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Vinyliminophosphorane-Mediated Preparation of 2-Arylquinoline and 4-Aryl-1-azaanthraquinone Derivatives. X-Ray Crystal Structure of 1,2-Dihydro-3*H*-indazolo[2,3-*a*]quinolin-4-one

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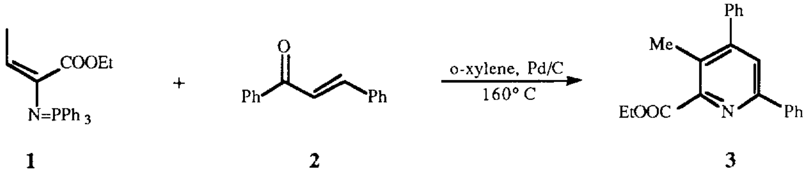
Abstract: The reaction of the iminophosphorane derived from 3-azidocyclohexen-2-enone with substituted cinnamyl aldehydes affords 2-aryl-tetrahydroquinoline derivatives, which are easily converted into 2-arylquinolines. By contrast, iminophosphorane derived from 2-azidocyclohex-2-enone reacts only with α,β-unsaturated aldehydes without substituent at β-position to give 5,6-dihydro-8(7H)quinolinones. The iminophosphorane derived from 2-azido-1,4-naphthoquinone reacts with substituted cinnamyl aldehydes providing directly 4-aryl-1-azaanthraquinones. The crystal and molecular structure of 1,2-dihydro-3*H*-indazolo[2,3-*a*]quinolin-4-one has been solved by X-Ray analysis.

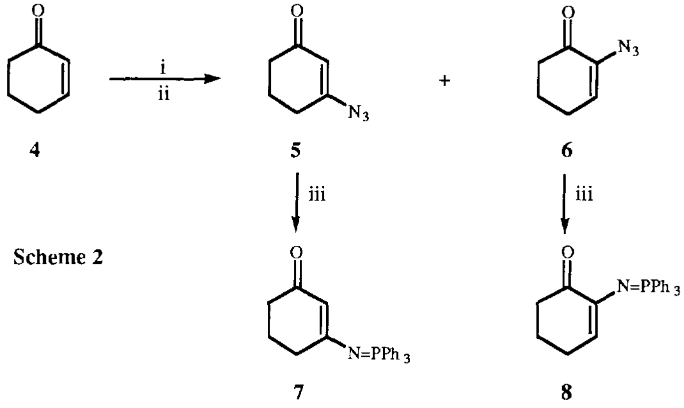
The utility of vinyliminophosphoranes for the synthesis of nitrogen-containing heterocycles has recently been demonstrated convincingly[1,2]. Vinyliminophosphoranes may be considered to be an equivalent of enamines and to contain two nucleophilic centers at the β-carbon atom and the iminophosphorane portion. Thus, this kind of compound undergoes a single step annulation with compounds containing two electrophilic centers such as α,β-unsaturated ketones[3] and related Michael acceptors[4] to give several kinds of azaheterocycles through an enamine-type carbon-carbon bond formation and subsequent aza Wittig reaction.

It has been previously reported[5] that vinyliminophosphoranes react with α,β-unsaturated ketones in toluene under refluxing in the presence of palladium on charcoal to give pyridines. However, enones bearing a substituent at the β-carbon atom, gave no product, and starting materials were recovered quantitatively even after a prolonged reaction time (168 h). Herein, we wish to report the reaction of α,β-unsaturated aldehydes



Scheme 1

with vinyliminophosphoranes bearing a cyclohexene or quinone residue on the nitrogen atom.

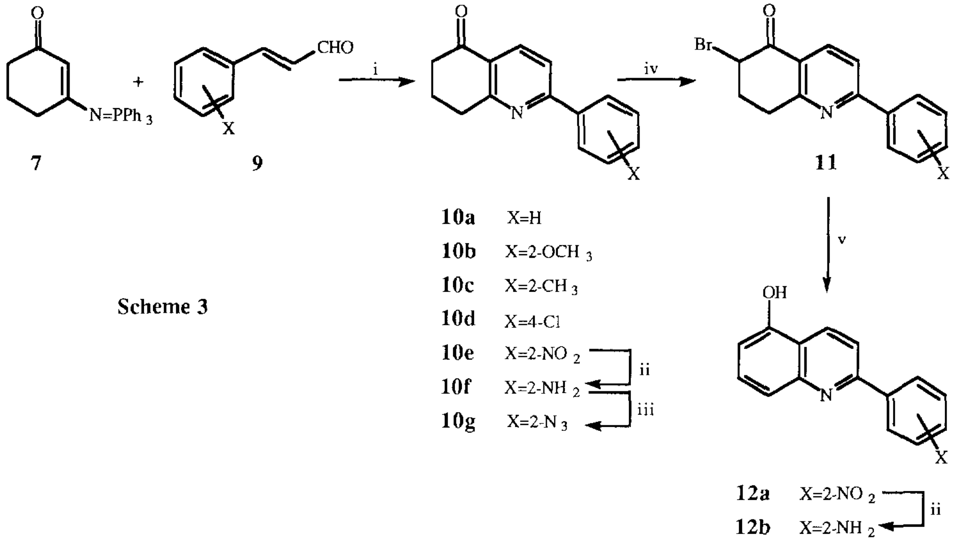


Scheme 2

Reagents and Conditions: i) IN_3, CH_3CN, r. t.; ii) NaN_3, DMF, 0°C; iii) PPh_3, CH_2Cl_2, r.t.

Vinyliminophosphorane **1**, derived from ethyl α-azido-2-butenoate[6], reacts with benzylideneacetophenone **2** in o-xylene at 160°C in the presence of Pd/C to give the pyridine **3** in 50% yield. This conversion could be explained either by an aza-Wittig/electrocyclic ring-closure process or by an enamine-type alkylation and a subsequent intramolecular aza-Wittig reaction (**Scheme 1**).

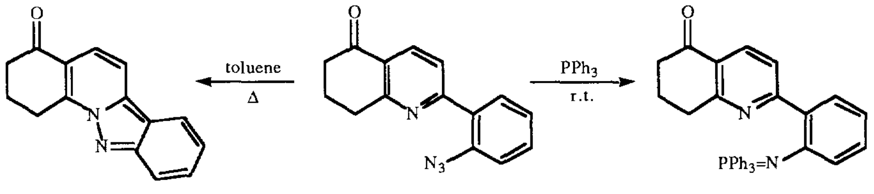
The next step was to study this reaction using vinyliminophosphoranes in which the vinylic portion belongs to a ring. Reaction of cyclohex-2-enone **4** with iodine azide and futher treatment with sodium azide[7], provides an equimolecular mixture of the vinyl azides **5** and **6**, which are separated by chromatography. Both



Scheme 3

Reagents and Conditions: i) o-xylene, Pd/C, 160°C; ii) Fe/AcOH, acetone; iii) HCl, $NaNO_2$, -5°C, then NaN_3; iv) Amberlyst-A26 Br_3^-, THF, reflux; v) 2,4,6-collidine, reflux compounds are converted in almost quantitative yield into the corresponding iminophosphoranes **7** and **8** by reaction with triphenylphosphine (**Scheme 2**).

Vinyliminophosphorane **7** reacts with several α,β-unsaturated aldehydes **9** in o-xylene at 160°C in the presence of Pd/C to produce directly 2-aryl-7,8-dihydro-5(6H)-quinolinones **10** in 39-58% yields. The reaction with acrolein under the same conditions provided the known compound[8] 7,8-dihydro-5(6H)quinolinone in 63% yield. The conversion **7** + **9** →**10** can be rationalised in terms of an initial addition of the β-carbon atom of the iminophosphorane **7** to the carbonyl carbon of the aldehyde followed by elimination of triphenylphosphine oxide with concomitant cyclization to give a tetrahydroquinoline which is dehydrogenated under the reaction conditions to give **10**[9]. The ready availability of dihydroquinolines possessing either electron-donating or electron-withdrawing substituents in the benzene ring is exemplified by entries **10b** and **10e**. Reduction of the nitro group in compound **10e** (78%) was straightforward using iron/acetic acid and acetone, and diazotisation of **10f** followed by reaction with sodium azide provided **10g** in 97% yield. Dihydroquinolinones **10** were readily converted into 2-arylquinolines **12** in two steps: a) α-bromination of the ketone group by using the polymeric brominating agent[10] Amberlyst-A26 Br_3^- to give **11** in 89%, and b) dehydrohalogenation by the action of 2,4,6-collidine affords **12a** in 73% yield, which is converted in 80% yield into **12b** by the action of iron/acetic acid (**Scheme 3**).



