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Iminophosphorane-mediated Bispyrido Annulation onto Five-membered Rings. X-Ray Crystal Structure of 6,7-Dibenzylamino-13-methoxymethyl-13Hdiquino[4,3-b:3',4'-d]pyrrole. Acetonitrile Complex.

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Abstract: Bispyrido annulation reaction onto a preformed five-membered heterocycle is achieved by the tandem aza Wittig/electrocyclic ring closure methodology. The method allows the one-step formation of diquinopyrroles, dipyridopyrroles, furodipyridines and thienodipyridines. The crystal and molecular structure of the 6,7-dibenzylamino-13-methoxymethyl-13H-diquino[4,3-b:3',4'-d]pyrrole. acetonitrile complex has been solved by X-ray analysis.

Pyrido annulation reaction based on the aza Wittig reaction of β -aryl(heteroaryl)vinyliminophosphoranes with iso(thio)cyanates or ketenes is a well-documented process.¹ Normally, the heterocyclization reaction takes place by electrocyclic ring-closure of the resulting heterocumulene (aza Wittig product) to give a *c*-fused pyridine.

Continuing our interest in the preparation and synthetic applications of C,C-bis(iminophosphoranes), we wish to report now a new one-flask bispyrido annulation reaction starting from appropriate C,C-bis(iminophosphoranes) in which both iminophosphorane groups are directly linked to different aromatic rings which are connected by a heteroaromatic ring.

The requisite bis(iminophosphorane) 3 was prepared from 2,5-bis(o-nitrophenyl)pyrrole² by the three-step sequence: a) protection with the methoxymethyl group (85%), b) hydrogenation of the N-protected pyrrole 1 in the presence of Pd on charcoal to give 2 (81%), and c) treatment of 2 with dibromotriphenylphosphorane in the presence of triethylamine to afford 3 (76%). Bis(iminophosphorane) 3 reacted with two equivalents of aromatic or aliphatic iso(thio)cyanates in toluene at reflux temperature to give the previously unreported pentacyclic compounds 4 in moderate to good yields (59-79%) (Scheme 1). In order to identify unambiguously the structure of compounds 4, the derivative 4b (R= C_6H_5 , CH₂) was recrystallized from different solvents and suitable crystals for X-ray analysis were obtained when acetonitrile was used.

The ¹H n.m.r. spectrum of the inclusion complex 4b.CH₃CN recorded in CDCl₃ showed signals due to both the free host 4b and free CH₃CN in a 1:1 ratio, at the same position as for the separate components. The IR spectrum of the crystalline complex in a nujol emulsion showed the nitrile band at 2247 cm⁻¹. We carried out a thermogravimetric (TG) analysis of the complex 4b.CH₃CN and we observed an experimental weight loss of 7.33 % at 100-107 °C, in good agreement with that required for the 1:1 complex (7.27 %).

The molecular structure of the acetonitrile complex with the atomic numbering is depicted in Fig. 1. The fiverings system is not planar and the five-membered ring (A) and the fused rings (B and D) makes angles of 1.6(1) and 1.2(1), while the angles between (B, C) and (D, E) are 2.0(1) and 4.3(1)° respectively. Some degree of delocalization has been observed along the N5-C16-N3 and C18-C8-N2 fragments. The acetonitrile molecule presents no significant differences with the averaged values retrieved from the Cambridge Structural Database³ (April 1995 release). Only 68 structures with R<0.10, no disorder, no metals and with located hydrogen bonds were retained, C-N= 1.123(29), C-C= 1.439(34)Å and NCC= 177(4)°(Table 1).

There is a total of four hydrogen interactions, of them only the N-H...N intramolecular bond could be considered strong when comparing with the result of the statistical analysis carried out for N-H...Nsp² interactions and secondary amines as donors (2.871Å and 167°). The N4...N5 distance of 2.766(5)Å is intermediate between the values reported for the neutral fluorene derivatives (2.861(2)-2.783(5)Å when there is no interaction) and those of the corresponding cation (2.588(3)-2.545(4)Å for N-H...N⁺ bond).⁴ The host and guest molecules are joined through weak N-H...N interactions so the whole crystal is built up of these discrete units (Table 1).



 $R = CH_3, C_6H_5.CH_2, 4-CH_3.C_6H_4, 4-CH_3O.C_6H_4. \qquad R = CH_3, C_6H_5.CH_2.$

Reagents and Conditions (a) H₂, Pd/C, EtOH, r.t.; (b) Ph₃PBr₂, Et₃N, benzene, reflux; (c) 2 R-NCO or 2 R-NCS, toluene, reflux; (d) 2 R-NCO or 2 R-NCS, Et₃NHBr, toluene, reflux.

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Scheme 1

The guest molecules are located in isolated cavities. The shape of the acetonitrile molecule can be described as spherical tipped rod when characterizing by the ratios of the inertial moments of volume over those of surface.⁵ The total packing coefficient is 0.68 while the local one is 0.38.



Fig.1.- Molecular structure of the acetonitrile complex of 4b and atomic numbering scheme. Displacement parameters are drawn at the 30% level and the hydrogen atoms are shown as spheres of arbitrary radii. Dotted lines mean hydrogen bonds.

In contrast to the only amino-imino tautomer observed in the solid state for 4b the compounds 4 show in solution a tautomeric equilibrium between the diamino and amino-imino forms 4A-4B, which is strongly dependent on the polarity of the solvent. In apolar solvents the tautomer 4A is the only tautomer observed whereas in polar solvents the tautomer 4B is found to be the predominant one.

Thus ¹H n.m.r. spectra of compound 4b in CDCl₃ or benzene-d₆ indicated only the presence of the tautomer A whereas in acetone-d₆ solution both tautomers appeared in 1:1 ratio, and in DMSO-d₆ in a ratio 1:4 wise B being the predominant tautomer. Thus for 4b in CDCl₃ the NH protons appeared at 6.36 ppm as a triplet and in DMSOd₆ two signals appeared, as a triplet at 12.80 ppm and as a singlet at 9.94 ppm, due to the exocyclic and endocyclic NH protons respectively. On the other hand, for compound 4a we have observed that in CDCl₃ only the tautomer A is observed whereas in DMSO-d₆ both tautomers appeared in a ratio 1:1. The low solubility of compounds 4c and 4d in the usual n.m.r. solvents do not allow us to study their possible tautomeric equilibria.

The reaction of bis(iminophosphorane) 3 with aliphatic iso(thio)cyanates and a proton source such as triethylammonium bromide led to the salts 5a-b as the only reaction products in moderate yields (45-52 %) (Scheme 1). The ¹H n.m.r. spectra of 5a-b in DMSO-d₆ showed a resonance in the range 16.02-16.71 ppm due to

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a strong N...H...N hydrogen bridge characteristic of protonated "proton sponges".⁶ In addition, both ¹H and ¹³C n.m.r. spectra showed a high degree of symmetry in the molecule, due, probably, to a rapid exchange of the bridging proton between the two exocyclic nitrogens, which confirms the proposed structure **5a-b**. The reaction of bis(iminophosphorane) **3** with aromatic isocyanates in the presence of the same proton source did not give the expected salts **5c-d**. The basic behaviour of compounds **4a-b** could be explained by the fact that they are vinylogue of pentasubstituted biguanides, which display a high basic strength.⁷ No protonation of compounds **4c-d** by the action of triethylammonium bromide may be ascribed to the fact that in the related biguanides alkylderivatives are stronger bases than are arylbiguanides. We should finally note that the transprotonation of **5a-b** with 1,8-bis(dimethylamino)naphthalene gives **4a-b**.

