C=C-Conjugated Carbodiimides as 2-Azadienes in Intramolecular [4 + 2] Cycloadditions. One-Pot Preparation of Quinoline, α-Carboline, and Quinindoline Derivatives

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Iminophosphoranes **2** derived from *o*-aminostyrenes react with aryl isocyanates to give the corresponding carbodiimides **13** which by thermal treatment at 160 °C undergo 6π-electrocyclization to give quinoline derivatives **14**. However, the reaction with styryl isocyanates leads to α-carbolines **19** through the intermediate carbodiimides **15** which undergo a tandem intramolecular hetero-Diels–Alder cycloaddition/aromatization process to give **19**. Similarly, related α-carbolines **20–22** can be obtained from the reaction of iminophosphoranes derived from *ortho*-substituted anilines containing an unsaturated side chain with styryl isocyanates. Iminophosphorane **6a**, derived from *o*-butadienylaniline, and related **10** and **12** react with aryl isocyanates under the same reaction conditions to give quinindoline derivatives **25–27**, respectively. Finally, iminophosphoranes **2** and **6** by reaction with ketenes lead directly to quinolines **32** and benzo[*b*]carbazoles **33**, respectively.

The hetero Diels–Alder reaction in its various forms continues to play an important role in the synthesis of functionalized heteroaromatic systems difficult to assemble by alternative methodology.[1] In recent years there has been an upsurge of interest in the [4 + 2] cycloaddition of unsaturated heterocumulenes as 4π-heterodiene partners: *N*-aryl ketene imines[2] and *N*-arylvinyl ketene imines[3] react with electron-rich ynamines to afford substituted quinolines by cycloaddition across the aza diene system. Similar observations have been made on the reaction of *N*-aryl ketene imines or *N*-arylvinyl ketene imines with thiobenzophenones.[4] *N*-Vinyl ketene imines react with diphenylketene to give 2*H*-1,3-oxazine derivatives;[5] in this case, the unsaturated ketene imine acts as a 2-azadiene which cycloadds to the C=O bond of the ketene. Aryl and vinyl isocyanates have been reported to give [4 + 2] cycloaddition products with ynamines,[6] benzyne[7] and ethoxyacetylene.[8] However, to the best of our knowledge, there have been no reports dealing with unsaturated carbodiimides as 2-azadienes.

Continuing our interest in the preparation and synthetic applications of unsaturated carbodiimides, we have recently shown that the thermal treatment of β-arylvinyl carbodiimides provides an efficient annulation route to highly substituted isoquinolines[9] (Scheme I). In this paper, we describe a new version of our annulation strategy that significantly expands the scope of the method. In particular, this new variant provides access to a variety of fused indoles such as pyrido[2,3-*b*]indoles (α-carbolines) and quinindolines which have received much attention because they are pharmacologically active compounds,

Scheme I

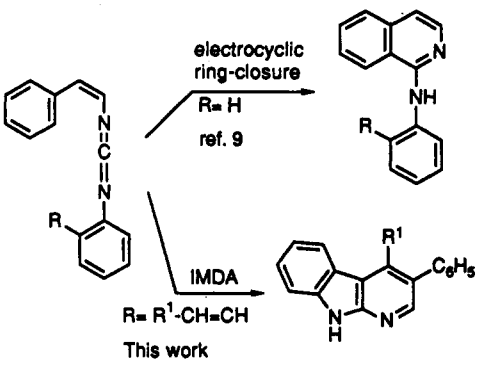

Table I. Quinoline Derivatives 14

entry	R^1	R^2	Ar	yield, %	mp, °C
14a	H	H	C_6H_5-CH_2	82	96–97
14b	H	H	C_6H_5	70	103–104
14c	H	H	4-$CH_3C_6H_4$	87	138–139
14d	H	H	4-$CH_3OC_6H_4$	63	129
14e	CH_3	H	4-$CH_3OC_6H_4$	81	139–141
14f	H	CH_3	C_6H_5	82	94
14g	H	CH_3	4-FC_6H_4	85	78–80
14h	CH_3	CH_3	4-$CH_3OC_6H_4$	63	132
14i	H	COOMe	C_6H_5	71	107–108
14j	H	COOMe	4-$CH_3C_6H_4$	69	121

displaying strong cytostatic antitumor activity.[10] This new annulation approach, based on the initial generation of *N*-aryl carbodiimides bearing an unsaturated chain in the *ortho* position, involves as a key step a tandem intramolecular Diels–Alder (IMDA) cycloaddition/oxidative aromatization process. The process has surprisingly been found to be useful in the simultaneous formation of pyrrole and pyridine rings in the synthesis of [*b*]fused indoles.

Results and Discussion

Preparation of Quinolines. A variety of iminophosphoranes **2** were prepared by treating an acetonitrile solution of the appropriate 2-aminosytrene **1** with a mixture of triphenylphosphine, carbon tetrachloride, and triethylamine at room temperature. The previously un-

(1) Boger, D. L.; Weinreb, S. M. In *Hetero Diels–Alder Methodology in Organic Synthesis*; Academic Press: New York, 1987. Boger, D. L. *Tetrahedron* **1983**, *39*, 2869. Boger, D. L. *Chem. Rev.* **1986**, *86*, 781. Weinreb, S. M.; Staib, R. R. *Tetrahedron* **1982**, *38*, 3128.
(2) Ghosez, L.; de Pérez, C. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 184.
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(4) Dondoni, A. *Heterocycles* **1980**, *14*, 1547.
(5) Saito, T.; Nakane, M.; Miyazaki, T.; Motoki,S. J. *J. Chem. Soc., Perkin Trans. 1* **1989**, 2140.
(6) Kuehne, M. E.; Sheeran, P. J. *J. Org. Chem.* **1968**, *33*, 4406. Dondoni, A.; Kniezo, L.; Medici, A. *J. Org. Chem.* **1982**, *47*, 3995.
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(8) Nieuwenhuis, J.; Arens, J. F. *Rec. Trav. Chim. Pays-Bas* **1957**, *76*, 999.
(9) Molina, P.; Tárraga, A.; Lidón, M. J. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1727. Molina, P.; Alajarín, M.; Vidal, A. *J. Org. Chem.* **1990**, *55*, 6140.
(10) Peczynska-Czoch, W. *Arch. Immunol. Ther. Exp.* **1987**, *35*, 221. Kaczmarek, J.; Balicki, R.; Nautka-Namirski, P.; Peczynska-Czoch, W.; Mordarski, M. *Arch. Pharm. (Weinheim)* **1988**, *321*, 463.

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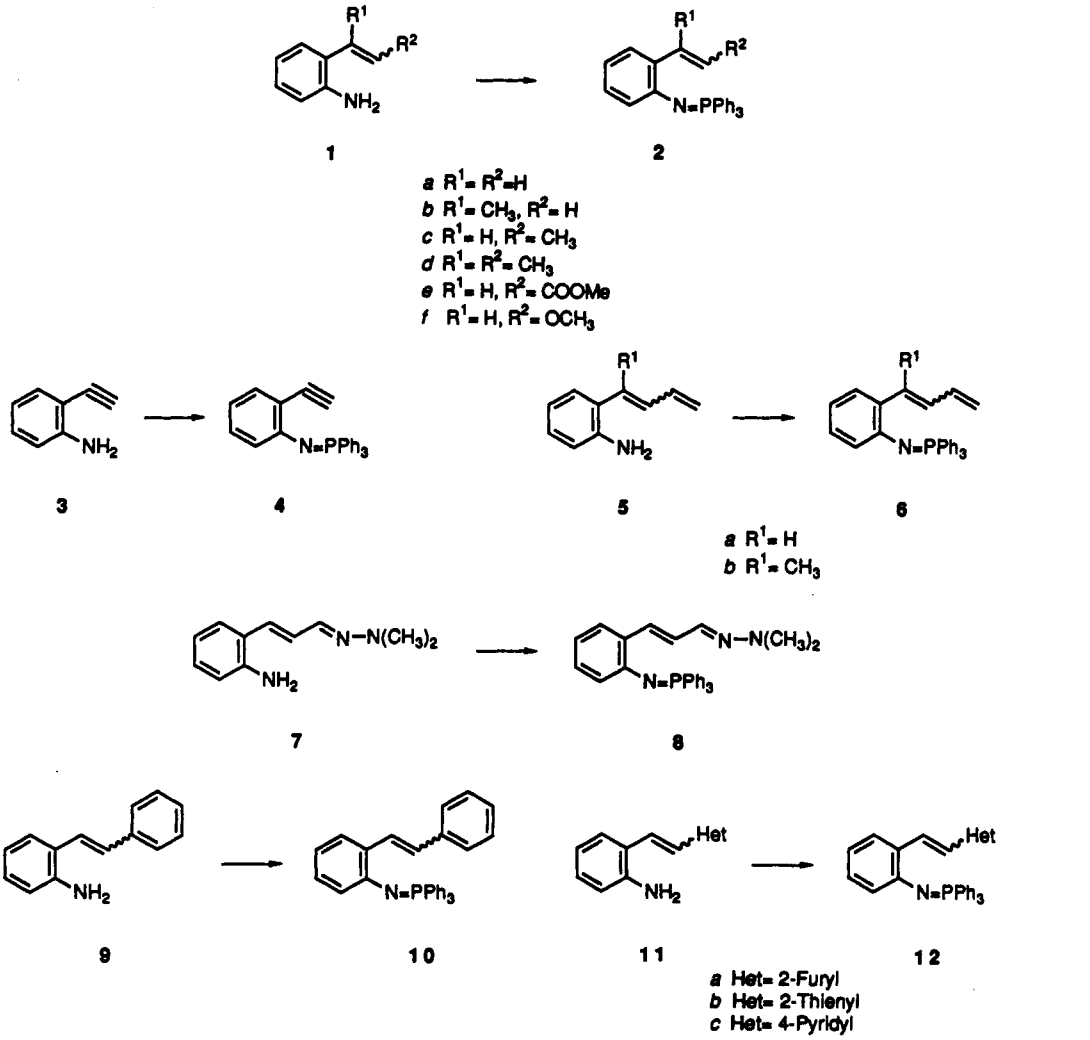
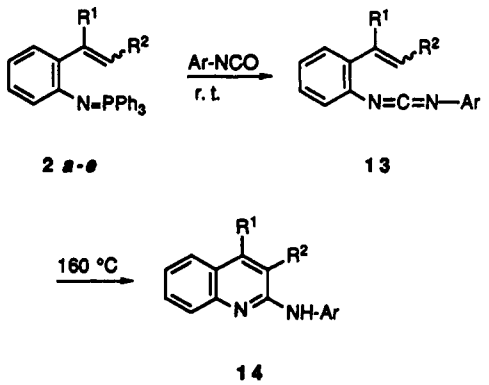
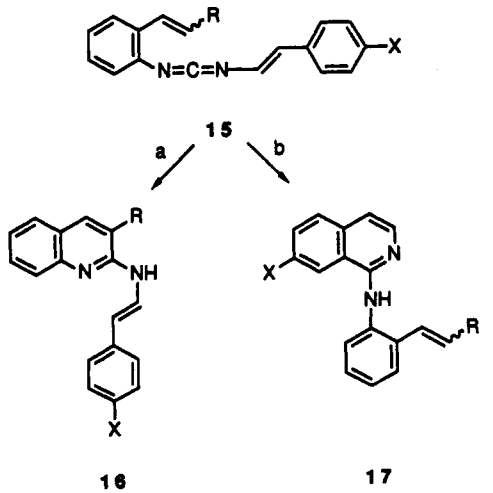
Scheme II



Scheme III



Scheme IV



reported 2-aminostyrene **1d** was prepared from 2-aminoacetophenone and ethylmagnesium bromide. Iminophosphoranes **2** were isolated as stable crystalline solids in 61–77% yields (Scheme II). Aza-Wittig type reaction of iminophosphoranes **2** with several aromatic isocyanates in dry toluene at room temperature gave triphenylphosphine oxide and the corresponding carbodiimide **13** which either could be isolated as viscous oils by column chromatography or used without purification in the next step. The cyclizations were performed by heating a solution of carbodiimide **13** at 160 °C in dry toluene in a sealed glass tube. The crude reaction mixture gave, after chromatographic purification over silica gel, the quinoline **14**; no byproducts were observed, and the yields of the isolated products were higher than 63% (Scheme III). Quinolines **14** can also be prepared directly in one pot from the precursor iminophosphoranes **2** and isocyanates without isolation of the intermedite carbodiimides. The cyclization **13** → **14** can be understood by an initial 6π-electrocyclization of the 2-azadiene system followed by a 1,3-hydrogen shift. The results are summarized in Table I.

Preparation of Pyrido[2,3-*b*]indoles (α-Carbolines). In accordance with the above-mentioned results and previous works,[9] carbodiimides of type **15** can undergo two

Table II. Pyrido[2,3-*b*]indoles 19–22

compd	R	X	yield, %	mp, °C
19a	H	H	35	275–276
19b	H	CH_3O	38	265–266
19c	COOMe	H	40	235–236
19d	COOMe	CH_3O	37	251–252
20a		H	44	253
20b		Cl	51	264–265
20c		CH_3O	43	276
21		H	32	227
21b		Cl	34	271
21c		CH_3O	31	266–267
22		CH_3O	55	290–292

different modes of 6π-electrocyclization leading either to quinolines **16** (pathway a) or isoquinolines **17** (pathway b) (Scheme IV). Aza-Wittig type reaction of iminophosphoranes **2a** and **2e** with styryl isocyanates in toluene at room temperature led to carbodiimides **15** which can be isolated as viscous oils or used without further purification in the next step. When toluene solutions of carbodiimides **15** were heated at 160 °C for 24 h the corresponding pyrido[2,3-*b*]indoles **19** were obtained as solids, in moderate yields (Table II), accompanied by minor amounts of unidentified compounds in which neither the quinoline **16** nor isoquinoline **17** could be detected. In light of the behavior of the previously reported conjugated carbodiimides, the intramolecular reactivity of the carbodiimides **15** came as a surprise. The conversion **15** → **19** includes a [4 + 2] cycloaddition whereby the unsaturated carbodiimide has functioned as a 2-azadiene using one cumulative double bond and a C=C double bond adjacent to the cumulative system, and the C=C double bond of the *o*-vinyl substituent has taken the role of the dienophile. A final oxidative aromatization of the cycloadduct **18** followed by a 1,3-proton shift furnishes the pyridoindole **19**.

This experimentally convenient sequence provides direct access to pyrido[2,3-*b*]indoles in a one-step process. In general, this cycloaddition reaction proceeded without complications in a range of substrates. Table II presents some of the pyrido[2,3-*b*]indoles rendered readily available via this methodology.

Iminophosphorane **4** prepared in 47% yield from (*o*-aminophenyl)acetylene, on reaction with cinnamyl isocyanate, also led to **19a** (R=H, X=H) in 68% yield. Iminophosphorane **6a** was easily prepared in 47% overall yield from 1-(*o*-nitrophenyl)buta-1,3-diene[11] (1:1 mixture of *E*/*Z* isomers) by standard chemistry: iodine-catalyzed isomerization to the *E* isomer, reduction with the iron–acetic acid system, and reaction with triphenylphosphine and carbon tetrachloride in the presence of triethylamine. Aza-Wittig reaction of iminophosphorane **6a** with several styryl isocyanates at 160 °C led directly to the pyrido[2,3-*b*]indoles **20**. Similarly, related iminophosphoranes **8** and **12b** afforded the tricyclic compounds **21** and **22**, respectively (Scheme V). It is worth noting that compounds related to **21**, under vigorous thermal conditions, undergo electrocyclic ring closure followed by loss of dimethylamine giving fused pyridines.[12] Efforts to improve the yields of pyrido[2,3-*b*]indoles by heating the carbodiimide **15** in the presence of palladium–charcoal as a dehydrogenation agent were unsuccessful.

