Preparation of [5 + 6]-, [6 + 6]-, and [6 + 7]-Bicyclic Guanidines from *C,C'*-Bis(iminophosphoranes)

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A one-pot synthesis of [5 + 6]-, [6 + 6]-, and [6 + 7]-rigid bicyclic guanidines (**6**, **8**, **19**, **21**, **23**) based on a bis(iminophosphorane)-mediated annulation strategy is reported. The crystal and molecular structure of the parent [5 + 6]-bicyclic guanidine **8** has been established by X-ray diffraction. The crystallographically independent molecule forms dimers through a centre of symmetry by N–H···N hydrogen bonds. The molecule, and therefore the dimer, is statistically disordered in a 65/35 ratio. A statistical study of N–H···N hydrogen bonds of this kind of dimers has been carried out by using the Cambridge Structural Database.

The cyclic guanidine moiety is found in a variety of naturally occurring compounds such as the potent ion-channel blockers saxitoxin and ptilocaulin, and the polycyclic marine-derived guanidine ptilomycalin A has been reported to exhibit remarkable antitumor, antiviral, and antifungal activities[1]. In addition, certain active secondary metabolites of marine origen are non-traditional, guanidine-based alkaloids in which the guanidino group is most frequently found as of a 2-amino-imidazole ring[2]. On the other hand, cyclic guanidines serve as binding sites for anionic functional groups[3] and in this sense rigid bicyclic guanidines have been utilized as enantioselective and/or substrate-specific oxo anion hosts[4].

The only two methods of general value for the preparation of bicyclic guanidines involve either the introduction of the central guanidine carbon atom by a double cyclization process in an non-cyclic triamine precursor[5] or an intramolecular cyclization of alkenylated monocyclic guanidines by aminomercuration[4].

Continuing our interest in the preparation and synthetic applications of bis(iminophosphoranes)[5], we have reported[6] a one-pot synthesis of [6 + *n*] (*n* = 6, 7, and 8) bicyclic guanidines based on a new method of dihydropyrimido annulation, which involves reaction of *C,C'*-bis(iminophosphoranes)[7] with isocyanates. As a further extension of this methodology, it was decided that the next logical step in the development of this chemistry would be an application to the preparation of [5 + 6]-bicyclic guanidines.

Results

For the [5 + 6] series as the key intermediates the bis(iminophosphoranes) **3** and **5** were chosen. Bis(iminophosphorane) **3** was readily prepared by a three-step sequence. Condensation of the iminophosphorane derived from *o*-azidobenzaldehyde[8] with *o*-azidoaniline afforded the azidoiminophosphorane **1** in a yield of 60%, which was converted into the bis(iminophosphorane) **2** by a Staudinger reaction with triphenylphosphane (80% yield). Reduction with $NaBH_4$ in ethanol provided the bis(iminophosphorane) **3** in 85% yield without affecting the iminophosphorane moieties. In a similar way, coupling of *o*-azidobenzoic acid with *o*-azidoaniline under standard carbodiimide conditions[9] provided the bisazide **4** in 60% yield, which was converted into the bis(iminophosphorane) **5** in 88% yield by reaction with triphenylphosphane in dichloromethane at room temperature (Scheme 1).

Aza Wittig-type reactions of bis(iminophosphorane) **3** with 2 equiv. of aryl isocyanates in dichloromethane at room temperature gave directly the bicyclic guanidines **6**, which were isolated as crystalline solids in 40–60% yields. Similar results were achieved when aryl isothiocyanates instead of aryl isocyanates were used. However, bis(iminophosphorane) **3** reacted with 1 equiv. of aryl isocyanates or isothiocyanates in dichloromethane at 0°C to give the iminophosphorane **7** derived from the benzimidazole ring. Traces of compounds **6** were detected in the reaction mixtures. The ^1H- and ^{13}C-NMR spectra of compounds **6** indicated that the two aryl groups are nonequivalent.

When compounds **6** were pyrolyzed at temperatures slightly higher than their melting points elimination of the corresponding diarylcarbodiimide took place, and the parent tetracyclic guanidine **8** was isolated as a crystalline solid in fair yields. Removal of the exocyclic guanidine moiety from **6** to give **8** could also be achieved by the action of tetrafluoroboric acid although in somewhat lower yields (Scheme 2). An X-ray structure analysis of compound **8** confirmed the proposed structure.