N1-C1	1.323(6)	N1-C2	1.388(6)	N2-C8	1.371(5)
N2-C9	1.403(5)	N3-C15	1.394(6)	N3-C16	1.361(6)
N4-C1	1.365(3)	N4-C19	1.437(6)	N5-C16	1.304(6)
N5-C28	1.471(6)	O1-C26	1.368(7)	O1-C27	1.459(6)
C1-C18	1.427(6)	C7-C8	1.437(6)	C8-C18	1.395(6)
C9-C10	1.431(6)	C9-C17	1.376(6)	C10-C15	1.421(6)
C16-C17	1.466(6)	C17-C18	1.445(6)	N35-C36	1.134(11)
C36-C37	1.431(18)				
C9-N2-C26	125.3(4)	C8-N2-C26	123.6(4)	C1-N4-C19	122.7(4)
C16-N5-C28	119.7(4)	C26-O1-C27	110.6(4)	N1-C1-N4	119.8(4)
N4-C1-C18	119.2(4)	N1-C1-C18	121.0(4)	N3-C16-N5	121.6(4)
N5-C16-C17	122.8(4)	N3-C16-C17	115.5(4)	N2-C26-O1	109.0(4)
N35-C36-C37	178.8(10)				
C8-N2-C26-O1	100.0(5)	C19-N4-C1-N1	8.4(7)	C1-N4-C19-C20	-95.4(5)
C28-N5-C16-N3	-0.1(7)	C16-N5-C28-C29	-173.6(4)	C27-O1-C26-N2	-178.2(4)
N4-C1-C18-C17	3.2(7)	N5-C16-C17-C18	1.5(8)	C16-C17-C18-C1	2.5(8)
N4-C19-C20-C25	19.6(7)	N5-C28-C29-C34	-51.1(7)		
Hydrogen interaction	ns				
Х-НҮ		Х-Н	XY	HY	X-HY
N4-H4N5		0.89(4)	2.766(5)	1.92(4)	158(4)
C6-H6O1		0.96(4)	3.303(6)	2.48(4)	143(3)
C11-H11O1		0.99(4)	3.353(6)	2.50(4)	145(3)
N3-H3NN35(-x+1	, -y, -z)	0.93(6)	3.694(9)	2.78(6)	170(5)

Table 1. Selected geometrical parameters (Å, °).

Bis(iminophosphorane) 3 also reacted with carbon disulfide in benzene solution at reflux temperature to give the corresponding bis(isothiocyanate) 6 in 69 % yield, which was recovered unaltered after prolonged heating at 160 °C in a sealed tube (Scheme 2).





This bispyrido annulation reaction allows the preparation of dipyrido[4,3-b:3',4'-d]pyrroles 11 and 12, structurally related to 9-azaellipticines but differing by deletion of a cycle, which exhibit good cytotoxicity on L1210 cultured cells and significant antitumor properties in the in vivo P388 leukemia system.⁸ Only two methods for the preparation of this tricyclic ring system have been described. The first involves Fischer indole reaction of



Scheme 3

4-hydrazino pyridine derivatives with N-acetyl piperidone and further dehydrogenation.⁹ The second method is based on a pyrido annulation reaction onto a preformed pyrrolo[3,2-c]pyridine.¹⁰

Our approach is based on the simultaneous construction of the two pyridine rings by using the so-called aza Wittig/electrocyclic ring closure process. The pyrroledicarboxaldehyde 8, readily available by reaction of *N*-methylpyrrole with α -dicarbonyl compounds and subsequent oxidation with periodate,¹¹ was subjected to reaction with ethyl azidoacetate at - 10 °C to give the bis(vinylazide) 9 in moderate yield (47 %). Staudinger reaction of compound 9 with triphenylphosphine in dichloromethane/diethyl ether at room temperature provided the key intermediate bis(iminophosphorane) 10 in almost quantitative yield (97 %). Bis(iminophosphorane) 10 reacted with two equivalents of isocyanates at 160 °C in a sealed tube for 8 h to give the tricyclic compounds 11 in 71-80 % yields, whereas the reaction with ketenes at room temperature gave 12 in 72-87 % yields (Scheme 3).

A logical step in this study was to extend this methodology to the preparation of the otherwise not readily available tricyclic compounds derived from furan and thiophene. The only method described for the preparation of furo[3,2-c:4,5-c']dipyridines involves formation of a pyridine ring onto a preformed appropriately substituted furo[3,2-c]pyridine.¹² Perhalogenated thieno[3,2-c:4,5-c']dipyridines have been prepared by photodehalogenation of perhalogenated 4-(4-pyridylthio)pyridines.¹³



(c) 2 PhRCCO, toluene, r.t.

Scheme 4

Bis(iminophosphoranes) 15 and 16 were prepared as described for compound 10. 2,5-Furandicarboxaldehyde¹⁴ was converted into the bis(vinylazide) 13 in 36 % yield by reaction with ethyl azidoacetate, and further treatment with triphenylphosphine provided 15 in 91 % yield. Similarly, bis(vinylazide)¹⁵ 14 afforded the bis(iminophosphorane) 16 in 98 % yield. The reaction of bis(iminophosphoranes) 15 and 16 with isocyanates yielded the furodipyridines 17 (73-86 %) and thienodipyridines 18 (50-80 %) respectively. With ketenes at room temperature the tricyclic compounds 19 (45-61 %) and 20 (67 %) were obtained (Scheme 4).

EXPERIMENTAL.

All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. IR spectra were obtained as nujol emulsions or films on a Nicolet 5DX spectrophotometer. NMR spectra were recorded on a Bruker AC-200 (200 MHz) or a Varian Unity 300 (300 MHz). Mass spectra were recorded on a Hewlett-Packard 5993C spectrometer and the FAB in a Autospec 5000VG Fisons instrument. Microanalyses were performed on a Perkin-Elmer 240C instrument. Thermogravimetric analysis was recorded on a Mettler TG-50 thermobalance.

X-Ray Analysis.- A summary of data collection and refinement process is given in Table 2. The structure was solved by direct methods (SIR92)¹⁶ and refined by least-squares procedures on Fobs. All hydrogens were obtained from difference Fourier synthesis and included and refined isotropically in the last cycles. The scattering factors were taken from the International Tables for X-Ray Crystallography.¹⁷ Table 3 list the final atomic coordinates and equivalent thermal factors for non-hydrogen atoms. The calculations were carried out with the XTAL,¹⁸ PESOS¹⁹ and PARST²⁰ set of programs running on a VAX 6410 computer.

N-Methoxymethyl-2,5-bis(o-nitrophenyl)pyrrole 1.

To a solution of 2,5-bis(*o*-nitrophenyl)pyrrole² (0.618 g, 2 mmol) in dry benzene (25 ml) potassium hydroxide (5 mmol) and 18-crown-6 (30 mg) were added. The resultant mixture was stirred at reflux temperature for 2 h. Then, a solution of chloromethyl methyl ether (0.402 g, 5 mmol) in dry benzene (10 ml) was added dropwise and the new solution stirred at reflux temperature for 4 h. After cooling at room temperature the reaction mixture was filtered over celite, which was washed with benzene (2 x 5 ml). The solvent was removed under reduced pressure and the residual material was chromatographed on a silica gel column with *n*-hexane/ethyl acetate (7:3) to give 1 in 85 % yield as orange prisms, m.p. 118-119 °C. (Found: C, 61.00; H, 4.32; N, 11.75. $C_{18}H_{15}N_3O_5$ requires: C, 61.19; H, 4.28; N, 11.89); i.r. (nujol): 1610, 1573, 1522, 1355, 1151, 1102, 919, 852, 788, 756, 720, 703 cm⁻¹; ¹H n.m.r. δ (CDCl₃): 2.95 (s, 3 H), 4.84 (s, 2 H), 6.25 (s, 2 H), 7.54-7.65 (m, 6 H), 7.95 (dd, 2 H, J = 0.60, 7.80 Hz); ¹³C n.m.r. δ (CDCl₃): 55.4, 76.0, 110.8, 124.2, 127.3, 129.3, 130.3, 132.3, 133.8, 150.1; m/z (%): 353 (M⁺, 5), 104 (11), 77 (7), 45 (100).

