(14%) of a mixture of **5b** and **6b** have been isolated. GLC analysis of the enriched mixture showed additionally the peaks of **7b** (t_R = 6.60 min; identical with that of purchased **7b**; 2%), acetic acid (t_R = 6.23 min; 18%), and acetic anhydride (t_R = 7.16 min; 4%).

Mixture of 4-acetyl-1-methylcyclopentene (5b) and 3-acetyl-1-methylcyclopentene (6b): colorless liquid; ^{1}H NMR ($CDCl_3$, TMS) δ 1.70 (s), 1.78 (s), 2.12 (s), 2.16 (s), 2.24–2.48 (m), 2.48–2.58 (m), 3.26 (quint), 3.49–3.61 (m), 5.19–5.23 (m), 5.32–5.36 (m); ^{13}C NMR ($CDCl_3$, TMS) δ 16.23, 16.52, 26.22, 27.71, 28.04, 35.31, 36.51, 38.97, 50.78, 59.71, 122.32, 122.37, 138.73, 144.51, 209.89, 209.93; GLC t_R = 12.49 min. Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.14; H, 9.63.

Photolysis of 3b for 9 h gave 0.17 g of a liquid residue from which 53 mg (20%) of **3b**, 50 mg (20%) of **4b**, and 31 mg (17%) of a mixture of **5b** and **6b** have been isolated. GLC analysis of the enriched mixture showed additionally the peaks of **7b** (2%), acetic acid (20%), and acetic anhydride (5%).

Ozonolysis of 1a in Pentane. A solution of 0.30 g (2.5 mmol) of **1a** in 30 mL of pentane was ozonized at −5 °C until it turned blue, flushed with nitrogen, and warmed up to room temperature. The solution was decanted from precipitated semisolid material, and pentane was removed at room temperature and ca. 18 Torr to leave 0.33 g of a liquid residue. ^{1}H and ^{13}C NMR and GC/MS analyses of the latter showed only the presence of **4a**. By flash chromatography (column 2 × 60 cm, 40 g of silica gel; 400 mL of pentane/diethyl ether, 25:1, followed by diethyl ether) 0.17 g (46%) of **4a** was isolated. It was identified by GLC (t_R = 18.69 min, condition 3) and ^{13}C NMR analysis ($CDCl_3$, TMS; δ 27.62, 28.05, 30.33, 51.67, 209.25).

Ozonolysis of 1b in Pentane. In the same way as described above, 0.36 g (2.7 mmol) of **1b** in 40 mL of pentane was ozonized at −20 °C to give 0.38 g of a liquid residue. Separation by flash chromatography (column 2 × 60 cm, 40 g of silica gel; 400 mL of pentane/diethyl ether, 30:1, followed by diethyl ether) gave 60 mg (12%) of a mixture of **2b** and **3b**, and 200 mg of **4b**. HPLC separation of the mixture of ozonides gave 50 mg (10%) of **2b** and 10 mg (2%) of **3b**.

Ozonolysis of 1c in Pentane. In the same way as described above, 0.28 g (1.7 mmol) of **1c** in 40 mL of pentane was ozonized at −5 °C to give 0.30 g of a liquid residue, from which 0.15 g (45%) of **4c** was isolated by flash chromatography (column 2 × 60 cm, 30 g of silica gel; 250 mL of pentane/diethyl ether, 20:1, followed by diethyl ether).

Acknowledgment. We are indebted to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support of our work.

Supplementary Material Available: Tables of atomic positional parameters and equivalent isotropic thermal parameters, bond distances and angles, and anisotropic thermal parameters and ORTEP views for **2a** and **3b** structure determinations (10 pages). Ordering information is given on any current masthead page.

Domino Reactions. One-Pot Preparation of Fluoreno[2,3,4-*ij*]isoquinoline Derivatives from Conjugated Ketene Imines

Pedro Molina,* Mateo Alajarín,* and Angel Vidal

Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Murcia, Campus de Espinardo, 30071, Murcia, Spain

J. Fenau-Dupont and J. P. Declerq

Laboratoire de Chimie Physique et de Cristallographie, Université Catholique de Louvain, 1 Place Louis Pasteur, 1348 Louvain la Neuve, Belgium

Received December 10, 1990

Iminophosphoranes **4**, derived from ethyl α-azido-2-(allyloxy)-3-methoxycinnamates, react with ketenes to give the corresponding ketene imines, which by thermal treatment at 150–160 °C undergo a consecutive electrocyclic ring closure/Claisen rearrangement/second ring closure/double aromatization process to give isoquinoline derivatives **7** and/or the previously unknown fluoreno[2,3,4-*ij*]isoquinolines **9** in moderate yields. Similarly, iminophosphoranes **14** derived from ethyl α-azido-2,3-disubstituted-4-(allyloxy)cinnamates reacted with diphenyl ketene to give the intermediate ketene imines, which at 150–160 °C undergo a cascade of pericyclic reactions to give the isoquinolines **15** and the pentacyclic compounds **16** in moderate yields.

Conjugated heterocumulenes exhibit a rich chemistry of unusual synthetic promise.[1] Cycloaddition reactions of such unsaturated heterocumulenic systems as ketenes, isocyanates, isothiocyanates, and carbodiimides provide an attractive entry to a variety of carbocycles and heterocycles. However, the chemistry of conjugated ketene imines has received limited attention. Only the preparation and some intra- and intermolecular reactions have been reported: *N*-arylvinyl ketene imines react with electron-deficient dienes in all-carbon Diels–Alder reactions, while their reactions with electron-rich ynamines afford quinoline derivatives by cycloaddition across the aza diene system.[2] Similar observations have been made on the reaction of *N*-arylvinyl ketene imines with thiobenzophenones.[3] *N*-Vinyl ketene imines react with diphenyl ketene to give 2*H*-1,3-oxazine derivatives.[4] In this case the unsaturated ketene imine acts as a 2-aza diene, which cycloadds to the C=O bond of the ketene.

We have recently shown that thermal treatment of β-arylvinyl carbodiimides provide an efficient annulation route to highly substituted isoquinolines and 1,9-diazaphenalene derivatives.[5] In our original version of this annulation strategy, the unsaturated carbodiimide is generated by aza-Wittig-type reactions of iminophosphoranes derived from ethyl α-azido-2-(allyloxy)-3-

(1) Moore, H. W.; Decker, O. H. W. *Chem. Rev.* **1986**, *86*, 821. Boger, D. L. *Tetrahedron* **1983**, *39*, 2869. Dondoni, A. *Heterocycles* **1980**, *14*, 1547. Snider, B. S. *Chem. Rev.* **1988**, *88*, 703. Arbuzov, B. A.; Zobova, N. N. *Synthesis* **1982**, 433 and references cited therein.

(2) Souveaux, E.; Ghosez, L. *J. Am. Chem. Soc.* **1973**, *95*, 5417.

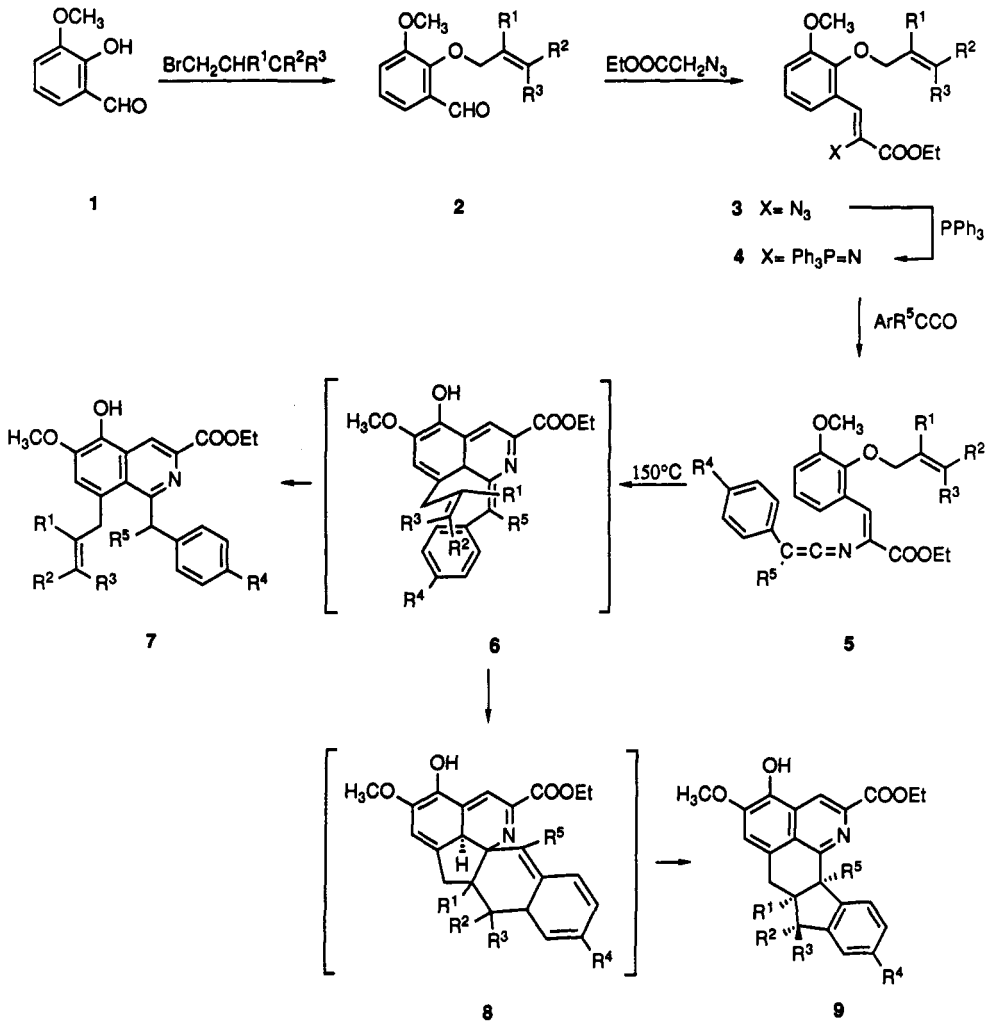
(3) Dondoni, A.; Battaglia, A.; Giorgianni, P. *J. Org. Chem.* **1982**, *47*, 3998.

(4) Saito, T.; Nakane, M.; Miyazaki, T.; Motoki, S. *J. Chem. Soc., Perkin Trans. 1* **1989**, 2140.

(5) Molina, P.; Alajarín, M.; Vidal, A. *J. Org. Chem.* **1990**, *55*, 6140.

0022-3263/91/1956-4008$02.50/0

Scheme I



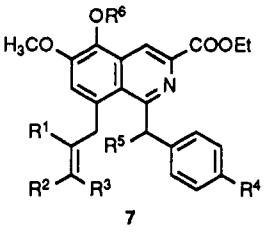
a R^1= H, R^2= H, R^3= H, R^4= H, R^5= C_6H_5
b R^1= H, R^2= CH_3, R^3= H, R^4= H, R^5= C_6H_5
c R^1= H, R^2= C_6H_5, R^3= H, R^4= H, R^5= C_6H_5
d R^1= CH_3, R^2= H, R^3= H, R^4= H, R^5= C_6H_5
e R^1= H, R^2= CH_3, R^3= CH_3, R^4= H, R^5= C_6H_5
f R^1= H, R^2= H, R^3= H, R^4= CH_3, R^5= 4-CH_3-C_6H_4
g R^1= H, R^2= CH_3, R^3= H, R^4= CH_3, R^5= 4-CH_3-C_6H_4
h R^1= H, R^2= H, R^3= H, R^4= H, R^5= C_2H_5
i R^1= H, R^2= CH_3, R^3= H, R^4= H, R^5= C_2H_5

methoxycinnamates with aromatic isocyanates. In this paper, we describe a "second generation" version of our annulation strategy that significantly expands the scope of the method. In particular, this new variant provides access to a variety of derivatives of the unknown fluoroeno[2,3,4-*ij*]isoquinoline ring system related to the isoaporphine skeleton. The new annulation method is based on the initial generation of the key *N*-vinyl ketene imine that undergoes a cascade of pericyclic reactions, some of them similar to those involved in our earlier method.

