A Short Synthesis of 2,3-Di(hetero)arylpyrido[3,2-*f*][1,4]thiazepines

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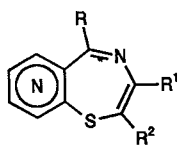
A reaction sequence leading to the new title compounds is described, the key step of which is the treatment of anions of *N*-arylmethyl(2-chloropyridyl) methylidene amines with aromatic and heteroaromatic *O*-ethyl thiocarboxylates.

Synthetic organic chemists have presently at their disposal a plethora of synthetic methods for the elaboration of sophisticated heterobicyclic compounds. The strategies usually adopted enable the control of the size of the fused models and equally the number, the nature and the position of the different heteroatoms in the heterocyclic framework.[1] Paradoxically, despite the considerable development of synthetic methodologies for efficiently constructing nitrogen- and sulfur-containing rings ascribable to the remarkable diversity of biological activities of this class of compounds,[2] a certain number of bicyclic systems incorporating these heteroatoms still remains hardly accessible. This is notably the case with pyrido[1,4]thiazepine derivatives **1**, whilst their benzo-analogs have recently aroused great interest from the scientific community as witnessed by recent patents dealing with their syntheses and emphasizing their pharmaceutical activities[3] expecially as antiarrhythmics,[4] antihyperlipidemics[5] and neurological agents.[6] An array of pyrido[2,3-*b*][1,5]benzothiazepine derivatives **2** (Z = O, S) have been recently prepared and evaluated as potential anti-HIV agents[7] and a variety of diversely substituted 2-dialkylaminoalkylpyrido-1,4-thiazepin-5-ones **3** possessing potent H_1 antihistaminic properties have been synthesized by treatment with oxalyl chloride[8] of the product obtained by condensing 2-chloronicotinic acid derivatives and 1-methyl-3-pyrrolidinethiol. However, the method is not general in scope and all products elaborated according to this protocol invariably possess a carbonyl function in the seven-membered heterocyclic moiety.



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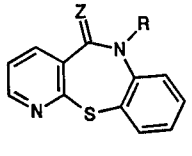

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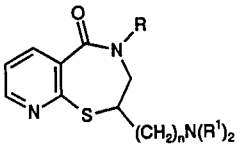

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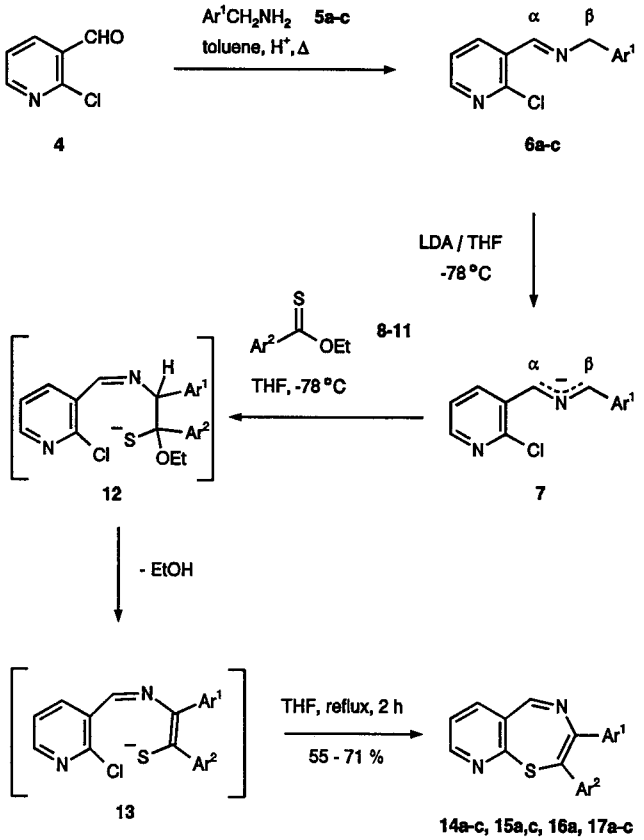
In this paper we wish to report a conceptually and experimentally simple approach to the pyrido[3,2-*f*][1,4]thiazepine skeleton. Our strategy hinges upon the ability of properly designed 2-azaallyl anions to transfer the C–N=C unit to unsaturated electrophiles like thiocarbonyl compounds[9] and on the ease of introducing functionality into π-deficient heterocycles like pyridine by traditional nucleophilic substitution. 2-Chloro-3-formylpyridine **(4)** is usually prepared by metallation of 2-chloropyridine and subsequent formylation of the *ortho*-chlorolithiated species.[10] After experimenting with a variety of metallation reagents including lithium diisopropylamide (LDA),[11] lithium 2,2,6,6-tetramethylpiperidide (LTMP), phenyllithium[12] and formyl donors like



