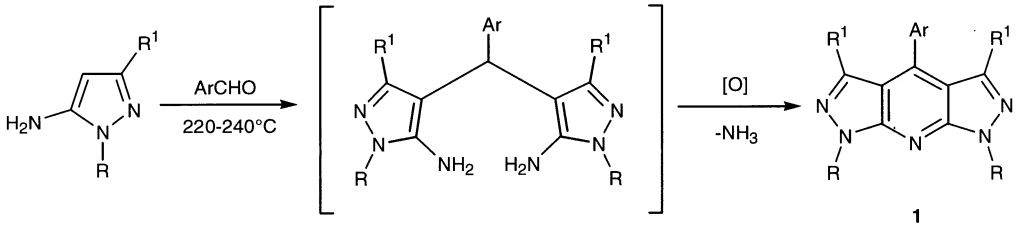
It has been shown in the literature that anilines react at elevated temperature with arylaldehydes yielding 4-aryl substituted acridines as a result of [2+1]-condensation.[1] 5-Aminopyrazoles with arylaldehydes by the same way gave 4-aryl substituted bispyrazolo[3,4-*b*;4′,3′-*e*]pyridines **1**.[2] The resulting products have antibacterial properties[2a] and their large conjugated π-systems are highly fluorescent and of potential use in photophysical processes and devices, such as photo-induced transfer reactions, pyrazole-based electroluminescent compounds and polymers.[3] The reaction is thought to occur via a bis(5-aminopyrazol-4-yl)phenylmethane intermediate, followed by the loss of ammonia with subsequent oxidative aromatization to the pyridine ring[3b] (Scheme 1).

To get access to analogs of bispyrazolo[3,4-*b*; 4′,3′-*e*]pyridines **1** we have studied the reactions of 5-amino-1,2-azoles **2** with the very reactive pentafluorobenzaldehyde. In this case we found that the result was a [1+1]-condensation and 1,2-azolo[3,4-*b*;4′,3′-*e*]tetrafluoroquinolines **3a**–**h** were formed in 52–87% yield (Table 1). Also this reaction is known in the literature as a synthetic method for (fused) quinolines from anilines.[4] Here the intermediate is thought to be an *ortho*-amino imine **A**, which undergoes thermal or acid-catalyzed ring closure (Scheme 2).

Joshi et al. reported on the basis of elemental analysis, IR, ^{1}H NMR and ^{19}F NMR spectroscopy that the reaction product of pentafluorobenzaldehyde and 1,3-diphenyl-5-aminopyrazole **2e** was bispyrazolo [3,4-*b*;4′,3′-*e*]pyridine

Table 1. Reactions of 5-amino-1,2-azoles **2a**–**h** with pentafluorobenzaldehyde

5-Amino-1,2-azole	X	R^1	Product	Yield (%)
2a	NMe	Me	**3a**	52
2b	NMe	*t*-Bu	**3b**	74
2c	NMe	Ph	**3c**	75
2d	NPh	Me	**3d**	80
2e	NPh	Ph	**3e**	87
2f	O	Me	**3f**	53
2g	O	Ph	**3g**	61
2h	S	Me	**3h**	58



Scheme 1.

Keywords: pyrazoles; aldehydes; cyclization; pyridines; fluorescence.
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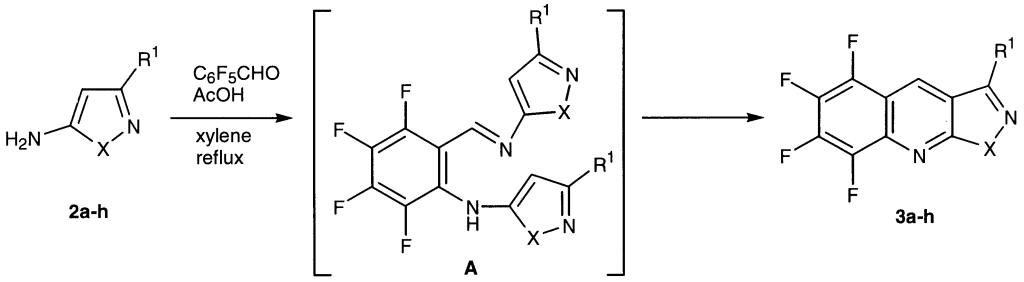
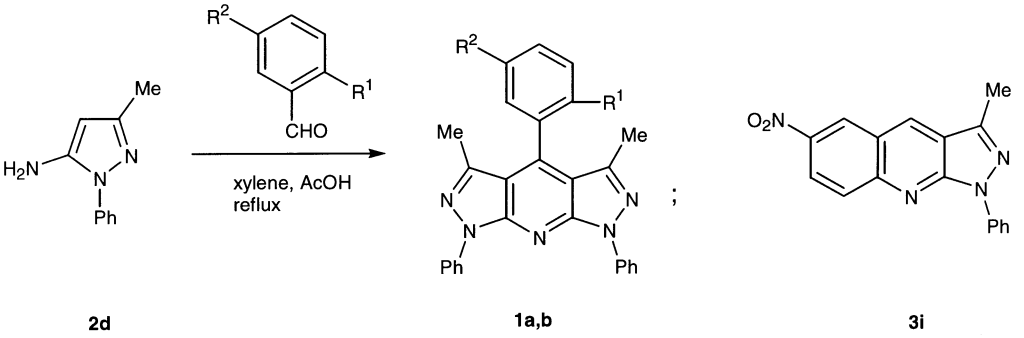
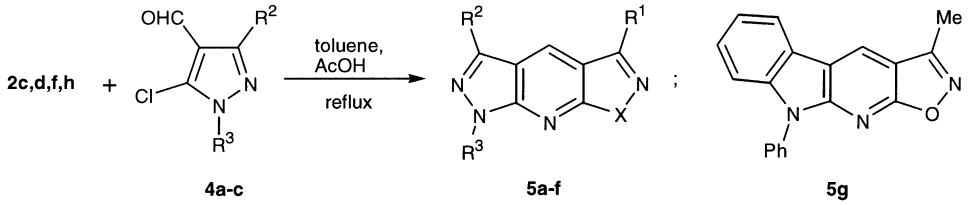


Scheme 2.