Preparation of Quinindolines. Aza-Wittig-type reaction of the iminophosphorane **6a** with several aromatic isocyanates in dry toluene at room temperature led to the corresponding carbodiimides **23**. When toluene solutions of **23** were heated at reflux temperature for 48 h, the starting carbodiimides were recovered unaltered. However, when toluene solutions of **23** were heated in a sealed tube at 160 °C for 16 h quinindolines **25** were directly obtained in moderate yields (Table III). The ^1H and ^{13}C NMR spectra of **25** indicated that the aryl group corresponding to the isocyanate reagent shows an *ortho*-disubstituted pattern. The original butadienyl moiety now appears as a vinyl substituent. In addition, the ^{13}C NMR spectra reveal the presence of two new quaternary carbon atoms.

Table III. Quinindolines 25–27

compd	R	Het	yield, %	mp, °C
25a	H		39	271
25b	Cl		43	318–319
25c	CH_3		35	263
25d	CH_3O		40	224
25e	F		34	287
26a	CH_3		42	279–281
26b	CH_3O		50	272–274
26c	F		37	263–265
27a	CH_3	2-furyl	51	316–318
27b	CH_3O	2-furyl	54	278–280
27c	F	2-furyl	40	297–299
27d	H	2-thienyl	30	252–254
27e	Cl	2-thienyl	34	223–225
27f	CH_3	2-thienyl	43	280–282
27g	Cl	4-pyridyl	31	342–344
27h	F	4-pyridyl	28	339–341
27i	CH_3	4-pyridyl	37	340–342

Table IV. Quinolines 32 and Benzo[*b*]carbazole 33

compd	R^1	R^2	R^3	yield, %	mp, °C
32a	H	H	C_2H_5	62	*a*
32b	H	CH_3	C_6H_5	73	175
33			C_2H_5	12	137–138

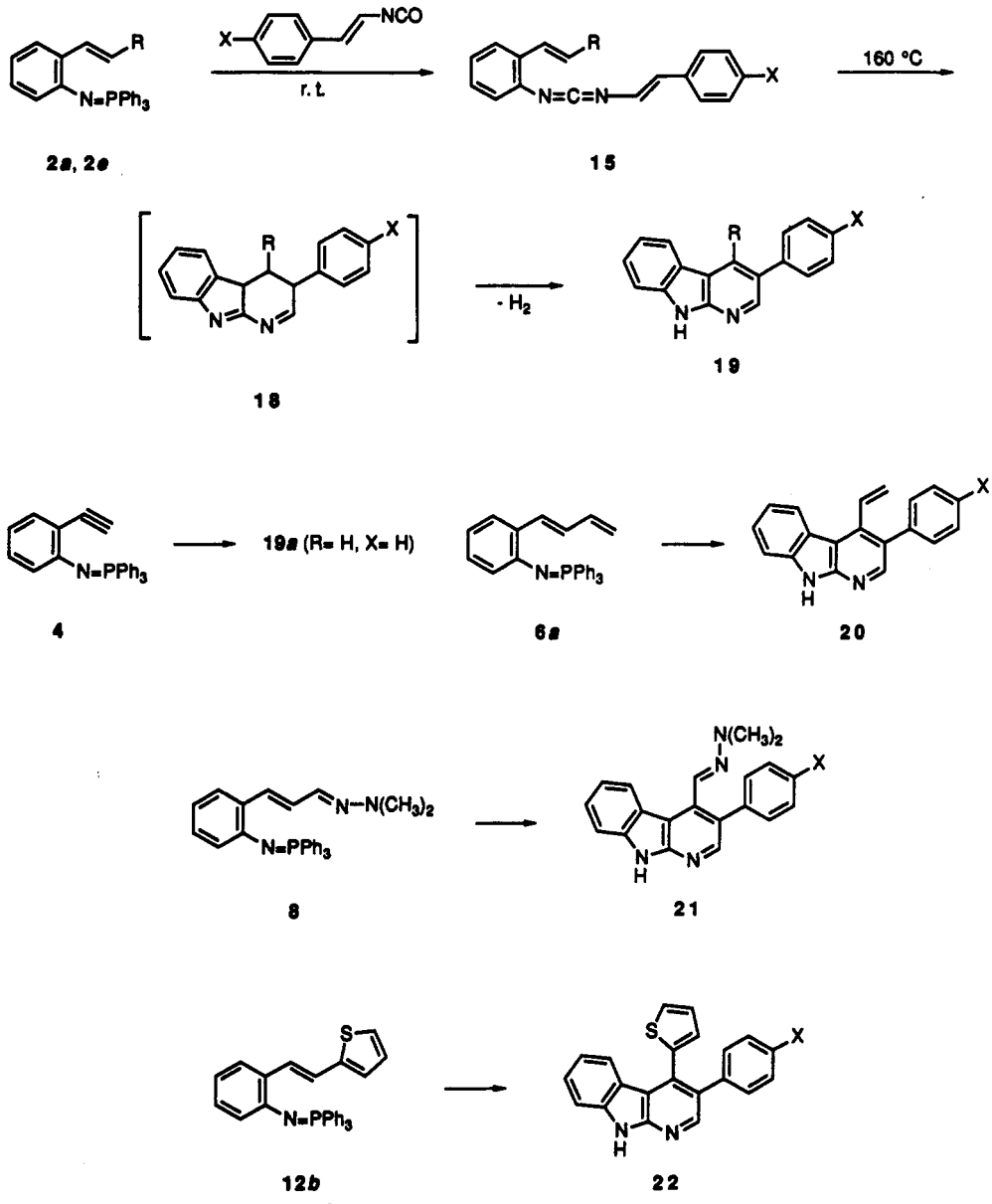
[a] Isolated as an oil.

Reaction of the related iminophosphoranes **10** and **12** also resulted in the smooth formation of the quinindoline derivatives **26** and **27**, respectively (Scheme VI). The ^1H and ^{13}C NMR spectra exhibited signals very similar to those of compounds **25**. Likewise, microanalytical and spectral data confirmed the structure shown. That conversions of the type **6a** → **25**, **10** → **26**, and **12** → **27** are reasonably general in nature is indicated by the examples given in Table III. In spite of the moderate yields, the syntheses of quinindolines **25–27** are competitive with known routes to comparable compounds and take place in a completely periselective fashion. These transformations include a [4 + 2] cycloaddition, whereby the aryl carbodiimide has functioned as a 2-azadiene and the C=C double bond of the *ortho*-butadienyl substituent directly linked to the aromatic ring has taken the role of the dienophile. This suggestion is supported by the fact that the carbodiimide derived from iminophosphorane **6a** and 2,6-dimethylphenyl isocyanate does not undergo cycloaddition: it was recovered unaltered after prolonged heating at 160 °C. Obviously, the two methyl groups at the *ortho* position prevent the cycloaddition step.

Most noticeable was that iminophosphorane **2f** by reaction with 4-methylphenyl isocyanate at 160 °C led to the quinindoline **28** in moderate yield and no trace of quinoline compound **29** was detected, whereas the iminophosphorane **6b** gave the quinoline derivative **31** as the only reaction product (Scheme VII). The conversion **2f** to **28** can be rationalized assuming an initial intramolecular inverse electron demand Diels–Alder cycloaddition between the electron-deficient 2-azadiene aryl carbodiimide and the electron-rich dienophile methyl vinyl ether moiety, followed by an aromatization step in which the methoxy

(11) Brander, E. A.; Fawcett, J. S. *J. Chem. Soc. C* **1951**, 3113.
(12) Gilchrist, T. L.; Healy, M. A. M. *Tetrahedron Lett.* **1990**, *31*, 5807.

Scheme V



group is concomitantly lost to give the quinindoline **28**. In other words, in carbodiimides of type **13** the presence of an electron-donating group at the dienophile portion leads to intramolecular cycloaddition instead of the expected electrocyclic ring closure. The formation of the electrocyclic ring closure product, quinoline **31**, by thermal treatment of the carbodiimide **30**, could be understood by the presence of a methyl group on the nonterminal carbon atom of the dienophile preventing the intramolecular cycloaddition[13] as well as the aromatization step.

In order to investigate the generality of this consecutive process, variations were considered. It was of interest to see what would happen if the carbodiimide moiety were replaced by another type of heterocumulene such as a ketene imine function. Thus, iminophosphoranes **2a** and **2c** were treated with ketenes in dry toluene at room temperature to give the corresponding ketene imines, which on heating at 160 °C in a sealed tube afforded the quinoline derivatives **32**. However, iminophosphorane **6a** under the same reaction conditions led to the tetracyclic compound **33** and no trace of the electrocyclic ring closure product was detected.

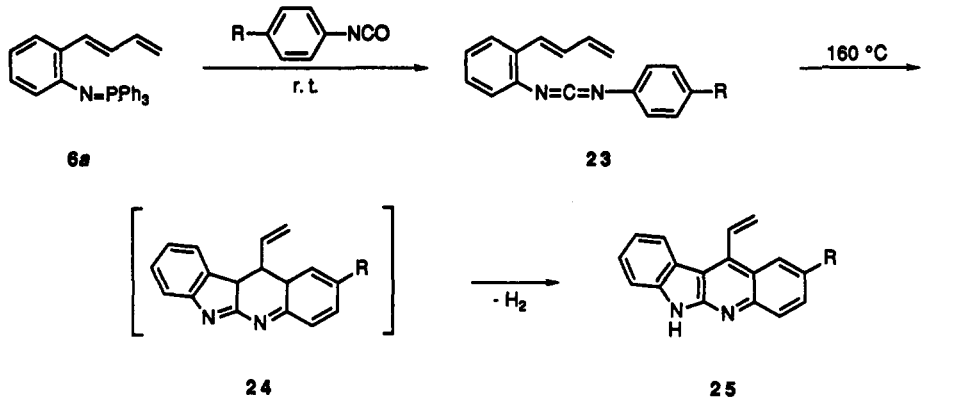
A final word about the dienophile geometry is relevant. The *E* and *Z* isomers of the iminophosphorane **12b**, isolated from an almost equimolecular mixture of the *E* and *Z* isomers by column chromatography, reacted with styryl and aryl isocyanates to give α-carbolines **22** and quinindolines **27**, respectively. The same compounds and yields were obtained when an equimolecular mixture of the *E* and *Z* isomers was used. In other words, the periselectivity of the reaction does not depend of the dienophile geometry.

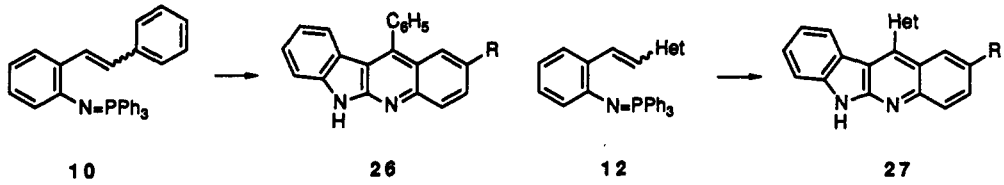
Concluding Remarks

In this paper, we have developed a simple but effective general one-pot strategy for the synthesis of a variety of quinoline, α-carboline, and quinindoline derivatives from readily available building blocks. Several trends have surfaced from our studies. First, *N,N'*-diaryl carbodiimides bearing one *o*-vinyl substituent undergo 6π-electrocyclization to give quinoline derivatives. Second, *N*-styryl-*N'*-aryl carbodiimides bearing either one *o*-vinyl or one *o*-butadienyl substituent undergo intramolecular hetero-Diels–Alder cycloaddition to give α-carbolines.

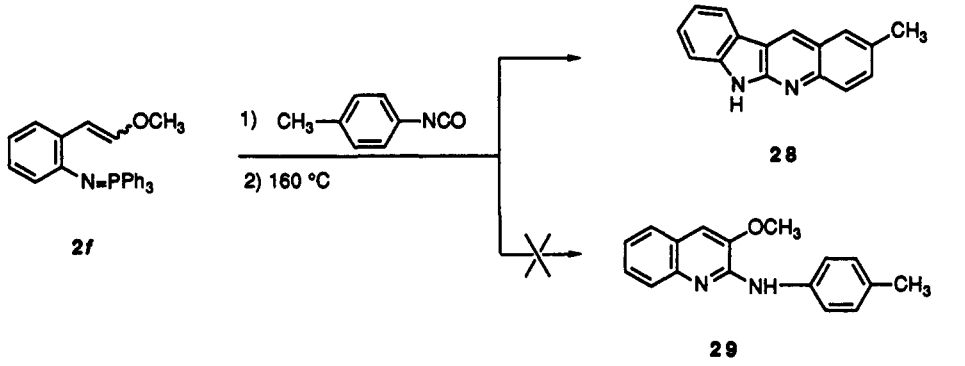
(13) Burke, S. D.; Strickland, S. M. S.; Powner, T. H. *J. Org. Chem.* **1983**, *48*, 454.

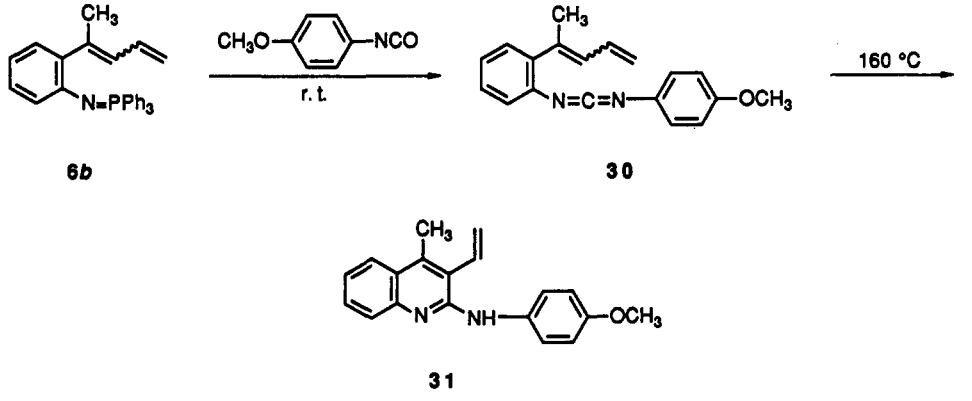
Scheme VI





Scheme VII

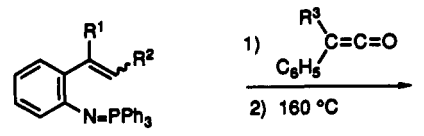




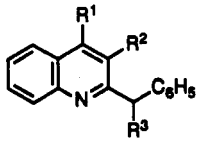
Third, *N,N'*-diaryl carbodiimides bearing one *o*-butadienyl substituent undergo intramolecular cyclization (IMDA) to give quinindoline derivatives. These results show a detailed and clear picture of the thermal behavior of the carbodiimides obtained from the reaction of iminophosphoranes derived from *ortho*-substituted anilines with an unsaturated side chain and aryl or styryl isocyanates; simply by changing either the nature of the *ortho* substituent or the isocyanate the reaction may be driven toward the production of quinolines, α-carbolines, or quinindolines. Fourthly, this work shows for the first time that easily available C=C-conjugated carbodiimides may react as 2-azadienes in intramolecular [4 + 2] cycloadditions; obviously the structural conditions in *N*-aryl(styryl)-*N'*-(*o*-butadienyl)(*o*-vinyl) carbodiimides provide an energetically favorable situation for this exceptional behavior.[14] Further studies are under way in our laboratory to explore the scope and generality of this methodology, and we hope that it will find further useful applications to produce structurally complex nitrogen heterocycles of demonstrated utility or theoretical interest.

