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Preparation and Synthetic Applications of Iminophosphoranes Derived from *o*-Substituted Arylazides: Preparation of Pyrazolo[1,2-*b*]Indazole, 4*H*-3,1-Benzoxazine and Quinoline Derivatives. Crystal Structure of 2-[2-(4-Methoxybenzoylamino)phenyl]-4-methylquinoline.

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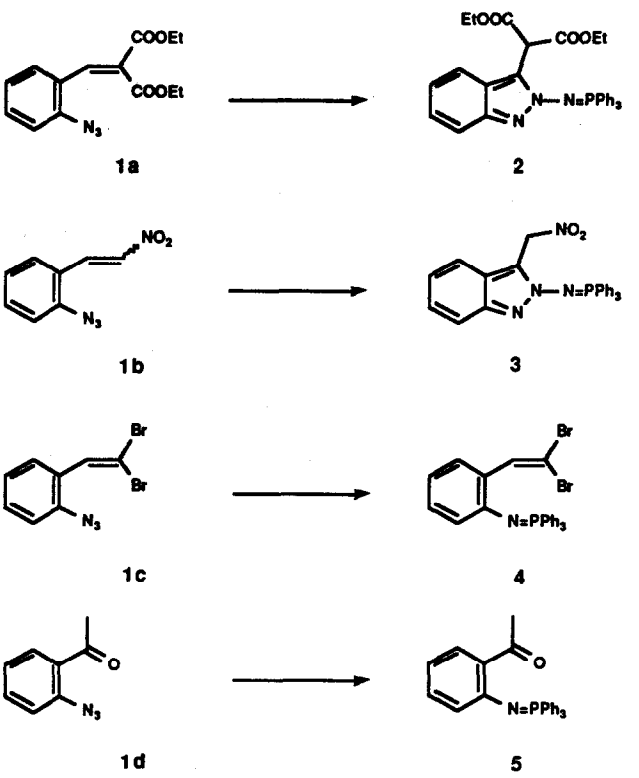
Abstract: The Staudinger reaction of several ortho-substituted arylazides with triphenylphosphine has been studied. The reaction product is found to be strongly dependent on the nature of the ortho-substituent. The Aza Wittig-type reaction of iminophosphorane derived from the ortho-azido acetophenone with isocyanates and aroyl chlorides leads to the previously unreported 4-methylene-4H-3,1-benzoxazine ring. The crystal and molecular structure of 2-[2-(4-methoxybenzoylamino)phenyl]-4-methylquinoline has been established by X-Ray diffraction methods.

The reaction of tertiary phosphines with an organic azide to produce an iminophosphorane after nitrogen evolution (Staudinger reaction) is a very useful reaction in synthetic organic chemistry. In the course of our studies directed towards the synthesis of nitrogen heterocycles we have developed the tactical combination[1] Staudinger reaction/aza Wittig reaction, which allows the preparation of functionalized heterocumulenes able to undergo a plethora of heterocyclization processes e.g. 6π-electrocyclization[2], intramolecular Diels-Alder cycloaddition[3], intramolecular amination[4]. Consequently, the discovery of novel functionalized azides bearing a functional group able to react either with the iminophosphorane moiety or the aza Wittig product is important in this respect.

In this context, we have found that aryl azides bearing an unsaturated functionality at the ortho-position e.g. *o*-azidobenzaldimines[5] and *o*-azidobenzaldehyde[6], react with triphenylphosphine under appropriate reac-

tion conditions to give iminophosphoranes derived from the 2-aminoindazole ring instead of the expected aryl-iminophosphorane. This conversion can be understood by an initial Staudinger reaction to give a phosphazide as a highly reactive intermediate which was converted into a ketenimine through [1,5] sigmatropic shift and subsequent ring–closure by nucleophilic attack of the central nitrogen atom of the phosphazide moiety on the central *sp* hybridized carbon atom of the ketenimine moiety.

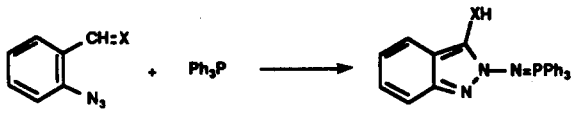


Scheme I

In order to develop this kind of conversion into an useful approach to synthesizing functionalized 2*H*-indazoles, we considered it essential to have access to a number of *o*-substituted aryl azides bearing an unsaturated functionality directly linked to the aromatic ring. The azide **1a** was prepared in 70% yield by condensation of *o*-azidobenzaldehyde with diethyl malonate in the presence of pyrrolidine. In a similar way, azide **1b** was prepared in 65% overall yield by condensation of *o*-azidobenzaldehyde with nitromethane and further dehydration with pyridine/acetic anhydride[7]. Compound **1c** was prepared in 35% yield by reaction of the reagent prepared from interaction of zinc dust, triphenylphosphine, and carbon tetrabromide[8] with *o*-azidobenzaldehyde. Azide **1d** was prepared from *o*-aminoacetophenone by the sequence diazotization/azidation[9].

Reaction of azides **1a** and **1b** with triphenylphosphine in dichloromethane at 0°C provided the iminophosphorane derived from the 2-aminoindazole **2** and **3** in 53% and 60% yield respectively. However, azides **1c** and **1d** under the same reaction conditions afforded the *o*-substituded aryliminophosphoranes **4** and **5** as the only reaction products (Scheme I). According to these results and those previously reported[5,6], the formation of the indazole ring in the reaction of arylazides *o*-substituted by unsaturated functionalities takes place only when the carbon atom, of the *o*-substituent, directly linked to the aromatic ring bears a hydrogen atom and it is linked through a double bond either to a heteroatom (oxygen or nitrogen) or a carbon atom substituted by electron-withdrawing groups (ethoxycarbonyl or nitro) (Scheme II).

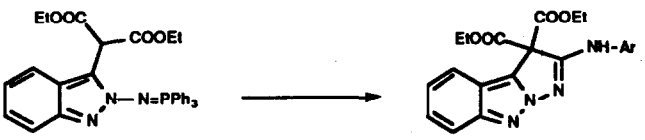
Iminophosphorane **2** reacted with aromatic isocyanates in dichloromethane at room temperature to give the



X=N–R	ref.5
X=O	ref.6
X=C(COOEt)$_2$	this work
X=CH–NO$_2$	this work

Scheme II

previously unreported pyrazolo [1,2-*b*] indoles **6**; the yields of the isolated products were higher than 50% (Scheme III). In the ^{13}C n.m.r. spectra of **6**, the new sp^3 quaternary carbon atom C-1 appears in the region δ 66.4-66.6 ppm. The mass spectra show the expected molecular ion peaks, a very informative peak was also found at m/z (M^+-COOEt). The conversion **2**→**6** involves initial aza Wittig-type reaction between the iminophosphorane and the isocyanate to give a highly reactive intermediate carbodiimide which undergoes a not too common cyclization by nucleophilic attack of the activated methine group on the central carbon atom of the carbodiimide moiety to form the pyrazole ring. Despite its apparent simplicity, addition of strongly acidic C-H to carbodiimides is rare. To our knowledge it has only been mentioned[10] in the case of the addition of Meldrum's acid and malononitrile to dicyclohexylcarbodiimide in the presence of bases.