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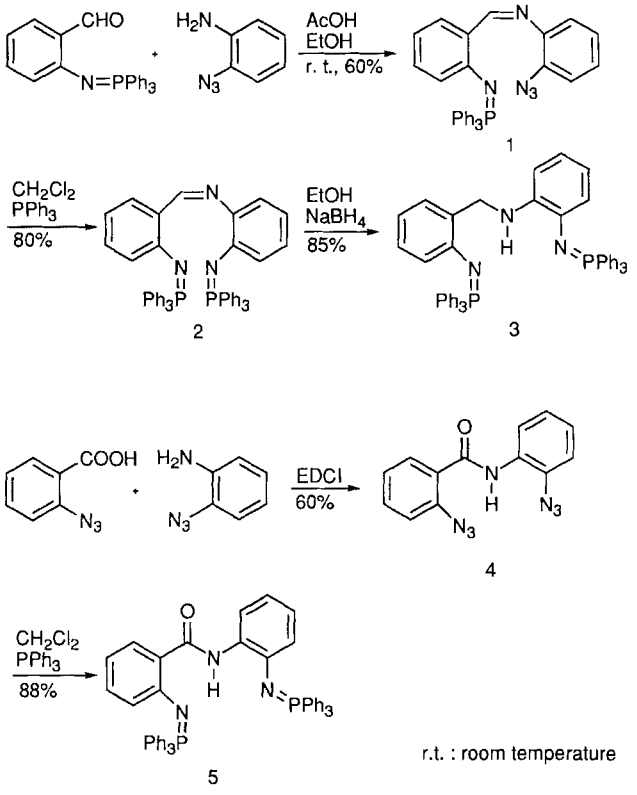
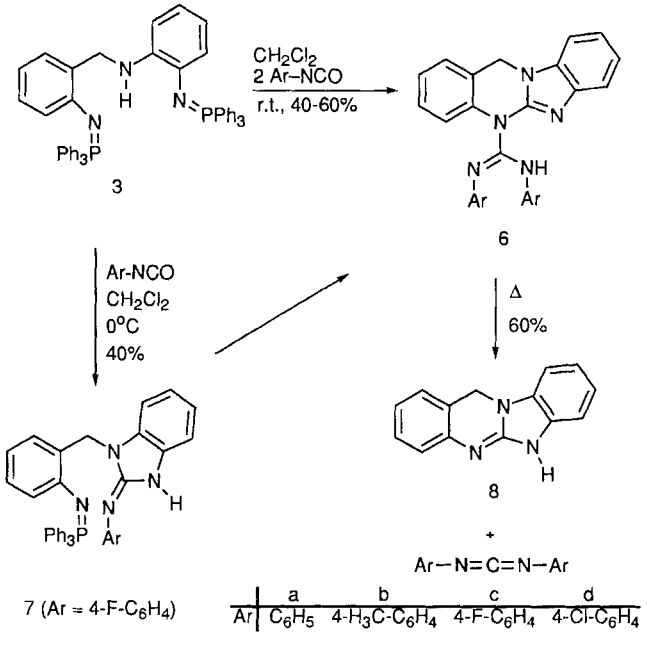
Scheme 1



Scheme 2



The main geometrical parameter of compound **8** corresponding to the most populated disordered positions are compiled in Table 1 according to the numbering scheme shown in Figure 1[10]. The model of disorder implies that the two central rings are interchanged and, in consequence, the N(1)–C(17) bond distances have intermediate values between single and double bonds [1.339(16) and 1.279(8) Å, respectively][11]. The heteroaromatic six-membered ring is significantly non-planar and, despite having a small total puckering amplitude[12], the ring shows a distorted 1,3-diplanar conformation (Table 1 versus the theoretical values: $\phi_2 = 90°$, $\Theta_2 = 67.5°$). The molecule, as a whole, is almost planar, the angles between the least-squares planes of contiguous rings (Figure 1) being $\Pi_1 \dagger \Pi_2 = 1.7(1)°$, $\Pi_2 \dagger \Pi_3 = 1.1(1)°$, and $\Pi_3 \dagger \Pi_4 = 1.3(1)°$.

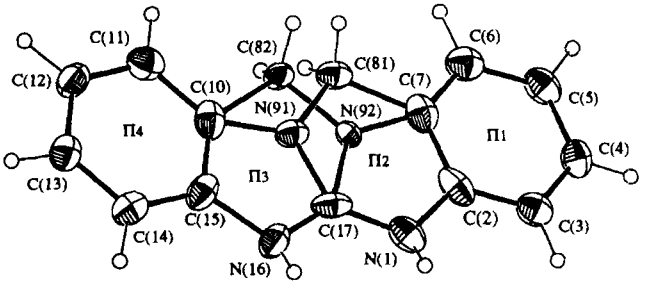


Figure 1. Molecular structure of compound **8** showing the disorder model (ellipsoids 30%)

The crystal structure consists of dimers formed by N–H···N hydrogen bonds through symmetry centers (Table 1, **A**).

The dimers, located parallel to the (1 0 −1) direction (Figure 2a), stack[13] along the *b* axis by unit translation (Figure 2b). The piles of the dimers form sheets parallel to the (1 0 1) direction by C–H···π electronic cloud interactions[13] related by a two-fold screw axis. No directional interactions between sheets have been found. The C–H···π contacts involve atoms in both possible disordered positions (Table 1), and they could be responsible for the disorder in the crystal, stabilizing the two different molecular orientations. There are no voids in the structure as tested by the HOLES[14] program; the total packing coefficient being 0.72.

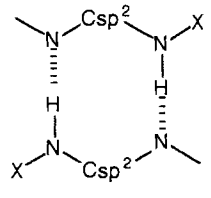
A statistical study of dimer interactions has been performed by using the Cambridge Structural Database[15] (October 1993 release). A skeleton similar to that observed in compound **8** and shown in the scheme was used for matching fragments, with hydrogen atoms in experimental positions. The restrictions imposed were: i) data free of error at a 0.02-Å level, ii) crystallographic *R* factor ≤ 0.075, iii) no metal atoms present, iv) H···N ≤ 2.75 Å, N···N ≤ 3.4 Å, and 120 ≤ N–H···N ≤ 180°. The mean values together with the standard deviation of the sample are shown in Table 2 (only 15 hits are in the 3.20–3.40-Å range). These results are in good agreement with those previously reported[16] for all R–NH_2···Nsp^2 and R,R'NH···Nsp^2 kinds of interactions (Table 2). Almost all of them [176 and 97 for NH_2 (X = H) and NH (X ≠ H) donor groups] correspond to symmetrically related dimers, and the distribution of their geometrical parameters is represented in Figure 3. Their mean values are not significantly different from those of the total set. The ring formed by the dimers seems to be quite favorable for linear interactions, although at the expense of the elongation of the N···N distances (the greater lower end of the range in dimers). In compound **8**, these