(14) Rzepa, H. S.; Molina, P.; Alajarín, M.; Vidal, A. Manuscript in preparation.

Scheme VIII



2a, 2c



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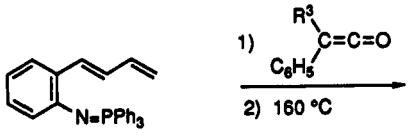
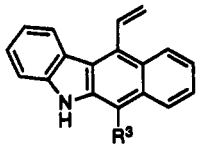


6a



33

Experimental Section

General Methods. General experimental conditions and spectroscopic instrumentation used have been described.[9]

Materials. *o*-Vinylaniline[15] (**1a**), *o*-(1-methylethenyl)aniline[16] (**1b**), (*E*)-*o*-(prop-1-enyl)aniline[17] (**1c**), methyl (*E*)-3-(*o*-aminophenyl)propenoate[18] (**1e**), *o*-ethynylaniline[19] (**3**), (*E*)-*o*-(butadienyl)aniline[20] (**5a**), (*E*)-3-(*o*-aminophenyl)propenal *N,N*-dimethylhydrazone[21] (**7**), 2-aminostilbene[22] (**9**), 2-(*o*-nitrostyryl)-furan, and 2-(*o*-nitrostyryl)thiophene[23] were prepared as mixtures of *E* and *Z* isomers as described in the literature. The previously unreported *o*-(1,2-dimethylethenyl)aniline (**2d**) and *o*-(1-methylbutadienyl)aniline (**5b**) were prepared from *o*-aminoacetophenone and ethylmagnesium bromide or allylmagnesium bromide by following the procedure reported for a similar preparation of 1-methyl-1-(*o*-aminophenyl)-2-phenylethylene.[24]

(*E*)-*o*-(2-Methoxyethenyl)aniline (2f). To a suspension of (methoxymethyl)triphenylphosphonium chloride (6.85 g, 20 mmol) in 50 mL of dry ether cooled at −20 °C was added 13 mL of *n*-butyllithium (1.6 M in hexane). The mixture was stirred at −20 °C for 2 h, then *o*-nitrobenzaldehyde (3.02 g, 20 mmol) was added. The resultant mixture was stirred at −20 °C for 2 h and then allowed to warm at room temperature. The precipitated solid was separated by filtration, and the filtrate was washed with water and dried on $MgSO_4$. The solvent was removed, and the residual materials were purified by column chromatography (silica gel, and *n*-hexane/ether (3:2) as eluent) to give (*E*)-*o*-(2-methoxyethenyl)nitrobenzene (57%). A mixture of (*E*)-*o*-(2-methoxyethenyl)nitrobenzene and ammonium chloride (7.5 g) in 400 mL of water was stirred vigorously at room temperature, and zinc (3.72 g) in 400 mL of water was stirred vigorously at room temperature, and zinc (3.72 g) was added in small portions. After being stirred for 5 h, the reaction mixture was diluted with 200 mL of ether and the organic layer was separated, washed with brine, and dried on $MgSO_4$. The solvent was removed under reduced pressure to afford the crude product **2f** which due to its instability was used without purification for the next step.

General Procedure for the Preparation of Amines (11). To a well-stirred mixture of 2-(*o*-nitrostyryl)furan, 2-(*o*-nitrostyryl)thiophene, or 4-(*o*-nitrostyryl)pyridine (20 mmol) and iron filings (11.17 g) in 150 mL of ethanol was added 150 mL of glacial acetic acid. The reaction mixture was heated at reflux temperature for 3 h. After cooling, the solution was poured into water (400 mL) and neutralized with Na_2CO_3. The resultant mixture was extracted with ether (3 × 250 mL), and the combined organic layer was washed with water (250 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude product **11** was purified by chromatography on silica gel column.

(*Z*)-2-(*o*-Aminostyryl)furan (11a): yield 85%; oil (eluent *n*-hexane/ethyl acetate (9:1); IR (neat) 3468, 3376 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.60 (s, 2 H), 6.08 (d, 1 H, J = 3.4 Hz), 6.24 (dd, 1 H, J = 1.6, 3.4 Hz), 6.31 (d, 1 H, J = 12.3 Hz), 6.51 (d, 1 H, J = 12.3 Hz), 6.67 (d, 1 H, J = 7.9 Hz), 6.73 (t, 1 H, J = 7.5 Hz), 7.09 (t, 1 H, J = 7.9 Hz), 7.24 (d, 1 H, J = 7.5 Hz), 7.25 (d, 1 H, J = 1.6 Hz), ^{13}C NMR ($CDCl_3$) δ 109.48 (C_3), 111.37 (C_4), 115.32 ($C_{3'}$), 118.18 ($C_{5'}$), 120.24 (C_α), 123.14 ($C_{1'}$), 123.95 (C_β), 128.59 ($C_{4'}$), 129.43 ($C_{6'}$), 141.61 (C_5), 143.63 ($C_{2'}$), 151.93 (C_2). Anal. Calcd for $C_{12}H_{11}NO$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.70; H, 5.83; N, 7.39.

(*E*)-2-(*o*-Aminostyryl)furan (11a): yield 70%; oil (eluent *n*-hexane/ethyl acetate (4:1); IR (neat) 3462, 3379 cm^{-1}; ^1H NMR ($CDCl_3$), δ 4.01 (s, 2 H), 6.31 (d, 1 H, J = 3.3 Hz), 6.40 (dd, 1 H, J = 1.5, 3.3 Hz), 6.67 (d, 1 H, J = 7.9 Hz), 6.78 (d, 1 H, J = 16.0 Hz), 6.78 (t, 1 H, J = 7.6 Hz), 7.07 (t, 1 H, J = 7.9 Hz), 7.09 (d, 1 H, J = 16.0 Hz), 7.35 (d, 1 H, J = 7.6 Hz), 7.37 (d, 1 H, J = 1.5 Hz); ^{13}C NMR ($CDCl_3$) δ 108.35 (C_3), 111.64 (C_4), 116.49 ($C_{3'}$), 117.78 ($C_{5'}$), 119.29 (C_α), 122.35 (C_β), 123.34 ($C_{1'}$), 126.67 ($C_{6'}$), 128.64 ($C_{4'}$), 142.01 (C_5), 143.70 ($C_{2'}$), 143.45 (C_2). Anal. Calcd for $C_{12}H_{11}NO$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.83; H, 5.82; N, 7.50.

(*Z*)-2-(*o*-Aminostyryl)thiophene (11b): yield 78%; oil (eluent *n*-hexane/ethyl acetate (9:1); IR (neat) 3467, 3375 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.53 (s, 2 H), 6.36 (d, 1 H, J = 11.6 Hz), 6.73 (t, 1 H, J = 8.1 Hz), 6.83 (d, 1 H, J = 11.6 Hz), 6.84 (d, 1 H, J = 7.6 Hz), 6.86 (d, 1 H, J = 4.6 Hz), 6.95 (d, 1 H, J = 3.5 Hz), 7.04 (dd, 1 H, J = 3.5, 4.6 Hz), 7.04–7.23 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 115.49 ($C_{3'}$), 118.64 ($C_{5'}$), 122.69 ($C_{1'}$), 124.38 (C_α), 125.67 (C_β), 126.25 (C_5), 126.41 (C_4), 128.45 ($C_{3'}$), 128.98 ($C_{4'}$), 129.82 ($C_{6'}$), 139.64 (C_2), 144.01 ($C_{2'}$). Anal. Calcd for $C_{12}H_{11}NS$: C, 71.60; H, 5.51; N, 6.96. Found: C, 71.43; H, 5.39; N, 6.80.

(*E*)- and (*Z*)-4-(*o*-Aminostyryl)pyridine (11c): yield 84% (as a 3:1 mixture of *Z* and *E* isomers); IR (Nujol) 3415, 3313 cm^{-1}; ^1H NMR ($CDCl_3$) δ *Z* isomer 5.12 (s, 2 H), 6.43 (d, 1 H, J = 14.5 Hz), 6.40–6.63 (m, 1 H), 6.76–6.88 (m, 1 H), 6.76–7.18 (m, 3 H), 7.17 (d, 2 H, J = 4.9 Hz), 8.40 (d, 2 H, J = 4.9 Hz); E isomer 5.12 (s, 2 H), 6.40–6.63 (m, 1 H), 6.96–7.18 (m, 1 H), 6.76–7.02 (m, 2 H), 7.57 (d, 1 H, J = 16.6 Hz), 7.60 (d, 2 H, J = 4.8 Hz), 7.70 (d, 1 H, J = 16.6 Hz), 8.53 (d, 2 H, J = 4.8 Hz); ^{13}C NMR ($CDCl_3$) δ *Z* isomer 115.15 ($C_{3'}$), 115.89 (C_α), 120.13 ($C_{1'}$), 122.99 (C_3 and C_5), 127.21 ($C_{5'}$), 128.71 (C_β), 128.91 ($C_{4'}$), 131.62 ($C_{6'}$), 144.26 ($C_{2'}$), 146.18 (C_4), 149.47 (C_1 and C_6); *E* isomer 116.36 ($C_{3'}$), 119.72 ($C_{1'}$), 120.74 (C_3 and C_5), 123.92 (C_α), 125.93 (C_β), 127.21 ($C_{5'}$), 129.02 ($C_{4'}$), 129.49 ($C_{6'}$), 145.00 ($C_{2'}$), 146.98 (C_4), 149.74 (C_1 and C_6); mass spectrum m/z (relative intensity) 196 (M^+, 100). Anal. Calcd for $C_{13}H_{12}N_2$: C, 79.56; H, 6.16; N, 14.27. Found: C, 79.48; H, 6.03; N, 14.12.

General Procedure for the Preparation of Iminophosphoranes 2, 4, 6, 8, 10, and 12. To a solution of the appropriate amine (20 mmol) in 50 mL of dry acetonitrile were added triphenylphosphine (10.48 g, 40 mmol), 30 mL of triethylamine, and 20 mL of CCl_4. The resultant mixture was stirred at room temperature for 24 h, whereupon triethylammonium chloride precipitated and was separated by filtration. The filtrate was concentrated to dryness. The residual material was purified by

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column chromatography on alumina, eluting with *n*-hexane/ether (7:3) to affort the title iminophosphorane. Compound **6b**, obtained as a mixture of *E* and *Z* isomers, was used without purification in the next step.

2a: yield 77%; mp 135–136 °C; colorless prisms (benzene/*n*-hexane); IR (Nujol) 1436, 1306, 1109 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.16 (dd, 1 H, J = 1.8, 11.0 Hz), 5.66 (dd, 1 H, J = 1.8, 17.9 Hz), 6.44 (dt, 1 H, J = 1.3, 7.9 Hz), 6.61 (t, 1 H, J = 7.0 Hz), 6.76 (dt, 1 H, J = 1.8, 7.9), 7.32–7.50 (m, 10 H), 7.67–7.82 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 110.72 (C_β), 117.32 (C_5), 121.77 (d, $^3J_{P-C}$ = 10.3 Hz, C_6), 125.33 (d, $^4J_{P-C}$ = 1.8 Hz, C_3), 127.70 (C_4), 128.45 (d, $^3J_{P-C}$ = 12.0 Hz, C_m), 131.34 (d, $^1J_{P-C}$ = 100.2 Hz, C_i), 131.48 (d, $^4J_{P-C}$ = 2.7 Hz, C_p), 131.87 (d, $^3J_{P-C}$ = 20.9 Hz, C_2), 132.43 (d, $^2J_{P-C}$ = 9.8 Hz, C_o), 135.51 (C_α), 148.83 (C_1); mass spectrum m/z (relative intensity) 379 (M^+, 3), 183 (100). Anal. Calcd for $C_{26}H_{22}NP$: C, 82.30; H, 5.84; N, 3.69. Found: C, 82.51; H, 5.83; N, 3.64.

2b: yield 73%; mp 118–120 °C; colorless prisms (benzene/*n*-hexane); IR 1435, 1336, 1109 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.27 (s, 3 H), 5.05–5.12 (m, 2 H), 6.46 (d, 1 H, J = 7.4 Hz), 6.60 (t, 1 H, J = 7.0 Hz), 6.75 (dt, 1 H, J = 2.2, 7.4 Hz), 7.10 (dt, 1 H, J = 2.2, 7.4 Hz), 7.30–7.42 (m, 9 H), 7.68–7.78 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 23.36 (CH_3), 112.95 (C_β), 117.12 (C_5), 121.74 (d, $^3J_{P-C}$ = 10.1 Hz, C_6), 127.10 (C_4), 128.48 (d, $^3J_{P-C}$ = 11.9 Hz, C_m), 128.93 (d, $^4J_{P-C}$ = 2.0 Hz, C_3), 131.60 (d, $^1J_{P-C}$ = 100.0 Hz, C_i), 131.40 (d, $^4J_{P-C}$ = 2.8 Hz, C_p), 132.50 (d, $^2J_{P-C}$ = 9.6 Hz, C_o), 139.09 (d, $^3J_{P-C}$ = 22.0 Hz, C_2), 148.24 (C_1), 148.57 (C_α); mass spectrum m/z (relative intensity) 393 (M^+, 7), 183 (86), 130 (100). Anal. Calcd for $C_{27}H_{24}NP$: C, 82.42; H, 6.15; N, 3.56. Found: C, 82.39; H, 6.19; N, 3.60.

2c: yield 66% (as a 3:1 mixture of *Z* and *E* isomers); colorless prisms (benzene/*n*-hexane); IR (Nujol) 1437, 1343, 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.86 (dd, 2.25 H, J = 1.8, 7.0 Hz), 1.90 (dd, 0.75 H, J= 1.7, 6.5 Hz), 5.75 (dq, 0.75 H, J = 7.0, 11.6 Hz), 6.14 (dq, 0.25 H, J = 6.5, 15.9 Hz), 6.43–6.82 (m, 3 H),7.02–7.09 (m, 1 H), 7.25 (dt, 1 H, J = 2.3, 7.4 Hz), 7.32–7.51 (m, 9 H), 7.68–7.79 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ *Z* isomer 14.87 (CH_3), 116.80 (d, $^4J_{P-C}$ = 0.9 Hz, C_5), 121.82 (d, $^3J_{P-C}$ = 9.8 Hz, C_6), 123.38 (C_β), 126.81 (C_4), 128.45 (d, $^3J_{P-C}$ = 12.0 Hz, C_m), 129.66 (d, $^4J_{P-C}$ = 1.5 Hz, C_3), 129.87 (C_α), 131.34 (d, $^1J_{P-C}$ = 100.9 Hz, C_i), 131.47 (d, $^4J_{P-C}$ = 2.8 Hz, C_p), 132.17 (d, $^3J_{P-C}$ = 20.4 Hz, C_2), 132.55 (d, $^2J_{P-C}$ = 9.6 Hz, C_o), 149.46 (d, $^2J_{P-C}$ = 1.4 Hz, C_1); mass spectrum m/z (relative intensity) 393 (M^+, 3), 183 (100). Anal. Calcd for $C_{27}H_{24}NP$: C, 82.42; H, 6.15; N, 3.56. Found: C, 82.48; H, 6.09; N, 3.52.

