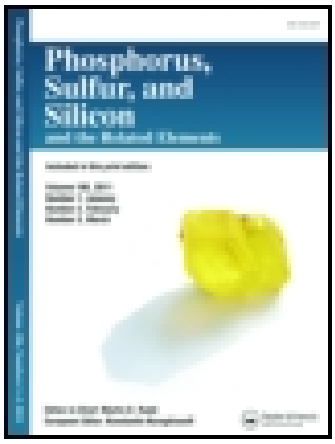

Phosphorus, Sulfur, and Silicon and the Related Elements

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SYNTHESIS, SPECTROSCOPIC STUDIES, AND X-RAY CRYSTAL STRUCTURE OF N-HETERYLIMINOPHOSPHORANES

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SYNTHESIS, SPECTROSCOPIC STUDIES, AND X-RAY CRYSTAL STRUCTURE OF N-HETERYLIMINOPHOSPHORANES

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N-[2-(α-Bromoacetyl)phenyl]imides (prepared in two steps from 2-aminoacetophenone) gave, upon treatment with sodium azide, fused azidoquinolines via an intramolecular cyclization. Reaction of the above azides with phosphines gave N-heteryliminophosphoranes. The IR, ^{1}H-, ^{13}C-, and ^{31}P-NMR and MS spectra of these compounds as well as the x-ray crystal structure of two of them is reported.

Keywords: 2-Aminoacetophenone; acid anhydrides; azides; iminophosphoranes; quinoline

Iminophosphoranes (phosphine imines) have been known for almost a century. They have been mostly prepared by either of two methods, reaction of phosphines with azides (Staudinger reaction) or reaction of primary amines with phosphine dihalides in the presence of a suitable base. The first method is the easiest and the most commonly used method for the preparation of these types of compounds. Nowadays, the most important application of iminophosphoranes is their use in the synthesis of nitrogen heterocyclic compounds via the inter- and intramolecular aza-Wittig reactions. A large number of nitrogen-containing heterocycles have been prepared using these reactions.[1–8] We have previously reported the use of iminophosphoranes via the aza- and bis-aza-Wittig reactions for the synthesis of heterocyclic systems such as imidazole, benzimidazole, perimidine, isoindole, and other systems.[9–11]

In the majority of the previous reports, iminophosphoranes were not isolated but rather used as intermediates in the aza-Wittig reactions.

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One of the difficulties in isolating them is that they are very susceptible to hydrolysis to give the corresponding amines and phosphine oxides. The cases were they have been isolated and fully characterized are scattered throughout the literature.[8,12–20]

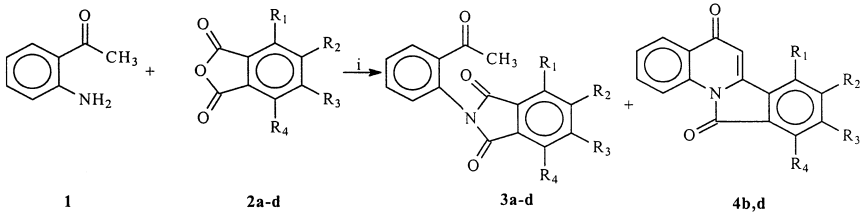
In a previous work we observed that N-heteryliminophosphoranes were stable to a degree that they did not hydrolyze or react under the aza-Wittig conditions.[21] Herein we report some further investigation on the synthesis and x-ray crystal structure of new derivatives of N-heteryliminophosphoranes.

RESULTS AND DISCUSSION

The imides **3a–d** were readily prepared by condensation of 2-aminoacetophenone with acid anhydrides (Scheme 1). In cases **2b** and **2d** where 3-nitro- and 3,4,5,6-tetrachlorophthalic anhydrides were used, the fused quinoline derivatives **4b** and **4d** were obtained along with **3b** and **3d** respectively. Percentages of **4b** and **4d** were dependent on the concentration of the base and reaction temperature. Increasing these two factors increases the percentages of **4b** and **4d**. Bromination of **3a–d** with copper bromide gave **5a–d**. These compounds showed in their ^{1}H-NMR spectra signals at about δ 4.50 ppm for the methylene group. Cyclization of **5a–d** with sodium azide gave the 6-azidoisoindolo[2,1-a]quinoline ring system **6a–d**. As it has been observed by Alkhathlan and Al-Farhan[21] and others,[22] reaction of the bromo derivatives **5a–d** with sodium azide did not give substitution products that would be the azido analogs of **5a–d** but gave instead the cyclized products **6a–d**. Although our attempts to isolate the azido analogs of **5a–d** by running the reaction at room temperature failed, it seems to be reasonable to assume that the conversion of **5a–d** to **6a–d** proceeds in a substitution step first followed by cyclization.

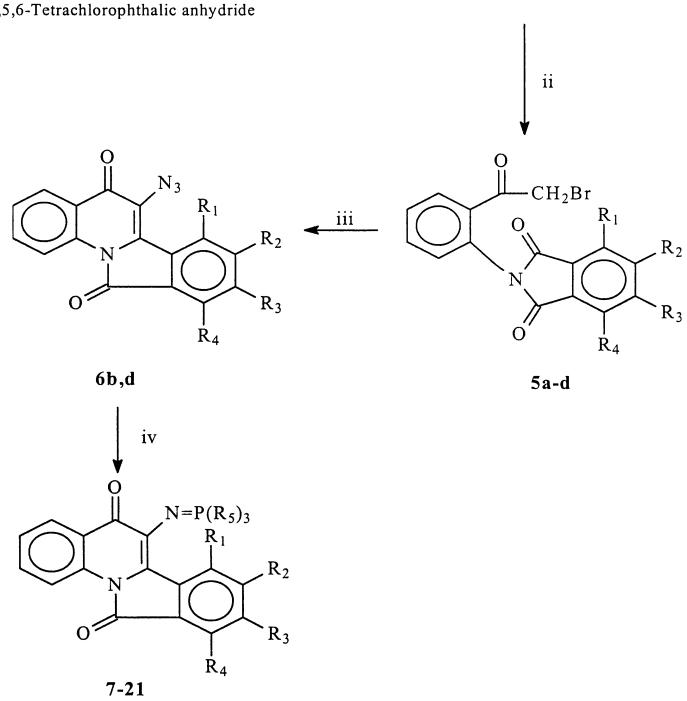
Structures of **6a–d** were confirmed by their IR, NMR, and MS spectra. Their IR spectra showed an absorbance for the azido group at about 2120 cm^{-1}, while the two carbonyl groups appeared as two absorption bands at about 1745 and 1620 cm^{-1}. Their ^{1}H- and ^{13}C-NMR spectra did not show any aliphatic signals. The position carrying the azido group (C_6) appeared in the ^{13}C-NMR at about δ 117 ppm. The MS spectra of the azido derivatives **6a–d** showed very weak molecular ions. They tend to lose N_2 very easily to give fragments at (M^+-28) with high intensities. Other main fragmentation pathways are loss of 2CO and the NO_2 group in **6b** and **6c**.