	Ar¹
a	Ph
b	4-MeC_6H_4
c	4-$MeOC_6H_4$

	Ar²
8, 14	Ph
9, 15	4-$MeOC_6H_4$
10, 16	3,4-$(OCH_2O)C_6H_3$
11, 17	2-thienyl

Scheme 1

Table. 2,3-Di(hetero)arylpyrido[3,2-*f*][1,4]thiazepines **14–17** Prepared

Product[a]	Yield[b] (%)	mp[c] (°C)	^{1}H NMR ($CDCl_3$/TMS) δ, J (Hz)	^{13}C NMR ($CDCl_3$/TMS) δ	MS (EI, 70 eV) m/z(%)
14a	65	145–146	7.30 (dd, 1H, J = 4.5, 8.1, H_{pyr}), 7.38 (m, 3H, H_{arom}), 7.52 (m, 3H, H_{arom}), 7.73 (m, 2H, H_{arom}), 7.92 (m, 2H, H_{arom}), 7.97 (dd, 1H, J = 1.6, 8.1, H_{pyr}), 8.57 (dd, 1H, J = 1.6, 4.5, H_{pyr}), 8.59 (s, 1H, CH=N)	C: 127.3 (C-5a), 129.4, 129.6, 136.3 (C-3), 136.5 (C-2), 159.0 (C-9a); CH: 119.8 (C-7), 128.6, 128.8, 129.1, 131.5 (C-6), 132.3, 146.8 (C-8), 163.7 (C-5)	314 (M^+, 65), 237 (100), 210 (29)
14b	68	103–104	2.44 (s, 3H, CH_3), 7.27–7.41 (m, 6H, 5 H_{arom} + 1 H_{pyr}), 7.74 (m, 2H, H_{arom}), 7.81 (d, 2H, J = 8.1, H_{arom}), 7.97 (dd, 1H, J = 1.7, 8.1, H_{pyr}), 8.54 (s, 1H, CH=N), 8.56 (dd, 1H, J = 1.7, 4.6, $_{pyr}$)	C: 127.2 (C-5a), 128.7, 129.9, 135.8 (C-3), 136.6 (C-2), 137.3, 159.9 (C-9a); CH: 120.0 (C-7), 128.4, 128.6, 128.9, 129.3, 132.3 (C-6), 146.6 (C-8), 165.3 (C-5); CH_3: 21.4	328 (M^+, 46), 237 (100), 210 (7)
14c	63	95–96	3.88 (s, 3H, OCH_3), 7.01 (d, 2H, J = 6.9, H_{arom}), 7.28 (dd, 1H, J = 4.6, 8.1, H_{pyr}), 7.37 (m, 3H, H_{arom}), 7.73 (m, 2H, H_{arom}), 7.86 (d, 2H, J = 6.9, H_{arom}), 7.95 (dd, 1H, J = 1.6, 8.1, H_{pyr}), 8.49 (s, 1H, CH=N), 8.55 (dd, 1H, J = 1.6, 4.6, H_{pyr})	C: 127.8 (C-5a), 129.3, 129.8, 135.8 (C-3), 136.9 (C-2), 157.1, 159.5 (C-9a); CH: 109.3, 119.6 (C-7), 123.6, 128.3, 129.2, 131.3 (C-6), 147.0 (C-8), 163.4 (C-5); CH_3: 56.2	344 (M^+, 30), 237 (69), 121 (100)
15a	59	115–116	3.82 (s, 3H, OCH_3), 6.92 (dd, 2H, J = 2.0, 6.8, H_{arom}), 7.28 (dd, 1H, J = 4.6, 8.1, H_{pyr}), 7.52 (m, 3H, H_{arom}), 7.68 (dd, 2H, J = 2.0, 6.8, H_{arom}), 7.91–7.96 (m, 3H, 2 H_{arom} + 1 H_{pyr}), 8.54 (dd, 2H, J = 1.6, 4.6, H_{pyr}), 8.63 (s, 1H, CH=N)	C: 127.5 (C-5a), 128.9, 129.6, 135.9 (C-3), 137.5 (C-2), 156.9, 159.1 (C-9a); CH: 108.8, 119.9 (C-7), 123.5, 128.4, 129.1, 130.9 (C-6), 146.6 (C-8), 165.4 (C-5); CH_3: 55.6	344 (M^+, 100), 264 (57), 224 (42)
