Aza-Wittig Reaction of *N*-Vinylic Phosphazenes with Carbonyl Compounds. Azadiene-Mediated Synthesis of Isoquinolines and 5,6-Dihydro-2*H*-1,3-oxazines

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N-Vinylic phosphazenes **4** are obtained by reaction of phosphorus ylide **5** and nitriles **6**. Aza-Wittig reaction of phosphazenes **4** with aldehydes leads to the formation of 2-azadienes **1**, which are easily converted into isoquinolines **2**. Reaction of conjugated phosphazenes **4** with ethyl glyoxalate affords 5,6-dihydro-2*H*-1,3-oxazines **9** in a regio- and stereoselective fashion, while heterodienes **1** react with ethyl glyoxalate and diethyl ketomalonate giving 1,3-oxazines **11** and **12**.

Introduction

Azadienes have been widely used as synthons in the building of nitrogen six-membered rings in a highly regio- and stereospecific way by using hetero-Diels−Alder processes, and in the last decade some new methods of generating 2-azadienes have been found that have increased the scope of this approach.[1] Likewise, phosphazenes[2] represent an important class of compounds and have attracted a great deal of attention in recent years because of their broad range of applications, showing that the use of phosphazenes represent an effective strategy for the construction of carbon−nitrogen double bonds.[3] Furthermore, the utility of *N*-vinylic phosphazenes[4] has been recently demonstrated in the synthesis of functionalized imine compounds such as 2-azadienes[5] and as key intermediates in the preparation of heterocycles such as pyridine derivatives,[5a,d,6] polycyclic compounds,[4,7] and benzodiazepines[8] as well as in elegant routes toward both the preparation of biologically active natural products[9a] and the construction of the framework of pharmacologically active alkaloids.[9b,c]

Elsewhere, we have used the aza-Wittig reaction of *N*-vinylic phosphazenes with carbonyl compounds, leading to a very efficient method for the preparation of 2-azadienes substituted with a phosphine oxide group in the 4-position[5d] and derived from α-[5b,c] and *β*-amino acids.[5a] Following on from our previous studies on the reactivity and the synthetic utility of phosphazenes[2] and azadienes,[5] here we aim to explore a new and effective strategy for the preparation of electronically neutral 2-azadienes **1** as well as their synthetic utility in the preparation of isoquinolines **2** and 5,6-dihydro-2*H*-1,3-oxazines **3**. Retrosynthetically, we envisaged the preparation of azadienes **1** by aza-Wittig reaction of *N*-vinylic phosphazenes **4**, obtained from the reaction between phosphorus ylide **5** and nitriles **6**; electrocyclic ring closure of azadienes **1** ($R^1 = C_6H_5$) provided isoquinolines **2**, while hetero-Diels−Alder reaction of azadienes **1** with carbonyl compounds led to the formation of oxazines **3** (Scheme 1).

Results and Discussion

The synthesis of conjugated phosphazenes **4** was accomplished very easily, with a high yield, by the reaction of commercially available aryl and heterocyclic nitriles **6** and phosphorus ylide **5** in benzene. This strategy had been previously used in the preparation of functionalized phosphazenes by reaction of phosphorus ylides[10] and simple phosphazenes[11] with aryl nitriles. Crystalline compounds **4** were characterized on the basis of their spectroscopic data. Thus, the ^{31}P NMR spectrum for **4a** showed an absorption at δ_P 2.51 ppm, and in the

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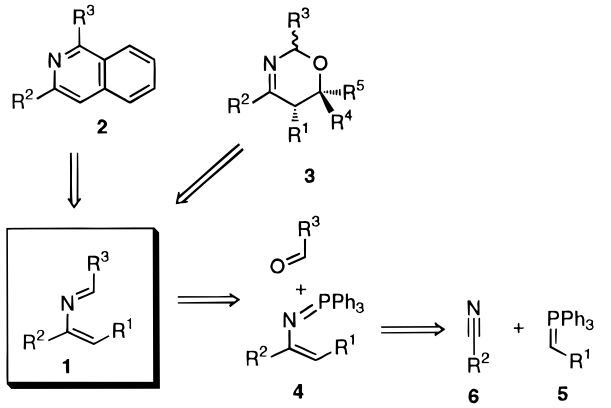
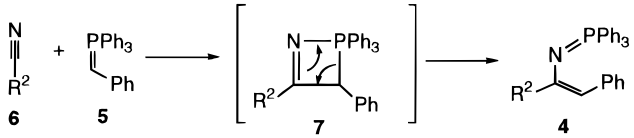
Scheme 1. General Strategy for Formation and Synthetic Use of 2-Azadienes

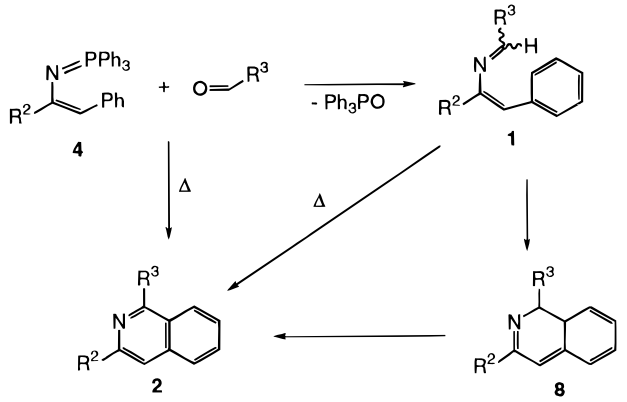


Scheme 2. Azadiene 1 Formation through Aza-Wittig Reaction



compound	**4a**	**4b**	**4c**	**4d**
R^2	2-Furyl	2-Thienyl	Phenyl[10a]	3-Pyridyl

Scheme 3. Phosphazenes 4 Formation through Reaction of Phosphorane 5 and Nitriles 6



^{1}H NMR spectrum of **4a** the vinylic proton resonated at δ_H 6.15 ppm as a well-resolved doublet with the long-range coupling constant of $^4J_{PH} = 3.7$ Hz, while in the ^{13}C NMR spectrum of **4a** the olefinic carbon in β position to the nitrogen atom gave a doublet at δ_C 111.0 ppm with a coupling constant of $^3J_{PC} = 19$ Hz. Formation of conjugated phosphazenes **4** can be explained through [2 + 2] cycloaddition[10a,11,12] followed by ring opening of the unstable cyclic pentavalent phosphorus compounds **7** (Scheme 2).

Aza-Wittig reaction of *N*-vinylic phosphazene **4a** containing a 2-furyl group as the substituent in the 3 position, with heteroaromatic and aromatic aldehydes in refluxing $CHCl_3$, gave high yields of electronically neutral azadienes **1aa**−**1ac** (Scheme 3, Table 1, entries 1−3). These compounds **1** were characterized on the basis of their spectroscopic data and mass spectrometry, which indicated that only the *E*,*Z*-isomers were obtained. For instance, the olefinic proton of **1ab** gave ^{1}H resonance at δ 6.63 ppm as a singlet, while the iminic proton showed absorption at δ 8.50 ppm also as a singlet. NOE difference experiments were combined with the information derived from the ^{1}H NMR spectra to confirm the stereochemistry of azadienes **1aa**−**1ac**. At room temperature in $CDCl_3$ the selective saturation of the singlet at 8.50 ppm of compound **1ab** afforded positive NOE over the furan proton and an absence of interaction with the olefinic proton (Figure 1). Therefore, this NOE observation was consistent with the *E* configuration around the carbon−nitrogen double bond (C=N), with a *Z* configuration around the carbon−carbon double bond (C=C) of azadiene **1ab** and supports an s-trans conformation for the azadiene backbone.[1g] Different behavior was observed, however, when phosphazenes **4b**−**d** reacted with aldehydes leading to the formation of azadienes **1** obtained as a mixture of *E*,*Z*- and *Z*,*Z*-isomers (Table 1, entries 4−16).

In order to test the synthetic usefulness of the new azadienes **1** as key intermediates in organic synthesis and especially in the preparation of new nitrogen-containing heterocycles, the electrocyclic ring closure of azadienes **1** was explored. Thus, heating azadienes **1**, not only the *E*,*Z*-isomers but also mixtures of *Z*,*Z*- and *E*,*Z*- isomers, in refluxing xylene afforded isoquinolines **2** in very high yields (Table 1, entries 17−20). The formation of heterocycles **2** (Scheme 3) could be explained *via* 1,6-electrocyclic ring-closure of azadienes **1** followed by dehydrogenation under the reaction conditions of the nonisolable annelated compound **8**. Several examples of synthesis of heterocyclic compounds by means of tandem aza-Wittig/electrocyclic ring-closure of conjugated phosphazenes containing an ethoxycarbonyl group have been reported in recent years,[3a] and this strategy has even been successfully utilized in the synthesis of β-carboline[13a] and azafluoranthene alkaloids.[13b] However, in our case the mild reaction conditions used allowed us to stop the aza-Wittig reaction of phosphazenes and aldehydes in the formation of electronically neutral azadienes **1**. On the other hand, from a preparative point of view, it is noteworthy that isoquinolines **2** can alternatively be obtained in a "one-pot" procedure, when phosphazenes **1** are directly heated in refluxing xylene with aldehydes.