A point worth mentioning here is that although the cyclization of **5b** and **5c** could give two products depending on the position of the nitro



1 **2a-d** **3a-d** **4b,d**

2a, Phthalic anhydride
2b, 3-Nitrophthalic anhydride
2c, 4-Nitrophthalic anhydride
2d, 3,4,5,6-Tetrachlorophthalic anhydride



6b,d **5a-d** **7-21**

Conditions: i: xylene, Et_3N, reflux; ii: $CuBr_2$, EtOAc, $CHCl_3$, reflux; iii: NaN_3, H_2O, acetone; iv: $(R_5)_3P$, THF, reflux.

SCHEME 1

group in the cyclized products (**5b** could give **6b** and another product were the NO_2 group is in position 7 while **5c** could give **6c** and another product were the NO_2 group is in position 8), only **6b** and **6c** were obtained. Their structures were confirmed based upon the structures of their iminophosphorane derivatives **14** and **18** respectively.

TABLE I Iminophosphorane Derivatives **7–21**

R_1	R_2	R_3	R_4	R_5	Compound
H	H	H	NO_2	Phenyl	**7**
H	H	NO_2	H	Phenyl	**8**
H	H	H	H	*p*-Tolyl	**9**
H	H	H	NO_2	*p*-Tolyl	**10**
H	H	NO_2	H	*p*-Tolyl	**11**
Cl	Cl	Cl	Cl	*p*-Tolyl	**12**
H	H	H	H	Benzyl	**13**
H	H	H	NO_2	Benzyl	**14**
H	H	NO_2	H	Benzyl	**15**
Cl	Cl	Cl	Cl	Benzyl	**16**
H	H	H	NO_2	Cyclohexyl	**17**
H	H	NO_2	H	Cyclohexyl	**18**
H	H	H	NO_2	Butyl	**19**
H	H	NO_2	H	Butyl	**20**
H	H	H	NO_2	Methoxy	**21**

Treatment of the azides **6a–d** with a variety of phosphines (Table I) resulted in the formation of the iminophosphoranes **7–21** in very good yields. Structures of these compounds were confirmed by their IR, ^{1}H-, ^{13}C-, and ^{31}P-NMR, MS, and x-ray crystallography. The IR spectra of **7–21** showed absorbances for the C_5 and C_{11} carbonyl groups at about 1620 and 1720 cm^{-1} respectively. The ^{1}H-NMR spectra of compounds **13–16** showed signals for the benzylic CH_2 groups in the range δ 3.40-3.57 ppm as doublets with J = 13.50–14.28 Hz as a result of the coupling with the phosphorous nuclei. This coupling was not as clear in compounds **17–20**, the signals appeared as multiplets because of coupling with other adjacent protons. A three-bond coupling could be observed between the phosphorous nuclei and protons of the methoxy group in **21**. The signal for the methoxy group in the latter compound appeared as doublet with J = 11.72 Hz.

The ^{13}C-NMR spectra of compounds **7–21** showed signals for the two carbonyl groups in the range δ 160–180 ppm, the heterocyclic ring system between δ 117–146 ppm and the R_5 groups depending on its nature. The signal for the ketonic carbonyl group at C_5 in all the above compounds was split by the phosphorous nuclei via a three-bond coupling with J = 33–42 Hz. The C_1 of the R_5 group attached to the phosphorous was also split to doublet with coupling constants varying depending on whether it has an aliphatic or aromatic character. As was the case in ^{1}H-NMR, the ^{13}C-NMR spectrum of compound **21** showed the signal for the methoxy group split into a doublet with J = 27.56 Hz. Table II shows the IR absorbances for the N=P and ^{13}C-NMR chemical shifts and coupling constants for the C_1 of the R_5 group attached to the phosphorous

TABLE II Selected IR, ^{13}C- and ^{31}P-NMR Data for Compounds **7–21**

Compound	IR N=P	^{13}C-NMR (J, Hz)		^{31}P-NMR
		P–C	C_5	
7	1438	128.50 (48.92)	177.38 (33.64)	19.34
8	1436	128.54 (48.96)	177.32 (36.72)	19.79
9	1440	128.77 (52.00)	173.10 (42.84)	22.72
10	1445	129.08 (52.00)	177.31 (33.64)	19.16
11	1435	129.14 (52.01)	177.28 (33.64)	19.66
12	1457	129.11 (59.02)	180.27 (33.74)	15.26
13	1435	35.22 (241.60)	174.52 (39.50)	31.81
14	1446	36.47 (241.61)	179.45 (36.68)	26.19
15	1420	36.52 (241.64)	179.34 (36.68)	23.62
16	1453	35.38 (238.56)	179.25 (36.86)	23.62
17	1445	39.16 (235.52)	178.75 (33.64)	36.39
18	1439	39.16 (232.44)	175.72 (33.69)	37.14
19	1443	28.47 (256.92)	179.25 (33.64)	32.64
20	1435	29.62 (256.95)	179.63 (33.63)	32.67
21	1466	55.13 (27.56) (P–O–C)	177.90 (33.64)	9.71

(P–C) and the ketonic carbonyl group (C_5) in addition to the ^{31}P-NMR signals for compounds **7–21**. The rest of the spectroscopic data is shown in the experimental section.

The MS spectra of the iminophosphoranes **7–21** showed molecular ions agreeing with the expected molecular weights. Compounds originating from the acid anhydrides **2b** and **2c** (i.e., **7**, **8**, **10**, **11**) have very stable molecular ions which in some cases represent the base peak. The main fragmentation pathways are the consequent loss of the three R_5 groups or the complete loss of the iminophosphorane moiety.

Structures of the iminophosphoranes **14** and **18** are confirmed using x-ray crystallography. Figures 1 and 2 show the crystal structures of **14** and **18** respectively. Relevant crystallographic data are summarized in Table III while selected geometrical parameters are given in Table IV.

EXPERIMENTAL

Melting points are uncorrected. IR spectra were recorded on a Perkin-Elmer 883 spectrophotometer as KBr pellets and expressed as ν in cm^{-1}. NMR spectra were recorded on JEOL ECP 400 (400 MHz) in $CDCl_3$ and chemical shifts are expressed as δ in ppm. MS spectra were recorded on Shimadzu QP 5050A GC/MS system. Microanalysis was performed at KACST Research Laboratories.