15c	58	147–148	3.82 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 6.91 (d, 2H, J = 8.9, H_{arom}), 7.01 (d, 2H, J = 8.8, H_{arom}), 7.28 (dd, 1H, J = 4.6, 8.1, H_{pyr}), 7.68 (d, 2H, J = 8.9, H_{arom}), 7.87 (d, 2H, J = 8.8, H_{arom}), 7.95 (dd, 1H, J = 1.6, 8.1, H_{pyr}), 8.52 (dd, 1H, J = 1.6, 4.6, H_{pyr}), 8.53 (s, 1H, CH=N)	C: 127.5 (C-5a), 129.3, 129.9, 135.7 (C-3), 137.2 (C-2), 157.0, 157.6, 159.2 (C-9a); CH: 108.8, 109.6, 119.8 (C-7), 123.1, 123.6, 131.5 (C-6), 146.5 (C-8), 164.2 (C-5); CH_3: 55.9, 55.7	374 (M^+, 10), 267 (14), 135 (100)
16a	71	150–151	5.92 (s, 2H, CH_2), 6.83 (d, 1H, J = 7.7, H_{arom}), 7.20–7.30 (m, 3H, 2 H_{arom} + 1 H_{pyr}), 7.50–7.53 (m + d, 3H, J = 7.7, H_{arom}), 7.92–7.95 (m, 3H, 2 H_{arom} + 1 H_{pyr}), 8.54 (dd, 1H, J = 1.5, 4.4, H_{pyr}), 8.56 (s, 1H, CH=N)	C: 127.0 (C-5a), 129.2, 129.3, 135.8 (C-3), 137.8 (C-2), 147.5, 147.9, 159.0 (C-9a); CH: 108.6, 109.6, 119.7 (C-7), 123.5, 128.7, 128.9, 129.0, 131.9 (C-6), 146.8 (C-8), 164.3 (C-5); CH_2: 101.3	358 (M^+, 100), 281 (67), 150 (29)
17a	55	144–145	7.08 (m, 1H, $H_{thiophene}$), 7.28 (dd, 1H, J = 4.6, 8.1, H_{pyr}), 7.48 (m, 2H, H_{arom}), 7.55 (m, 3H, 1 H_{arom} + 2 $H_{thiophene}$), 7.95 (dd, 1H, J = 1.5, 8.1, H_{pyr}), 8.05 (m, 2H, H_{arom}), 8.52 (dd, 1H, J = 1.5, 4.6, H_{pyr}), 8.77 (s, 1H, CH=N)	C: 127.8 (C-5a), 129.6, 134.9, 136.0 (C-3), 136.6 (C-2), 159.1 (C-9a); CH: 119.9 (C-7), 126.5, 127.0, 128.7, 128.8, 128.9, 129.2, 132.0 (C-6), 146.8 (C-8), 162.8 (C-5)	320 (M^+, 94), 243 (37), 160 (20)
17b	60	104–105	2.46 (s, 3H, CH_3), 7.08 (m, 1H, $H_{thiophene}$), 7.28 (dd, 1H, J = 4.6, 8.1, H_{pyr}), 7.36 (d, 2H, J = 8.1, H_{arom}), 7.40 (m, 2H, $H_{thiophene}$), 7.94 (d, 2H, J = 8.1, H_{arom}), 7.95 (dd, 1H, J = 1.6, 8.1, H_{pyr}), 8.52 (dd, 1H, J = 1.6, 4.6, H_{pyr}), 8.73 (s, 1H, CH=N)	C: 127.2 (C-5a), 129.9, 134.8, 135.8 (C-3), 136.7 (C-2), 137.1, 158.9 (C-9a); CH: 119.7 (C-7), 126.1, 127.6, 128.2, 129.3, 132.1 (C-6), 146.3 (C-8), 164.3 (C-5); CH_3: 21.5	334 (M^+, 100), 237 (37), 210 (15)
17c	57	112–113	3.91 (s, 3H, OCH_3), 7.06 (d, 2H, J = 8.6, H_{arom}), 7.07 (m, 1H, $H_{thiophene}$), 7.32 (dd, 1H, J = 4.6, 8.1, H_{pyr}), 7.39 (m, 2H, $H_{thiophene}$), 7.94 (dd, 1H, J = 1.6, 8.1, H_{pyr}), 8.00 (d, 2H, J = 8.6, H_{arom}), 8.51 (dd, 1H, J = 1.6, 4.6, H_{pyr}), 8.68 (s, 1H, CH=N)	C: 127.2 (C-5a), 129.4, 134.8, 136.9 (C-3), 137.5 (C-2), 157.1, 158.9 (C-9a); CH: 109.9, 119.8 (C-7), 123.9, 126.5, 127.1, 128.7, 131.8 (C-6), 146.7 (C-8), 162.9 (C-5); CH_3: 55.3	350 (M^+, 10), 263 (24), 121 (100)