Crystal aala						
Chemical formula	C,H,NO.C,H,N	Crystal system	Monoclinic			
Mr	564.69	Space group	P2,/c			
a (Å)	11.4605(5)	α (°)	90			
<i>b</i> (Å)	8.8523(8)	β (°)	90.105(8)			
c (Å)	28.9376(41)	γ(°)	90			
Z	4	Dx (gr/cm ³)	1.28			
V (Å ³)	2935.8(5)	Radiation	CuKα			
Wavelength (Å)	1.5418	No. of reflections for	eflections for			
θ range for lattice parameters (°)	2-45	Lattice parameters:	67			
Absorption coefficient (cm ⁻¹)	5.91	Temperature (K)	295			
Crystal colour	Dark yellow	Crystal description	Prism			
Crystal size (mm)	0.46 x 0.17 x 0.17					
Data collection						
Diffractometer type	iffractometer type Philips PW1100, four circle. Graphite oriented monocromator.					
Measurement time	1 min./reflection Detector apertures (°)		1 1			
			1 X 1			
Collection method	ω/2θ scans	θmax (°)	65			
Collection method No. of standard reflections (interval)	ω/2θ scans 2 (90 min.). 46% decay	θmax (°) Scan width (°)	65 1.5			
Collection method No. of standard reflections (interval) No. of independent reflections	ω/2θ scans 2 (90 min.). 46% decay 5013	θmax (°) Scan width (°) No. of observed reflections, I>3	65 1.5 σ(I) 3104			
Collection method No. of standard reflections (interval) No. of independent reflections Refinement	ω/20 scans 2 (90 min.). 46% decay 5013	θmax (°) Scan width (°) No. of observed reflections, I>3	65 1.5 σ(I) 3104			
Collection method No. of standard reflections (interval) No. of independent reflections <i>Refinement</i> Treatment of hydrogen atoms	 ω/2θ scans 2 (90 min.). 46% decay 5013 See experimental part Re 	θmax (°) Scan width (°) No. of observed reflections, I>3 finement: Least-Squares of Fo. Fu	65 1.5 σ(I) 3104			
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Collection method No. of standard reflections (interval) No. of independent reflections <i>Refinement</i> Treatment of hydrogen atoms Secondary extintion correction (10 ⁴) R	ω/2θ scans 2 (90 min.). 46% decay 5013 See experimental part Re 0.25(3) 0.076	 θmax (°) Scan width (°) No. of observed reflections, I>3 finement: Least-Squares of <i>Fo</i>. Fo No. of parameters refined 	65 1.5 σ(I) 3104 ull matrix 516			
Collection method No. of standard reflections (interval) No. of independent reflections <i>Refinement</i> Treatment of hydrogen atoms Secondary extintion correction (10 ⁴) R wR	ω/2θ scans 2 (90 min.). 46% decay 5013 See experimental part Re 0.25(3) 0.076 0.081	 θmax (°) Scan width (°) No. of observed reflections, I>3 finement: Least-Squares of Fo. Fo No. of parameters refined Degrees of freedom 	65 1.5 σ(I) 3104 ull matrix 516 2588			
Collection method No. of standard reflections (interval) No. of independent reflections <i>Refinement</i> Treatment of hydrogen atoms Secondary extintion correction (10 ⁴) R wR $(\Delta \rho)$ max (e/Å ³)	 ω/2θ scans 2 (90 min.). 46% decay 5013 See experimental part Re 0.25(3) 0.076 0.081 0.44 	 θmax (°) Scan width (°) No. of observed reflections, I>3 finement: Least-Squares of Fo. Fo No. of parameters refined Degrees of freedom Ratio of freedom 	65 1.5 σ(I) 3104 will matrix 516 2588 6.0			
Collection method No. of standard reflections (interval) No. of independent reflections <i>Refinement</i> Treatment of hydrogen atoms Secondary extintion correction (10 ⁴) R wR (Δp)max (e/Å ³) <shift error=""></shift>	 ω/2θ scans 2 (90 min.). 46% decay 5013 See experimental part Re 0.25(3) 0.076 0.081 0.44 0.14 	 θmax (°) Scan width (°) No. of observed reflections, I>3 finement: Least-Squares of Fo. Fo No. of parameters refined Degrees of freedom Ratio of freedom Max. thermal value (Å²) U11[C. 	1×1 65 1.5 $\sigma(I)$ 3104 ull matrix 516 2588 6.0 33]= 0.23(1)			
Collection method No. of standard reflections (interval) No. of independent reflections <i>Refinement</i> Treatment of hydrogen atoms Secondary extintion correction (10^4) R wR (Δp)max (e/Å ³) <shift error=""> Weighting scheme: Empirical as to give</shift>	 ω/2θ scans 2 (90 min.). 46% decay 5013 See experimental part Re 0.25(3) 0.076 0.081 0.44 0.14 we no trends in <ωΔ²F> v 	θ max (°) Scan width (°) No. of observed reflections, I>3 finement: Least-Squares of <i>Fo</i> . Fo No. of parameters refined Degrees of freedom Ratio of freedom Max. thermal value (Å ²) U11[C: s. < Fobs > and <sin<math>\theta/\lambda>.</sin<math>	$\begin{array}{c} 1 \times 1 \\ 65 \\ 1.5 \\ \sigma(I) & 3104 \end{array}$ ull matrix $\begin{array}{c} 516 \\ 2588 \\ 6.0 \\ 33] = 0.23(1) \end{array}$			

Table 2. Crystal analysis parameters at room temperature.

N-Methoxymethyl-2,5-bis(o-aminophenyl)pyrrole 2.

To a solution of *N*-methoxymethyl-2,5-bis(*o*-nitrophenyl)pyrrole 1 (0.706 g, 2 mmol) in ethanol (30 ml) was added 10 % Pd on charcoal (0.075 g), and the reaction mixture was stirred at room temperature under hydrogen at 2 atm for 4 h. The reaction mixture was filtered on celite, which was washed with ethanol (2 x 10 ml). The filtrate and the ethanolic extracts were combined and concentrated to dryness under reduced pressure and the residual material was chromatographed on a silica gel column with *n*-hexane/ethyl ether (3:7) to give 2 in 81 % yield as a viscous oil. (Found: C, 73.78; H, 6.45; N, 14.37. $C_{18}H_{19}N_3O$ requires: C, 73.69; H, 6.53; N, 14.32); i.r. (neat): 3461, 3365, 1619, 1488, 1453, 1384, 1301, 1149, 1086, 916, 756 cm⁻¹; ¹H n.m.r. δ (CDCl₃): 2.93 (s, 3 H), 4.05 (br s, 4 H), 4.92 (s, 2 H), 6.31 (s, 2 H), 6.73-6.81 (m, 4 H), 7.14-7.24 (m, 4 H); ¹³C n.m.r. δ (CDCl₃): 5.5, 7.5.3,

109.9, 115.4, 118.1, 118.5, 129.3, 131.9, 132.0, 145.7; m/z (%): 293 (M⁺, 33), 260 (54), 231 (35), 155 (72), 144 (97), 131 (100), 94 (58), 77 (27).

Bis(iminophosphorane) 3.

To a cooled at 0 °C solution of triphenylphosphine (1.311 g, 5 mmol) in dry benzene (30 ml), bromine (0.799 g, 5 mmol) in the same solvent (20 ml) was added dropwise. The mixture was allowed to warm at room temperature and then *N*-methoxymethyl-2,5-bis(*o*-aminophenyl)pyrrole **2** (0.733g, 2.5 mmol) and triethylamine (1.012 g, 10 mmol) were added. The resultant mixture was refluxed for 8 h. After cooling, the precipitated solid was separated by filtration, the filtrate was concentrated to dryness and the residual material was recrystallized from benzene/ *n*-hexane to give the bis(iminophosphorane) **3** in 76 % yield as colourless prisms, m.p. 245-247 °C. (Found: C, 79.80; H, 5.51; N, 5.21. $C_{54}H_{45}N_3OP_2$ requires: C, 79.69; H, 5.57; N, 5.16); i.r. (nujol): 1590, 1435, 1362, 1314, 1113, 1083, 1026, 753, 742, 722, 693 cm⁻¹; ¹H n.m.r. δ (CDCl₃): 2.68 (s, 3 H), 5.22 (s, 2 H), 6.32 (s, 2 H), 6.56 (d, 2 H, *J* = 7.86 Hz), 6.68 (t, 2 H, *J* = 7.36 Hz), 6.88 (dd, 2 H, *J* = 1.63, 7.55 Hz), 7.30-7.50 (m, 20 H), 7.62-7.73 (m, 12 H); ³¹P n.m.r. δ (CDCl₃): - 2.12.