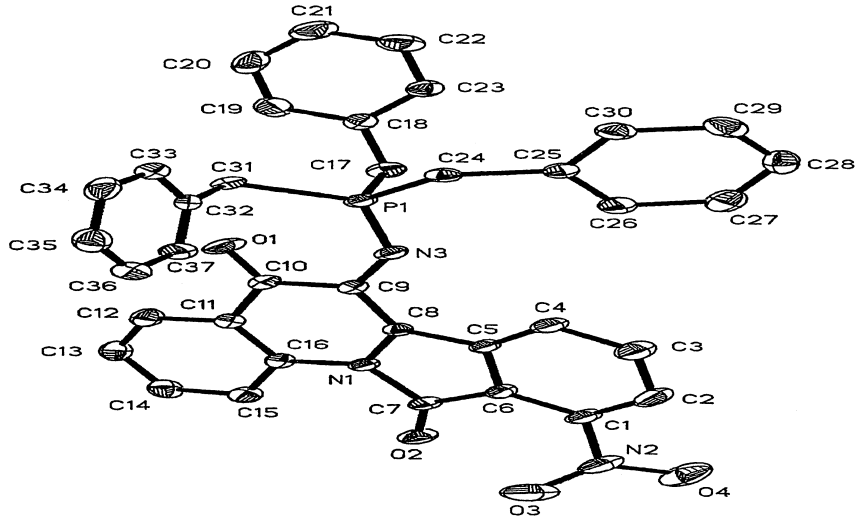


FIGURE 1 X-ray crystal structure of **14**.

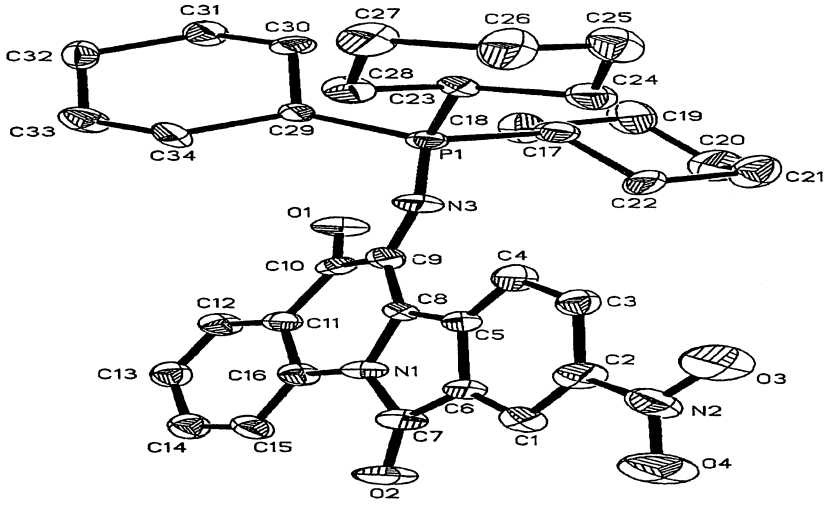


FIGURE 2 X-ray crystal structure of **18**.

TABLE III Crystal Data, Intensity Data Collection Parameters, and Structure Refinement Results for **14** and **18**

	18	**14**
Crystal data		
Chemical formula	$C_{34}H_{40}N_3O_4P$	$C_{37}H_{28}N_3O_4P$
Formula weight	585.66	609.59
Colour of crystal	Red	Red
Size of specimen (mm)	$0.20 \times 0.20 \times 0.10$	$0.36 \times 0.24 \times 0.22$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	18.716(1)	10.9239(1)
b (Å)	10.869(1)	16.3707(3)
c (Å)	16.059(1)	17.2625(3)
β (°)	114.320(6)	99.094(1)
V (Å^3)	2976.9(4)	3048.28(8)
Z	4	4
$D_{calc.}$ (g cm^{-3})	1.307	1.328
μ (Mo-K$_\alpha$) (mm^{-1})	0.255	0.137
F(000)	1248	1272
Data collection		
Diffractometer	Siemens P4	Siemens SMART CCD
Radiation, λ (Å)	Mo-K$_\alpha$, 0.71073	Mo-K$_\alpha$, 0.71073
Monochromator	Graphite	Graphite
Range of h, k, l	$-20 \le h \ge 18$, $-11 \le k \ge 1$, $-1 \le l \ge 17$	$-12 \le h \ge 12$, $-19 \le k \ge 15$, $-18 \le l \ge 20$
No. of independent reflections	4855	5338
R_{int}	0.0427	0.1507
No. of observed reflections	2083	3008
Cut-off criteria	$F_o > 4\sigma(F_o)$	$F_o > 4\sigma(F_o)$
Absorption corrections	Non	Non
Structure refinement		
Refinement on	F^2	F^2
$R[F > 4\sigma(F)]$	0.0524	0.0617
$wR(F^2)$	0.0981	0.1252
w	$1/[\sigma^2(F_0^2) + (0.0524P)^2 + 0.0P]$ where $P = (F_0^2 + 2F_c^2)/3$	$1/[\sigma^2(F_0^2) + (0.0003P)^2 + 0.0P]$ where $P = (F_0^2 + 2F_c^2)/3$
S	0.998	0.861
No. of independent reflections	4440	5325
No. of parameters refined	380	407
$\Delta\rho$ (e Å^{-3})	0.189, −0.254	0.416, −0.637

TABLE IV Selected Geometrical Parameters. Lengths (Å) and Angles (°) for **14** and **18**

	18	**14**
Bond lengths		
P(1)—C(23)	1.831 (4)	
P(1)—C(29)	1.829 (4)	
P(1)—C(24)		1.825 (3)
P(1)—C(31)		1.838 (3)
P(1)—C(17)	1.846 (4)	1.847 (3)
P(1)—N(3)	1.586 (3)	1.593 (2)
N(3)—C(9)	1.346 (5)	1.375 (3)
C(10)—O(1)	1.241 (4)	1.243 (3)
C(7)—O(2)	1.209 (5)	1.212 (3)
N(2)—O(3)	1.223 (5)	1.234 (4)
N(2)—O(4)	1.223 (5)	1.217 (4)
N(2)—C(2)	1.471 (5)	
N(2)—C(1)		1.471 (4)
C(9)—C(8)	1.382 (5)	1.389 (3)
C(8)—C(5)	1.441 (6)	1.458 (3)
C(5)—C(6)	1.401 (5)	1.402 (4)
C(6)—C(7)	1.468 (6)	1.497 (4)
N(1)—C(7)	1.429 (5)	1.424 (3)
N(1)—C(8)	1.408 (5)	1.417 (3)
N(1)—C(16)	1.396 (5)	1.411 (3)
C(16)—C(11)	1.400 (5)	1.411 (4)
C(11)—C(10)	1.464 (6)	1.481 (4)
C(10)—C(9)	1.464 (6)	1.491 (4)
Bond angles		
N(3)—P(1)—C(17)	114.2 (2)	114.7 (1)
N(3)—P(1)—C(23)	103.3 (2)	104.6 (1)
N(3)—P(1)—C(29)	119.3 (2)	119.6 (1)
P(1)—N(3)—C(9)	133.5 (3)	131.8 (2)
N(3)—C(9)—C(8)	120.8 (4)	119.7 (2)
N(3)—C(9)—C(10)	123.5 (4)	123.6 (2)
C(8)—C(9)—C(10)	115.7 (4)	116.7 (3)
O(1)—C(10)—C(9)	119.6 (4)	119.7 (3)
O(1)—C(10)—C(11)	122.0 (4)	121.7 (3)
C(9)—C(10)—C(11)	118.4 (4)	118.6 (2)
O(2)—C(7)—N(1)	125.9 (4)	126.1 (3)
O(2)—C(7)—C(6)	129.6 (4)	129.1 (3)
N(1)—C(7)—C(6)	104.6 (4)	104.8 (2)
O(3)—N(2)—O(4)	123.2 (4)	124.4 (3)
Torsion angles		
C(17)—P(1)—N(3)—C(9)	−75.4 (4)	66.5 (3)
C(23)—P(1)—N(3)—C(9)	171.5 (4)	175.8 (2)
C(29)—P(1)—N(3)—C(9)	52.9 (5)	62.3 (3)
C(24)—P(1)—N(3)—C(9)		175.8 (2)
C(31)—P(1)—N(3)—C(9)		62.3 (3)