14 **10g** **13**

Scheme 4

Azide **10g** was converted in 91% yield into the iminophosphorane **13** by reaction with triphenylphosphine at room temperature, while by heating in toluene provided the tetracyclic indazolo[2,3-*a*]quinolinone **14** in 94% yield (**Scheme 4**).

A view of the molecular structure of **14** with the atom numbering scheme is shown in **fig. 1**[11]. Significant geometrical parameters are reported in **Table 1**. It is worth noticing the localization of the double bond character at C(1)-C(2), C(3)-C(4), C(8)-C(14) and C(15)-C(16) bonds while delocalization is observed in the C(5)-N(6)-N(7)-C(8)-C(14)-C(12)-O(13) fragment. The pyrido[*c*]indazole three ring system (A,B,C) is

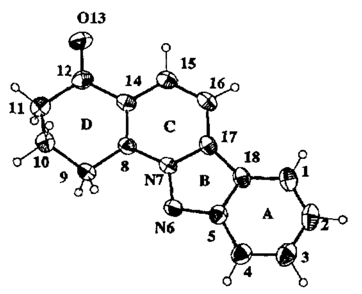


Fig 1. Molecular Structure (Ellipsoids 30%).

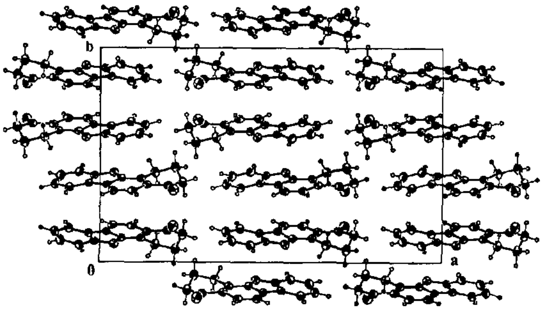


Fig 2. Crystal packing along the **c** axis showing the stacking of the molecules.

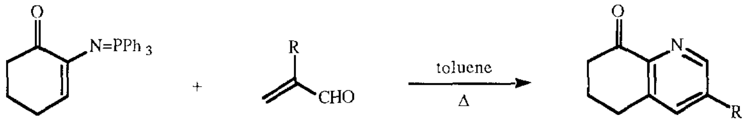
almost planar, although each ring deviates significantly from planarity (χ^2 (ring A/C)=84.57, 146.95 versus 7.81 and χ^2 (ring B)=16.88 versus 5.99). The angles between the pair of planes A,B and B,C are 1.8(1) and 1.4(1)° respectively. Ring D has an intermediate envelope-half chair conformation[12] (**Table 1**, versus the theoretical values envelope/half-chair: $\phi2=0/30°$, $\theta_2=54.7/50.8°$).

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

C(1)-C(2)	1.360(4)	N(7)-C(8)	1.363(3)	C(12)-O(13)	1.223(3)
C(1)-C(18)	1.406(3)	N(7)-C(17)	1.392(3)	C(12)-C(14)	1.476(3)
C(2)-C(3)	1.420(5)	C(8)-C(9)	1.491(3)	C(14)-C(15)	1.421(3)
C(3)-C(4)	1.362(4)	C(8)-C(14)	1.377(3)	C(15)-C(16)	1.352(4)
C(4)-C(5)	1.417(4)	C(9)-C(10)	1.523(4)	C(16)-C(17)	1.404(3)
C(5)-N(6)	1.352(3)	C(10)-C(11)	1.503(4)	C(17)-C(18)	1.404(3)
N(6)-N(7)	1.364(2)	C(11)-C(12)	1.500(4)	C(18)-C(5)	1.417(3)
C(9)-C(8)-C(14)-C(11)	-0.7(3)	C(9)-C(10)-C(11)-C(12)	-53.5(3)	Cremer and Pople Parameters:	
C(14)-C(8)-C(9)-C(10)	-18.4(3)	C(10)-C(11)-C(12)-C(14)	34.1(3)	q2=0.333(3)Å	q3=0.262(3)Å
C(8)-N(9)-C(10)-C(11)	44.9(3)	C(11)-C(12)-C(14)-C(8)	-7.2(3)	ϕ2=15.5(4)°	θ2=51.8(3)°
C-H...Centroid*		C-H	C..Centr.	H...Centr.	C-H...Centr.
C(15)-H(15)..C(**C**)(x, 1/2-y, -1/2+z)		1.03(3)	3.547(2)	2.87(3)	124(2)
C(16)-H(16)..C(**B**)(x, 1/2-y, -1/2+z)		0.97(3)	3.400(2)	2.97(2)	108(2)
Centroid....Centroid			C..Centr.		
C(A)...C(C)(1-x, -y, 1-z)			3.777(1)		
C(**B**)...C(**B**)(1-x, -y, 1-z)			3.524(1)		

The packing of the molecules is illustrated in **Fig. 2**. The molecules stack along the **b** axis, through symmetry centers involving the three ring of the planar system. These pairs of molecules do not bear additional interactions except two weak C-H...π electronic cloud interactions[13].

On the other hand, the reaction of vinyliminophosphorane **8** with α,β-unsaturated aldehydes **15a-b**, both which have no substituent at the β-position, provides 5,6-dihydro-8(7H)quinolinones **16** in moderate yields (52-54%). However, the attempted reaction of **8** with α,β-unsaturated aldehydes such as: crotonaldehyde and cinnamaldehyde, both of which have a substituent at the β-carbon atom, gave no product, and iminophosphorane **8** was recovered unchanged (**Scheme 5**). 5,6-Dihydro-8(7H)quinolinones **16** are useful building blocks for the preparation of pyrido[2,3-*g*]indoles, which have been used as hosts for urea derivatives[14], however, the only synthetic method described for their preparation is based on the oxidation of the 2-methylene position of 5,6,7,8-tetrahydroquinolines by a two-step sequence: condensation with benzaldehyde followed by ozonolysis of the resulting α-benzylidene derivative[15].



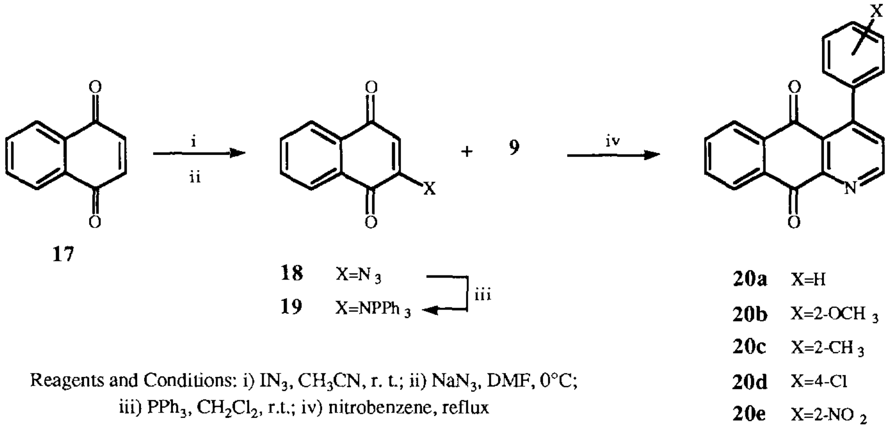
8

15a R=H
15b R=CH$_3$

16a R=H
16b R=CH$_3$

Scheme 5

Having established that the reaction of vinyliminophosphoranes type **7** and **8** with α,β-unsaturated aldehydes provides annelated pyridines, we considered the suitability of this reaction for the synthesis of the otherwise not readily available 4-aryl-1-azaanthraquinones. To this end, the 2-azido-1,4-naphthoquinone **18** was prepared from 1,4-naphthoquinone **17** and iodine azide. Staudinger reaction of the azide **18** with triphenylphosphine furnished the iminophosphorane **19** in 92% yield. Reaction of iminophosphorane **19** with aldehydes **9** in nitrobenzene at reflux temperature for 3 h gives directly compounds **20** in moderate yields (45-56%). The reaction with acrolein under the same conditions afforded 1-azaanthraquinone[16] in 47% yield (**Scheme 6**). The conversion **19** + **9** →**20** can be rationalised in terms of an initial aza-Wittig reaction to give an azahexatriene as intermediate, which undergoes ring-closure further and dehydrogenation under the reaction conditions. The two general methods for the preparation of 1-azaanthraquinones: a) [4+2]cycloaddition reaction of 1,4-naphthoquinone with α,β-unsaturated hydrazones[17] and b) [4+2]cycloaddition reaction of quinoline-5,8-diones with cyclic and alicyclic dienes[18], failed to give 4-arylsubstituted 1-azaanthraquinones. Thus, reaction of 1,4-naphthoquinone with o-substituted cinnamyl N,N-dimethylhydrazones failed, yielding intractable mixtures of products[19].