Scheme 3. (a) $R^1=R^2=F$; (b) $R^1=Cl$, $R^2=NO_2$.



Scheme 4.

Table 2. Reactions of azoles **2c**,**d**,**f**,**h** with heterocyclic *o*-chlorocarbaldehydes **4a–c**

Azole	R^1	X	Aldehyde	R^2	R^3	Product	Yield (%)
2d	Me	NPh	**4a**	Me	Ph	**5a**	34
2d	Me	NPh	**4b**	Ph	Ph	**5b**	36
2f	Me	O	**4a**	Me	Ph	**5c**	64
2f	Me	O	**4b**	Ph	Ph	**5d**	87
2h	Me	S	**4a**	Me	Ph	**5e**	71
2c	Ph	NMe	**4c**	Ph	Me	**5f**	25
2f	Me	O	2-chloro-1-phenyl-3-indolecarbaldehyde			**5g**	48

1 (Ar=C_6F_5).[2a] Comparing the MS (*m*/*e*=393), ^{1}H- and ^{13}C NMR data of the product we obtained under their conditions with the spectral data of compounds **3a**–**d**, we now showed beyond doubt that this compound was the 1,2,3,4-tetrafluoropyrazolo[3,4-*b*; 4′,3′-*e*]quinoline **3e**. Furthermore, the less reactive *o*-halosubstituted benzaldehydes 2,5-difluorobenzaldehyde and 2-chloro-5-nitrobenzaldehyde yielded the [2+1]-condensation products when reacted with 5-aminopyrazoles. From the NMR and mass spectroscopic data we could decide that these were the symmetrical bispyrazolo[3,4-*b*;4′,3′-*e*]pyridines **1a**,**b**. In the case of 2-chloro-5-nitrobenzaldehyde, an additional amount (3%) of pyrazolo[3,4-*b*;2,3-*b*]quinoline **3i** was separated. In fact, this is the only case reported so far where the two types of products **1** and **3** are obtained from the same reaction. 5-Amino-3-methylisoxazole **2f** and -isothiazole **2h** did not form the analogs of bispyrazolo[3,4-*b*;4′,3′-*e*]pyridines **1** and no defined products were isolated from the reaction mixture. Apparently, the thermally labile isoxazole and isothiazole ring systems did not survive the rather drastic reaction conditions (Scheme 3).

To show the scope and limitations of the [1+1] condensation of heterocyclic α-chloroaldehydes with amines we have studied the reaction of 5-amino-1,2-azoles **2** with the reactive heterocyclic 5-chloropyrazole-4-carbaldehydes **4a**–**c** (Scheme 4 and Table 2).[5] It should be mentioned that in the literature only one example of the [1+1] condensation reaction of 5-chloro-3-methyl-1-phenylpyrazole-4-carbaldehyde **4a** and 5-aminopyrazole **2a** to give bispyrazolo[3,4-*b*;4′,3′-*e*]pyridine **5a** was found.[6]

As expected, the reaction goes the same way as in the reactions leading to **3a**–**e** and only the [1+1]-condensation products **5a**–**e** form. Further examples were the tricyclic

Table 3. Selected data from absorption and emission spectra of pyridines **3a–h** and **5e,f**

Compound	Absorption[a] λ_{max} (nm) (ϵ, M^{-1} cm^{-1})		Emission λ_{max} (nm) (ϵ, M^{-1} cm^{-1})	
	Ethanol	Toluene	Ethanol	Toluene
3a	382(4310)	386(5220)	435(1.00)	419(0.79)
3b	384(4510)	386(4890)	434(1.00)	421(0.81)
3c	398(5720)	401(5820)	485(0.73)	461(0.74)
3d	395(3180)		495(0.16)	
3e	409(5660)	415(4910)	505(0.47)	491(0.61)
3f	335(3400)		408(0.14)	
3g	342(5230)		415(0.11)	
3h	363(3520)		418(0.15)	
5e	342(3850)		445(0.08)	
5f	375(7940)	377(7260)	440(0.36)	419(0.21)

[a] Range reported: 300–450 nm.

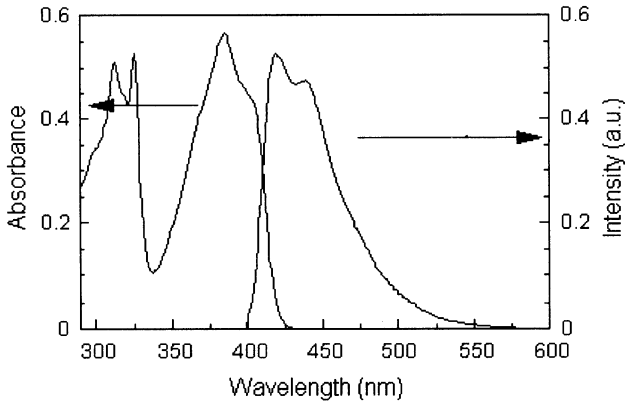


Figure 2. Absorption spectrum of a 1.08×10^{-4} M solution of compound **3a** I toluene (left); fluorescence spectrum (excitation at 386 nm) of compound **3a** in toluene (right).

pyridine **5f**, and the tetracyclic indolopyridine **5g**, which were smoothly prepared from the corresponding *o*-chloroaldehyde and 5-amino-3-methylisoxazole.