N-(2-Acetylphenyl)phthalimide, **3a**: A solution of 10.0 g (74.0 mmol) of 2-aminoacetophene (**1**), 13.1 g (88.5 mmol) of phthalic anhydride (**2a**) and 2 mL of triethylamine in 350 mL of xylene was refluxed for 5 h. The resulting solid was collected and recrystallized from ethanol. Yield, 90%, colorless solid, m.p. 134°C (136°C).[23]

N-(2-Acetylphenyl)-3-nitrophthalimide, **3b**; 10-Nitro-5H,11H-isoindolo [2,1-a]quinoline-5,11-dione, **4b**: These two compounds were obtained from (**1**) and 3-nitrophthalic anhydride (**2b**) in a procedure similar to that described for (**3a**). Compound (**4b**) was obtained from the filtrate of (**3b**). **3b**, 52% yield, pale yellow solid, m.p. 185°C (184°C).[23] **4b**, 30% yield, yellow solid, m.p. 231°C (233°C).[23]

N-(2-Acetylphenyl)-4-nitrophthalimide, **3c**: This compound was obtained from (**1**) and 4-nitrophthalic anhydride (**2d**) in a procedure similar to that described for (**3a**). 93% yield, yellow solid, m.p. 139°C; IR: 1784, 1719, 1620. ^{1}H-NMR: 2.58 (s, 3H), 7.45–8.72 (m, 7H); MS: m/z (%) 310 (M^+, 23), 295 (100), 249 (48), 193 (10), 164 (10), 75 (25). *Anal. Calcd*. for $C_{16}H_{10}N_2O_5$: C, 61.93; H, 3.22; N, 9.03. Found: C, 61.75; H, 3.28; N, 8.91.

N-(2-Acetylphenyl)-3,4,5,6-tetrachlorophthalimide, **3d**; 7,8,9,10-Tetrachloro-5H,11H-isoindolo[2,1-a]quinoline-5,11-dione, **4d**: These two compounds were obtained from (**1**) and 3,4,5,6-tetrachlorophthalic anhydride (**2d**) in a procedure similar to that described for (**3b**) and (**4b**). **3d**, 88% yield, pale yellow solid, m.p. 219°C; IR: 1785, 1715, 1685. ^{1}H-NMR: 2.59 (s, 3H), 7.64–7.93 (m, 4H). MS: m/z (%) 407 (M^{+6}, 3), 405 (M^{+4}, 9.5), 403 (M^{+2}, 21), 401 (M^+, 16), 388 (100), 360 (22), 214 (12), 90 (16). *Anal. Calcd*. for $C_{16}H_7Cl_4NO_3$: C, 47.64; H, 1.73; N, 3.47. Found: C, 47.60; H, 1.69; N, 3.40. **4d**, 8% yield, yellow solid, m.p. 316°C; IR: 1733, 1633. ^{1}H-NMR: 6.95 (s, 1H), 7.20–7.80 (m, 4H). MS: m/z (%) 389 (M^{+6}, 11), 387 (M^{+4}, 48), 385 (M^{+2}, 97), 383 (M^+, 78), 357 (100), 292 (24), 178 (35), 111 (15), 91 (8). *Anal. Calcd*. for $C_{16}H_5Cl_4NO_2$: C, 49.87; H, 1.30; N, 3.63. Found: C, 49.71; H, 1.26; N, 3.72.

N-[2-(α-Bromoacetyl)phenyl]phthalimide, **5a**: A solution of 5.0 g (22.3 mmol) of $CuBr_2$ in 200 mL of ethyl acetate was heated to reflux after which a solution of 3.0 g (11.3 mmol) of (**3a**) in 100 mL of chloroform was added. Reflux was continued for 5 h. The mixture was filtered while hot and the filtrate washed with water (2 × 50 mL). The organic layer was dried over anhydrous magnesium sulphate and then evaporated to dryness. The resulting solid was recrystallized from ethanol. 82% yield, yellow solid, m.p. 190°C (m.p. 194°C).[21]

N-[2-(α-Bromoacetyl)phenyl]-3-nitrophthalimide, **5b**: This compound was obtained from (**3b**) and $CuBr_2$ in a procedure similar to that described for (**5a**). 90% yield, pale yellow solid, m.p. 191°C; IR: 1785, 1708, 1615. ^{1}H-NMR: 4.56 (s, 2H), 7.41–8.19 (m, 7H). MS: m/z (%) 390 (M^{+2},

1), 388 (M^+, 1), 295 (100), 248 (21), 193 (5), 90 (6), 75 (20). *Anal. Calcd*. for $C_{16}H_9BrN_2O_5$: C, 49.38; H, 2.33; N, 7.19. Found: C, 49.27; H, 2.21; N, 7.01.

N-[2-(α-Bromoacetyl)phenyl]-4-nitrophthalimide, **5c**: This compound was obtained from (**3c**) and $CuBr_2$ in a procedure similar to that described for (**5a**). 70% yield, colorless solid, m.p. 180°C; IR: 1783, 1720, 1620. ^{1}H-NMR: 4.49 (s, 2H), 7.44–8.18 (m, 7H). MS: m/z (%) 390 (M^{+2}, 1), 388 (M^+, 1), 295 (100), 249 (37), 193 (8), 90 (3), 75 (21). *Anal. Calcd*. for $C_{16}H_9BrN_2O_5$: C, 49.38; H, 2.33; N, 7.19. Found: C, 48.92; H, 2.25; N, 7.25.

N-[2-(α-Bromoacetyl)phenyl]-3,4,5,6-tetrachlorophthalimide, **5d**: This compound was obtained from (**3d**) and $CuBr_2$ in a procedure similar to that described for (**5a**). 95% yield, yellow solid, m.p. 227°C; IR: 1783, 1716, 1633. ^{1}H-NMR: 4.49 (s, 2H), 7.46–7.92 (m, 4H). MS: m/z (%) 481 (M^{+2}, 1), 479 (M^+, 1), 392 (12), 388 (100), 386 (76), 216 (6), 146 (7), 90 (13). *Anal. Calcd*. for $C_{16}H_6BrCl_4NO_3$: C, 39.83; H, 1.24; N, 2.90. Found: C, 39.72; H, 1.17; N, 2.83.