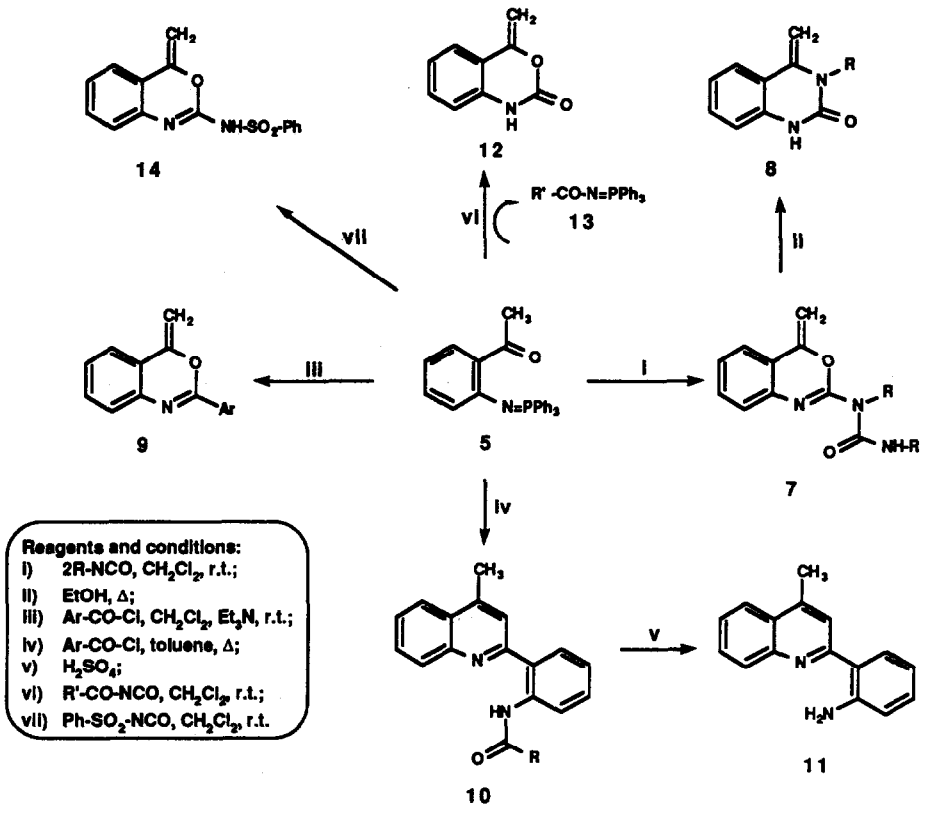
2 **6**

Scheme III

On the other hand, iminophosphorane **5** reacted with 2 equivalents of aliphatic or aromatic isocyanates in dichloromethane at room temperature to give the corresponding 4-methylen-*4H*-3,1-benzoxazine **7** in 51-86% yields. Reaction of iminophosphorane **5** with one equivalent of isocyanate under the same reaction conditions also led to **7** albeit in moderate yields. When compounds **7** were heated in ethanol they underwent elimination of isocyanate followed by a typical Dimroth rearrangement to furnish **8** in excellent yields (86-92%). In the ^1H n.m.r. spectra of compounds **7** the olefinic protons appear as two doublets at δ 4.20-4.67 and 4.68-4.86 ppm respectively, while in the ^{13}C n.m.r. spectra the exocyclic olefinic carbon atom appears at δ 86.6-87.9 ppm. The ^1H and ^{13}C n.m.r. spectra of **8** exhibited signals very similar to those of compounds **7**

The conversion **5**→**7** can be rationalized in terms of an initial aza Wittig-type reaction with the isocyanate to give a carbodiimide which cyclizes across the enol form of the carbonyl function with concomitant addition on the formed NH group of the second equivalent of the isocyanate.

In a similar way, iminophosphorane **5** reacted with aroyl chlorides in dichloromethane in the presence of triethylamine at room temperature to afford 4*H*-3,1-benzoxazines **9** in moderate to good yields. We believe that the conversion **5**→**9** takes place through an imidoyl chloride intermediate, formed by aza Wittig-type reaction between the iminophosphorane and the acyl chloride[11], which also cyclizes across the enol form of the carbonyl function. We have recently reported[12] the synthesis of 2,5-disubstituted oxazoles based on a conceptually similar heterocyclization. However, the reaction of iminophosphorane **5** with aroyl chlorides (2:1 molar ratio) in dry toluene at reflux temperature without triethylamine gave the corresponding 4-methyl-2-arylquinolines **10** in moderate yields and triphenylphosphine oxide.



Scheme IV

The first indication of a structure type **10** was obtained from ^{1}H and ^{13}C-n.m.r. spectra which clearly showed that there were two groups of signals for the iminophosphorane residue; in addition, in the ^{13}C-n.m.r. the signal corresponding to the carbonyl carbon atom of the iminophosphorane was absent. In order to identify unambiguously the structure of the reaction product X-ray structure determination of crystalline compound **10a** has been performed. The main characteristics of the molecular and crystal structure are reported in Table 1 according to the atom labelling shown in Fig. 1. The main peculiarity of the structure is the presence of the N-H···N intramolecular hydrogen bond with formation of a six-membered ring, Fig. 1a, and giving rise to a roughly planar molecule. All rings in the molecule deviate significantly from planarity in terms of the achieved precision. This is probably induced by steric crowding, mainly in O(19), as a consequence of hydrogen interactions O(19)···H(13)/H(21)=2.31(2)Å respectively. Moreover two additional C-H···O intramolecular interactions are observed, Table 1. The deformations of the exocyclic angles could also be due to these effects and those of the endocyclic angles in the benzene rings, up to 2.4°, reflect the influence of the substituent[14].The packing diagram down the c axis illustrates the stacking of aromatic rings, Fig. 1b. The corresponding distances between the centroids of the rings related through symmetry centers are as follows: C(5-10)···C(5-10)$_{-x,1-y,1-z}$=

3.792(1), C(11-16)···C(11-16)$_{1-x,1-y,-z}$= 3.813(1)Å and the separation between their planes are 3.637(1) and 3.586(1)Å respectively.

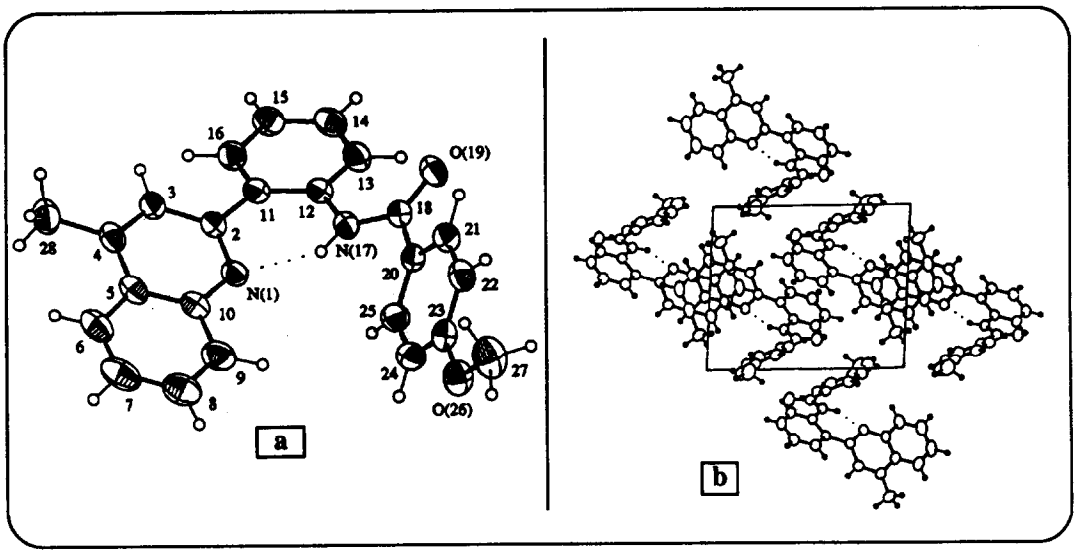


Fig. 1 a) A perspective view[13] of the molecular structure displaying the numbering scheme; b) Crystal packing down the c axis showing the molecular overlapping. Thermal ellipsoids are drawn at 30% probability level and H-atoms are represented by spheres of 0.1 Å radius.

Table 1. Selected geometrical parameters and hydrogen interactions (Å, °). C(5-10), C(11-16) and C(20-25) stand for the centroids of the corresponding 6-membered rings.