Reagents and Conditions: i) IN_3, CH_3CN, r. t.; ii) NaN_3, DMF, 0°C; iii) PPh_3, CH_2Cl_2, r.t.; iv) nitrobenzene, reflux

Scheme 6

In conclusion, the pyrido annulation reaction described here represents an alternative route to 2-arylquinoline derivatives and to the previously unreported 4-aryl-1-azaanthraquinones.

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 Impact 400 spectrophotometer. NMR spectra were recorded on a Bruker AC200 (200MHz) or a Varian Unity 300 (300MHz). Mass spectra were recorded on a Hewlett-Packard 5993C spectrometer. Microanalyses were performed on a Perkin Elmer 240C instrument.

X-ray Analysis.- A summary of data collection and refinement process is given in **Table 2**. The structure was solved by direct methods (SIR92)[20] and refined by least-squares procedures on Fobs. All hydrogens were obtained from difference Fourier synthesis and included in the refinement process as isotropic. The scattering factors were taken from the International Tables for X-Ray Crystallography[21]. Two reflection were affected by secondary extinction and were considered as unobserved in the last cycles of refinement. **Table 3** list the final atomic coordinates and equivalent thermal factors for non-hydrogen atoms. The calculations were carried out with the XRAY80[22], PESOS[23] and PARST[24] set of programs running on a VAX6410 computer.

Table 2. Crystal analysis parameters at room temperature.

Crystal data

Chemical formula	$C_{15}H_{12}N_2O$	Crystal system	Orthorhombic
Mr	236.27	Space group	*Pbca*
a (Å)	23.0444(19)	α (°)	90
b (Å)	14.7359(8)	β (°)	90
c (Å)	6.7600(2)	γ (°)	90
Z	8	*Dx* (gr/cm^3)	1.37
V (Å^3)	2295.6(2)	Radiation	CuKα
Wavelength (Å)	1.5418	No. of reflections for lattice parameters:	7
θ range for lattice parameters (°)	2-45	Temperature (K)	295
Absorption coefficient (cm-1)	6.60		
Crystal colour	Yellow	Crystal description	Plate like
Crystal size (mm)	0.50 x 0.50 x 0.05		

Data collection

Diffractometer type	Philips PW1100, four circle. Graphite oriented monocromator.		
Measurement time	1 min./reflection	Detector apertures (°)	1 x 1
Collection method	ω/2θ scans	θmax (°)	65
No. of standard reflections (interval)	2 (90 min.). No variation	Scan width (°)	1.5
No. of independent reflections	1944	No. of observed reflections, I>3σ(I)	1507

Refinement

Treatment of hydrogen atoms	See experimental part	Refinement: Least-Squares on F*o*. Full matrix	
R	0.052	No. of parameters refined	211
wR	0.060	Degrees of freedom	1296
(Δρ)max (e/Å^3)	0.22	Ratio of freedom	7.1
<Shift/error>	0.08	Max. thermal value (Å^2)	U33[C(2)]=0.115(3)

Weighting scheme: Empirical as to give no trends in <ωΔ^{2}F> vs. <|Fobs|> and <sinθ/λ>.

Table 3. Final atomic coordinates and Ueq=(1/3)Σ[Uij·a$_i$*·a$_j$*·a$_i$·a$_j$·cos(a$_i$,a$_j$)]x10^4

Atom	x	y	z	Ueq	Atom	x	y	z	Ueq
C(1)	0.4099(1)	0.1542(2)	0.4693(5)	680(9)	C(10)	0.7213(1)	0.0587(2)	0.5630(4)	688(9)
C(2)	0.3693(1)	0.1382(2)	0.6110(6)	794(11)	C(11)	0.7420(1)	0.1278(2)	0.4156(4)	671(10)
C(3)	0.3850(1)	0.0994(2)	0.7956(5)	772(11)	C(12)	0.6988(1)	0.1450(2)	0.2541(4)	574(8)
C(4)	0.4408(1)	0.0778(2)	0.8415(4)	660(9)	O(13)	0.7141(1)	0.1645(2)	0.0860(3)	781(7)
C(5)	0.4839(1)	0.0960(1)	0.6973(3)	522(7)	C(14)	0.6367(1)	0.1402(1)	0.3066(3)	503(7)
N(6)	0.5417(1)	0.0824(1)	0.7152(3)	518(6)	C(15)	0.5942(1)	0.1686(2)	0.1676(3)	557(8)
N(7)	0.5629(1)	0.1100(1)	0.5367(3)	457(6)	C(16)	0.5373(1)	0.1694(2)	0.2170(4)	559(8)
C(8)	0.6205(1)	0.1107(1)	0.4920(3)	469(7)	C(17)	0.5204(1)	0.1403(1)	0.4061(3)	493(7)
C(9)	0.6620(1)	0.0814(2)	0.6490(4)	582(8)	C(18)	0.4680(1)	0.1323(1)	0.5109(4)	539(7)

Reaction of Vinyliminophosphorane 1 with Benzylideneacetophenone 2.

A mixture of vinyliminophosphorane **1** (1.0 g, 2.57 mmol), benzylideneacetophenone **2** (0.56 g, 2.69 mmol) and palladium on charcoal (0.075 g) in dry o-xylene (5 ml) was heated at reflux temperature for 24 h. After cooling, the mixture was filtered and the filtrate was concentrated to dryness. The residual material was chromatographed on a silica gel column with dichloromethane as eluent to give **3** in 50% yield as colourless prisms, m.p. 98-101°C (Found: C, 79.27; H, 6.26; N, 4.23. $C_{21}H_{19}NO_2$ requires: C, 79.47; H, 6.03; N, 4.41); i.r. (nujol) 1724, 1591, 1217, 1090, 773, 720, 687 cm^{-1}; ^{1}H n.m.r. δ($CDCl_3$): 1.46 (t, 3H, ^{3}J=7.1 Hz, OCH_2CH_3), 2.37 (s, 3H, Het-CH_3), 4.49 (q, 2H, ^{3}J=7.1 Hz, OCH_2CH_3), 7.30-7.48 (m, 8H, aromatics), 7.68 (s, 1H, H-5), 8.02 (dd, 2H, ^{3}J=7.7 Hz, ^{4}J=1.7 Hz, aromatics); ^{13}C n.m.r. δ($CDCl_3$): 14.3 (OCH_2CH_3), 16.0 (Het-CH_3), 61.7 (OCH_2CH_3), 122.8 (C-5), 127.0, 128.2, 128.4 (q), 128.6, 128.7, 129.1, 138.5 (q), 139.2 (q), 150.7 (q), 152.2 (q), 154.4 (q), 167.6 (C=O); m/z (%): 317 (M$^+$, 2), 215 (22), 140 (31), 115 (62), 77 (60).

General Procedure for the Preparation of Azides 5, 6 and 18.

To a stirred slurry of sodium azide (15.0 g, 0.25 mol) in dry acetonitrile (100 ml) at -10°C under nitrogen was added iodine monochloride (18.3 g, 0.113 mol) over a period of 20 min. The reaction mixture was stirred for an additional 10 min and cyclohex-2-enone **4** (9.6 g, 0.1 mol) was added, allowed to warm to room temperature and stirred for 20 h. The resultant solution was poured into water (250 ml) and extracted with diethyl ether (3x50 ml). The combined organic layers were washed with 5% sodium thiosulfate (150 ml), saturated solution of NaCl (4x225 ml) and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure at room temperature and the residual material was dissolved in DMF (425 ml) and sodium azide (5.98 g, 92 mmol) was added. The mixture was stirred at 0°C for 4 h and then poured into water (400 ml) and extracted with diethyl ether (5x100 ml). The combined organic layers were washed with a saturated solution of NaCl (3x100 ml) and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure at room temperature and the residual material was chromatographed on a silica gel column with AcOEt/n-hexane (1:3) as eluent to give 3-azido cyclohex-2-enone **5** (R_f=0.26) and 2-azido cyclohex-2-enone **6** (R_f=0.5).