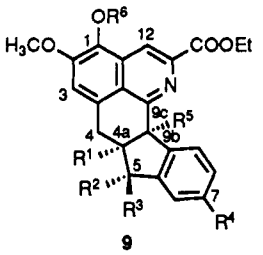
Results and Discussion

The commercially available starting material 2-hydroxy-3-methoxybenzaldehyde 1 was converted into the key iminophosphorane 4 by standard chemistry: O-allylation with allyl bromides in acetone in the presence of potassium carbonate gave 2 in 50–81% yield. Condensation with ethyl azidoacetate in the presence of sodium ethoxide at ~20 °C led to 3 in 50–65% yield. Finally, reaction with triphenylphosphine in ether at room temperature afforded 4 in 60–95% yield. Aza-Wittig-type reaction of the iminophosphoranes 4 with ketenes in dry toluene at room temperature led to the corresponding ketene imines 5, which could be isolated as viscous oils by means of short-column chromatography. When a toluene solution of **5a** was heated at reflux temperature for 48 h, the starting ketene imine was recovered unalterated. However, when a toluene solution of **5a** was heated in a sealed tube at 150 °C for 16 h, two compounds were obtained and separated by column chromatography (Scheme I). The minor product (17%, see Table I) was found to be the 1-(diphenylmethyl)isoquinoline derivative **7a**. The major product (36%) has a complex structure. The ^1H and ^{13}C NMR spectra indicated that the two phenyl groups are nonequivalent and one of them shows an ortho-disubsituted pattern. The original allyl moiety now appears as

Table I. Isoquinoline Derivatives 7 and Fluoreno[2,3,4-*ij*]isoquinolines 9



7



9

entry	R^1	R^2	R^3	R^4	R^5	R^6	7 (%)	9 (%)
a	H	H	H	H	C_6H_5	H	17	36
b	H	CH_3	H	H	C_6H_5	H	28	35
c	H	C_6H_5	H	H	C_6H_5	H		46
d	CH_3	H	H	H	C_6H_5	H	46	
e	H	CH_3	CH_3	H	C_6H_5	H	29	28
f	H	H	H	CH_3	4-$CH_3C_6H_4$	H	20	45
g	H	CH_3	H	CH_3	4-$CH_3C_6H_4$	H	20	43
h	H	H	H	H	C_2H_5	H	63	
i	H	CH_3	H	H	C_2H_5	H	67[a]	
j	H	H	H	H	C_6H_5	$C_6H_5CH_2$	25	32

[a] A 1:1 mixture of cis/trans isomers.

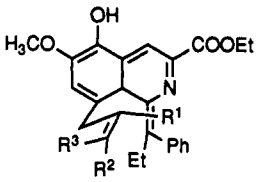
a three sp^3-carbon chain with two methylene and one central methine group, all of them linked to quaternary carbons; the methylene protons of the ester moiety and the previously mentioned methylene protons are nonequivalent, which clearly indicates the presence of at least one asymmetric center. In addition, the ^{13}C NMR spectrum reveals the presence of one sp^3 quaternary carbon atom. An X-ray structure determination confirmed the structure **9a**.

Reaction of the related ketene imine **5f** also resulted in the smooth formation of the isoquinoline derivative **7f** and the pentacyclic compound **9f**. The ^1H and ^{13}C NMR spectra of **9f** exhibited signals very similar to those of compound **9a**. Likewise, microanalytical and spectral data confirmed the structure shown. Ketene imines **5b**, **5e**, and **5g** containing substituents on the double bond of the allylic side chain behaved similarly although the ratio of products was somewhat different. Most noticeable was that ketene imine **5c** by thermal treatment led to the pentacyclic compound **9c** as the only reaction product in moderate yield, whereas ketene imine **5d** gave the isoquinoline derivative **7d** and no trace of the pentacyclic compound was detected. In a similar way, ketene imines **5h** and **5i** derived from ethyl phenyl ketene by thermal treatment led to the corresponding isoquinoline derivatives **7h** (63%) and **7i** (67%), respectively, as the only reaction products.

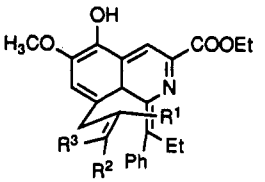
The ^1H NMR and the X-ray analysis of compounds **9** show that the conversion **6** → **9** takes place with a high degree of stereochemical control. The relative stereochemistry of the substituents on the allylic chain is retained, and the two carbocycles are cis fused.

Unfortunately, efforts to improve the yield of **9** under a variety of reaction conditions were unsuccessful, and compounds **7** were recovered unchanged after prolonged heating at temperatures higher than 160 °C. This observation and the fact that heating **5** in the presence of radical scavengers did not affect the product composition strongly suggest a mechanism for the conversion **5** → **7** + **9** involving initial 6π-electrocyclization with the aryl group as a 2π-component and subsequent Claisen rearrangement to give **6**. Aromatization of **6** to **7** occurs by a [1,3] proton shift. The formation of the pentacyclic compound **9** from the intermediate **6** can be explained if an initial intramolecular Diels–Alder cycloaddition leading to the pentacyclic fused blocked ring system **8** takes place. This cycloadduct,

Chart I



10



11

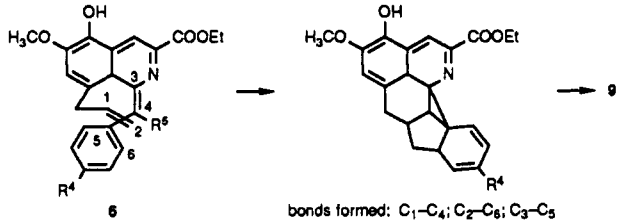
under the reaction conditions, undergoes aromatization of both phenyl and isoquinoline rings with concomitant migration of a substituent at the ring juncture of the fused blocked ring, involving a ring-opening/ring-closure sequence to afford **9**. The conversion of intermediate **6** to **8** represents a clear example of an intramolecular Diels–Alder cycloaddition of unactivated dienophiles on stilbene derivatives.[6] On the other hand, rearrangements in which the migration of a single substituent results in the simultaneous aromatization of two nonaromatic rings have previously been reported,[7] however, to the best of our knowledge, this is the first example reported involving a ring-opening/ring-closure sequence.[8]

Assuming this mechanism for the conversion of **5** to **7** + **9**, the thermal behavior of ketene imines **5c** and **5d** can be rationalized. It is well-known that dienophiles with a phenyl group on the terminal carbon atom of the olefin cyclize easier than do the unsubstituted analogues.[9]

(6) Wagner-Jauregg, T. *Synthesis* **1980**, 769. Ciganek, E. *Org. React.* **1984**, *32*, 1.

(7) Miller, B.; Baghdadchi, J. *J. Chem. Soc., Chem. Commun.* **1986**, 1257.

(8) A reviewer has pointed out a reasonable alternative pathway for the formation of **9** from the intermediate **6**. It involves the formation of an intermediate with a cyclopropane ring that by loss of hydrogen and ring opening leads directly to **9** without molecular rearrangement.



6

bonds formed: C_1–C_4; C_2–C_6; C_3–C_5

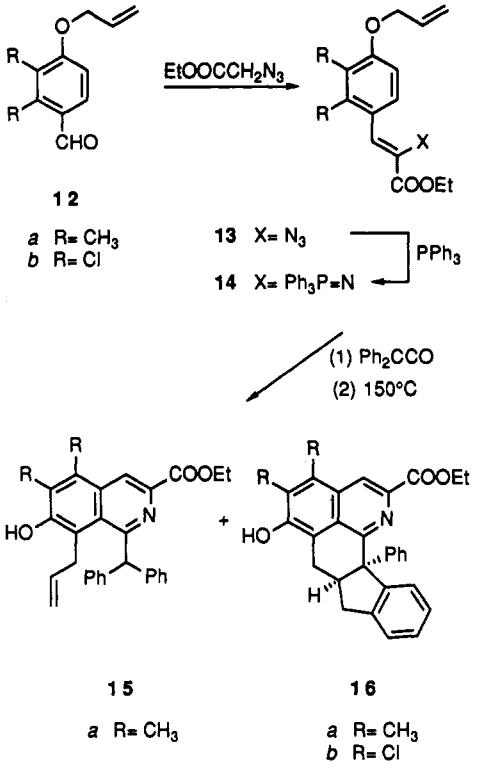
Ketene imine **5c** only gave the pentacyclic compound whereas an alkyl group on the nonterminal carbon atom of the dienophile decreases or even prevents the intramolecular cyclization.[10] Ketene imine **5d** only led to the isoquinoline derivative. On the other hand, thermal electrocyclizations of allenyl dienes[11] and (*Z*)-hexa-1,3,5-trienes[12] have been demonstrated to be stereospecific processes. At this point, we believe that ketene imines **5h** and **5i**, derived from ethyl phenyl ketene, undergo a concerted electrocyclic process proceeding in a stereospecific disrotatory manner to give intermediate **10** in which the phenyl group is antiperiplanar to the forming C–C bond (Chart I). Since there are two possible modes of disrotation, the other allowed geometric isomer of **10**, namely **11**, is presumably not formed for steric reasons. Consequently, in the thermal treatment of ketene imines **5h** and **5i** only the [1,3] proton shift product, the isoquinoline derivatives **7**, were obtained and no intramolecular Diels–Alder cycloaddition products, pentacyclic compounds **9**, were formed due to the unfavorable geometry of the diene in the intermediate **10**.

In order to investigate the generality of this consecutive process, variations were considered. At first, it was of interest to see what would happen if the ketene imine moiety and the allyloxy side chain were in the para position. Thus, *p*-(allyloxy)benzaldehydes **12**, available from the corresponding *p*-hydroxybenzaldehydes and allyl bromide, were converted into the iminophosphoranes **14** by sequential treatment with ethyl azidoacetate in the presence of sodium ethoxide at −20 °C and triphenylphosphine at room temperature. When a toluene solution of iminophosphorane **14a** (R = CH_3) was treated with diphenyl ketene at room temperature for 1 h and then heated at 160 °C in a sealed tube, the isoquinoline derivative **15a** (56%) and the pentacyclic compound **16a** (28%) were isolated by column chromatography. However, iminophosphorane **14b** (R = Cl) under the same reaction conditions led to the pentacyclic compound **16b** (45%), and no trace of the isoquinoline derivative was detected (Scheme II). This result shows that this consecutive process is also applicable when the Claisen rearrangement takes place at the ortho-position; in this case, the aromatic ring of the reaction products is fully substituted.

Variations were also considered by inverting the sequence of reactions. Thus, iminophosphorane **17**[5] reacted with diphenyl ketene at 160 °C to give the isoquinoline derivative **18** in 67% yield (tandem aza-Wittig/electrocyclic ring closure product). Deprotection of **18** to **19** by catalytic hydrogenolysis followed by O-allylation furnished **20** in 67% yield, which when subjected to the previously mentioned thermal conditions led to the isolation of the Claisen rearrangement product **7b** in 35% yield (Scheme III). On the other hand, iminophosphorane **21** reacted with diphenyl ketene at 160 °C to afford the isoquinoline derivative **7j** in 25% yield and the pentacyclic compound **9j** in 32% yield (Scheme IV).

A final word about the sequence electrocyclic ring closure/Claisen rearrangement is relevant. During our previous experiences on thermally induced electrocyclization of heterocumulenes we have found the following facts:

Scheme II



12

a R = CH_3
b R = Cl

13 X = N_3

14 X = $Ph_3P{=}N$

15

a R = CH_3

16

a R = CH_3
b R = Cl

carbodiimides of type **22** undergo electrocyclic ring closure in toluene at reflux temperature; carbodiimides of type **23** undergo electrocyclic ring closure/Claisen rearrangement at 150 °C; and isothiocyanates of type **24** at 150 °C were recovered unalterated (Scheme V). These results clearly show that electrocyclization takes place at lower temperatures than the Claisen rearrangement, and from the comparison of the thermal behavior of compounds **23** and **24** the Claisen rearrangement could occur simultaneously or after the electrocyclization.