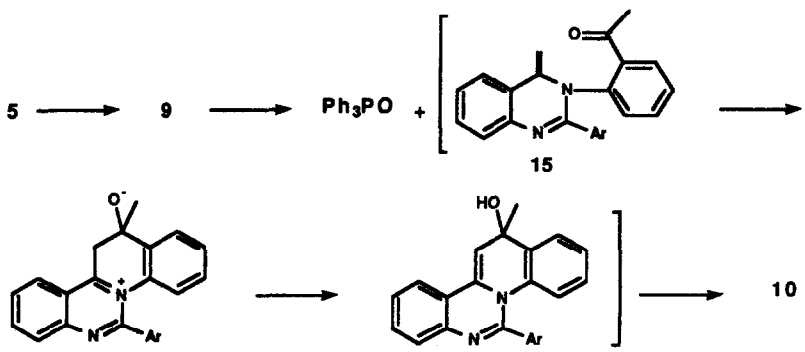
N(1)-C(2)	1.323(2)	C(4)-C(5)	1.420(3)
N(1)-C(10)	1.374(2)	C(5)-C(10)	1.409(3)
C(2)-C(3)	1.418(3)	C(12)-N(17)	1.407(3)
C(2)-C(11)	1.490(2)	N(17)-C(18)	1.358(3)
C(3)-C(4)	1.361(2)	C(18)-O(19)	1.225(2)
N(1)-C(2)-C(11)	118.5(2)	C(12)-N(17)-C(18)	127.4(2)
C(2)-C(11)-C(16)	118.7(2)	N(17)-C(18)-C(20)	114.4(2)
C(2)-C(11)-C(12)	123.7(2)	N(17)-C(18)-O(19)	124.3(2)
C(12)C(11)-C(16)	117.6(2)	O(19)-C(18)-C(20)	121.3(2)
C(11)-C(12)-N(17)	119.4(2)	C(18)-C(20)-C(21)	118.6(2)
C(11)-C(12)-C(13)	119.8(2)	C(21)-C(20)-C(25)	117.8(2)
C(13)-C(12)-N(17)	120.8(2)	C(20)-C(21)-C(22)	121.8(2)
N(1)-C(2)-C(11)-C(12)	-25.1(3)	C(12)-N(17)-C(18)-C(20)	176.9(2)
C(2)-C(11)-C(12)-N(17)	0.9(3)	N(17)-C(18)-C(20)-C(25)	30.7(3)
C(13)-C(12)-N(17)-C(18)	29.5(3)	C(22)-C(23)-O(26)-C(27)	4.0(3)
C(12)-N(17)-C(18)-O(19)	-1.7(3)		

D-H...A	D-H	D...A	H...A	D-H...A
N(17)-H(17)...N(1)	0.86(2)	2.693(2)	1.97(2)	140(2)
C(3)-H(3)...O(19)$_1$	0.94(2)	3.661(2)	2.75(2)	162(2)
C(27)-H(271)...O(19)$_2$	0.97(3)	3.481(4)	2.65(4)	144(2)
C(8)-H(8)...O(26)$_3$	0.96(3)	3.557(4)	2.79(3)	137(2)
C(28)-H(283)...O(26)$_4$	1.06(3)	3.342(3)	2.65(3)	123(3)
C(13)-H(13)...C(20-25)$_5$	0.97(2)	3.622(2)	3.00(2)	123(2)

1: 1-x, 1-y, -z 2: 1-x, -y, 1-z 3: -x, -y, 1-z
4: -x, 1-y, 1-z 5: 1-x, -y, -z

Hydrolytic cleavage of compounds **10** under strongly acidic conditions provides **11** in good yields. The reaction of iminophosphorane **5** with electron–withdrawing substituted iso-cyanates was also studied. Compound **5** reacted with benzoyl– and ethoxycarbonyl isocyanate in dry dichloromethane at room temperature to give 4*H*–3,1–benzoxazin–2–one **12** and the corresponding iminophosphorane **13**. The conversion **5**→**12** + **13** can be understood by initial abnormal aza Wittig–type reaction[15] to give the iminophosphorane **13** (R=Ph, EtO) and *o*–acetylphenyl isocyanate as intermediate which undergoes ring–closure across the enol form to give **12**. However, the reaction with benzenesulphonyl isocyanate under the same conditions provided **14** in 80% yield.

At first it seemed likely that the formation of compounds **10** took place through a Friedländer–type cyclization between two molecules of the starting iminophosphorane followed by acylation of the remaining iminophosphorane moiety and further hydrolysis of the imidoyl function during the work–up. However, all attempts to cyclize the iminophosphorane **5** to compound **10** by heating in toluene at reflux temperature in the presence of either acids or even strong bases failed, and the starting material was recovered unchanged. However, reaction of iminophosphorane **5** with 4*H*–3,1–benzoxazines **9** in dry toluene provided **10** in good yields, together with triphenylphosphine oxide. According to these results a tentative mechanism for the conversion **5**→**10** is despicted in Scheme V.



Scheme V

The initial formed 4*H*–3,1-benzoxazine **9** reacts with a second equivalent of the starting iminophosphorane **5** to give triphenylphosphine oxide and the intermediate **15** which by a ring–opening ring–closure sequence furnishes **10**.

EXPERIMENTAL.

All melting points were determined on a Kofler hot–plate melting point apparatus and are uncorrected. IR spectra were obtained as Nujol emulsions on a Nicolet–5DX spectrophotometer. NMR spectra were recorded on a Bruker AC–200 (200MHz) or a Varian Unity–300 (300 MHz). Mass spectra were recorded on a Hewlett–Packard 5993C spectrometer. Microanalyses were performed on a Perkin–Elmer 240C instrument.

X–Ray Crystallography. The structure was solved by direct methods, SIR88[16]. Most of the calculations were performed on a Vax 6410 computer using the XRAY80 program package[17], PESOS[18] and PARST[19]. All hydrogen atoms were located in a Fourier difference synthesis and the atomic scattering factors were taken from the International Tables for X–Ray Crystallography[20].

Table 2. Crystal analysis parameters at room temperature.

Crystal data			
Chemical Formula	$C_{24}H_{20}N_2O_2$	Crystal system	Triclinic
Mr	368.4	Space group	P-1
a(Å)	11.7783(8)	α(°)	106.129(7)
b(Å)	9.9346(10)	β(°)	74.462(5)
c(Å)	8.7608(7)	γ(°)	91.134(9)
Z	2		
V(Å^3)	947.1(1)	*Dx* (Mg/m^3)	1.292
Radiation	CuKα	No.of reflections for lattice parameters:	80
Wavelength (Å)	1.5418	Θ range for lattice parameters (°)	2-45
Absorption coefficient (mm^{-1})	6.231	Temperature (K)	295
Crystal Colour	Colourless	Crystal description	Plate
Crystal size (mm)	0.13 x 0.33 x 0.40		
Data collection			
Diffractometer type	Four circle Philips Pw1100, bisecting geometry, graphite monocromator		
Collection method	ω/2Θ scans	Scan width	1.6°
No. of independent reflections	3225	Θ_{max}(°)	65
No. of observed reflections	2718	No. of standard reflections (interval)	2(90 min.)
Criterion for observed	I>3σ(I)	Variation of standards	No variation
Refinement			
Treatment of hydrogen atoms	isotropic	Refinement: Least-Squares on *Fo*.Full matrix	
R	0.046	No.of parameters refined	333
*w*R	0.053	No. of reflections used in refinement	2718
Weighting scheme: Empirical as to give no trends in <wΔ^{2}F>vs.<|Fobs|> and <sinΘ/λ>			
$(\Delta/\sigma)_{max}$	0.11	$(\Delta\rho)_{max}$ (e/Å^3)	0.12

Table 3. Final atomic coordinates.