3-Azido cyclohex-2-enone 5: (42%), oil; (Found: C, 52.78; H, 5.28; N, 30.40. $C_6H_7N_3O$ requires: C, 52.55; H, 5.15; N, 30.64); i.r. (neat) 2108, 1661, 1607, 1188 cm^{-1}; ^{1}H n.m.r. $\delta(CDCl_3)$: 2.06 (qn, 2H, ^3J=6.0 Hz, H-5), 2.36-2.43 (m, 4H, H-4 and H-6), 5.77 (s, 1H, H-2); ^{13}C n.m.r. $\delta(CDCl_3)$: 21.3 (C-5), 27.2 (C-4), 36.4 (C-6), 114.3 (C-2), 161.2 (C-3), 197.6 (C=O); m/z (%): 137 (M^+, 20), 109 (10), 54 (100).

2-Azido cyclohex-2-enone 6: (33%), oil; (Found: C, 52.74; H, 4.94; N, 30.87. $C_6H_7N_3O$ requires: C, 52.55; H, 5.15; N, 30.64); i.r. (neat) 2118, 1686, 1620, 1232 cm^{-1}; ^{1}H n.m.r. $\delta(CDCl_3)$: 2.02 (qn, 2H, ^3J=6.6 Hz, H-5), 2.41-2.58 (m, 4H, H-4 and H-6), 6.46 (t, 1H, ^3J=4.6 Hz, H-3); ^{13}C n.m.r. $\delta(CDCl_3)$: 22.5(C-5), 25.1 (C-4), 38.2 (C-6), 133.0 (C-3), 135.1 (C-2), 194.1 (C=O); m/z (%): 137 (M^+, 25), 109 (5), 80 (27), 54 (100).

By this procedure and using 1,4-naphthoquinone **17** as the carbonyl partner, 2-azido-1,4-naphthoquinone **18** was obtained in 78% yield, m.p. 111-114°C (lit.[25] 118°C dec.) (yellow prisms): i.r. (nujol) 2123, 1680, 1649, 1123 cm^{-1}; ^{1}H n.m.r. $\delta(CDCl_3)$: 6.45 (s, 1H, H-3), 7.73-7.79 (m, 2H, H-6 and H-7), 8.05-8.09 (m, 2H, H-5 and H-8); ^{13}C n.m.r. $\delta(CDCl_3)$: 120.1 (C-3), 126.4, 126.9, 131.0 (q), 132.1 (q), 133.6, 134.8, 146.2 (C-2), 180.8 (C=O), 183.6 (C=O); m/z (%): 199 (M^+, 3), 171 (76), 76 (100).

General Procedure for the Preparation of Vinyliminophosphoranes 7, 8 and 19.

To a solution of triphenylphosphine (1.30 g, 4.96 mmol) in dry dichloromethane (20 ml), a solution of the appropriate vinylazide (4.96 mmol) in the same solvent (20 ml) was added dropwise at room temperature under nitrogen. The reaction mixture was stirred at room temperature for 2 h. The solvent was removed under reduced pressure at 35°C and the residual material was purified by crystallization from the appropriate solvent.

Compound 7: (94%), m.p. 169-171°C (lit.[26] 163-163.5°C) (colourless prisms from diethyl ether/dichloromethane); (Found: C, 77.44; H, 6.20; N, 3.58. $C_{24}H_{22}NOP$ requires: C, 77.61; H, 5.97; N, 3.77); i.r. (nujol) 1609, 1518, 1435, 1244, 1107 cm^{-1}; ^{1}H n.m.r. $\delta(CDCl_3)$: 1.94 (qn, 2H, ^3J=6.3 Hz, H-5), 2.25 (t, 2H, ^3J=6.5 Hz, H-6), 2.57 (t, 2H, ^3J=6.0 Hz, H-4), 5.09 (s, 1H, H-2), 7.43-7.57 (m, 9H, H_m and H_p), 7.69 (ddd, 6H, $^3J_{P-H}$=12.6 Hz, ^3J=8.3 Hz, ^4J=1.3 Hz, H_o); ^{13}C n.m.r. $\delta(CDCl_3)$: 22.6 ($^4J_{P-C}$=3.1 Hz, C-5), 35.8 ($^3J_{P-C}$=23.7 Hz, C-4), 36.3 (C-6), 109.3 ($^3J_{P-C}$=13.0 Hz, C-2), 128.0 (q, $^1J_{P-C}$=102.2 Hz, C_i), 128.8 ($^3J_{P-C}$=12.1 Hz, C_m), 132.3 ($^4J_{P-C}$=2.6 Hz, C_p), 132.5 ($^2J_{P-C}$=9.6 Hz, C_o), 175.2 ($^2J_{P-C}$=5.5 Hz, C-3), 198.1 (C=O); m/z (%): 371 (M^+, 6), 262 (5), 183 (100), 108 (73).

Compound 8: (97%), m.p. 146-148°C (colourless prisms from diethyl ether/dichloromethane); (Found: C, 77.85; H, 5.84; N, 3.98. $C_{24}H_{22}NOP$ requires: C, 77.61; H, 5.97; N, 3.77); i.r. (nujol) 1667, 1591, 1435, 1221, 1107 cm^{-1}; ^{1}H n.m.r. $\delta(CDCl_3)$: 1.85 (qn, 2H, ^3J=6.3 Hz, H-5), 2.28-2.36 (m, 4H, H-4 and H-6), 6.38 (t, 1H, ^3J=4.5 Hz, H-3), 7.36-7.42 (m, 9H, H_m and H_p), 7.72 (ddd, 6H, $^3J_{P-H}$=12.0 Hz, ^3J=7.8 Hz, ^4J=1.6 Hz, H_o); ^{13}C n.m.r. $\delta(CDCl_3)$: 23.6 (C-5), 26.1 ($^4J_{P-C}$=2.5 Hz, C-4), 38.5 (C-6), 128.0 ($^3J_{P-C}$=12.1 Hz, C_m), 128.2 ($^3J_{P-C}$=22.6 Hz, C-3), 130.7 ($^4J_{P-C}$=2.5 Hz, C_p), 132.3 ($^2J_{P-C}$=9.6 Hz, C_o), 133.6 ($^1J_{P-C}$=101.7 Hz, C_i), 143.3 ($^2J_{P-C}$=6.0 Hz, C-2), 197.5 ($^3J_{P-C}$=8.1 Hz, C=O); m/z (%): 371 (M^+, 7), 262 (6), 183 (100), 108 (86).

Compound 19: (92%), m.p. 188-190°C (red prisms from diethyl ether/dichloromethane); (Found: C, 77.46; H, 4.83; N, 3.03. $C_{28}H_{20}NO_2P$ requires: C, 77.59; H, 4.65; N, 3.23); i.r. (nujol) 1672, 1626, 1443, 1107 cm^{-1}; ^{1}H n.m.r. δ(CDCl$_3$): 6.32 (s, 1H, H-3), 7.43-7.62 (m, 11H, aromatics), 7.79 (dd, 6H, $^3J_{P-H}$=12.0 Hz, ^3J=7.7 Hz, H$_o$), 7.85 (d, 1H, ^3J=7.5 Hz, aromatic), 8.01 (d, 1H, ^3J=7.5 Hz, aromatic); ^{13}C n.m.r. δ(CDCl$_3$): 116.4 ($^3J_{P-C}$=19.6 Hz, C-3), 125.5, 126.4, 128.7 ($^3J_{P-C}$=12.6 Hz, C$_m$), 129.6 ($^1J_{P-C}$=102.7 Hz, C$_i$), 131.4, 131.5 (J_{P-C}=1.1 Hz, q), 132.0 ($^4J_{P-C}$=3.0 Hz, C$_p$), 132.4 ($^2J_{P-C}$=9.6 Hz, C$_o$), 133.5, 133.8 (q), 156.8 ($^2J_{P-C}$=5.1 Hz, C-2), 183.5 ($^3J_{P-C}$=14.6 Hz, C=O), 184.5 ($^4J_{P-C}$=3.5 Hz, C=O); m/z (%): 433 (M$^+$, 100), 262 (37), 183 (17), 108 (4).

General Procedure for Preparation of 2-Aryl-7,8-dihydro-5(6H)quinolinones 10.

A mixture of vinyliminophosphorane **7** (0.5 g, 1.35 mmol), the appropriate α,β-unsaturated aldehyde **9** (1.60 mmol), palladium on charcoal (0.035 g) in dry o-xylene was heated at 160°C for 24 h. After cooling, the solution was filtered and the filtrate was concentrated to dryness under reduced pressure. The residual material was chromatographed on a silica gel column with n-hexane/AcOEt (3:1) as eluent to give **10** which were recristallized from the adequate solvent.