Concluding Remarks

This second-generation version of our annulation strategy shows for the first time that easily available conjugated ketene imines undergo a one-pot consecutive electrocyclization ring closure/Claisen rearrangement/intramolecular Diels–Alder cycloaddition/double aromatization process to afford derivatives of the previously unreported fluoreno[2,3,4-*ij*]isoquinoline ring system. Essentially, this process involves the formation of four C–C single bonds and two stereocenters, one of them being a quaternary carbon atom, with a high degree of stereochemical control. Further studies are underway in our laboratory aimed at the application of this methodology to the preparation of structurally complex nitrogen heterocycles related to the isoaporphine alkaloids.

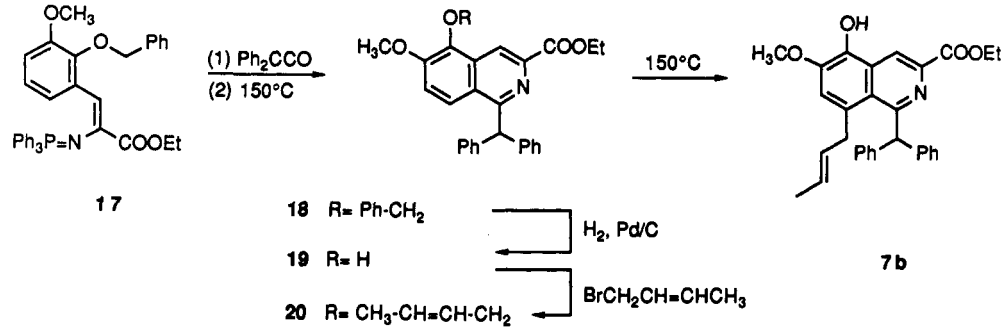
Experimental Section

General Methods. General experimental conditions and spectroscopic instrumentation used have been described.[5]

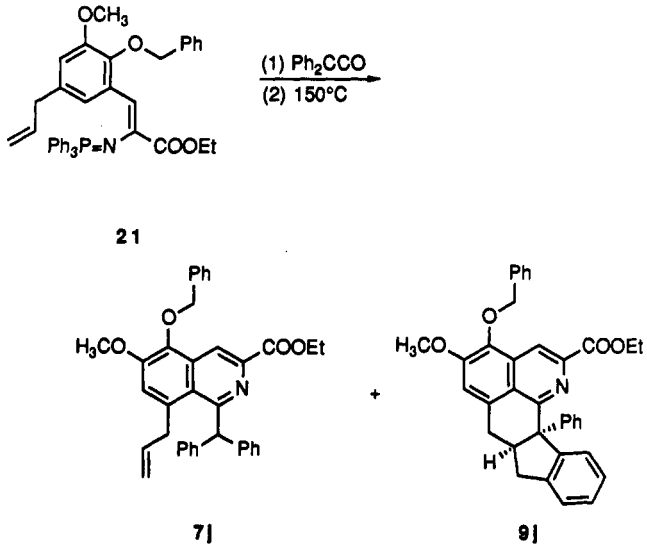
Materials. 2-(Allyloxy)-3-methoxybenzaldehyde[13] (**2a**), aldehydes 2,3-dichloro-4-hydroxybenzaldehyde and 2,3-dimethylbenzaldehyde,[14] iminophosphoranes[5] **4a**, **17**, and **21**, and ketenes diphenyl ketene[15] and ethyl phenyl ketene[16] were prepared as

(9) Oppolzer, W.; Achini, R.; Pfenninger, E.; Weber, H. P. *Helv. Chim. Acta* **1976**, *59*, 1186.
(10) Burke, S. D.; Strickland, S. M. S.; Powner, T. M. *J. Org. Chem.* **1983**, *48*, 454.
(11) Okamura, W. H.; Peter, R.; Reischl, W. *J. Am. Chem. Soc.* **1985**, *107*, 1034.
(12) Padwa, A.; Brodsky, L.; Clough, S. *J. Am. Chem. Soc.* **1972**, *94*, 6767. Marvell, E. N.; Caple, G.; Schatz, B.; Pippin, W. *Tetrahedron* **1973**, *29*, 3781. Vogel, E.; Grimme, W.; Dinné, E. *Tetrahedron Lett.* **1965**, 391.
(13) Martin, S. F.; Garrison, P. J. *J. Org. Chem.* **1982**, *47*, 1513.
(14) Bicking, J. B.; Holtz, W. J. Watson, L. S.; Cragoe, E. J. *J. Med. Chem.* **1976**, *19*, 530.
(15) Taylor, E. C.; McKillop, A.; Hawks, G. H. *Org. Synth.* **1973**, *52*, 36.

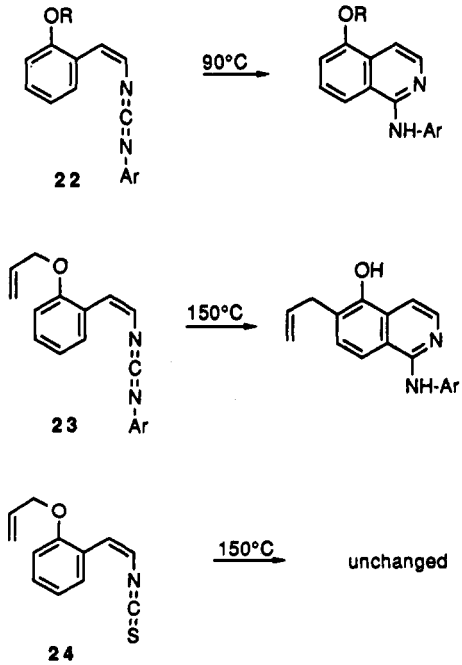
Scheme III



Scheme IV



Scheme V



described in the literature. Di-*p*-tolyl ketene was prepared by the same method described for diphenyl ketene.

Preparation of the Substituted Benzaldehydes 2 and 12. To a solution of the appropriate benzaldehyde (20 mmol) in 40 mL of dry acetone was added potassium carbonate (2.76 g, 20 mmol) and the corresponding alkenyl bromide (20 mmol). The resultant mixture was stirred at reflux temperature for 24 h. After the mixture was cooled, the solvent was removed under reduced pressure, and the residual material was treated with 35 mL of water and extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with water (3 × 25 mL), dried over anhydrous magnesium sulfate, and filtered. The solution was concentrated to dryness, and the crude product was purified by crystallization or chromatography (silica gel column, eluting with *n*-hexane/ethyl acetate (4:1)). For compound **12b**, dimethylformamide was used as solvent and the reaction mixture was heated at 80 °C for 24 h.

2b: yield 60%; oil; IR (Nujol) 1689 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.69 (d, 3 H, J = 4.5 Hz), 3.88 (s, 3 H), 4.56–4.59 (m, 2 H), 5.72–5.77 (m, 2 H), 7.09–7.15 (m, 2 H), 7.39 (dd, 1 H, J = 2.7, 6.7 Hz), 10.41 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 17.5, 55.8, 74.8, 117.7, 118.6, 123.8, 125.9, 131.7, 151.1 (q), 152.9 (q), 190.3 (CO), one quaternary carbon atom was not observed; mass spectrum m/z (relative intensity) 206 (M^+, 40). Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 70.12; H, 6.63.

2c: yield 71%; mp 76 °C; colorless prisms (ether/*n*-hexane); IR (Nujol) 1691 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.86 (s, 3 H), 4.79 (d, 2 H, J = 6.3 Hz), 6.40 (dt, 1 H, J = 15.9, 6.3 Hz), 6.65 (d, 1 H, J = 15.9 Hz), 7.04–7.43 (m, 8 H), 10.48 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 55.9, 74.9, 117.9, 119.0, 124.0, 124.2, 126.5, 128.0, 128.5, 130.1, 134.2, 136.1 (q), 151.1 (q), 152.9 (q), 190.2 (CO); mass spectrum m/z (relative intensity) 268 (M^+, 15). Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 75.93; H, 5.89.

2d: yield 50%; oil; IR (Nujol) 1693 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.86 (s, 3 H), 3.87 (s, 3 H), 4.54 (s, 2 H), 4.97 (m, 1 H), 5.08 (m, 1 H), 7.05–7.15 (m, 2 H), 7.39 (dd, 1 H, J = 2.5, 6.9 Hz), 10.44 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 19.5, 55.7, 77.9, 113.5, 117.8, 118.7, 123.8, 129.7 (q), 140.7 (q), 151.3 (q), 152.7 (q), 189.9 (CO); mass spectrum m/z (relative intensity) 206 (M^+, 24). Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.71; H, 7.03.

2e: yield 81%; oil; IR (Nujol) 1692 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.60 (s, 3 H), 1.73 (s, 3 H), 3.90 (s, 3 H), 4.65 (d, 2 H, J = 7.6 Hz), 5.46–5.54 (m, 1 H), 7.09–7.15 (m, 2 H), 7.39 (dd, 1 H, J = 2.9, 6.5 Hz), 10.39 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 17.6, 25.5, 55.8, 70.2, 117.6, 118.5, 119.1, 123.8, 130.3 (q), 140.0 (q), 151.1 (q), 153.1 (q), 190.3 (CO); mass spectrum m/z (relative intensity) 220 (M^+, 15). Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.88; H, 7.32. Found: C, 71.03; H, 7.42.

12a: yield 79%; oil; IR (Nujol) 1684 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.17 (s, 3 H), 2.54 (s, 3 H), 4.55 (d, 2 H, J = 4.8 Hz), 5.25–5.46 (m, 2 H), 5.94–6.14 (m, 1 H), 6.74 (d, 1 H, J = 8.6 Hz), 7.58 (d, 1 H, J = 8.6 Hz), 10.08 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.2, 14.5, 68.6, 108.4, 117.3, 126.4 (q), 127.8 (q), 132.3, 132.6, 140.6 (q), 160.4 (q), 191.6 (CO); mass spectrum m/z (relative intensity) 190 (M^+, 94). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.61; H, 7.65.

12b: yield 73%; mp 85 °C; colorless prisms (ether/ethanol); IR (Nujol) 1684 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.69–4.72 (m, 2 H), 5.34–5.54 (m, 2 H), 5.59–6.13 (m, 1 H), 6.93 (d, 1 H, J = 8.8 Hz), 7.81 (d, 1 H, J = 8.8 Hz), 10.31 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 70.1, 111.0, 118.7, 122.8 (q), 126.9 (q), 128.5, 131.3, 137.7 (q), 159.6 (q), 188.3 (CO); mass spectrum m/z (relative intensity) 232 (M + 2, 36) 230 (M^+, 60). Anal. Calcd for $C_{10}H_8Cl_2O_2$: C, 51.98; H, 3.49. Found: C, 52.19; H, 3.37.

Preparation of Ethyl α-Azidocinnamates 3 and 13. A mixture of ethyl azidoacetate (10.32 g, 80 mmol) and the ap-

(16) Brady, W. T.; Dorsey, E. D.; Parry, F. H. *J. Org. Chem.* **1969**, *34*, 2846.

propriate aldehyde (20 mmol) was added dropwise under nitrogen at −20 °C to a well-stirred solution containing sodium (0.76 g) in 50 mL of anhydrous ethanol. The reaction mixture was stirred for 6 h, poured into aqueous 30% ammonium chloride (100 mL), and then extracted with ether (3 × 80 mL). The combined organic layers were washed with water, dried over anhydrous sodium sulfate, and filtered. Concentration to dryness yielded a crude material that was purified by crystallization from the appropriate solvent or by chromatography.

3b: yield 60%; mp 74 °C; colorless prisms (ethanol); IR (Nujol) 2115, 1707 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.39 (t, 3 H, J = 7.0 Hz), 1.72 (dd, 3 H, J = 1.0, 4.0 Hz), 3.84 (s, 3 H), 4.35 (q, 2 H, J = 7.0 Hz), 4.39–4.41 (m, 2 H), 5.74–5.79 (m, 2 H), 6.90 (dd, 1 H, J = 1.5, 8.2 Hz), 7.07 (t, 1 H, J = 8.1 Hz), 7.39 (s, 1 H), 7.81 (dd, 1 H, J = 1.5, 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 14.1, 17.6, 55.8, 61.9, 74.5, 113.7, 120.1, 122.1, 123.5, 125.9 (q), 126.8, 127.8 (q), 130.5, 147.1 (q), 152.7 (q), 163.5 (CO); mass spectrum m/z (relative intensity) 317 (M^+, 7), 162 (100). Anal. Calcd for $C_{16}H_{19}N_3O_4$: C, 60.56; H, 6.03; N, 13.24. Found: C, 60.43; H, 5.85; N, 13.20.