Atom	x	y	z	Atom	x	y	z
N(1)	0.1881(1)	0.3742(1)	0.0960(2)	C(15)	0.5327(2)	0.4265(2)	-0.3226(2)
C(2)	0.2509(1)	0.4585(2)	0.0171(2)	C(16)	0.4208(2)	0.4659(2)	-0.2198(2)
C(3)	0.2055(1)	0.5943(2)	0.0334(2)	N(17)	0.3952(1)	0.2419(2)	0.0592(2)
C(4)	0.0938(1)	0.6416(2)	0.1264(2)	C(18)	0.4562(1)	0.1876(2)	0.1418(2)
C(5)	0.0246(1)	0.5520(2)	0.2109(2)	O(19)	0.5640(1)	0.1823(2)	0.1123(2)
C(6)	-0.0922(2)	0.5893(3)	0.3151(3)	C(20)	0.3809(1)	0.1361(2)	0.2777(2)
C(7)	-0.1516(2)	0.5002(4)	0.3971(3)	C(21)	0.4226(2)	0.1397(2)	0.4122(3)
C(8)	-0.0997(2)	0.3700(4)	0.3791(3)	C(22)	0.3587(2)	0.0914(2)	0.5412(2)
C(9)	0.0116(2)	0.3293(3)	0.2790(3)	C(23)	0.2513(2)	0.0356(2)	0.5354(2)
C(10)	0.0760(1)	0.4200(2)	0.1942(2)	C(24)	0.2078(2)	0.0311(2)	0.4026(2)
C(11)	0.3720(1)	0.4076(2)	-0.0905(2)	C(25)	0.2714(2)	0.0814(2)	0.2757(2)
C(12)	0.4413(1)	0.3039(2)	-0.0689(2)	O(26)	0.1813(1)	-0.0187(2)	0.6530(2)
C(13)	0.5538(2)	0.2627(2)	-0.1757(2)	C(27)	0.2189(3)	-0.0090(4)	0.7982(3)
C(14)	0.5986(2)	0.3244(2)	-0.3003(2)	C(28)	0.0461(2)	0.7847(3)	0.1395(3)

Diethyl *o*–azidobenzylidenemalonate 1a.

To a 0°C cooled solution of *o*–azidobenzaldehyde[21] (1.47 g, 10 mmol) and pyrrolidine (2.13 g, 30 mmol) in anhydrous ethanol (30 ml) was added dropwise a solution of diethyl malonate (4.8 g, 30 mmol) in the same solvent (20ml).The resultant solution was stirred at this temperature for 5h, then poured into water (40 ml) and acidified with concentrated hydrochloric acid (10 ml). The mixture was extracted with dichloromethane (3x30 ml) and the extracts were combined and dried on anhydrous magnesium sulfate. After filtration, the solvent was chromatographed on silica gel colum, eluting with ethyl acetate/n–hexane (1:1) to afford **1a** (70%), m.p. 32°C. (Found: C, 57.92; H, 5.35; N, 14.35. $C_{14}H_{15}N_3O_4$ requires: C, 58.12; H, 5.22; N, 14.52); i.r. (Nujol) 2129 (azide), 1732 (COOEt) cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 1.22 (t, 3H, J= 7.1 Hz), 1.33 (t, 3H, J= 7.1 Hz), 4.19–4.37 (m, 4H), 7.09 (t, 1H, J= 7.5 Hz), 7.19 (dd, 1H, J= 8.2, 1.2 Hz), 7.39-7.46 (m, 2H), 7.94 (s, 1H, H_β); ^{13}C n.m.r. δ ($CDCl_3$) : 13.8 (CH_3), 14.1 (CH_3), 61.5 (CH_2), 61.6 (CH_2), 118.4 (C–3), 124.6 (C–5), 124.8 (C–1), 127.7 (C_α), 129.1 (C–6)*, 131.5 (C–4)*, 137.3 (C_β), 139.4 (C–2), 163.8 (C=O), 166.2 (C=O); m/z (%) 289 (M^+, 3), 187 (100).

2–(*o*–Azidobenzyl)nitroethylene 1b.

To a 0°C cooled solution of *o*-azidobenzaldehyde (1.47 g, 10 mmol), and nitromethane (1.22 g, 20 mmol) in anhydrous ethanol (15 ml) was added dropwise with stirring a solution of potassium hydrochloride (0.61 g, 11 mmol) in the same solvent (15 ml). The resultant solution was stirred at this temperature for 1h. Acetic acid (5 ml) and water (30 ml) were added and the mixture was extracted with dichloromethane (3x20 ml). The combined organic layers were dried on anhydrous magnesium sulfate, filtered and concentrated to dryness to give the 2–hydroxy-(*o*–azidophenyl)nitroethane (90%). The crude product was used directly in the subsequent reaction very effectively withouth the need further purification. A mixture of the azido alcohol (2 g, 10 mmol), acetic anhydride (20 ml) and pyridine (2 ml) was stirred at 0°C for 20h, the poured into water (40ml)

and extracted with dichloromethane (3x20 ml). The combined organic layers were dried on anhydrous magnesium sulfate, filtered and concentrated to dryness. The residual material was chromatographed on a silica gel column using dichloromethane as eluent to give **1b** (72%), m.p. 86–87°C.(Found: C, 50.31; H, 3.10; N, 29.54. $C_8H_6N_4O_2$ requires: C, 50.52; H, 3.18; N, 29.46); i.r. (Nujol) 2129 (azide) cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 7.16–7.28 (m, 2H, H–3, H–5), 7.48–7.55 (m, 2H, H–4, H–6), 7.77 (d, 1H, J=13.7 Hz, H_α), 8.16 (d, 1H, J =13.7 Hz, H_β); ^{13}C n.m.r. δ ($CDCl_3$): 119.1 (C–3), 121.6 (C–1), 125.2 (C–5), 130.5 (C–6)*, 133.0 (C–4)*, 133.9 (C_β), 138.6 (C_α), 140.5 (C–2); m/z (%) 190 ($M^{+\cdot}$ 14), 116 (100).

1-(*o*-Azidophenyl)-2,2-dibromoethylene 1c.

To a solution of triphenylphosphine (5.24 g, 20mmol) and carbon tetrabromide (6.62 g, 20 mmol) in dry dichloromethane (30 ml) was added zinc dust (1.3 g). The mixture was stirred at room temperature for 24h. A solution of *o*-azidobenzaldehyde (1.47 g, 10 mmol) in the same solvent (15 ml) was added and the resulting mixture was stirred at room temperature for 5h wherupon *n*-pentane (20 ml) was added. The separated solid was collected and the filtrate was extracted with dichloromethane/n-pentane (1:1) (3 x 30 ml). The combined organic layer was concentrated to dryness and the residual material was chromatographed on a silica gel column eluting with dichloromethane to give **1c** (35%), m. p. 30°C. (Found: C, 31.57; H, 1.79; N, 13.71. $C_8H_5Br_2N_3$ requires : C, 31.71; H, 1.71; N, 13.86); i. r. (Nujol) 2123 (azide) cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 7.09-7.15 (m, 2H, H-3, H-5), 7.35 (t, 1H, J=7.6 Hz, H-4), 7.45 (s, 1H, H_β), 7.65 (d, 1H, J=8.0 Hz, H-6); $^{13}Cn.m.r.$ δ ($CDCl_3$): 91.7 (C_α), 118.1 (C-3), 124.4 (C-5), 126.9 (C-1), 129.5 (C-6), 129.7 (C-4), 132.6 (C_β), 137.7 (C-2); m/z (%) 303 (M^+, 5), 115 (100).

General Procedure for the Preparation of Iminophosphoranes 2-5.

A solution of the appropiate azide **1** (10 mmol) in dry dichloromethane (30 ml) was added dropwise under nitrogen to a well-stirred solution of triphenylphosphine (2.60 g, 10 mmol) in the same solvent (10 ml) at 0°C. After the stirring was continued for 1h at the same temperature, the mixture was slowly warmed for 12h, and then the solvent was removed under reduced pressure. The resultant crude product was purified by recrystallization from the appropiate solvent to give **2-5** as crystalline solids.

Compound 2: (53%), m. p. 127-128°C (yellow prisms from dichloromethane/diethyl ether); (Found: C, 69.03; H, 5.55; N, 7.50. $C_{32}H_{30}N_3O_4P$ requires: C, 69.68; H, 5.48; N, 7.61); i. r. (Nujol) 1748, 1729, 1280, 1175 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) 1.17 (t, 6H, J=7.2 Hz), 4.16 (q, 2H, J=7.1 Hz), 4.17 (q, 2H, J=7.1 Hz), 5.87 (s, 1H), 6.92 (td, 1H, J=6.9, 1.0 Hz), 7.05 (td, 1H, J=7.0, 1.0 Hz), 7.38-7.56 (m, 9H), 7.62-7.69 (m, 2H), 7.81 (ddd, 6H, J=12.3, 7.5, 2.4 Hz); ^{13}C n.m.r. δ ($CDCl_3$): 13.9 (CH_3), 50.1 (CH), 61.6 (CH_2), 115.3 (C-7), 118.5 (C-5), 119.3 (^3J_P=11.6 Hz, C-3), 119.7 (C-4), 119.9 (C-3a), 123.0 (C-6), 128.5 (^1J_P=99.9 Hz), 128.5 (^3J_P=12.2 Hz), 132.1 (^4J_P=2.4 Hz), 133.3(^2J_P=9.5 Hz), 143.3 (C-7a), 167.2 (C=O); m/z % 551 (M^+, 3), 183 (100).