Aza-Wittig reaction of phosphazenes **4** and aldehydes was extended, and the reaction with ethyl glyoxalate was also explored. Surprisingly, when ethyl glyoxalate was added to compounds **4** at room temperature, formation of the expected azadienes **10** was not observed, and the six-membered heterocycle **9** was isolated instead (Scheme 4, Table 2, entries 1−3) in a regio- and stereoselective fashion. 1,3-Oxazines **9** proved to be single stereoisomers and were characterized on the basis of their spectroscopic data and mass spectrometry. For instance, mass spectrometry of **9a** showed the molecular ion peak (*m*/*z* 371, 5). Vicinal H-5 and H-6 coupling constants of compounds **9** in the range of 3.0−3.5 Hz suggested that both proton atoms were relatively *cis*,[14] while the absence of coupling between H-5 and H-2 could support the *trans* configuration of these protons. NOE difference experiments were used to confirm the stucture of compound **9c**. At room temperature in $CDCl_3$, the selective saturation at 5.36 δ (H-6) afforded significant NOE (13%) over the adjacent

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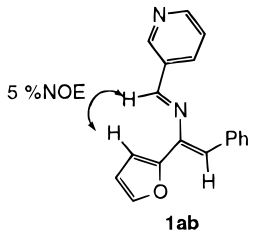
Table 1. 2-Azadienes 1 and Isoquinolines 2 Obtained

entry	starting material	products	R^2	R^3	reaction condns: T (°C)	reaction condns: time (h)	yield[a] (%)	E/Z ratio[b]
1	**4a**	**1aa**	2-furyl	phenyl	80	15	83	100/0
2	**4a**	**1ab**	2-furyl	3-pyridyl	80	17	95	100/0
3	**4a**	**1ac**	2-furyl	2-pyrrolyl	80	136	65	100/0
4	**4b**	**1ba**	2-thienyl	phenyl	80	15	80	50/50
5	**4b**	**1bb**	2-thienyl	3-pyridyl	80	17	98	100/0
6	**4b**	**1bc**	2-thienyl	3-indolyl	80	192	60	50/50
7	**4b**	**1bd**	2-thienyl	2-thienyl	80	40	70	40/60
8	**4c**	**1ca**	phenyl	phenyl	80	24	95	40/60
9	**4c**	**1cb**	phenyl	3-pyridyl	80	15	70	50/50
10	**4c**	**1cc**	phenyl	5-Me-2-furyl	80	144	60	40/60
11	**4c**	**1cd**	phenyl	2-thienyl	80	14	90	40/60
12	**4c**	**1ce**	phenyl	2-pyrrolyl	80	192	77	50/50
13	**4c**	**1cf**	phenyl	3-indolyl	80	136	62	40/60
14	**4d**	**1da**	3-pyridyl	phenyl	80	63	81	80/20
15	**4d**	**1db**	3-pyridyl	3-pyridyl	80	15	99	50/50
16	**4d**	**1dc**	3-pyridyl	5-Me-2-furyl	80	66	90	40/60
17	**1aa**	**2a**	2-furyl	phenyl	140	12	83 (94)[c]	
18	**1bb**	**2b**	2-thienyl	3-pyridyl	140	15	70	
19	**1cb**	**2c**	phenyl	3-pyridyl	140	15	82	
20	**1da**	**2d**	3-pyridyl	phenyl	140	17	78	

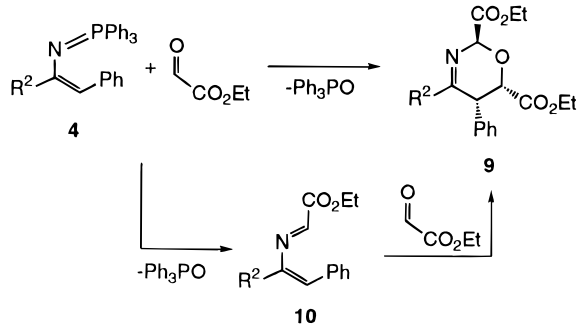
[a] Purified by flash chromatography. [b] E/Z ratio by GC and ^{1}H-NMR assignment. [c] Yield of product **2a** in "one-pot" reaction from **4a** and benzaldehyde.



1ab

Figure 1.

Scheme 4. 2*H*-1,3-Oxazines 9 Formation through Reaction of Phosphazenes 4 and Ethyl Glyoxalate



proton (H-5) and low positive NOE (3%) over the proton at C-2, while an appreciable integral enhancement was seen between the proton at C-2 and one of the aryl protons of the C-5 phenyl group (Figure 2). Both observations were compatible with structure **9**, in which three new stereogenic centers are created.

Formation of azadienes **9** can be explained by aza-Wittig reaction of phosphazenes **4** and the aldehyde to give azadienes **10** followed by [4 + 2] cycloaddition reaction of heterodiene **10** with a second molecule of ethyl glyoxalate (Scheme 4). Interestingly, heterocycles **9** were obtained as single stereoisomers and therefore suggested that the reaction of azadienes **10** with ethyl glyoxalate underwent *exo* selectivity (Figure 2). Although [4 + 2] cycloaddition processes of electronically neutral 2-azadienes with *endo* selectivity have also been reported,[15,16] this behavior may be consistent with our previous result obtained for 2-azadienes derived from β-amino acids[5a] as well as in intramolecular Diels–Alder cyclization processes.[17] Hetero-Diels–Alder reactions represent a great potential for the efficient construction of heterocycles,[18] natural products,[19a,b] and asymmetric synthesis.[19b–e] In our case, the reaction of phosphazenes **4** with ethyl glyoxalate led to a new approach to the formation of 5,6-dihydro-2*H*-1,3-oxazines **9** with controlled stereochemistry of three stereocenters. In this context, it is noteworthy that 2*H*-1,3-oxazines are excellent synthetic intermediates in organic synthesis.[20]

In order to test whether azadienes **10** are intermediates in this process, we tried to stop the reaction at the first step, i.e., in the azadienes **10**, but the isolation of compounds **10** was cumbersome to carry out on a routine basis. However, the presence of the azadiene **10a** in the crude reaction mixture was detected by ^{1}H NMR[21] when phosphazene **4a** was treated with ethyl glyoxalate at 0 °C. The addition of a second equivalent of aldehyde to the reaction mixture used "in situ" without isolation of the azadiene **10a** gave 1,3-oxazine **9a**.

To enhance and generalize the synthetic use of azadienes **1** obtained through aza-Wittig reaction of phosphazenes and aldehydes (Scheme 3) as well as the preparation of 1,3-oxazines, the reaction of heterodienes **1** with ethyl glyoxalate was studied. Thus, cycloaddition of (*Z*,*Z*) azadienes **1** with ethyl glyoxalate was attempted at 120 °C using toluene as solvent, but no reaction took place.

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(21) The reaction was monitored by ^{31}P and ^{1}H NMR showing the disappearance of phosphazene **4** and the formation of azadiene **10**.

Table 2. Compounds 9, 11, 12, and 12′ Obtained

entry	starting material	products	R^2	R^3	reaction condns: *T* (°C)	reaction condns: time (h)	yield[a] (%)	**12**/**12′** ratio[b]
1	**4a**	**9a**	2-furyl		rt	12	72	
2	**4b**	**9b**	2-thienyl		rt	48	60	
3	**4c**	**9c**	phenyl		rt	68	80	
4	**1ab**	**11a**	2-furyl	3-pyridyl	80/rt[c]	144/20[c]	76/78[c]	
5	**1bb**	**11b**	2-thienyl	3-pyridyl	80/rt[c]	144/14[c]	65/70[c]	
6	**1cb**	**11c**	phenyl	3-pyridyl	80/rt[c]	144/18[c]	63/65[c]	
7	**1aa**	**12a**	2-furyl	phenyl	rt[c]	4	78	100/0
8	**1ab**	**12b**	2-furyl	3-pyridyl	rt[c]	1	62	100/0
9	**1ac**	**12c**	2-furyl	2-pyrrolyl	rt[c]	1	58	100/0
10	**1ba**	**12d**	2-thienyl	phenyl	rt[c]	2	78	70/30
11	**1bb**	**12e**	2-thienyl	3-pyridyl	rt[c]	2	43	70/30
12	**1cb**	**12f**	phenyl	3-pyridyl	rt[c]	4	80	100/0
13	**1cc**	**12g**	phenyl	5-Me-2-furyl	rt[c]	17	68	70/30
14	**1cd**	**12h**	phenyl	2-thienyl	rt[c]	96	88	70/30
15	**1cf**	**12i**	phenyl	3-indolyl	rt[c]	48	63	100/0
16	**1db**	**12j**	3-pyridyl	3-pyridyl	rt[c]	96	66	100/0
17	**1dc**	**12k**	3-pyridyl	5-Me-2-furyl	rt[c]	72	55	70/30

[a] Purified by flash chromatography. [b] **12**/**12′** ratio by GC and ^{1}H-NMR assignment. [c] Reaction was performed in the presence of LP−Et_2O.

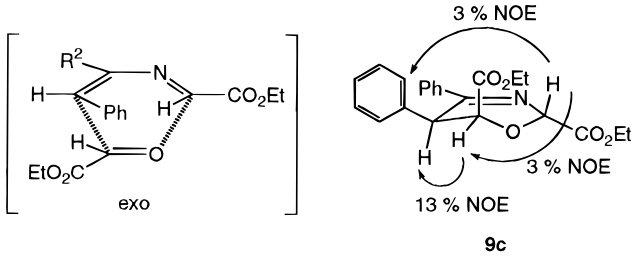
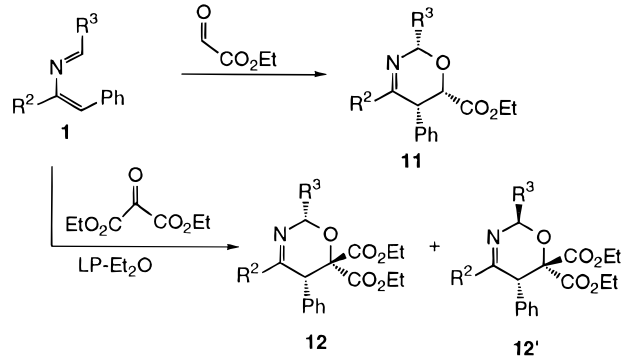


Figure 2.