3c: yield 50%; oil (chromatographed on silica gel with ether/*n*-hexane (7:3) as eluent); IR (Nujol) 2118, 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.24 (t, 3 H, J = 7.1 Hz), 3.87 (s, 3 H), 4.22 (q, 2 H, J = 7.1 Hz), 4.66 (d, 2 H, J = 6.4 Hz), 6.41 (dt, 1 H, J = 6.4, 15.9 Hz), 6.65 (d, 1 H, J = 15.9 Hz), 6.89–7.41 (m, 8 H), 7.80 (d, 1 H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ 14.0, 55.8, 62.1, 77.4, 113.4, 119.7, 122.1, 123.8, 124.8, 126.0 (q), 126.5, 127.8, 127.9 (q), 128.5, 133.4, 136.5 (q), 146.8 (q), 152.6 (q), 163.5 (CO); mass spectrum m/z (relative intensity) 379 (M^+, 5). Anal. Calcd for $C_{21}H_{21}N_3O_4$: C, 66.48; H, 5.58; N, 11.07. Found: C, 66.31; H, 5.82; N, 10.85.

3d: yield 65%; mp 38 °C; colorless prisms (chromatographed on silica gel with ether/*n*-hexane (4:1) as eluent); IR (Nujol) 2106, 1705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.36 (t, 3 H, J = 7.2 Hz), 2.14 (s, 3 H), 3.85 (s, 3 H), 4.33 (q, 2 H, J = 7.2 Hz), 4.37 (s, 2 H), 4.97 (m, 1 H), 5.12 (m, 1 H), 6.90 (dd, 1 H, J = 1.4, 8.1 Hz), 7.07 (t, 1 H, J = 8.1 Hz), 7.44 (s, 1 H), 7.84 (dd, 1 H, J = 1.4, 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ 14.0, 19.8, 55.8, 62.0, 77.4, 113.2, 113.5, 119.4, 122.0, 123.6, 125.9 (q), 127.5 (q), 141.4 (q), 147.0 (q), 152.6 (q), 163.6 (CO); mass spectrum m/z (relative intensity) 317 (M^+, 19). Anal. Calcd for $C_{16}H_{19}N_3O_4$: C, 60.56; H, 6.03; N, 13.24. Found: C, 60.43; H, 5.91; N, 13.12.

3e: yield 56%; mp 52 °C; colorless prisms (ethanol); IR (Nujol) 2112, 1713 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.39 (t, 3 H, J = 7.0 Hz), 1.68 (s, 3 H), 1.76 (s, 3 H), 3.85 (s, 3 H), 4.35 (q, 2 H, J = 7.0 Hz), 4.47 (d, 2 H, J = 7.4 Hz), 5.50–5.57 (m, 1 H), 6.90 (dd, 1 H, J = 1.0, 8.0 Hz), 7.07 (t, 1 H, J = 8.0 Hz), 7.40 (s, 1 H), 7.82 (dd, 1 H, J = 1.0, 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 14.1, 17.8, 25.7, 55.8, 62.0, 70.0, 113.4, 120.0, 120.1, 122.0, 123.5, 125.7 (q), 127.9 (q), 138.9 (q), 147.1 (q), 152.8 (q), 163.6 (CO); mass spectrum m/z (relative intensity) 331 (M^+, 10), 69 (100). Anal. Calcd for $C_{17}H_{21}N_3O_4$: C, 61.62; H, 6.39; N, 12.68. Found: C, 61.52; H, 6.58; N, 12.92.

13a: yield 75%; mp 56 °C; colorless prisms (ethanol/water); IR (Nujol) 2123, 1704 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.38 (t, 3 H, J = 7.0 Hz), 2.19 (s, 3 H), 2.25 (s, 3 H), 4.35 (q, 2 H, J = 7.0 Hz), 4.53 (d, 2 H, J = 4.9 Hz), 5.23–5.46 (m, 2 H), 5.96–6.50 (m, 1 H), 6.70 (d, 1 H, J = 8.7 Hz), 7.18 (s, 1 H), 7.74 (d, 1 H, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$) δ 11.6, 13.7, 15.8, 61.6, 68.4, 108.1, 116.6, 124.2 (q), 124.3, 125.1 (q), 127.7, 132.9, 137.2 (q), 156.3 (q), 163.2 (CO), one quaternary carbon atom was not observed; mass spectrum m/z (relative intensity) 301 (M^+, 10), 200 (100). Anal. Calcd for $C_{16}H_{19}N_3O_3$: C, 63.77; H, 6.35; N, 13.94. Found: C, 63.98; H, 6.18; N, 14.21.

13b: yield 65%; mp 119–120 °C; colorless prisms (ethanol); IR (Nujol) 2122, 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.41 (t, 3 H, J = 7.1 Hz), 4.38 (q, 2 H, J = 7.1 Hz), 4.60 (d, 2 H, J = 5.0 Hz), 5.32–5.52 (m, 2 H), 5.96–6.15 (m, 1 H), 6.87 (d, 1 H, J = 9.0 Hz), 7.26 (s, 1 H), 8.11 (d, 1 H, J = 9.0 Hz); ^{13}C NMR ($CDCl_3$) δ 14.3, 62.5, 70.1, 110.8, 118.5, 120.6, 122.7 (q), 125.4 (q), 126.5 (q), 129.4, 132.0, 134.5 (q), 155.5 (q), 163.4 (CO); mass spectrum m/z (relative intensity) 343 (M + 2, 3), 341 (M^+, 9). Anal. Calcd for $C_{14}H_{13}Cl_2N_3O_3$: C, 49.14; H, 3.83; N, 12.28. Found: C, 48.95; H, 3.73; N, 12.31.

Preparation of Ethyl α-[(Triphenylphosphoranylidene)amino]cinnamates 4 and 14. A solution of triphenylphosphine (2.62 g, 10 mmol) in 30 mL of dry ether was added dropwise under nitrogen at room temperature to a solution of the appropriate ethyl α-azidocinnamate **3** or **13** (10 mmol) in 10 mL of the same solvent. The reaction mixture was stirred at room temperature for 12 h, and the solvent was removed under reduced pressure. The residual material was purified by column chromatography or recrystallized from the appropriate solvent.

4b: yield 95%; mp 105–106 °C; colorless prisms (ether); IR (Nujol) 1690, 1261, 1105 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.03 (t, 3 H, J = 7.0 Hz), 1.71 (d, 3 H, J = 4.0 Hz), 3.81 (s, 3 H), 3.85 (q, 2 H, J = 7.0 Hz), 4.41 (d, 2 H, J = 4.0 Hz), 5.81–5.83 (m, 2 H), 6.72 (d, 1 H, J = 8.0 Hz), 6.95 (t, 1 H, J = 8.0 Hz), 7.14 (d, 1 H, J = 7.2 Hz), 7.31–7.46 (m, 9 H), 7.67–7.77 (m, 6 H), 8.72 (d, 1 H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 14.0, 17.8, 55.9, 60.6, 74.0, 109.6 (d, $^3J_{P-C}$ = 19.5 Hz, C_β), 110.1, 122.6, 122.9, 127.6, 128.0 (d, $^3J_{P-C}$ = 12.1 Hz, C_m), 129.5, 130.8 (d, $^4J_{P-C}$ = 2.5 Hz, C_p), 132.3 (d, $^2J_{P-C}$ = 9.5 Hz, C_o), 132.7 (q), 133.0 (d, $^1J_{P-C}$ = 103.1 Hz, C_i), 136.7 (d, $^2J_{P-C}$ = 6.8 Hz, C_α), 145.6 (q), 152.4 (q), 168.0 (d, $^3J_{P-C}$ = 7.1 Hz, CO); mass spectrum m/z (relative intensity) 551 (M^+, 10), 183 (100). Anal. Calcd for $C_{34}H_{34}NO_4P$: C, 74.03; H, 6.21; N, 2.54. Found: C, 73.76; H, 6.39; N, 2.62.

4c: yield 78%; mp 103–104 °C; colorless prisms (ether); IR (Nujol) 1693, 1210, 1168, 1108 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, 3 H, J = 7.1 Hz), 3.77 (q, 2 H, J = 7.1 Hz), 3.83 (s, 3 H), 4.66 (d, 2 H, J = 5.7 Hz), 6.56 (dt, 1 H, J = 5.7, 15.8 Hz), 6.69–6.76 (m, 2 H), 6.98 (t, 1 H, J = 8.1 Hz), 7.13–7.45 (m, 15 H), 7.67–7.77 (m, 6 H), 8.75 (d, 1 H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 13.9, 55.9, 60.7, 74.0, 109.4 (d, $^3J_{P-C}$ = 19.6 Hz, C_β), 110.1, 122.6, 123.1, 126.1, 126.5, 127.4, 128.0 (d, $^3J_{P-C}$ = 12.1 Hz, C_m), 128.4, 130.8 (d, $^4J_{P-C}$ = 2.7 Hz, C_p), 132.3 (d, $^2J_{P-C}$ = 7.8 Hz, C_o), 132.6, 132.8 (q), 133.0 (d, $^1J_{P-C}$ = 103.2 Hz, C_i), 137.0 (d, $^2J_{P-C}$ = 6.6 Hz, C_α), 137.1 (q), 145.4 (q), 152.4 (q), 168.0 (d, $^3J_{P-C}$ = 7.0 Hz, CO); mass spectrum m/z (relative intensity) 603 (M^+, 6), 183 (100). Anal. Calcd for $C_{39}H_{36}NO_4P$: C, 76.33; H, 5.91; N, 2.28. Found: C, 76.18; H, 6.15, N, 2.39.

4d: yield 65%; mp 98 °C; colorless crystals (ether/*n*-hexane); IR (Nujol) 1692, 1217, 1166, 1080 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (t, 3 H, J = 7.0 Hz), 1.95 (s, 3 H), 3.83 (s, 3 H), 3.85 (q, 2 H, J = 7.0 Hz), 4.39 (s, 2 H), 4.96 (s, 1 H), 5.18 (s, 1 H), 6.74 (dd, 1 H, J = 1.3, 8.1 Hz), 6.96 (t, 1 H, J = 8.1 Hz), 7.18 (d, 1 H, J = 7.3 Hz), 7.33–7.48 (m, 9 H), 7.68–7.86 (m, 6 H), 8.72 (dd, 1 H, J = 1.2, 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ 14.0, 20.0, 56.0, 60.7, 76.9, 109.4 (d, $^3J_{P-C}$ = 19.6 Hz, C_β), 110.3, 112.6, 122.7, 123.1, 128.1 (d, $^3J_{P-C}$ = 12.1 Hz, C_m), 130.9 (d, $^4J_{P-C}$ = 2.6 Hz, C_p), 132.4 (d, $^2J_{P-C}$ = 9.8 Hz, C_o), 133.1 (d, $^1J_{P-C}$ = 103.4 Hz, C_i), 136.9 (d, $^2J_{P-C}$ = 6.5 Hz, C_α), 142.3 (q), 145.6 (q), 152.5 (q), 168.1 (d, $^3J_{P-C}$ = 7.4 Hz, CO), one quaternary carbon atom was not observed; mass spectrum m/z (relative intensity) 551 (M^+, 8), 183 (100). Anal. Calcd for $C_{34}H_{34}NO_4P$: C, 74.03; H, 6.21; N, 2.54. Found: C, 73.89; H, 6.39; N, 2.37.