2d: yield 65%; mp 132–134 °C; colorless prisms (benzene/*n*-hexane); IR (Nujol) 1436, 1327, 1109 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.76 (d, 3 H, J = 6.7 Hz), 2.10 (s, 3 H), 5.52 (q, 1 H, J = 6.7 Hz), 6.45–6.76 (m, 2 H), 6.72–6.81 (m, 1 H), 7.03 (dt, 1 H, J = 2.2, 7.3 Hz), 7.30–7.47 (m, 9 H), 7.66–7.76 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 13.92 (CH_3C_β), 17.27 (CH_3C_α), 117.32 (d, $^4J_{P-C}$ = 0.9 Hz, C_5), 121.58 (C_β), 121.92 (d, $^3J_{P-C}$ = 9.7 Hz, C_6), 126.63 (C_4), 128.29 (d, $^3J_{P-C}$ = 11.9 Hz, C_m), 129.21 (d, $^4J_{P-C}$ = 1.6 Hz, C_3), 131.37 (d, $^4J_{P-C}$ = 2.7 Hz, C_p), 131.81 (d, $^1J_{P-C}$ = 99.4 Hz, C_i), 132.55 (d, $^2J_{P-C}$ = 9.6 Hz, C_o), 139.38 (C_α), 141.34 (d, $^3J_{P-C}$ = 21.2 Hz, C_2), 148.21 (C_1); mass spectrum m/z (relative intensity) 407 (M^+, 5), 183 (100). Anal. Calcd for $C_{28}H_{26}NP$: C, 82.53; H, 6.42; N, 3.44. Found: C, 82.48; H, 6.35; N, 3.48.

2e: yield 61%, mp 135 °C; yellow prisms (benzene/*n*-hexane); IR (Nujol) 1712, 1437, 1345, 1114 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.78 (s, 3 H), 6.45 (d, 1 H, J = 8.0 Hz), 6.51 (d, 1 H, J = 16.2 Hz), 6.61 (t, 1 H, J = 7.3 Hz), 6.85 (dt, 1 H, J = 1.6, 7.4 Hz), 7.37–7.54 (m, 10 H), 7.69–7.80 (m, 6 H), 8.78 (d, 1 H, J = 16.2 Hz); ^{13}C NMR ($CDCl_3$) δ 51.16 (CH_3O), 114.41 (C_3), 117.24 ($C_{4'}$), 122.22 (d, $^3J_{P-C}$ = 10.4 Hz, $C_{3'}$), 127.54 (d, $^4J_{P-C}$ = 2.2 Hz, $C_{6'}$), 128.38 (d, $^3J_{P-C}$ 21.3 Hz, $C_{1'}$), 128.60 (d, $^3J_{P-C}$ = 12.1 Hz, C_m), 130.35 ($C_{5'}$), 130.76 (d, $^1J_{P-C}$ = 99.7 Hz, C_i), 131.72 (d, $^4J_{P-C}$ = 2.9 Hz, C_p), 132.44 (d, $^2J_{P-C}$ = 9.8 Hz, C_o), 144.63 (C_2), 151.52 ($C_{2'}$), 168.60 (C_1); mass spectrum m/z (relative intensityi) 437 (M^+, 6), 378 (100), 183 (95). Anal. Calcd for $C_{28}H_{24}NO_2P$: C, 76.87; H, 5.53; N, 3.20. Found: C, 76.85; H, 5.57; N, 3.26.

2f: yield 67%; colorless prisms (benzene); IR (Nujol) 1435, 1350, 1106 cm^{-1}, ^1H NMR ($CDCl_3$) δ 3.68 (s, 3 H), 6.43–6.70 (m, 4 H), 7.15 (d, 1 H, J = 13.1 Hz), 7.18–7.20 (m, 1 H), 7.36–7.49 (m, 9 H), 7.70–7.80 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 56.15 (CH_3O), 104.71 (C_α), 117.68 (d, $^4J_{P-C}$ = 0.6 Hz, C_5), 121.75 (d, $^3J_{P-C}$ = 9.8 Hz, C_6), 125.03 (d, $^4J_{P-C}$ = 1.8 Hz, C_3), 125.78 (C_4), 128.52 (d,$^3J_{P-C}$ = 11.9 Hz, C_m), 130.55 (d, $^3J_{P-C}$ = 20.9 Hz, C_2), 131.55 (d, $^4J_{P-C}$ = 2.9 Hz, C_p), 131.63 (d, $^1J_{P-C}$ = 100.0 Hz, C_i), 132.57 (d, $^2J_{P-C}$ = 9.7 Hz, C_o), 147.42 (C_β), 147.71 (d, $^2J_{P-C}$ = 1.1 Hz, C_1); mass spectrum m/z (relative intensity) 409 (M^+, 5), 183 (100). Anal. Calcd for $C_{27}H_{24}NOP$: C, 79.12; H, 5.91; N, 3.42. Found: C, 79.09; H, 5.82; N, 3.38.

4: yield 47%; mp 141 °C; colorless prisms (benzene/*n*-hexane); IR (Nujol) 3284, 1438, 1342, 1109 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.32 (s, 1 H), 6.44 (d, 1 H, J = 7.9 Hz), 6.55 (t, 1 H, J = 7.9 Hz), 6.83 (t, 1 H, J = 7.9 Hz), 7.33–7.51 (m, 10 H), 7.76–7.86 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 79.29 (C_β), 85.25 (C_α), 116.92 (C_5), 117.41 (d, $^3J_{P-C}$ = 22.9 Hz, C_2), 121.36 (d, $^3J_{P-C}$ = 9.7 Hz, C_6), 128.54 (d, $^3J_{P-C}$ = 12.0 Hz, C_m), 128.89 (C_4), 131.11 (d, $^1J_{P-C}$ = 100.4 Hz, C_i), 131.68 (d, $^4J_{P-C}$ = 2.7 Hz, C_p), 132.68 (d, $^2J_{P-C}$ = 9.8 Hz, C_o), 133.65 (d, $^4J_{P-C}$ = 1.9 Hz, C_3), 153.62 (C_1); mass spectrum m/z (relative intensity) 377 (M^+, 15), 183 (100). Anal. Calcd for $C_{26}H_{20}NP$: C, 82.74; H, 5.34; N, 3.71. Found: C, 82.80; H, 5.41; N, 3.77.

6a: yield 56%; mp 121–122 °C; colorless prisms (benzene/*n*-hexane); IR (Nujol) 1436, 1338, 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.04 (dd, 1 H, J = 1.5, 9.6 Hz), 5.22 (dd, 1 H, J = 1.5, 16.2 Hz), 6.43–6.92 (m, 5 H), 7.34–7.51 (m, 10 H), 7.59 (d, 1 H, J = 15.6 Hz), 7.69–7.79 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 114.62 (C_β), 117.46 (C_5), 122.03 (d, $^3J_{P-C}$ = 10.2 Hz, C_6), 125.82 (d, $^4J_{P-C}$ = 1.4 Hz, C_3), 127.23, 127.67, 128.55 (d, $^3J_{P-C}$ = 12.0 Hz, C_m), 131.10 (d, $^3J_{P-C}$ = 21.1 Hz, C_2), 131.31 (d, $^1J_{P-C}$ = 99.9 Hz, C_i), 131.61 (d, $^4J_{P-C}$ = 2.5 Hz, C_p), 132.50 (d, $^2J_{P-C}$ = 9.7 Hz, C_o), 138.95, 149.29 (C_1), one carbon was not observed; mass spectrum m/z (relative intensity) 405 (M^+, 4), 183 (100). Anal. Calcd for $C_{28}H_{24}NP$: C, 82.94; H, 5.96;, N, 3.45. Found: C, 82.99; H, 6.02; N, 3.51.

8: yield 67%; mp 127–128 °C; colorless prisms (benzene); IR (Nujol) 1437, 1347, 1113 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.87 (s, 6 H), 6.44 (d, 1 H, J = 7.8 Hz), 6.61 (t, 1 H, J = 7.3 Hz), 6.74 (dt, 1 H, J = 1.6, 7.3 Hz), 6.93 (dd, 1 H, J = 9.0, 16.2 Hz), 7.34 (d, 1 H, J = 9.0 Hz), 7.35–7.53 (m, 11 H), 7.69–7.79 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 43.17 [$(CH_3)_2N$], 117.63 ($C_{4'}$), 122.06 (d, $^3J_{P-C}$ = 10.3 Hz, $C_{3'}$), 124.63 (C2), 125.37 (d, $^4J_{P-C}$ = 1.7 Hz, $C_{6'}$), 127.72 ($C_{5'}$), 128.56 (d, $^3J_{P-C}$ = 12.0 Hz, C_m), 131.20 (d, $^3J_{P-C}$ = 20.8 Hz, $C_{1'}$), 131.28 (d, $^1J_{P-C}$ = 99.8 Hz, C_i), 131.63 (d, $^4J_{P-C}$ = 2.8 Hz, C_p), 132.16, 132.53 (d, $^2J_{P-C}$ = 9.6 Hz, C_o), 138.96, 149.11 (d, $^2J_{P-C}$ = 0.9 Hz, $C_{2'}$); mass spectrum m/z (relative intensity) 442 (M^+, 2), 183 (100). Anal. Calcd for $C_{29}H_{28}N_3P$: C, 77.48; H, 6.28; N, 9.34. Found: C, 77.37; H, 6.09; N, 9.39.

10: yield 54% (as a 4:1 mixture of *Z* and *E* isomers); yellow prisms (benzene/*n*-hexane); IR (Nujol) 1438, 1339, 1111 cm^{-1}; ^1H NMR (DMSO-d_6) δ 6.53 (d, 0.8 H, J = 12.3 Hz), 6.32–7.39 (m, 9 H), 7.44–7.66 (m, 10 H), 7.71–7.84 (m, 6 H), 8.16 (d, 0.2 H, J = 16.8 Hz); mass spectrum m/z (relative intensity) 455 (M^+, 12), 183 (100). Anal. Calcd for $C_{32}H_{26}NP$: C, 84.37; H, 5.75; N, 3.07. Found: C, 84.19; H, 5.63; N, 2.92.

***Z*-12a**: yield 64%; mp 108–109 °C; yellow prisms (benzene/*n*-hexane); IR (Nujol) 1586, 1439, 1314, 1112 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.23–6.29 (m, 2 H), 6.37 (d, 1 H, J = 12.6 Hz), 6.50 (d, 1 H, J = 7.9 Hz), 6.62 (d, 1 H, J = 7.9 Hz), 6.83 (t, 1 H, J = 7.9 Hz), 7.06 (d, 1 H, J = 12.6 Hz), 7.25 (d, 1 H, J = 1.0 Hz), 7.34–7.53 (m, 10 H), 7.69–7.79 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 108.24 (C_3), 111.05 (C_4), 115.55 (C_α), 116.98 (d, $^4J_{P-C}$ = 1.0 Hz, $C_{4'}$), 121.91 (d, $^3J_{P-C}$ 9.6 Hz, $C_{3'}$), 127.93 ($C_{5'}$), 128.52 (d, $^3J_{P-C}$ = 11.9 Hz, C_m), 129.48 (d, $^4J_{P-C}$ = 1.3 Hz, $C_{6'}$), 129.57 (C_β), 131.55 (d, $^4J_{P-C}$ = 2.8 Hz, C_p), 131.60 (d, $^1J_{P-C}$ = 104.6 Hz, C_i), 132.17 (d, $^3J_{P-C}$ = 20.3 Hz, $C_{1'}$), 132.67 (d, $^2J_{P-C}$ = 9.5 Hz, C_o), 140.59 (C_5), 149.63 (d, $^2J_{P-C}$ = 1.4 Hz, $C_{2'}$), 153.42 (C_2); mass spectrum m/z (relative intensity) 445 (M^+, 3), 183 (100). Anal. Calcd for $C_{30}H_{24}NOP$: C, 80.88; H, 5.43; N, 3.14. Found: C, 80.69; H, 5.31; N, 3.01.

***E*-12a**: yield 30%; mp 96–98 °C; orange prisms (benzene/*n*-hexane); IR (Nujol) 1586, 1437, 1345, 1109 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.24 (d, 1 H, J = 3.2 Hz), 6.37 (dd, 1 H, J = 1.8, 3.2 Hz), 6.45 (d, 1 H, J = 7.8 Hz), 6.63 (t, 1 H, J = 7.8 Hz), 6.77 (t, 1 H, J = 7.8 Hz), 7.01 (d, 1 H, J = 16.6 Hz), 7.36 (d, 1 H, J = 1.8 Hz), 7.35–7.53 (m, 10 H), 7.78–7.83 (m, 6 H), 8.04 (d, 1 H, J = 16.6 Hz); ^{13}C NMR ($CDCl_3$) δ 106.25 (C_3), 111.34 (C_4), 114.45 (C_α), 117.58 (d, $^4J_{P-C}$ = 1.0 Hz, $C_{4'}$), 122.13 (d, $^3J_{P-C}$ = 10.0 Hz, $C_{3'}$), 125.86 (d, $^4J_{P-C}$ = 2.0 Hz, $C_{6'}$), 127.11 (C_β), 127.59 ($C_{5'}$), 128.52 (d, $^3J_{P-C}$ = 12.0 Hz, C_m), 131.12 (d, $^3J_{P-C}$ = 20.7 Hz, $C_{1'}$), 131.26 (d, $^1J_{P-C}$ = 100.0 Hz, C_i), 131.57 (d, $^4J_{P-C}$ = 2.8 Hz, C_p), 132.53 (d, $^2J_{P-C}$ = 9.7 Hz, C_o), 141.10 (C_5), 149.24 (d, $^2J_{P-C}$ = 0.8 Hz, $C_{2'}$), 155.09 (C_2); mass spectrum m/z (relative intensity) 445 (M^+, 6),

183 (100). Anal. Calcd for $C_{30}H_{24}NOP$: C, 80.88; H, 5.43; N, 3.14. Found: C, 80.81; H, 5.33; N, 3.02.