Compound 3: (60%), m.p. 147-148°C (yellow prims from dichloromethane/diethyl ether); (Found: C, 68.82; H, 4.60; N, 12.29. $C_{26}H_{21}N_4O_2P$ requires: C, 69.02; H, 4.67; N, 12.38); i.r. (Nujol) 1556, 1309, 1125 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 6.04 (s, 2H), 7.00-7.12 (m, 2H), 7.36 (d, 1H, J=7.8 Hz), 7.38-7.55 (m, 10H), 7.73 (ddd, 6H, J=12.3, 6.9, 1.5 Hz); ^{13}C n. m.r. δ ($CDCl_3$): 68.9 (CH_2), 115.8*(C-7), 116.2 (^3J_P=13.0 Hz, C-3), 116.5* (C-4), 121.0# (C-6), 123.4# (C-5), 127.3 (^4J_P=1.1 Hz, C-3a), 128.4 (^1J_P=97.8 Hz), 128.6 (^3J_P=12.0 Hz), 132.3 (^4J_P=3.0Hz), 133.3 (^2J_P=9.5 Hz), 143.3 (C-7a); m/z (%) 452 (M^+, 2), 277 (100), 183 (56).

Compound 4: (68%), m.p. 113-114°C (yellow prims from dichloromethane/diethyl ether); (Found: C, 57.95, H, 3.69; N, 2.65. $C_{26}H_{20}Br_2NP$ requires: C, 58.12; H, 3.75; N, 2.60); i.r. (Nujol) 1585, 1438, 1110 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 6.43(d, 1H, J=6.8 Hz), 6.63 (t, 1H, J=7.3 Hz), 6.84 (t, 1H, J=7.6 Hz), 7.36-7.52 (m, 10H), 7.70 (ddd, 6H, J=12.0, 6.5, 3.9 Hz), 8.18 (s, 1H, H_β); ^{13}C n.m.r. δ ($CDCl_3$): 86.0 (C_α), 116.9 (C-5), 121.6 (^3J_P=9.5 Hz, C-3), 128.5 (C-6), 128.7 (^3J_P=12.0 Hz), 128.9 (C-4), 130.0 (^3J_P=21.0 Hz, C-1), 131.0

(^1J_P=99.6 Hz), 131.8 (^4J_P=2.4 Hz), 132.5 (^2J_P=9.5 Hz), 137.7 (C_β), 149.6 (C-2); m/z (%) 537 (M^+, 5), 183 (100).

Compound 5: (81%), m.p. 120-122°C (white prisms from diethyl ether); (Found: C, 78.89; H, 5.66; N, 3.56. $C_{26}H_{22}NOP$ requires: C, 78.97; H, 5.61; N, 3.54); i.r. (Nujol) 1647, 1109 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 2.81 (s, 3H), 6.44 (d, 1H, J=8.0 Hz), 6.61 (t, 1H, J=7.4 Hz), 6.89 (ddd, 1H, J=8.0, 7.4, 1.8 Hz), 7.36-7.55 (m, 9H), 7.65–7.76 (m, 7H); ^{13}C n.m.r. δ ($CDCl_3$): 31.5 (CH_3), 116.6 (C-4), 122.7 (^3J_P=11.6 Hz, C-6), 128.6 (^2J_P=12.0 Hz), 129.2 (^4J_P=2.5 Hz, C-3), 130.6 (^1J_P=120.5 Hz), 131.3 (C-5), 131.8 (^4J_P=2.6 Hz), 133.2 (^3J_P=9.6 Hz), 135.0 (^3J_P=22.9 Hz, C-2), 151.2 (C-1), 204.9 (C=O); m/z (%) 395 (M^+, 21), 183 (100).

General Procedure for the Preparation of Pyrazolo[1,2-*b*]indoles 6.

To a solution of iminophosphorane **2** (0.55 g, 1mmol) in dry dichloromethane (20 ml) was added a solution of the appropiate isocyanate (1 mmol) in the same solvent. The reaction mixture was removed under reduced pressure and the crude product was chromatographed on a silica gel column eluting with ethyl acetate/n-hexane (1:2) to give **6**.

6a (Ar=4-CH_3-C_6H_4): (53%), m.p. 132-133°C, (yellow prisms) ; (Found C, 65.21; H, 5.39,; N, 13.88. $C_{22}H_{22}N_4O_4$ requires : C, 65.01; H, 5.45; N, 13.78); i.r. (Nujol) 3358, 1742, 1726, 1623 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 1.28 (t, 6H, J=7.2 Hz), 2.35 (s, 3H), 4.18-4.45 (m, 4H), 7.15-7.32 (m, 4H), 7.62-7.68 (m, 3H), 7.77-7.82 (m, 2H), ^{13}C n.m.r. δ ($CDCl_3$): 13.8 (CH_3), 20.8 (CH_3), 64.2 (CH_2), 66.5 (C-1), 117.0 (C-9b), 117.9* (C-9), 118.5* (C-6), 119.3 (CH, C-9a), 122.7# (C-8), 124.5# (C-7), 129.7 (CH), 133.9, 135.4, 148.9 (C-5a), 158.3 (C-2), 163.9 (C=O); m/z (%) 406 (M^+, 10), 333 (24), 332 (100).

6b (Ar=4-CH_3O-C_6H_4): (58%) m.p. 93-94°C (yellow prisms); (Found: C, 62.40; H, 5.17; N, 13.35. $C_{22}H_{22}N_4O_5$ requires: C, 62.55,; H, 5.24; N, 13.26); i.r. (Nujol) 3341, 1748, 1722, cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 1.28 (t, 6H, J=7.1 Hz), 3.81 (s, 3H), 4.22-4.42 (m, 4H), 6.93 (d, 2H, J=9.0 Hz), 7.15-7.33 (m, 2H), 7.65-7.83 (m, 5H); ^{13}C n.m.r. δ ($CDCl_3$): 13.8 (CH_3), 55.4 (CH_3O), 64.4 (CH_2), 66.4 (C-1), 114.3 (CH), 117.0* (C-9b), 117.9# (C-9), 118.5# (C-6), 119.3* (C-9a), 120.8 (CH), 122.7Δ (C-8), 124.4Δ (C-7), 131.1, 148.8 (C-5a), 156.3, 158.4 (C-2), 163.9 (C=O); m/z (%) 422 (M^+, 23), 350 (22), 349 (100).

6c (Ar=4-F-C_6H_4): (50%), m.p. 149-150°C (yelllow prisms); (Found: C, 61.61; H, 4.72; N, 13.75). $C_{21}H_{19}FN_4O_4$ requires: C, 61.47, H, 4.66; N, 13.65); i.r. (Nujol) 3358, 1742, 1720, 1621 cm^{-1}; ^1Hn.m.r. δ ($CDCl_3$): 1.29 (t, 6H, J=7.1 Hz), 4.22-4.39 (m, 4H), 7.10 (t,2H, J=8.6 Hz), 7.16-7.29 (m, 2H), 7.65-7.82 (m, 5H); ^{13}C n.m.r. δ ($CDCl_3$): 13.8 (CH_3), 64.3 (CH_2), 66.5 (C-1), 115.9 (^2J_F=22.8 Hz, CH), 117.0* (C-9b), 117.9# (C-9), 118.6# (C-6), 119.3* (C-9a), 121.0 (^3J_F=8.0 Hz, CH), 122.9Δ (C-8), 124.6Δ (C-7), 134.0 (^4J_F=2.4 Hz), 148.9 (C-5a), 158.4 (C-2), 159.2 (^1J_F=244.1 Hz), 163.8 (C=O); m/z (%) 410 (M^+, 15), 338 (23) 337 (100).