All of the compounds obtained (**1a**,**b**, **3a–i**, **5a–g**) are highly fluorescent. In Table 3 are shown the selected data from absorption and emission spectra of fused pyridines **3a–h** and **5e**,**f** and on Fig. 1 absorption and fluorescence spectra of compound **3c** are drawn.

The strong fluorescent properties of some of the compounds makes them interesting as potential (electro)luminescent dye or scintillator or fluorescent probe. In compounds **3** the presence of the *N*-alkyl or *N*-aryl group in the pyrazine ring is necessary for an absorption maximum above 380 nm and a fluorescent quantum yield larger than 0.3. The long wavelength absorption band is structureless in toluene or both solvents (toluene, ethanol) for compounds **3c**, **3e** and **5f**, while it shows some vibrational fine structure in **3a** (Fig. 2) and **3b**. This may indicate that the dihedral angle between the heterocycle and the phenyl substituents in position 3 changes upon excitation in compounds **3c**, **3e** and **5f**. Besides the long wavelength absorption band of which the data are shown in Table 3 the compounds **3** with an *N*-alkyl or *N*-aryl moiety in the pyrazole ring show a structured absorption band below 350 nm. This

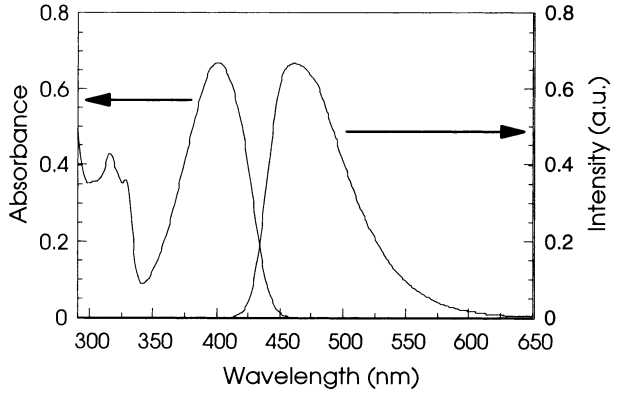


Figure 1. Absorption spectrum of a 1.147×10^{-4} M solution of compound **3c** in toluene (left); fluorescence spectrum (excitation at 401 nm) of compound **3c** in toluene (right).

excitation is apparently not accompanied with a change in the dihedral angle between the phenyl and the heterocycle. While the emission spectra of the compounds **3a** and **3b** with an alkyl substituent in the 3 position show a vibrational structure in toluene the latter is blurred in compounds **3c**, **3e** and **5f**. In ethanol, all vibrational structures of the emission bands disappear, indicating a difference in dipole moment for the ground and excited state. The small bathochromic shift observed for the emission spectra between toluene and ethanol indicates that the excited state dipole moment is larger than the ground state dipole moment. The difference will however not be very large, as for solvent probes with strongly polar excited states, shifts up to 100 or 200 nm are observed.[7–14] The small hypsochromic shift of the absorption spectra observed between toluene and ethanol can be attributed to a decreased polarizability of the solvent.[15–18] The long wavelength of absorption and emission maxima, the high fluorescence quantum yield, and the independence of the photophysical properties upon the polarity and hydrogen donor properties of the environment make **3c**, **3e** and **5f** interesting as fluorescent labels. The last two properties make them potentially interesting scintillators in electroluminescent devices.[19–21] Furthermore, the non-planarity indicated by the structureless spectra of compounds **3c**, **3e** and **5f** will probably reduce the aggregation which is an advantage to use them at high concentration in a polymer matrix or glass.[22] For a possible use as probe and/or scintillator compounds **3d** and **3f**, **3g** and **3h** are less interesting due to a shorter excitation and emission wavelength and a lower fluorescence quantum yield.

1. Experimental

Mps were determined using a Reichert Thermovar apparatus. NMR spectra were acquired on commercial instrumentation (Bruker Avance 300 MHz or Bruker AMX 400 MHz) and chemical shifts are reported in ppm (δ) referenced to internal residual solvent protons (^1H) or the carbon signal of deuterated solvents (^{13}C). Mass spectrometry data were obtained with a HP MS-engine 5989A (EI=electron impact, 70 eV). 5-Amino-1,2-azoles were obtained from Maybridge Chemical and benzaldehydes

from Aldrich. Heterocyclic *o*-chlorobenzaldehydes were synthesized by known procedures.[5]

1.1. General procedure for synthesis of fused pyridines

In a typical experimental procedure 30 μL of acetic acid were added at room temperature to a mixture of 5-aminopyrazole **2a**–**h** (5 mmol) and aldehyde (3 mmol) in toluene (3 mL) and *p*-xylene (7 mL) and refluxed while removing water azeotropically. The xylene solution obtained was refluxed for 6–24 h (monitoring with TLC), and allowed to cool to room temperature. Then, methanol (10 mL) was added, the crystalline solid was filtered off and washed with methanol. The filtrate was evaporated to dryness under reduced pressure and the residue was washed with water and dried. The precipitates were combined and the reaction product was purified by column chromatography on silica gel.