[a] Satisfactory microanalysis obtained: C ± 0.35, H ± 0.26, N ± 0.30, O ± 0.28, S ± 0.34.
[b] Yields are of purified products.
[c] Uncorrected.

dimethylformamide, *N*-formylpiperidine (NFP) and *N*-formyl-*N'*-methylpiperazine[13] it was found that the best result was obtained by using LTMP (3 mol equiv) and NFP (4 mol equiv) at low temperature. The *N*-arylmethyl(2-chloropyridyl)methylidene amines **6a–c** were quantitatively obtained in a conventional manner by refluxing the appropriate arylmethylamines **5a–c** with **4** in toluene with azeotropic elimination of water (Scheme 1). The aromatic and heteroaromatic *O*-ethyl thiocaboxylates **8–11** were efficiently prepared by treatment of the corresponding carboxamidic esters, readily accessible from the nitriles via the Pinner reaction, with hydrogen sulfide.[14]

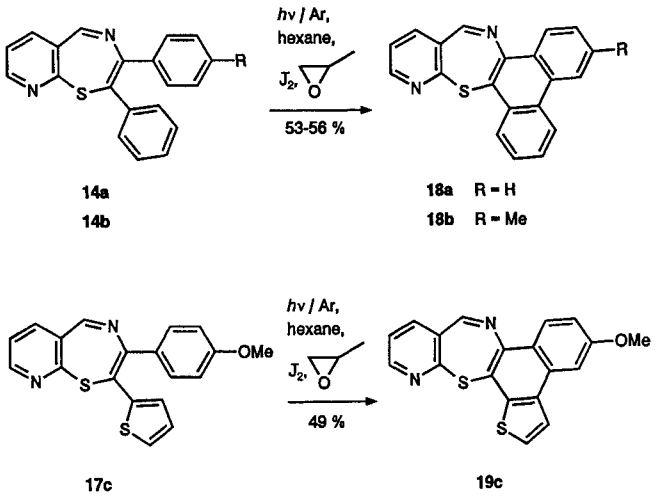
Deprotonation[15] of the aldimines **6a–c** with LDA at −78 °C yielded the corresponding 1,3-diaryl-2-azaallyl

anions **7** which are stable in THF at low temperature (Scheme 1). The *O*-ethyl thiocarboxylates **8–11** dissolved in THF were added at −78 °C to the anions and the addition occurred when the mixture was slowly warmed as evidenced by the disappearance of the characteristic deep purple colour of the anions **7**. Refluxing the reaction mixture for 2 hours ensured the completion of the annulation reaction and this protocol delivered the heterobicyclic compounds **14–17** with satisfactory yields. The results of a representative series of 2,3-diaryl and heteroarylpyrido[3,2-*f*][1,4]thiazepines **14a–c**, **15a, c**, **16a** and **17a–c** accessible by this method are presented in the Table.