12b: yield 98% (as a 3:2 mixture of *Z* and *E* isomers); yellow prisms (benzene/*n*-hexane); IR (Nujol) 1586, 1438, 1326, 1113 cm^{-1}; ^1H NMR ($CDCl_3$) δ *Z* isomer 6.67 (d, 1 H, J = 12.0 Hz), 7.03 (d, 1 H, J = 12.0 Hz), 6.50–7.11 (m, 6 H), 7.31–7.39 (m, 10 H), 7.67–7.78 (m, 6 H); *E* isomer 6.46–7.20 (m, 6 H), 7.27 (d, 1 H, J = 16.4 Hz), 7.31–7.50 (m, 10 H), 7.60–7.83 (m, 6 H), 8.04 (d, 1 H, J = 16.4 Hz); ^{13}C NMR ($CDCl_3$) δ *Z* isomer 117.20 (d, $^4J_{P-C}$ = 1.2 Hz, $C_{4'}$), 120.58 (C_4), 121.96 (d, $^3J_{P-C}$ = 9.5 Hz, $C_{3'}$), 124.25 (C_o), 125.98 (C_5), 127.03 (C_3), 127.07 ($C_{5'}$), 128.38 (d, $^3J_{P-C}$ = 12.0 Hz, C_m), 129.91 (d, $^4J_{P-C}$ = 1.3 Hz, $C_{8'}$), 130.42 (C_8), 131.52 (d, $^1J_{P-C}$ = 103.0 Hz, C_i), 131.72 (d, $^4J_{P-C}$ = 2.8 Hz, C_p), 131.88 (d, $^3J_{P-C}$ = 20.7 Hz, $C_{1'}$), 132.48 (d, $^2J_{P-C}$ = 9.7 Hz, C_o), 141.23 (C_2), 149.74 (d, $^2J_{P-C}$ = 1.0 Hz, $C_{2'}$); *E* isomer 117.58 (d, $^4J_{P-C}$ = 1.0 Hz, $C_{4'}$), 119.18 (C_4), 122.04 (d, $^3J_{P-C}$ = 9.8 Hz, $C_{3'}$), 122.84 (C_o), 124.44 (C_5), 125.62 (d, $^4J_{P-C}$ = 1.8 Hz, $C_{8'}$), 127.32 ($C_{5'}$), 127.70 (C_3), 128.57 (d, $^3J_{P-C}$ = 12.0 Hz, C_m), 131.06 (d, $^3J_{P-C}$ = 20.9 Hz, $C_{1'}$), 131.33 (d, $^1J_{P-C}$ = 100.0 Hz, C_i), 131.47 (d, $^4J_{P-C}$ = 2.9 Hz, C_p), 131.87 (C_8), 132.57 (d, $^2J_{P-C}$ = 9.7 Hz, C_o), 145.33 (C_2), 149.21 (d, $^2J_{P-C}$ = 1.1 Hz, $C_{2'}$); mass spectrum m/z (relative intensity) 461 (M^+, 11), 183 (100). Anal. Calcd for $C_{30}H_{24}NPS$: C, 78.07; H, 5.24; N, 3.03. Found: C. 77.86; H, 5.13; N, 2.88.

12c: yield 59% (as a 9:1 mixture of the *Z* and *E* isomers); yellow prisms (benzene/*n*-hexane); IR (Nujol) 1590, 1439, 1342, 1114 cm^{-1}; ^1H NMR (DMSO-d_6) δ *Z* isomer 6.42 (t, 1 H, J = 7.8 Hz), 6.52 (d, 1 H, J = 12.3 Hz), 6.67–6.74 (m, 2 H), 7.17 (d, 2 H, J = 5.0 Hz), 7.31 (d, 1 H, J = 12.3 Hz), 7.59–7.71 (m, 10 H), 7.71–7.81 (m, 6 H), 8.36 (d, 2 H, J = 5.0 Hz); ^{13}C NMR ($CDCl_3$) δ *Z* isomer 116.82 (d, $^4J_{P-C}$ = 1.0 Hz, $C_{4'}$), 121.43 (d, $^3J_{P-C}$ = 9.5 Hz, $C_{3'}$), 123.14 (C_3 and C_5), 127.11 ($C_{5'}$), 128.75 (C_o), 128.77 (d, $^3J_{P-C}$ = 11.7 Hz, C_m), 129.10 (d, $^4J_{P-C}$ = 1.3 Hz, $C_{8'}$), 130.95 (C_8), 131.57 (d, $^1J_{P-C}$ = 103.7 Hz, C_i), 131.90 (d, $^3J_{P-C}$ = 20.5 Hz, $C_{1'}$), 132.08 (d, $^4J_{P-C}$ = 2.8 Hz, C_p), 132.18 (d, $^2J_{P-C}$ = 9.5 Hz, C_o), 145.14 (C_4), 149.40 (C_2 and C_6), 149.52 (d, $^2J_{P-C}$ = 1.2 Hz, $C_{2'}$); mass spectrum m/z (relative intensity) 456 (M^+, 5), 183 (100). Anal. Calcd for $C_{31}H_{25}N_2P$: C, 81.56; H, 5.62; N, 6.14. Found: C, 81.41; H, 5.51; N, 6.18.

General Procedure for the Preparation of 2-Aryl(alkyl)aminoquinolines 14. Reaction of Iminophosphoranes 2 with Aryl(alkyl) Isocyanates. To a solution of the adequate iminophosphorane **2** (3 mmol) in 30 mL of dry toluene was added the appropriate isocyanate (3 mmol). The reaction mixture was stirred at room temperature for 1 h, and the resulting carbodiimide **13** was heated in a sealed tube at 160 °C for 24 h. After the mixture was cooled, the solvent was removed under reduced pressure, and the residual material was purified by chromatography on a silica gel column, eluting with ethyl acetate/*n*-hexane (3:7), and recrystallized from the appropriate solvent to afford **14** as crystalline solid.

14a: yield 82%; mp 96–97 °C, colorless prisms (ethyl ether/*n*-hexane); IR (Nujol) 3262, 1621 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.63 (d, 2 H, J = 5.6 Hz), 5.24 (t, 1 H, J = 5.6 Hz), 6.48 (d, 1 H, J = 8.8 Hz), 7.12–7.35 (m, 6 H), 7.43–7.52 (m, 2 H), 7.68 (d, 1 H, J = 8.8 Hz), 7.70 (d, 1 H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$) δ 45.65 (CH_2), 111.31 (C_3), 122.01 (C_6), 123.47 (C_{4a}), 126.13 ($C_{4'}$), 127.15 (C_8), 127.37 (C_5), 127.65 ($C_{3'}$ and $C_{5'}$), 128.51 ($C_{2'}$ and $C_{6'}$), 129.46 (C_7), 137.23 (C_4), 139.32 ($C_{1'}$), 147.95 (C_{8a}), 156.69 (C_2); mass spectrum m/z (relative intensity) 234 (M^+, 16), 106 (100). Anal. Calcd for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.95. Found: C, 81.91; H, 6.12: N, 11.89.

14b: yield 70%; mp 103–104 °C; colorless prisms (ether/*n*-hexane); IR (Nujol) 3403, 1623 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.88 (d, 1 H, J = 9.0 Hz), 7.03 (t, 1 H, J = 7.3 Hz), 7.19–7.37 (m, 4 H), 7.49–7.56 (m, 4 H), 7.60 (d, 1 H, J = 8.2 Hz), 7.79 (d, 1 H, J = 9.0 Hz); ^{13}C NMR ($CDCl_3$) δ 111.74 (C_3), 120.49 ($C_{2'}$ and $C_{8'}$), 122.98 ($C_{4'}$), 123.00 (C_6), 124.05 (C_{4a}), 126.56 (C_8), 127.38 (C_5), 129.14 ($C_{3'}$ and $C_{5'}$), 129.71 (C_7), 137.64 (C_4), 140.18 ($C_{1'}$), 147.55 (C_{8a}), 154.47 (C_2); mass spectrum m/z (relative intensity) 220 (M^+, 49), 219 (100). Anal. Calcd for $C_{15}H_{12}N_2$: C, 81.79; H, 5.49; N, 12.72. Found: C, 81.82; H, 5.40; N, 12.71.

14c: yield 87%; mp 138–139 °C; colorless prisms (ether/*n*-hexane); IR (Nujol) 3409, 1623 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.28 (s, 3 H), 6.85 (d, 1 H, J = 9.0 Hz), 7.13 (d, 2 H, J = 8.3 Hz), 7.20 (t, 1 H, J = 7.3 Hz), 7.33 (s, 1 H), 7.34 (d, 2 H, J = 8.3 Hz), 7.46–7.53 (m, 2 H), 7.73 (d, 1 H, J = 7.8 Hz), 7.75 (d, 1 H, J = 9.0 Hz); ^{13}C NMR ($CDCl_3$) δ 20.77 (CH_3), 111.41 (C_3), 121.29 ($C_{2'}$ and $C_{8'}$), 122.74 (C_6), 123.96 (C_{4a}), 126.42 (C_8), 127.35 (C_5), 129.62 (C_7), 129.67 ($C_{3'}$ and $C_{5'}$), 132.83 ($C_{4'}$), 137.48 ($C_{1'}$), 137.53 (C_4), 147.67 (C_{8a}), 154.99 (C_2); mass spectrum m/z (relative intensity) 234 (M^+, 51), 233 (100). Anal. Calcd for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.95. Found: C, 82.11; H, 6.00; N, 11.87.

14d: yield 63%; mp 129 °C; colorless prisms (ether/*n*-hexane); IR (Nujol) 3194, 1615 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.74 (s, 3 H), 6.69 (d, 1 H, J = 8.9 Hz), 6.85 (d, 2 H, J = 8.8 Hz), 7.20 (t, 1 H, J = 7.2 Hz), 7.37 (d, 2 H, J = 8.8 Hz), 7.40 (s, 1 H), 7.47 (d, 1 H, J = 7.8 Hz), 7.54 (d, 1 H, J = 7.8 Hz), 7.69 (d, 1 H, J = 8.3 Hz), 7.76 (d, 1 H, J = 8.9 Hz); ^{13}C NMR ($CDCl_3$) δ 55.42 (CH_3O), 111.06 (C_3), 114.45 ($C_{3'}$ and $C_{5'}$), 122.57 (C_6), 123.87 ($C_{2'}$ and $C_{8'}$), 126.27 (C_8), 127.37 (C_5), 129.62 (C_7), 133.04 ($C_{1'}$), 137.57 (C_4), 147.70 (C_{8a}), 155.58 (C_2), 156.19 ($C_{4'}$) (one quaternary carbon was not observed); mass spectrum m/z (relative intensity) 250 (M^+, 35), 128 (100). Anal. Calcd for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N, 11.19. Found: C, 76.68; H, 5.53; N, 11.01.

14e: yield 81%; mp 139–141 °C; colorless prisms (ether/*n*-hexane); IR (Nujol) 3171, 1622 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.44 (s, 3 H), 3.73 (s, 3 H), 6.62 (s, 1 H), 6.84 (d, 2 H, J = 8.8 Hz), 7.17–7.25 (m, 1 H), 7.37 (d, 2 H, J = 8.8 Hz), 7.40–7.51 (m, 2 H), 7.68–7.72 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.72 (CH_3C_4), 55.37 (CH_3O), 111.16 (C_3), 119.38 ($C_{3'}$ and $C_{5'}$), 122.30 (C_6), 123.49 (C_8), 123.79 ($C_{2'}$ and $C_{8'}$), 124.17 (C_{4a}), 126.75 (C_5), 129.28 (C_7), 133.20 ($C_{1'}$), 145.38 (C_4), 147.68 (C_{8a}), 155.37 (C_2), 156.04 ($C_{4'}$); mass spectrum m/z (relative intensity) 264 (M^+, 31), 115 (100). Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60. Found: C, 77.12; H, 6.16; N, 10.69.

14f: yield 82%; mp 94 °C; colorless prisms (*n*-hexane); IR (Nujol) 3443, 1632 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.15 (s, 3 H), 6.33 (s, 1 H), 7.00 (t, 1 H, J = 7.7 Hz), 7.19 (t, 1 H, J = 7.7 Hz), 7.31 (t, 2 H, J = 7.7 Hz), 7.43–7.48 (m, 2 H), 7.51 (s, 1 H), 7.78–7.82 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 17.40 (CH_3-C_3), 119.38 ($C_{2'}$ and $C_{8'}$), 119.92 (C_3), 122.11 ($C_{4'}$), 122.93 (C_6), 124.36 (C_{4a}), 126.43 (C_8), 126.68 (C_5), 128.45 (C_7), 128.74 ($C_{3'}$ and $C_{5'}$), 136.19 (C_4), 140.39 ($C_{1'}$), 146.17 (C_{8a}), 152.54 (C_2); mass spectrum m/z (relative intensity) 234 (M^+, 49), 233 (100). Anal. Calcd for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.95. Found: C, 82.13; H, 5.89; N, 11.90.

14g: yield 85%; mp 78–80 °C; colorless prisms (*n*-hexane); IR (Nujol) 3455, 1632 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.06 (s, 3 H), 6.23 (s, 1 H), 6.95 (t, 2 H, J = 8.7 Hz), 7.20 (t, 1 H, J = 7.8 Hz), 7.43–7.63 (m, 3 H), 7.65 (dd, 2 H, J = 4.8, 9.1 Hz), 7.66–7.76 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 17.07 (CH_3C_3), 114.97 (d, $^2J_{F-C}$ = 22.2 Hz, $C_{3'}$ and $C_{5'}$), 119.65 (C_3), 121.03 (d, $^3J_{F-C}$ = 7.6 Hz, $C_{2'}$ and $C_{8'}$), 122.78 (C_6), 124.26 (C_{4a}), 126.36 (C_5 and C_8), 128.36 (C_7), 136.08 (C_4), 136.33 (d, $^4J_{F-C}$ = 2.3 Hz, $C_{1'}$), 145.92 (C_{8a}), 152.39 (C_2), 158.00 (d, $^1J_{F-C}$ = 240.5 Hz, $C_{4'}$); mass spectrum m/z (relative intensity) 252 (M^+, 60), 251 (100). Anal. Calcd for $C_{16}H_{13}FN_2$: C, 76.17; H, 5.19; N, 11.10. Found: C, 76.10; H, 5.25; N, 11.00.

14h: yield 63%; mp 132 °C; colorless prisms (ether/*n*-hexane); IR (Nujol) 3392, 1595 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.11 (s, 3 H), 2.41 (s, 3 H), 3.73 (s, 3 H), 6.29 (s, 1 H), 6.35 (d, 2 H, J = 8.9 Hz), 7.21 (t, 1 H, J = 8.1 Hz), 7.45 (t, 1 H, J = 8.1 Hz), 7.62 (d, 2 H, J = 8.9 Hz), 7.69–7.76 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.24 (CH_3), 14.40 (CH_3), 55.35 (CH_3O), 113.86 ($C_{3'}$ and $C_{5'}$), 117.15 (C_3), 121.52 ($C_{2'}$ and $C_{8'}$), 122.34 (C_6), 123.28 (C_8), 124.19 (C_{4a}), 127.21 (C_5), 127.88 (C_7), 133.97 ($C_{1'}$), 140.60 (C_4), 145.45 (C_{8a}), 152.64 (C_2), 154.89 ($C_{4'}$); mass spectrum m/z (relative intensity) 278 (M^+, 84), 263 (100). Anal. Calcd for $C_{18}H_{18}N_2O$: C, 77.67; H, 6.52; N, 10.06. Found: C, 77.55; H, 6.58; N, 9.98.

14i: yield 71%; mp 107–108 °C; yellow needles (ether); IR (Nujol) 3307, 1710, 1624 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.87 (s, 3 H), 7.04 (t, 1 H, J = 7.0) Hz), 7.18 (t, 1 H, J = 7.0 Hz), 7.36 (t, 2 H, J = 7.6 Hz), 7.53–7.74 (m, 3 H), 7.95 (d, 2 H, J = 8.1 Hz), 8.60 (s, 1 H), 10.22 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 52.45 (CH_3O), 110.19 (C_3), 120.02 ($C_{2'}$ and $C_{8'}$), 122.22 (C_{4a}), 122.36 ($C_{4'}$), 123.28 (C_6), 126.81 (C_8), 128.75 ($C_{3'}$ and $C_{5'}$), 128.85 (C_5), 132.47 (C_7), 140.23 ($C_{1'}$), 142.46 (C_4), 149.66 (C_{8a}), 152.42 (C_2), 167.50 (CO); mass spectrum m/z (relative intensity) 278 (M^+, 54), 218 (100). Anal. Calcd for $C_{17}H_{14}N_2O_2$: C, 73.37; H, 5.07; N, 10.06. Found: C, 73.21; H, 5.18, N, 10.11.