General Procedure for the Preparation of Diquino[4,3-b:3',4'-d]pyrroles 4.

To a solution of the bis(iminophosphorane) **3** (0.407 g, 0.5 mmol) in dry toluene (20 ml) a solution of the appropriate iso(thio)cyanate (1 mmol) in the same solvent (5 ml) was added at once. The reaction mixture was heated at reflux temperature for 6 h. After cooling, the product was isolated by one of the following procedures: a) the solvent was concentrated to dryness under reduced pressure and the residual material was chromatographed on a silica gel column using ethanol as solvent (for **4a**); b) the solvent was removed under reduced pressure and the resulting material was treated with cold ethanol, the precipitated solid was filtered and recrystallized (for **4b**); or c) the precipitated solid was filtered and recrystallized (for **4c** and **4d**).

4a (R = CH₃) (79 %), m.p. 216-217 °C (from ethanol/diethyl ether as colourless prisms). (Found: C, 71.05; H, 5.65; N, 18.81. $C_{22}H_{21}N_5O$ requires: C, 71.14; H, 5.70; N, 18.85); i.r. (nujol): 3365, 1613, 1570, 1533, 1519, 1239, 1228, 1202, 1087, 971, 852, 761 cm⁻¹; ¹H n.m.r. δ (CDCl₃): 3.11 (br s, 6 H), 3.53 (s, 3 H), 5.21 (s, 3 H), 5.92 (br s, 2 H), 7.10 (t, 2 H, *J* = 7.48 Hz), 7.29 (t, 2 H, *J* = 7.60 Hz), 7.67 (d, 2 H, *J* = 7.08 Hz), 7.76 (d, 2 H, *J* = 7.35 Hz); ¹³C n.m.r. δ (CDCl₃): 28.9, 54.7, 78.8, 105.6, 113.9, 120.8, 122.1, 127.1, 127.6, 140.8, 146.2, 152.4; m/z (%): 371 (M⁺, 58), 327 (24), 326 (100), 297 (13), 283 (8), 268 (9).

4b (R = C₆H₅.CH₂) (59 %), m.p. 186-188 °C (from ethanol as colourless prisms). (Found: C, 77.78; H, 5.56; N, 13.41. C₃₄H₂₉N₅O requires: C, 77.99; H, 5.58; N, 13.37); i.r. (nujol): 3324, 1635, 1609, 1569, 1544, 1513, 1223, 1080, 1031, 963, 752, 715, 699 cm⁻¹; ¹H n.m.r. δ (CDCl₃): 3.64 (s, 3 H), 4.61 (d, 4 H, *J* = 4.46 Hz), 5.48 (s, 2 H), 6.36 (t, 2 H, *J* = 4.46 Hz), 7.14-7.36 (m, 14 H), 7.74 (d, 2 H, *J* = 7.87 Hz), 7.93 (d, 2 H, *J* = 7.87 Hz); ¹³C n.m.r. δ (CDCl₃): 46.1, 54.8, 79.1, 105.6, 114.3, 120.9, 122.5, 127.2, 127.4, 127.8, 128.6, 139.7, 141.4, 146.2, 151.4; m/z (%): 523 (M⁺, 25), 478 (35), 432 (44), 283 (34), 209 (27), 118 (100), 91 (56), 77 (31).

4c (R = 4-CH₃.C₆H₄) (64 %), m.p. 299-300 °C (from toluene as colourless prisms). (Found: C, 77.71; H, 5.52; N, 13.09. C₃₄H₂₉N₅O requires: C, 77.99; H, 5.58; N, 13.13); i.r. (nujol): 3390, 1681, 1628, 1604, 1569, 1511, 1089,

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971, 828, 753, 716 cm⁻¹; ¹H n.m.r. δ (CDCl₃ + CF₃COOH) (tautomers ratio 3:1): 2.33 (s, Ar.CH₃, minor tautomer), 2.36 (s, Ar.CH₃, major tautomer), 2.42 (s, Ar.CH₃, minor tautomer), 3.87 (s, CH₃OCH₂, minor tautomer), 3.91 (s, CH₃OCH₂, major tautomer), 5.86 (s, CH₃OCH₂, minor tautomer), 5.97 (s, CH₃OCH₂, major tautomer), 7.05-8.44 (m, aromatic, major and minor tautomers); HRMS (FAB⁺) M⁺+1 524.2457, theor. 524.2450.

4d (R = 4-CH₃O.C₆H₄) (72 %), m.p. 237-238 °C (from toluene as colourless prisms). (Found: C, 73.41; H, 5.20; N, 12.64. C₃₄H₂₉N₅O₃ requires: C, 73.49; H, 5.26; N, 12.60); i.r. (nujol): 3387, 1668, 1629, 1572, 1550, 1504, 1246, 1085, 1037, 830, 748 cm⁻¹; ¹H n.m.r. δ (CDCl₃ + CF₃COOH) (tautomers ratio 2.5:1): 3.84 (s), 3.88 (s), 3.92 (s), 5.89 (s, CH₃OCH₂, minor tautomer), 5.97 (s, CH₃OCH₂, major tautomer), 6.99-8.45 (m, aromatic, major and minor tautomers); HRMS (FAB⁺) M⁺+1 556.2342, theor. 556.2348.

General Procedure for the Preparation of Diquino[4,3-b:3',4'-d]pyrrole Hydrobromides 5.

To a mixture of the bis(iminophosphorane) **3** (0.407 g, 0.5 mmol) and triethylammonium bromide (0.5 mmol) in dry toluene (20 ml), a solution of the appropriate iso(thio)cyanate (1 mmol) in the same solvent (5 ml) was added at once. The reaction mixture was heated at reflux temperature for 6 h. After cooling, the precipitated solid was filtered, washed with cold water (2.5 ml) and dried. An analytical sample was obtained by recrystallization.

5a (R = CH₃) (45 %), m.p. 280-282 °C (from ethanol as colourless prisms). (Found: C, 58.40; H, 4.95; N, 14.93. $C_{22}H_{21}N_5$ O.HBr requires: C, 58.41; H, 4.90; N, 15.48); i.r. (nujol): 3193, 1648, 1593, 1333, 1307, 1252, 1206, 1085, 974, 772, 753, 741 cm⁻¹; ¹H n.m.r. δ (DMSO-d₆): 2.95 (s, 6 H), 3.52 (s, 3 H), 5.21 (s, 2 H), 7.15 (t, 2 H), *J* = 7.23 Hz), 7.38-7.47 (m, 4 H), 7.75 (d, 2 H, *J* = 8.12 Hz), 10.59 (s, 2 H), 16.02 (s, 1 H); ¹³C n.m.r. δ (DMSO-d₆): 31.1, 54.6, 77.6, 109.4, 111.3, 117.2, 121.4, 123.2, 129.4, 137.0, 137.6, 148.5; MS (FAB⁻) 452 (M⁺, 54).