Table 1. Selected bond distances, angles, torsion angles, and intermolecular hydrogen bonds [Å, °]. * Due to disorder only the centroids of the six-membered rings are considered

N(1)-C(2)	1.408(3)	N(1)-C(17)	1.332(3)	C(2)-C(7)	1.396(3)
C(7)-C(81)	1.562(5)	C(81)-N(91)	1.444(4)	N(91)-C(10)	1.407(4)
N(91)-C(17)	1.401(3)	C(10)-C(15)	1.396(3)	C(15)-N(16)	1.403(3)
N(16)-C(17)	1.324(3)				
C(2)-N(1)-C(17)	114.8(2)	N(1)-C(2)-C(7)	117.2(2)	C(2)-C(7)-C(81)	129.7(2)
C(7)-C(81)-N(91)	105.7(2)	C(81)-N(91)-C(17)	120.9(2)	C(81)-N(91)-C(10)	121.7(2)
C(10)-N(91)-C(17)	117.3(2)	N(91)-C(10)-C(15)	96.9(2)	C(10)-C(15)-N(16)	113.8(2)
C(15)-N(16)-C(17)	109.1(2)	N(91)-C(17)-N(16)	102.9(2)	N(1)-C(17)-N(16)	125.5(2)
N(1)-C(17)-N(91)	131.6(2)				
C(81)-N(91)-C(17)-N(1)	−1.9(4)	C(7)-C(81)-N(91)-C(17)	3.2(3)	Cremer and Pople Parameters:	
C(2)-C(7)-C(81)-N(91)	−2.6(4)	N(1)-C(2)-C(7)-C(81)	0.2(4)	q_2=0.031(2)Å	q_3=0.009(2)Å
C(17)-N(1)-C(2)-C(7)	1.7(3)	C(2)-N(1)-C(17)-N(91)	−1.0(3)	ϕ_2=103(4)°	θ_2=75(4)°

N-H···N	N-H	N···N	H···N	N-H···N
N(1)-H(101)···N(16)(1-x, 1-y, 1-z)	0.80(4)	2.918(2)	2.12(4)	170(5)
N(16)-H(102)···N(1)(1-x, 1-y, 1-z)	0.73(-)	2.918(2)	2.21(-)	167(-)
C-H···Centroid*	**C-H**	**C···Centr.**	**H···Centr.**	**C-H···Centr.**
C(11)-H(11)···C(2-7)(½-x, ½+y, ½-z)	0.96(3)	3.597(2)	2.89(4)	131(2)
C(81)-H(812)···C(10-82)(½-x, ½+y, ½-z)	1.05(3)	3.860(3)	2.84(3)	162(3)
C(82)-H(821)···C(10-82)(½-x, ½+y, ½-z)	0.94(-)	3.894(5)	3.00(-)	161(-)
C(81)-H(812)···C(10-15)(½-x, ½+y, ½-z)	1.05(3)	3.848(3)	2.94(3)	145(2)
C(82)-H(821)···C(10-15)(½-x, ½+y, ½-z)	0.94(-)	3.824(5)	3.05(-)	141(-)
Centroid···Centroid		**C···Centr.**		
C(1-17)···C(10-82)(1-x, 2-y, 1-z)		3.515(1)		
C(1-17)···C(10-15)(1-x, 2-y, 1-z)		3.891(1)		

A



interactions appear to be linear and stronger than the reported average value as measured by the N···N distance. In the H···N distance plot, the distribution is bimodal with a principal maximum at 2.14 Å and a secondary one at 2.26 Å.

Probably, the conversion **3** → **6** could involve an initial aza Wittig-type reaction between the *o*-amino-substituted iminophosphorane moiety and 1 equiv. of the isocyanate to give the carbodiimide **9** which undergoes cyclization by nucleophilic attack of the secondary amino group on the central carbon atom of the carbodiimide moiety to give **7**. An aza Wittig-type reaction between the iminophosphorane moiety of **7** and the second equivalent of the isocyanate led to **10**, and an intramolecular [2 + 2] cycloaddition between the carbodiimide moiety and the exocyclic C=N bond and subsequent opening of the four-membered ring of 1,4-diazetidine **11** afforded **6**. Strong support for this mechanism was found for the conversion **7** → **6** by the action of 1 equiv of isocyanate under the same reaction conditions. The preferential reactivity of the *o*-amino-substituted iminophosphorane moiety with respect to the *o*-methylene-substituted iminophosphorane in compound **3** in aza Wittig-type reactions with isocyanates was confirmed by model experiments. Thus, iminophosphorane **12** reacted with 1 equivalent of isocyanate in dichloromethane at room temperature to give the benzimidazole derivative **13** via the aza Wittig product carbodiimide, whereas the isomeric iminophosphorane **14** afforded the carbamoyl derivative **15** under the same reaction conditions (Scheme 3).