From a mechanistic point of view it is likely that the cycloaddition involves, through the intermediacy of the primary adduct **12**, a transition state **13** with a high degree of conjugation which accounts for the remarkable stabilization of the negative charge. The annulation reaction that gives rise to the pyrido[3,2-*f*][1,4]thiazepines **14–17** is actually the combined result of the sensitivity of halogen atoms of halogenopyridines with respect to nucleophilic attack and the nucleophilicity of the intermediate sulfur anion. The steric congestion of the aldimine carbon centre Cα of **6a–c** caused by the presence of the chloropyridine unit accounts for two notable phenomena observed during the annulation process. First the nucleophilic attack of the unsymmetrically substituted 2-azaallyl anions **7** at the anionophiles **8–11** occurs regioselectively at the β position and consequently gives rise exclusively to the transient sulfur anion **13**. On the other hand the displacement of the chlorine atom of the pyridine ring by the heteroanionic species **13** is favoured vs the attack of the aldimine function which survived the preliminary steps.[16]

These annulation reactions enrich the repertoire of reactions involving 1,3-diaryl-2-azaallyl anions. These carbanionic species have proven to be useful 4π electron partners in [π4s + π2s] cycloaddition processes thus giving ready access to a wide array of five-membered azaheterocyclic frameworks.[15,17] However, their use for the elaboration of six- and especially seven-membered rings is extremely rare,[18] and it is only very recently that the azepine ring system has been assembled by combination of azaallyl anions with *s-cis*-fixed dienes.[19] Furthermore, the reactions reported here represent a rare example in which one of the aromatic units which flanks the peripheric carbon atoms of the azaallyl anionic species is directly implicated in the annulation process.

The exclusive utilization of non-enolizable *O*-ethyl thiocarboxylates which prevents their deactivation by a competitive transmetallation reaction with concomitant consumption of the azaallyllithium species may set a limit to the applicability of the method. However, the possibility to incorporate two aromatic units on the neighbouring olefinic carbon atoms in the fused models **14–17** endows the procedure with interesting synthetic potential. Indeed, one can envisage the formation of highly condensed pentacyclic models of synthetically challenging structures by photoinduced electrocyclization of the 6π electron hexatrienic systems[20] present in the primary annulation products. The photoconversion of the diaryl and heteroaryl models **14a, b** and **17c** to the fused compounds **18a, b**, **19c** respectively under the oxidative conditions developed by Katz[21] illustrates this potentiality and these reactions broaden the scope of the cyclocondensation process reported here (Scheme 2).



Scheme 2

In conclusion, the reaction of aromatic and heteroaromatic *O*-ethyl thiocarboxylates with the anions of *N*-arylmethyl(2-chloropyridyl)methylidene amines represents a convenient route to the barely accessible 2,3-di(hetero)arylpyrido[3,2-*f*][1,4]thiazepines. The simplicity of the experimental procedure, the ready access to the precursors, the good yields and the relatively short reaction time render this process particularly attractive and the other terms of the series would be undoubtedly accessible from suitable chloroformylpyridines by this method.

All reactions were performed in flame-dried glassware with assembly under Ar. ^{1}H NMR spectra were measured at 300 MHz and ^{13}C NMR were measured at 75 MHz on a Bruker AM 300 instrument using $CDCl_3$ as solvent and TMS as the internal standard. Mass spectra (EI, 70 eV) were recorded on a Ribermag 10-10 mass spectrometer. For flash column chromatography, the technique described by Still[22] was adopted using mixtures of petroleum ether (bp 40–60 °C) and EtOAc as eluents. Elemental analyses were determined by the CNRS microanalysis centre. Compounds **18a, b** and **19c** gave C ± 0.21, H ± 0.12, N ± 0.33, O ± 0.14, S ± 0.29. The reactions involving organometallic reagents were carried out under Ar in solvents distilled from sodium/benzophenone ketyl and reagent transfer was performed by syringe or cannula techniques. Unless otherwise stated, solutions were dried with $MgSO_4$ and evaporated in a rotary evaporator under diminished pressure.