5b (R= C₆H₅.CH₂) (52 %), m.p. 244-246 °C (from ethanol as colourless prisms). (Found: C, 67.37; H, 5.06; N, 11.52. C₃₄H₂₉N₅O.HBr requires: C, 67.55; H, 5.00; N, 11.58); i.r. (nujol): 3166, 1634, 1595, 1301, 1247, 1203, 1110, 1085, 973, 752, 704 cm⁻¹; ¹H n.m.r. δ (DMSO-d₆): 3.64 (s, 3 H), 4.43 (s, 4 H), 5.58 (s, 2 H), 7.16-7.25 (m, 10 H), 7.36 (t, 2 H, J = 7.81 Hz), 7.56 (t, 2 H, J = 7.81 Hz), 7.56 (t, 2 H, J = 7.81 Hz), 7.56 (t, 2 H, J = 7.81 Hz), 11.12 (s, 2 H), 16.71 (s, 1 H); ¹³C n.m.r. δ (DMSO-d₆): 47.3, 54.9, 78.2, 110.0, 112.0, 117.6, 122.2, 123.9, 127.2, 127.5, 128.6, 130.1, 137.3, 138.1, 139.2, 148.4; MS (FAB⁺) 524 (M⁺ - Br, 97).

Reaction of Bis(iminophosphorane) 3 with Carbon Disulfide.

A mixture of bis(iminophosphorane) **3** (0.407 g, 0.5 mmol), dry benzene (15 ml) and carbon disulfide (4 ml) was refluxed for 12 h. After cooling, the solvent was removed under reduced pressure and the crude product was chromatographed on a silica gel column with petroleum ether/dichloromethane (1:1) to give **6** in 69 % yield, as colourless prisms, m.p. 124-125 °C. (Found: C, 63.59; H, 4.09; N, 11.19. $C_{20}H_{15}N_3OS_2$ requires: C, 63.64; H, 4.00; N, 11.13); i.r (nujol): 2173, 2114, 1600, 1568, 1331, 1230, 1162, 1081, 949, 923, 753 cm⁻¹; ¹H n.m.r. δ (CDCl₃): 2.89 (s, 3 H), 4.99 (s, 2 H), 6.44 (s, 2 H), 7.31-7.38 (m, 6 H), 7.58-7.61 (m, 2 H); ¹³C n.m.r. δ (CDCl₃): 55.5, 75.6, 112.2, 126.1, 127.3, 129.1, 130.6, 131.4, 131.6, 132.1, 136.6; m/z (%): 377 (M⁺, 100), 287 (17), 274 (72), 257 (26), 242 (18).

Atom	n x	у	z	Ueq	Atom	x	у	Z	Ueq
- N1	0.2495(3)	-0.0505(4)	0.0610(1)	54(1)	C17	0.4951(3)	0.2183(5)	0.0300(1)	44(1)
N2	0.4086(3)	0.1977(4)	-0.0407(1)	45(1)	C18	0.3948(3)	0.1201(5)	0.0327(1)	46(1)
N3	0.6657(3)	0.3640(4)	0.0470(1)	56(1)	C19	0.3423(4)	-0.0405(6)	0.1507(2)	62(2)
N4	0.3820(3)	0.0524(5)	0.1131(1)	57(1)	C20	0.2479(4)	0.0312(6)	0.1784(2)	56(2)
N5	0.5836(3)	0.2227(4)	0.1065(1)	56(1)	C21	0.2281(5)	-0.0265(7)	0.2226(2)	72(2)
01	0.3351(3)	0.2873(5)	-0.1102(1)	81(1)	C22	0.1405(5)	0.0348(9)	0.2490(2)	88(2)
C1	0.3400(3)	0.0383(5)	0.0692(2)	49(1)	C23	0.0746(5)	0.1522(9)	0.2327(2)	91(3)
C2	0.2025(4)	-0.0607(5)	0.0168(2)	54(2)	C24	0.0924(5)	0.2093(7)	0.1889(2)	85(2)
C3	0.1068(4)	-0.1585(6)	0.0095(2)	68(2)	C25	0.1796(4)	0.1488(6)	0.1623(2)	65(2)
C4	0.0505(5)	-0.1684(7)	-0.0331(2)	80(2)	C26	0.4064(4)	0.1794(6)	-0.0915(2)	72(2)
C5	0.0844(4)	-0.0791(7)	-0.0695(2)	76(2)	C27	0.3279(7)	0.2697(8)	-0.1602(2)	101(3)
C6	0.1789(4)	0.0133(6)	-0.0637(2)	64(2)	C28	0.6762(4)	0.2749(6)	0.1379(2)	64(2)
C7	0.2416(3)	0.0233(5)	-0.0212(2)	51(1)	C29	0.6678(4)	0.1954(6)	0.1833(2)	61(2)
C8	0.3441(3)	0.1108(5)	-0.0110(1)	45(1)	C30	0.7628(5)	0.1227(7)	0.2030(2)	76(2)
C9	0.4991(3)	0.2650(5)	-0.0153(1)	45(1)	C31	0.7586(8)	0.0444(9)	0.2436(2)	123(3)
C10	0.5857(3)	0.3685(5)	-0.0316(1)	45(1)	C32	0.6565(11)	0.0385(14)	0.2657(3)	154(5)
C11	0.5922(4)	0.4302(5)	-0.0761(2)	55(2)	C33	0.5601(10)	0.1046(14)	0.2481(3)	144(5)
C12	0.6804(4)	0.5282(6)	-0.0877(2)	65(2)	C34	0.5632(6)	0.1914(9)	0.2062(2)	96(3)
C13	0.7647(4)	0.5664(6)	-0.0545(2)	69(2)	N35	-0.0789(7)	-0.4833(9)	0.1095(3)	140(4)
C14	0.7595(4)	0.5131(6)	-0.0102(2)	63(2)	C36	-0.0161(7)	-0.3935(10)	0.1223(3)	100(3)
C15	0.6700(4)	0.4151(5)	0.0015(2)	50(1)	C37	0.0622(14)	-0.2780(18)	0.1378(4)	145(5)
C16	0.5828(4)	0.2683(5)	0.0636(2)	50(2)					

Table 3. Final atomic coordinates and Ueq= $(1/3)\Sigma[Uij.a_i^*.a_j^*.a_i.a_j.cos(a_i,a_j)]x10^3$

Preparation of Bis(azides) 9 and 13.

A mixture of ethyl azidoacetate (10.32 g, 80 mmol) and N-methyl-2,5-pyrroledicarboxaldehyde¹¹ or 2,5furandicarboxaldehyde¹⁴ (10 mmol) was added dropwise to a well-stirred solution containing sodium (1.84 g, 80 mmol) in dry ethanol (100 ml), under nitrogen at - 10 °C. The reaction mixture was stirred at - 10 °C for 5 h and for 1 h at 0 °C. Then, it was poured into saturated aqueous ammonium chloride (200 ml) and extracted with diethyl ether (3 x 100 ml). The organic layers were washed with water (2 x 150 ml) and dried over MgSO₄. The MgSO₄ was removed by filtration and the solvent concentrated to dryness. The resulting solid was treated with cold ethanol and recrystallized.

9 (47 %), m.p. 121-124 °C (from ethanol as yellow needles). (Found: C, 50.03; H, 4.71; N, 27.35. $C_{15}H_{17}N_7O_4$ requires: C, 50.14; H, 4.77; N, 27.28); i.r. (nujol): 2107, 1699, 1598, 1261, 1141, 1098, 1075, 772, 748 cm⁻¹; ¹H n.m.r. δ (CDCl₃): 1.39 (t, 6 H, *J* = 7.04 Hz), 3.61 (s, 3 H), 4.36 (q, 4 H, *J* = 7.04 Hz), 6.84 (s, 2 H), 7.26 (s, 2 H); ¹³C n.m.r. δ (CDCl₃): 14.3, 30.4, 62.2, 112.2, 116.6, 122.6, 130.6, 163.5; m/z (%): 359 (M⁺, 5), 230 (77), 184 (62), 158 (100), 131 (44), 90 (29), 54 (42).