General Procedure for the Preparation of 2-Arylamino-4-methylene-4*H*-3,1-benzoxazines 7.

To a solution of the iminophosphorane **5** (0.514 g, 1.3 mmol) in dry dichloromethane (20ml) was added the appropiate isocyanate (2.6 mmol). The solution was stirred under nitrogen at room temperature for 9h, and then concetrated to dryness. The crude product was chromatographed on a silica gel column using *n*-hexane/ethyl acetate (3:1) as eluent to give **7** as crystalline solid after recrystallization from n-hexane/dichlorometane (5:1).

7a (R=*n*-C_3H_7): (86%), colourless oil; (Found: C, 66.93; H, 7.40; N, 14.70. $C_{16}H_{21}N_3O_2$ requires: C, 66.97; H, 7.37; N, 14.62); i.r. (Nujol) 3290, 1703, 1663, 1635 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 0.80-1.02 (m, 6H), 1.50-1.65 (m, 4H), 3.20 (q, 2H, J=6.9 Hz), 3.81 (t, 2H, J=7.5 Hz), 4.56 (d, 1H, J=2.9 Hz), 4.78 (d, 1H, J=2.9 Hz), 6.92 (dd, 1H, J=7.6, 1.0 Hz), 7.01 (dt, 1H, J=7.6, 1.0 Hz), 7.22 (dd, 1H, J=7.6, 1.3 Hz), 7.35 (dd, 1H, J=7.6, 1.3 Hz), 10.17 (s broad, 1H); ^{13}C n.m.r. δ ($CDCl_3$): 11.2 (CH_3), 11.6 (CH_3), 22.6 (CH_2), 22.7 (CH_2),

42.4 (CH_2-N), 44.9 (CH_2-NH), 86.6 (=CH_2), 117.9 (C-4a), 122.7 (C-8), 123.8 (C-6), 125.3 (C-5), 131.0 (C-7), 139.1 (C-8a), 151.8* (C-4), 154.4* (C-2), 163.6 (C=O); m/z (%) 287 (M^+, 5), 160 (100).

7b (R=*i*-C_3H_7): (71%), colourless oil; (Found: C, 66.76; H, 7.40; N, 14.66. $C_{16}H_{21}N_3O_2$ requires: C, 66.88; H, 7.37; N, 14.62); i.r. (Nujol) 3262, 1697, 1662, 1634 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 1.24 (d, 6H, J=6.6 Hz), 1.44 (d, 6H, J=6.8 Hz), 3.88-4.06 (m, 1H), 4.67 (d, 1H, J=2.9 Hz), 4.86 (d, 1H, J=2.9 Hz), 5.09 (sp, 1H, J=6.8 Hz), 6.99 (dd, 1H, J=7.7, 1.0 Hz), 7.11 (dt, 1H, J=7.7, 1.0 Hz), 7.30 (dt, 1H, J=7.7, 1.0 Hz), 7.43 (dd, 1H J=7.7, 1.0 Hz), 9.87 (d, 1H, J=6.2 Hz); ^{13}C n.m.r. δ ($CDCl_3$): 21.2 (CH_3), 22.9 (CH_3), 42.9 (CH-N), 47.1 (CH-NH), 86.6 (=CH_2), 118.4 (C-4a), 122.8 (C-8), 123.9 (C-6), 125.5 (C-5), 131.0 (C-7), 139.2 (C-8a), 151.7* (C-4), 153.7* (C-2), 163.7 (C=O); m/z (%) 287 (M^+, 2), 146 (100).

7c (R=4-CH_3O-C_6H_4): (72%), m.p. 146-148°C (white prisms); (Found: C, 69.49; H, 5.11; N, 10.16. $C_{24}H_{21}N_3O_4$ requires: C, 69.39; H, 5.09; N, 10.11); i.r. (Nujol) 3317, 1710, 1644 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 3.74 (s, 3H), 3.79 (s, 3H), 4.20 (d, 1H, J=2.7 Hz), 4.68 (d, 1H, J=2.7 Hz), 6.82 (d, 2H, J=9.0 Hz), 6.91 (d, 2H, J=9.0 Hz), 7.06-7.17 (m, 4H), 7.27-7.33 (m, 2H), 7.46 (d, 2H, J=9.0 Hz), 12.49 (s, 1H); ^{13}C n.m.r. δ ($CDCl_3$): 55.5 (CH_3O), 55.6 (CH_3O), 87.6 (=CH_2), 114.2 (CH), 114.3 (CH), 118.3 (C-4a), 122.2 (CH), 122.9 (C-8), 124.0 (C-6), 126.0 (c-5), 128.5, 130.1 (CH), 131.2 (C-7), 131.6, 138.4 (C-8a), 151.4* (C-4), 151.8* (C-2), 156.0, 159.2, 164.0 (C=O); m/z (%) 415 (M^+, 2), 134 (100).

7d (R=4-F-C_6H_4): (51%), m.p. 140-142°C (white prisms); (Found: C, 67.62; H, 3.90; N, 10.80. $C_{22}H_{15}F_2N_3O_2$ requires: C, 67.52; H, 3.86; N, 10.74); i.r. (Nujol) 3231, 1716, 1652, 1624 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 4.35 (d, 1H, J=3.0 Hz), 4.82 (d, 1H, J=3.0 Hz), 7.05-7.11 (m, 2H), 7.18-7.25 (m, 4H), 7.31-7.36 (m, 2H), 7.39-7.47 (m, 2H), 7.59-7.62 (m, 2H), 12.72 (s, 1H); ^{13}C n.m.r. δ ($CDCl_3$): 87.9 (=CH_2), 115.7 (^2J_F=26.2 Hz, CH), 116.0 (^2J_F=26.0 Hz, CH), 118.3 (C-4a), 121.4 (^3J_F=7.5 Hz, CH), 123.0 (C-8), 124.1 (C-6), 126.4 (C-5), 130.9 (^3J_F=9.1 Hz, CH), 131.3 (C-7), 134.2 (2xq), 138.0 (C-8a), 151.3* (C-4), 151.6* (C-2), 159.2 (^1J_F=243.0 Hz), 162.3 (^1J_F=247.0 Hz), 164.1 (C=O); m/z (%) 391 (M^+, 2), 137 (100).

Thermal Treatment of Compounds 7.

A solution of the appropiate 3,1-benzoxazine **7** (0.5 mmol) in ethanol (10 ml) was heated at reflux temperature for 24h. After cooling, the solvent was removed and the residual material was slurried with cold *n*-hexane. The formed solid was chromatographed on a silica gel column eluting with *n*-hexane/ethyl acetate (3:1) and then recrystallized from *n*-hexane to give **8**.

8a (R=*n*-C_3H_7): (92%), m.p. 132-134°C (white prisms); (Found: C, 71.16, H, 6.72; N, 13.91. $C_{12}H_{14}N_2O$ requires: C, 71.26; H, 6.98; N, 13.85); i.r. (Nujol) 3200, 1720, 1644 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 0.95 (t, 3H, J=7.4 Hz), 1.70 (sx, 2H, J=7.4 Hz), 3.78 (t, 2H, J=7.4 Hz), 4.24 (s broad, 1H), 4.79 (s broad, 1H), 6.78 (d, 1H, J=7.8 Hz), 6.94 (t, 1H, J=7.8 Hz), 7.20 (t, 1H, J=7.8 Hz), 7.51 (d, 1H, J=7.8 Hz), 9.07 (s, 1H); ^{13}C n.m.r. δ ($CDCl_3$): 11.3 (CH_3), 18.9 (CH_2), 44.9 (CH_2-N), 84.1 (=CH_2), 114.7 (C-8), 115.1 (C-4a), 122.5 (C-6), 123.9 (C-5), 130.0 (C-7), 134.7, 140.2, 151.3 (C-2); m/z (%) 202 (M^+, 4), 146 (100).

