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The synthesis of pyrido[2,1-*c*]-1,2,4-triazines **6**, pyrido[1,2-*b*]-1,2,4-triazines **7** and pyrido[1,2-*b*]pyridazines **8** respectively by cycloacylation of derivatives of pyridine with imidoylchlorides of type **2** is described. The heterocycles of type **6** as well as of type **7** can be ring-transformed with dimethyl acetylenedicarboxylate. In contrast to pyrido[1,2-*a*]pyrazines **1**, a complex reaction including cleavage of the acetylene subunit takes place. Starting from compound **6a**, the pyrrolo[2,3-*d*]imidazole **11a** could be isolated from a mixture of unidentified by-products, whereas derivatives **7** gave nearly quantitatively the tricyclic products of type **12**.

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Introduction.

Pyrido[1,2-*a*]pyrazines of type **1**, which can easily be prepared *via* cycloacylation of 2-aminomethylpyridine with bis-imidoylchlorides of oxalic acid **2** [1], represent suitable starting materials for the synthesis of a variety of highly substituted heterocycles. For example, starting from cycloamidines of type **1** by a cycloaddition/ring transformation sequence new compounds such as 2,2-bipyridines [2], azaquinones [3], 1,2,4-triazines [4] and 1,2,5-oxadiazines [4] are accessible. Our work in this area is aimed at the synthesis of further pyridine derivatives, and the 2-hydrazinopyridine **3**, 1,2-diaminopyridinium iodide **4** and 1-amino-2-methylpyridinium iodide **5** were chosen as starting materials. By reaction with the building blocks of type **2** the binuclear heterocycles should be accessible which, similar to pyrido[1,2-*a*]pyrazines **1** and quinolizines [5], also have a zwitterionic mesomeric structure suitable for cycloaddition reactions.

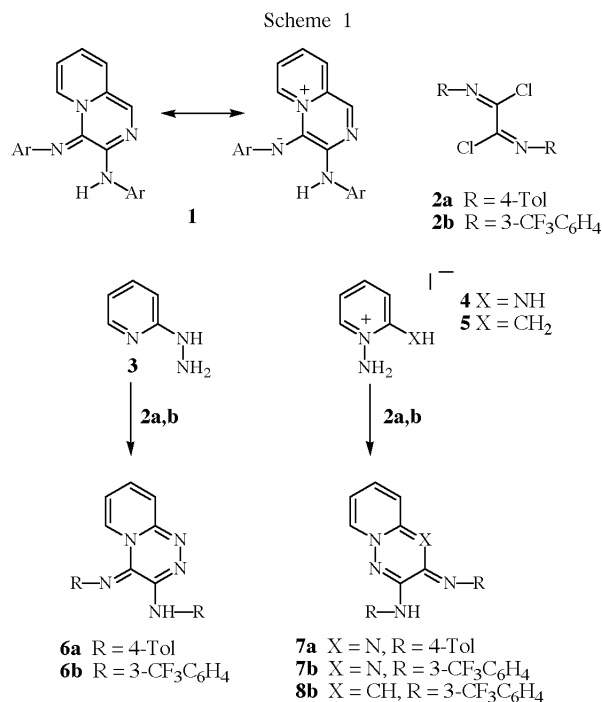
Results and Discussion.

Under mild conditions 2-hydrazinopyridine **3** reacts with imidoylchlorides **2a** and **2b** to produce pyrido[2,1-*c*]triazines **6a,b** in good yields. The structure has been identified using ¹³C nmr spectra especially by long-range C-F coupling constants. Using 2D nmr experiments all connectivities for pyrido[1,2-*a*]pyrazines **1** could be determined. For azaanalogues of type **6**, however, such characterization was not possible although the ¹H nmr spectra revealed the coexistence of several tautomeric forms which are in a state of equilibrium with each other.

The cycloacylation of 1,2-diamino derivative **4** can also be accomplished with the educt **2b** at slightly elevated temperature and with triethylamine as base yielding the yellow colored pyrido[1,2-*b*]-1,2,4-triazine **7b**. In the case

of the less reactive electrophile **2a** the cyclization to **7a** requires a longer heating time. Both the ¹H and ¹³C nmr data confirm the presence of a bicyclic system and therefore are in agreement with the structure of **7**.

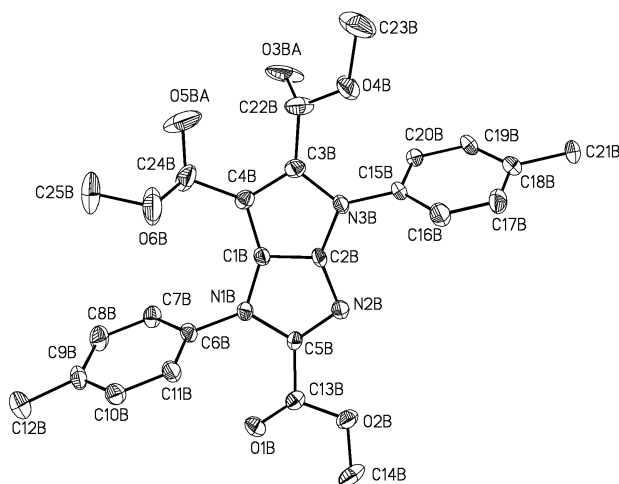
The cycloacylation of 1-amino-2-methylpyridinium iodide **5** with the building block **2b** involved, firstly, a deprotonization using butyl lithium followed by reaction with the electrophile **2b** at -78 °C. A complicated chromatographic purification of the tarry reaction mixture yielded a yellow substance (<10 %) which, based on the nmr und ms data confirmed the structure as **8b**. No yield increase could be realised by varying the reaction conditions.



As could already be determined from its physico-chemical data, pyrido[2,1-*c*]triazine **6** does not have the tendency shown by the lower azahomologues **1** towards delocalization of the π -system, and thereby the tendency to form a dipolar mesomeric structure. In contrast to pyrido[1,2-*a*] pyrazines **1**, the heterocycles **6a,b** are quite stable towards atmospheric oxygen. Oxidation of these derivatives succeeds only with hydrogen peroxide or MCPBA at raised temperature yielding a resin-like product. Singlet oxygen however, reacted with the bicycle **6a** through a [4+2]-cycloaddition reaction. The intermediate adduct **9** extruded nitrogen to form the 2-pyridone **10**. These types of pyridones are difficult to obtain by other methods and are of interest for their biological activity [6].

Heating **6a** with dimethyl acetylenedicarboxylate gave a small amount of the pyrrolo[2,3-*d*]imidazole **11a**. The structure of this formerly unknown heterocycle has been confirmed by a single crystal x-ray structure analysis (Figure 1).

Figure 1. ORTEP drawing of the molecule **11a**.