The incorporation of a carbonyl group into the bond connecting the two aromatic rings has also been examined. At first, aza Wittig-type reactions of bis(iminophosphorane) **5** with isocyanates may take place by two different ways, i.e. either via the *o*-amino-substituted iminophosphorane moiety to give a benzimidazole derivative as it has been mentioned before for bis(iminophosphorane) **3** or with participation of the *o*-acyl-substituted iminophosphorane functionality to give a 4*H*-3,1-benzoxazin-4-imine derivative in analogy with the observed behavior of iminophosphoranes derived from *N*-substituted *o*-azidobenzamides in aza Wittig-type reactions[17]. Actually, bis(iminophosphorane) **5** reacted with 1 equiv. of aryl or alkyl isocyanates in dichloromethane at 0°C to give iminophosphoranes **16** derived from the benzimidazole ring in modest yields (30−56%). Compounds **16** were also prepared by an

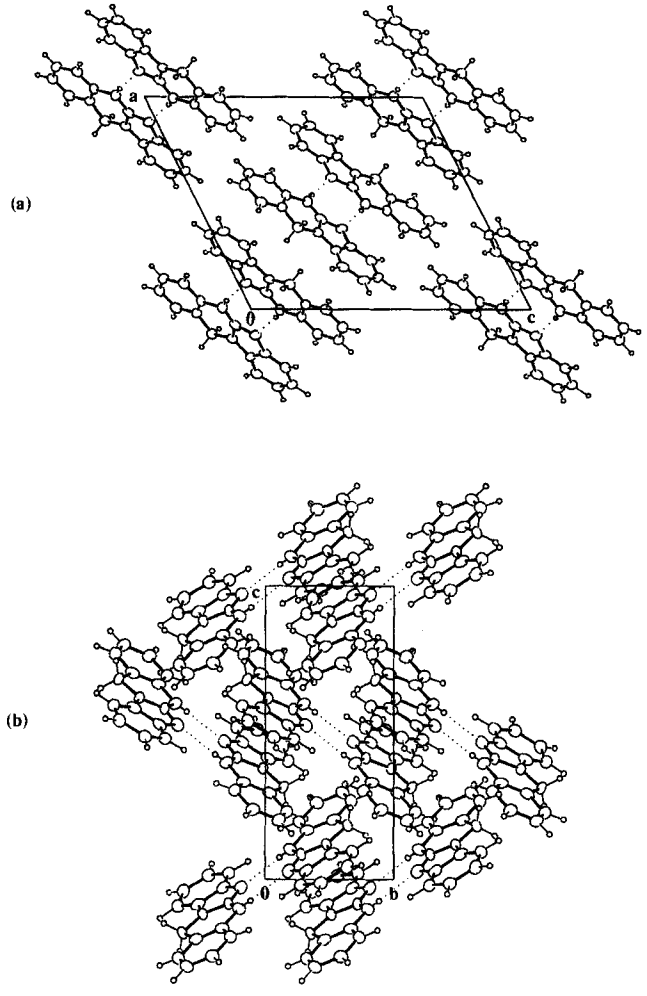


Figure 2. Crystal packing of **8** along the *b* and *a* axis showing dimers and stacking of molecules. Only molecules corresponding to the most populated positions are represented

alternative route which involves an aza Wittig-type reaction of iminophosphorane **17**, available by coupling of *o*-azidobenzoic acid with the iminophosphorane derived from *o*-azidoaniline, with isocyanates to give **18** which was converted into **16** by a Staudinger reaction with triphenylphosphane.