Scheme 5. Reaction of Azadienes 1 with Ethyl Glyoxalate and Diethyl Ketomalonate



However, 2*H*-1,3-oxazines **11** (Scheme 5) were obtained as single isomers when (*E*,*Z*)-heterodienes **1** reacted with ethyl glyoxalate in refluxing $CHCl_3$ (Table 2, entries 4−6). Even higher yields were obtained when this reaction was performed in the presence of lithium perchlorate in a nonaqueous solvent such as diethyl ether (LP-Et_2O) in a similar way as in processes previously reported.[5a] In contrast to 1,3-oxazines **9**, heterocycle **11** seemed to show a different configuration at C-2, given that the long-range coupling constant ($^5J_{H^2H^5}$) for compounds **11** appeared in the range of 2.0−2.5 Hz, and these results could be consistent with the *cis*-configuration between both protons (H-2 and H-5). ^{1}H NMR NOE experiments confirmed the structure of 1,3-oxazines **11** because a significant integral enhancement was seen between the proton at C-6 and both protons at C-2 and C-5 (Figure 3). Formation of heterocycles **11** can be assumed in terms of a *formal* [4 + 2] cycloaddition but in a different pathway to that observed in the formation

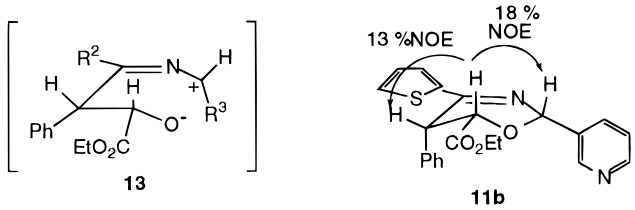


Figure 3.

of compounds **9**. This process occurred with high stereospecificity and can be regarded as a two-step cycloaddition through zwitterionic species **13** (Figure 3); subsequent cyclization can afford oxazines **11** containing the 2,6-*cis*-configuration, which is more stable than the *trans* one. In this context, it is noteworthy that zwitterionic intermediates have been proposed as participants in Lewis acid-catalyzed Diels−Alder processes,[1c,22] while, to the best of our knowledge, these types of intermediates are less frequent in this kind of cycloaddition carried out in the absence of a catalyst. From a preparative point of view, it is noteworty that 1,3-oxazines **11** can also be obtained when a mixture of (*Z*,*Z*)- and (*E*,*Z*)-azadienes **1** is directly heated in $CHCl_3$ with ethyl glyoxalate.

Diethyl ketomalonate also reacted with azadienes **1**. However, in this case the presence of LP−Et_2O as a catalyst was required[23] and afforded a mixture of cycloadducts **12** and **12′** (Scheme 5), with a higher proportion of *cis* isomer **12** than the *trans* isomer **12′** (Table 3, entries 7−17). Formation of 1,3-oxazines **12**/**12′** can also be explained through a two-step cycloaddition process, although now the presence of two substituents in position 6 of compounds **12**/**12′** as opposed to the presence of only one substituent in heterocycles **11** could explain the formation of both isomers **12** and **12′**, but with a higher proportion of the more stable **12**.

We conclude that *N*-vinylic phosphazenes **4**, easily obtained by reaction of phosphorane **5** and nitriles **6**, can be intermediates in the preparation of azadienes **1**, isoquinolines **2**, and 5,6-dihydro-2*H*-1,3-oxazines **9**, in

(22) (a) Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779. (b) Larson, E. R.; Danishefsky, S. *J. Am. Chem. Soc.* **1982**, *104*, 6458.

(23) Cycloaddition of azadienes **4** with diethyl ketomalonate was attempted at 120 °C using toluene as solvent, but no reaction took place and starting materials were recovered.

which three chiral centers are created. Electronically neutral 2-azadienes **1** are suitable 4π systems in [4 + 2] cycloaddition reactions with ethyl glyoxalate and diethyl ketomalonate to yield 1,3-oxazines **11** and **12**. The striking difference between the structure of oxazines **9** and that of **11**, both containing three new stereogenic centers, may be described as a symmetry-allowed one-step mechanism in the first case and a two-step mechanism involving a zwitterionic intermediate in the second. It is worth noting that 2*H*-1,3-oxazines are potentially useful synthons for stereoselective construction of acyclic derivatives.[20]

Experimental Section

General Methods. Melting points were determined with a Büchi SPM-20 apparatus and are uncorrected. Elemental analyses were performed in a LECO CHNS-932 apparatus. IR spectra were obtained as neat oils or solids in KBr on a Nicolet IRFT Magna 550 spectrometer. ^{1}H (250 MHz), and ^{13}C (75 MHz), ^{31}P (120 MHz) spectra and NOE experiments were recorded on a Variant VXR 300 MHz spectrometer in $CDCl_3$ solution with TMS as internal reference for ^{1}H and ^{13}C NMR spectra and phosphoric acid (85%) for ^{31}P NMR spectra. Mass spectra were obtained on a Hewlett-Packard 5971 spectrometer (70 eV). TLC's were developed on Kieselgel 60 F_{254} sheets (Merck); column chromatography was performed on silica gel 60 and on aluminum oxide 90 active, neutral (0.063−0.200 mm). Benzene, xylene, and diethyl ether were distilled from benzophenone ketyl and sodium, while chloroform was distilled from P_2O_5. Standard experimental parameters for the acquisition of NOE difference spectra were used. Phosphazene **4c** was prepared as described in the literature.[10a] Additional spectral data (^{13}C NMR, IR, and MS) for compounds **1aa**−**1dc** and **12a**−**12k** are given in the Supporting Information.

General Procedure for the Preparation of *N*-Vinylic Phosphazenes 4. A solution in benzene (10 mL) and 3.125 mL of 1.6 M solution of methyllithium in ether (5 mmol) was added dropwise to a solution of 2.400 g (5 mmol) of benzyltriphenylphosphonium iodide in benzene (20 mL) cooled to 0 °C under N_2.The clear red solution was heated to reflux for 1 h. A solutionof nitrile **6** (5 mmol) in benzene (5 mL) was added dropwise and stirred as was shown for **4a**−**d**. The mixture was cooled at rt, filtered, and concentrated to afford an oil.

1,1,1,4-Tetraphenyl-3-(2-furyl)-2-aza-1λ^5-phosphabuta-1,3-diene (4a). The general procedure was followed using 0.437 mL (5 mmol) of 2-furonitrile, and the mixture was stirred at rt for 96 h. The crude product was chromatographed on neutral aluminum oxide (AcOEt) to give 1.446 g (65%) of a yellow oil that was dissolved in AcOEt, and the solution deposited yellow crystals (1.335 g, 60%) of **4a**: mp 131−132 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.98−6.78 (m, 21H), 6.15 (d, $^4J_{PH}$ = 3.7 Hz, 1H), 6.04 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.7 (s), 139.8 (s), 139.5 (s), 137.3 (s), 133.0−124.1 (m), 111.0 (d, $^3J_{PC}$ = 19 Hz), 110.7 (s), 105.8 (s); ^{31}P NMR ($CDCl_3$, 120 MHz) δ 2.51; IR (KBr) 1446, 1123; MS (EI) *m*/*z* 445 (M^+, 38). Anal. Calcd for $C_{30}H_{24}NOP$: C, 80.87; H, 5.43; N, 3.15. Found: C, 80.72; H, 5.40; N, 3.16.

1,1,1,4-Tetraphenyl-3-(2-thienyl)-2-aza-1λ^5-phosphabuta-1,3-diene (4b). The general procedure was followed using 0.466 mL (5 mmol) of 2-thiophenecarbonitrile, and the mixture was stirred at rt for 72 h. The crude product was chromatographed on neutral aluminum oxide (AcOEt) to give 1.498 g (65%) of a yellow oil that was dissolved in AcOEt, and the solution deposited yellow crystals (1.383 g, 60%) of **4b**: mp 118−119 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.92−6.48 (m, 23H), 6.02 (d, $^4J_{PH}$ = 2.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 141.1 (s), 139.5 (s), 132.8−123.0 (m), 113.4 (d, $^3J_{PC}$ = 17.5 Hz); ^{31}P NMR ($CDCl_3$, 120 MHz) δ 1.30; IR (KBr) 1386; MS (EI) *m*/*z* 461 (M^+, 10). Anal. Calcd for $C_{30}H_{24}NSP$: C, 78.07; H, 5.25; N, 3.04. Found: C, 78.02; H, 5.27; N, 3.04.

1,1,1,4-Tetraphenyl-3-(3-pyridyl)-2-aza-1λ^5-phosphabuta-1,3-diene (4d). The general procedure was followed using 0.520 g (5 mmol) of 3-cyanopyridine, and the mixture was stirred at reflux for 48 h. The crude product was chromatographed on neutral aluminum oxide (AcOEt) to give 1.938 g (85%) of a yellow oil that was dissolved in AcOEt, and the solution deposited yellow crystals (1.892 g, 83%) of **4d**: mp 134−135 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.34 (d, $^4J_{HH}$ = 1.4 Hz, 1H), 8.14−8.07 (m, 3H), 7.65−7.07 (m, 19H), 6.64−6.59 (m, 1H), 5.69 (d, $^4J_{PH}$ = 3.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 148.5 (s),147.1 (s), 139.6 (s), 134.8 (s), 132.7−128.0 (m), 123.4 (d, $^1J_{PC}$ = 141.5 Hz), 113.5 (d,$^3J_{PC}$ = 19 Hz); ^{31}P NMR ($CDCl_3$, 120 MHz) δ 0.49; IR (KBr) 1394; MS (EI) *m*/*z* 456 (M^+, 81). Anal. Calcd for $C_{31}H_{25}N_2P$: C, 81.55; H, 5.52; N, 6.14. Found: C, 81.52; H, 5.51; N, 6.15.