1.1.1. 5,6,7,8-Tetrafluoro-1,3-dimethyl-1*H*-pyrazolo[3,4-*b*]-quinoline 3a. From pentafluorobenzaldehyde (4.2 g, 21.7 mmol) and 5-amino-1,3-dimethyl-1*H*-pyrazole **2a** (4.0 g, 36.1 mmol). Yield 3.0 g (52%), mp 155–6°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.71 (s, 1H, C^4H), 4.13 (s, 3H, CH_3N^1), 2.69 (s, 3H, CH_3C^3). ^{13}C NMR ($CDCl_3$, δ, ppm): 12.5 (CH_3–C^3), 33.7(CH_3–N^1), 111.2 (d×m, C^{4a}, $^2J_{CF}$=14.3 Hz), 117.0 (br s, C^{3a}), 123.2 (C^4), 134.7 (d, C^{8a}, $^2J_{CF}$=14.3 Hz), 135.3 (d×m, CF, $^1J_{CF}$=251 Hz), 141.5 (C^3), 141.8 (d×m, 3×CF, $^2J_{CF}$=251 Hz), 150.8 (C^{9a}). Mass spectrum, *m*/*z* (EI, %): 269 (M^+, 100). Found, %: C 53.51; H 2.87; N 15.47. $C_{12}H_7F_4N_3$. Calcd, %: C 53.54; H 2.62; N 15.61.

1.1.2. 5,6,7,8-Tetrafluoro-3-*tert*-butyl-1-methyl-1*H*-pyrazolo[3,4-*b*]quinoline 3b. From pentafluorobenzaldehyde (4.0 g, 20.4 mmol) and 5-amino-3-*tert*-butyl-1-methyl-1*H*-pyrazole **2b** (5.0 g, 32.7 mmol). Yield 4.7 g (74%), mp 177–178°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.91 (s, 1H, C^4H), 4.18 (s, 3H, CH_3N^1), 1.59 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$, δ, ppm): 30.0 (CH_3C), 33.7 (CH_3CC^3), 34.5 (CH_3N^1), 110.9 (d, C^{4a}, $^2J_{CF}$=15.7 Hz), 115.0 (br s, C^{3a}), 124.8 (C^4), 134.1 (d×m, C^{4a}, $^2J_{CF}$=15.7 Hz), 135.6 (d×m, CF, $^1J_{CF}$=250 Hz), 141.7 (d×m, 3×CF, $^1J_{CF}$=250 Hz), 151.2 (C^{9a}), 152.7(C^3). Mass spectrum, *m*/*z* (EI, %): 311 (M^+, 100). Found, %: C 57.74; H 4.16; N 13.45. $C_{15}H_{13}F_4N_3$. Calcd, %: C 57.88; H 4.21; N 13.50.

1.1.3. 5,6,7,8-Tetrafluoro-1-methyl-3-phenyl-1*H*-pyrazolo[3,4-*b*]quinoline 3c. From pentafluorobenzaldehyde (4.25 g, 21.7 mmol) and 5-amino-1-methyl-3-phenyl-1*H*-pyrazole **2c** (6.25 g, 36.1 mmol). Yield 5.4 g (75%), mp 157–158°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 9.05 (s, 1H, C^4H), 8.02 (d, 2H, *ortho*-Ph), 7.56 (t, 2H, *meta*-Ph), 7.48 (t, 1H, *para*-Ph), 2.77 (s, 3H, CH_3N^1). ^{13}C NMR ($CDCl_3$, δ, ppm): 34.9 (CH_3–N^1), 112.0 (d, C^{4a}, $^2J_{CF}$=14.8 Hz), 115.2 (C^{3a}), 124.5 (C^4), 127.1, 129.1, 129.2, 134.4 (d, C^{8a}, $^2J_{CF}$=14.8 Hz), 135.9 (d×m, CF, $^1J_{CF}$=253 Hz), 141.7 (d×m, 3×CF, $^2J_{CF}$=253 Hz), 151.1(C^{9a}). Mass spectrum, *m*/*z* (EI, %): 331 (M^+, 100). Found, %: C 61.61; H 2.76; N 12.62. $C_{17}H_9F_4N_3$. Calcd, %: C 61.64; H 2.74; N 12.68.

1.1.4. 5,6,7,8-Tetrafluoro-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]quinoline 3d. From pentafluorobenzaldehyde (1.56 g, 7.9 mmol) and 5-amino-3-methyl-1-phenyl-1*H*-pyrazole **2d** (2.3 g, 13.3 mmol). Yield 2.1 g (80%), mp 179–180°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 9.04 (s, 1H, C^4H), 8.44 (d, 2H, *ortho*-Ph) 7.55 (t, 2H, *meta*-Ph), 7.30 (t, 1H, *para*-Ph), 2.77 (s, 3H, CH_3C^3). ^{13}C NMR ($CDCl_3$, δ, ppm): 13.6 (CH_3C^3), 112.3 (d, C^{4a}, $^2J_{CF}$=14.3 Hz), 119.9 (*ortho*-Ph), 125.0 (C^4), 127.6 (*para*-Ph), 129.0 (*meta*-Ph), 134.7 (d×m, C^{8a}, $^2J_{CF}$=14.8 Hz), 135.6 (d×m, CF, $^1J_{CF}$=251 Hz), 139.9 (C^3 and *ipso*-Ph), 142.2 (d×m, 3×CF, $^1J_{CF}$=251 Hz), 150.6 (C^{9a}). Mass spectrum, *m*/*z* (EI, %): 331 (M^+, 100). Found, %: C 61.38; H 2.73; N 12.53. $C_{17}H_9F_4N_3$. Calcd, %: C 61.64; H 2.74; N 12.68.