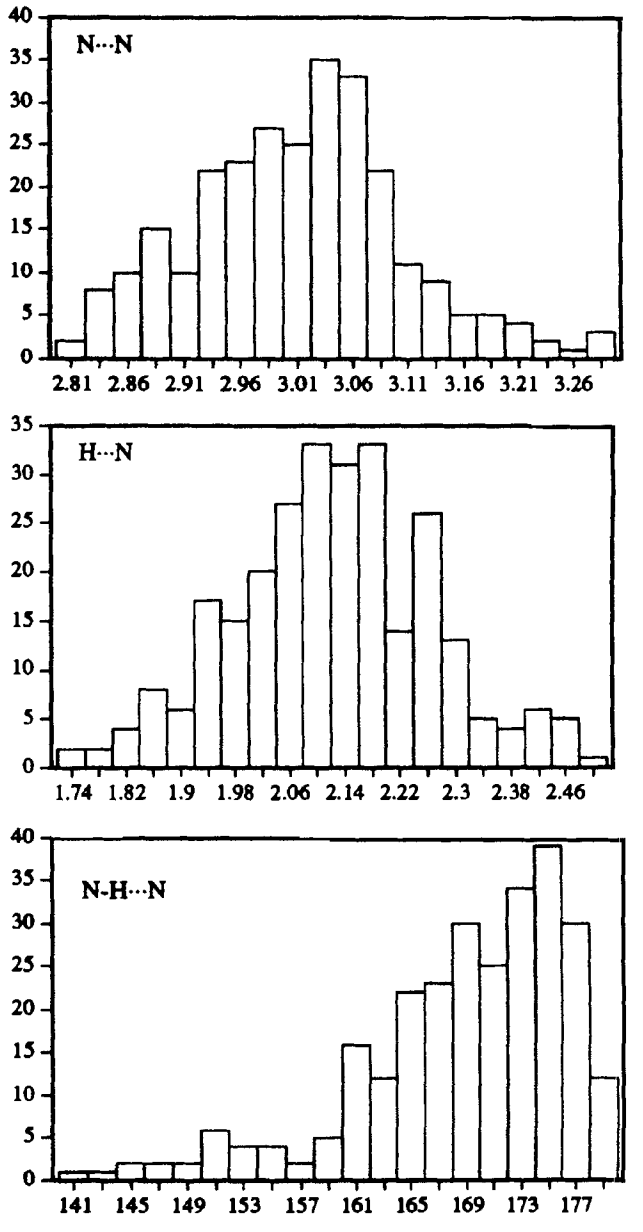
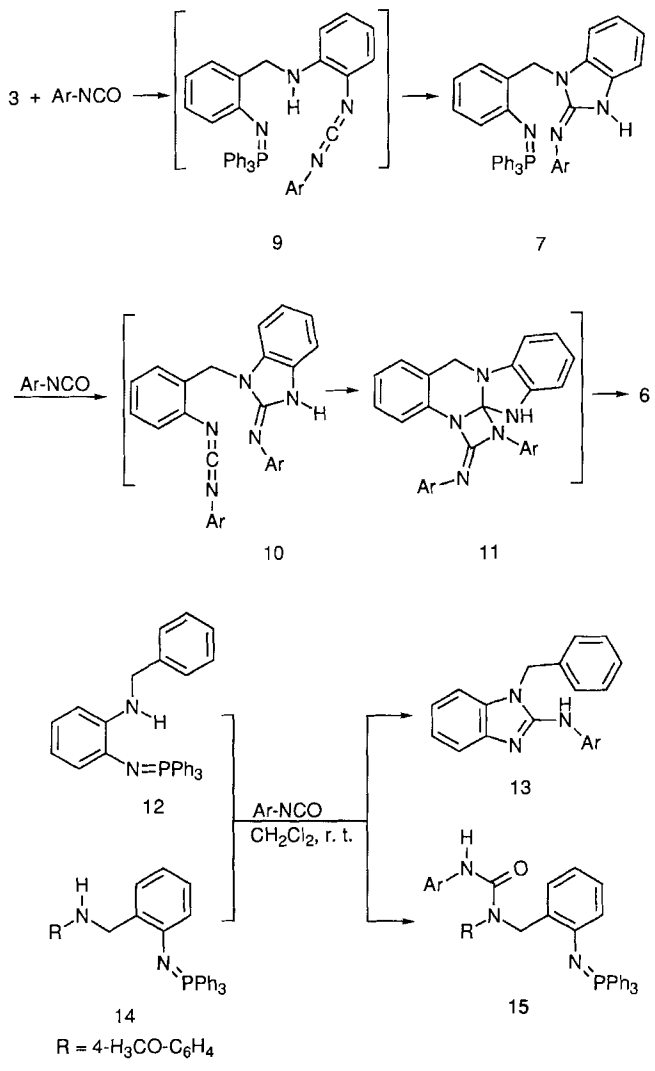


Figure 3. Histograms of the geometrical characteristics of the N−H···N interaction in symmetric dimers

Table 2. Geometrical values of the interactions N−H···N in dimers [Å, °]; σ stands for the standard deviation of the sample

		DIMERS			Ref. 16	
		Total	X=H	X≠H	$R\text{-}NH_2$	R,R'-NH
No. Hits		341	223	118	307	284
N···N	$\bar{x}(\sigma)$	3.022(91)	3.052(75)	2.964(92)	3.037	2.949
	Range	2.801-3.392	2.876-3.392	2.801-3.261	2.805-3.199	2.697-3.196
H···N	$\bar{x}(\sigma)$	2.13(14)	2.16(12)	2.07(16)	2.16	2.05
	Range	1.72-2.63	1.73-2.63	1.72-2.47	1.86-2.43	1.75-2.46
N-H···N	$\bar{x}(\sigma)$	168(8)	168(7)	167(8)	164	165
	Range	134-179	135-179	138-179	140-179	140-180

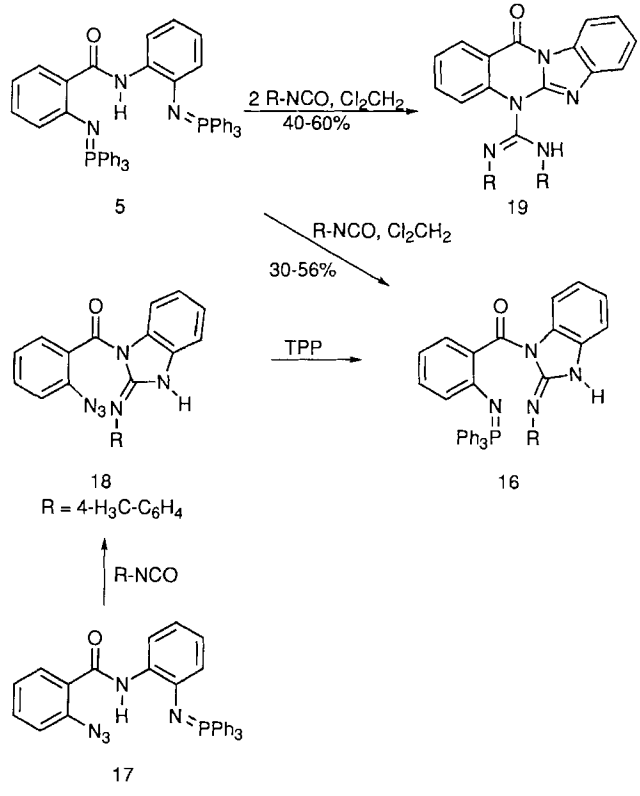
Scheme 3



Reaction of bis(iminophosphorane) **5** with 2 equivalents of isocyanates in dichloromethane at room temperature afforded the bicyclic guanidines **19** in 40–60% yields which has previously not been reported. Attempts to remove the exocyclic guanidine unit from **19** either by thermal treatment or acid-promoted failed (Scheme 4).