General Procedure for the Preparation of 2-Azadienes 1. Aldehyde (5 mmol) was added to a 0−10 °C solution of phosphazene **4** (5 mmol) in $CHCl_3$ (15 mL) under N_2, and the mixture was refluxed until TLC indicated the disappearance of phosphazene. Evaporation of solvent under reduced pressure afforded an oil that was chromatographed on neutral aluminum oxide to give the 2-azadienes **1**.

(1*E*,3*Z*)-1,4-Diphenyl-3-(2-furyl)-2-azabuta-1,3-diene (1aa). The general procedure was followed using benzaldehyde (0.505 mL, 5 mmol) and 2.225 g (5 mmol) of phosphazene **4a** (15 h). The crude oil was chromatographed on neutral aluminum oxide (Et_2O/hexane1/3) to give 1.133 g (83%) of **1aa** as a yellow oil (R_f = 0.53): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.94−7.05 (m, 11H), 6.59 (s, 1H), 6.42 (m, 1H), 6.28 (d, $^3J_{HH}$ = 3.3 Hz, 1H). Anal. Calcd for $C_{19}H_{15}NO$: C, 83.48; H, 5,54; N, 5.13. Found: C, 83.16 H, 5.56; N, 5.12.

(1*E*,3*Z*)-3-(2-Furyl)-4-phenyl-1-(3-pyridyl)-2-azabuta-1,3-diene (**1ab**). The general procedure was followed using 3-pyridinecarboxaldehyde (0.472 mL, 5 mmol) and 2.225 g (5 mmol) of phosphazene **4a** (17 h). The crude oil was chromatographed on neutral aluminum oxide (Et_2O/hexane 1/1) to give 1.301 g (95%) of **1ab** as a yellow oil (R_f = 0.28): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.02 (d, $^4J_{HH}$ = 1.9 Hz, 1H), 8.74 (dd, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 1.9 Hz, 1H), 8.50 (s, 1H), 8.3 (m, 1H), 7.60−7.17 (m, 8H), 6.63 (s, 1H), 6.44 (dd, $^3J_{HH}$ = 1.8 Hz, $^3J_{HH}$ = 3.3 Hz, 1H), 6.30 (d, $^3J_{HH}$ = 3.3 Hz). Anal. Calcd for $C_{18}H_{14}N_2O$: C, 78.80; H, 5.15; N, 10.22. Found: C, 78.82; H, 5.13; N, 10.20.

(1*E*,3*Z*)-3-(2-Furyl)-4-phenyl-1-(2-pyrrolyl)-2-azabuta-1,3-diene (1ac). The general procedure was followed using 2-pyrrolecarboxaldehyde (0.475 g, 5 mmol) and 2.225 g (5 mmol) of phosphazene **4a** (136 h). The crude oil was chromatographed on neutral aluminum oxide (Et_2O/hexane 1/1) to give 0.851 g (65%) of **1ac** as a yellow oil (R_f = 0.60): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.04 (s, 1 H), 8.14 (s, 1H), 7.88−6.85 (m, 7H), 6.54 (m, 1H), 6.51 (s, 1H), 6.32 (m, 1H), 6.2 (m, 2H). Anal. Calcd for $C_{17}H_{14}N_2O$: C, 77.83; H, 5.38; N, 10.69. Found: C, 77.81; H, 5.39; N, 10.65.

(3*Z*)-1,4-Diphenyl-3-(2-thienyl)-2-azabuta-1,3-diene (1ba). The general procedure was followed using benzaldehyde (0.505 mL, 5 mmol) and 2.305 g (5 mmol) of phosphazene **4b** (15 h). The crude oil was chromatographed on neutral aluminum oxide (Et_2O/hexane 1/1) to give 1.156 g (80%) of a 50:50 diastereomeric mixture of *E*/*Z* isomers of **1ba** as a yellow oil (R_f = 0.62): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.52 (s, 1H) for the *E*-isomer, 8.30 (s, 1H) for the *Z*-isomer, 8.00−7.06 (m, 21 H), 7.02 (s, 1H) for the *Z*-isomer, 6.55 (s, 1H) for the *E*-isomer. Anal. Calcd for $C_{19}H_{15}NS$: C, 78.86; H, 5.23; N, 4.84. Found: C, 78.89; H, 5.22; N, 4.86.

(1*E*,3*Z*)-4-Phenyl-1-(3-pyridyl)-3-(2-thienyl)-2-azabuta-1,3-diene (1bb). The general procedure was followed using 3-pyridinecarboxaldehyde (0.472 mL, 5 mmol) and 2.305 g (5 mmol) of phosphazene **4b** (17 h). The crude oil was chromatographed on neutral aluminum oxide (Et_2O/hexane 1/1) to give 1.421 g (98%) of **1bb** as a yellow oil (R_f = 0.28): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.99 (d, $^4J_{HH}$ = 1.8 Hz, 1H), 8.72 (dd, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 1.8 Hz, 1H), 8.49 (s, 1H), 8.31−8.28 (m, 2 H), 7.80−7.00 (m, 8H), 6.53 (s, 1H). Anal. Calcd for $C_{18}H_{14}N_2S$: C, 74.46; H, 4.86; N, 9.65. Found: C, 74.50; H, 4.85; N, 9.68.

(3*Z*)-1-(3-Indolyl)-4-phenyl-3-(2-thienyl)-2-azabuta-1,3-diene (1bc). The general procedure was followed using 3-indolecarboxaldehyde (0.726 g, 5 mmol) and 2.305 g (5 mmol) of phosphazene **4b** (192 h). The crude oil was chromatographed on neutral aluminum oxide (Et_2O/hexane 1/1) to give

0.984 g (60%) of a 50:50 diastereomeric mixture of *E*/*Z* isomers of **1bc** as a yellow oil ($R_f = 0.42$): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.34 (s, 1H),10.10 (s, 1H), 8.60−8.54 (m, 2H), 8.52 (s, 1H) for the *E*-isomer, 8.45 (s, 1H) for the *Z*-isomer 7.74−7.00 (m, 24 H), 6.80 (s, 1H) for the *Z*-isomer, 6.42 (s, 1H) for the *E*-isomer. Anal. Calcd for $C_{21}H_{16}N_2S$: C, 76.80; H, 4.91; N, 8.53. Found: C, 76.02; H, 4.90 N, 8.50.

(3*Z*)-1,3-Bis-(2-thienyl)-4-phenyl-2-azabuta-1,3-diene (1bd). The general procedure was followed using 2-thiophenecarboxaldehyde (0.460 mL, 5 mmol) and 2.305 g (5 mmol) of phosphazene **4b** (40 h). The crude oil was chromatographed on neutral aluminum oxide (Et_2O/hexane 1/1) to give 1.032 g (70%) of a 40:60 diastereomeric mixture of *E*/*Z* isomers of **1bd** as a yellow oil ($R_f = 0.59$): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.52 (s, 1H) for the *E*-isomer, 8.24 (s, 1H) for the *Z*-isomer, 7.65−6.96 (m, 23 H), 6.44 (s, 1H) for the *E*-isomer. Anal. Calcd for $C_{17}H_{13}NS_2$: C, 69.13; H, 4.44; N, 4.75. Found: C, 69.08; H, 4.46; N, 4.74.

(3*Z*)-1,3,4-Triphenyl-2-azabuta-1,3-diene (1ca). The general procedure was followed using benzaldehyde (0.505 mL, 5 mmol) and 2.275 g (5 mmol) of phosphazene **4c** (24 h). The crude oil was chromatographed on neutral aluminum oxide (Et_2O/hexane 1/2) to give 1.344 g (95%) of a (40:60) diastereomeric mixture of *E*/*Z* isomers of **1ca** as a yellow oil ($R_f = 0.54$): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (s, 1H) for the *E*-isomer, 8.02 (s, 1H) for the *Z*-isomer 7.87−6.95 (m, 31 H), 6.48 (s, 1H) for the *E*-isomer. Anal. Calcd for $C_{21}H_{17}N$: C, 89.00; H, 6.05; N, 4.95. Found: C, 88.97; H, 6.06; N, 4.97.

(3*Z*)-3,4-Diphenyl-1-(3-pyridyl)-2-azabuta-1,3-diene (1cb). The general procedure was followed using 3-pyridinecarboxaldehyde (0.472 mL, 5 mmol) and 2.275 g (5 mmol) of phosphazene **4c** (15 h). The crude oil was chromatographed on neutral aluminum oxide (Et_2O/hexane 1/1) to give 0.944 g (70%) of a 50:50 diastereomeric mixture of *E*/*Z* isomers of **1cb** as a yellow oil ($R_f = 0.35$): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.96 (d, $^4J_{HH} = 2$ Hz, 1H), 8.85 (d, $^4J_{HH} = 2$ Hz, 1H), 8.70 (dd, $^3J_{HH} = 4.8$ Hz, $^4J_{HH} = 2$ Hz, 1H), 8.62 (dd, $^3J_{HH} = 4.8$ Hz, $^4J_{HH} = 2$ Hz, 1H), 8.30 (s, 1H) for the *E*-isomer, 8.28−8.19 (m, 2H), 7.71−7.04 (m, 23 H), 6.46 (s, 1H) for the *E*-isomer. Anal. Calcd for $C_{20}H_{16}N_2$: C, 84.47; H, 5.68; N, 9.86. Found: C, 84.51; H, 5.66; N, 9.83.