Compound 10a (X=H): (58%), m.p. 134-136°C (colourless prisms from n-hexane/ dichloromethane); (Found: C, 80.52; H, 6.11; N, 6.38. C$_{15}$H$_{13}$NO requires: C, 80.69; H, 5.87; N, 6.27); i.r. (nujol) 1678, 1584, 1271, 1125 cm^{-1}; ^{1}H n.m.r. δ(CDCl$_3$): 2.22 (qn, 2H, ^3J=6.4 Hz, H-7), 2.72 (t, 2H, ^3J=6.5 Hz, H-6), 3.22 (t, 2H, ^3J=6.2 Hz, H-8), 7.46-7.52 (m, 3H, aromatics), 7.70 (d, 1H, ^3J=8.2 Hz, H-3), 8.03-8.08 (m, 2H, aromatics), 8.32 (d, 1H, ^3J=8.2 Hz, H-4); ^{13}C n.m.r. δ(CDCl$_3$): 22.0 (C-7), 32.9 (C-8), 38.6 (C-6), 119.0 (C-3), 126.6 (C-4a), 127.5, 128.9, 130.0, 135.8 (C-4), 138.4 (q), 160.8 (C-2), 163.8 (C-8a), 197.9 (C=O); m/z (%): 223 (M$^+$, 100), 195(39), 167(7).

Compound 10b (X=2-OCH$_3$): (50%), m.p. 99-101°C (colourless prisms from n-hexane/ dichloromethane); (Found: C, 76.08; H, 5.80; N, 5.41. C$_{16}$H$_{15}$NO$_2$ requires: C, 75.87; H, 5.97; N, 5.53); i.r. (nujol) 1680, 1582, 1269, 1125 cm^{-1}; ^{1}H n.m.r. δ(CDCl$_3$): 2.21 (qn, 2H, ^3J=6.4 Hz, H-7), 2.70 (t, 2H, ^3J=6.6 Hz, H-6), 3.20 (t, 2H, ^3J=6.2 Hz, H-8), 3.85 (s, 3H, OCH_3), 7.00 (d, 1H, ^3J=8.4 Hz, aromatic), 7.08 (td, 1H, ^3J=7.7 Hz, ^4J=0.8 Hz, aromatic), 7.40 (td, 1H, ^3J=8.7 Hz, ^4J=1.8 Hz, aromatic), 7.81 (d, 1H, ^3J=8.4 Hz, H-3), 7.82 (dd, 1H, ^3J=7.5 Hz, ^4J=2.0 Hz, aromatic), 8.26 (d, 1H, ^3J=8.1 Hz, H-4); ^{13}C n.m.r. δ(CDCl$_3$): 22.0 (C-7), 32.7 (C-8), 38.6 (C-6), 55.5 (OCH_3), 111.4, 121.1 (C-3), 123.6, 126.1 (C-4a), 128.2 (q), 130.8, 131.3, 134.4 (C-4), 157.2 (q), 159.8 (C-2), 163.3 (C-8a), 197.9 (C=O); m/z (%): 253 (M$^+$, 28), 195 (38), 167 (21), 148 (100).

Compound 10c (X=2-CH$_3$): (39%), m.p. 116-119°C (colourless prisms from n-hexane/ AcOEt); (Found: C, 80.85; H, 6.61; N, 6.01. C$_{16}$H$_{15}$NO requires: C, 80.98; H, 6.37; N, 5.90); i.r. (nujol) 1676, 1582, 1272, 1126 cm^{-1}; ^{1}H n.m.r. δ(CDCl$_3$): 2.24 (qn, 2H, ^3J=6.4 Hz, H-7), 2.39 (s, 3H, Ar-CH_3), 2.73 (t, 2H, ^3J=6.6 Hz, H-6), 3.21 (t, 2H, ^3J=6.2 Hz, H-8), 7.30-7.43 (m, 5H, aromatics), 8.33 (d, 1H, ^3J=8.0 Hz, H-4); ^{13}C n.m.r. δ(CDCl$_3$): 20.4 (Ar-CH_3), 21.9 (C-7), 32.7 (C-8), 38.6 (C-6), 122.7 (C-3), 126.0, 126.1 (C-4a), 128.9, 129.5, 131.0, 135.1 (C-4), 135.8 (q), 139.7 (q), 163.2 (C-2), 163.7 (C-8a), 197.9 (C=O); m/z (%): 237 (M$^+$, 58), 236 (100), 181 (11), 180 (23).

Compound 10d (X=4-Cl): (41%), m.p. 116-122°C (colourless prisms from n-hexane/ diethyl ether); (Found: C, 69.76; H, 4.91; N, 5.62. C$_{15}$H$_{12}$ClNO requires: C, 69.91; H, 4.69; N, 5.44); i.r. (nujol) 1685, 1577, 1279, 1089 cm^{-1}; ^{1}H n.m.r. δ(CDCl$_3$): 2.20 (qn, 2H, ^3J=6.4 Hz, H-7), 2.70 (t, 2H, ^3J=6.5 Hz, H-6), 3.19 (t, 2H, ^3J=6.1 Hz, H-8), 7.43 (d, 2H, ^3J=8.5 Hz, aromatics), 7.63 (d, 1H, ^3J=8.2 Hz, H-3), 7.98 (d, 2H, ^3J=8.5 Hz, aromatics), 8.28 (d, 1H, ^3J=8.2 Hz, H-4); ^{13}C n.m.r. δ(CDCl$_3$): 21.8 (C-7), 32.8 (C-8), 38.5 (C-6), 118.5 (C-3), 126.6 (C-4a), 128.6, 129.0, 135.9 (C-4), 136.2 (q), 136.7 (q), 159.2 (C-2), 163.8 (C-8a), 197.6 (C=O); m/z (%): 259 (M$^+$+2, 31), 257 (M$^+$, 87), 231 (35), 229 (100), 166 (54), 139 (21).

Compound 10e (X=2-NO$_2$): (47%), m.p. 170-172°C (colourless prisms from n-hexane/ AcOEt); (Found: C, 67.01; H, 4.72; N, 10.69. C$_{15}$H$_{12}$NO$_2$ requires: C, 67.16; H, 4.51; N, 10.44); i.r. (nujol) 1678, 1584, 1269, 1128 cm^{-1}; ^{1}H n.m.r. δ(CDCl$_3$): 2.22 (qn, 2H, ^3J=6.4 Hz, H-7), 2.73 (t, 2H, ^3J=6.6 Hz, H-6), 3.15 (t, 2H, ^3J=6.2 Hz, H-8), 7.45 (d, 1H, ^3J=8.1 Hz, H-3), 7.59 (td, 1H, ^3J=7.1 Hz, ^4J=1.6 Hz, aromatic), 7.62 (dd, 1H, ^3J=7.5 Hz, ^4J=1.8 Hz, aromatic), 7.69 (td, 1H, ^3J=7.5 Hz, ^4J=1.3 Hz, aromatic), 7.94 (dd, 1H, ^3J=8.1 Hz, ^4J=1.2 Hz, aromatic), 8.37 (d, 1H, ^3J=8.1 Hz, H-4); ^{13}C n.m.r. δ(CDCl$_3$): 21.7 (C-7), 32.4 (C-8), 38.5 (C-6), 121.2 (C-3), 124.6, 127.1 (C-4a), 129.9, 131.0, 132.6, 134.7 (q), 136.0 (C-4), 149.1 (q), 159.2 (C-

2), 163.7 (C-8a), 197.5 (C=O); m/z (%): 268 (M$^+$, 43), 210 (100), 140 (92), 127 (83).

2-(2-Amino)phenyl-7,8-dihydro-5(6H)quinolinone 10f.