4e: yield 95%; mp 127–128 °C; colorless prisms (benzene/*n*-hexane); IR (Nujol) 1690, 1221, 1181, 1101 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.01 (t, 3 H, J = 7.2 Hz), 1.37 (s, 3 H), 1.76 (s, 3 H), 3.83 (s, 3 H), 3.85 (q, 2 H, J = 7.2 Hz), 4.47 (d, 2 H, J = 7.2 Hz), 5.56 (t, 1 H, J = 7.2 Hz), 6.74 (d, 1 H, J = 7.2 Hz), 6.95 (t, 1 H, J = 7.2 Hz), 7.14 (d, 1 H, J = 7.2 Hz), 7.31–7.46 (m, 9 H), 7.67–7.77 (m, 6 H), 8.72 (d, 1 H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$) δ 14.0, 18.0, 25.8, 55.9, 60.6, 69.8, 109.7 (d, $^3J_{P-C}$ = 19.6 Hz, C_β), 110.2, 121.1, 122.7, 122.9, 128.1 (d, $^3J_{P-C}$ = 12.2 Hz, C_m), 130.8 (d, $^4J_{P-C}$ = 2.8 Hz, C_p), 132.4 (d, $^2J_{P-C}$ = 9.6 Hz, C_o), 132.8 (q), 133.1 (d, $^1J_{P-C}$ = 103.0 Hz, C_i), 136.8 (d, $^2J_{P-C}$ = 6.8 Hz, C_α), 137.5 (q), 145.7 (q), 152.5 (q), 168.1 (d, $^3J_{P-C}$ = 7.1 Hz, CO); mass spectrum m/z (relative intensity) 565 (M^+, 7), 183 (100). Anal. Calcd for $C_{35}H_{36}NO_4P$: C, 74.32; H, 6.41; N, 2.48. Found: C, 74.18; H, 6.59; N, 2.30.

14a: yield 97%; mp 129–130 °C; colorless prisms (benzene/*n*-hexane); IR (Nujol) 1688, 1219, 1105 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.01 (t, 3 H, J = 7.2 Hz), 2.31 (s, 3 H), 2.25 (s, 3 H), 3.90 (q, 2 H, J = 7.2 Hz), 4.55 (d, 2 H, J = 4.9 Hz), 5.24–5.52 (m, 2 H), 6.01–6.20 (m, 1 H), 6.67 (d, 1 H, J = 8.7 Hz), 6.96 (d, 1 H, J = 5.8 Hz), 7.34–7.49 (m, 9 H), 7.65–7.79 (m, 6 H), 8.52 (d, 1 H, J = 8.7 Hz); ^{13}C NMR ($CDCl_3$) δ 12.3, 14.1, 16.2, 60.5, 69.1, 108.5, 115.5 (d, $^3J_{P-C}$ = 19.0 Hz, C_β), 116.6, 124.7 (q), 128.1 (d, $^3J_{P-C}$ = 12.1 Hz, C_m), 128.2, 129.7 (d, $^4J_{P-C}$ = 1.3 Hz), 130.8 (d, $^4J_{P-C}$ = 2.9 Hz, C_p), 132.5 (d, $^2J_{P-C}$ = 9.7 Hz, C_o), 133.3 (d, $^1J_{P-C}$ = 103.0 Hz, C_i), 134.1, 134.7 (d, $^2J_{P-C}$ = 6.0 Hz, C_α), 136.4 (q), 154.9 (q), 168.5 (d, $^3J_{P-C}$ = 6.1 Hz, CO); mass spectrum m/z (relative intensity) 535 (M^+, 25), 183 (100). Anal. Calcd for $C_{34}H_{34}NO_3P$:

C, 76.24; H, 6.40; N, 2.61. Found: C, 76.11; H, 6.66; N, 2.87.

14b: yield 82%; mp 135 °C dec; colorless prisms (benzene/*n*-hexane); IR (Nujol) 1693, 1238, 1112, 1026 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (t, 3 H, J = 7.0 Hz), 3.87 (q, 2 H, J = 7.0 Hz), 4.61 (d, 2 H, J = 4.2 Hz), 5.27–5.50 (m, 2 H), 5.99–6.10 (m, 1 H), 6.74 (d, 1 H, J = 8.9 Hz), 7.01 (d, 1 H, J = 8.9 Hz), 7.41–7.50 (m, 9 H), 7.65–7.75 (m, 6 H), 9.02 (d, 1 H, J = 8.6 Hz); ^{13}C NMR ($CDCl_3$) δ 14.1, 61.0, 70.1, 110.9 (d, $^3J_{P-C}$ = 19.0 Hz, C_β), 111.0, 118.0, 121.9 (q), 128.2 (d, $^3J_{P-C}$ = 12.2 Hz, C_m), 128.8, 130.7 (d, $^4J_{P-C}$ = 1.1 Hz), 131.1 (d, $^4J_{P-C}$ = 2.8 Hz, C_p), 132.2 (q), 132.4 (d, $^2J_{P-C}$ = 9.7 Hz, C_o), 132.7 (d, $^1J_{P-C}$ = 103.5 Hz, C_i), 132.7, 137.3 (d, $^2J_{P-C}$ = 6.0 Hz, C_α), 152.7 (q), 167.8 (d, $^3J_{P-C}$ = 7.2 Hz, CO); mass spectrum m/z (relative intensity) 579 (M + 4, 0.5), 577 (M + 2, 2.5), 575 (M^+, 41), 183 (100). Anal. Calcd for $C_{32}H_{28}Cl_2NO_3P$: C, 66.67; H, 4.90; N, 2.43. Found: C, 66.42; H, 5.19; N, 2.27.

General Procedure for the Preparation of Ethyl 1-Hydroxy-2-methoxy-4a,9b-dihydro-4*H*-fluoreno[2,3,4-*ij*]-isoquinoline-11-carboxylates 9. To a solution of the iminophosphorane **4** (2.5 mmol) in 40 mL of dry toluene was added the appropriate ketene (2.5 mmol). The reaction mixture was stirred at room temperature for 1 h, and the ketene imine **5** was heated in a sealed tube at 150–160 °C for 16 h. After the mixture was cooled, the solvent was removed under reduced pressure, and the residual material was chromatographed on a silica gel column, eluting with ethyl acetate/*n*-hexane (2:3), and recrystallized from the appropriate solvent to afford **7** and/or **9** as crystalline solids.

7a: yield 17%; mp 204–205 °C; colorless prisms (ethyl acetate/*n*-hexane); IR (Nujol) 3375, 1699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.37 (t, 3 H, J = 7.1 Hz), 3.80–3.82 (m, 2 H), 3.94 (s, 3 H), 4.35 (q, 2 H, J = 7.1 Hz), 4.92–5.02 (m, 1 H), 5.40–5.54 (m, 1 H), 6.20 (br s, 1 H), 6.26–6.37 (m, 1 H), 6.41 (s, 1 H), 7.10–7.35 (m, 11 H), 8.77 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.3, 40.2, 56.1, 56.5, 61.0, 116.4, 117.3, 119.6, 124.4 (q), 126.2, 128.0, 128.1 (q), 128.7 (q), 130.0, 138.4, 138.9 (q), 139.1 (q), 143.4 (q), 144.2 (q), 160.1 (q), 166.2 (q); mass spectrum m/z (relative intensity) 453 (M^+, 66), 161 (100). Anal. Calcd for $C_{29}H_{27}NO_4$: C, 76.80; H, 6.00; N, 3.09. Found: C, 76.55; H, 5.87; N, 3.24.

Ethyl 1-Hydroxy-2-methoxy-9b-phenyl-4a,9b-dihydro-4*H*-fluoreno[2,3,4-*ij*]isoquinoline-11-carboxylate (9a): yield 36%; mp 205–206 °C, colorless prisms (ethyl acetate/*n*-hexane); IR (Nujol) 3392, 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.34 (t, 3 H, J = 7.1 Hz, CH_3CH_2), 2.67 (dd, 1 H, J = 10.4, 14.8 Hz, 5-H), 2.91 (dd, 1 H, J = 1.7, 15.6 Hz, 4-H), 3.00 (dd, 1 H, J = 2.3, 14.8 Hz, 5-H), 3.14 (dddd, 1 H, J = 1.7, 2.3, 4.4, 10.4 Hz, 4a-H), 3.23 (dd, 1 H, J = 4.4, 15.6 Hz, 4-H), 3.90 (s, 3 H, CH_3O), 4.33 (dq, 1 H, J = 7.1, 11.0 Hz, $CH_3CH_aH_b$), 4.40 (dq, 1 H, J = 7.1, 11.0 Hz, $CH_3CH_aH_b$), 6.22 (s, 1 H, OH), 6.85–6.90 (m, 2 H, aromatic), 7.13–7.31 (m, 7 H, aromatic), 7.80 (d, 1 H, J = 7.2 Hz, aromatic), 8.63 (s, 1 H, 12-H); ^{13}C NMR ($CDCl_3$) δ 14.3 (CH_3CH_2), 28.5 (C_4), 35.8 (C_5), 50.9 (C_{4a}), 58.5 (CH_3O), 61.0 (CH_3CH_2), 62.3 (C_{9b}), 114.2 (C_3), 115.9 (C_{12}), 122.2 (q), 123.6, 126.0, 126.1 (q), 126.3, 127.1, 127.9, 128.3, 129.2, 138.0 (q), 141.4 (q), 142.6 (q), 144.5 (q), 148.2 (q), 148.9 (q), 159.9 (C_{9c}), 166.2 (CO), one quaternary carbon atom was not observed; mass spectrum m/z (relative intensity) 451 (M^+, 100). Anal. Calcd for $C_{29}H_{25}NO_4$: C, 77.14; H, 5.58; N, 3.10. Found: C, 76.95; H, 5.69; N, 2.96.

7b: yield 28%; mp 204 °C; colorless prisms (chloroform); IR (Nujol) 3358, 1696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40 (t, 3 H, J = 7.2 Hz), 1.81 (dd, 3 H, J = 1.5, 6.4 Hz), 3.76–3.79 (m, 2 H), 3.99 (s, 3 H), 4.38 (q, 2 H, J = 7.2 Hz), 5.30–5.44 (m, 1 H), 5.92–6.05 (m, 1 H), 6.15 (s, 1 H), 6.53 (s, 1 H), 7.16 (s, 1 H), 7.18–7.33 (m, 10 H), 8.79 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.2, 18.1, 39.2, 55.9, 56.4, 60.9, 116.4, 119.5, 124.2 (q), 126.1, 127.7, 127.9, 128.6 (q), 129.1 (q), 129.9, 131.2, 138.8, (q), 138.9 (q), 143.3 (q), 144.2 (q), 160.1 (q), 166.2 (q); mass spectrum m/z (relative intensity) 467 (M^+, 60), 165 (100). Anal. Calcd for $C_{30}H_{29}NO_4$: C, 77.06; H, 6.25; N, 2.99. Found: C, 76.83; H, 6.17; N, 3.15.

Ethyl 1-Hydroxy-2-methoxy-5-methyl-9b-phenyl-4a,9b-dihydro-4*H*-fluoreno[2,3,4-*ij*]isoquinoline-11-carboxylate (9b): yield 35%; mp 241 °C; colorless crystals (chloroform/*n*-hexane); IR (Nujol) 3409, 1698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.37 (t, 3 H, J = 7.2 Hz, CH_3CH_2), 1.39 (d, 3 H, J = 7.2 Hz, 5-CH_3), 2.64 (ddd, 1 H, J = 1.7, 4.6, 10.7 Hz, 4a-H), 2.79 (dq, 1 H, J = 7.2, 10.7 Hz, 5-H_a), 3.09 (dd, 1 H, J = 1.7, 16.7 Hz, 4-H_a), 3.26 (dd, 1 H, J = 4.6, 16.7 Hz, 4-H_a), 4.01 (s, 3 H, CH_3O), 4.30 (dq, 1 H, J = 7.2, 11.0 Hz, $CH_3CH_aH_b$), 4.38 (dq, 1 H, J = 7.2, 11.0 Hz, $CH_3CH_aH_b$), 6.15 (s, 1 H, OH), 6.90–7.34 (m, 9 H, aromatic), 7.82 (d, 1 H, J = 7.4 Hz, aromatic), 8.64 (s, 1 H, 12-H); ^{13}C NMR ($CDCl_3$) δ 14.3 (CH_3CH_2), 16.8 (CH_3C_5), 26.2 (C_4), 39.7 (C_5), 56.6 (CH_3O), 59.4 (C_{4a}), 61.0 (CH_3CH_2), 61.6 (C_{9b}), 114.3 (C_3), 115.9 (C_{12}), 122.0, 122.3 (q), 126.0, 126.1 (q), 126.4, 127.2, 128.0, 128.3, 129.1, 138.0 (q), 141.4 (q), 144.2 (q), 146.8 (q), 148.3 (q), 148.5 (q), 161.7 (C_{9c}) 166.2 (CO), one quaternary carbon atom was not observed; mass spectrum m/z (relative intensity) 465 (M^+, 66), 77 (100). Anal. Calcd for $C_{30}H_{27}NO_4$: C, 77.40; H, 5.84; N, 3.01. Found: C, 77.58; H, 5.66; N, 3.27.