6-Azido-5H,11H-isoindolo[2,1-a]quinoline-5,11-dione, **6a**: To a solution of 2.0 g (5.8 mmol) of (**5a**) in 70 mL of acetone was added a solution of 0.45 g (6.9 mmol) of NaN_3 in 20 mL of water. The mixture was heated at 65°C for 2 h. The resulting solid was collected and recrystallized from ethanol. 76% yield, brownish solid, m.p. 126°C (m.p. 126°C).[21]

6-Azido-10-nitro-5H,11H-isoindolo[2,1-a]quinoline-5,11-dione, **6b**: This compound was obtained from (**5b**) and NaN_3 in a procedure similar to that described for (**6a**). 53% yield, brownish solid, m.p. 195°C; IR: 2125, 1746, 1624. ^{1}H-NMR: 7.42–7.88 (m, 4H), 8.20–8.70 (m, 2H), 9.13 (d, J = 8.2 Hz, 1H); ^{13}C-NMR: 117.90, 119.52, 123.47, 125.34, 126.41, 126.82, 129.36, 130.29, 133.87, 134.64, 135.40, 136.75, 141.20, 146.96, 160.37, 176.95. MS: m/z (%) 333 (M^+, 5), 305 (49), 293 (17), 275 (17), 231 (43), 203 (49), 176 (49), 146 (40), 90 (16), 75 (100). *Anal. Calcd*. for $C_{16}H_7N_5O_4$: C, 57.65; H, 2.10; N, 21.02. Found: C, 57.84; H, 2.21; N, 21.22.

6-Azido-9-nitro-5H,11H-isoindolo[2,1-a]quinoline-5,11-dione, **6c**: This compound was obtained from (**5c**) and NaN_3 in a procedure similar to that described for (**6a**). 59% yield, brownish solid, m.p. 208°C; IR: 2128, 1746, 1622. ^{1}H-NMR: 7.14–7.75 (m, 4H), 8.23 (d, J = 8.3 Hz, 1H), 9.05–9.15 (m, 2H); ^{13}C-NMR: 116.18, 117.50, 123.10, 124.08, 124.82, 125.11, 127.90, 131.21, 133.01, 133.54, 133.62, 134.60, 139.52, 145.89, 160.75, 175.85. MS: m/z (%) 333 (M^+, 8), 305 (88), 275 (22), 261 (46), 231 (79), 203 (89), 175 (35), 151 (56), 102 (34), 75 (100). *Anal. Calcd*. for $C_{16}H_7N_5O_4$: C, 57.65; H, 2.10; N, 21.02. Found: C, 57.77; H, 2.16; N, 21.10.

6-Azido-7,8,9,10-tetrachloro-5H,11H-isoindolo[2,1-a]quinoline-5,11-dione, **6d**: This compound was obtained from (**5d**) and NaN_3 in a procedure similar to that described for (**6a**). 42% yield, brownish solid, m.p. 215°C; IR: 2119, 1787, 1610. ^{1}H-NMR: 7.05–7.90 (m, 4H); ^{13}C-NMR: 116.88, 119.94, 120.74, 125.11, 127.64, 127.98, 129.87, 135.88, 136.27, 137.18, 137.92, 140.34, 160.14, 186.87. MS: m/z (%) 424 (M^+, 5), 396 (82), 361 (100), 317 (78), 214 (39), 142 (19), 76 (41). *Anal. Calcd*. for $C_{16}H_4Cl_4N_4O_2$: C, 45.07; H, 0.93; N, 13.14. Found: C, 45.23; H, 1.02; N, 13.05.

General Procedure for the Synthesis of Iminophosphoranes 7–21

A solution of the appropriate azide (1.5 mmol) and the appropriate phosphine (2.2 mmol) in 60 mL of dry THF was heated to reflux for 2 h. The solvent was evaporated under vacuum and the resulting solid was recrystallized from ethanol or mixture of ethanol and chloroform.

N-[(10-Nitro-5H,11H-isoindolo[2,1-a]quinoline-5,11-dione)-6-yl] iminotriphenylphosphorane, **7**: This compound was obtained from (**6b**) and Ph_3P. 86% yield, red solid, m.p. 260°C; IR: 1719, 1623, 1438. ^{1}H-NMR: 7.18 (t, J = 8.1 Hz, 1H), 7.46-7.63 (m, 7H), 7.74–7.92 (m, 11H), 8.0 (d, J = 8.1 Hz, 1H), 9.09 (d, J = 7.9 Hz, 1H), 9.22 (d, J = 8.1 Hz, 1H). ^{13}C-NMR: 118.04, 118.28, 121.98, 122.05, 124.72, 126.55, 127.37, 128.50 (d, J = 48.92 Hz), 128.91, 131.30, 132.14 (d, J = 39.76 Hz), 132.65, 133.71 (d, J = 18.36 Hz), 134.02, 136.57 (d, J = 21.40 Hz), 136.85, 138.95, 146.96, 160.32, 177.38 (d, J = 33.64 Hz). MS: m/z (%) 567 (M^+, 100), 539 (13), 304 (24), 277 (10), 262 (43), 201 (10), 183 (86), 108 (25), 77 (7). *Anal. Calcd*. for $C_{34}H_{22}N_3O_4P$: C, 71.95; H, 3.92; N, 7.49. Found: C, 71.88; H, 3.81; N, 7.35.

N-[(9-Nitro-5H,11H-isoindolo[2,1-a]quinoline-5,11-dione)-6-yl]-iminotriphenylphosphorane, **8**: This compound was obtained from (**6c**) and Ph_3P. 80% yield, red solid, m.p. 331°C; IR: 1720, 1625, 1436. ^{1}H-NMR: 7.12 (t, J = 7.8 Hz, 1H), 7.42–7.67 (m, 9H), 7.55 (t, J = 7.8 Hz, 1H), 7.72–7.83 (m, 6H), 7.89 (d, J = 8.4 Hz, 1H), 8.35 (d, J = 7.8 Hz, 1H), 8.68 (d, J = 1.6 Hz, 1H), 8.82 (d, J = 7.8 Hz, 1H), 9.15 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H). ^{13}C-NMR: 117.78, 117.91, 120.24, 121.94, 124.73, 125.16, 125.48, 127.51, 128.54 (d, J = 48.96 Hz), 128.66, 131.41, 132.51 (d, J = 36.68 Hz), 132.27, 133.38, 134.17, 137.14, 141.21, 146.88, 163.63, 177.32 (d, J = 36.72 Hz). MS: m/z (%) 567 (M^+, 69), 539 (7), 490 (8), 399 (6), 288 (11), 277 (11), 262 (18), 233 (8), 183 (100), 133 (7), 108 (45), 77 (19). *Anal. Calcd*. for $C_{34}H_{22}N_3O_4P$: C, 71.95; H, 3.92; N, 7.49. Found: C, 71.98; H, 3.96; N, 7.55.