8b (R=4-CH_3O-C_6H_4): (86%), m.p. 141-143°C (white prisms); (Found: C, 72.26; H, 5.32; N, 10.58. $C_{16}H_{14}N_2O_2$ requires: C, 72.17; H, 5.30; N, 10.52); i.r. (Nujol) 3352, 1719, 1673 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 3.73 (s, broad, 1H), 3.88 (s, 3H), 4.75 (s broad, 1H), 6.72 (d, 1H, J=8.1 Hz), 6.99-7.07 (m, 3H), 7.21-7.28 (m, 3H), 7.56 (d, 1H, J=8.1 Hz), 8.84 (s broad, 1H); ^{13}C n.m.r δ ($CDCl_3$): 55.4 (CH_3O), 87.2 (=CH2), 114.7 (C-8), 115.1 (CH), 116.9 (C-4a), 122.7 (C-6), 123.9 (C-5), 130.0 (CH), 130.2 (C-7), 130.9, 139.0, 143.5, 151.1 (C-2), 159.2; m/z (%) 266 (M^+, 42), 265 (100), 146 (87).

8c (R=4-F-C_6H_4): (87%), m.p. 136-138°C (white prisms); (Found; C, 70.96; H, 4.40; N, 11.05. $C_{15}H_{11}FN_2O$ requires: C, 70.86; H, 4.36; N, 11.01); i.r. (Nujol) 3341, 1722, 1669 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$); 3.65 (s broad, 1H), 4.74 (s broad, 1H), 6.70 (d, 1H, J= 7.8 Hz), 7.00 (t, 1H, J= 7.8 Hz), 7.15-7.31 (m, 5H), 7.53 (d, 1H, J=7.8 Hz), 8.92 (s broad, 1H); ^{13}C n.m.r. δ ($CDCl_3$): 87.5 (=CH_2), 115.1 (C-8), 116.9 (C-4a),

116.9 (^2J_F= 22.6 Hz, CH), 122.9 (C-6), 123.9 (C-5), 130.3 (C-7), 130.9 (^3J_F=8.5 Hz, CH) 134.2 (^4J_F=3.3 Hz), 135.0, 143.3, 150.9 (C-2), 162.2 (^1J_F= 245.8 Hz); m/z (%) 254 (M^+, 36), 253 (100), 146 (10).

General Procedure for the Preparation of 2-Aryl-4-methylene-4*H*-3,1-benzoxazines 9.

To a solution of the iminophosphorane **5** (0.5 g, 1.26 mmol) in dry dichloromethane (20 ml) were added the appropiate aroyl chloride (1.26 mmol) and triethylamine (0.13 g, 1.26 mmol). The resultant solution was stirred at room temperature for 8h, and then concetrated to dryness. The residual material was chromatographed on a silica gel column using *n*-hexane/ethyl acetate (3:1) as eluent to give **9**.

9a (Ar=C_6H_5): (30%), m.p. 57–59°C (yellow prisms from *n*–hexane); (Found: C, 81.52; H, 5.07; N, 6.39; $C_{15}H_{11}NO$ requires: C, 81.43; H, 5.01; N, 6.33); i.r. (Nujol) 1658, 1634 cm^{-1}; ^1H n.m.r. δ (DMSO–d_6): 4.78 (d, 1H, J=2.7 Hz), 5.13 (d, 1H, J=2.7 Hz), 7.30 –7.60 (m, 6H), 7.72 (d, 1H, J=8.0 Hz), 8.1 (d, 2H, J=8.1 Hz); ^{13}C n.m.r. δ (DMSO–d_6): 86.9 (=CH_2), 120.3 (C–4a), 123.2 (C–8), 126.2 (C–6), 127.4 (CH), 128.0 (C–5), 128.7 (CH), 130.5 , 131.3 (C–7), 132.2 (CH), 138.2 (C–8a), 150.8 (C–4)*, 154.3 (C–2)*; m/z (%) 221 (M^+, 6), 105 (100).

9b (Ar=4–Cl–C_6H_4): (48%), m.p. 119–121°C (yellow prisms from *n*–hexane); (Found: C, 70.39; H, 3.98; N, 5.52; $C_{15}H_{10}ClNO$ requires: C, 70.46; H, 3.94; N, 5.48); i.r. (Nujol) 1658, 1629 cm^{-1}; ^1H n.m.r. δ (DMSO–d_6): 4.77 (d, 1H, J=2.7 Hz), 5.13 (d, 1H, J=2.7 Hz) , 7.25–7.31 (m, 2H), 7.48 (dt, 1H, J= 7.6, 1.5 Hz), 7.58 (d, 2H, J= 8.8 Hz), 7.72 (dd, 1H, J= 7.6, 1.5 Hz), 8.07 (d, 2H, J= 8.8 Hz); ^{13}C n.m.r. δ (DMSO–d_6): 87.1 (=CH_2), 120.2 (C–4a), 123.3 (C–8), 126.2 (C–6), 128.2 (C–5), 128.8 (CH), 129.2 (CH), 129.4 , 131.3 (C–7), 136.9, 137.9 (C–8a), 150.7(C–4)*, 153.5 (C–2)*; m/z (%) 257 (M^++2, 8), 255 (M^+, 25), 227 (100).

9c (Ar=4–Br–C_6H_4): (62%), m.p. 79–81°C (yellow prisms from *n*–hexane); (Found: C, 60.10; H, 3.40; N, 4.62; $C_{15}H_{10}BrNO$ requires: C, 60.02; H, 3.36; N, 4.67); i.r. (Nujol) 1659, 1632 cm^{-1}; ^1H n.m.r. δ (DMSO–d_6): 4.75 (s broad,1H), 5.11 (s broad, 1H), 7.24–7.30 (m, 2H), 7.41 (t, 1H, J=7.6 Hz), 7.68–7.72 (m, 3H), 7.98 (d, J= 8.2 Hz); ^{13}C n.m.r. δ (DMSO–d_6): 87.0 (=CH_2), 120.3 (C–4a), 123.3 (C–8), 125.9, 126.2 (C–6), 128.2 (C–5), 129.3 (CH), 129.7, 131.3 (C–7), 131.8 (CH), 137.9 (C–8a), 150.7 (C–2)*, 153.6 (C–4)*; m/z (%) 301 (M^++2, 27), 299 (M^+, 24), 55 (100).

General Procedure for the Preparation of 2-Aryl-4-methylquinolines 10.

A mixture of iminophosphorane **5** (0.7g, 1.8 mmol) the corresponding aroyl chloride (0.9 mmol) and dry toluene (30 ml) was heated at reflux temperature for 9h. Then the solution was cooled at 0°C and the precipitated solid was collected by filtration and recrystallized from toluene to give **10**.

10a (R=C_6H_5): (32%); m.p. 144-147°C (white prisms); (Found: C, 81.70; H, 5.42; N, 8.32; $C_{23}H_{18}N_2O$ requires: C, 81.63; H, 5.36; N, 8.28); i.r. (Nujol) 3262, 1681 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 2.73 (s, 3H), 7.20 (t, 1H, J=6.3 Hz), 7.43-7.57 (m, 5H), 7.70 (m, 2H), 7.81 (d, 1H, J=7.2 Hz), 7.96-8.02 (m, 4H), 8.79 (d, 1H, J=6.3 Hz), 13.41 (s, 1H); ^{13}C n.m.r. δ ($CDCl_3$): 19.3 (CH_3), 121.8 (CH), 123.9 (3xCH), 126.8 (C-4a), 127.0 (C-5), 127.6 (CH), 128.1, 128.5 (2xCH), 129.6 (CH), 130.5* (C-7), 130.8* (C-8), 131.6 (CH), 135.7, 138.3, 145.2 (C-4, C-8a), 157.3 (C-2), 166.1 (C=O); m/z (%) 338 (M^+, 14), 261 (52), 77 (100).