Ethyl 1-Hydroxy-2-methoxy-5,9b-diphenyl-4a,9b-dihydro-4*H*-fluoreno[2,3,4-*ij*]isoquinoline-11-carboxylate (9c): yield 46%; mp 190–191 °C; colorless prisms (chloroform/*n*-hexane); IR (Nujol) 3409, 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.37 (t, 3 H, J = 7.1 Hz, CH_3CH_2), 2.89 (dd, 1 H, J = 3.9, 18.4 Hz, 4-H_a), 3.12 (m, 2 H, 4-H_a + 4a-H), 3.91 (d, 1 H, J = 10.4 Hz, 5-H_a), 3.97 (s, 3 H, CH_3O), 4.33 (dq, 1 H, J = 7.1, 11.1 Hz, $CH_3CH_aH_b$), 4.40 (dq, 1 H, J = 7.1, 11.1 Hz, $CH_3CH_aH_b$), 6.29 (br s, 1 H, OH), 6.78 (d, 1 H, J = 7.5 Hz, aromatic), 6.97–7.38 (m, 13 H, aromatic), 7.90 (d, 1 H, J = 7.4 Hz, aromatic), 8.69 (s, 1 H, 12-H); ^{13}C NMR ($CDCl_3$) δ 14.4 (CH_3CH_2), 25.7 (C_4), 52.7 (C_5), 56.6 (CH_3O), 60.8 (C_{4a}), 61.1 (CH_3CH_2), 61.4 (C_{9b}), 114.4 (C_3), 116.1 (C_{12}), 122.5 (q), 123.9, 126.1, 126.3 (q), 126.8, 126.9, 127.4, 128.1, 128.3, 128.6, 128.9, 129.1, 138.2 (q), 141.4 (q), 142.5 (q), 144.7 (q), 145.6 (q), 147.8 (q), 149.0 (q), 159.6 (C_{9c}), 166.2 (CO), one quaternary carbon atom was not observed; mass spectrum m/z (relative intensity) 527 (M^+, 100). Anal. Calcd for $C_{35}H_{29}NO_4$: C, 79.67; H, 5.54; N, 2.65. Found: C, 79.52; H, 5.32; N, 2.83.

7d: yield 46%; mp 218–219 °C; colorless prisms (chloroform); IR (Nujol) 3358, 1698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.36 (t, 3 H, J = 7.1 Hz), 1.98 (s, 3 H), 3.65 (s, 2 H), 3.90 (s, 3 H), 4.35 (q, 2 H, J = 7.1 Hz), 4.43 (s, 1 H), 5.12 (s, 1 H), 6.30 (br s, 2 H, Ph_2CH + OH), 7.10 (s, 1 H), 7.13–7.28 (m, 10 H), 8.82 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.3, 23.5, 44.7, 55.6, 56.5, 61.0, 113.2, 116.6, 120.2, 124.4 (q), 126.1, 127.9, 128.2 (q), 128.7 (q), 130.0, 138.9 (q), 139.2 (q), 143.4 (q), 144.5 (q), 146.9 (q), 160.1 (q), 166.3 (q); mass spectrum m/z (relative intensity) 467 (M^+, 69), 165 (100). Anal. Calcd for $C_{30}H_{29}NO_4$: C, 77.06; H, 6.25; N, 2.99. Found: C, 76.89; H, 6.13; N, 3.21.

7e: yield 29%; mp 190–191 °C; colorless prisms (chloroform/*n*-hexane); IR (Nujol) 3330, 1703 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.36 (t, 3 H, J = 7.1 Hz), 1.71 (s, 3 H), 1.85 (s, 3 H), 3.80 (d, 2 H, J = 4.8 Hz), 3.88 (s, 3 H), 4.35 (q, 2 H, J = 7.1 Hz), 5.40–5.43 (m, 1 H), 6.26 (br s, 1 H, OH), 6.54 (s, 1 H), 7.09–7.29 (m, 11 H), 8.79 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.3, 18.4, 25.6, 36.0, 56.4, 56.6, 61.0, 116.5, 118.6, 123.9 (q), 124.5, 126.1, 127.9, 128.8 (q), 130.1, 131.4 (q), 133.7 (q), 138.8 (q), 143.3 (q), 144.2 (q), 160.3 (q), 166.3 (q), one quaternary carbon atom was not observed; mass spectrum m/z (relative intensity) 481 (M^+, 14), 165 (100). Anal. Calcd for $C_{31}H_{31}NO_4$: C, 77.31; H, 6.49; N, 2.90. Found: C, 77.11; H, 6.72; N, 3.17.

Ethyl 5,5-Dimethyl-1-hydroxy-2-methoxy-9b-phenyl-4a,9b-dihydro-4*H*-fluoreno[2,3,4-*ij*]isoquinoline-11-carboxylate (9e): yield 28%; mp 276–278 °C; colorless crystals (chloroform); IR (Nujol) 3330, 1696 cm^{-1}; ^1H NMR (DMSO-d_6) δ 0.41 (s, 3 H, 5-CH_3), 1.32 (t, 3 H, J = 7.1 Hz, CH_3CH_2), 1.41 (s, 3 H, 5-CH_3), 2.52 (dd, 1 H, J = 1.7, 6.5 Hz, 4$_a$-H), 3.12 (dd, 1 H, J = 6.5, 17.8 Hz, 4-H_a), 3.26 (dd, 1 H, J = 1.7, 17.8 Hz, 4-H_a), 4.03 (s, 3 H, CH_3O), 4.35 (dq, 1 H, J = 7.1, 11.0 Hz, $CH_3CH_aH_b$), 4.40 (dq, 1 H, J = 7.1, 11.0 Hz, $CH_3CH_aH_b$), 6.69–6.73 (m, 2 H), 7.15–7.31 (m, 6 H, aromatic), 7.61 (s, 1 H, aromatic), 7.69–7.73 (m, 1 H, aromatic), 8.58 (s, 1 H, 12-H), 9.61 (br s, 1 H, OH); ^{13}C NMR (DMSO-d_6) δ 14.1 (CH_3CH_2), 23.6 (C_4), 26.3 (CH_3C_5), 28.1 (CH_3C_5), 45.4 (C_5), 56.4 (CH_3O), 59.0 (C_{4a}), 59.7 (C_{9b}), 60.6 (CH_3CH_2), 115.5 (C_3), 116.1 (C_{12}), 121.3, 121.6 (q), 125.8, 126.0, 126.2 (q), 127.3, 127.5, 128.0, 128.6 (q), 129.3, 138.2 (q), 139.5 (q), 146.0 (q), 146.2 (q), 149.3 (q), 151.3 (q), 160.4 (C_{9c}), 165.1 (CO); mass spectrum m/z (relative intensity) 479 (M^+, 100). Anal. Calcd for $C_{31}H_{29}NO_4$: C, 77.64; H, 6.09; N, 2.92. Found: C, 77.41; H, 5.83; N, 2.74.

7f: yield 20%; mp 205–207 °C; colorless prisms (ethyl acetate/*n*-hexane): IR (Nujol) 3443, 1691 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.38 (t, 3 H, J = 7.1 Hz), 2.24 (s, 6 H), 3.80–3.82 (m, 2 H), 3.87 (s, 3 H), 4.36 (q, 2 H, J = 7.1 Hz), 4.92–5.02 (m, 1 H), 5.32–5.37 (m, 1 H), 6.33 (s, 1 H), 6.27–6.41 (br s, 2 H, Ph_2CH + OH), 7.02 (d, 4 H, J = 8.0 Hz), 7.11 (s, 1 H), 7.21 (d, 4 H, J = 8.0 Hz), 8.79

(s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.2, 21.0, 40.2, 55.2, 56.4, 61.0, 116.3, 117.1, 119.6, 124.3 (q), 128.0 (q), 128.6, 129.7, 135.4 (q), 138.5, 138.8 (q), 139.1 (q), 141.4 (q), 143.3 (q), 160.4 (q), 166.3 (q), one quaternary carbon atom was not observed; mass spectrum *m/z* (relative intensity) 481 (M^+, 100). Anal. Calcd for $C_{31}H_{31}NO_4$: C, 77.31; H, 6.49; N, 2.91. Found: C, 77.13; H, 6.67; N, 3.17.

Ethyl 1-Hydroxy-2-methoxy-7-methyl-9b-*p*-tolyl-4a,9b-dihydro-4*H*-fluoreno[2,3,4-*ij*]isoquinoline-11-carboxylate (9f): yield 45%; mp 225 °C; colorless prisms (ethyl acetate/*n*-hexane); IR (Nujol) 3358, 1712 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.36 (t, 3 H, *J* = 7.1 Hz, CH_3CH_2), 2.26 (s, 3 H, $ArCH_3$), 2.30 (s, 3 H, $ArCH_3$), 2.57 (dd, 1 H, *J* = 10.7, 14.8 Hz, 5-H_a), 2.92 (dd, 1 H, *J* = 1.2, 16.2 Hz, 4-H_a), 2.98 (dd, 1 H, *J* = 2.6, 14.8 Hz, 5-H_b), 3.13 (dddd, 1 H, *J* = 1.2, 2.6, 5.0, 10.7 Hz, 4$_a$-H), 3.27 (dd, 1 H, *J* = 5.0, 16.2 Hz, 4-H_a), 3.99 (s, 3 H, CH_3O), 4.25 (dq, 1 H, *J* = 7.1, 10.9 Hz, $CH_3CH_aH_b$), 4.95 (dq, 1 H, *J* = 7.1, 10.9 Hz, $CH_3CH_aH_b$), 6.09 (br s, 1 H, OH), 6.78 (d, 2 H, *J* = 8.1 Hz, aromatic), 6.93 (s, 1 H, aromatic), 6.99 (d, 2 H, *J* = 8.1 Hz, aromatic), 7.07 (d, 1 H, *J* = 7.8 Hz, aromatic), 7.19 (s, 1 H, aromatic), 7.68 (d, 1 H, *J* = 7.8 Hz, aromatic), 8.60 (s, 1 H, 12-H); ^{13}C NMR ($CDCl_3$) δ 14.3 (CH_3CH_2), 20.9 ($ArCH_3$), 21.4 ($ArCH_3$), 28.6 (C_4), 35.7 (C_5), 51.1 (C_{4a}), 56.6 (CH_3O), 61.0 (CH_3CH_2), 61.6 (C_{9b}), 114.2 (C_3), 115.7 (C_{12}), 122.3 (q), 124.3, 126.1 (q), 127.3, 128.1, 128.7, 128.9, 135.4 (q), 136.7 (q), 137.9 (q), 141.6 (q), 142.7 (q), 144.4 (q), 145.4 (q), 146.2 (q), 160.4 (C_{9c}), 166.2 (CO), one quaternary carbon atom was not observed; mass spectrum *m/z* (relative intensity) 479 (M^+, 100). Anal. Calcd for $C_{31}H_{29}NO_4$: C, 77.64; H, 6.09; N, 2.92. Found: C, 77.51; H, 5.83; N, 3.18.