1.1.5. 5,6,7,8-Tetrafluoro-1,3-diphenyl-1*H*-pyrazolo-[3,4-*b*]quinoline 3e. From pentafluorobenzaldehyde (0.39 g, 2 mmol) and 5-amino-1,3-diphenyl-1*H*-pyrazole **2e** (0.94 g, 4 mmol). Yield 0.69 g (87%), mp 207–208°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 9.11 (s, 1H, C^4H), 8.56 (d, 2H, *ortho*-PhN^1), 8.10 (d, 2H, *ortho*-PhC^3), 7.56 (m, 5H, *meta*-PhN^1, *meta*-PhC^3, and *para*-PhC^3), 7.34 (t, 1H, *para*-PhN^1). ^{13}C NMR ($CDCl_3$, δ, ppm): 112.2 (d, C^{4a}, $^2J_{CF}$=15 Hz), 116.9 (C^{3a}), 120.4 (*ortho*-PhN^1), 124.7 (C^4), 126.0 (*para*-PhC^3 and *para*-PhN^1), 127.5 (*ortho*-PhC^3), 129.1 (*meta*-PhN^1), 129.2 (*meta*-PhC^3), 131.6 (*ipso*-PhC^3), 134.1 d (C^{8a}, $^2J_{CF}$=15 Hz), 135.6 (d×m, CF, $^1J_{CF}$=252 Hz), 139.2 (*ipso*-PhN^1), 141.6 (d×m, 3×CF, $^2J_{CF}$=252 Hz), 144.7, 150.3 (C^{9a}). Mass spectrum, *m*/*z* (EI, %): 393 (M^+, 100). Found, %: C 67.22; H 2.80; N 10.59. $C_{22}H_{11}F_4N_3$. Calcd, %: C 67.18; H 2.82; N 10.68.

1.1.6. 5,6,7,8-Tetrafluoro-3-methyl-isoxazolo[5,4-*b*]quinoline 3f. From pentafluorobenzaldehyde (1.20 g, 6.1 mmol) and 5-amino-3-methylisoxazole **2f** (0.69 g, 7.0 mmol). Yield 0.83 g (53%), mp 142–143°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.83 (s, 1H, C^4H), 2.73 (s, 3H, CH_3C^3). ^{13}C NMR ($CDCl_3$, δ, ppm): 12.5(CH_3C^3), 113.6 (d, C^{4a}, $^2J_{CF}$=14.4 Hz), 116.5(C^{3a}), 126.6 (C^4), 135.7 (d, C^{8a}, $^2J_{CF}$=14.4 Hz), 137.3 (d×m, CF, $^1J_{CF}$=252 Hz), 142.0 (d×m, 3×CF, $^2J_{CF}$=252 Hz), 156.2 (C^3), 167.6 (C^{9a}). Mass spectrum, *m*/*z* (EI, %): 256 (M^+, 100). Found, %: C 51.41; H 1.58; N 10.71. $C_{11}H_4F_4N_2O$. Calcd, %: C 51.58; H 1.57; N 10.94.

1.1.7. 5,6,7,8-Tetrafluoro-3-phenyl-isoxazolo[5,4-*b*]quinoline 3g. From pentafluorobenzaldehyde (1.0 g, 5.1 mmol) and 5-amino-3-methylisoxazole **2g** (1.0 g, 6.25 mmol). Yield 0.98 g (61%), mp 189–190°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 9.09 (s, 1H, C^4H), 8.05–8.02 (m, 2H, *meta*-PhC^3), 7.67–7.64 (m, 3H, *ortho*-PhC^3 and *para*-PhC^3). ^{13}C NMR ($CDCl_3$, δ, ppm): 113.6 (d, C^{4a}, $^2J_{CF}$=14.0 Hz), 114.5 (C^{3a}), 127.4 (C^4 and *ipso*-PhC^3), 127.8 (*ortho*-PhC^3), 129.6 (*meta*-PhC^3), 131.6 (*para*-PhC^3), 134.5 (m, C^{8a}, $^2J_{CF}$=14.0 Hz), 137.1 (d×m, CF, $^1J_{CF}$=254 Hz), 142.0 (d×m, 2×CF, $^2J_{CF}$=254 Hz), 142.7 (d×m, CF, $^2J_{CF}$=254 Hz), 157.4 (C^3), 167.7 (C^{9a}). Mass spectrum, *m*/*z* (EI, %): 256 (M^+, 100). Found, %: C 51.41; H 1.58; N 10.71. $C_{11}H_4F_4N_2O$. Calcd, %: C 51.58; H 1.57; N 10.94.

1.1.8. 5,6,7,8-Tetrafluoro-3-methyl-isothiazolo[5,4-*b*]-quinoline 3h. From pentafluorobenzaldehyde (1.20 g, 6.1 mmol) and 5-amino-3-methylisothiazole **2h** hydrochloride (1.05 g, 7.0 mmol) and triethylamine (1 mL). Yield 0.96 g (58%), mp 139–140°C. ^{1}H NMR ($CDCl_3$, δ,

ppm): 8.99 (s, 1H, C^4H), 2.90 (s, 3H, CH_3C^3). ^{13}C NMR ($CDCl_3$, δ, ppm): 18.3 (CH_3C^3), 112.7 (d, C^{4a}, $^2J_{CF}$= 14.5 Hz), 125.6 (C^{4a}), 127.1 (C^4), 134.5 (d, C^{8a}, $^2J_{CF}$= 14.5 Hz), 137.4 (d×m, CF, $^1J_{CF}$=255 Hz), 141.8 (d×m, 3×CF, $^2J_{CF}$=252 Hz), 161.8 (C^{3a}), 172.2 (C^{9a}). Mass spectrum, *m/z* (EI, %): 272 (M^+, 100). Found, %: C 48.58; H 1.58; N 10.11. $C_{11}H_4F_4N_2S$. Calcd, %: C 48.53; H 1.48; N 10.29.