On reacting pyrido[1,2-*b*][1,2,4]triazine **7** with dimethyl acetylenedicarboxylate an unexpected ring transformation takes place. Here, at a reaction temperature of 40 °C, in nearly quantitative yields the tricyclic compounds **12a,b** were obtained. The cleavage of one aryl residues of the starting material as well as the incorporation of three various methyl ester groups were deduced by nmr spectroscopy and again confirmed by an x-ray crystal structure analysis of derivative **12a**. As depicted in scheme 2 the reaction occurred exclusively on the exocyclic arylamino moieties. The compounds **12a,b** can not be described as heteroaromatic but exhibit rather a conjugated system with localized double

Table 1
Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **11a**. U(eq) is Defined as One Third of the Trace of the Orthogonalized U^{ij} Tensor

	x	y	z	U(eq)
O(1A)	6367(2)	1010(2)	11035(1)	30(1)
O(2A)	5911(2)	-433(2)	11011(1)	29(1)
O(3A)	7194(2)	-610(2)	7277(2)	44(1)
O(4A)	5828(2)	-1268(2)	7237(1)	34(1)
O(5A)	6469(2)	1219(2)	7400(2)	47(1)
O(6A)	6447(2)	2010(2)	8306(2)	43(1)
N(1A)	6335(2)	824(2)	9632(1)	20(1)
N(2A)	6183(2)	-684(2)	9799(1)	21(1)
N(3A)	6346(2)	-1012(2)	8645(1)	22(1)
C(1A)	6408(2)	387(2)	9062(2)	19(1)
C(2A)	6306(2)	-514(2)	9191(2)	20(1)
C(3A)	6480(2)	-420(2)	8171(2)	20(1)
C(4A)	6511(2)	464(2)	8404(2)	22(1)
C(5A)	6207(2)	146(2)	10056(2)	21(1)
C(6A)	6333(2)	1772(2)	9756(2)	20(1)
C(7A)	7140(3)	2271(2)	9819(2)	26(1)
C(8A)	7135(3)	3173(2)	9970(2)	28(1)
C(9A)	6339(3)	3596(2)	10070(2)	28(1)
C(10A)	5530(3)	3074(3)	9982(2)	27(1)
C(11A)	5519(2)	2175(2)	9829(2)	23(1)
C(12A)	6355(3)	4560(3)	10289(2)	39(1)
C(13A)	6166(2)	300(2)	10745(2)	21(1)
C(14A)	5905(3)	-347(3)	11699(2)	34(1)
C(15A)	6294(2)	-1970(2)	8600(2)	20(1)
C(16A)	5533(3)	-2408(3)	8725(2)	28(1)
C(17A)	5469(3)	-3333(3)	8665(2)	32(1)
C(18A)	6154(3)	-3839(2)	8483(2)	29(1)
C(19A)	6916(3)	-3383(2)	8361(2)	29(1)
C(20A)	6997(3)	-2457(2)	8422(2)	25(1)
C(21A)	6081(4)	-4843(3)	8409(2)	44(1)
C(22A)	6552(3)	-747(3)	7517(2)	28(1)
C(23A)	5877(4)	-1701(4)	6628(2)	54(1)
C(24A)	6488(3)	1248(3)	7985(2)	26(1)
C(25A)	6372(4)	2827(3)	7926(3)	50(1)

bonds. This has been established not only through the bond length alternation but also by the relatively long wave absorption in their uv/vis spectra ($\lambda_{\text{max}} = 554 \text{ nm}$). On treatment with acids, the color of solutions of **12a,b** in ethanol faded to yellowish to give protonated heterocycles of type **13**.

The pyrido[1,2-*b*]pyridazine **8b** reacted with acetylenedicarboxylates under similar conditions to produce a wide spectrum of products which have not been further characterized.

A mechanistic interpretation of the described ring transformation reactions has not yet been formulated. Despite the large number of well-documented reactions involving acetylenedicarboxylates [7,8] there exist only a few examples which show any similarity to ours [9,10].

Table 2
Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **11a**. The
Anisotropic Displacement Factor Exponent Takes the Form:
 $-2\pi^2[h^2 a^{*2}U^{11} + \dots + 2 h k a^*b^*U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
O(1A)	34(2)	26(2)	28(1)	-5(1)	6(1)	-4(1)
O(2A)	35(2)	28(2)	25(1)	1(1)	7(1)	-9(1)
O(3A)	45(2)	49(2)	47(2)	-8(2)	27(2)	-7(2)
O(4A)	40(2)	34(2)	26(1)	-9(1)	2(1)	-4(1)
O(5A)	64(2)	41(2)	42(2)	10(2)	23(2)	13(2)
O(6A)	71(2)	19(2)	42(2)	0(1)	18(2)	1(1)
N(1A)	21(2)	17(2)	22(2)	-2(1)	6(1)	-2(1)
N(2A)	23(2)	19(2)	21(2)	-2(1)	8(1)	0(1)
N(3A)	23(2)	19(2)	24(2)	-5(1)	8(1)	-1(1)
C(1A)	17(2)	17(2)	21(2)	-4(1)	4(1)	-2(1)
C(2A)	22(2)	16(2)	23(2)	-3(1)	8(2)	-1(1)
C(3A)	21(2)	19(2)	19(2)	2(1)	3(1)	-2(1)
C(4A)	19(2)	24(2)	23(2)	-2(2)	5(2)	0(1)
C(5A)	20(2)	20(2)	23(2)	4(1)	6(1)	-1(1)
C(6A)	20(2)	17(2)	23(2)	-3(1)	6(1)	-2(1)
C(7A)	24(2)	23(2)	31(2)	-3(2)	7(2)	0(2)
C(8A)	26(2)	22(2)	33(2)	-6(2)	3(2)	-5(2)
C(9A)	45(2)	15(2)	22(2)	-2(2)	7(2)	1(2)
C(10A)	30(2)	25(2)	27(2)	1(2)	8(2)	6(2)
C(11A)	21(2)	23(2)	26(2)	0(2)	5(2)	2(1)
C(12A)	47(3)	20(2)	50(3)	-7(2)	14(2)	2(2)
C(13A)	14(2)	22(2)	25(2)	-3(2)	3(1)	1(1)
C(14A)	34(2)	47(3)	20(2)	4(2)	6(2)	-1(2)
C(15A)	24(2)	16(2)	20(2)	-7(1)	6(1)	-3(1)
C(16A)	27(2)	25(2)	35(2)	-7(2)	11(2)	-3(2)
C(17A)	42(2)	26(2)	33(2)	-9(2)	17(2)	-11(2)
C(18A)	49(2)	16(2)	23(2)	-6(2)	11(2)	-6(2)
C(19A)	44(2)	20(2)	25(2)	-1(2)	13(2)	6(2)
C(20A)	27(2)	20(2)	31(2)	-1(2)	12(2)	2(2)
C(21A)	77(3)	19(2)	38(3)	-8(2)	20(2)	-5(2)
C(22A)	26(2)	29(2)	31(2)	-3(2)	9(2)	0(2)
C(23A)	66(3)	57(3)	35(3)	-21(2)	8(2)	-4(3)
C(24A)	28(2)	25(2)	30(2)	7(2)	13(2)	2(2)
C(25A)	70(3)	18(2)	64(3)	10(2)	21(3)	-1(2)