The aromatic and heteroaromtic *O*-ethyl thiocarboxylates **8–11** were prepared according to already reported procedures.[14]

2-Chloro-3-formylpyridine (4):
To a cooled (−70 °C) solution of freshly distilled (over CaH_2) 2,2,6,6-tetramethylpiperidine (53.4 mmol, 7.29 g) in THF (250 mL) was added dropwise a 1.6 M solution of BuLi in hexanes (36.7 mL, 58.7 mmol). The mixture was stirred at −70 °C for 30 min and a solution of 2-chloropyridine (17.8 mmol, 2.0 g) in THF (5 mL) was added dropwise at a rate such that the reaction temperature did not exceed −60 °C. The mixture was maintained at −60 °C for 1 h

and a solution of *N*-formylpiperidine (71.2 mmol, 7.32 g, dried over 4Å molecular sieves before distillation) in THF (10 mL) was slowly added by a syringe. The mixture was stirred at −60 °C for 2 h, then warmed to r.t. and quenched with dil NH_4Cl. The mixture was partitioned between Et_2O and brine and after classical workup the product was purified by flash chromatography and finally recrystallized from hexane to afford **4** in 65% yield as a pale yellow solid; mp 49–50 °C (Lit.[12] mp 50 °C).

N-Arylmethyl(2-chloropyridyl)methylidene amines 6a–c; General Procedure:

The aldimines **6a–c** were prepared by refluxing in toluene a mixture of 2-chloro-3-formylpyridine **(4)** (1 mol equiv) and the commercially available arylmethylamines **5a–c** (1.1 mol equiv) in the presence of a catalytic amount of 2-naphthalenesulfonic acid for 3 h. After neutralization with aq $NaHCO_3$ the organic phase was dried, the solvent removed and the slight excess of the starting arylmethylamines was eliminated under high vacuum (0.01 Torr). ^{1}H NMR spectra of the product unambiguously indicated the exclusive presence of the aldimines **6a–c** which were immediately used as obtained in subsequent reactions.

N-Phenylmethyl(2-chloropyridyl)methylidene amine **(6a)**:

^{1}H NMR: δ = 4.86 (s, 2H, CH_2), 7.30 (m, 6H, 5 H_{arom} + 1 H_{pyr}), 8.39 (m, 2H, H_{pyr}), 8.75 (s, 1H, CH=N).

MS: *m/z* (%) = 230 (M^+, 7), 195 (24), 91 (100).

N-(4-Methylphenyl)methyl(2-chloropyridyl)methylidene amine **(6b)**:

^{1}H NMR: δ = 2.37 (s, 3H, CH_3), 4.83 (s, 2H, CH_2), 7.10–7.35 (m, 5H, 4 H_{arom} + 1 H_{pyr}), 8.38 (dd, 2H, J = 1.7, 3.9, H_{pyr}), 8.74 (s, 1H, CH=N).

MS: *m/z* (%) = 244 (M^+, 7), 105 (100).

N-(4-Methoxyphenyl)methyl(2-chloropyridyl)methylidene amine **(6c)**:

^{1}H NMR: δ = 3.77 (s, 3H, OCH_3), 4.79 (s, 2H, CH_2), 6.84 (d, 2H, J = 8.7, H_{arom}), 7.20 (d, 2H, J = 8.7, H_{arom}), 7.24 (m, 1H, H_{pyr}), 8.37 (m, 2H, H_{pyr}), 8.71 (s, 1H, CH=N).

MS: *m/z* (%) = 260 (M^+, 3), 121 (100).

2,3-Di(hetero)arylpyrido[3,2-*f*][1,4]thiazepines 14a–c, 15a, c, 16a, 17a–c; General Procedure:

A solution of LDA in THF was prepared by the slow addition at −70 °C of BuLi (1.6 M in hexanes, 2.2 mmol, 1.4 mL) to a solution of an equimolar amount of freshly distilled $(i\text{-Pr})_2NH$ in THF (10 mL). The resulting solution of LDA was warmed to 0 °C for 30 min and then recooled to −78 °C. The aldimine **6a–c** (2 mmol) dissolved in THF (5 mL) was added by syringe during a 5 min period and the deep purple solution was stirred for 15 min which was followed by the dropwise addition of 2 mmol of *O*-ethyl thiocarboxylates **8–11** dissolved in THF (5 mL). The mixture was slowly warmed to r.t. and then gently refluxed for an additional 2 h. Water (20 mL) was then added to the crude mixture and the aqueous layer was extracted with Et_2O (2 × 50 mL) and then with CH_2Cl_2 (20 mL). The combined organic extracts were washed with brine, dried and then evaporated to give the annulated products **14–17** which were finally purified by flash chromatography followed by recrystallization from hexane/toluene.