N-[(5H,11H-isoindolo[2,1-a]quinoline-5,11-dione)-6-yl]iminotri-*p*-tolylphosphorane, **9**: This compound was obtained from (**6a**) and tri-*p*-tolylphosphine. 53% yield, orange solid, m.p. 241°C; IR: 1719, 1621, 1440. ^{1}H-NMR: 2.39 (s, 9H), 7.19–7.24 (m, 9H), 7.32 (t, J = 7.32 Hz, 1H), 7.45–7.90 (m, 8H), 7.63 (dd, J_1 = 7.68 Hz, J_2 = 1.46 Hz, 1H), 8.0 (dd, J_1 = 7.68 Hz, J_2 = 1.46 Hz, 1H). ^{13}C-NMR: 20.96, 114.29, 115.21, 121.74, 122.70, 122.99, 123.72, 128.19, 128.77 (d, J = 52.00 Hz), 128.97, 129.90, 131.47, 131.92, 132.13, 132.24 (d, J = 42.80 Hz), 133.09, 135.51, 135.79, 165.98, 173.10 (d, J = 42.84 Hz). MS: m/z (%) 448 (M^+-116, 2), 419 (4), 346 (17), 319 (100), 267 (10), 229 (15), 182 (7), 91 (21), 76 (8). *Anal. Calcd*. for $C_{37}H_{29}N_2O_2P$: C, 78.72; H, 5.14; N, 4.96. Found: C, 78.55; H, 5.05; N, 4.85.

N-[(10-Nitro-5H,11H-isoindolo[2,1-a]quinoline-5,11-dione)-6-yl] iminotri-*p*-tolylphosphorane, **10**: This compound was obtained from (**6b**) and tri-*p*-tolylphosphine. 98% yield, red solid, m.p. 290°C; IR: 1710, 1619, 1445. ^{1}H-NMR: 2.38 (s, 9H), 7.20 (t, J = 7.9 Hz, 1H), 7.25–7.45 (m, 7H), 7.63–7.81 (m, 8H), 7.99 (t, J = 8.02 Hz, 1H), 9.14 (d, J = 8.02 Hz, 1H), 9.22 (d, J = 7.9 Hz, 1H). ^{13}C-NMR: 21.51, 117.92, 118.05, 121.69, 122.06, 124.50, 126.48, 127.35, 128.81, 129.08 (d, J = 52.00 Hz), 129.49, 130.55, 132.02 (d, J = 39.76 Hz), 133.52, 133.79, 136.74, 138.89, 141.43 (d, J = 12.20 Hz), 146.83, 160.19, 177.31 (d, J = 33.64 Hz). MS: m/z (%) 609 (M^+, 100), 579 (23), 346 (16), 319 (11), 304 (81), 213 (120), 183 (14), 122 (25), 76 (14). *Anal. Calcd*. for $C_{37}H_{28}N_3O_4P$: C, 72.89; H, 4.62; N, 6.89. Found: C, 72.52; H, 4.56; N, 6.84.

N-[(9-Nitro-5H,11H-isoindolo[2,1-a]quinoline-5,11-dione)-6-yl]-iminotri-*p*-tolylphosphorane, **11**: This compound was obtained from (**6c**) and tri-*p*-tolylphosphine. 83% yield, red solid, m.p. 306°C; IR: 1717, 1625, 1435. ^{1}H-NMR: 2.31 (s, 9H), 7.10–7.25 (m, 7H), 7.51–7.62 (m, 7H), 7.91 (t, J = 8.78 Hz, 1H), 8.32 (dd, J_1 = 8.42 Hz, J_2 = 1.83 Hz, 1H), 8.65 (d, J = 1.83 Hz, 1H), 8.83 (d, J = 8.78 Hz, 1H), 9.13 (d, J = 8.78 Hz, 1H). ^{13}C-NMR: 21.54, 117.65, 117.78, 120.09, 121.96, 124.50, 125.34, 127.48, 128.19, 129.14 (d, J = 52.01 Hz), 129.23, 130.24, 132.08 (d, J = 42.84 Hz), 132.11, 133.72, 133.93, 141.12, 141.62 (d, J = 12.24 Hz), 146.61, 163.50, 177.28 (d, J = 33.64 Hz). MS: m/z (%) 609 (M^+, 100), 518 (10), 346 (13), 319 (49), 304 (26), 265 (11), 213 (25), 183 (15), 122 (25), 75 (33). *Anal. Calcd*. for $C_{37}H_{28}N_3O_4P$: C, 72.89; H, 4.62; N, 6.89. Found: C, 72.44; H, 4.71; N, 6.69.

N-[(7,8,9,10-Tetrachloro-5H,11H-isoindolo[2,1-a]quinoline-5,11-dione)-6-yl]iminotri-*p*-tolylphosphorane, **12**: This compound was obtained from (**6d**) and tri-*p*-tolylphosphine. 78% yield, red solid, m.p. 291°C; IR: 1716, 1623, 1457. ^{1}H-NMR: 2.30 (s, 9H), 7.10–7.32 (m, 13H), 7.64 (t, J = 8.4 Hz, 1H), 7.88 (d, J = 8.4 Hz, 1H), 9.12 (d, J = 8.4 Hz,

1H). ^{13}C-NMR: 21.65, 118.26, 121.43, 123.01, 124.95, 126.89, 127.75, 127.98, 129.11 (d, J = 59.02 Hz), 130.10, 130.36, 131.65, 132.40 (d, J = 40.73 Hz), 134.24, 135.52, 136.29, 137.15, 138.45, 141.05, 160.34, 180.27 (d, J = 33.74 Hz). MS: m/z (%) 702 (M^{+2}, 6), 700 (M^+, 6), 414 (11), 360 (23), 346 (100), 319 (20), 227 (14), 213 (19), 91 (15), 75 (12). *Anal. Calcd*. for $C_{37}H_{25}Cl_4N_2O_2P$: C, 63.24; H, 3.56; N, 3.98. Found: C, 63.42; H, 3.61; N, 3.81.

N-[(5H,11H-isoindolo[2,1-a]quinoline-5,11-dione)-6-yl]iminotribenzylphosphorane, **13**: This compound was obtained from (**6a**) and tribenzylphosphine. 67% yield, orange solid, m.p. 183°C; IR: 1719, 1620, 1435. ^{1}H-NMR: 3.57 (d, J = 14.28 Hz, 6H), 7.16–7.78 (m, 21H), 8.28 (dd, J_1 = 8.05 Hz, J_2 = 1.46 Hz, 1H), 9.25 (t, J = 8.42 Hz, 1H). ^{13}C-NMR: 35.22 (d, J = 241.60 Hz), 115.25, 117.77, 118.50, 121.79, 122.36, 124.67, 126.52, 127.27, 128.88 (d, J = 9.20 Hz), 130.28 (d, J = 21.40 Hz), 131.52, 131.92, 134.25, 135.17, 135.93, 137.24, 138.12, 163.29, 174.52 (d, J = 39.50 Hz). MS: m/z (%) 564 (M^+, 2), 473 (2), 320 (2), 307 (100), 279 (3), 251 (7), 223 (5), 91 (77), 75 (12). *Anal. Calcd*. for $C_{37}H_{29}N_2O_2P$: C, 78.72; H, 5.14; N, 4.96. Found: C, 78.48; H, 5.19; N, 4.89.