Table 4
Bond angles [$^\circ$] for **11a**

C(13A)-O(2A)-C(14A)	114.8(3)	C(7A)-C(6A)-N(1A)	120.2(3)
C(22A)-O(4A)-C(23A)	115.6(3)	C(8A)-C(7A)-C(6A)	119.2(3)
C(24A)-O(6A)-C(25A)	116.8(3)	C(7A)-C(8A)-C(9A)	121.7(4)
C(1A)-N(1A)-C(5A)	105.1(3)	C(8A)-C(9A)-C(10A)	117.2(3)
C(1A)-N(1A)-C(6A)	128.4(3)	C(8A)-C(9A)-C(12A)	121.7(4)
C(5A)-N(1A)-C(6A)	126.4(3)	C(10A)-C(9A)-C(12A)	121.0(4)
C(5A)-N(2A)-C(2A)	102.0(3)	C(11A)-C(10A)-C(9A)	121.9(4)
C(3A)-N(3A)-C(2A)	107.3(3)	C(10A)-C(11A)-C(6A)	119.1(3)
C(3A)-N(3A)-C(15A)	127.3(3)	O(1A)-C(13A)-O(2A)	124.5(3)
C(2A)-N(3A)-C(15A)	125.4(3)	O(1A)-C(13A)-C(5A)	123.8(3)
N(1A)-C(1A)-C(2A)	104.5(3)	O(2A)-C(13A)-C(5A)	111.7(3)
N(1A)-C(1A)-C(4A)	147.4(3)	C(20A)-C(15A)-C(16A)	120.4(3)
C(2A)-C(1A)-C(4A)	108.0(3)	C(20A)-C(15A)-N(3A)	120.3(3)
N(2A)-C(2A)-C(1A)	114.3(3)	C(16A)-C(15A)-N(3A)	119.3(3)
N(2A)-C(2A)-N(3A)	136.4(3)	C(17A)-C(16A)-C(15A)	119.4(4)
C(1A)-C(2A)-N(3A)	109.3(3)	C(16A)-C(17A)-C(18A)	121.6(4)
N(3A)-C(3A)-C(4A)	110.5(3)	C(19A)-C(18A)-C(17A)	117.9(3)
N(3A)-C(3A)-C(22A)	120.8(3)	C(19A)-C(18A)-C(21A)	120.4(4)
C(4A)-C(3A)-C(22A)	128.7(3)	C(17A)-C(18A)-C(21A)	121.7(4)
C(3A)-C(4A)-C(1A)	104.9(3)	C(20A)-C(19A)-C(18A)	121.4(4)
C(3A)-C(4A)-C(24A)	123.5(3)	C(19A)-C(20A)-C(15A)	119.3(3)
C(1A)-C(4A)-C(24A)	130.8(3)	O(3A)-C(22A)-O(4A)	123.4(4)
N(2A)-C(5A)-N(1A)	114.1(3)	O(3A)-C(22A)-C(3A)	125.5(4)
N(2A)-C(5A)-C(13A)	122.0(3)	O(4A)-C(22A)-C(3A)	111.0(3)
N(1A)-C(5A)-C(13A)	123.8(3)	O(5A)-C(24A)-O(6A)	123.1(4)
C(11A)-C(6A)-C(7A)	120.7(3)	O(5A)-C(24A)-C(4A)	124.6(4)
C(11A)-C(6A)-N(1A)	119.1(3)	O(6A)-C(24A)-C(4A)	112.3(3)

Table 3
Bond Lengths [\AA] for **11a**

O(1A)-C(13A)	1.218(4)	C(3A)-C(4A)	1.400(5)
O(2A)-C(13A)	1.322(4)	C(3A)-C(22A)	1.479(5)
O(2A)-C(14A)	1.444(4)	C(4A)-C(24A)	1.453(5)
O(3A)-C(22A)	1.200(5)	C(5A)-C(13A)	1.473(5)
O(4A)-C(22A)	1.333(5)	C(6A)-C(11A)	1.390(5)
O(4A)-C(23A)	1.445(5)	C(6A)-C(7A)	1.385(5)
O(5A)-C(24A)	1.216(5)	C(7A)-C(8A)	1.378(5)
O(6A)-C(24A)	1.326(5)	C(8A)-C(9A)	1.398(5)
O(6A)-C(25A)	1.442(5)	C(9A)-C(10A)	1.401(5)
N(1A)-C(1A)	1.385(4)	C(9A)-C(12A)	1.504(5)
N(1A)-C(5A)	1.386(4)	C(10A)-C(11A)	1.374(5)
N(1A)-C(6A)	1.435(4)	C(15A)-C(20A)	1.393(5)
N(2A)-C(5A)	1.343(4)	C(15A)-C(16A)	1.384(5)
N(2A)-C(2A)	1.351(4)	C(16A)-C(17A)	1.384(5)
N(3A)-C(3A)	1.376(4)	C(17A)-C(18A)	1.392(6)
N(3A)-C(2A)	1.374(4)	C(18A)-C(19A)	1.394(6)
N(3A)-C(15A)	1.429(4)	C(18A)-C(21A)	1.503(5)
C(1A)-C(2A)	1.384(5)	C(19A)-C(20A)	1.386(5)
C(1A)-C(4A)	1.426(5)		

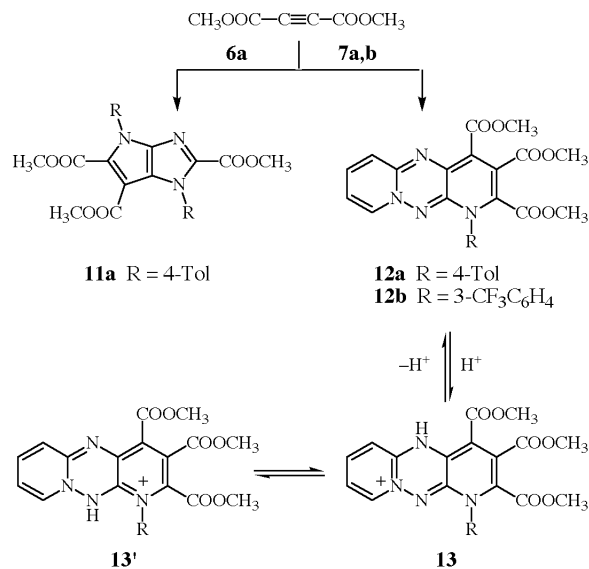
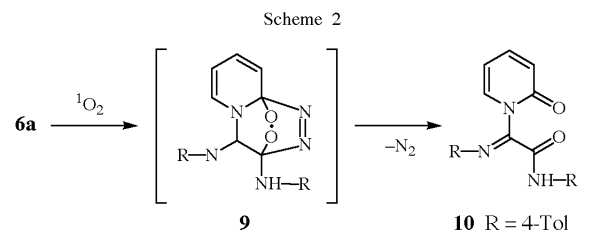