(3*Z*)-3,4-Diphenyl-1-(5-methyl-2-furyl)-2-azabuta-1,3-diene (1cc). The general procedure was followed using 5-methyl-2-furfural (0.497 mL, 5 mmol) and 2.275 g (5 mmol) of phosphazene **4c** (144 h). The crude oil was chromatographed on neutral aluminum oxide (Et_2O/hexane 1/2) to give 0.861 g (60%) of a 40:60 diastereomeric mixture of *E*/*Z* isomers of **1cc** as a yellow oil ($R_f = 0.35$): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (s, 1H) for the *E*-isomer, 7.72 (m, 2H), 7.62 (s, 1H) for the *Z*-isomer, 7.45−6.92 (m, 21 6H), 6.72 (d, $^3J_{HH} = 3.3$Hz, 1H), 6.56 (d, $^3J_{HH} = 3.3$Hz, 1H), 6.32 (s, 1H) for the *E*-isomer, 6.10 (d, $^3J_{HH} = 3.3$Hz, 1H), 6.05 (d, $^3J_{HH} = 3.3$ Hz, 1H), 2.38 (s, 3H), 2.36 (s, 3H). Anal. Calcd for $C_{20}H_{17}NO$: C, 83.59; H, 5.97; N, 4.88. Found: C, 83.50; H, 5.98; N, 4.87.

(3*Z*)-3,4-Diphenyl-1-(2-thienyl)-2-azabuta-1,3-diene (1cd). The general procedure was followed using 2-thiophenecarboxaldehyde (0.460 mL, 5 mmol) and 2.275 g (5 mmol) of phosphazene **4c** (14 h). The crude oil was chromatographed on neutral aluminum oxide (Et_2O/hexane 1/1) to give 1.300 g (90%) of a 40:60 diastereomeric mixture of *E*/*Z* isomers of **1cd** as a yellow oil ($R_f = 0.74$): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (s, 1H) for the *E*-isomer, 7.89 (s, 1H) for the *Z*-isomer, 7.63−6.79 (m, 27 H), 6.20 (s, 1H) for the *E*-isomer. Anal. Calcd for $C_{19}H_{15}NS$: C, 78.86; H, 5.23; N, 4.84. Found: C, 78.66; H, 5.22; N, 4.86.

(3*Z*)-3,4-Diphenyl-1-(2-pyrrolyl)-2-azabuta-1,3-diene (1ce). The general procedure was followed using 2-pyrrolecarboxaldehyde (0.475 g, 5 mmol) and 2.275 g (5 mmol) of phosphazene **4c** (192 h). The crude oil was chromatographed on neutral aluminum oxide (Et_2O/hexane 1/2) to give 0.970 g (77%) of a 50:50 diastereomeric mixture of *E*/*Z* isomers of **1ce** as a yellow oil ($R_f = 0.34$): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.00 (s,1H), 8.09−7.96 (m, 3H), 7.70 (s, 1H) for the *Z*-isomer, 7.60−6.70 (m, 21 H), 6.55 (d, $^3J_{HH} = 3.6$ Hz, 1H), 6.42 (d, $^3J_{HH} = 3.6$ Hz, 1H), 6.36 (s, 1H) for the *E*-isomer, 6.26−6.17 (m, 2H). Anal. Calcd for $C_{19}H_{16}N_2$: C, 83.78; H, 5.93; N, 10.29. Found: C, 83.80; H, 5.92; N, 10.28.

(3*Z*)-3,4-Diphenyl-1-(3-indolyl)-2-azabuta-1,3-diene (1cf). The general procedure was followed using 3-indolecarboxaldehyde (0.726 g, 5 mmol) and 2.275 g (5 mmol) of phosphazene **4c** (136 h). The crude oil was chromatographed on neutral aluminum oxide (Et_2O/hexane 1/2) to give 0.998 g (62%) of a 40:60 diastereomeric mixture of *E*/*Z* isomers of **1cf** as a yellow oil ($R_f = 0.17$): ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.12 (s, 1H), 10.02 (s, 1H), 8.55 (m, 1H), 8.48 (m, 1H), 8.29 (s, 1H) for the *E*-isomer, 8.14 (s, 1H) for the *Z*-isomer, 7.76−6.90 (m, 28 H), 6.84 (s, 1H) for the *Z*-isomer, 6.29 (s, 1H) for the *E*-isomer. Anal. Calcd for $C_{23}H_{18}N_2$: C, 85.68; H, 5.63; N, 8.69. Found: C, 85.65; H, 5.65; N, 8.70.

(3*Z*)-1,4-Diphenyl-3-(3-pyridyl)-2-azabuta-1,3-diene (1da). The general procedure was followed using benzaldehyde (0.505 mL, 5 mmol) and 2.280 g (5 mmol) of phosphazene **4d** (63 h). The crude oil was chromatographed on neutral aluminum oxide (Et_2O/hexane 1/1) to give 1.150 g (81%) of an 80:20 diastereomeric mixture of *E*/*Z* isomers of **1da** as a yellow oil ($R_f = 0.48$): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.56 (m, 2H), 8.25 (s, 1H) for the *E*-isomer, 8.1 (s, 1H) for the *Z*-isomer, 8.09−7.05 (m, 25H), 6.92 (s, 1H) for the *Z*-isomer, 6.42 (s, 1H) for the *E*-isomer. Anal. Calcd for $C_{20}H_{16}N_2$: C, 84.47; H, 5.68; N, 9.86. Found: C, 84.44; H, 5.68; N, 9.88.

(3*Z*)-4-Phenyl-1,3-bis(3-pyridyl)-2-azabuta-1,3-diene (1db). The general procedure was followed using 3-pyridinecarboxaldehyde (0.472 mL, 5 mmol) and 2.280 g (5 mmol) of phosphazene **4d** (15 h). The crude oil was chromatographed on neutral aluminum oxide (AcOEt) to give 1.411 g (99%) of a 50:50 diastereomeric mixture of *E*/*Z* isomers of **1db** as a yellow oil ($R_f = 0.12$): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.97−8.53 (m, 6 H), 8.28 (s, 1H) for the *E*-isomer, 8.09 (s, 1H) for the *Z*-isomer, 7.74−7.00 (m, 19 H), 6.47 (s, 1H) for the *E*-isomer. Anal. Calcd for $C_{19}H_{15}N_3$: C, 79.97; H, 5.30; N, 14.73. Found: C, 79.95; H, 5.31; N, 14.74.

(3*Z*)-1-(5-Methyl-2-furyl)-4-phenyl-3-(3-pyridyl)-2-azabuta-1,3-diene (1dc). The general procedure was followed using 5-methyl-2-furfural (0.497 mL, 5 mmol) and 2.280 g (5 mmol) of phosphazene **4d** (66 h). The crude oil was chromatographed on neutral aluminum oxide (AcOEt) to give 0.518 g (36%) of the *E*-isomer and 0.777 g (54%) of the *Z* -isomer of **1dc** as yellow oils ($R_f = 0.33$ for the *E*-isomer and $R_f = 0.43$ for the *Z* -isomer). Data for *E*-isomer:^{1}H NMR (300 MHz, $CDCl_3$) δ 8.62 (m, 1H), 8.42 (dd, $^3J_{HH} = 1.5$ Hz, $^3J_{HH} = 0.9$ Hz, 1H), 7.81 (s, 1H), 7.8−6.8 (m, 6H), 6.68 (d, $^3J_{HH} = 3.6$ Hz, 1H), 6.25 (s, 1H), 6.05 (m, 1H), 2.3 (s, 3H). Anal. Calcd. for $C_{19}H_{16}N_2O$: C, 79.13; H, 5.60; N, 9.72. Found: C, 79.00; H, 5.58; N, 9.70.

Data for *Z*-isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.65 (dd, $^3J_{HH} = 4.8$ Hz, $^3J_{HH} = 1.8$ Hz, 1H), 8.5 (dd, $^3J_{HH} = 2$ Hz, $^3J_{HH} = 1$ Hz, 1H), 7.7 (s, 1H), 7.6−6.9 (m, 7H), 6.67 (d, $^3J_{HH} = 3.3$ Hz, 1H), 6.12 (m, 1H), 2.4 (s, 3H). Anal. Calcd for $C_{19}H_{16}N_2O$: C, 79.13; H, 5.60; N, 9.72. Found: C, 78.98; H, 5.61; N, 9.70.

General Procedure for the Preparation of Isoquinolines 2. A solution of 2-azadiene (5 mmol) in xylene (20 mL) was warmed at 140 °C under N_2. Evaporation of solvent under reduced pressure afforded an oil that was chromatographed on silica gel to give the isoquinolines **2**.

3-(2-Furyl)-1-phenyl isoquinoline (2a). The general procedure was followed using 1.365 g (5 mmol) of 2-azadiene **1aa**, and the solution was warmed for 12 h. The crude oil was chromatographed on silica gel (hexane/Et_2O 10/1) to give 1.125 g (83%) of **2a** as a yellow solid: mp 149−150 °C (recrystallized from hexane/CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08−7.25 (m, 11 H), 7.18 (d, $^3J_{HH} = 3.3$ Hz, 1H), 6.55 (dd, $^3J_{HH} = 1.8$ Hz, $^3J_{HH} = 3.3$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.7, 154.6, 142.9, 139.5−113.5 (m), 112.1, 108.6; IR (KBr) 1616, 1558, 1484, 1010; M/S (EI) *m*/*z* 271 (M^+, 100). Anal. Calcd for $C_{19}H_{13}NO$: C, 84.11; H, 4.83; N, 5.16. Found: C, 84.01; H, 4.82; N, 5.18.