N-[(10-Nitro-5H,11H-isoindolo[2,1-a]quinoline-5,11-dione)-6-yl]-iminotribenzylphosphorane, **14**: This compound was obtained from (**6b**) and tribenzylphosphine. 78% yield, red solid, m.p. 235°C; IR: 1718, 1632, 1446. ^{1}H-NMR: 3.47 (d, J = 13.56 Hz, 6H), 7.09–7.31 (m, 17H), 7.45 (t, J = 8.41 Hz, 1H), 7.62 (t, J = 8.41 Hz, 1H), 8.15 (dd, J_1 = 8.05 Hz, J_2 = 1.46 Hz, 1H), 8.25 (dd, J_1 = 8.05 Hz, J_2 = 1.46 Hz, 1H), 9.17 (d, J = 8.41 Hz, 1H). ^{13}C-NMR: 36.47 (d, J = 241.61 Hz), 117.82, 118.07, 121.79, 122.51, 124.93, 126.99, 127.12, 128.63, 128.74 (d, J = 9.16 Hz), 129.87, 130.27 (d, J = 21.40 Hz), 132.65 (d, J = 27.52 Hz), 133.63, 134.25, 136.77, 137.09, 139.01, 146.70, 160.32, 179.45 (d, J = 36.68 Hz). MS: m/z (%) 609 (M^+, 22), 579 (4), 518 (23), 488 (6), 336 (8), 306 (11), 262 (5), 91 (100), 77 (6). *Anal. Calcd*. for $C_{37}H_{28}N_3O_4P$: C, 72.89; H, 4.62; N, 6.89. Found: C, 72.56; H, 4.62; N, 6.90.

X-Ray Structure Determination for 14 and 18

Suitable crystals for single-crystal diffraction studies were prepared by crystallization from ethanol. The structure was solved by direct methods using SHELXS[24] and refined by full-matrix least squares method using SHELXLT97.[25] Each of the hydrogen atoms was included in the refinement at calculated position with isotropic thermal parameter equal to $1.2U_{eq}$ of the atom to which it is bonded.

N-[(9-Nitro-5H,11H-isoindolo[2,1-a]quinoline-5,11-dione)-6-yl]iminotribenzylphosphorane, **15**: This compound was obtained from (**6c**)

and tribenzylphosphine. 94% yield, red solid, m.p. 211°C; IR: 1716, 1617, 1420. ^{1}H-NMR: 3.49 (d, J = 13.50 Hz, 6H), 7.08–7.29 (m, 15H), 7.32 (t, J = 8.04 Hz, 1H), 7.65 (t, J = 8.04 Hz, 1H), 7.89 (d, J = 7.90 Hz, 1H), 8.02 (dd, J_1 = 7.90 Hz, J_2 = 1.46 Hz, 1H), 8.28 (d, J = 8.04 Hz), 8.61 (d, J = 1.46 Hz, 1H), 9.20 (d, J = 8.04 Hz, 1H). ^{13}C-NMR: 36.52 (d, J = 241.64 Hz), 117.92, 118.04, 120.01, 122.33, 125.00, 125.32, 127.08, 127.20, 127.38, 128.28, 128.91 (d, J = 6.12 Hz), 130.32 (d, J = 18.36 Hz), 132.55 (d, J = 27.56 Hz), 134.46, 136.92, 137.15, 141.00, 146.79, 163.72, 179.34 (d, J = 36.68 Hz). MS: m/z (%) 609 (M^+, 15), 518 (41), 336 (20), 320 (10), 290 (18), 262 (4), 123 (5), 91 (100), 76 (7). *Anal. Calcd*. for $C_{37}H_{28}N_3O_4P$: C, 72.89; H, 4.62; N, 6.89. Found: C, 72.96; H, 4.51; N, 6.73.

N-[(7,8,9,10-Tetrachloro-5H,11H-isoindolo[2,1-a]quinoline-5,11-dione)-6-yl]iminotribenzylphosphorane, **16**: This compound was obtained from (**6d**) and tribenzylphosphine. 60% yield, red solid, m.p. 237°C; IR: 1716, 1620, 1453. ^{1}H-NMR: 3.40 (d, J = 13.90 Hz, 6H), 7.05–7.27 (m, 15H), 7.30 (t, J = 8.42 Hz, 1H), 7.61 (t, J = 8.42 Hz, 1H), 8.27 (d, J = 8.42 Hz, 1H), 9.15 (d, J = 8.42 Hz, 1H). ^{13}C-NMR: 35.38 (d, J = 238.56 Hz), 118.31, 121.63, 124.17, 124.81, 126.96, 127.02, 127.29, 128.68 (d, J = 9.16 Hz), 129.85 (d, J = 21.76 Hz), 130.33 (d, J = 21.44 Hz), 131.54, 131.61, 132.29 (d, J = 27.56 Hz), 134.37, 136.81, 137.08, 138.01, 138.33, 160.37, 179.25 (d, J = 36.86 Hz). MS: m/z (%) 702 (M^{+2}, 3), 700 (M^+, 2), 667 (3), 611 (4), 429 (5), 400 (33), 320 (18), 211 (5), 91 (100), 76 (13). *Anal. Calcd*. for $C_{37}H_{25}Cl_4N_2O_2P$: C, 63.26; H, 3.58; N, 3.98. Found: C, 63.29; H, 3.54; N, 3.96.

N-[(10-Nitro-5H,11H-isoindolo[2,1-a]quinoline-5,11-dione)-6-yl]-iminotricyclohexylphosphorane, **17**: This compound was obtained from (**6b**) and tricyclohexylphosphine. 82% yield, red solid, m.p. 254°C; IR: 1715, 1620, 1445. ^{1}H-NMR: 1.24–1.46 (m, 9H), 1.57–1.70 (m 9H), 1.76–1.91 (m, 12H), 2.30–2.63 (m, 3H), 7.25 (t, J = 8.0 Hz, 1H), 7.57–7.72 (m, 3H), 8.15–8.22 (m, 1H), 9.20-9.33 (m, 2H). ^{13}C-NMR: 26.25, 26.93 (d, J = 45.88 Hz), 27.65 (d, J = 15.28 Hz), 39.16 (d, J = 235.52 Hz), 117.49, 118.12, 121.09, 121.94, 124.56, 127.16, 128.29, 132.94, 133.85, 136.83, 139.07, 139.18, 139.24, 147.00, 160.13, 178.75 (d, J = 33.64 Hz). MS: m/z (%) 585 (M^+, 41), 502 (5), 420 (7), 322 (11), 295 (9), 280 (17), 214 (13), 198 (10), 81 (10), 75 (15), 67 (27), 55 (100). *Anal. Calcd*. for $C_{34}H_{40}N_3O_4P$: C, 69.74; H, 6.83; N, 7.17. Found: C, 69.89; H, 6.75; N, 7.25.