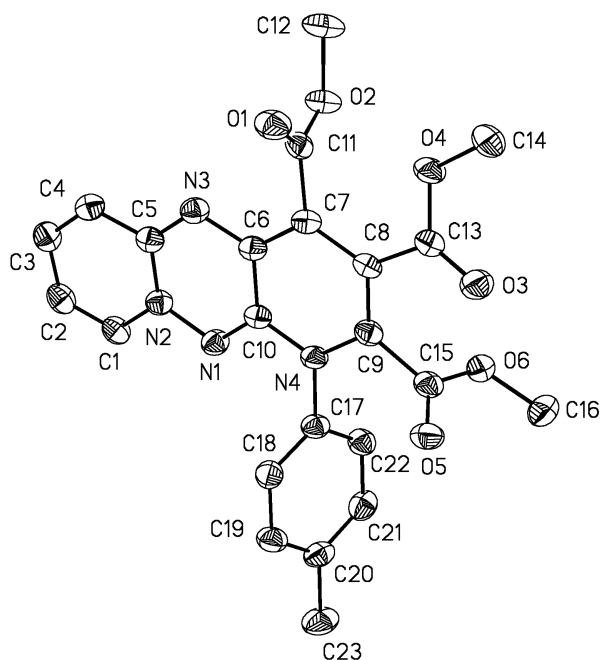
Figure 2. ORTEP Drawing of the Molecule **12a**.

Table 5
Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **12a**. $U(\text{eq})$ is Defined as One Third of the Trace of the Orthogonalized U^{ij} Tensor

	x	y	z	$U(\text{eq})$
O(1)	2242(2)	5838(2)	3549(2)	36(1)
O(2)	3204(2)	7683(2)	2215(2)	32(1)
O(3)	255(2)	8578(2)	6903(2)	37(1)
O(4)	658(2)	8147(2)	4828(2)	33(1)
O(5)	1906(2)	8163(2)	8681(2)	35(1)
O(6)	2306(2)	9989(2)	7103(2)	31(1)
N(1)	6833(3)	6649(2)	4719(2)	29(1)
N(2)	7643(3)	5916(2)	3646(2)	27(1)
N(3)	5708(3)	5930(2)	3014(2)	29(1)
N(4)	4627(3)	7598(2)	6005(2)	26(1)
C(1)	9023(3)	5557(3)	3491(3)	30(1)
C(2)	9906(4)	4814(3)	2522(3)	35(1)
C(3)	9362(3)	4414(3)	1688(3)	34(1)
C(4)	7984(3)	4789(3)	1849(3)	31(1)
C(5)	7049(3)	5571(3)	2850(3)	26(1)
C(6)	4863(3)	6647(3)	4051(3)	24(1)
C(7)	3477(3)	7090(3)	4280(3)	25(1)
C(8)	2617(3)	7799(3)	5417(3)	25(1)
C(9)	3207(3)	8025(3)	6248(3)	26(1)
C(10)	5497(3)	6939(3)	4902(3)	24(1)
C(11)	2884(3)	6777(3)	3345(3)	26(1)
C(12)	2602(4)	7521(4)	1282(4)	43(1)
C(13)	1065(3)	8220(3)	5818(3)	27(1)
C(14)	-874(4)	8410(4)	5183(4)	37(1)
C(15)	2379(3)	8705(3)	7497(3)	28(1)
C(16)	1438(5)	10728(4)	8208(4)	45(1)
C(17)	5220(3)	7790(3)	6941(3)	27(1)
C(18)	5500(3)	6725(3)	7777(3)	30(1)
C(19)	6037(3)	6916(3)	8690(3)	33(1)
C(20)	6298(3)	8154(3)	8769(3)	33(1)
C(21)	5996(3)	9206(3)	7920(3)	35(1)
C(22)	5471(3)	9031(3)	6990(3)	31(1)
C(23)	6893(5)	8339(5)	9753(4)	47(1)

Table 6
Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **12a**. The Anisotropic Displacement Factor Exponent Takes the Form:
 $-2\pi^2[h^2 a^{*2}U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	41(1)	36(1)	43(1)	-3(1)	-27(1)	-10(1)
O(2)	34(1)	44(1)	25(1)	0(1)	-19(1)	-9(1)
O(3)	28(1)	53(1)	32(1)	-14(1)	-14(1)	2(1)
O(4)	25(1)	50(1)	33(1)	-11(1)	-19(1)	5(1)
O(5)	40(1)	40(1)	25(1)	-2(1)	-17(1)	-2(1)
O(6)	35(1)	31(1)	31(1)	-8(1)	-17(1)	1(1)
N(1)	25(1)	35(1)	29(1)	-9(1)	-12(1)	-2(1)
N(2)	24(1)	30(1)	26(1)	-4(1)	-11(1)	-3(1)
N(3)	28(2)	32(1)	28(1)	-6(1)	-14(1)	-3(1)
N(4)	25(1)	34(1)	26(1)	-7(1)	-16(1)	0(1)
C(1)	22(2)	35(2)	34(2)	-2(2)	-14(2)	-3(1)
C(2)	26(2)	38(2)	37(2)	1(2)	-13(2)	-2(2)
C(3)	30(2)	36(2)	29(2)	-2(2)	-7(2)	1(1)
C(4)	34(2)	34(2)	27(2)	-4(1)	-12(2)	-5(1)
C(5)	28(2)	26(2)	25(2)	0(1)	-12(1)	-6(1)
C(6)	26(2)	25(2)	23(2)	-1(1)	-12(1)	-6(1)
C(7)	26(2)	30(2)	21(2)	-1(1)	-12(1)	-6(1)
C(8)	26(2)	27(2)	25(2)	2(1)	-16(1)	-3(1)
C(9)	23(2)	30(2)	25(2)	-1(1)	-12(1)	-4(1)
C(10)	26(2)	26(2)	23(2)	-1(1)	-13(1)	-5(1)
C(11)	20(2)	30(2)	27(2)	-3(1)	-11(1)	0(1)
C(12)	44(2)	62(3)	33(2)	-2(2)	-27(2)	-9(2)
C(13)	25(2)	29(2)	27(2)	-1(1)	-14(2)	-3(1)
C(14)	24(2)	46(2)	47(2)	-13(2)	-20(2)	3(2)
C(15)	25(2)	34(2)	32(2)	-6(2)	-17(2)	-2(1)
C(16)	62(3)	39(2)	39(2)	-17(2)	-25(2)	10(2)
C(17)	23(2)	36(2)	26(2)	-7(1)	-13(1)	-3(1)
C(18)	28(2)	32(2)	34(2)	-9(1)	-16(2)	1(1)
C(19)	32(2)	42(2)	31(2)	-5(2)	-19(2)	0(1)
C(20)	22(2)	53(2)	28(2)	-14(2)	-11(1)	-1(1)
C(21)	28(2)	41(2)	39(2)	-16(2)	-14(2)	-3(1)
C(22)	28(2)	34(2)	34(2)	-5(2)	-17(2)	-1(1)
C(23)	42(2)	71(3)	42(2)	-19(2)	-27(2)	-5(2)