13 (36 %), m.p. 92-96 °C (from ethanol as yellow needles). (Found: C, 48.49; H, 4.11; N, 24.36. C₁₄H₁₄N₆O₅ requires: C, 48.56; H, 4.07; N, 24.27); i.r. (nujol): 2125, 1712, 1613, 1289,1230, 1192, 1083, 1017, 794, 754

cm⁻¹; ¹H n.m.r. δ (CDCl₃): 1.38 (t, 6 H, *J* = 7.02 Hz), 4.35 (q, 4 H, *J* = 7.02 Hz), 6.81 (s, 2 H), 7.21 (s, 2 H); ¹³C n.m.r. δ (CDCl₃): 14.2, 62.4, 112.3, 117.8, 124.4, 150.4, 162.9; m/z (%): 346 (M⁺, 6), 146 (13), 145 (100), 90 (16), 69 (13), 57 (9).

Preparation of Bis(iminophosphoranes) 10, 15 and 16.

To a solution of triphenylphosphine (1.31 g, 5 mmol) in a mixture of diethyl ether/dichloromethane (2:1) the corresponding bis(azide) 9, 13 or 14¹⁵ (2.5 mmol) was added in small portions. The reaction mixture was stirred at room temperature for 12 h, and the separated solid was filtered and recrystallized.

10 (97 %), m.p. 223-225 °C (from dichloromethane/diethyl ether as yellow prisms). (Found: C, 73.92; H, 5.76; N, 5.00. $C_{s_1}H_{47}N_3O_4P_2$ requires; C, 73.99; H, 5.72; N, 5.08); i.r. (nujol): 1685, 1579, 1408, 1247, 1209, 1107, 788, 752, 717, 696 cm⁻¹; ¹H n.m.r. δ (DMSO-d₆): 0.88 (t, 6 H, J = 7.20 Hz), 3.53 (s, 3 H), 3.77 (q, 4 H, J = 7.20 Hz), 6.70 (d, 2 H, $J_{H-P} = 7.19$ Hz), 7.24 (s, 2 H), 7.37-7.55 (m, 18 H), 7.63-7.69 (m, 12 H); ³¹P n.m.r. δ (DMSO-d₆): 5.65.

15 (91 %), m.p. 222-223 °C (from dichloromethane/diethyl ether as yellow prisms). (Found: C, 73.63; H, 5.38; N, 3.46. $C_{50}H_{44}N_2O_5P_2$ requires: C, 73.70; H, 5.44; N, 3.44); i.r. (nujol): 1691, 1583, 1263, 1206, 1169, 1109, 746, 717, 695 cm⁻¹; ¹H n.m.r. δ (CDCl₃): 1.01 (t, 6 H, *J* = 7.03 Hz), 3.87 (q, 4 H, *J* = 7.03 Hz), 6.87 (d, 2 H, *J*_H. _p = 7.00 Hz), 7.11 (br s, 2 H), 7.34-7.46 (m, 18 H), 7.69-7.80 (m, 12 H); ¹³C n.m.r. δ (CDCl₃): 14.2, 60.6, 107.7 (d, *J* = 20.8 Hz), 113.6, 128.1 (d, *J* = 12.1 Hz), 130.9 (d, *J* = 2.6 Hz), 132.5 (d, *J* = 9.3 Hz), 133.1 (d, *J* = 102.4 Hz), 133.8 (d, *J* = 6.7 Hz), 152.7, 167.3 (d, *J* = 6.5 Hz); ³¹P n.m.r δ (CDCl₃): 8.27; m/z (%): 407 (5), 263 (40), 262 (69), 201 (29), 183 (100), 145 (61), 108 (79), 69 (31), 57 (48).

16 (98 %), m.p. 231-232 °C (from dichloromethane/diethyl ether as yellow prisms). (Found: C, 72.19; H, 5.39; N, 3.31. $C_{50}H_{44}N_2O_4P_2S$ requires: C, 72.28; H, 5.34; N, 3.37); i.r. (nujol): 1685, 1570, 1438, 1402, 1233, 1209, 1109, 1042, 744, 717, 695 cm⁻¹; ¹H n.m.r. δ (CDCl₃): 0.98 (t, 6 H, *J* = 7.21 Hz), 3.82 (q, 4 H, *J* = 7.21 Hz), 6.98 (d, 2 H, *J*_{H-P} = 7.20 Hz), 7.32-7.40 (m, 18 H), 7.53 (s, 2 H), 7.70-7.77 (m, 12 H); ¹³C n.m.r. δ (CDCl₃): 14.0, 60.5, 112.8 (d, *J* = 20.6 Hz), 126.9, 127.9 (d, *J* = 12.1 Hz), 130.7 (d, *J* = 3.0 Hz), 132.4 (d, *J* = 9.6 Hz), 132.7 (d, *J* = 102.7 Hz), 133.7 (d, *J* = 7.0 Hz), 140.4, 167.2 (d, *J* = 6.5 Hz); ³¹P n.m.r. δ (CDCl₃): 9.58; m/z (%): 496 (5), 415 (5), 262 (92), 183 (100), 149 (18), 108 (37), 77 (19).

General Procedure for the Preparation of Dipyrido[4,3-b:3',4'-d]pyrroles 11, Furo[3,2-c:4,5-c']dipyridines 17 and Thieno[3,2-c:4,5-c']dipyridines 18.

To a suspension of the corresponding bis(iminophosphorane) **10**, **15** or **16** (0.5 mmol) in dry toluene (25 ml) the isocyanate (1 mmol) in the same solvent (5 ml) was added at once. The reaction mixture was heated at 80 °C for 30 min and then 8 h at 160 °C in a sealed tube. After cooling, the solvent was removed under reduced pressure and the residual material was treated with cold ethanol (5 ml), the separated solid was filtered and recrystallized.

11a (R = C₆H₅.CH₂) (77 %), m.p. 172-173 °C (from ethanol as yellow prisms). (Found: C, 69.31; H, 5.74; N, 13.00. C₃₁H₃₁N₅O₄ requires: C, 69.26; H, 5.81; N, 13.03); i.r. (nujol): 3381, 3364, 3256, 1735, 1715, 1569, 1242, 1206, 1189, 1115, 780, 756, 706 cm⁻¹; ¹H n.m.r. δ (CDCl₄): 1.47 (t, 6 H, *J* = 7.08 Hz), 3.75 (s, 3 H), 4.45 (q, 4 H, 1.206).

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 $J = 7.08 \text{ Hz}), 4.63 \text{ (d, 4 H, } J = 5.51 \text{ Hz}), 6.05 \text{ (t, 2 H, } J = 5.51 \text{ Hz}), 7.15-7.36 \text{ (m, 10 H)}, 7.63 \text{ (s, 2 H)}; {}^{13}\text{C n.m.r.}$ $\delta \text{ (CDCL}): 14.3, 29.7, 46.6, 61.4, 99.8, 106.7, 127.2, 128.5, 128.6, 139.4, 142.8, 146.2, 152.2, 166.1; m/z (%): 537 \text{ M}^{\star}, 6), 446 \text{ (16)}, 298 \text{ (22)}, 209 \text{ (6)}, 91 \text{ (100)}, 65 \text{ (14)}.$

11b (R = 4-Cl.C₆H₄) (71 %), m.p. 299-301 °C (from ethanol as orange prisms). (Found: C, 60.15; H, 4.31; N, 12.07. C₂₉H₂₅Cl₂N₅O₄ requires: C, 60.22; H, 4.36; N, 12.11); i.r. (nujol): 3359, 1717, 1706, 1636, 1601, 1566, 1271, 1180, 1094, 828, 759, 726 cm⁻¹; ¹H n.m.r. δ (CDCl₃ + CF₃COOH): 1.44 (t, 6 H, *J* = 7.15 Hz), 4.23 (s, 3 H), 4.55 (q, 4 H, *J* = 7.15 Hz), 7.33 (d, 4 H, *J* = 8.68 Hz), 7.56 (d, 4 H, *J* = 8.68 Hz), 8.08 (s, 2 H); ¹³C n.m.r. δ (CDCl₃ + CF₃COOH): 13.5, 32.1, 65.7, 103.7, 108.5, 125.0, 131.6, 131.8, 132.8, 136.2, 147.8, 149.0, 159.4.