1.1.9. 4-(2,5-Difluorophenyl)-3,5-dimethyl-1,7-diphenyl-1,7-dihydro-dipyrazolo[3,4-*b*;4′,3′-*e*]pyridine 1a. From pentafluorobenzaldehyde (1.0 g, 7.0 mmol) and 5-amino-3-methyl-1-phenylpyrazole **2g** (1.60 g, 9.1 mmol) and triethylamine (1 mL). Yield 0.75 g (38%), mp 277°C. ^1H NMR ($CDCl_3$, δ, ppm): 8.39 (d, 4H, *ortho*-PhN^1 and *ortho*-PhN^7), 8.54 (t, 4H, *meta*-PhN^1 and *meta*-PhN^7), 7.51–7.25 (m, 3H, arom), 7.17 (t, 2H, *para*-PhN^1 and *para*-PhN^7), 2.21 (s, 6H, CH_3C^3 and CH_3C^5). ^{13}C NMR ($CDCl_3$, δ, ppm): 14.4 (CH_3C^3 and CH_3C^5), 113.4 (C^{3a} and C^{4a}), 116.9–118.1 (m, $^2J_{CF}$=14 Hz, $^3J_{CF}$=8 Hz, *ortho*-CF_{arom}), 118.8 (d, $^1J_{CF}$=240 Hz, *ipso*-CF_{arom}), 120.3 (*meta*-PhN^1 and *meta*-PhN^7), 121.6 (d, $^1J_{CF}$=240 Hz, *ipso*-CF_{arom}), 125.3 (*para*-PhN^1 and *para*-PhN^7), 128.9 (*ortho*-PhN^1 and *ortho*-PhN^7), 132.5 and 139.5 (C^4, *ipso*-PhN^1 and *ipso*-PhN^7), 143.7 (C^3 and C^5), 150.5 (C^{7a} and C^{8a}). Mass spectrum, *m/z* (EI, %): 272 (M^+, 100). Found, %: C 48.58; H 1.58; N 10.11. $C_{11}H_4F_4N_2S$. Calcd, %: C 48.53; H 1.48; N 10.29.

1.1.10. 4-(2-Chloro-5-nitrophenyl)-3,5-dimethyl-1,7-diphenyl-1,7-dihydro-dipyrazolo[3,4-*b*;4′,3′-*e*]pyridine 1b and 3-methyl-6-nitro-1-phenyl-1*H*-pyrazolo[3,4-*b*]quinoline 3i. From 2-chloro-5-nitrobenzaldehyde (1.0 g, 5.4 mmol) and 5-amino-3-methyl-1-phenyl-1*H*-pyrazole **2d** (1.0 g, 5.8 mmol). After column chromatography a mixture of two compounds was obtained. This mixture was suspended in chloroform (3 mL), the suspension was filtered and precipitate was washed again with chloroform (1 mL). The filtrates were evaporated under reduced pressure and 4-(2-chloro-5-nitrophenyl)-3,5-dimethyl-1,7-diphenyl-1,7-dihydro-dipyrazolo[3,4-*b*;4′,3′-*e*]pyridine (0.56 g, 39%) was isolated as crystals with mp 215°C. ^1H NMR ($CDCl_3$, δ, ppm): 8.47 (s, 1H, *ortho*-NO_2), 8.35–8.43 (m, 5H, arom), 7.80 (d, 1H, *ortho*-NO_2), 7.52 (t, 4H, *meta*-PhN^1 and *meta*-PhN^7), 7.29 (t, 2H, *para*-PhN^1 and *para*-PhN^7), 2.00 (s, 6H, CH_3C^3 and CH_3C^5). ^{13}C NMR ($CDCl_3$, δ, ppm): 14.1 (CH_3C^3 and CH_3C^5), 112.8 (C^{3a} and C^{4a}), 120.1 (*meta*-PhN^1 and *meta*-PhN^7), 125.3 (*para*-PhN^1 and *para*-PhN^7), 125.5, 128.9 (*ortho*-PhN^1 and *ortho*-PhN^7), 130.6, 134.1, 135.0, 139.3 (*ipso*-PhN^1 and *ipso*-PhN^7), 140.2 (C^4), 143.1 (C^3 and C^5), 146.1, 150.3 (C^{7a} and C^{8a}). Mass spectrum, *m/z* (EI, %): 494 (M^+, 100). Found, %: C 65.65; H 3.92; N 16.67. $C_{27}H_{19}ClN_6O_2$. Calcd, %: C 65.52; H 3.87; N 16.98. The precipitate from the chloroform suspension (7 mg) was identified as 3-methyl-6-nitro-1-phenyl-1*H*-pyrazolo[3,4-*b*]quinoline. ^1H NMR ($CDCl_3$, δ, ppm): 9.00 (s, 1H, C^4H), 8.75 (s, 1H, *ortho*-NO_2), 8.55–8.34 (m, 3H, arom), 8.25 (d, 1H, *ortho*-NO_2), 7.57 (m, 2H, *meta*-PhN^1), 7.32 (t, 1H, *para*-PhN^1), 2.80 (s, 3H, CH_3C^3). Mass spectrum, *m/z* (EI, %): 304 (M^+, 100).