1-(3-Pyridyl)-3-(2-thienyl)isoquinoline (2b). The general procedure was followed using 1.450 g (5 mmol) of 2-azadiene **1bb**, and the solution was warmed for 15 h. The crude oil was chromatographed on silica gel (hexane/Et_2O 5/1) to give

1.008 g (70%) of **2b** as a white solid: mp 132−133 °C (recrystallized from hexane/CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.99 (d, $^4J_{HH}$ = 1.5 Hz, 1H), 8.70 (dd, $^3J_{HH}$ = 4.7 Hz, $^4J_{HH}$ = 1.5 Hz, 1H), 8.10−7.08 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.4, 151.2, 150.0, 146.2−123.5 (m), 114.4; IR (KBr) 1606, 1557, 1430, 1050; M/S (EI) *m*/*z* 288 (M^+, 83). Anal. Calcd for $C_{18}H_{12}N_2S$: C, 74.97; H, 4.19; N, 9.72. Found: C, 74.79; H, 4.20; N, 9.71

3-Phenyl-1-(3-pyridyl) isoquinoline (2c). The general procedure was followed using 1.420 g (5 mmol) of a 50:50 diastereomeric mixture of *E*/*Z* isomers of 2-azadiene **1cb**, and the solution was warmed for 15 h. The crude oil was chromatographed on silica gel (hexane) to give 1.156 g (82%) of **2c** as a yellow solid: mp 51−52 °C (recrystallized from hexane/CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.07 (d, $^4J_{HH}$ = 2.1Hz, 1H), 8.76 (dd, $^4J_{HH}$ = 2.1 Hz, $^3J_{HH}$ = 4.8 Hz, 1H), 8.22−7.20 (m, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.1, 150.8−123.3 (m), 116.2; IR (KBr) 1622, 1575, 1390, 1031; M/S (EI) *m*/*z* 282 (M^+, 70). Anal. Calcd for $C_{20}H_{14}N_2$: C, 85.08; H, 5.00; N, 9.92. Found: C, 85.28; H, 5.02; N, 9.92.

1-Phenyl-3-(3-pyridyl)isoquinoline (2d). The general procedure was followed using 1.420 g (5 mmol) of an 80:20 diastereomeric mixture of *E*/*Z* isomers of 2-azadiene **1da**, and the solution was warmed for 17 h. The crude oil was chromatographed on silica gel (hexane/Et_2O 1/1) to give 1.100 g (78%) of **2d** as a brown oil (R_f = 0.39 in AcOEt): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.07 (d, $^4J_{HH}$ = 2.2Hz, 1H), 8.55 (dd, $^3J_{HH}$ = 2.4 Hz, $^3J_{HH}$ = 4.7 Hz, 1H), 8.10 (m, 1H), 8.02−7.05 (m, 11 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.0, 152.8, 150.1, 149.8, 140.8−122.5 (m); IR (film) 1680, 1591, 1196, 1124; M/S (EI) *m*/*z* 282 (M^+, 40). Anal. Calcd for $C_{20}H_{14}N_2$: C, 85.08; H, 5.00; N, 9.92. Found: C, 85.28; H, 5.00; N, 9.93.

General Procedure for the Preparation of 9. To a solution of phosphazene **4** (5 mmol) in $CHCl_3$ (20 mL) was added 1.020 g (10 mmol) of freshly distilled ethyl glyoxalate, and the mixture was stirred at rt under N_2. Evaporation of solvent under reduced pressure afforded an oil that was chromatographed on silica gel to give the compounds **9**.

2,6-Bis(ethoxycarbonyl)-4-(2-furyl)-5-phenyl-5,6-dihydro-2*H*-1,3-oxazines (9a). The general procedure was followed using 2.225 g (5 mmol) of phosphazene **4a**, and the mixture was stirred for 12 h. The crude oil was chromatographed on silica gel (AcOEt/hexane 1/1) to give 1.336 g (72%) of **9a** as a brown oil (R_f = 0.30); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36−7.10 (m, 6 H), 6.72 (d, $^3J_{HH}$ = 3.5 Hz, 1H), 6.31 (m,1H), 6.12 (s,1H), 5.33 (d, $^3J_{HH}$ = 3.5 Hz, 1H), 4.32−4.20 (m, 3H), 4.10−3.85 (m, 2H), 1.25 (t, 3H), 1.00 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.2, 158.0,144.8−128.0 (m), 113.9, 111.7, 85.6, 70.4, 61.9, 61.2, 43.1, 14.1, 14.0; IR (film) 1759, 1750, 1632, 1232, 1197; M/S (EI) *m*/*z* 371 (M^+, 5). Anal. Calcd for $C_{20}H_{21}NO_6$: C, 64.68; H, 5.70; N, 3.77. Found: C, 64.58; H, 5.68; N, 3.78.

2,6-Bis(ethoxycarbonyl)-5-phenyl-4-(2-thienyl)-5,6-dihydro-2*H*-1,3-oxazines (9b). The general procedure was followed using 2.305 g (5 mmol) of phosphazene **4b**, and the mixture was stirred for 48 h. The crude oil was chromatographed on silica gel (hexane) to give 1.160 g (60%) of **9b** as a white solid: mp 125−126 °C (recrystallized from hexane/Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28−6.85 (m, 8 H), 6.03 (s,1H), 5.31 (d, $^3J_{HH}$ = 3.4 Hz, 1H), 4.30 (d, $^3J_{HH}$ = 3.4 Hz, 1H), 4.31−4.17 (m, 2H), 4.09−3.85 (m, 2H), 1.26 (t, 3H), 1.03 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.2, 160.1, 135.0, 129.9, 129.1−127.5 (m), 85.5, 70.7, 61.9, 61.2, 44.4, 14.1, 14.0; IR (KBr) 1762, 1631, 1229, 1196, 1111; M/S (EI) *m*/*z* 387 (M^+, 3). Anal. Calcd for $C_{20}H_{21}NO_5S$: C, 62.00; H, 5.46; N, 3.62. Found: C, 62.18; H, 5.47; N, 3.62.

2,6-Bis(ethoxycarbonyl)-4,5-diphenyl-5,6-dihydro-2*H*-1,3-oxazines (9c). The general procedure was followed using 2.275 g (5 mmol) of phosphazene **4c**, and the mixture was stirred for 68 h. The crude oil was chromatographed on silica gel (hexane/AcOEt: 5/1) to give 0.762 g (80%) of **9c** as a white solid: mp 138−140 °C (recrystallized from hexane/Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81−7.20 (m, 10 H), 6.23 (s,1H), 5.36 (d, $^3J_{HH}$ = 3.3 Hz, 1H), 4.43 (d, $^3J_{HH}$ = 3.3 Hz, 1H), 4.39−4.21 (m, 2H), 4.08−3.92 (m, 2H), 1.36 (t, 3H), 1.10 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.5, 164.9, 136.7, 134.9, 131.0−127.3 (m), 86.3, 71.2, 62.0, 61.3, 43.8, 14.3, 14.1; IR (KBr) 1768, 1743, 1216, 1117; M/S (EI) *m*/*z* 381 (M^+, 5). Anal. Calcd for $C_{22}H_{23}NO_5$: C, 69.28; H, 6.08; N, 3.67. Found: C, 69.09; H, 6.07; N, 3.68.

General Procedure A for the Preparation of 11. To a solution of 2-azadiene **1** (5 mmol) in $CHCl_3$ (20 mL) was added 0.510 g (5 mmol) of freshly distilled ethyl glyoxalate, and the mixture was refluxed at 80 °C for 144 h under N_2. Evaporation of solvent under reduced pressure afforded an oil that was chromatographed on silica gel to give the compounds **11**.

General Procedure B for the Preparation of 11. To a solution of 2-azadiene **1** (5 mmol) in Et_2O (10 mL) were added 0.510 g (5 mmol) of freshly distilled ethyl glyoxalate and 5.320 g (0.050 mol) of $LiClO_4$. The mixture was stirred at rt under N_2 and was poured on CH_2Cl_2 (20 mL), washed with a satured solution of $NaHCO_3$, extracted with three 20 mL portions of CH_2Cl_2, and dried ($MgSO_4$). Evaporation of solvent under reduced pressure afforded an oil that was chromatographed on silica gel to give the compounds **11**.