A mixture of **10e** (0.15 g, 0.56 mmol), acetone (10 ml), acetic acid (1 ml), water (1 ml) and powder iron (0.36 g) was refluxed for 1 h and then filtered. A saturated solution of sodium carbonate (5 ml) was added to the filtrate. The organic layer was separated and dried over anhydrous magnesiun sulfate. The solvent was removed under reduced pressure and the crude product was chromatographed on a silica gel column with n-hexane/ AcOEt (1:1) as eluent and then recrystallized from n-hexane/dichloromethane (1:1) to give **10f** in 78% yield, as yellow prisms, m.p. 202°C; (Found: C, 75.48; H, 5.73; N, 11.98. $C_{15}H_{14}N_2O$ requires: C, 75.61; H, 5.92; N, 11.76); i.r. (nujol) 3417, 3305, 1671, 756 cm^{-1}; ^{1}H n.m.r. δ(CDCl$_3$): 2.21 (qn, 2H, ^{3}J=6.1 Hz, H-7), 2.70 (t, 2H, ^{3}J=6.5 Hz, H-6), 3.15 (t, 2H, ^{3}J=6.2 Hz, H-8), 5.75-6.19 (s, 2H, NH$_2$), 6.76 (d, 1H, ^{3}J=7.8 Hz, aromatic), 6.77 (t, 1H, ^{3}J=8.3 Hz, aromatic), 7.20 (t, 1H, ^{3}J=7.8 Hz, aromatic), 7.60 (d, 1H, ^{3}J=7.8 Hz, aromatic), 7.65 (d, 1H, ^{3}J=8.4 Hz, H-3), 8.30 (d, 1H, ^{3}J=8.4 Hz, H-4); ^{13}C n.m.r. δ(CDCl$_3$): 22.0 (C-7), 32.7 (C-8), 38.5 (C-6), 117.6, 120.2 (C-3), 120.3 (q), 125.1 (C-4a), 129.6, 131.1, 135.5 (C-4), 147.5 (q), 162.2 (C-2), 163.0 (C-8a), 197.5 (C=O); m/z (%): 238 (M$^+$, 66), 237 (100), 154 (34), 130 (34), 91 (48).

2-(2-Azido)phenyl-7,8-dihydro-5(6H)quinolinone 10g.

To a solution of the **10f** (0.25 g, 1.05 mmol) in 2N HCl (6 ml) cooled at -5°C was added dropwise a solution of sodium nitrite (0.08 g, 1.15 mmol) in water (1 ml). After 90 min of stirring, a solution of sodium azide (0.082 g, 1.26 mmol) in water (1 ml) was added dropwise and stirring was continued for 2 h. Then a 2M solution of KOH (6 ml) was added and the mixture was extracted with diethyl ether (3x10 ml), and the organic layers were dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the residual material was purified by chromatography using a silica gel column with n-hexane/ AcOEt (1:1) and then recrystallized from n-hexane/dichloromethane (1:1) as eluent to give **10g** in 97% yield, as colourless prisms, m.p. 94-96°C; (Found: C, 67.99; H, 4.71; N, 21.03. $C_{15}H_{12}N_4O$ requires: C, 68.17; H, 4.58; N, 21.20); i.r. (nujol) 2126, 1672, 1582, 1297, 1128, 756 cm^{-1}; ^{1}H n.m.r. δ(CDCl$_3$): 2.21 (qn, 2H, ^{3}J=6.3 Hz, H-7), 2.70 (t, 2H, ^{3}J=6.6 Hz, H-6), 3.19 (t, 2H, ^{3}J=6.2 Hz, H-8), 7.24 (t, 1H, ^{3}J=7.1 Hz, aromatic), 7.25 (dd, 1H, ^{3}J=6.6 Hz, ^{4}J=0.3 Hz, aromatic), 7.45 (td, 1H, ^{3}J=7.8 Hz, ^{4}J=1.4 Hz, aromatic), 7.65 (d, 1H, ^{3}J=8.1 Hz, H-3), 7.69 (dd, 1H, ^{3}J=8.1 Hz, ^{4}J=1.7 Hz, aromatic), 8.29 (d, 1H, ^{3}J=8.4 Hz, H-4); ^{13}C n.m.r. δ(CDCl$_3$): 21.9 (C-7), 32.7 (C-8), 38.6 (C-6), 119.0, 123.5 (C-3), 125.2, 126.5 (C-4a), 130.6, 131.4 (q), 131.5, 134.9 (C-4), 137.6 (q), 159.5 (C-2), 163.5 (C-8a), 197.8 (C=O); m/z (%): 264 (M$^+$, 1), 236 (100), 207 (46), 181 (16).

6-Bromo-2-(2-nitro)phenyl-7,8-dihydro-5(6H)quinolinone 11.

To a solution of **10e** (0.1g, 0.37 mmol) in tetrahydrofurane (3 ml), Amberlyst-A26 Br$_3^-$ (0.29 g) was added. The resultant suspension was heated at reflux temperature for 3 h. After cooling, the resin was removed by filtration and the filtrate was concentrated to dryness. The residue was chromatographed on a silica gel column with dichloromethane as eluent to give **11** in 89% yield, as colourless prisms, m.p. 119-123°C; (Found: C, 51.75; H, 3.40; N, 7.98. $C_{15}H_{11}BrN_2O_3$ requires: C, 51.90; H, 3.19; N, 8.07); i.r. (nujol) 1692, 1586, 1271, 752 cm^{-1}; ^{1} Hn.m.r. δ(CDCl$_3$): 2.47-2.67 (m, 2H, H-7), 3.13 (dt, 1H, ^{1}J=18.0 Hz, ^{3}J=4.5 Hz, H-8), 3.44 (ddd, 1H, ^{1}J=18.0 Hz, ^{3}J=9.9 Hz, ^{3}J=5.3 Hz, H-8), 4.77 (t, 1H, ^{3}J=4.2 Hz, H-6), 7.51 (d, 1H, ^{3}J=8.1 Hz, H-3), 7.58-7.64 (m, 2H, aromatics), 7.71 (td, 1H, ^{3}J=7.5 Hz, ^{4}J=1.2 Hz, aromatic), 7.96 (dd, 1H, ^{3}J=8.1 Hz, ^{4}J=1.4 Hz, aromatic), 8.43 (d, 1H, ^{3}J=8.1 Hz, H-4); ^{13}C n.m.r. δ(CDCl$_3$): 28.9 (C-8), 30.3 (C-7), 49.1 (C-6), 121.6 (C-3), 124.6, 124.7 (C-4a), 130.1, 131.1, 132.7, 134.5 (q), 137.4 (C-4), 149.1 (q), 159.9 (C-2), 162.0 (C-8a), 190.0 (C=O); m/z (%): 348 (M$^+$+2, 1), 346 (M$^+$, 1), 208 (60), 193 (100), 165 (52), 127 (29).

5-Hydroxy-2-(2-nitro)phenylquinoline 12a.

A solution of compound **11** (0.14 g, 0.4 mmol) in 2,4,6-collidine (2 ml) was refluxed for 1 h. After cooling, the solution was extracted with diethyl ether (4x5 ml). The combined organic layers were washed with 15% HCl (5x5 ml), water (5x5 ml) and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the crude product was chromatographed on a silica gel column with n-hexane/ AcOEt (1:1) to give **12a** in 73% yield as colourless prisms m.p. 217-224°C; (Found: C, 67.82; H, 3.58; N, 10.76. $C_{15}H_{10}N_2O_3$ requires: C, 67.67; H, 3.79; N, 10.52); i.r. (nujol) 3300-2600, 1593, 1263, 1083, 727, 703 cm^{-1}; ^{1}H n.m.r. δ(DMSO-d^6): 7.00 (d, 1H, ^{3}J=7.5 Hz, H-6), 7.39 (d, 1H, ^{3}J=8.4 Hz, H-8), 7.60 (t, 1H, ^{3}J=8.1 Hz, H-7), 7.74 (td, 1H, ^{3}J=7.5 Hz, ^{4}J=1.8 Hz, aromatic), 7.75 (d, 1H, ^{3}J=9.0 Hz, H-3), 7.85 (t, 1H, ^{3}J=7.5 Hz, aromatic), 7.89 (dd, 1H, ^{3}J=7.8 Hz, ^{4}J=1.8 Hz, aromatic), 8.04 (d, 1H, ^{3}J=8.1 Hz, aromatic), 8.65 (d, 1H, ^{3}J=8.7 Hz, H-4), 10.63 (s, 1H, OH); ^{13}C n.m.r. δ(DMSO-d^6): 109.1 (C-6), 118.6 (C-4a), 119.3 (C-3), 119.4 (C-8), 124.5, 130.1, 130.7 (C-7), 131.4, 132.2 (C-4), 132.9, 134.5 (q), 148.4 (C-8a), 149.3 (q), 153.4 (C-5), 154.9 (C-2); m/z (%): 266 (M$^+$, 41), 236 (27), 190 (43), 95 (100).

5-Hydroxy-2-(2-amino)phenylquinoline 12b.