1.1.11. 3,5-Dimethyl-1,7-diphenyl-1,7-dihydro-dipyrazolo[3,4-*b*;4′,3′-*e*]pyridine 5a. From 4-chloro-3-methyl-1-phenylpyrazole **4a** (0.50 g, 2.27 mmol) and 5-amino-3-methyl-1-phenylpyrazole **2d** (0.40 g, 2.27mmol). Yield 0.26 g, 34%, mp 217–218°C. ^1H NMR ($CDCl_3$, δ): 8.27 (s, 1H, C^4H), 8.40 (d, 4H, *ortho*-PhN^1 and *ortho*-PhN^7), 7.53 (t, 4H, *meta*-PhN^1 and *meta*-PhN^7), 7.27 (t, 2H, *meta*-PhN^1 and *meta*-PhN^7) and 2.70 (s, 6H, CH_3C^3 and CH_3C^5). ^{13}C NMR ($CDCl_3$, δ): 12.6 (CH_3C^3 and CH_3C^5), 114.9 (C^{3a}), 122.8 (C^4), 120.1 (*meta*-PhN^1 and *meta*-PhN^7), 125.1 (*para*-PhN^1 and *para*-PhN^7), 129.0 (*ortho*-PhN^1 and *ortho*-PhN^7), 139.7 (*ipso*-PhN^1 and *ipso*-PhN^7), 144.1 (C^3) and 150.5 (C^{8a}). Mass spectrum, *m/z* (EI, %): 340 (M^++H, 100), 339 (M^+, 21). HRMS: 399.1487. $C_{21}H_{17}N_5$. Calcd: 339.1484.

1.1.12. 3-Methyl-1,5,7-triphenyl-1,7-dihydro-dipyrazolo-[3,4-*b*;4′,3′-*e*]pyridine 5b. From 5-chloro-1,3-diphenyl-1*H*-pyrazole **4b** (0.50 g, 1.77 mmol) and 5-amino-3-methyl-1-phenylpyrazole **2d** (0.30 g, 1.77 mmol). Yield 0.25 g, 36%, mp 209–210°C. ^1H NMR ($CDCl_3$, δ): 8.49 (s, 1H, C^4H), 8.45 and 8.36 (2×d, 4H, *ortho*-PhN^1 and *ortho*-PhN^7), 7.56–7.47 (m, 7H, *meta*-PhN^1 and *meta*-PhN^7, *meta*-PhC^5, *para*-PhC^5), 7.31–7.23 (2 t, 2H, *para*-PhN^1 and *para*-PhN^7), 8.01 (d, 2H, *ortho*-PhC^5), and 2.65 (s, 3H, CH_3C^3). ^{13}C NMR ($CDCl_3$, δ): 12.6 (CH_3C^3), 113.0 (C^4H), 115.6 (C^{3a}), 123.8 (C^{4a}), 119.9, 120.5, 125.0, 125.5, 127.5, 128.9, 129.0 and 128.92 (Ph), 139.62 and 139.64 (*ipso*-PhN^1 and *ipso*-PhN^7), 132.5 (*ipso*-PhC^5), 144.2 (C^3), 145.4 (C^5), 150.1 (C^{8a}), and 150.7 (C^{7a}). Mass spectrum, *m/z* (EI, %): 402 (M^++H, 100), 401 (M^+, 25). HRMS: 401.1651. $C_{26}H_{19}N_5$. Calcd: 401.1640.

1.1.13. 3,5-Dimethyl-7-phenyl-1*H*-pyrazolo[4′,3′-*b*;5,4-*e*]-isoxazolopyridine 5c. From 5-chloro-3-methyl-1-phenyl-1*H*-pyrazole-4-carbaldehyde **4a** (0.20 g, 0.91 mmol) and 5-amino-3-methyl-isoxazole **2f** (0.09 g, 0.91 mmol). Yield 0.15 g, 64%, mp 193°C. ^1H NMR ($CDCl_3$, δ): 8.27 (d, 2H, *ortho*-PhN^7), 8.19 (s, 1H, C^4H), 7.51 (d, 2H, *meta*-PhN^7), 7.29 (t, 1H, *para*-PhN^7), 2.64 (s, 3H, CH_3C^5) and 2.59 (s, 3H, CH_3C^3). ^{13}C NMR ($CDCl_3$, δ): 10.7 (CH_3C^3), 12.5 (CH_3C^5), 110.1 (C^3), 116.0 (C^{4a}), 120.6 (*ortho*-PhN^7), 124.4 (C^4), 125.8 (*para*-PhN^7), 129.0 (*meta*-PhN^7), 139.0 (*ipso*-PhN^7), 144.1 (C^5), 150.5 (C^{7a}), 156.1 (C^5), and 168.9 (C^{8a}). Mass spectrum, *m/z* (EI, %): 264 (M^+, 100). HRMS: 264.1013. $C_{15}H_{12}N_4O$. Calcd: 264.1011.

1.1.14. 3-Methyl-5,7-diphenyl-1*H*-pyrazolo[4′,3′-*b*;5,4-*e*]-isoxazolopyridine 5d. From 5-chloro-1,3-diphenyl-1*H*-pyrazole-4-carbaldehyde **4b** (0.21 mg, 0.75 mmol) and 5-amino-3-methylisoxazole **2f** (73 mg, 0.74 mmol). Yield 214 mg, 87%, mp 208–209°C. ^1H NMR ($CDCl_3$, δ): 8.55 (s, 1H, C^4H), 8.36 (d, 2H *ortho*-PhN^7), 8.00 (d, 2H *ortho*-PhC^5), 7.58–7.49 (m, 5H, Ph), 7.35–7.32 (t, 1H, *para*-$PhCN^7$) and 2.65 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 10.9 (CH_3C^3), 111.1 (C^{3a}), 114.3 (C^{4a}), 121.2 (*ortho*-PhN^7), 125.6 (C^4H), 126.3 (*para*-PhN^7), 127.6, 129.1 and 129.3 (Ph), 132.0 (*ipso*-PhC^5), 138.9 (*ipso*-PhN^7), 145.7 (C^{4a}), 151.1 (C^{7a}), 156.2 (C^3), and 168.7 (C^{8a}). Mass spectrum, *m/z* (EI, %): 327 (M^+, 100). Found, %: C 73.4; H 4.6. $C_{20}H_{15}N_4O$. Calcd: C 73.42; H 4.41.