7g: yield 20%; mp 198–200 °C; colorless crystals (ethyl acetate/*n*-hexane); IR (Nujol) 3392, 1693 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.39 (t, 3 H, *J* = 7.1 Hz), 1.78 (dd, 3 H, *J* = 1.6, 6.4 Hz), 2.26 (s, 6 H), 3.75–3.78 (m, 2 H), 3.96 (s, 3 H), 4.36 (q, 2 H, *J* = 7.1 Hz), 5.27–5.41 (m, 1 H), 5.90–6.01 (m, 1 H), 5.87–6.31 (br s, 1 H, OH), 6.42 (s, 1 H), 7.03 (d, 4 H, *J* = 8.0 Hz), 7.13 (s, 1 H), 7.18 (d, 4 H, *J* = 8.0 Hz), 8.75 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.3, 18.2, 21.1, 39.4, 55.3, 56.5, 61.0, 116.3, 119.4, 124.2 (q), 127.7, 128.7, 129.4 (q), 129.8, 131.3, 135.3 (q), 135.5 (q), 138.9 (q), 141.4 (q), 141.7 (q), 143.3 (q)l, 160.6 (q), 166.3 (q); mass spectrum *m/z* (relative intensity) 495 (M^+, 64), 165 (100). Anal. Calcd for $C_{32}H_{33}NO_4$: C, 77.55; H, 6.71; N, 2.83. Found: C, 77.42; H, 6.94; N, 2.61.

Ethyl 1-Hydroxy-2-methoxy-5,7-dimethyl-9b-*p*-tolyl-4a,9b-dihydro-4*H*-fluoreno[2,3,4-*ij*]isoquinoline-11-carboxylate (9g): yield 43%; mp 228 °C; colorless prisms (ethyl acetate/*n*-hexane); IR (Nujol) 3390, 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.35 (t, 3 H, *J* = 7.1 Hz, CH_3CH_2), 1.36 (d, 3 H, *J* = 7.2 Hz, CH_3C_5) 2.25 (s, 3 H, $ArCH_3$), 2.32 (s, 3 H, $ArCH_3$), 2.58 (ddd, 1 H, *J* = 1.7, 5.7, 10.7 Hz, 4a-H), 2.72 (dq, 1 H, *J* = 7.2, 10.7 Hz, 5-H_a), 3.06 (dd, 1 H, *J* = 1.7, 16.4 Hz, 4-H_e), 3.22 (dd, 1 H, *J* = 5.7, 16.4 Hz, 4-H_a), 3.98 (s, 3 H, CH_3O), 4.37 (dq, 1 H, *J* = 7.1, 11.0 Hz, $CH_3CH_aH_b$), 4.42 (dq, 1 H, *J* = 7.1, 11.0 Hz, $CH_3CH_aH_b$), 6.50 (br s, 1 H, OH), 6.79 (d, 2 H, *J* = 8.2 Hz, aromatic), 6.88 (s, 1 H, aromatic), 6.98 (d, 2 H, *J* = 8.2 Hz, aromatic), 7.09 (d, 1 H, *J* = 7.8 Hz, aromatic), 7.20 (s, 1 H, aromatic), 7.70 (d, 1 H, *J* = 7.8 Hz, aromatic), 8.61 (s, 1 H, 12-H); ^{13}C NMR ($CDCl_3$) δ 14.3 (CH_3CH_2), 16.8 (CH_3C_5), 20.9 ($ArCH_3$), 21.5 ($ArCH_3$), 26.3 (C_4), 39.6 (C_5), 56.6 (CH_3O), 59.6 (C_{4a}), 60.9 (C_{9b}), 61.0 (CH_3CH_2), 114.3 (C_3), 115.8 (C_{12}), 122.3 (q), 122.8 (C_6), 126.2 (q), 127.4, 128.1, 128.7, 128.8, 135.5 (q), 136.8 (q), 138.0 (q), 141.4 (q), 144.4 (q), 145.5 (q), 147.0 (q), 159.7 (q), 160.5 (C_{9c}), 166.3 (CO); mass spectrum *m/z* (relative intensity) 493 (M^+, 100). Anal. Calcd for $C_{32}H_{31}NO_4$: C, 77.87; H, 6.33; N, 2.84. Found: C, 78.12; H, 6.21; N, 2.65.

7h: yield 63%; mp 182 °C, colorless prisms (chloroform/*n*-hexane); IR (Nujol) 3375, 1715 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.74 (t, 3 H, *J* = 7.2 Hz), 1.46 (t, 3 H, *J* = 7.1 Hz), 2.09 (ddq, 1 H, *J* = 7.2, 7.2, 13.6 Hz), 2.46 (ddq, 1 H, *J* = 7.2, 7.2, 13.6 Hz), 3.56–3.67 (m, 1 H), 3.90 (s, 3 H), 4.07–4.18 (m, 1 H), 4.49 (q, 2 H, *J* = 7.1 Hz), 4.76 (t, 1 H, *J* = 7.2 Hz), 4.87–4.97 (m, 1 H), 5.22–5.29 (m, 1 H), 6.13–6.30 (m, 1 H), 6.31 (s, 1 H), 7.09 (s, 1 H), 7.11–7.28 (m, 3 H), 7.41–7.48 (m, 2 H), 8.79 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 12.8, 14.4, 32.2, 40.4, 52.1, 56.4, 61.1, 116.2, 117.1, 119.1, 124.6 (q), 126.0, 128.2, 128.5 (q), 128.6 (q), 128.7, 138.0, 138.6 (q), 138.7 (q), 143.2 (q), 144.3 (q), 161.7 (q), 166.4 (q); mass spectrum *m/z* (relative intensity) 405 (M^+, 6), 91 (100). Anal. Calcd for $C_{25}H_{27}NO_4$: C, 74.05; H, 6.71; N, 3.45. Found: C, 73.87; H, 6.53; N, 3.33.

7i: yield 67%; IR (Nujol) 3381, 1690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.76 (t, 1.5 H, *J* = 7.3 Hz), 0.81 (t, 1.5 H, *J* = 7.3 Hz), 1.47 (t, 3 H, *J* = 7.1 Hz), 1.70–1.78 (m, 3 H), 2.10 (ddq, 1 H, *J* = 6.5, 7.3, 22.6 Hz), 2.45 (ddq, 1 H, *J* = 7.3, 7.6, 20.8 Hz), 3.52–3.85 (m, 1 H), 3.94 (s, 1.5 H), 3.95 (s, 1.5 H), 3.99–4.17 (m, 1 H), 4.49 (q, 2 H, *J* = 7.1 Hz), 4.79–4.88 (m, 1 H), 5.31 (m, 0.5 H), 5.64 (m, 0.5 H), 5.73 (m, 0.5 H), 5.86 (m, 0.5 H), 6.10 (s, 1 H), 7.09–7.22 (m, 4 H), 7.37–7.47 (m, 2 H), 8.75 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 12.9, 13.0, 14.4, 18.0, 31.9, 32.2, 34.6, 39.5, 52.1, 52.9, 56.4, 56.5, 61.1, 116.1, 117.9, 119.1, 124.3 (q), 124.5 (q), 125.8, 126.0, 127.7, 128.1, 128.4 (q), 128.5 (q), 128.8, 129.7, 130.8, 130.9 (q), 138.6 (q), 138.7 (q), 138.9 (q), 143.1 (q), 144.3 (q), 144.5 (q), 161.9 (q), 166.4 (q); mass spectrum *m/z* (relative intensity) 419 (M^+, 15), 391 (100). Anal. Calcd for $C_{26}H_{29}NO_4$: C, 74.44; H, 6.97; N, 3.34. Found: C, 74.21; H, 7.22; N, 3.11.

Preparation of Ethyl 1,2-Disubstituted-3-hydroxy-4a,9b-dihydro-4*H*-fluoreno[2,3,4-*ij*]isoquinoline-11-carboxylates 16. The reaction of iminophosphoranes **14** with diphenyl ketene under the same reaction conditions described for the preparation of **9** led to **15** and/or **16**.

15a: yield 56%; mp 217 °C; colorless prisms (toluene); IR (Nujol) 3455, 1690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.36 (t, 3 H, *J* = 7.1 Hz), 2.41 (s, 3 H), 2.56 (s, 3 H), 3.76–3.80 (m, 2 H), 4.34 (q, 2 H, *J* = 7.1 Hz), 5.00–5.15 (m, 1 H), 5.36–5.45 (m, 1 H), 6.42 (s, 1 H), 6.36–6.50 (m, 1 H), 7.11–7.42 (m, 10 H), 8.41 (s, 1 H), 9.06 (br s, 1 H, OH); ^{13}C NMR ($CDCl_3$) δ 14.0, 14.1, 14.9, 32.1, 54.6, 60.4, 115.3 (q), 115.6, 117.7, 125.9, 127.8, 129.3, 129.6 (q), 130.3 (q), 131.5 (q), 132.8 (q), 136.7 (q), 137.2, 144.3 (q), 155.8 (q), 158.6 (q), 165.2 (q); mass spectrum *m/z* (relative intensity) 451 (M^+, 97), 360 (100). Anal. Calcd for $C_{30}H_{29}NO_3$: C, 79.79; H, 6.47; N, 3.10. Found: C, 79.93; H, 6.25; N, 2.87.

Ethyl 1,2-Dimethyl-3-hydroxy-4a,9b-dihydro-4*H*-fluoreno[2,3,4-*ij*]isoquinoline-11-carboxylate (16a): yield 28%; mp 235 °C; colorless prisms (ethyl acetate/*n*-hexane); IR (Nujol) 3403, 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.34 (t, 3 H, *J* = 7.2 Hz, CH_3CH_2), 2.40 (s, 3 H, $ArCH_3$), 2.60 (s, 3 H, $ArCH_3$), 2.85–3.10 (m, 5 H, 2 × 4-H + 4a-H + 2 × 5-H), 4.30 (dq, 1 H, *J* = 7.2, 11.2 Hz, $CH_3CH_aH_b$), 4.37 (dq, 1 H, *J* = 7.2, 11.2 Hz, $CH_3CH_aH_b$), 6.12 (br s, 1 H, OH), 6.81–6.86 (m, 2 H, aromatic), 7.06–7.22 (m, 6 H, aromatic), 7.77 (d, 1 H, *J* = 7.1 Hz, aromatic), 8.47 (s, 1 H, 12-H); ^{13}C NMR ($CDCl_3$) δ 13.4 (CH_3CH_2), 14.3 ($ArCH_3$) 14.7 ($ArCH_3$), 21.8 (C_4), 36.3 (C_5), 49.9 (C_{4a}), 61.1 (CH_3CH_2), 62.0 (C_{9b}), 113.6 (C_3), 118.5 (C_{12}), 123.6, 126.0, 126.3, 127.1, 127.2 (q), 128.0, 128.2, 129.2, 130.3 (q), 131.7 (q), 139.6 (q), 142.5 (q), 144.3 (q), 148.2 (q), 149.3 (q), 152.2 (q), 158.8 (C_{9c}), 166.9 (CO); mass spectrum *m/z* (relative intensity) 449 (M^+, 100). Anal. Calcd for $C_{30}H_{27}NO_3$: C, 80.15; H, 6.05; N, 3.11. Found: C, 79.93; H, 5.90; N, 3.31.