Photocyclization of 14a, b, 17c; General Procedure:

Dry Ar was bubbled through a solution of **14a, b, 17c** (0.5 mmol) in hexane (200 mL) for 15 min. Propylene oxide (5 mL, 70 mmol) and I_2 (110 mg, 0.5 mmol) was added and the mixture irradiated for 1.5 h in a Rayonet RPR 208 photochemical reactor equipped with eight RUL 350 nm lamps. The mixture was washed with 5% $Na_2S_2O_3$ and the organic layer was passed through a short plug of silica gel, eluting with EtOAc/hexane. During evaporation of the solvent at r.t., the compounds **18a, b, 19c** precipitated. Filtration and recrystallization from EtOH afforded pure samples of the cyclized products **18a, b** and **19c**.

Phenanthro[9,10-b]pyrido[3,2-f][1,4]thiazepine **(18a)**: yield 56%; mp 276–277 °C.

IR (KBr): ν = 1631 cm^{-1}.

^{1}H NMR: δ = 7.49 (dd, 1H, J = 4.7, 8.1, H_{pyr}), 7.57 (m, 2H, 1 H_{arom} + 1 H_{pyr}), 7.64 (m, 1H, H_{arom}), 7.79 (2d, 2H, J = 8.1, 8.3, H_{arom}), 7.85 (m, 1H, H_{arom}), 8.18 (d, 1H, J = 8.1, H_{arom}), 8.23 (d, 1H, J = 8.3, H_{arom}), 8.73 (dd, 1H, J = 1.7, 4.7, H_{pyr}), 8.79 (dd, 1H, J = 1.7, 8.1, CH=N).

MS: *m/z* (%) = 312 (M^+, 76), 131 (100), 156 (50), 142 (11).

10-Methylphenanthro[9,10-b]pyrido[3,2-f][1,4]thiazepine **(18b)**: yield 53%; mp 231–232 °C.

IR (KBr): ν = 1637 cm^{-1}.

^{1}H NMR: δ = 2.49 (s, 3H, CH_3), 7.40 (d, 2H, J = 7.8, H_{arom}), 7.49 (dd, 1H, J = 4.7, 7.8, H_{pyr}), 7.63 (ddd, 1H, J = 1.2, 1.3, 8.3, H_{arom}), 7.69 (m, 2H, H_{arom} + H_{pyr}), 7.84 (ddd, 1H, J = 1.2, 1.3, 8.1, H_{arom}), 8.18 (d, 1H, J = 7.8, H_{arom}), 8.25 (d, 1H, J = 8.3, H_{arom}), 8.72 (dd, 1H, J = 1.7, 4.7, H_{pyr}), 8.80 (dd, 1H, J = 1.7, 7.8, CH=N).

MS: *m/z* (%) = 326 (M^+, 100), 311 (43), 162 (45), 156 (27).

10-Methoxythieno[4',5':1,2]naphtho[3,4-b]pyrido[3,2-f][1,4]thiazepine **(19c)**: yield 49%; mp 241–242 °C.

IR (KBr): ν = 1635 cm^{-1}.

^{1}H NMR: δ = 3.92 (s, 3H, OCH_3), 7.12 (d, 2H, J = 6.8, H_{arom}), 7.49 (dd, 1H, J = 4.7, 7.9, H_{pyr}), 7.57 (d, 1H, J = 5.5, $H_{thiophene}$), 7.77 (d, 1H, J = 5.5, $H_{thiophene}$), 7.91 (m, 2H, H_{arom} + H_{pyr}), 8.72 (dd, 1H, J = 1.7, 4.7, H_{pyr}), 8.79 (dd, 1H, J = 1.7, 7.9, CH=N).

MS: *m/z* (%) = 348 (M^+, 100), 333 (7), 317 (5).

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