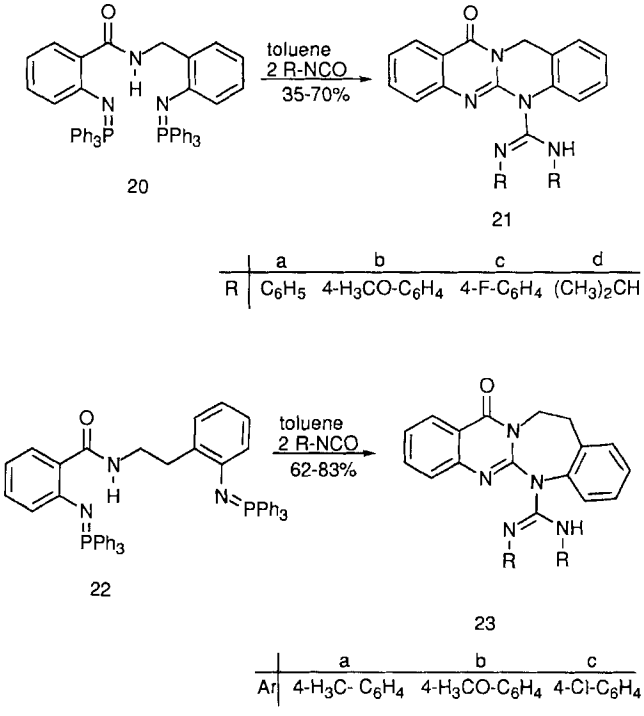
Varying the length of the amino group-bearing side chain in compound **5** was effective in producing bicyclic guanidines of varying ring size. The bis(iminophosphorane) **20** was successfully employed in the preparation of [6 + 6]-bicyclic guanidines **21**. Compound **20** was prepared by coupling of *o*-azidobenzoic acid with *o*-azidobenzylamine[18] (45%) and subsequent Staudinger reaction with triphenylphosphane (yield 85%). Starting from **20** and 2 equivalents of the corresponding aryl or alkyl isocyanate, we obtained the [6 + 6]-bicyclic guanidines **21** in 35–70% yields in a one-pot reaction. Similarly, the [6 + 7]-bicyclic guanidines **23** were obtained in 62–83% yield from the bis(iminophosphorane) **22**, available in 50% overall yield from *o*-azidobenzoic acid and 2-(*o*-azidophenyl)ethylamine[6] by using the method described for the preparation of **20** (Scheme 5).

Scheme 4



The ^{1}H-NMR spectra of bis(iminophosphorane) **20** and **22** show that the protons of the methylene groups are magnetically equivalent: a singlet at $\delta = 4.99$ for compound **20**

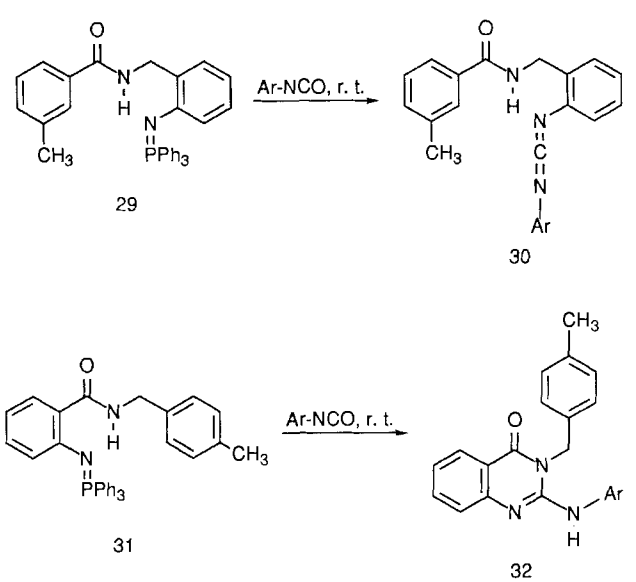
Scheme 5



and two triplets at δ = 3.07 and 3.80 for compound **22**. However, for the guanidines **21** the methylene protons appear as two doublets with a geminal coupling constant of 15 Hz, whereas for the guanidines **23** the two methylene protons appear as an ABMN system. In addition, the ^{13}C-NMR spectra of **21** and **23** show among others the carbon atoms of the two guanidine moieties, whose chemical shifts are in good agreement with the previously reported values for the related compounds[6].