Ethyl 1,2-Dichloro-3-hydroxy-4a,9b-dihydro-4*H*-fluoreno[2,3,4-*ij*]isoquinoline-11-carboxylate (16b): yield 45%; mp 199–200 °C; colorless prisms (ethyl acetate/*n*-hexane); IR (Nujol) 3352, 1721 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.36 (t, 3 H, *J* = 7.1 Hz, CH_3CH_2), 2.56 (dd, 1 H, *J* = 10.5, 14.7 Hz, 5-H_a), 2.94 (dd, 1 H, *J* = 1.6, 15.6 Hz, 4-H_e), 3.01 (dd, 1 H, *J* = 2.3, 14.7 Hz, 5-H_e), 3.16 (dddd, 1 H, *J* = 1.6, 2.3, 4.4, 10.5 Hz, 4$_a$-H), 3.25 (dd, 1 H, *J* = 4.4, 15.6 Hz, 4-H_a), 4.33 (dq, 1 H, *J* = 7.1, 11.0 Hz, $CH_3CH_aH_b$), 4.41 (dq, 1 H, *J* = 7.1, 11.0 Hz, $CH_3CH_aH_b$), 6.61–6.81 (m, 3 H, aromatic + OH), 7.03–7.30 (m, 6 H, aromatic), 7.78 (d, 1 H, *J* = 7.3 Hz, aromatic), 8.61 (s, 1 H, 12-H); ^{13}C NMR ($CDCl_3$) δ 14.3 (CH_3CH_2), 22.3 (C_4), 36.2 (C_5), 49.7 (C_{4a}), 61.5 (CH_3CH_2), 62.1 (C_{9b}), 118.2, 118.5 (q), 123.8, 126.2, 126.5, 127.1 (q), 127.4, 128.1, 128.2, 128.3 (q), 129.0 (q), 129.1, 141.6 (q), 142.4 (q), 147.6 (q), 148.7 (q), 148.9 (q), 160.2 (C_{9c}), 165.8 (CO), one quaternary carbon atom was not observed; mass spectrum *m/z* (relative intensity) 493 (M + 4, 5), 491 (M + 2, 25), 489 (M^+, 35), 77 (100). Anal. Calcd for $C_{28}H_{21}Cl_2NO_3$: C, 68.58; H, 4.32; N, 2.86. Found: C, 68.33; H, 4.17; N, 2.99.

Ethyl 5-(Benzyloxy)-1-(diphenylmethyl)-6-methoxyisoquinoline-3-carboxylate (18). To a solution of iminophosphorane **17** (1.76 g, 3 mmol) in 35 mL of dry toluene was added diphenyl ketene (0.53 g, 3 mmol). The reaction mixture was stirred at room temperature for 1 h and then was heated in a sealed tube at 160 °C for 16 h. Workup similar to that previously described for the preparation of **7** led to **18**: yield 67%; mp 165–166 °C; colorless prisms (chloroform/*n*-hexane); IR (Nujol) 1727, 1226 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.37 (t, 3 H, *J* = 7.2 Hz), 3.92 (s, 3 H), 4.36 (q, 2 H, *J* = 7.2 Hz), 5.16 (s, 2 H), 6.32 (s, 1 H), 7.12–7.51 (m, 16 H), 7.97 (d, 1 H, *J* = 9.3 Hz), 8.67 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.2, 55.7, 56.4, 61.1, 75.7, 116.9, 117.1, 122.4, 124.0

(q), 126.5, 128.2, 128.3, 128.5, 129.6, 132.9 (q), 137.1 (q), 140.7 (q), 141.9 (q), 142.5 (q), 151.3 (q), 161.0 (q), 166.0 (q), one aromatic carbon atom was not observed; mass spectrum m/z (relative intensity) 503 (M^+, 36), 91 (100). Anal. Calcd for $C_{33}H_{29}NO_4$: C, 78.71; H, 5.80; N, 2.78. Found: C, 78.52; H, 6.13; N, 2.61.

Ethyl 1-(Diphenylmethyl)-5-hydroxy-6-methoxyisoquinoline-3-carboxylate (19). To a solution of isoquinoline 18 (1.51 g, 3 mmol) in 100 mL of ethanol was added 10% Pd on charcoal (0.25 g), and the reaction mixture was stirred at room temperature under hydrogen at 2 atm for 2 h. Then, the reaction mixture was filtered, and the filtrate was concentrated to dryness under reduced pressure. The residual material was recrystallized from chloroform/*n*-hexane (1:1) to give 19: yield 87%; mp 179–181 °C; colorless prisms; IR (Nujol) 3347, 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.38 (t, 3 H, J = 7.1 Hz), 3.82 (s, 3 H), 4.39 (q, 2 H, J = 7.1 Hz), 6.31 (s, 1 H), 6.51 (s, 1 H), 7.14–7.38 (m, 11 H), 7.71 (d, 1 H, J = 9.2 Hz), 8.87 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.3, 55.7, 56.5, 61.2, 115.1, 116.9, 117.8, 123.8 (q), 126.4 (q), 126.9 (q), 128.1, 129.6, 139.7 (q), 140.5 (q), 142.5 (q), 144.3 (q), 160.9 (q), 166.3 (q); mas spectrum m/z (relative intensity) 413 (M^+, 100). Anal. Calcd for $C_{26}H_{23}NO_4$: C, 75.53; H, 5.61; N, 3.39. Found: C, 75.41; H, 5.84; N, 3.18.

Ethyl 5-(Crotonyloxy)-1-(diphenylmethyl)-6-methylisoquinoline-3-carboxylate (20). The reaction of the isoquinoline 19 with crotonyl bromide under the same conditions described for the preparation of 2 and 12 led to 20: yield 67%; mp 114–115 °C; colorless prisms (chloroform/*n*-hexane); IR (Nujol) 1728, 1235 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.39 (t, 3 H, J = 7.0 Hz), 1.70 (d, 3 H, J = 3.7 Hz), 3.90 (s, 3 H), 4.40 (q, 2 H, J = 7.0 Hz), 4.58 (d, 2 H, J = 4.3 Hz), 5.70–5.85 (m, 2 H), 6.32 (s, 1 H), 7.13–7.40 (m, 11 H), 7.97 (d, 1 H, J = 9.3 Hz), 8.72 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.2, 17.8, 55.6, 56.3, 61.1, 74.5, 116.9, 117.1, 122.1, 124.0 (q), 126.4, 126.6, 128.1, 129.5, 131.2, 133.1 (q), 140.6 (q), 142.0 (q), 142.5 (q), 151.3 (q), 160.9 (q), 166.2 (q); mass spectrum m/z (relative intensity) 467 (M^+, 100). Anal. Calcd for $C_{30}H_{29}NO_4$: C, 77.06; H, 6.25; N, 2.99. Found: C, 76.81; H, 6.49; N, 3.22.

When a solution of compound 20 in dry toluene was heated at 160 °C for 16 h, compound 7b (35%) was obtained.

Reaction of Iminophosphorane 21 with Diphenyl Ketene. The reaction of iminophosphorane 21 with diphenyl ketene under the same conditions described for the preparation of 7 and 9 led to 7j and 9j.

7j: yield 22%; mp 117 °C; colorless prisms (ether); IR (Nujol) 1737, 1237 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.36 (t, 3 H, J = 7.1 Hz), 3.80–3.85 (m, 2 H), 3.95 (s, 3 H), 4.33 (q, 2 H, J = 7.1 Hz), 4.94–5.03 (m, 1 H), 5.15 (s, 2 H), 5.36–5.42 (m, 1 H), 6.26–6.45 (m, 1 H), 6.42 (s, 1 H), 7.14–7.54 (m, 16 H), 8.72 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.2, 40.3, 55.9, 56.4, 60.9, 75.7, 116.6, 117.5, 121.4, 124.7 (q), 126.2, 127.9, 128.2, 128.5, 128.6, 129.9, 132.9 (q), 134.7 (q), 137.1 (q), 138.0, 139.8 (q), 140.6 (q), 144.1 (q), 150.3 (q), 160.2 (q), 166.0 (q); mass spectrum m/z (relative intensity) 543 (M^+, 10), 91 (100). Anal. Calcd for $C_{36}H_{33}NO_4$: C, 79.53; H, 6.12; N, 2.58. Found: 79.79; H, 5.92; N, 2.84.

Ethyl 1-(Benzyloxy)-2-methoxy-9b-phenyl-4a,9b-dihydro-4*H*-fluoreno[2,3,4-*ij*]isoquinoline-11-carboxylate (9j): yield 32%; mp 150–152 °C; colorless crystals (ether); IR (Nujol) 1738, 1226 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 (t, 3 H, J = 7.1 Hz, CH_3CH_2), 2.62 (dd, 1 H, J = 10.3, 14.8 Hz, 5-H_a), 2.97 (dd, 1 H, J = 1.3, 15.6 Hz, 4-H_e), 3.02 (dd, 1 H, J = 2.6, 14.8 Hz, 5-H_e), 3.17 (dddd, 1 H, J = 1.3, 2.6, 5.0, 10.3 Hz, 4$_a$-H), 3.21 (dd, 1 H, J = 5.0, 15.6 Hz, 4-H_a), 4.02 (s, 3 H, CH_3O), 4.27 (dq, 1 H, J = 7.1, 11.0 Hz, $CH_3CH_aH_b$), 4.35 (dq, 1 H, J = 7.1, 11.0 Hz, $CH_3CH_aH_b$), 5.15 (s, 2 H, $PhCH_2O$), 6.86–6.91 (m, 3 H, aromatic), 7.09–7.42 (m, 9 H, aromatic), 7.50–7.56 (m, 2 H, aromatic), 7.75–7.80 (m, 1 H, aromatic), 8.55 (s, 1 H, 12-H); ^{13}C NMR ($CDCl_3$) δ 14.2 (CH_3CH_2), 28.8 (C_4), 35.8 (C_5), 50.8 (C_{4a}), 56.5 (CH_3O), 61.0 (CH_3CH_2), 62.2 (C_{9b}), 75.8 ($PhCH_2O$), 115.8 (C_3), 116.0 (C_{12}), 122.6 (q), 123.6, 126.1, 126.4, 127.2, 128.0, 128.2, 128.3, 128.4, 128.5, 129.2, 132.1 (q), 133.3 (q), 137.3 (q), 139.7 (q), 142.4 (q), 142.6 (q), 148.1 (q), 148.8 (q), 151.6 (q), 160.1 (C_{9c}), 166.1 (CO); mass spectrum m/z (relative intensity) 541 (M^+, 15), 91 (100). Anal. Calcd for $C_{36}H_{31}NO_4$: C, 79.83; H, 5.77; N, 2.58. Found: C, 80.10; H, 5.51; N, 2.82.

Acknowledgment. We are indebted to Dirección General de Investigación Científica y Técnica for financial support, Project Number PB89-0436, and the reviewers for valuable comments.

Registry No. 1, 148-53-8; **2b**, 133495-63-3; **2c**, 133495-64-4; **2d**, 110124-13-5; **2e**, 92736-73-7; **3b**, 133495-67-7; **3c**, 133495-68-8; **3d**, 133495-69-9; **3e**, 133495-70-2; **4a**, 133495-73-5; **4b**, 133495-74-6; **4c**, 133495-75-7; **4d**, 133495-76-8; **4e**, 133495-77-9; **7a**, 129199-76-4; **7b**, 133495-80-4; **7d**, 129199-78-6; **7e**, 133495-82-6; **7f**, 133495-84-8; **7g**, 133495-86-0; **7h**, 133495-88-2; *cis*-**7i**, 133495-89-3; *trans*-**7i**, 133495-90-6; **7j**, 133522-74-4; **9a**, 129199-79-7; **9b**, 129199-80-0; **9c**, 133495-81-5; **9e**, 133495-83-7; **9f**, 133495-85-9; **9g**, 133495-87-1; **9h**, 133495-98-4; **12a**, 133495-65-5; **12a** hydroxy aldehyde, 58380-40-8; **12b**, 133495-66-6; **12b** hydroxy aldehyde, 16861-22-6; **13a**, 133495-71-3; **13b**, 133495-72-4; **14a**, 133495-78-0; **14b**, 133495-79-1; **15a**, 133495-91-7; **16a**, 133495-92-8; **16b**, 133495-93-9; **17**, 133495-94-0; **18**, 133495-95-1; **19**, 133522-73-3; **20**, 133495-96-2; **21**, 133495-97-3; (*E*)-$BrCH_2CH{=}CHCH_3$, 29576-14-5; (*E*)-$BrCH_2CH{=}CHC_6H_5$, 26146-77-0; $BrCH_2C(CH_3){=}CH_2$, 1458-98-6; $BrCH_2CH{=}C(CH_3)_2$, 870-63-3; $EtOOCCH_2N_3$, 637-81-0; $(C_6H_5)_2C{=}C{=}O$, 525-06-4; $(4\text{-}CH_3CoH_4)_2C{=}C{=}O$, 40195-52-6; $C_6H_5(C_2H_5)C{=}C{=}O$, 20452-67-9.

Supplementary Material Available: Crystal structure data for **9a** (7 pages). Ordering information is given on any current masthead page.