Table 7
Bond Lengths [\AA] for **12a**

O(1)-C(11)	1.201(3)	C(1)-C(2)	1.361(5)
O(2)-C(11)	1.344(3)	C(2)-C(3)	1.415(5)
O(2)-C(12)	1.456(4)	C(3)-C(4)	1.367(4)
O(3)-C(13)	1.211(3)	C(4)-C(5)	1.421(4)
O(4)-C(13)	1.343(3)	C(6)-C(7)	1.370(4)
O(4)-C(14)	1.454(4)	C(6)-C(10)	1.451(4)
O(5)-C(15)	1.210(4)	C(7)-C(8)	1.452(4)
O(6)-C(15)	1.341(4)	C(7)-C(11)	1.511(4)
O(6)-C(16)	1.449(4)	C(8)-C(9)	1.370(4)
N(1)-C(10)	1.305(4)	C(8)-C(13)	1.491(4)
N(1)-N(2)	1.412(3)	C(9)-C(15)	1.518(4)
N(2)-C(1)	1.367(4)	C(17)-C(18)	1.384(4)
N(2)-C(5)	1.391(4)	C(17)-C(22)	1.388(4)
N(3)-C(5)	1.327(4)	C(18)-C(19)	1.397(4)
N(3)-C(6)	1.381(4)	C(19)-C(20)	1.399(5)
N(4)-C(9)	1.396(4)	C(20)-C(21)	1.393(5)
N(4)-C(10)	1.398(4)	C(20)-C(23)	1.511(4)
N(4)-C(17)	1.463(4)	C(21)-C(22)	1.399(4)

Table 8
Bond Angles [°] for **12a**

C(11)-O(2)-C(12)	115.3(3)	C(7)-C(8)-C(13)	123.8(2)
C(13)-O(4)-C(14)	115.7(2)	C(8)-C(9)-N(4)	120.9(3)
C(15)-O(6)-C(16)	115.0(2)	C(8)-C(9)-C(15)	123.5(3)
C(10)-N(1)-N(2)	114.2(2)	N(4)-C(9)-C(15)	115.6(2)
C(1)-N(2)-C(5)	123.7(3)	N(1)-C(10)-N(4)	116.4(2)
C(1)-N(2)-N(1)	114.5(2)	N(1)-C(10)-C(6)	125.4(3)
C(5)-N(2)-N(1)	121.7(2)	N(4)-C(10)-C(6)	118.2(2)
C(5)-N(3)-C(6)	117.9(2)	O(1)-C(11)-O(2)	123.8(3)
C(9)-N(4)-C(10)	121.3(2)	O(1)-C(11)-C(7)	125.5(3)
C(9)-N(4)-C(17)	120.3(2)	O(2)-C(11)-C(7)	110.7(3)
C(10)-N(4)-C(17)	118.4(2)	O(3)-C(13)-O(4)	123.5(3)
C(2)-C(1)-N(2)	120.5(3)	O(3)-C(13)-C(8)	124.7(3)
C(1)-C(2)-C(3)	118.6(3)	O(4)-C(13)-C(8)	111.7(2)
C(4)-C(3)-C(2)	120.2(3)	O(5)-C(15)-O(6)	125.0(3)
C(3)-C(4)-C(5)	122.0(3)	O(5)-C(15)-C(9)	124.5(3)
N(3)-C(5)-N(2)	122.8(3)	O(6)-C(15)-C(9)	110.4(2)
N(3)-C(5)-C(4)	122.2(3)	C(18)-C(17)-C(22)	121.3(3)
N(2)-C(5)-C(4)	115.0(3)	C(18)-C(17)-N(4)	119.0(3)
C(7)-C(6)-N(3)	122.3(3)	C(22)-C(17)-N(4)	119.6(3)
C(7)-C(6)-C(10)	120.0(3)	C(17)-C(18)-C(19)	118.8(3)
N(3)-C(6)-C(10)	117.7(2)	C(20)-C(19)-C(18)	121.4(3)
C(6)-C(7)-C(8)	120.1(2)	C(19)-C(20)-C(21)	118.4(3)
C(6)-C(7)-C(11)	117.7(3)	C(19)-C(20)-C(23)	120.6(3)
C(8)-C(7)-C(11)	122.2(2)	C(21)-C(20)-C(23)	121.0(3)
C(9)-C(8)-C(7)	119.4(3)	C(22)-C(21)-C(20)	121.0(3)
C(9)-C(8)-C(13)	116.6(3)	C(17)-C(22)-C(21)	119.1(3)

EXPERIMENTAL

All reagents were of commercial quality (Aldrich, Fluka, Merck). Solvents were dried and purified using standard techniques. Reactions were monitored by thin layer chromatography (tlc), Polygram SIL G/UV₂₅₄ from Macherey-Nagel or Polygram ALOX N/UV₂₅₄ from Macherey-Nagel. Flash chromatography was carried out on silica gel (Merck, Silica gel 60, particle size 0.063 mm - 0.2 mm, 70 - 230 mesh ASTM) or neutral alumina (Merck, aluminium oxide 90 active neutral, activity V, particle size 0.063 mm - 0.2 mm, 70 - 230 mesh ASTM). Melting points were measured with a Galen III (Boëtius system) from Cambridge Instruments and are uncorrected. The uv-vis spectra were obtained using a Perkin Elmer Lambda 19 spectrophotometer. The ¹H nmr and ¹³C nmr spectra were obtained on Bruker DRX 400 (400 MHz) and Bruker AC 250 (250 MHz) spectrometers. Mass spectra were taken from measurements on a Finnigan MAT SAQ 710 mass spectrometer. Elemental analyses were carried out using an automatic analyzer LECO CHNS 932.