14j: yield 69%; mp 121 °C; yellow needles (ether); IR (Nujol) 3296, 1703, 1621 cm^{-1}, ^1H NMR ($CDCl_3$) δ 2.32 (s, 3 H), 3.86 (s, 3 H), 7.14 (d, 2 H, J = 8.4 Hz), 7.17–7.20 (m, 1 H), 7.51–7.60 (m, 2 H), 7.70 (d, 1 H, J = 8.2 Hz), 7.82 (d, 2 H, J = 8.4 Hz), 8.58 (s, 1 H), 10.12 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.84 (CH_3), 52.35

(CH_3O), 110.08 (C_3), 120.17 ($C_{2'}$ and $C_{6'}$), 122.11 (C_{4a}), 123.03 (C_6), 126.74 (C_8), 128.81 (C_5), 129.20 ($C_{3'}$ and $C_{5'}$), 131.77 ($C_{4'}$), 132.37 (C_7), 137.60 ($C_{1'}$), 142.38 (C_4), 149.79 (C_{8a}), 152.50 (C_2), 167.48 (CO); mass spectrum m/z (relative intensity) 292 (M^+, 22), 115 (100). Anal. Calcd for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.28. Found: C, 73.89; H, 5.50; N, 9.15.

General Procedure for the Preparation of Pyrido[2,3-*b*]indoles (α-Carbolines). Reaction of Iminophosphoranes 2, 4, 6, 8, and 12 with Styryl Isocyanates. To a solution of the appropriate iminophosphorane **2**, **4**, **6**, **8**, or **12** (3 mmol) in 30 mL of dry toluene was added the corresponding styryl isocyanate (3 mmol). The resultant mixture was stirred at room temperature for 30 min, and the resulting carbodiimide **15** was heated in a sealed tube at 160 °C for 24 h. After the mixture was cooled, the solvent was removed under reduced pressure, the residual material was slurried with cold ethanol (10 mL), and the separated solid was dried and recrystallized from the appropriate solvent to give the title compounds as crystalline solids.

19a: yield 35%; mp 275–276 °C; colorless prisms (ethanol); IR (Nujol) 3126, 1609 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.25–7.63 (m, 6 H), 7.83 (d, 2 H, J = 7.5 Hz), 8.20 (d, 1 H, J = 7.7 Hz), 8.80 (d, 1 H, J = 2.0 Hz), 8.86 (d, 1 H, J = 2.0 Hz), 12.00 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 111.35 (C_8), 115.36 (C_3), 119.46 (C_6), 120.53 (C_{4a}), 121.38 (C_5), 126.43 (C_4), 126.71 (C_7), 126.77 ($C_{2'}$ and $C_{6'}$), 126.87 ($C_{4'}$), 127.62 (C_{4b}), 128.95 ($C_{3'}$ and $C_{5'}$), 138.62 ($C_{1'}$), 139.43 (C_{8a}), 144.74 (C_2), 151.49 (C_{9a}); mass spectrum m/z (relative intensity) 244 (M^+, 100), 122 (45). Anal. Calcd for $C_{17}H_{12}N_2$: C, 83.58; H, 4.95; N, 11.47. Found: C, 83.50; H, 4.88; N, 11.32.

19b: yield 38%; mp 265–266 °C; colorless prisms (ethanol); IR (Nujol) 3080, 1610 cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.82 (s, 3 H), 7.08 (d, 2 H, J = 8.7 Hz), 7.26 (t, 1 H, J = 7.0 Hz), 7.46–7.59 (m, 2 H), 7.74 (d, 2 H, J = 8.7 Hz), 8.26 (d, 1 H, J = 7.7 Hz), 8.72 (d, 1 H, J = 2.0 Hz), 8.77 (d, 1 H, J = 2.0 Hz), 11.89 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 55.10 (CH_3O), 111.30 (C_8), 114.45 ($C_{3'}$ and $C_{5'}$), 115.29 (C_3), 119.37 (C_6), 120.52 (C_{4a}), 121.36 (C_5), 125.93 (C_4), 126.66 (C_7), 127.43 (C_{4b}), 127.86 ($C_{2'}$ and $C_{6'}$), 130.96 ($C_{1'}$), 139.39 (C_{8a}), 144.42 (C_2), 151.11 (C_{9a}), 158.57 ($C_{4'}$); mass spectrum m/z (relative intensity) 274 (M^+, 100), 259 (57). Anal. Calcd for $C_{18}H_{14}N_2O$: C, 78.81; H, 5.14; N, 10.21. Found: C, 78.75; H, 5.09; N, 10.25.

19c: yield 40%; mp 235–236 °C; colorless prisms (ethanol); IR (Nujol) 3109, 1730 cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.86 (s, 3 H), 7.24–7.63 (m, 8 H), 7.90 (d, 1 H, J = 7.9 Hz), 8.58 (s, 1 H), 12.29 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 52.66 (CH_3O), 110.53 (s), 111.75 (C_8), 118.38 (s), 120.02 (C_6), 121.84 (C_5), 125.37 (s), 127.44 (C_7), 127.51 ($C_{4'}$), 128.52 ($C_{2'}$ and $C_{6'}$), 128.72 ($C_{3'}$ and $C_{5'}$), 131.99 (s), 137.36 ($C_{1'}$), 139.74 (C_{8a}), 146.88 (C_2), 151.26 (C_{9a}), 167.93 (CO); mass spectrum m/z (relative intensity) 302 (M^+, 100), 271 (46). Anal. Calcd for $C_{19}H_{14}N_2O_2$: C, 75.48; H, 4.67; N, 9.26. Found: C, 75.42; H, 4.59; N, 9.20.

19d: yield 37%; mp 251–252 °C; colorless prisms (ethanol); IR (Nujol) 3114, 1724 cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.82 (s, 3 H), 3.91 (s, 3 H), 7.06 (d, 2 H, J = 8.5 Hz), 7.29 (t, 1 H, J = 7.2 Hz), 7.42 (d, 2 H, J = 8.5 Hz), 7.49–7.66 (m, 2 H), 7.92 (d, 1 H, J = 7.8 Hz), 8.57 (s, 1 H), 12.27 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 52.64 ($COOCH_3$), 55.08 (CH_3O), 110.51 (s), 111.21 (C_8), 114.21 ($C_{3'}$), 118.45 (s), 119.94 (C_6), 121.77 (C_5), 125.10 (s), 127.39 (C_7), 129.54 ($C_{1'}$), 129.69 ($C_{2'}$ and $C_{6'}$), 131.89 (s), 139.74 (C_{8a}), 146.90 (C_2), 151.05 (C_{9a}), 158.79 ($C_{4'}$), 168.11 (CO); mass spectrum m/z (relative intensity) 332 (M^+, 100), 158 (47). Anal. Calcd for $C_{20}H_{16}N_2O_3$: C, 72.28; H, 4.85; N, 8.42. Found: C, 72.20; H, 4.79; N, 8.35.

20a: yield 44%; mp 253 °C; colorless needles (ethanol); IR (Nujol) 3100, 1569 cm^{-1}; ^1H NMR (DMSO-d_6) δ 5.55 (dd, 1 H, J = 1.1, 17.8 Hz), 5.73 (dd, 1 H, J = 1.1, 11.5 Hz), 7.10–7.25 (m, 2 H), 7.36–7.53 (m, 6 H), 7.62 (d, 1 H, J = 7.9 Hz), 8.27 (d, 1 H, J = 7.9 Hz), 8.36 (s, 1 H), 12.06 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 111.35 (C_8), 111.79 (C_3), 119.20 (C_6), 120.38 (C_{4a}), 122.79 (C-H=CH_2), 122.84 (C_5), 126.36 (C_7), 126.71 ($C_{4'}$), 127.46 (C_{4b}), 128.09 ($C_{2'}$ and $C_{6'}$), 130.26 ($C_{3'}$ and $C_{5'}$), 132.89 (CH=CH_2), 138.31 ($C_{1'}$), 139.23 (C_{8a}), 139.52 (C_4), 146.79 (C_2), 151.67 (C_{9a}); mass spectrum m/z (relative intensity) 270 (M^+, 91), 269 (100). Anal. Calcd for $C_{19}H_{14}N_2$: C, 84.42; H, 5.22; N, 10.36. Found: C, 84.51; H, 5.17; N, 10.31.

20b: yield 51%; mp 264–265 °C; colorless needles (benzene); IR (Nujol) 3140, 1581 cm^{-1}; ^1H NMR (DMSO-d_6) δ 5.49 (dd, 1 H, J = 1.3, 17.8 Hz), 5.74 (dd, 1 H, J = 1.3, 11.5 Hz), 7.09–7.24 (m, 2 H), 7.37–7.61 (m, 6 H), 8.23 (d, 1 H, J = 7.9 Hz), 8.32 (s, 1 H), 12.05 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 111.37 (C_8), 111.83 (C_3), 119.32 (C_6), 120.29 (C_{4a}), 122.85 (C_5), 123.12 (CH=CH_2), 126.12 (C_{4b}), 126.47 (C_7), 128.10 ($C_{2'}$ and $C_{6'}$), 131.77 ($C_{4'}$), 132.03 ($C_{3'}$ and $C_{5'}$), 132.73 (CH=CH_2), 137.17 ($C_{1'}$), 139.40 (C_{8a}), 139.48 (C_4), 146.65 (C_2), 151.72 (C_{9a}); mass spectrum m/z (relative intensity) 306 (M^+ + 2, 11), 304 (M^+, 33), 269 (100). Anal. Calcd for $C_{19}H_{13}ClN_2$: C, 74.88; H, 4.30; N, 9.19. Found: C, 74.77; H, 4.23; N, 9.11.

20c: yield 43%; mp 276 °C; colorless needles (benzene); IR (Nujol) 3120, 1590 cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.80 (s, 3 H), 5.55 (dd, 1 H, J = 1.7, 17.9 Hz), 5.73 (dd, 1 H, J = 1.7, 11.5 Hz), 7.00 (d, 2 H, J = 8.6 Hz), 7.06–7.22 (m, 2 H), 7.33 (d, 2 H, J = 8.6 Hz), 7.42–7.58 (m, 2 H), 8.25 (d, 1 H, J = 8.1 Hz), 8.29 (s, 1 H), 11.94 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 55.03 (CH_3O), 111.31 (C_8), 111.69 (C_3), 113.63 ($C_{3'}$ and $C_{5'}$), 119.14 (C_6), 120.34 (C_{4a}), 122.63 (C-H=CH_2), 122.77 (C_5), 126.31 (C_7), 127.16 (C_{4b}), 130.35 ($C_{1'}$), 131.32 ($C_{2'}$ and $C_{6'}$), 133.05 (CH=CH_2), 139.33 (C_{8a}), 139.46 (C_4), 146.83 (C_2), 151.48 (C_{9a}), 158.24 ($C_{4'}$); mass spectrum m/z (relative intensity) 300 (M^+, 100), 285 (45). Anal. Calcd for $C_{20}H_{16}N_2O$: C, 79.98; H, 5.37; N, 9.32. Found: C, 79.87; H, 5.31; N, 9.18.

21a: yield 32%; mp 227 °C; colorless prisms (ethanol); IR (Nujol) 3100, 1598 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.99 (s, 6 H), 7.18 (d, 1 H, J = 7.1 Hz), 7.36 (s, 1 H), 7.39–7.57 (m, 8 H), 8.63 (d, 1 H, J = 8.0 Hz), 11.97 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 41.86 [$(CH_3)_2N$], 110.20 (C_3), 110.71 (C_8), 118.65 (C_6), 121.16 (C_{4a}), 125.43 (C_5), 126.23 (C_7), 126.96 ($C_{4'}$), 127.83 (C_{4b}), 128.20 ($C_{2'}$ and $C_{6'}$), 128.48 (CH=N), 130.29 ($C_{3'}$ and $C_{5'}$), 137.14 ($C_{1'}$), 138.64 (C_{8a}), 139.43 (C_4), 146.69 (C_2), 152.19 (C_{9a}); mass spectrum m/z (relative intensity) 314 (M^+, 100), 270 (64). Anal. Calcd for $C_{20}H_{18}N_4$: C, 76.41; H, 5.77; N, 17.82. Found: C, 76.50; H, 5.68; N, 17.77.

21b: yield 34%; mp 271 °C; colorless prisms (ethanol); IR (Nujol) 3150, 1543 cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.00 (s, 6 H), 7.19 (t, 1 H, J = 7.9 Hz), 7.35 (s, 1 H), 7.43–7.59 (m, 6 H), 8.27 (s, 1 H), 7.79 (d, 1 H, J = 7.9 Hz), 11.98 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 41.89 [$(CH_3)_2N$], 110.31 (C_3), 110.78 (C_8), 118.78 (C_6), 121.08 (C_{4a}), 125.31 (C_5), 126.30 (C_{4b}), 126.34 (C_7), 127.70 (CH=N), 128.14 ($C_{2'}$ and $C_{6'}$), 131.81 ($C_{4'}$), 132.01 ($C_{3'}$ and $C_{5'}$), 137.18 ($C_{1'}$), 137.64 (C_{8a}), 139.43 (C_4), 146.65 (C_2), 152.29 (C_{9a}); mass spectrum m/z (relative intensity) 350 (M^+ + 2, 33), 348 (M^+, 100). Anal. Calcd for $C_{20}H_{17}ClN_4$: C, 68.86; H, 4.91; N, 16.06. Found: C, 68.79; H, 4.93; N, 15.93.

21c: yield 31%; mp 266–267 °C; colorless prisms (ethanol); IR (Nujol) 3114, 1553 cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.00 (s, 6 H), 3.80 (s, 3 H), 7.02 (d, 2 H, J = 8.6 Hz), 7.17 (t, 1 H, J = 7.2 Hz), 7.33–7.56 (m, 5 H), 8.25 (s, 1 H), 8.84 (d, 1 H, J = 8.0 Hz), 11.89 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 41.91 [$(CH_3)_2N$], 55.05 (CH_3O), 110.17 (C_3), 110.66 (C_8), 113.67 ($C_{3'}$ and $C_{5'}$), 118.56 (C_6), 121.18 (C_{4a}), 125.47 (C_5), 126.17 (C_7), 127.57 (C_{4b}), 128.91 (CH=N), 130.60 ($C_{1'}$), 131.37 ($C_{2'}$ and $C_{6'}$), 137.15 (C_{8a}), 139.39 (C_4), 146.82 (C_2), 152.02 (C_{9a}), 158.36 ($C_{4'}$); mass spectrum m/z (relative intensity) 344 (M^+, 100), 300 (45). Anal. Calcd for $C_{21}N_{20}N_4O$: C, 73.23; H, 5.85; N, 16.27. Found: C, 73.16; H, 5.79; N, 16.20.