This compound was prepared in 80% yield from **12a** by the same method as described for preparation of **10f**: m.p. 195-198°C (yellow prisms from n-hexane/dichloromethane); (Found: C, 76.43; H, 4.99; N, 11.68. $C_{15}H_{12}N_2O$ requires: C, 76.25; H, 5.12; N, 11.86); i.r. (nujol) 3329, 3324, 3300-2600, 1597, 1237, 792, 762 cm^{-1}; ^{1}H n.m.r. δ(DMSO-d^6): 6.68 (td, 1H, ^{3}J=7.5 Hz, ^{4}J=1.8 Hz, aromatic), 6.87 (dd, 1H, ^{3}J=8.0 Hz, ^{4}J=0.9 Hz, aromatic), 6.95 (dd, 1H, ^{3}J=7.2 Hz, ^{4}J=1.3 Hz, H-6), 7.17 (td, 1H, ^{3}J=7.6 Hz, ^{4}J=1.2 Hz, aromatic), 7.20 (s, 2H, NH$_2$), 7.46-7.61 (m, 2H, H-7 and H-8), 7.79 (dd, 1H, ^{3}J=8.1 Hz, ^{4}J=1.3 Hz, aromatic), 7.95 (d, 1H, ^{3}J=9.1 Hz, H-3), 8.56 (d, 1H, ^{3}J=9.0 Hz, H-4), 10.50 (s, 1H, OH); ^{13}C n.m.r. δ(DMSO-d^6): 108.4 (C-6), 115.6, 116.7, 117.2 (q), 118.5 (C-3), 118.8 (C-8), 119.2 (C-4a), 129.4, 130.1, 130.2 (C-7), 131.3 (C-4), 147.4 (q), 148.6 (C-8a), 153.2 (C-5), 158.9 (C-2); m/z (%): 236 (M$^+$, 59), 235 (100), 206 (12), 118 (7), 103 (7).

2-(2-Triphenylphosphoranylidenamino)phenyl-7,8-dihydro-5(6H)quinolinone 13.

This compound was prepared in 91% yield from **10g** by the same method as described for the preparation of vinyliminophosphoranes **7**, **8** and **19**: m.p. 228°C (yellow prisms from n-hexane/dichloromethane); (Found: C, 79.37; H, 5.27; N, 5.86. $C_{33}H_{27}N_2OP$ requires: C, 79.50; H, 5.46; N, 5.62); i.r. (nujol) 1678, 1582, 1435, 1340, 1109, 743, 721, 692 cm^{-1}; ^{1}H n.m.r. δ(CDCl$_3$): 2.22 (qn, 2H, ^{3}J=6.2 Hz, H-7), 2.71 (t, 2H, ^{3}J=6.4 Hz, H-6), 3.21 (t, 2H, ^{3}J=6.0 Hz, H-8), 6.55 (d, 1H, ^{3}J=7.9 Hz, aromatic), 6.77 (t, 1H, ^{3}J=7.7 Hz, aromatic), 6.92 (td, 1H, ^{3}J=7.6 Hz, ^{4}J=1.5 Hz, aromatic), 7.41-7.55 (m, 9H, H$_m$ and H$_p$), 7.64-7.73 (m, 7H, H$_o$ and aromatic), 8.22 (d, 1H, ^{3}J=8.3 Hz, H-3), 8.43 (d, 1H, ^{3}J=8.3 Hz, H-4); ^{13}C n.m.r. δ(CDCl$_3$): 22.2 (C-7), 32.9 (C-8), 38.7 (C-6), 117.9, 122.7 (J_{P-C}=11.1 Hz), 124.8 (C-3), 125.3 (C-4a), 128.6 ($^3J_{P-C}$=12.1 Hz, C$_m$), 129.6, 130.8 ($^1J_{P-C}$=97.0 Hz, C$_i$), 131.1 (J_{P-C}=2.0 Hz), 131.7 ($^4J_{P-C}$=2.8 Hz, C$_p$), 132.5 ($^2J_{P-C}$=9.9 Hz, C$_o$), 132.8 (C-4), 133.3 (J_{P-C}=22.0 Hz, q), 149.4 (q), 163.2 (C-8a), 164.1 (C-2), 198.6 ($^6J_{P-C}$=1.7 Hz, C=O); m/z (%): 498 (M$^+$, 100), 497 (28), 421 (20), 352 (11), 262 (7), 183 (42).

1,2-Dihydro-3*H*-indazolo[2,3-*a*]quinolin-4-one 14.

A solution of **10g** (0.18g, 0.68 mmol) in dry toluene (10 ml) was refluxed for 12 h. After cooling, the solvent was removed under reduced pressure and the residue was recrystallized from n-hexane/dichloromethane (1:1) to give **14** in 94% yield, as yellow prisms, m.p. 221°C; (Found: C, 76.41; H, 5.23; N, 11.05. $C_{15}H_{12}N_2O$ requires: C, 76.25; H, 5.12; N, 11.86); i.r. (nujol) 1668, 1638, 1296, 755, 739, 729 cm^{-1}; ^{1}H n.m.r. δ(CDCl$_3$): 2.37 (qn, 2H, ^{3}J=6.9 Hz, H-2), 2.77 (t, 2H, ^{3}J=6.6 Hz, H-3), 3.62 (t, 2H, ^{3}J=6.3 Hz, H-1), 7.22 (ddd, 1H, ^{3}J=8.3 Hz, ^{3}J=6.9 Hz, ^{4}J=0.8 Hz, H-8), 7.57 (ddd, 1H, ^{3}J=8.7 Hz, ^{3}J=6.8 Hz, ^{4}J=1.1Hz, H-9), 7.86 (dt, 1H, ^{3}J=8.7 Hz, ^{4}J=0.8 Hz, H-10), 7.90 (d, 1H, ^{3}J=9.0 Hz, H-5), 7.99 (d, 1H, ^{3}J=9.3 Hz, H-6), 8.01 (dt, 1H, ^{3}J=8.4 Hz, ^{4}J=1.1 Hz, H-7); ^{13}C n.m.r. δ(CDCl$_3$): 21.1 (C-2), 25.1 (C-1), 37.5 (C-3), 115.3 (C-6), 115.6 (C-4a), 116.2 (C-10), 118.8 (C-5), 120.2 (C-7), 120.8 (C-8), 122.0 (C-6b), 129.4 (C-9), 136.6 (C-10a), 146.1 (C-1a), 151.1 (C-6a), 196.1 (C=O); m/z (%): 236 (M$^+$, 100), 235 (23), 207 (78), 180 (22).

General Procedure for the Preparation of 5,6-Dihydro-8(7H)quinolinones 16.

A solution of the vinyliminophosphorane **8** (0.5 g, 1.35 mmol) and the appropriate α,β-unsaturated aldehyde **15** (2 mmol) in dry toluene (10 ml) was heated at reflux temperature for 24 h. After cooling, the solvent was removed under reduced pressure and the crude product was chromatographed on a silica gel column with AcOEt as eluent to give **16**.

Compound 16a (R=H): (52%), oil; (Found: C, 73.27; H, 6.32; N, 9.39. C_9H_9NO requires: C, 73.45; H, 6.16; N, 9.52); i.r. (neat) 1692, 1296, 1198, 1036, 820, 802 cm^{-1}; ^{1} Hn.m.r. δ(CDCl$_3$): 2.14 (qn, 2H, ^{3}J=6.4 Hz, H-6), 2.75 (t, 2H, ^{3}J=6.6 Hz, H-7), 2.97 (t, 2H, ^{3}J=6.1 Hz, H-5), 7.33 (ddd, 1H, ^{3}J=7.9 Hz, ^{3}J=4.5 Hz, H-3), 7.60 (d, 1H, ^{3}J=7.7 Hz, H-4), 8.65 (dd, 1H, ^{3}J=4.4 Hz, ^{4}J=0.9 Hz, H-2); ^{13}C n.m.r. δ(CDCl$_3$): 22.7 (C-6), 29.2 (C-5), 39.7 (C-7), 127.0 (C-3), 137.8 (C-4), 140.8 (C-4a), 148.1 (C -8a), 149.1 (C-2), 189.5 (C=O); m/z (%): 147 (M$^+$, 81), 118 (53), 93 (37), 91 (100).

Compound 16b (R=CH$_3$): (54%), oil; (Found: C, 74.27; H, 7.03; N, 8.92. $C_{10}H_{11}NO$ requires: C, 74.51; H, 6.88; N, 8.69); i.r. (neat) 1696, 1599, 1223, 1202, 1037, 727 cm^{-1}; ^{1}H n.m.r. δ(CDCl$_3$): 2.09 (qn, 2H, ^{3}J=6.4 Hz, H-6), 2.31 (s, 3H, Het-CH_3), 2.69 (t, 2H, ^{3}J=6.6 Hz, H-7), 2.91 (t, 2H, ^{3}J=6.0 Hz, H-5), 7.37 (s, 1H, H-4), 8.43 (s, 1H, H-2); ^{13}C n.m.r. δ(CDCl$_3$): 18.6 (Het-CH_3), 22.6 (C-6), 29.0 (C-5), 39.5 (C-7), 137.4 (C-4), 137.5 (C-3), 140.4 (C-4a), 145.9 (C-8a), 149.9 (C-2), 196.7 (C=O); m/z (%): 161 (M$^+$, 58), 132 (28), 107 (29), 105 (100).