N-(4-Methylphenyl)-4-[(4-methylphenyl)imino]-4*H*-pyrido[2,1-*c*][1,2,4]triazin-3-amine (**6a**, R = Toly).l)

A mixture of 2-hydrazinopyridine (**3**) [11] (10 mmoles, 1.09 g), bis-imidoylchloride **2a** [12] (10 mmoles, 3.05 g) and triethylamine (20 mmoles, 2.02 g) in 100 ml of acetonitrile was stirred under reflux for three hours. After cooling to room temperature, triethylamine hydrochloride was separated and the filtrate was evaporated to dryness *in vacuo*. The residue was purified by recrystallization from ethanol. Compound **6a** was obtained as yellow crystals, 2.94 g (86 %), mp 165 °C; uv/vis (acetonitrile): λ(logε) 278 (4.23), 375 (4.28); ¹H nmr (deuteriodichloromethane): δ 2.29 (s, 3H), 2.39 (s, 3H), 6.43 (br. d, 1H), 6.25 - 6.83 (m, 11H), 7.30 (br. s, 1H, N-H); ¹³C nmr (deuteriodichloromethane): δ 20.8, 21.0, 112.8, 119.5,

120.4, 125.5, 127.2, 128.7, 129.6, 130.1, 132.3, 133.7, 137.3, 143.6, 144.7 ppm; ms: m/z 341 (M⁺), 235, 224, 197, 171, 118, 91.

Anal. Calcd. for C₂₁H₁₉N₅: C, 73.88; H, 5.61; N, 20.51. Found: C, 73.69; H, 5.62; N, 20.50.

N-(3-Trifluoromethylphenyl)-4-[(3-trifluoromethylphenyl)imino]-4*H*-pyrido[2,1-*c*][1,2,4]triazin-3-amine (**6b**, R = 3-Trifluoromethylphenyl).

This compound was obtained as yellow needles, mp 174 - 176 °C; yield 78 %; uv/vis (acetonitrile): λ(logε) 271 (4.20), 380 (4.24); ¹³C nmr (deuteriotrichloromethane): δ 113.5, 115.5 (q, J = 7.8 Hz), 117.1 (q, J = 7.8 Hz), 119.1 (q, J = 7.7 Hz), 120.4 (q, J = 7.7 Hz), 121.9, 123.4, 125.6 (q, J = 270 Hz, CF₃), 123.9 (q, J = 270 Hz, CF₃), 125.4, 126.5, 128.2, 129.3, 129.8, 130.2, 131.5 (q, J = 30 Hz, *ipso*-C-CF₃), 131.6 (q, J = 30 Hz, *ipso*-C-CF₃), 139.4, 143.2, 143.4, 146.8 ppm; ms: m/z 450 (M⁺+1), 430, 278.

Anal. Calcd. for C₂₁H₁₃F₆N₅: C, 56.13; H, 2.92; N, 15.59. Found: C, 55.98; H, 3.12; N, 15.87.

N-(4-Methylphenyl)-2-[(4-methylphenyl)imino]-2*H*-pyrido[1,2-*b*][1,2,4]triazin-3-amine (**7a**, X = N, R = Toly).l)

To a solution of 1,2-diaminopyridinium iodide (**4**) [13] (1 mmole, 0.24 g) and triethylamine (3 mmoles, 0.31 g) in 50 ml of acetonitrile a solution of imidoylchloride **2a** (1 mmole, 0.31 g) in 20 ml of acetonitrile was added. After heating under reflux for 12 hours the solvent was evaporated *in vacuo*. The solid residue was treated in 50 ml of toluene in an ultrasonic bath for about ten minutes and then filtered from triethylamine hydrochloride. The filtrate was purified by column chromatography (alumina, toluene/acetone 5:1). Removal of the solvent and addition of a small amount of *n*-hexane gave **7a** as a yellow solid, 0.28 g (82 %), mp 182 °C; ¹H nmr (deuteriodichloromethane): δ 2.34 (s, 3H), 2.35 (s, 3H), 6.66 (t, 1H, J = 7.6 Hz), 6.99 (d, 1H, J = 8.9 Hz), 7.14 (d, 2H, J = 8.2 Hz), 7.21 (d, 2H, J = 8.3 Hz), 7.34 (d, 2H, J = 8.2 Hz), 7.40 (t, 1H, J = 7.9 Hz), 7.67 (d, 2H, J = 8.5 Hz), 7.92 (d, 2H, J = 8.2 Hz), 8.50 - 10.00 ppm (br. s, 1H, N-H); ¹³C nmr (deuteriodichloromethane): δ 20.9, 21.1, 111.6, 120.3, 122.9, 125.0, 129.3, 129.9, 132.8, 133.5, 135.1, 136.4, 141.9, 146.5, 146.9, 148.2 ppm; ms:m/z 341 (M⁺), 340, 235, 208, 91.

Anal. Calcd. for C₂₁H₁₉N₅: C, 73.88; H, 5.61; N, 20.51. Found: C, 73.53; H, 5.68; N, 20.34.

N-(3-Trifluoromethylphenyl)-2-[(3-trifluoromethylphenyl)imino]-2*H*-pyrido [1,2-*b*][1,2,4]triazin-3-amine (**7b**, X = N, R = 3-Trifluoromethylphenyl).

This compound was obtained, in an analogous manner as derivative **7a** by stirring the reaction mixture for 6 hours at 40 °C, as yellow crystals, 0.38 g (85 %), mp 127 °C, ¹H nmr (deuteriotrichloromethane): δ 6.72 (t, 1H, J = 6.7 Hz), 7.08 (d, 1H, J = 8.8 Hz), 7.30 (d, 1H, J = 7.7 Hz), 7.35 (d, 1H, J = 7.9 Hz), 7.41 - 7.50 (m, 3H), 7.71 (d, 1H, J = 7.9 Hz), 7.81 (d, 1H, J = 9.1 Hz), 7.83 (s, 1H), 7.92 (d, 1H, J = 6.9 Hz), 8.18 (s, 1H), 8.50 - 10.50 ppm (br. s, 1H, N-H); ¹³C nmr (deuteriotrichloromethane): δ 112.2 (q, J = 7.7 Hz), 116.4 (q, J = 7.6 Hz), 119.9 (q, J = 7.7 Hz), 120.0 (q, J = 7.6 Hz), 121.1, 122.8, 123.0, 124.0 (q, J = 271 Hz, CF₃), 124.3 (q, J = 269 Hz, CF₃), 127.4, 128.8, 129.5, 130.7 (q, J = 31 Hz, *ipso*-C-CF₃), 131.4 (q, J = 32 Hz, *ipso*-C-CF₃), 135.3, 136.0, 138.7, 141.9, 146.3, 147.7, 148.2 ppm; ms: m/z 450 (M⁺), 430, 263, 215, 96.