6-(Ethoxycarbonyl)-2-(3-pyridyl)-4-(2-furyl)-5,6-dihydro-2*H*-1,3-oxazines (11a). The general procedure A was followed using 2.225 g (5 mmol) of 2-azadiene **1ab**. The crude oil was chromatographed on silica gel (hexane) to give 1.428 g (76%) of **11a** as a white solid. Following the general procedure B 2.225 g (5 mmol) of 2-azadiene **1ab** was used for 20 h, and the crude oil was chromatographed on silica gel (hexane) to give 1.362 g (78%) of **11a** as a white solid: mp 150−152 °C (recrystallized from hexane/Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.01 (s, 1H), 8.65 (m, 1H), 8.04 (m, 1H), 7.71−7.23 (m, 7 H), 6.78 (d, $^5J_{HH}$ = 2.4 Hz, 1H), 6.39 (m, 2H), 4.92 (d, $^3J_{HH}$ = 3.2 Hz, 1H), 4.38 (dd, $^5J_{HH}$ = 2.4 Hz, $^3J_{HH}$ = 3.2 Hz, 1H), 4.04−3.90 (m, 2H), 1.25 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.9, 154.8−144.8 (m), 135.2−123.2 (m), 113.8, 111.9, 87.3, 75.3, 61.3, 44.2, 14.1; IR (KBr) 1732, 1437, 1188, 1120; M/S (EI) *m*/*z* 376 (M^+, 6). Anal. Calcd for $C_{22}H_{20}N_2O_4$: C, 70.20; H, 5.36; N, 7.44. Found: C, 70.10; H, 5.35; N, 7.43

6-(Ethoxycarbonyl)-2-(3-pyridyl)-4-(2-thienyl)-5,6-dihydro-2*H*-1,3-oxazines (11b). The general procedure A was followed using 2.305 g (5 mmol) of 2-azadiene **1bb**. The crude oil was chromatographed on silica gel (hexane) to give 1.274 g (65%) of **11b** as a white solid. Following the general procedure B 2.305 g (5 mmol) of 2-azadiene **1bb** was used for 14 h, and the crude oil was chromatographed on silica gel (hexane) to give 1.372 g (70%) of **11b** as a white solid: mp 162−163 °C (recrystallized from hexane/Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.97 (d, $^3J_{HH}$ = 2.0 Hz, 1H), 8.58 (dd, $^3J_{HH}$ = 4.9 Hz, $^3J_{HH}$ = 1.7 Hz, 1H), 8.00 (dd, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 2.0 Hz, 1H), 7.35−6.84 (m, 9 H), 6.30 (d, $^5J_{HH}$ = 2.4 Hz, 1H), 4.80 (d, $^3J_{HH}$ = 3.7 Hz, 1H), 4.35 (dd, $^5J_{HH}$ = 2.4 Hz, $^3J_{HH}$ = 3.7 Hz, 1H), 4.06−3.98 (m, 2H), 1.01 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.2, 164.4, 149.6−117.0 (m), 87.8, 75.2, 61.2, 44.8,14.0; IR (KBr) 1754, 1630, 1210; M/S (EI) *m*/*z* 392 (M^+, 5). Anal. Calcd for $C_{22}H_{20}N_2O_3S$: C, 67.33; H, 5.14; N, 7.14. Found: C, 67.30; H, 5.13; N, 7.14.

6-(Ethoxycarbonyl)-2-(3-pyridyl)-4-phenyl-5,6-dihydro-2*H*-1,3-oxazines (11c). The general procedure A was followed using 2.275 g (5 mmol) of a 50:50 diastereomeric mixture of *E*/*Z* isomers of 2-azadiene **1cb**. The crude oil was chromatographed on silica gel (hexane) to give 1.216 g (63%) of **11c** as a white solid. Following the general procedure B 2.275 g (5 mmol) of 2-azadiene **1cb** was used for 18 h, and the crude oil was chromatographed on silica gel (hexane) to give 1.255 g (65%) of **11c** as a white solid: mp 148−149 °C (recrystallized from hexane/Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.11 (s, 1H), 8.69 (d, $^3J_{HH}$ = 4.8 Hz, 1H), 8.17 (d, $^3J_{HH}$ = 6.3 Hz, 1H), 7.92−7.19 (m, 11 H), 6.44 (d, $^5J_{HH}$ = 2.1 Hz, 1H), 4.88 (d, $^3J_{HH}$ = 3.6 Hz, 1H), 4.51 (d, $^5J_{HH}$ = 2.1 Hz, $^3J_{HH}$ = 3.6 Hz, 1H), 4.07−3.99 (m, 2H), 1.14 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.4, 164.8, 150.1−120.3 (m), 88.1, 74.9, 61.0, 44.5,14.1; IR (KBr) 1762, 1631, 1210; M/S (EI) *m*/*z* 386 (M^+, 5).

Anal. Calcd for $C_{24}H_{22}N_2O_3$: C, 74.59; H, 5.74; N, 7.25. Found: C, 74.69; H, 5.73; N, 7.24.

General Procedure for the Preparation of 12. To a solution of 2-azadiene **1** (5 mmol) in Et_2O (10 mL) were added 0.762 mL of diethyl ketomalonate and 5.320 g (0.050 mol) of $LiClO_4$. The mixture was stirred at rt under N_2 and was poured on CH_2Cl_2 (20 mL), washed with a satured solution of

$NaHCO_3$, extracted with three 20 mL portions of CH_2Cl_2, and dried ($MgSO_4$). Evaporation of solvent under reduced pressure afforded an oil that was chromatographed on silica gel to give the compounds **12**.

6,6-Bis(ethoxycarbonyl)-4-(2-furyl)-2,5-diphenyl-5,6-dihydro-2*H*-1,3-oxazines (12a). The general procedure was followed using 1.365 g (5 mmol) of 2-azadiene **1aa** for 4 h. The crude oil was chromatographed on silica gel (hexane/AcOEt 5/1) to give 1.743 g (78%) of **12a** as a white solid: mp 148−149 °C (recrystallized from hexane/CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74−7.13 (m, 11 H), 6.71 (d, $^5J_{HH}$ = 2.7 Hz, 1H), 6.34−6.14 (m, 2H), 4.72 (d, $^5J_{HH}$ = 2.7 Hz,1H), 4.31−4.18 (m, 2H), 4.00−3.78 (m, 2H), 1.24 (t, 3H), 0.95 (t, 3H). Anal. Calcd for $C_{26}H_{25}NO_6$: C, 69.79; H, 5.63; N, 3.13. Found: C, 69.88; H, 5.61; N, 3.13.

6,6-Bis(ethoxycarbonyl)-4-(2-furyl)-5-phenyl-2-(3-pyridyl)-5,6-dihydro-2*H*-1,3-oxazines (12b). The general procedure was followed using 1.370 g (5 mmol) of 2-azadiene **1ab** for 1 h. The crude oil was chromatographed on silica gel (hexane/AcOEt 5/1) to give 1.389 g (62%) of **12b** as a yellow solid: mp 173−174 °C (recrystallized from hexane/CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.99 (d, $^3J_{HH}$ = 1.5 Hz, 1H), 8.59 (dd, $^3J_{HH}$ = 3.3 Hz, $^3J_{HH}$ = 1.5 Hz, 1H), 8.03 (dd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 2.1 Hz, 1H), 7.36−7.13 (m, 7 H), 6.75 (d, $^5J_{HH}$ = 2.7 Hz, 1H), 6.30 (dd, $^3J_{HH}$ = 3.0 Hz, $^3J_{HH}$ = 1.5 Hz, 1H), 6.25 (d, $^3J_{HH}$ = 3.0 Hz, 1H), 4.75 (d, $^5J_{HH}$ = 2.7 Hz, 1H), 4.30 (q, 2H), 3.96−3.82 (m, 2H), 1.25 (t, 3H), 0.96 (t, 3H). Anal. Calcd for $C_{25}H_{24}N_2O_6$: C, 66.96; H, 5.39; N, 6.25. Found: C, 67.00; H, 5.37; N, 6.23.

6,6-Bis(ethoxycarbonyl)-4-(2-furyl)-5-phenyl-2-(2-pyrrolyl)-5,6-dihydro-2*H*-1,3-oxazines (12c). The general procedure was followed using 1.310 g (5 mmol) of 2-azadiene **1ac** for 1 h. The crude oil was chromatographed on silica gel (hexane/AcOEt 5/1) to give 1.264 g (58%) of **12c** as a yellow solid: mp 198−199 °C (recrystallized from hexane/Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.34 (s, 1H), 7.70−7.19 (m, 11 H), 6.80 (d, $^5J_{HH}$ = 2.7 Hz, 1H), 6.49−6.34 (m, 4H), 4.76 (d, $^5J_{HH}$ = 2.7 Hz, 1H), 4.37−4.26 (m, 2H), 4.03−3.88 (m, 2H),1.28 (t, 3H), 1.02 (t, 3H). Anal. Calcd for $C_{24}H_{24}N_2O_6$: C, 66.04; H, 5.54; N, 6.42. Found: C, 66.24 H, 5.53; N, 6.41.

6,6-Bis(ethoxycarbonyl)-4-(2-thienyl)-2,5-diphenyl-5,6-dihydro-2*H*-1,3-oxazines (12d). The general procedure was followed using 1.445 g (5 mmol) of a 50:50 diastereomeric mixture of *E*/*Z* isomers of 2-azadiene **1ba** for 2 h. The crude oil was chromatographed on silica gel (hexane/AcOEt 5/1) to give 1.806 g (78%) of a 70:30 diastereomeric mixture of **12d** and **12d′** as a white solid: mp 66−68 °C (recrystallized from hexane/Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86−6.95(m, 27H), 6.30 (d, $^5J_{HH}$ = 2.4 Hz, 1H) for **12d**, 4.90 (d, $^5J_{HH}$ = 2.4 Hz, 1H) for **12d**, 4.79 (s, 1H) for **12d′**, 4.43−4.36 (m, 2H), 4.11−3.92 (m, 4H), 3.65 (m, 1H), 2.93 (m, 1H), 1.36 (t, 3H), 1.22−1.01 (m, 6H), 0.90 (t, 3H). Anal. Calcd for $C_{26}H_{25}NO_5S$: C, 67.37; H, 5.44; N, 3.02. Found: C, 67.28; H, 5.42; N, 3.01.