1.1.15. 3,5-Dimethyl-7-phenyl-1*H*-pyrazolo[4′,3′-*b*;5,4-*e*]-isothiazolopyridine 5e. From 5-chloro-3-methyl-1-phenyl-1*H*-pyrazole-1-4-carbaldehyde **4a** (0.66 g, 3 mmol) and

5-amino-3-methyl-isothiazole **2h** hydrochloride (0.75 g, 5 mmol) and triethylamine (0.6 g). Yield 0.6 g (71%), mp 157–159°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.42 (s, 1H, C^4H), 8.32 (d, 2H, *ortho*-PhN^7), 7.52 (t, 2H, *meta*-PhN^7) 7.29 (t, 1H, *para*-PhN^7), 2.70 (s, 3H, CH_3C^3), 2.67 (s, 3H, CH_3C^5). ^{13}C NMR ($CDCl_3$, δ, ppm): 12.5 (CH_3C^5), 18.0 (CH_3–C^3), 115.9 (C^{4a}), 120.4 (*ortho*-PhN^7), 124.7 (C^4), 125.6 (*para*-PhN^7), 129.0 (*meta*-PhN^7), 139.0 (*ipso*-PhN^7), 144.1 (C^{5a}), 150.4 (C^{7a}), 161.9 (C^{3a}), and 172.5 (C^{8a}). Mass spectrum, *m*/*z* (EI, %): 280 (M^+, 100). Found, %: C 63.82; H 4.40; N 19.46. $C_{15}H_{12}N_4S$. Calcd, %: C 64.26; H 4.31; N 19.98.

1.1.16. 1,7-Dimethyl-3,5-diphenyl-1,7-dihydro-dipyrazolo[3,4-*b*;4′,3′-*e*]pyridine 5f. From 5-chloro-1-methyl-3-phenyl-1*H*-pyrazole-4-carbaldehyde **4c** (0.66 g, 3 mmol) and 5-amino-1-methyl-3-phenyl-1*H*-pyrazole **2c** (1.04 g, 6 mmol). Yield 0.25 g (25%), mp 185–186°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.86 (s, 1H, C^4H), 7.96 (d, 4H, *ortho*-PhC^3 and *ortho*-PhC^5), 7.54 (t, 4H, *meta*-PhC^3 and *meta*-PhC^5), 7.45 (t, 2H, *para*-PhC^3 and *para*-PhC^5), 4.22 (s, 6H, CH^3N^1 and CH_3N^7). ^{13}C NMR ($CDCl_3$, δ, ppm): 33.9 (CH_3N^1), 112.1 (C^{3a} and C^{4a}), 124.6 (C^4), 127.3 (*ortho*-PhC^3 and *ortho*-PhC^5), 128.5 (*para*-PhC^3 and *para*-PhC^5), 129.0 (*meta*-PhC^3 and *meta*-PhC^5), 133.1 (*ipso*-PhC^3 and *ipso*-PhC^5), 144.0 (C^3 and C^5), 152.0 (C^{7a} and C^{8a}). Mass spectrum, *m*/*z* (EI, %): 339 (M^+, 100). Found, %: C 74.13; H 5.14; N 20.47. $C_{21}H_{17}N_5$. Calcd, %: C 74.32; H 5.05; N 20.63.

1.1.17. 3-Methyl-9-phenyl-1*H*-indolo[2′,3′-*b*;5,4-*e*]isoxazolopyridine 5g. From 2-chloro-1-phenyl-1*H*-indole-3-carbaldehyde (0.51 g, 2.0 mmol) and 5-amino-3-methyl-isoxazole **2f** (0.20 g, 2.0 mmol). Yield 285 mg, 48%, mp 197°C. ^{1}H NMR ($CDCl_3$, δ): 8.58 (s, 1H, C^4H) 8.15–8.13 (d, 1H, C^5H, indole), 7.63 and 7.49 (2×m, 7H, PhN^9, C^6H and C^8H), 7.38 (m, 1H, C^7H) and 2.67 (br s, 3H, CH_3C^3). ^{13}C NMR ($CDCl_3$, δ): 10.9 (CH_3C^3), 107.9 (C^{3a}), 110.9 (C^8), 115.2, 120.4 (C^6), 120.8 (C^{4b}), 121.6 (C^5), 122.2 (C^4), 127.2 (C^7), 127.3 (*ortho*-PhN^{10}), 128.2 (*para*-PhN^{10}), 129.7 (*meta*-PhN^7), 135.4 and 141.2 (C^{8a} and *ipso*-PhN^7), 153.2 (C^{9a}), 155.8 (C^3), and 168.8 (C^{10a}). Mass spectrum, *m*/*z* (EI, %): 299 (M^+, 100).

1.2. Absorption and emission spectra

Toluene (ACROS, spectrophotometric grade) and ethanol (BDH, p.a.) were used as received. The absorption spectra were recorded with a DW-2000 Aminco or Perkin Elmer Lamda 40 spectrophotometer. The fluorescence and excitation spectra were determined on a SPEX Fluorolog in a rectangular configuration. The spectra were obtained in S/R (sample over reference) mode and corrected for the wavelength dependence of the detection. The fluorescence quantum yields were determined versus a solution of perylene in toluene (φ_f=0.87).[23] As a fluorescence decay time below 5 ns was expected for all molecules the solutions were not degassed. For all fluorescence spectra the absorbance at the excitation wavelength (close the maximum of the absorption spectrum) was always less than 0.1 in a 1 cm cell. Taking into account a molar extinction coefficient of at least 10^4 $M^{-1}cm^{-1}$, this corresponds to a concentration of 1.0×10^{-5} M or lower.

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