Anal. Calcd. for $C_{21}H_{13}F_6N_5$: C, 56.12; H, 2.90; N, 15.59. Found: C, 55.56; H, 2.77; N, 15.27.

N-(3-Trifluoromethylphenyl)-3-[(3-trifluoromethylphenyl)imino]-3*H*-pyrido[1,2-*b*]pyridazin-2-amine (**8b**, X = CH, R = 3-Trifluoromethylphenyl).

A solution of 1.6 *M* *n*-butyllithium in *n*-hexane (2 mmoles, 1.25 ml) was added dropwise to a suspension of 1-amino-2-methylpyridinium iodide (**5**) (1 mmole, 0.24 g) in tetrahydrofuran at -78 °C under an argon atmosphere. The reaction mixture was stirred for another 40 minutes at -78 °C and then a solution of imidoylchloride **2b** (1 mmole, 0.41 g) was added dropwise. After the addition was complete and the mixture stirred for two hours 1.6 *M* *n*-butyllithium in *n*-hexane (1 mmole, 0.6 ml) was slowly added under stirring. The reaction mixture was then allowed to slowly warm up to room temperature. After standing overnight the solvent was evaporated *in vacuo*. The solid residue was treated in 50 ml of toluene in an ultrasonic bath for about ten minutes and then filtered off. The filtrate was purified by column chromatography (alumina, toluene). Removal of the solvent and drying *in vacuo* resulted in a yellow amorphous solid, yield 8 %. ¹H nmr (deuteriotrichloromethane): δ 6.13 (s, 1H), 6.50 (t, 1H, J = 6.9 Hz), 6.85 (d, 1H, J = 7.9 Hz), 7.07 (t, 1H, J = 7.4 Hz), 7.08 - 7.28 (m, 3H), 7.30 (s, 1H), 7.37 - 7.50 (m, 2H), 7.55 (d, 1H, J = 8.1 Hz), 7.84 (d, 1H, J = 7.9 Hz), 7.95 (d, 1H, J = 7.0 Hz), 8.26 ppm (s, 1H); ¹³C nmr (deuteriotrichloromethane): δ 92.2, 110.8, 112.5, 116.1, 118.8, 119.1, 121.0, 122.1, 122.5, 123.6 (q, J = 275 Hz, CF₃), 124.1 (q, J = 275 Hz, CF₃), 125.5, 129.5 (q, J = 32 Hz, *ipso*-C-CF₃), 129.9 (q, J = 33 Hz, *ipso*-C-CF₃), 130.6, 136.0, 139.6, 140.9, 141.0, 149.9 ppm; ms: m/z 449 (M⁺), 429, 391, 334, 291.

Anal. Calcd. for $C_{22}H_{14}F_6N_4$: C, 58.93; H, 3.13; N, 12.50. Found: C, 58.44; H, 3.01; N, 12.36.

N-(4-Methylphenyl)- α -[(4-methylphenyl)imino]-2-oxo-1(2*H*)-pyridineacetamide (**10**, R = 4-Tol).

The triazine derivative **6a** (1 mmole, 0.34 g) was dissolved in 20 ml of dichloromethane and 5 mg of tetraphenylporphyrin were added. A constant stream of dry oxygen was passed through the reaction mixture at -20 °C for 3 hours, while externally irradiating with a sodium vapour lamp. The solvent was evaporated *in vacuo* and the solid residue was dissolved in 50 ml of toluene and then purified by column chromatography (alumina, toluene/acetone 9:1). Removal of the solvent and addition of a small amount of *n*-hexane resulted in colorless crystals, 0.31 g (88 %), mp 219 °C (decomposition). ¹H nmr (deuteriotrichloromethane): δ 2.29 (s, 3H), 2.31 (s, 3H), 6.07 (t, 1H, J = 8.4 Hz), 6.57 (d, 1H, J = 9.4 Hz), 6.79 (d, 2H, J = 6.9 Hz), 6.90 (d, 2H, J = 8.4 Hz), 7.09 - 7.14 (m, 4H), 7.32 (t, 1H, J = 8.0 Hz), 7.56 (d, 2H, J = 8.5 Hz), 9.10 ppm (s, 1H, N-H); ¹³C nmr (deuteriotrichloromethane): δ 20.9, 21.1, 106.4, 119.6, 121.2, 121.7, 129.5, 134.4, 134.5, 134.6, 137.5, 141.0, 141.2, 146.8, 156.9, 162.3 ppm; ms: m/z 345 (M⁺), 239, 211, 118, 95.

Anal. Calcd. for $C_{21}H_{19}N_3O_2$: C, 73.04; H, 5.51; N, 12.17. Found: C, 73.44; H, 5.92; N, 11.81.

General Procedure for the Reaction Between Heterocycles **6**, **7** and **8** and Dimethylacetylenedicarboxylate.

A mixture of the corresponding heterocyclic derivative (1 mmole) and dimethyl acetylenedicarboxylate (2 mmoles, 0.29 g) in 80 ml of toluene was heated at reflux for several hours. The reaction progress was monitored by tlc. After the reaction was complete by tlc analysis the solvent was removed *in vacuo*, and

the residue was chromatographed on neutral alumina using toluene:acetone 3:1. The products **11a**, **12a** and **12b** were obtained as crystalline solids after removing most of the eluent, addition of some ml of diethyl ether and cooling.

Trimethyl 1,4-Dihydro-1,4-bis(4-methylphenyl)pyrrolo[2,3-*d*]-imidazole-2,5,6-tricarboxylate (**11a**, R = 4-Tolyl).

This compound was obtained after a reaction time of 6 hours as yellow needles, mp 238 - 240 °C; yield 10 %; ¹H nmr (dimethylformamide-*d*₇): δ 2.43 (s, 3H), 2.45 (s, 3H), 3.32 (s, 3H), 3.75 (s, 3H), 3.81 (s, 3H), 7.22 (d, 2H, J = 8.0 Hz), 7.38 - 7.49 (m, 4H), 7.83 (d, 2H, J = 8.0 Hz); ms: m/z 461 (M⁺), 430, 402, 91.

Anal. Calcd. for $C_{25}H_{23}N_3O_6$: C, 65.07; H, 5.02; N, 9.11. Found: C, 64.88; H, 4.88; N, 9.00.