A final word about the position of the exocyclic guanidine moiety in compound **21** and **23** is relevant. An unambiguous structural assignment could not be achieved on the basis of the spectroscopic data, and all attempts to obtain suitable crystals for an X-ray crystallographic analysis failed. However, model studies revealed the following facts: a) Iminophosphorane **29** reacted with isocyanates to give the corresponding carbodiimide **30**, and no cyclized product could be detected in the crude products, b) the isomeric iminophosphorane **31** provided the cyclized product **32** by reaction with isocyanates under the same reaction conditions (Scheme 6). The results clearly indicated the preferential formation of the quinazolinone ring with respect to the dihydropyrimidine ring. Accordingly, with the conversions **3** → **6** and **5** → **19**, which show that the exocyclic guanidine moiety is linked to the nitrogen atom of the last ring formed, this exocyclic guanidine portion is tentatively assigned in compounds **21** and **23** on the dihydropyrimidine ring.

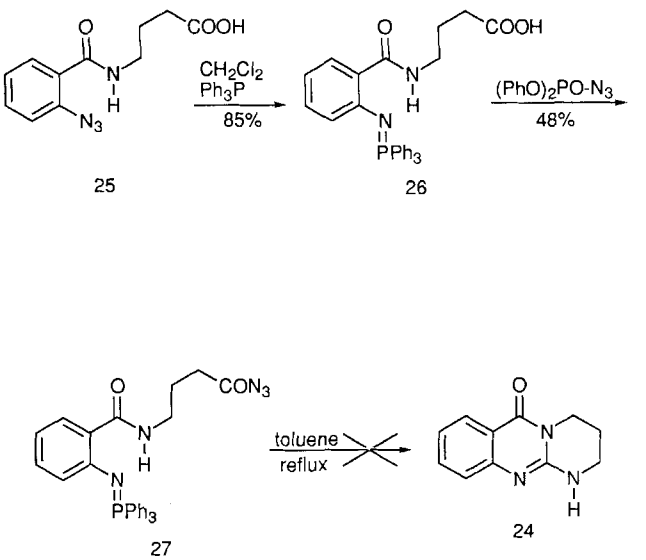
Scheme 6



29 30 31 32

Having established that the reaction of bis(iminophosphoranes) **5**, **20**, and **22** with isocyanates provided bicyclic guanidines, we considered the suitability of the intramolecular version of this reaction for the synthesis of the bicyclic guanidine **24**. To this end, iminophosphorane **26** was selected as starting material. Reaction of *o*-azidobenzoyl chloride with 4-aminobutyric acid afforded **25** in 54% yield, which was converted into **26** in 85% yield by reaction with triphenylphosphane. Compound **26** reacted with the Shioiri-Yamada reagent, diphenylphosphoryl azide[19], to give the acyl azide **27**, isolated as a crystalline solid in 48% yield. Thermal treatment of **27** in toluene at reflux temperature did not lead to the expected bicyclic guanidine **24** (Scheme 7).

Scheme 7



25 26 27 24

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Experimental

Melting points, uncorrected: Kofler hot-stage apparatus. – IR: Nicolet FT 5DX; nujol emulsions in NaCl plates. – ^{1}H and ^{13}C NMR: Bruker AC 200. – MS (70 eV): Hewlett-Packard 5993C, EI. – CC: Silica gel 60 (Merck) as stationary phase; columns of 4.5 cm diameter and 70 cm height.

X-Ray Analysis of **8**: Details of data collection and refinement process are given in Table 3. The structure was solved by direct methods (SIR92)[20] and refined by least-squares procedures on F_{obs}. The presence of large and elongate anisotropic displacement parameters in atoms C(81) and N(91) was indiative of some disorder. A model that interchanges the two central 5- and 6-membered rings was established and refined giving a disorder ratio of 65/35. Non-hydrogen atoms were refined anistropically. All hydrogen atoms were obtained from difference Fourier synthesis and included in the refinement process as isotropic. The thermal factor of H(101) and all parameters of H(102), H(821), and H(822) were kept fixed in the last stages of refinement. The scattering factors were taken from the International Tables for X-Ray Crystallography[21]. The calculations were carried out with the XRAY80[22], PESOS[23], and PARST[24] set of programs on a VAX6410 computer[25].

Imine **1**: To a mixture of *o*-[(triphenylphosphoranyliden)amino]-benzaldehyde (1.00 g, 2.62 mmol) and *o*-azidoaniline (0.70 g, 5.24 mmol) in anhydrous ethanol (10 ml) was added a catalytic amount of acetic acid. The reaction mixture was stirred at room temp. for 3 h, and the separated solid was collected by filtration and was recrystallized from ethanol to give **1**: Yield 0.78 g (60%), m.p.

Table 3. Crystal analysis parameters of **8** at room temperature

Crystal data

Chemical formula	$C_{14}H_{11}N_3$	Crystal system	Monoclinic
Mr	221.26	Space group	$P2_1/n$
a (Å)	13.5853(13)	α (°)	90
b (Å)	5.8338(3)	β (°)	114.414(4)
c (Å)	14.4696(14)	γ (°)	90
Z	4	*Dx* (gr/cm³)	1.41
V (Å³)	1044.2(2)	Radiation	CuKα
Wavelength (Å)	1.5418	No. of reflections for	
θ range for lattice parameters (°)	2-45	lattice parameters:	71
Absorption coefficient (cm^{-1})	6.45	Temperature (K)	295
Crystal colour	Colourless	Crystal description	Prism
Crystal size (mm)	0.50 x 0.23 x 0.13		

Data collection

Diffractometer type	Philips PW1100, four circle. Graphite oriented monocromator.		
Measurement time	1 min./reflection	Detector apertures (°)	1 x 1
Collection method	ω/2θ scans	θ_{max} (°)	65
No. of standard reflections (interval)	2 (90 min.). No variation	Scan width (°)	1.6
No. of independent reflections	1769	No. of observed reflections, I>3σ(I)	1682