10b (R=4-CH_3-C_6H_4): (36%), m.p. 67-70°C (white prisms); (Found: C, 80.94, H, 6.13; N, 7.63. $C_{24}H_{20}N_2O$ requires: C, 81.79; H, 5.72; N, 7.95); i.r. (Nujol) 3341, 1671 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 2.41 (s, 3H), 2.74 (s, 3H), 7.17-7.28 (m, 3H), 7.44-7.61 (m, 2H), 7.71-7.84 (m, 3H), 7.94-8.01 (m, 3H), 8.10 (d, 1H, J=8.2 Hz), 8.84 (d, 1H, J=8.2 Hz), 13.50 (s, 1H); ^{13}C n.m.r. δ ($CDCl_3$): 19.2 (CH_3), 21.6 (CH_3), 121.7 (CH), 121.9 (CH), 123.5 (CH), 123.9 (CH), 125.9 (C-4a), 126.7 (C-5), 126.8, 127.7 (CH), 128.7 (CH), 129.2 (CH), 129.5 (CH), 130.0$^{\Delta}$ (C-7), 130.5$^{\Delta}$ (C-8), 133.1, 138.6, 142.1, 146.2* (C-4), 146.3* (C-8a), 157.9 (C-2), 166.0 (C=O); m/z (%) 352 (M^+, 100), 261 (69).

10c (R=4-CH_3O-C_6H_4): (34%), m.p. 147-149°C (white prisms); (Found: C, 78.32; H, 5.50; N, 7.53.

$C_{24}H_{20}N_2O_2$ requires: C, 78.24; H, 5.47; N, 7.60); i.r. (Nujol) 3370, 1671 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 2.74 (s, 3H), 3.85 (s, 3H), 6.95 (d, 2H, J=8.8 Hz), 7.19 (ddd, 1H, J=8.8, 7.6, 1.2 Hz), 7.43-7.60 (m, 2H), 7.70-7.77 (m, 2H), 7.82 (dd, 1H, J=7.9, 1.4 Hz), 7.97-8.08 (m, 4H), 8.83 (d, 1H, J=8.3 Hz), 13.47 (s, 1H); ^{13}C n.m.r. δ ($CDCl_3$): 19.1 (CH_3), 55.4 (CH_3O), 113.7 (CH), 121.6 (CH), 121.7 (CH), 123.2 (CH), 123.9 (CH), 125.6 (C-4a), 126.6 (C-5), 126.7, 128.3, 128.6 (CH), 129.4 (2xCH), 129.9* (C-7), 130.3* (C-8), 138.7, 146.0# (C-4), 146.1# (C-8a), 157.9 (C-2), 162.2, 165.5 (C=O); m/z (%) 368 (M^+, 5), 261 (7), 135 (100).

10d (R=4-Br-C_6H_4): (40%), m.p. 165-167°C (white prisms); (Found: C, 66.31; H, 4.08; N, 6.76. $C_{23}H_{17}BrN_2O$ requires: C, 66.20; H, 4.11; N, 6.71); i.r. (Nujol) 3375, 1659 cm^{-1}; ^1H n.m.r. δ (DMSO-d_6): 2.84 (s, 3H), 7.47 (t, 1H, J=7.4 Hz), 7.60-7.70 (m, 3H), 7.80-8.08 (m, 7H), 8.26 (d, 1H, J=8.2 Hz), 8.46 (d, 1H, J=8.2 Hz), 11.60 (s, 1H); ^{13}C n.m.r. δ (DMSO-d_6): 19.1 (CH_3), 122.7 (2xCH), 125.1 (2xCH), 125.5, 125.6 (CH), 126.5 (CH), 126.6, 128.5, 129.6 (CH), 131.3 (CH), 130.8 (CH), 131.8* (C-7), 132.9* (C-8), 133.1, 136.5, 139.3# (C-8a), 139.4# (C-4), 154.3 (C-2), 164.7 (C=O); m/z (%) 418 (M^++2, 10), 416 (M^+, 10), 261 (100).

The appropiate quinoline **10** (0.25 mmol) in 70% sulfuric acid (15 ml) was heated at reflux temperature for 30 min. After cooling, the separated solid was collected by filtation and to the filtrate was added 10% aqueous solution of sodium hydroxide (50 ml), then extracted with diethyl ether (2x25 ml) and dried on anhydrous sodium sulfate. The solvent was removed under reduced pressure and recrystallized from diethyl ether to give **11** (92%), m.p. 58-60°C (yellow prisms); (Found: C, 82.12; H, 6.06; N, 11.82. $C_{16}H_{14}N_2$ requires: C, 82.02; H, 6.02; N, 11.95); i.r. (Nujol) 3392, 3251, 1613 cm^{-1}; ^1H n.m.r δ ($CDCl_3$): 2.72 (s, 3H), 5.72 (s, 2H), 6.77-6.85 (m, 2H), 7.18 (ddd, 1H, J=9.7, 5.4, 1.4 Hz), 7.51 (ddd, 1H, J=8.1, 7.0, 1.1 Hz), 7.65-7.71 (m, 3H), 7.95 (dd, 1H, J=8.2, 1.1 Hz), 8.07 (d, 1H, J=8.2 Hz); ^{13}C n.m.r. δ ($CDCl_3$): 19.0 (CH_3), 117.4 (CH), 117.6 (CH), 121.1 (C-3), 121.7, 123.5 (C-6), 125.9 (C-5), 126.4, 129.1 (CH), 129.8 (CH), 129.2 (CH), 130.2 (CH), 145.0, 146.3, 146.9, 158.6 (C-2); m/z (%) 234 (M^+, 7), 219 (100).

Reaction of Iminophosphorane 5 with Electron-Withdrawing Substituted Isocyanates.

A mixture of the iminophosphorane **5** (0.51 g, 1.3 mmol), the appropriate isocyanate (1.3 mmol) and dichloromethane (20 ml) was stirred at room temperature for 24h. The solvent was removed under reduced pressure and the residual material was slurried with diethyl ether (20 ml) and the separated solid which was collected by filtration was found to be the corresponding iminophosphorane **13**. The filtrate was concentrated to dryness and the residual material was chromatographed on a silica gel column, eluting with *n*-hexane/ethyl acetate (3:1) to give **12** (30%), m.p. 176-178°C; (Found: C, 67.16; H, 4.42; N, 8.65. $C_9H_7NO_2$ requires: C, 67.07; H, 4.38; N, 8.69); i.r (Nujol) 3222, 1736, 1633 cm^{-1}; ^1H n.m.r. δ (DMSO-d_6): 4.66 (d, 1H, J=2.7 Hz), 5.06 (d, 1H, J=2.7 Hz), 6.87 (dd, 1H, J=8.1, 1.5 Hz), 6.99 (ddd, 1H, J=8.1, 7.5, 1.5 Hz), 7.28 (ddd, 1H, J=8.1, 7.5, 1.5), 7.59 (dd, 1H, J=8.1, 1.5 Hz), 10.63 (s, 1H); ^{13}C n.m.r. δ (DMSO-d_6): 89.2 (=CH_2), 113.9 (C-4a), 114.7 (CH), 123.1 (CH), 123.8 (CH), 130.9 (CH), 135.0, 147.0, 151.9 (C=O); m/z (%) 161 (M^+, 71), 133 (100).

When benzenesulfonyl isocyanate was used under the above mentioned reaction conditions, the reaction product was found to be 2-benzenesulfonylamino-4-methylen-4*H*-3,1-benzoxazine **14** (80%), m.p. 164-166°C (yellow prisms from dichloromethane); (Found: C, 60.08; H, 3.98; N, 9.37. $C_{15}H_{12}N_2O_3S$ requires: C, 59.99; H, 4.03; N, 9.33); i.r. (Nujol) 3234, 1663, 1623 cm^{-1}; ^1H n.m.r. δ (DMSO-d_6): 4.66 (d, 1H, J=3.3 Hz), 5.09 (d, 1H, J=3.3 Hz), 6.91 (d, 1H, J=7.7 Hz), 7.02 (t, 1H, J=7.7 Hz), 7.26 (t, 1H, J=7.7 Hz), 7.48-7.56 (m, 4H), 7.87-7.92 (m, 2H), 11.75 (s, 1H); ^{13}C n.m.r. δ (DMSO-d_6): 91.0 (=CH_2), 114.1 (C-4a), 115.8 (C-8), 123.8 (C-6), 124.7 (C-5), 126.8 (CH), 128.7 (CH), 131.4 (C-7), 132.0 (CH), 132.6 (C-8a), 142.9, 149.5, 150.0; m/z (%) 300 (M^+, 8), 77 (100).

***, #, Δ: Interchangeable assignment.**

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