The X-ray crystallography, solution and refinements of **11a**: molecular formula $C_{25}H_{23}N_3O_6$, Mr = 461.46 gmol⁻¹, colourless prism, size 0.40 x 0.38 x 0.36 mm³, monoclinic, space group P2₁/c, a = 14.819(2), b = 14.878(2), c = 20.891(3) Å, β = 104.59(1)°, V = 4457(1) Å³, T = -90 °C, Z = 8, ρ_{calcd.} = 1.375 gcm⁻³, μ (Mo-K_α) = 1.0 cm⁻¹, F(000) = 1936, 8957 reflections in h(-17/17), k(0/18), l(-26/11), measured in the range 2.37° ≤ θ ≤ 26.32°, completeness Θ_{max} = 95.8 %, 8698 independent reflections, R_{int} = 0.057, 4811 reflections with F_o > 4σ(F_o), 633 parameters, 0 restraints, R1_{obs} = 0.081, wR₂^{obs} = 0.233, R1_{all} = 0.152, wR₂^{all} = 0.307, GOOF = 1.160, largest difference peak and hole: 0.590 / -0.513 e Å⁻³.

The intensity data for the compound **11a** were collected on a Nonius CAD4 diffractometer, using graphite-monochromatic Mo-K_α radiation. Data were corrected for Lorentz and polarization effects, but not for absorption [13].

The structures were solved by direct methods (SHELXS [16]) and refined by full-matrix least squares techniques against Fo² (SHELXL-97 [17]). The hydrogen atoms of the structure were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically [16]. Compound **11a** has two symmetry-nonequivalent molecules in the asymmetric unit. The molecule B is disordered. The disorder could be solved. For the discussion and the Tables only the results for molecule A will be published. XP [17] (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

The atomic coordinates and thermal parameters of **11a** are shown in Tables 1 and 2, and the bond lengths, and angles are listed in Tables 3 and 4. Further details of the crystal structure investigations are available on requests from the director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ, on quoting the depository number CCSD-142366 (**11a**) the names of the authors, and the journal citation.

Trimethyl 1-(4-Methylphenyl)-1*H*-dipyrido[1,2-*b*:3,2-*e*]-[1,2,4]triazine-2,3,4-tricarboxylate (**12a**, R = 4-Tolyl).

This compound was obtained after a reaction time of 20 hours as a black microcrystalline solid, mp 209 °C; yield 70 %; uv/vis (chloroform): λ(logε) 278 (4.59), 389 (3.93), 554 (2.79); ¹H nmr (deuteriodichloromethane): δ 2.34 (s, 3H), 3.29 (s, 3H), 3.60 (s, 3H), 3.64 (s, 3H), 5.81 (t, 1H, J = 6.8 Hz), 6.00 (d, 1H, J = 9.0 Hz), 6.36 (d, 1H, J = 6.7 Hz), 6.81 (t, 1H, J = 7.8 Hz), 7.05 (d, 2H, J = 8.4 Hz), 7.19 ppm (d, 2H, J = 8.3 Hz); ¹³C nmr (deuteriodichloromethane): δ 21.3, 51.9, 52.5, 52.6, 107.7,

110.3, 115.4, 121.2, 128.4, 130.2, 134.2, 134.4, 136.8, 138.7, 139.6, 141.3, 153.4, 157.4, 162.1, 164.7, 166.4 ppm; ms:m/z 449 (M⁺+1), 417, 93.

Anal. Calcd. for C₂₃H₂₀N₄O₆: C, 61.61; H, 4.46; N, 12.50. Found: C, 61.35; H, 4.65; N, 12.32.

The X-ray crystallography, solution and refinements of **12a**: molecular formula C₂₃H₂₀N₄O₆, Mr = 448.43 g mol⁻¹, black prism, size 0.38 x 0.32 x 0.28 mm³, triclinic, space group P-1, a = 10.3434(5), b = 10.5708(5), c = 10.9432(6) Å, α = 78.386(2), β = 63.735(2), γ = 81.927(2)°, V = 1049.21(9) Å³, T = -90 °C, Z = 2, ρ_{calcd.} = 1.419 g cm⁻³, μ (Mo-K_α) = 1.05 cm⁻¹, F(000) = 468, 5620 reflections in h(0/11), k(-11/11), l(-10/12), measured in the range 2.10° ≤ Θ ≤ 23.24°, completeness Θ_{max} = 94.6 %, 2852 independent reflections, R_{int} = 0.036, 2285 reflections with F_o > 4σ(F_o), 378 parameters, 0 restraints, R_{1obs} = 0.046, wR_{2obs} = 0.125, R_{1all} = 0.070, wR_{2all} = 0.167, GOOF = 1.262, largest difference peak and hole: 0.418/-0.526 e Å⁻³.

The intensity data for the compound **12a** were collected on a Nonius KappaCCD diffractometer, using graphite-monochromatic Mo-K_α radiation. Data were corrected for Lorentz and polarization effects, but not for absorption [14,15].

The structures were solved by direct methods (SHELXS [16]) and refined by full-matrix least squares techniques against Fo² (SHELXL-97 [17]). The hydrogen atoms were located by difference Fourier synthesis and refined isotropically. All non-hydrogen atoms were refined anisotropically [16]. XP [17] (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

The atomic coordinates and thermal parameters of **12a** are shown in Tables 5 and 6, and the bond lengths, and angles are listed in Tables 7 and 8. Further details of the crystal structure investigations are available on requests from the director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ, on quoting the depository number CCSD-142367 (**12a**) the names of the authors, and the journal citation.

Trimethyl 1-(3-Trifluoromethylphenyl)-1*H*-dipyrido-[1,2-*b*:3,2-*e*][1,2,4]triazine-2,3,4-tricarboxylate (**12b**, R = 3-Trifluoromethylphenyl).

This compound was obtained after a reaction time of 20 hours as a black microcrystalline solid, mp 201 °C; yield 80 %; ¹H nmr (deuteriotrichloromethane): δ 3.30 (s, 3H), 3.64 (s, 3H), 3.71 (s, 3H), 5.84 (t, 1H, J = 7.3 Hz), 6.15 (d, 1H, J = 8.7 Hz), 6.39 (d, 1H, J = 6.8 Hz), 6.82 (t, 1H, J = 7.2 Hz), 7.39 (d, 1H, J = 8.0 Hz), 7.46 (s, 1H), 7.50 (t, 1H, J = 7.9 Hz), 7.58 ppm (d, 1H, J = 7.8 Hz); ¹³C nmr (deuteriotrichloromethane): δ 51.9,

52.3, 52.4, 106.8, 110.6, 117.8, 121.6, 123.3 (q, J = 271 Hz, CF₃), 125.6, 125.7, 125.8, 129.9, 131.4 (q, J = 34 Hz, *ipso*-C-CF₃), 131.9, 136.2, 137.4, 138.2, 141.7, 152.7, 156.3, 161.5, 164.5, 165.8 ppm; ms:m/z 504 (M⁺), 503, 471.

Anal. Calcd. for C₂₃H₁₇F₃N₄O₆: C, 54.98; H, 3.39; N, 11.16. Found: C, 54.40; H, 3.36; N, 10.90.

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