N-[(9-Nitro-5H,11H-isoindolo[2,1-a]quinoline-5,11-dione)-6-yl]iminotricyclohexylphosphorane, **18**: This compound was obtained from (**6c**) and tricyclohexylphosphine. 70% yield, red solid, m.p. 296°C; IR: 1718, 1625, 1439. ^{1}H-NMR: 1.31–1.46 (m, 9H), 1.58–1.79 (m, 9H), 1.85–1.98 (m, 12H), 2.41–2.53 (m, 3H), 7.27 (t, J = 8.0 Hz, 1H), 7.68 (t, J = 8.0 Hz,

1H), 8.25 (d, J = 8.8 Hz, 1H), 8.42 (dd, J_1 = 8.80 Hz, J_2 = 2.0 Hz, 1H), 8.74 (d, J = 2.0 Hz), 9.05 (d, J = 8.0 Hz, 1H), 9.28 (d, J = 8.0 Hz, 1H). ^{13}C-NMR: 26.31, 26.99 (d, J = 48.96 Hz), 27.71 (d, J = 12.24 Hz), 39.16 (d, J = 232.44 Hz), 118.07, 118.56, 120.43, 121.85, 124.66, 127.35, 127.89, 133.45, 133.79, 134.14, 137.25, 138.89, 141.18, 146.16, 160.01, 175.72 (d, J = 33.69 Hz). MS: m/z (%) 585 (M^+, 44), 502 (16), 420 (100), 390 (9), 338 (32), 290 (28), 279 (11), 228 (8), 197 (9), 81 (9), 67 (7), 55 (6). *Anal. Calcd*. for $C_{34}H_{40}N_3O_4P$: C, 69.74; H, 6.83; N, 7.17. Found: C, 69.69; H, 6.79; N, 7.14.

N-[(10-Nitro-5H,11H-isoindolo[2,1-a]quinoline-5,11-dione)-6-yl]-iminotributylphosphorane, **19**: This compound was obtained from (**6b**) and tributylphosphine. 50% yield, red solid, m.p. 160°C; IR: 1712, 1615, 1443. ^{1}H-NMR: 0.86 (t, J = 7.32 Hz, 9H), 1.38–1.43 (m, 6H), 1.46–1.58 (m, 6H), 2.03–2.25 (m, 6H), 7.27 (t, J = 8.0 Hz, 1H), 7.56–7.71 (m, 3H), 8.14 (d, J = 8.05 Hz, 1H), 8.93 (d, J = 8.05 Hz, 1H), 9.19 (d, J = 8.0 Hz, 1H). ^{13}C-NMR: 13.69, 24.15 (d, J = 58.12 Hz), 24.70 (d, J = 15.28 Hz), 28.47 (d, J = 256.92 Hz), 117.70, 118.11, 121.41, 122.13, 124.67, 126.99, 128.26, 130.25, 133.26, 133.96, 136.80, 138.25, 139.00, 146.91, 160.18, 179.25 (d, J = 33.64 Hz). MS: m/z (%) 507 (M^+, 58), 477 (10), 450 (8), 321 (8), 291 (20), 279 (13), 263 (23), 244 (27), 189 (30), 147 (23), 92 (100), 75 (62), 63 (60), 55 (85). *Anal. Calcd*. for $C_{28}H_{34}N_3O_4P$: C, 66.27; H, 6.70; N, 8.28. Found: C, 66.48; H, 6.59; N, 8.18.

N-[(9-Nitro-5H,11H-isoindolo[2,1-a]quinoline-5,11-dione)-6-yl]iminotributylphosphorane, **20**: This compound was obtained from (**6c**) and tributylphosphine. 65% yield, red solid, m.p. 156°C; IR: 1720, 1624, 1435. ^{1}H-NMR: 0.92 (t, J = 7.4 Hz, 9H), 1.43–1.51 (m, 6H), 1.55–1.74 (m, 6H), 2.09–2.25 (m, 6H), 7.29 (t, J = 8.04 Hz, 1H), 7.71 (d, J = 8.04 Hz, 1H), 8.28 (d, J = 8.8 Hz, 1H), 8.52 (dd, J_1 = 8.8 Hz, J_2 = 1.8 Hz, 1H), 8.74 (d, J = 8.04 Hz, 1H), 9.05 (d, J = 1.8 Hz, 1H), 9.28 (d, J = 8.04 Hz, 1H). ^{13}C-NMR: 13.70, 24.25 (d, J = 58.20 Hz), 24.91 (d, J = 15.16 Hz), 29.62 (d, J = 256.95 Hz), 118.01, 118.70, 122.15, 122.93, 124.70, 127.32, 128.61, 129.78, 133.85, 134.39, 137.45, 138.91, 139.13, 145.73, 162.03, 179.63 (d, J = 33.63 Hz). MS: m/z (%) 507 (M^+, 100), 478 (20), 377 (21), 355 (15), 291 (21), 263 (28), 235 (42), 103 (12), 76 (16). *Anal. Calcd*. for $C_{28}H_{34}N_3O_4P$: C, 66.27; H, 6.70; N, 8.28. Found: C, 66.35; H, 6.63; N, 8.22.

N-[(10-Nitro-5H,11H-isoindolo[2,1-a]quinoline-5,11-dione)-6-yl]-iminotrimethoxyphosphorane, **21**: This compound was obtained from (**6b**) and trimethylphosphite. 73% yield, pale yellow solid, m.p. 210°C; IR: 1726, 1634, 1466. ^{1}H-NMR: 3.85 (d, J = 11.72 Hz, 9H), 7.32 (t, J = 7.32 Hz, 1H), 7.65–7.98 (m, 3H), 8.25 (d, J = 7.32 Hz, 1H), 9.01 (d, J = 7.32 Hz, 1H), 9.16 (d, J = 8.79 Hz, 1H). ^{13}C-NMR: 55.13 (d, J = 27.56 Hz), 117.98, 118.79, 122.24, 122.90, 125.19, 127.25, 127.65,

128.89, 133.46, 134.03, 134.27, 136.69, 138.59, 146.86, 160.46, 177.90 (d, J = 33.64 Hz). MS: m/z (%) 429 (M^+, 30), 353 (2), 305 (6), 279 (4), 246 (7), 229 (10), 217 (12), 177 (18), 166 (100), 150 (23), 109 (54), 93 (59), 76 (21). *Anal. Calcd*. for $C_{19}H_{16}N_3O_7P$: C, 53.14; H, 3.73; N, 9.79. Found: C, 53.32; H, 3.65; N, 9.74.

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