General Procedure for the Preparation of 4-Aryl-1-azaanthraquinones 20.

A mixture of iminophosphorane **19** (0.25 g, 0.58 mmol) the appropriate α,β-unsaturated aldehyde **9** (0.70 mmol) in nitrobenzene (5 ml) was heated at reflux temperature for 3 h. The solvent was removed under reduced pressure and the residue was chromatographed on a silica gel column with diethyl ether as eluent to give **20** which were recrystallized from n-hexane/dichloromethane (1:1).

Compound 20a (X=H): (55%), m.p. 216-218°C (colourless prisms from n-hexane/ dichloromethane); (Found: C, 80.15; H, 4.00; N, 4.82. $C_{19}H_{11}NO_2$ requires: C, 79.99; H, 3.89; N, 4.91); i.r. (nujol) 1688, 1298, 1286, 721, 706 cm^{-1}; ^{1}H n.m.r. δ(CDCl$_3$): 7.27-7.34 (m, 2H, aromatics), 7.48-7.53 (m, 4H, H-3 and aromatics), 7.77-7.81 (m, 2H, H-6 and H-7), 8.10-8.15 (m, 1H, H-5), 8.35-8.40 (m, 1H, H-8), 9.05 (d, 1H, ^{3}J=4.8 Hz, H-2); ^{13}C n.m.r. δ(CDCl$_3$): 127.4 (C-3), 127.5 (C-5), 127.7, 128.3, 128.4 (C-8), 130.6, 130.7 (C-4a), 132.6 (q), 133.8 (q), 134.3, 134.7, 139.1 (q), 150.2 (C-4), 152.7 (C-10a), 153.6 (C-2), 181.7 (C=O), 182.9 (C=O); m/z (%): 285 (38), 284 (62), 126 (17), 76 (100).

Compound 20b (X=2-OCH$_3$): (45%), m.p. 187-189°C (colourless prisms from n-hexane/ dichloromethane); (Found: C, 76.42; H, 3.99; N, 4.29. $C_{20}H_{13}NO_3$ requires: C, 76.18; H, 4.16; N, 4.44); i.r. (nujol) 1680, 1593, 1290, 1242, 754, 722 cm^{-1}; ^{1}H n.m.r. δ(CDCl$_3$): 3.57 (s, 3H, OCH_3), 6.89 (d, 1H, ^{3}J=8.1 Hz, aromatic), 7.01 (t, 1H, ^{3}J=7.5 Hz, aromatic), 7.14 (dd, 1H, ^{3}J=7.2 Hz, ^{4}J=0.9 Hz, aromatic), 7.37 (td, 1H, ^{3}J=7.5 Hz, ^{4}J=0.9 Hz, aromatic), 7.42 (d, 1H, ^{3}J=4.8 Hz, H-3), 7.67-7.71 (m, 2H, H-6 and H-7), 8.01-8.04 (m, 1H, H-5), 8.26-8.29 (m, 1H, H-8), 8.97 (d, 1H, ^{3}J=4.5 Hz, H-2); ^{13}C n.m.r. δ(CDCl$_3$): 55.3 (OCH_3), 110.5, 120.9, 127.0 (C-3), 127.4 (C-5), 128.3 (q), 128.4 (C-8), 129.6 (C-4a), 130.1, 130.7, 132.7 (q), 133.9 (q), 134.0, 134.5, 148.7 (C-4), 149.3 (C-10a), 153.7 (C-2), 155.7 (q), 181.9 (C=O), 182.9 (C=O); m/z (%): 315 (14), 285 (20), 284 (100), 256 (4), 76 (4).

Compound 20c (X=2-CH$_3$): (46%), m.p. 213-214°C (colourless prisms from n-hexane/ AcOEt); (Found: C, 80.37; H, 4.54; N, 4.47. $C_{20}H_{13}NO_2$ requires: C, 80.25; H, 4.38; N, 4.68); i.r. (nujol) 1685, 1593, 1300, 752, 721 cm^{-1}; ^{1}H n.m.r. δ(CDCl$_3$): 2.04 (s, 3H, Ar-CH_3), 7.07 (dd, 1H, ^{3}J=7.8 Hz, ^{4}J=1.2 Hz, aromatic), 7.31-7.43 (m, 3H, aromatics), 7.48 (d, 1H, ^{3}J=4.8 Hz, H-3), 7.77-7.84 (m, 2H, H-6 and H-7), 8.11-8.15 (m, 1H, H-5), 8.38-8.43 (m, 1H, H-8), 9.10 (d, 1H, ^{3}J=4.8 Hz, H-2) ; ^{13}C n.m.r. δ(CDCl$_3$): 20.0 (Ar-CH_3), 126.0, 126.9, 127.5 (C-3), 127.6 (C-5), 128.4 (C-8), 128.5 (C-4a), 129.9, 130.5, 132.8 (q), 133.6 (q), 134.3 (q), 134.4, 134.7, 139.1 (q), 150.1 (C-4), 152.4 (C-10a), 153.9 (C-2), 181.9 (C=O), 182.9 (C=O); m/z (%): 299 (M$^+$, 36), 298 (14), 285 (23), 283 (100), 282 (23), 270 (9), 254 (9).

Compound 20d (X=4-Cl): (48%), m.p. 225-228°C (colourless prisms from n-hexane/ AcOEt); (Found: C, 71.54; H, 3.02; N, 4.17. $C_{19}H_{10}ClNO_2$ requires: C, 71.37; H, 3.15; N, 4.38); i.r. (nujol) 1687, 1668, 1595, 1300, 1260, 819, 803, 724 cm^{-1}; ^{1}H n.m.r. δ(CDCl$_3$): 7.18 (d, 2H, ^{3}J=8.3 Hz, aromatics), 7.38 (d, 2 H, ^{3}J=7.2 Hz, aromatics), 7.41 (d, 1H, ^{3}J=4.5 Hz, H-3), 7.71-7.75 (m, 2H, H-6 and H-7), 8.02-8.07 (m, 1H, H-5), 8.28-8.32 (m, 1H, H-8), 8.98 (d, 1H, ^{3}J=4.8 Hz, H-2) ; ^{13}C n.m.r. δ(CDCl$_3$): 127.4 (C-3), 127.6 (C-5), 128.2 (C-4a), 128.6, 129.2, 130.4 (C-8), 132.6 (q), 133.7 (q), 134.5, 134.7 (q), 134.8, 137.5 (q), 150.2 (C-4), 151.4 (C-10a), 153.7 (C-2), 181.5 (C=O), 183.0 (C=O); m/z (%): 321 (M$^+$+2, 29), 320 (47), 319 (M$^+$, 68), 318 (100), 284 (45), 227 (51), 200 (31), 76 (20).

Compound 20e (X=2-NO$_2$): (56%), m.p. 245-250°C (colourless prisms from n-hexane/ dichloromethane); (Found: C, 68.90; H, 2.93; N, 8.66. $C_{19}H_{10}N_2O_4$ requires: C, 69.09; H, 3.05; N, 8.48); i.r. (nujol) 1673, 1520, 1345, 1295, 724 cm^{-1}; ^{1}H n.m.r. δ(CDCl$_3$): 7.28 (dd, 1H, ^{3}J=7.4 Hz, ^{4}J=1.4 Hz, aromatic), 7.47 (d, 1H, ^{3}J=4.8 Hz, H-3), 7.65-7.83 (m, 4H, H-6 and H-7 and aromatics), 8.03 (dd, 1H, ^{3}J=7.5

Hz, ^4J=1.2 Hz, aromatic), 8.35 (td, 2H, ^3J=7.5 Hz, ^4J=1.1 Hz, H-5 and H-8), 9.12 (d, 1H, ^3J=5.1 Hz, H-2) ; ^{13}C n.m.r. δ($CDCl_3$): 124.7, 127.3 (C-3), 127.5 (C-5), 128.5 (C-8), 129.3, 129.8, 129.9 (C-4a), 132.6 (q), 133.0 (q), 133.9, 134.6, 134.7, 135.2 (q), 146.7 (q), 149.4 (C-4), 149.5 (C-10a), 154.2 (C-2), 181.3 (C=O), 183.0 (C=O); m/z (%): 330 (M^+, 1), 285 (15), 284 (65), 129 (100), 102 (21).

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