6,6-Bis(ethoxycarbonyl)-4-(2-thienyl)-5-phenyl-2-(3-pyridyl)-5,6-dihydro-2*H*-1,3-oxazines (12e). The general procedure was followed using 1.450 g (5 mmol) of 2-azadiene **1bb** for 2 h. The crude oil was chromatographed on silica gel (hexane/AcOEt 5/1) to give 0.998 g (43%) of a 70:30 diastereomeric mixture of **12e** and **12e′** as a white solid: mp 116−118 °C (recrystallized from hexane/Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.01 (s, 1H), 8.84 (s, 1H), 8.60 (d, $^3J_{HH}$ = 3.4 Hz, 1H), 8.48 (d, $^3J_{HH}$ = 3.4 Hz, 1H), 8.05 (d, $^3J_{HH}$ = 7.9 Hz, 1H), 7.84 (d, $^3J_{HH}$ = 7.9 Hz, 1H), 7.37−6.85 (m, 19H), 6.24 (d, $^5J_{HH}$ = 2.6 Hz, 1H) for **12e**, 4.82 (d, $^5J_{HH}$ = 2.6 Hz, 1H) for **12e**, 4.69 (s, 1H) for **12e′**, 4.34−4.24 (m, 2H), 4.03−3.83 (m, 4H), 3.60 (m, 1H), 2.95 (m, 1H), 1.26 (t, 3H), 0.98 (t, 6H), 0.79 (t, 3H). Anal. Calcd for $C_{25}H_{24}N_2O_5S$: C, 64.64; H, 5.21; N, 6.03. Found: C, 64.80; H, 5.23 N, 6.01.

6,6-Bis(ethoxycarbonyl)-4,5-diphenyl-2-(3-pyridyl)-5,6-dihydro-2*H*-1,3-oxazines (12f). The general procedure was followed using 1.420 g (5 mmol) of a 50:50 diastereomeric mixture of *E*/*Z* isomers of 2-azadiene **1cb** for 4 h. The crude oil was chromatographed on silica gel (hexane/AcOEt 5/1) to give 1.832 g (80%) of **12f** as a white solid: mp 105−106 °C (recrystallized from hexane/CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.06 (d, $^3J_{HH}$ = 1.5 Hz, 1H), 8.60 (d, $^3J_{HH}$ = 4.8 Hz, 1H), 8.10 (m, 1H), 7.78−7.09 (m, 11 H), 6.31 (d, $^5J_{HH}$ = 2.4 Hz, 1H), 4.92 (d, $^3J_{HH}$ = 2.4 Hz, 1H), 4.30 (m, 2H), 4.00 (m, 2H), 1.22 (t, 3H), 1.00 (t, 3H). Anal. Calcd for $C_{27}H_{26}N_2O_5$: C, 70.73; H, 5.72; N, 6.11. Found: C, 70.62; H, 5.72; N, 6.13.

6,6-Bis(ethoxycarbonyl)-4,5-diphenyl-2-(5-methyl-2-furyl)-5,6-dihydro-2*H*-1,3-oxazines (12g). The general procedure was followed using 1.435 g (5 mmol) of a 40:60 diastereomeric mixture of *E*/*Z* isomers of 2-azadiene **1cc** for 17 h. The crude oil was chromatographed on silica gel (hexane/AcOEt 10/1) to give 1.567 g (68%) of a 70:30 diastereomeric mixture of **12g** and **12g′** as a white solid: mp 142−144 °C (recrystallized from hexane/Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88−7.18 (m, 20 H), 6.89 (s, 1H) for **12g′**, 6.50 (d, $^3J_{HH}$ = 3.1 Hz, 1H), 6.28 (d, $^5J_{HH}$ = 2.4 Hz, 1H) for **12g**, 6.09 (d, $^3J_{HH}$ = 3.0 Hz, 1H), 6.03 (m, 1H), 5.88 (d, $^3J_{HH}$ = 3.0 Hz, 1H), 4.93 (d, $^5J_{HH}$ = 2.4 Hz, 1H) for **12g**, 4.86 (s, 1H) for **12g′**, 4.40−4.25 (m, 2H), 4.07−3.86 (m, 5H), 3.52−3.46 (m, 1H), 2.37 (s, 3H), 2.32 (s, 3H), 1.30 (t, 3H), 1.05−0.98 (m, 9H). Anal. Calcd for $C_{27}H_{27}NO_6$: C, 70.27; H, 5.90; N, 3.03. Found: C, 70.20; H, 5.88; N, 3.01.

6,6-Bis(ethoxycarbonyl)-4,5-diphenyl-2-(2-thienyl)-5,6-dihydro-2*H*-1,3-oxazines (12h). The general procedure was followed using 1.445 g (5 mmol) of a 40:60 diastereomeric mixture of *E*/*Z* isomers of 2-azadiene **1cd** for 96 h. The crude oil was chromatographed on silica gel (hexane/AcOEt 2/1) to give 1.984 g (88%) of a (70:30) diastereomeric mixture of **12h** and **12h′** as a brown oil (R_f = 0.41): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95−6.95 (m, 27 H), 6.54 (d, $^5J_{HH}$ = 2.4 Hz, 1H) for **12h**, 4.98 (d, $^5J_{HH}$ = 2.4 Hz, 1H) for **12h**, 4.80 (s, 1H) for **12h′**, 4.42−4.80 (m, 2H), 4.03−3.81 (m, 4H), 3.75 (m, 1H), 3.25 (m, 1H), 1.32 (t, 3H), 1.09−0.96 (m, 9H). Anal. Calcd for $C_{25}H_{25}NO_5S$: C, 66.50; H, 5.58; N, 3.10. Found: C, 66.43; H, 5.57; N, 3.12.

6,6-Bis(ethoxycarbonyl)-4,5-diphenyl-2-(3-indolyl)-5,6-dihydro-2*H*-1,3-oxazines (12i). The general procedure was followed using 1.440 g (5 mmol) of a 40:60 diastereomeric mixture of *E*/*Z* isomers of 2-azadiene **1cf** for 48 h. The crude oil was chromatographed on silica gel (hexane/AcOEt 5/1) to give 1.562 g (63%) of **12i** as a white solid: mp 78−80 °C (recrystallized from hexane/Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.08−6.86 (m, 15H), 6.65 (d, $^5J_{HH}$ = 2.7 Hz, 1H), 4.96 (d, $^5J_{HH}$ = 2.7 Hz, 1H), 4.40−4.12 (m, 2H), 4.08−3.86 (m, 2H), 1.97−1.30 (m, 6H). Anal. Calcd for $C_{30}H_{28}N_2O_5$: C, 72.56; H, 5.68; N, 5.64. Found: C, 72.59; H, 5.67; N, 5.63.

6,6-Bis(ethoxycarbonyl)-5-phenyl-2,4-bis(3-pyridyl)-5,6-dihydro-2*H*-1,3-oxazines (12j). The general procedure was followed using 1.425 g (5 mmol) of a 50:50 diastereomeric mixture of *E*/*Z* isomers of 2-azadiene **1db** for 96 h. The crude oil was chromatographed on silica gel (hexane/AcOEt 1/1) to give 1.515 g (66%) of **12j** as a white solid: mp 169−171 °C (recrystallized from hexane/CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.05 (d, $^3J_{HH}$ = 1.5 Hz, 1H), 8.96 (d, $^3J_{HH}$ = 1.5 Hz, 1H), 8.61 (m, 1H), 8.50 (m, 1H), 8.09 (m, 2H), 7.39−7.07 (m, 7 H), 6.30 (d, $^5J_{HH}$ = 2.4 Hz, 1H), 4.85 (d, $^5J_{HH}$ = 2.4 Hz, 1H), 4.30 (m, 2H), 4.00 (m, 2H), 1.25 (t, 3H), 0.99 (t, 3H). Anal. Calcd for $C_{26}H_{25}N_3O_5$: C, 67.96; H, 5.48; N, 9.14. Found: C, 67.90; H, 5.47; N, 9.16.

6,6-Bis(ethoxycarbonyl)-2-(5-methyl-2-furyl)-5-phenyl-4-(3-pyridyl)-5,6-dihydro-2*H*-1,3-oxazines (12k). The general procedure was followed using 1.440 g (5 mmol) of (1*E*,3*Z*)-2-azadiene **1dc** for 72 h. The crude oil was chromatographed on silica gel (hexane/AcOEt 2/1) to give 1.271 g (55%) of a (70:30) diastereomeric mixture of **12k** and **12k′** as a yellow solid: mp 94−96 °C (recrystallized from hexane/Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.06 (s, 1H), 9.00 (s, 1H), 8.60 (d, $^3J_{HH}$ = 4.5 Hz, 1H), 8.56 (d, $^3J_{HH}$ = 4.8 Hz, 1H), 8.13 (d, $^3J_{HH}$ = 7.5 Hz, 1H), 8.10 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 7.41−7.20 (m, 12 H), 6.90 (s, 1H) for **12k′**, 6.50 (d, $^3J_{HH}$ = 3.00 Hz, 1H), 6.26 (d, $^5J_{HH}$ = 2.7 Hz, 1H) for **12k**, 6.07 (d, $^3J_{HH}$ = 3.0 Hz, 1H), 6.05 (d, $^3J_{HH}$ = 3.0 Hz, 1H), 5.89 (m, 1H), 4.85 (d, $^5J_{HH}$ = 2.7 Hz, 1H) for the **12k**, 4.81 (s, 1H) for **12k′**, 4.42−4.85 (m, 2H), 4.07−3.89 (m, 5H), 3.50 (m, 1H), 2.38 (s, 3H), 2.36 (s, 3H), 1.28−1.09 (m, 6H), 1.02−0.81 (m, 6H). Anal. Calcd for $C_{26}H_{26}N_2O_6$: C, 67.52; H, 5.67; N, 6.06. Found: C, 67.47 H, 5.66; N, 6.08.

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Supporting Information Available: Additional spectral data (^{13}C NMR, IR, and MS) for compounds **1aa**−**1dc** and **12a**−**12k** (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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