22: yield 55%; mp 290–292 °C; colorless prisms (benzene); IR (Nujol) 3194, 1568 cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.74 (s, 3 H), 6.82–7.70 (m, 11 H), 8.44 (s, 1 H), 12.04 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 54.98 (CH_3O), 111.36 (C_8), 113.59 ($C_{3''}$ and $C_{5''}$), 114.19 (C_3), 119.18 (C_6), 119.98 (C_{4a}), 121.80 (C_5), 126.63 (C_7), 127.34 ($C_{3'}$ or $C_{4'}$), 127.59 ($C_{3'}$ or $C_{4'}$), 128.30 ($C_{5'}$), 129.00 (C_{4b}), 130.10 ($C_{1''}$), 131.07 ($C_{2''}$ and $C_{6''}$), 134.81 ($C_{2'}$), 137.20 (C_4), 139.50 (C_{8a}), 146.69 (C_2), 150.99 (C_{9a}), 158.07 ($C_{4''}$); mass spectrum m/z (relative intensity) 357 (M^+, 26), 356 (100). Anal. Calcd for $C_{22}H_{16}N_2OS$: C, 74.13; H, 4.52; N, 7.86. Found: C, 74.01; H, 5.45; N, 7.78.

General Procedure for the Preparation of Quinindolines 25–27. Reaction of Iminophosphoranes 6, 10, and 12 with Aryl Isocyanates. The reaction of iminophosphoranes **6**, **10**, and **12** with aryl isocyanates under the same reaction conditions described for the preparation of α-carbolines **19–22** led to quinindolines **25–27**.

25a: yield 39%; mp 271 °C; yellow needles (ethanol); IR (Nujol) 3143, 1598 cm^{-1}; ^1H NMR (DMSO-d_6) δ 5.92 (dd, 1 H, J = 1.3, 17.8 Hz), 6.15 (dd, 1 H, J = 1.3, 11.6 Hz), 7.20–7.66 (m, 5 H), 7.75 (t, 1 H, J = 7.0 Hz), 8.04 (d, 1 H, J = 8.4 Hz), 8.22–8.32 (m, 2 H), 11.81 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 110.80 (C_7), 114.06 (C_{10a}), 119.41 (C_9), 120.41 (C_{10b}), 121.70 (C_{11a}), 122.65 (C_2), 123.47 (C_{10}), 123.94 (CH=CH_2), 125.13 (C_1), 127.37 (C_3), 127.83 (C_8), 128.48

(C_4), 131.65 ($CH{=}CH_2$), 138.78 (C_{11}), 141.48 (C_{6a}), 146.37 (C_{5a}), 152.55 (C_{4a}); mass spectrum m/z (relative intensity) 244 (M^+, 100), 243 (98). Anal. Calcd for $C_{17}H_{12}N_2$: C, 83.58; H, 4.95; N, 11.47. Found: C, 83.47; H, 4.96; N, 11.35.

25b: yield 43%; mp 318–319 °C; yellow needles (ethanol); IR (Nujol) 3133, 1613 cm^{-1}; ^1H NMR (DMSO-d_6) δ 5.91 (dd, 1 H, J = 1.6, 17.9 Hz), 6.16 (dd, 1 H, J = 1.6, 11.7 Hz), 7.19–7.27 (m, 1 H), 7.52–7.61 (m, 3 H), 7.68 (dd, 1 H, J = 2.2, 8.7 Hz), 7.99 (d, 1 H, J = 9.0 Hz), 8.20–8.27 (m, 2 H), 11.85 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 110.92 (C_7), 114.71 (C_{10a}), 119.61 (C_9), 120.04 (C_{10b}), 122.29 (C_{11a}), 123.63 (C_{10}), 123.72 (C_1), 124.44 ($CH{=}CH_2$), 126.94 (C_2), 128.23 (C_8), 128.72 (C_3), 129.32 (C_4), 131.23 ($CH{=}CH_2$), 137.94 (C_{11}), 141.71 (C_{6a}), 144.66 (C_{5a}), 152.66 (C_{4a}); mass spectrum m/z (relative intensity) 280 (M^+ + 2, 14), 278 (M^+, 40), 243 (100). Anal. Calcd for $C_{17}H_{11}ClN_2$: C, 73.25; H, 3.98; N, 10.05. Found: C, 73.30; H, 3.89; N, 9.98.

25c: yield 35%; mp 263 °C; yellow needles (benzene); IR (Nujol) 3131, 1603 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.51 (s, 3 H), 5.90 (dd, 1 H, J = 1.4, 17.8), 6.13 (dd, 1 H, J = 1.4, 11.6 Hz), 7.18–7.26 (m, 1 H), 7.52–7.57 (m, 4 H), 7.92 (d, 1 H, J = 8.6 Hz), 8.02 (s, 1 H), 8.28 (d, 1 H, J = 7.8 Hz), 11.72 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 21.22 (CH_3), 110.72 (C_7), 113.95 (C_{10a}), 119.22 (C_9), 120.46 (C_{10b}), 121.66 (C_{11a}), 123.37 (C_{10}), 123.66 ($CH{=}CH_2$), 123.81 (C_1), 127.16 (C_4), 127.66 (C_8), 130.60 (C_3), 131.61 (C_2), 131.80 ($CH{=}CH_2$), 138.07 (C_{11}), 141.55 (C_{6a}), 144.82 (C_{5a}), 152.17 (C_{4a}); mass spectrum m/z (relative intensity) 258 (M^+, 82), 243 (100). Anal. Calcd for $C_{18}H_{14}N_2$: C, 83.69; H, 5.46; N, 10.85. Found: C, 83.58; H, 5.36; N, 10.80.

25d: yield 40%; mp 224 °C; yellow needles (benzene); IR (Nujol) 3171, 1625 cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.90 (s, 3 H), 5.95 (dd, 1 H, J = 1.7, 17.8 Hz), 6.13 (dd, 1 H, J = 1.7, 11.6 Hz), 7.16–7.67 (m, 6 H), 7.95 (d, 1 H, J = 9.1 Hz), 8.28 (d, 1 H, J = 7.8 Hz), 11.68 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 55.12 (CH_3O), 103.26 (C_1), 110.67 (C_7), 114.07 (C_{10a}), 119.04 (C_9), 120.25 (C_{10b}), 120.71 (C_3), 122.18 (C_{11a}), 123.38 (C_{10}), 123.48 ($CH{=}CH_2$), 127.52 (C_8), 128.73 (C_4), 131.95 ($CH{=}CH_2$), 137.32 (C_{11}), 141.55 (C_{6a}), 142.15 (C_{5a}), 151.38 (C_{4a}), 154.68 (C_2); mass spectrum m/z (relative intensity) 274 (M^+, 100), 259 (70). Anal. Calcd for $C_{18}H_{14}N_2O$: C, 78.81; H, 5.14; N, 10.21. Found: C, 78.72; H, 5.09; N, 10.17.

25e: yield 34%; mp 287 °C; yellow needles (benzene); IR (Nujol) 3140, 1607 cm^{-1}; ^1H NMR (DMSO-d_6) δ 5.92 (dd, 1 H, J = 1.5, 17.6 Hz), 6.16 (dd, 1 H, J = 1.5, 11.8 Hz), 7.15–7.25 (m, 1 H), 7.52–7.67 (m, 4 H), 7.88–8.09 (m, 2 H), 8.27 (d, 1 H, J = 7.8 Hz), 11.81 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 107.71 (d, $^2J_{F-C}$ = 22.9 Hz, C_1), 110.84 (C_7), 114.82 (C_{10a}), 118.24 (d, $^2J_{F-C}$ = 25.8 Hz, C_3), 119.45 (C_9), 119.93 (C_{10b}), 121.79 (d, $^3J_{F-C}$ = 8.9 Hz, C_{11a}), 123.62 (C_{10}), 124.18 ($CH{=}CH_2$), 128.16 (C_8), 129.67 (d, $^3J_{F-C}$ = 9.1 Hz, C_4), 131.37 ($CH{=}CH_2$), 138.03 (d, $^4J_{F-C}$ = 5.4 Hz, C_{11}), 141.75 (C_{6a}), 143.29 (C_{5a}), 152.28 (d, $^4J_{F-C}$ = 1.6 Hz, C_{4a}), 157.62 (d, $^1J_{F-C}$ = 240.2 Hz, C_2); mass spectrum m/z (relative intensity) 262 (M^+, 100), 261 (90). Anal. Calcd for $C_{17}H_{11}FN_2$: C, 77.85; H, 4.23; N, 10.68. Found: C, 77.78; H, 4.15; N, 10.59.

26a: yield 42%; mp 279–281 °C; yellow prisms (ethanol); IR (Nujol) 3143, 1632 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.39 (s, 3 H), 6.94–6.96 (m, 2 H), 7.45–7.70 (m, 9 H), 8.01 (d, 1 H, J = 8.5 Hz), 11.85 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 21.12 (CH_3), 110.78 (C_7), 115.40 (C_{10a}), 119.07 (C_9), 120.28 (C_{10b}), 122.21 (C_{10}), 122.77 (C_{11a}), 124.27 (C_1), 127.10 (C_4), 127.71 (C_8), 128.52 ($C_{4'}$), 129.00 ($C_{3'}$ and $C_{5'}$), 129.04 ($C_{2'}$ and $C_{6'}$), 130.63 (C_3), 131.71 (C_2), 136.16 ($C_{1'}$), 140.75 (C_{11}), 141.63 (C_{6a}), 144.92 (C_{5a}), 152.09 (C_{4a}); mass spectrum m/z (relative intensity) 308 (M^+, 100), 146 (56). Anal. Calcd for $C_{22}H_{16}N_2$: C, 85.69; H, 5.23; N, 9.08. Found: C, 85.61; H, 5.15; N, 8.92.

26b: yield 50%; mp 273–275 °C; yellow prisms (ethanol); IR (Nujol) 3149, 1633 cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.70 (s, 3 H), 6.97–7.01 (m, 3 H), 7.42–7.74 (m, 8 H), 8.05 (d, 1 H, J = 9.2 Hz), 11.82 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 54.98 (CH_3O), 104.04 (C_1), 110.78 (C_7), 115.50 (C_{10b}), 118.98 (C_9), 120.07 (C_{10b}), 120.54 (C_3), 122.27 (C_{10}), 123.32 (C_{11a}), 127.74 (C_8), 128.62 ($C_{4'}$), 128.70 (C_4), 129.00 ($C_{3'}$ and $C_{5'}$), 129.15 ($C_{2'}$ and $C_{6'}$), 136.17 ($C_{1'}$), 140.11 (C_{11}), 141.68 (C_{6a}), 142.27 (C_{5a}), 151.39 (C_{4a}), 154.71 (C_2); mass spectrum m/z (relative intensity) 324 (M^+, 100), 140 (74). Anal. Calcd for $C_{22}H_{16}N_2O$: C, 81.46; H, 4.97; N, 8.64. Found: C, 81.39; H, 4.83; N, 8.59.

26c: yield 37%; mp 263–265 °C; yellow prisms (ethanol); IR (Nujol) 3148, 1633 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.00–7.02 (m, 2 H), 7.25 (dd, 1 H, J = 2.6, 10.5 Hz), 7.49–7.74 (m, 8 H), 8.15 (dd, 1 H, J = 5.6, 9.2 Hz), 11.95 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 108.40 (d, $^2J_{F-C}$ = 22.6 Hz, C_1), 110.92 (C_7), 116.02 (C_{10a}), 118.25 (d, $^2J_{F-C}$ = 25.9 Hz, C_3), 119.29 (C_9), 119.73 (C_{10b}), 122.43 (C_{10}), 123.01 (d, $^3J_{F-C}$ = 8.9 Hz, C_{11a}), 128.15 (C_8), 128.81 ($C_{4'}$), 128.94 ($C_{3'}$ and $C_{5'}$), 129.16 ($C_{2'}$ and $C_{6'}$), 129.63 (d, $^3J_{F-C}$ = 8.8 Hz, C_4), 135.46 ($C_{1'}$), 140.64 (d, $^4J_{F-C}$ = 5.4 Hz, C_{11}), 141.87 (C_{6a}), 143.29 (C_{5a}), 152.25 (d, $^4J_{F-C}$ = 1.6 Hz, C_{4a}), 157.57 (d, $^1J_{F-C}$ = 240.6 Hz, C_2); mass spectrum m/z (relative intensity) 312 (M^+, 100), 155 (31). Anal. Calcd for $C_{21}H_{13}FN_2$: C, 80.75; H, 4.19; N, 8.97. Found: C, 80.63; H, 4.07; N, 8.78.

27a: yield 51%; mp 316–318 °C; yellow prisms (toluene); IR (Nujol) 3160, 1579 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.49 (s, 3 H), 6.99 (dd, 1 H, J = 1.7, 2.9 Hz), 7.09 (d, 1 H, J = 2.9 Hz), 7.08–7.19 (m, 1 H), 7.37–7.61 (m, 4 H), 7.83 (s, 1 H), 7.99 (d, 1 H, J = 8.5 Hz), 8.19 (d, 1 H, J = 1.7 Hz), 11.88 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 21.25 (CH_3), 110.95 (C_7), 112.01 ($C_{4'}$), 112.42 ($C_{3'}$), 116.42 (C_{10a}), 119.44 (C_9), 119.63 (C_{10b}), 122.58 (C_{11a}), 122.87 (C_{10}), 124.07 (C_1), 128.31 (C_4), 128.65 (C_8 and C_{11}), 130.92 (C_3), 132.45 (C_2), 141.91 (C_{6a}), 144.12 ($C_{5'}$), 144.90 (C_{5a}), 147.52 ($C_{2'}$), 152.10 (C_{4a}); mass spectrum m/z (relative intensity) 298 (M^+, 100), 91 (44). Anal. Calcd for $C_{20}H_{14}N_2O$: C, 80.52; H, 4.73; N, 9.39. Found: C, 80.41; H, 4.62; N, 9.30.

27b: yield 54%; mp 278–280 °C; yellow prisms (toluene); IR (Nujol) 3162, 1634 cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.86 (s, 3 H), 7.01 (dd, 1 H, J = 1.5, 3.2 Hz), 7.19 (d, 1 H, J = 3.2 Hz), 7.13–7.20 (m, 1 H), 7.44 (d, 1 H, J = 9.3 Hz), 7.46 (s, 1 H), 7.41–7.57 (m, 3 H), 8.05 (d, 1 H, J = 9.3 Hz), 8.21 (d, 1 H, J = 1.5 Hz), 11.86 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 55.09 (CH_3O), 103.58 (C_1), 110.93 (C_7), 112.13 ($C_{4'}$), 112.35 ($C_{3'}$), 116.41 (C_{10a}), 119.34 (C_9), 119.47 (C_{10b}), 121.06 (C_3), 122.75 (C_{11a}), 123.00 (C_{10}), 128.00 (C_{11}), 128.29 (C_8), 128.87 (C_4), 141.92 (C_{6a}), 142.29 (C_{5a}), 144.07 ($C_{5'}$), 147.69 ($C_{2'}$), 151.35 (C_{4a}), 155.21 (C_2); mass spectrum m/z (relative intensity) 314 (M^+, 20), 91 (100). Anal. Calcd for $C_{20}H_{14}N_2O_2$: C, 76.42; H, 4.49; N, 8.91. Found: C, 76.38; H, 4.44; N, 8.82.