11c (R = 4-CH₃.C₆H₄) (80 %), m.p. 282-283 °C (from ethanol as orange prisms). (Found: C, 69.21; H, 5.77; N, 13.10. C₃₁H₃₁N₅O₄ requires: C, 69.26; H, 5.81; N, 13.03); i.r. (nujol): 3349, 1732, 1704, 1631, 1513, 1287, 1238, 1195, 1028, 760 cm⁻¹; ¹H n.m.r. δ (CDCl₃ + CF₃COOH): 1.42 (t, 6 H, *J* = 7.21 Hz), 2.44 (s, 6 H), 4.21 (s, 3 H), 4.52 (q, 4 H, *J* = 7.21 Hz), 7.28 (d, 4 H, *J* = 7.40 Hz), 7.40 (d, 4 H, *J* = 7.40 Hz), 8.01 (s, 2 H): ¹³C n.m.r. δ (CDCl₃ + CF₃COOH): 13.5, 21.0, 31.9, 65.2, 103.2, 108.1, 123.7, 129.9, 132.1, 132.2, 140.7, 148.1, 148.5, 159.3.

17a (R = C₆H₅, CH₂) (82 %), m.p. 176-177 °C (from ethanol as yellow prisms). (Found: C, 68.60; H, 5.32; N, 10.74. C₃₀H₂₈N₄O₅ requires: C, 68.69; H, 5.38; N, 10.68); i.r. (nujol): 3322, 3243, 1739, 1716, 1604, 1422, 1312, 1299, 1237, 1114, 1027, 781, 753, 725 cm⁻¹; ¹H n.m.r. δ (CDCl₃): 1.45 (t, 6 H, *J* = 7.21 Hz), 4.42 (q, 4 H, *J* = 7.21 Hz), 4.62 (d, 4 H, *J* = 5.41 Hz), 5.93 (t, 2 H, *J* = 5.41 Hz), 7.27-7.32 (m, 10 H), 7.73 (s, 2 H); ¹³C n.m.r. δ (CDCl₃): 14.3, 46.6, 61.7, 102.1, 108.0, 127.4, 128.6, 138.8, 145.2, 152.5, 162.0, 165.0; m/z (%): 524 (M⁺, 7), 433 (10), 359 (5), 285 (7), 196 (6), 106 (5), 91 (100), 65 (10).

17b (R = 4-Cl.C₆H₄) (73 %), m.p. 251-253 °C (from ethanol as orange prisms). (Found: C, 59.55; H, 3.96; N, 9.87. C₂₈H₂₂Cl₂N₄O₅ requires: C, 59.48; H, 3.92; N, 9.91); i.r. (nujol): 3354, 1714, 1643, 1606, 1593, 1496, 1287, 1254, 1220, 1029, 835, 767 cm⁻¹; ¹H n.m.r. δ (CDCl₃ + CF₃COOH): 1.40 (t, 6 H, *J* = 7.11 Hz), 4.46 (q, 4 H, *J* = 7.11 Hz), 7.18 (d, 4 H, *J* = 8.59 Hz), 7.48 (d, 4 H, *J* = 8.59 Hz), 7.57 (s, 2 H); ¹³C n.m.r. δ (CDCl₃ + CF₃COOH): 13.7, 64.6, 101.9, 114.6, 123.6, 131.3, 133.2, 133.8, 136.5, 146.9, 159.9, 161.5; m/z (%): 568 (M⁺ + 4, 4), 566 (M⁺ + 2, 25), 564 (M⁺, 40), 455 (20), 381 (20), 127 (40), 111 (100), 77 (48), 68 (44), 55 (44).

17c (R = 4-CH₃.C₆H₄) (86 %), m.p. 232-233 °C (from ethanol as orange prisms). (Found: C, 68.64; H, 5.31; N, 10.61. C₃₀H₂₈N₄O₅ requires: C, 68.69; H, 5.38; N, 10.68); i.r. (nujol): 3357, 1711, 1658, 1604, 1512, 1290, 1254, 1220, 1105, 1031, 814, 767 cm⁻¹; ¹H n.m.r. δ (CDCl₃ + CF₃COOH): 1.43 (t, 6 H, J = 7.21 Hz), 2.44 (s, 6 H), 4.53 (q, 4 H, J = 7.21 Hz), 7.24 (d, 4 H, J = 8.40 Hz), 7.41 (d, 4 H, J = 8.40 Hz), 8.05 (s, 2 H); ¹³C n.m.r. δ (CDCl₃ + CF₃COOH): 13.4, 20.9, 65.8, 104.3, 111.0, 123.7, 129.6, 132.3, 135.3, 141.4, 148.7, 158.8, 164.8; m/z (%): 524 (M^{*}, 10), 421 (13), 376 (14), 285 (10), 188 (17), 149 (17), 91 (95), 69 (56), 55 (100).

18a (R = C₆H₅.CH₂) (50 %), m.p. 171-172 °C (from ethanol as yellow prisms). (Found: C, 66.60; H, 5.31; N, 10.30. C₃₀H₂₈N₄O₄S requires: C, 66.65; H, 5.22; N, 10.36); i.r. (nujol): 3362, 1735, 1725, 1571, 1548, 1274, 1219, 1038, 856, 782, 704 cm⁻¹; ¹H n.m.r. δ (CDCl₃): 1.44 (t, 6 H, *J* = 7.22 Hz), 4.41 (q, 4 H, *J* = 7.22 Hz), 4.62 (d, 4 H, *J* = 5.25 Hz), 6.03 (t, 2 H, *J* = 5.25 Hz), 7.28 (s, 10 H), 7.94 (s, 2 H); ¹³C n.m.r. δ (CDCl₃): 14.4, 46.7, 61.7, 110.3, 117.8, 127.6, 128.7, 128.8, 138.7, 142.9, 149.1, 152.3, 165.3; m/z (%): 540 (M⁺, 13), 450 (27), 449 (100), 375 (42), 301 (64), 91 (35).

18b (R = 4-CH₃.C₆H₄) (76 %), m.p. 228-230 °C (from ethanol as orange prisms). (Found: C, 66.71; H, 5.17; N, 10.39. C₃₀H₂₈N₄O₄S requires: C, 66.65; H, 5.22; N, 10.36); i.r. (nujol): 3339, 1736, 1707, 1599, 1509, 1252, 1223, 1197, 865, 833, 762, 728 cm⁻¹; ¹H n.m.r. δ (DMSO-d₆): 1.38 (t, 6 H, *J* = 7.05 Hz), 2.24 (s, 6 H), 4.36 (q, 4 H, *J* = 7.05 Hz), 7.03 (d, 4 H, *J* = 8.16 Hz), 7.52 (d, 4 H, *J* = 8.16 Hz), 8.33 (s, 2 H), 9.45 (s, 2 H); ¹³C n.m.r. δ (DMSO-d₆): 14.1, 20.4, 61.1, 111.5, 118.9, 119.1, 128.9, 130.5, 138.6, 141.9, 149.3, 149.4, 164.5; m/z (%): 540 (M⁺, 100), 539 (53), 467 (17), 465 (25), 451 (44), 437 (56), 393 (20), 91 (21).

18c (R = 4-CH₃O.C₆H₄) (80 %), m.p. 249-250 °C (from ethanol as orange prisms). (Found: C, 62.85; H, 4.98; N, 9.74. C₃₀H₂₈N₄O₆S requires: C, 62.93; H, 4.93; N, 9.78); i.r. (nujol): 3335, 1735, 1706, 1665, 1606, 1508, 1300, 1248, 1033, 837, 760, 731, 694 cm⁻¹; ¹H n.m.r. δ (DMSO-d₆): 1.37 (t, 6 H, *J* = 6.93 Hz), 3.75 (s, 6 H), 4.36 (q, 4 H, *J* = 6.93 Hz), 6.84 (d, 4 H, *J* = 8.71 Hz), 7.61 (d, 4 H, *J* = 8.71 Hz), 8.32 (s, 2 H), 9.30 (s, 2 H); ¹³C n.m.r. δ (DMSO-d₆): 14.3, 55.3, 61.2, 111.2, 113.8, 118.7, 120.7, 134.4, 142.0, 149.2, 149.7, 154.5, 164.7; m/z (%): 573 (M⁺, 35), 467 (65), 449 (73), 304 (38), 301 (61), 170 (91), 149 (65), 91 (100), 77 (50).