27c: yield 40%; mp 297–299 °C; yellow prisms (toluene): IR (Nujol) 3164, 1628 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.02 (dd, 1 H, J = 1.7, 3.3 Hz), 7.20 (d, 1 H, J = 3.3 Hz), 7.15–7.23 (m, 1 H), 7.51 (d, 1 H, J = 7.9 Hz), 7.49–7.78 (m, 4 H), 8.16 (dd, 1 H, J = 5.6, 9.2 Hz), 8.21 (d, 1 H, J = 1.7 Hz), 12.01 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 108.47 (d, $^2J_{F-C}$ = 23.4 Hz, C_1), 111.06 (C_7), 116.89 (C_{10a}), 118.57 (d, $^2J_{F-C}$ = 25.8 Hz, C_3), 119.15 (C_{10a}), 119.64 (C_9), 122.21 ($C_{4'}$), 122.29 (d, $^3J_{F-C}$ = 9.1 Hz, C_{11a}), 122.39 ($C_{3'}$), 123.16 (C_{10}), 128.61 (d, $^4J_{F-C}$ = 5.6 Hz, C_{11}), 128.79 (C_8), 129.83 (d, $^3J_{F-C}$ = 9.0 Hz, C_4), 142.16 (C_{6a}), 143.32 (C_{5a}), 144.42 ($C_{5'}$), 147.02 ($C_{2'}$), 152.30 (d, $^4J_{F-C}$ = 1.7 Hz, C_{4a}), 158 (d, $^1J_{F-C}$ = 241.2 Hz, C_2); mass spectrum m/z (relative intensity) 302 (M^+, 100), 273 (42). Anal. Calcd for $C_{19}H_{11}FN_2O$: C, 75.48; H, 3.67; N, 9.27. Found: C, 75.36; H, 3.39; N, 9.15.

27d: yield 30%; mp 252–254 °C; yellow prisms (ethanol); IR (Nujol) 3126, 1631 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.05–7.20 (m, 2 H), 7.47–7.63 (m, 5 H), 7.79 (t, 1 H, J = 8.4 Hz), 7.89 (d, 1 H, J = 8.3 Hz), 8.03 (d, 1 H, J = 4.7 Hz), 8.14 (d, 1 H, J = 8.4 Hz), 12.00 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 110.96 (C_7), 117.19 (C_{10a}), 119.45 (C_9), 119.85 (C_{10b}), 122.52 (C_{10}), 123.09 (C_2), 123.87 (C_{11a}), 125.39 (C_1), 127.22 (C_3), 128.13 ($C_{4'}$), 128.15 ($C_{5'}$), 128.28 ($C_{3'}$), 128.47 (C_8), 128.64 (C_4), 133.77 ($C_{2'}$), 135.30 (C_{11}), 141.81 (C_{6a}), 146.14 (C_{5a}), 152.25 (C_{4a}); mass spectrum m/z (relative intensity) 300 (M^+, 100), 299 (41). Anal. Calcd for $C_{19}H_{12}N_2S$: C, 75.97; H, 4.03; N, 9.33. Found: C, 75.83; H, 3.89; N, 9.19.

27e: yield 34%; mp 323–325 °C; yellow prisms (ethanol); IR (Nujol) 3130, 1612 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.13–7.15 (m, 2 H), 7.52–8.13 (m, 8 H), 12.07 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 111.12 (C_7), 117.85 (C_{10a}), 119.47 (C_{10b}), 119.68 (C_9), 122.67 (C_{10}), 123.72 (C_1), 124.43 (C_{11a}), 127.37 (C_2), 128.30 (C_3), 128.62 (C_8), 128.75 ($C_{5'}$), 128.87 ($C_{4'}$), 128.90 ($C_{3'}$), 129.31 (C_4), 132.86 ($C_{2'}$), 134.42 (C_{11}), 141.97 (C_{6a}), 144.44 (C_{5a}), 152.37 (C_{4a}); mass spectrum m/z (relative intensity) 335 (M^+ + 2, 41), 334 (M^+, 100). Anal. Calcd for $C_{19}H_{11}ClN_2S$: C, 68.82; H, 3.31; N, 8.37. Found: C, 68.71; H, 3.13; N, 8.19.

27f: yield 43%; mp 280–282 °C; yellow prisms (toluene); IR (Nujol) 3126, 1602 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.44 (s, 3 H), 7.05–7.07 (m, 2 H), 7.41–7.61 (m, 6 H), 7.97–8.03 (m, 2 H), 12.02 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 21.80 (CH_3), 111.10 (C_7), 117.46 (C_{10a}), 119.59 (C_9), 119.82 (C_{10b}), 122.43 (C_{10}), 123.68 (C_{11a}), 124.10 (C_1), 126.35 ($C_{5'}$), 128.17 (C_4), 128.31 ($C_{3'}$ and $C_{4'}$), 128.47 (C_8),

131.17 (C_3), 132.51 (C_2), 133.81 ($C_{2'}$), 135.21 (C_{11}), 141.70 (C_{6a}), 143.64 (C_{5a}), 151.16 (C_{4a}); mass spectrum m/z (relative intensity) 314 (M^+, 100), 149 (39). Anal. Calcd for $C_{20}H_{14}N_2S$: C, 76.40; H, 4.49; N, 8.91. Found: C, 76.40; H, 4.37; N, 8.82.

27g: yield 31%; mp 342–344 °C; yellow prisms (ethanol); IR (Nujol) 3149, 1633, 1615 cm^{-1}; ^1H NMR (DMSO-d_6) δ 6.95–7.00 (m, 2 H), 7.31–7.68 (m, 4 H), 7.67 (d, 2 H, J = 3.9 Hz), 8.07 (d, 1 H, J = 8.5 Hz), 8.96 (d, 2 H, J = 3.9 Hz), 12.07 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 111.26 (C_7), 115.52 (C_{10a}), 119.29 (C_{10b}), 119.79 (C_9), 122.36 (C_{10}), 122.49 (C_{11a}), 123.57 (C_1), 124.22 ($C_{3'}$ and $C_{5'}$), 127.40 (C_2), 128.73 (C_3), 129.02 (C_8), 129.44 (C_4), 137.37 (C_{11}), 142.00 (C_{6a}), 143.46 ($C_{4'}$), 144.53 (C_{5a}), 150.79 ($C_{2'}$ and $C_{6'}$), 152.48 (C_{4a}); mass spectrum m/z (relative intensity) 331 (M^+ + 2, 6), 329 (M^+, 15), 127 (100). Anal. Calcd for $C_{20}H_{12}ClN_3$: C, 72.84; H, 3.67; N, 12.74. Found: C, 72.72; H, 3.52; N, 12.91.

27h: yield 28%; mp 339–341 °C; yellow prisms (ethanol); IR (Nujol) 3149, 1633, 1614 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.00–7.02 (m, 2 H), 7.19 (dd, 1 H, J = 2.6, 10.3 Hz), 7.53–7.69 (m, 3 H), 7.67 (d, 2 H, J = 5.3 Hz), 8.12 (dd, 1 H, J = 5.6, 9.2 Hz), 8.97 (d, 2 H, J = 5.3 Hz), 12.01 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 108.13 (d, $^2J_{F-C}$ = 23.0 Hz, C_1), 111.18 (C_7), 115.38 (C_{10a}), 118.61 (d, $^2J_{F-C}$ = 25.7 Hz, C_3), 119.16 (C_{10b}), 119.63 (C_9), 121.99 (d, $^3J_{F-C}$ = 8.9 Hz, C_{11a}), 122.36 (C_{10}), 124.22 ($C_{3'}$ and $C_{5'}$), 128.66 (C_8), 129.84 (d, $^3J_{F-C}$ = 9.1 Hz, C_4), 137.58 (d, $^4J_{F-C}$ = 5.4 Hz, C_{11}), 142.02 (C_{6a}), 143.16 ($C_{4'}$), 143.66 (C_{5a}), 150.70 ($C_{2'}$ and $C_{5'}$), 152.08 (d, $^4J_{F-C}$ = 1.5 Hz, C_{4a}), 157.76 (d, $^1J_{F-C}$ = 241.6 Hz, C_2); mass spectrum m/z (relative intensity) 313 (M^+, 100), 156 (34). Anal. Calcd for $C_{20}H_{12}FN_2$: C, 76.67; H, 3.86; N, 13.41. Found: C, 76.60; H, 3.82; N, 13.30.

27i: yield 37%; mp 340–342 °C; yellow prisms (ethanol); IR (Nujol) 3154, 1633, 1612 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.39 (s, 3 H), 6.95–7.00 (m, 2 H), 7.17–7.64 (m, 3 H), 7.32 (s, 1 H), 7.63 (d, 2 H, J = 4.2 Hz), 7.98 (d, 1 H, J = 8.5 Hz), 8.95 (d, 2 H, J = 4.2 Hz), 11.91 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 21.15 (CH_3), 111.03 (C_7), 114.67 (C_{10a}), 119.38 (C_9), 119.67 (C_{10b}), 121.77 (C_{11a}), 122.09 (C_{10}), 123.77 (C_1), 124.31 ($C_{3'}$ and $C_{5'}$), 127.24 (C_3), 128.14 (C_8), 130.92 (C_4), 132.30 (C_2), 137.61 (C_{11}), 141.78 (C_{6a}), 144.38 ($C_{4'}$), 144.77 (C_{5a}), 150.55 ($C_{2'}$ and $C_{6'}$), 151.91 (C_{4a}); mass spectrum m/z (relative intensity) 309 (M^+, 100), 154 (31). Anal. Calcd for $C_{21}H_{15}N_3$: C, 81.53; H, 4.89; N, 13.58. Found: C, 81.40; H, 4.74; N, 13.64.

Preparation of Quinindoline 28. The reaction of the iminophosphorane **2f** (3 mmol) with *p*-tolyl isocyanate (3 mmol) under the same reaction conditions described for the preparation of quinindolines **25–27** led to **28**.

28: yield 39%; mp 327–328 °C; colorless prisms (ethanol); IR (Nujol) 3137, 1615 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.52 (s, 3 H), 7.21–7.28 (m, 1 H), 7.49–7.58 (m, 3 H), 7.84–9.91 (m, 2 H), 8.24 (d, 1 H, J = 7.7 Hz), 8.92 (s, 1 H), 11.62 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 20.93 (CH_3), 110.81 (C_7), 117.78 (C_{10a}), 119.43 (C_9), 120.29 (C_{10b}), 121.69 (C_{10}), 123.63 (C_{11a}), 126.69 (C_1), 126.76 (C_{11}), 127.2 (C_4), 127.99 (C_8), 130.79 (C_3), 131.66 (C_2), 141.40 (C_{6a}), 144.83 (C_{5a}), 152.51 (C_{4a}); mass spectrum m/z (relative intensity) 232 (M^+, 100). Anal. Calcd for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21; N, 12.06. Found: C, 82.68; H, 5.15; N, 12.00.

Preparation of 4-Methyl-2-[(*p*-methoxyphenyl)amino]-3-vinylquinoline (31). The reaction of the iminophosphorane **6b** (3 mmol) with *p*-methoxyphenyl isocyanate (3 mmol) under the same reaction conditions described for the preparation of quinolines **14** led to **31**.

31: yield 67%; mp 106 °C; colorless prisms (ether); IR (Nujol) 3410, 1525, 1244 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.44 (s, 3 H), 3.75 (s, 3 H), 5.50 (dd, 1 H, J = 1.8, 18.0 Hz), 5.75 (dd, 1 H, J = 1.8, 11.3 Hz), 6.63 (dd, 1 H, J = 11.3, 18.0 Hz), 6.85 (d, 2 H, J = 8.8 Hz), 6.80–6.89 (m, 1 H), 7.22 (t, 1 H, J = 7.2 Hz), 7.49 (t, 1 H, J = 7.2 Hz), 7.70 (d, 2 H, J = 8.8 Hz), 7.68–7.77 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 15.40 (CH_3), 55.50 (CH_3O), 114.02 ($C_{3'}$ and $C_{5'}$), 121.09 ($C_{2'}$ and $C_{6'}$), 121.46 (C_3), 122.59 (C_6), 123.64 (C_8), 123.69 (CH=CH_2), 123.90 (C_{4a}), 127.31 (C_5), 128.84 (C_7), 132.42 (CH=CH_2), 133.91 ($C_{1'}$), 140.91 (C_4), 146.17 (C_{8a}), 151.19 (C_2), 154.95 ($C_{4'}$); mass spectrum m/z (relative intensity) 290 (M^+, 60), 289 (83), 63 (100). Anal. Calcd for $C_{19}H_{18}N_2O$: C, 78.59; H, 6.25; N, 9.65. Found: C, 78.51; H, 6.17; N, 9.58.

Reaction of Iminophosphoranes 2 and 6a with Ketenes. Preparation of Quinolines 32 and Benzo[*b*]carbazoles 33. The reaction of iminophosphoranes **2a** and **2c** (5 mmol) with the appropriate ketene (5 mmol) under the conditions described for the preparation of quinolines **14** led to **32**, whereas iminophosphorane **6a** led to the corresponding benzo[*b*]carbazoles **33**.

32a: yield 62%; IR (neat) 1493, 754 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.94 (t, 3 H, J = 7.3 Hz), 2.28 (ddq, 2 H, J = 7.3, 7.7, 21.5 Hz), 4.17 (t, 1 H, J = 7.7 Hz), 6.99–7.44 (m, 8 H), 7.65–7.71 (m, 1 H), 7.93 (d, 1 H, J = 8.4 Hz), 8.10 (d, 1 H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 12.62, 27.79, 56.21, 120.97, 125.81, 126.40, 126.85 (s), 127.42, 128.21, 128.44, 129.19, 129.29, 136.26, 143,45 (s), 147.80 (s), 164.17 (s); mass spectrum m/z (relative intensity) 247 (M^+, 100). Anal. Calcd for $C_{18}H_{17}N$: C, 87.41; H, 6.93; N, 5.66. Found: C, 87.35; H, 6.88; N, 5.57.

32b: yield 73%; mp 175 °C; colorless prisms (*n*-hexane); IR (Nujol) 1492, 756, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.39 (s, 3 H), 5.88 (s, 1 H), 7.14–7.42 (m, 11 H), 7.52 (t, 1 H, J = 6.8 Hz), 7.63 (d, 1 H, J = 7.9 Hz), 7.78 (s, 1 H), 7.94 (d, 1 H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ 19.76, 55.86, 126.08, 126.37, 126.54, 127.27 (s), 128.19, 129.61, 129.80, 130.13 (s), 136.29, 142.54 (s), 146.57 (s), 161.83 (s), one carbon was not observed; mass spectrum m/z (relative intensity) 309 (M^+, 60), 165 (98), 51 (100). Anal. Calcd for $C_{23}H_{19}N$: C, 89.28; H, 6.19; N, 4.53. Found: C, 89.21; H, 6.12; N, 4.47.

33: yield 12%; mp 137–138 °C; yellow needles (ether); IR (Nujol) 3420, 1609, 754 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.36 (t, 3 H, J = 7.5 Hz), 3.21 (q, 2 H, J = 7.5 Hz), 5.72 (dd, 1 H, J = 2.1, 17.9 Hz), 5.98 (dd, 1 H, J = 2.1, 11.3 Hz), 7.17 (t, 1 H, J = 8.3 Hz), 7.32–7.59 (m, 5 H), 7.79 (s, 1 H), 8.09 (d, 1 H, J = 8.3 Hz), 8.40 (d, 2 H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$) δ 14.31, 20.58, 110.06, 117.11 (s), 119.19, 121.88, 122.09, 122.25, 122.64, 124.10, 124.20 (s), 124.87, 126.40, 126.91, 126.96 (s), 129.48 (s), 130.04 (s), 134.17, 137.00 (s), 142.12 (s); mass spectrum m/z (relative intensity) 271 (M^+, 65), 242 (100). Anal. Calcd for $C_{20}H_{17}N$: C, 88.52; H, 6.31; N, 5.17. Found: C, 88.45; H, 6.27; N, 5.10.