General Procedure for the Preparation of Dipyrido[4,3-b:3',4'-d]pyrroles 12, Furo[3,2-c:4,5-c']dipyridines 19 and Thieno[3,2-c:4,5-c']dipyridines 20.

To a suspension of the corresponding bis(iminophosphorane) 10, 15 or 16 (0.5 mmol) in dry toluene (25 ml) the ketene (1 mmol) in the same solvent (5 ml) was added at once. The reaction mixture was stirred at 80 °C for 30 min and then 8 h at room temperature. The solvent was removed under reduced pressure and the residual material was treated with cold ethanol (5 ml), the separated solid was filtered and recrystallized (for 12a, 19a and 20) or the residual material was chromatographed on a silica gel column using *n*-hexane/ethyl acetate (3:2) as eluent (for 12b and 19b).

12a ($\mathbf{R} = \mathbf{C}_{6}\mathbf{H}_{5}$) (87 %), m.p. 282-283 °C. (Found: C, 78.21; H, 5.59; N, 6.39. $\mathbf{C}_{43}\mathbf{H}_{37}\mathbf{N}_{3}\mathbf{O}_{4}$ requires: C, 78.28; H, 5.65; N, 6.37); i.r. (nujol): 1721, 1578, 1297, 1268, 1164, 1033, 983, 877, 787, 737, 703 cm⁻¹; ¹H n.m.r. δ (CDCl₃): 1.41 (t, 6 H, J = 7.17 Hz), 3.95 (s, 3 H), 4.39 (q, 4 H, J = 7.17 Hz), 6.15 (s, 2 H), 6.98-7.03 (m, 8 H), 7.16-7.26 (m, 12 H), 8.10 (s, 2 H); ¹³C n.m.r. δ (CDCl₃): 14.2, 29.7, 56.7, 61.5, 103.8, 119.4, 126.4, 127.8, 130.2, 144.0, 144.2, 147.6, 156.6, 165.8; m/z (%): 660 (M⁺, 60), 418 (12), 330 (17), 201 (21), 167 (86), 166 (41), 165 (100), 152 (67), 91 (47), 77 (60).

12b (R = C_2H_5) (72 %) diastereomeric ratio 2:1. (Found: C, 74.52; H, 6.69; N, 7.42. $C_{35}H_{37}N_3O_4$ requires: C, 74.58; H, 6.62; N, 7.45); i.r. (nujol): 1738, 1714, 1596, 1549, 1295, 1268, 1175, 981, 867, 789, 740, 702 cm⁻¹; ¹H n.m.r. δ (CDCl₃): 0.65 (t, CH₂CH₃, major diastereomer), 0.86 (t, CH₂CH₃, minor diastereomer), 1.48 (t, OCH₂CH₃, major diastereomer), 1.49 (t, OCH₂CH₃, minor diastereomer), 2.27-2.40 (m, CH₂CH₃, both diastereomers), 2.56-2.69 (m, CH₂CH₃, both diastereomers), 3.91 (s, NCH₃, minor diastereomer), 3.92 (s, NCH₃, major diastereomer), 4.49 (q, OCH₂CH₃, both diastereomers), 5.04 (t, -CHPhEt, both diastereomers), 7.11-7.44 (m, aromatic, both diastereomers), 8.05 (s, H₄ and H₆, minor diastereomer), 8.06 (s, H₄ and H₆, major diastereomer); ¹³C n.m.r. δ (CDCl₃) (both diastereomers): 12.3, 12.6, 14.1, 14.3, 29.6, 29.9, 31.3, 52.8, 61.6, 103.5, 103.7, 119.3, 126.2, 126.3, 128.0, 128.1, 128.6, 129.0, 142.9, 143.5, 144.0, 147.4, 158.6, 158.8, 165.8, 165.9; m/z (%): 563 (M⁺, 75), 548 (63), 535 (50), 472 (35), 444 (64), 342 (20), 282 (31), 179 (24), 91 (100).

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19a (R = C₆H₅) (61 %), m.p. 279-280 °C (from ethanol as yellow prisms). (Found: C, 78.07; H, 5.25; N, 4.39. C₄₂H₃₄N₂O₅ requires: C, 78.00; H, 5.30; N, 4.33); i.r. (nujol): 1718, 1582, 1547, 1311, 1245, 1108, 1028, 889, 792, 739, 699 cm⁻¹; ¹H n.m.r. δ (CDCl₃): 1.39 (t, 6 H, *J* = 7.12 Hz), 4.38 (q, 4 H, *J* = 7.12 Hz), 6.11 (s, 2 H), 6.95-6.98 (m, 8 H), 7.21-7.23 (m, 12 H), 8.25 (s, 2 H); ¹³C n.m.r. δ (CDCl₃): 14.1, 56.6, 61.7, 106.9, 120.7, 126.7, 128.0, 130.0, 143.3, 146.8, 157.3, 162.7, 164.6; m/z (%): 646 (M⁺, 36), 405 (8), 210 (15), 165 (88), 152 (57), 92 (71), 91 (100), 77 (50).

19b (R = C₂H₅) (45 %) diastereomeric ratio 3:1. (Found: C, 74.09; H, 6.27; N, 5.01. C₃₄H₃₄N₂O₅ requires: C, 74.16; H, 6.22; N, 5.09); i.r. (nujol): 1743, 1723, 1560, 1310, 1286, 1215, 1100, 788, 733, 699 cm⁻¹; ¹H n.m.r. δ (CDCl₃): 0.48 (t, CH₂CH₃, major diastereomer), 0.86 (t, CH₂CH₃, minor diastereomer), 1.37 (t, OCH₂CH₃, major diastereomer), 1.38 (t, OCH₂CH₃, minor diastereomer), 2.03-2.18 (m, CH₄H₆CH₃, major diastereomer), 2.20-2.32 (m, CH₄H₆CH₃, minor diastereomer), 2.42-2.76 (m, CH₄H₆CH₃, both diastereomer), 4.39 (q, OCH₂CH₃, both diastereomers), 4.93 (t, CHPhEt, both diastereomers), 7.02-7.35 (m, aromatic, both diastereomers), 8.09 (s, H₄ and H₆, major diastereomer); ¹³C n.m.r. δ (CDCl₃) (both diastereomers): 12.2, 12.6, 14.2, 29.6, 30.2, 31.0, 52.5, 52.8, 61.8, 106.6, 106.9, 120.3, 120.9, 126.4, 126.5, 128.1, 128.3, 129.0, 142.1, 143.1, 146.4, 146.5, 159.3, 159.4, 162.5, 164.7; m/z (%): 551 (M⁺, 13), 536 (13), 523 (12), 431 (12), 283 (12), 173 (13), 91 (100), 77 (17).

20 (R = C_6H_5) (67 %), m.p. 316 °C (from ethanol as yellow prisms). (Found: C, 76.07; H, 5.11; N, 4.20. $C_{42}H_{34}N_2O_4S$ requires: C 76.11; H, 5.17; N, 4.23); i.r. (nujol): 1717, 1494, 1302, 1181, 1159, 1119, 1020, 746, 734, 707 cm⁻¹; ¹H n.m.r. δ (CDCl₃): 1.42 (t, 6 H, *J* = 7.06 Hz), 4.45 (q, 4 H, *J* = 7.06 Hz), 6.01 (s, 2 H), 7.12 (s, 20 H), 8.38 (s, 2 H); ¹³C n.m.r. δ (CDCl₃): 14.4, 57.4, 61.8, 116.4, 126.7, 127.9, 130.0, 130.3, 143.1, 144.6, 149.8, 158.6, 164.8.

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