Refinement

Treatment of hydrogen atoms	See experimental part	Refinement: Least-Squares on *Fo*. Full matrix	
R	0.056	No. of parameters refined	216
wR	0.062	Degrees of freedom	1466
$(\Delta\rho)_{max}$ (e/Å³)	0.18	Ratio of freedom	7.8
<Shift/error>	0.08	Max. thermal value (Å²)	U22[C(10)]=0.072(1)
Weighting scheme: Empirical as to give no trends in $<\omega\Delta^2F>$ vs. <|Fobs|> and $<\sin\theta/\lambda>$			

117–118°C, brown prisms. – IR: $\tilde{\nu}$ = 2142, 2112, 1606, 1594, 1483, 1342, 1113, 757, 717, 694 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 8.62–8.54 (m, 1H), 7.78 (ddd, ^3J = 12.3, ^3J = 6.9, ^4J = 1.8 Hz, 6H), 7.70–7.45 (m, 11H), 7.22–7.12 (m, 3H), 6.93 (td, ^3J = 7.2, ^4J = 1.5 Hz, 1H), 6.84 (t, ^3J = 7.2 Hz, 1H), 6.55 (d, ^3J = 7.8 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ = 161.41 (CH=N), 153.28 (q), 146.57 (q), 134.53, 132.49 (^2J_P = 9.7 Hz), 131.90 (^4J_P = 2.4 Hz), 130.93 (q, ^1J_P = 99.6 Hz), 129.18 (q, ^3J_P = 19.5 Hz), 128.73 (^3J_P = 12.0 Hz), 128.03, 125.61 (q), 125.44, 122.53 (^3J_P = 10.5 Hz), 120.21, 119.74, 117.78, 115.87. – MS; *m/z* (%): 469 (88) [M^+ – 28], 468 (58), 392 (74), 183 (100). – $C_{31}H_{24}N_5P$ (497.5): calcd. C 74.84, H 4.86, N 14.08; found C 74.92, H 4.91, N 13.90.

Bis(iminophosphorane) **3**: To a solution of imine **1** (0.60 g, 1.20 mmol) in dry dichloromethane (10 ml) was added dropwise a solution of triphenylphosphane (0.31 g, 1.20 mmol) in the same solvent (10 ml) at 0°C under N_2. The reaction mixture was stirred for 1 h, then allowed to warm at room temp., and stirring was continued for 12 h. The solvent was removed under reduced pressure, and the residue was recrystallized from diethyl ether to give **2**: Yield 0.70 g (80%), m.p. 228–229°C, orange prisms. – IR: $\tilde{\nu}$ = 1637, 1619, 1595, 1583, 1438, 1340, 1321, 1256, 1108, 746, 714, 696 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 11.08 (s, CH=N, 1H), 7.82–7.71 (m, 12H), 7.60–7.41 (m, 19H), 7.02 (td, ^3J = 6.6, ^4J = 1.8 Hz, 1H), 6.75–6.70 (m, 1H), 6.65 (t, ^3J = 7.8 Hz, 1H), 6.56 (td, ^3J = 6.6, ^4J = 1.8 Hz, 1H), 6.44 (d, ^3J = 7.8 Hz, 1H), 6.40–6.32 (m, 2H). – MS, *m/z* (%): 352 (5), 277 (18), 183 (100). – $C_{49}H_{39}N_3P_2$ (731.8): calcd. C 80.42, H 5.37, N 5.74; found C 80.55, H 5.22, N 5.65.

To a cooled solution of compound **2** (0.60 g, 0.82 mmol) in dry dichloromethane (10 ml) and dry methanol (10 ml) was added with stirring $NaBH_4$ (0.04 g, 1.23 mmol). Stirring was continued for 1 h. Then the solvent was removed under reduced pressure, and the residue was treated with cold water, filtered, and dried initially at room temp. and then at 70°C to give **3**: Yield 0.51 g (85%), m.p. 105–106°C, yellow prisms. – IR: $\tilde{\nu}$ = 3300, 1620, 1589, 1496, 1264, 1107, 719, 694 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 7.72 (ddd, ^3J_P = 13.0, ^3J = 6.8, ^4J = 1.5 Hz, 12H), 7.50–7.24 (m, 19H), 6.79 (t, ^3J = 7.8 Hz, 1H), 6.64–6.59 (m, 3H), 6.48 (d, ^3J = 7.8 Hz, 1H), 6.38 (d, ^3J = 7.3 Hz, 1H), 6.27 (td, ^3J = 6.7, ^4J = 2.0 Hz, 1H), 5.90 (br. s, 1H, NH), 4.73 (s, 2H, CH_2). – ^{13}C NMR ($CDCl_3$): δ = 148.73 (q), 144.47 (q, ^3J_P = 19.5 Hz), 137.15 (q), 134.50 (q, ^3J_P = 20.5 Hz), 132.50 (^2J_P = 9.4 Hz), 131.56 (^2J_P = 9.4 Hz), 131.54 (^4J_P = 2.3 Hz), 131.32 (^4J_P = 2.3 Hz), 128.45 (^3J_P = 11.9 Hz), 128.37 (^3J_P = 11.9 Hz), 127.53, 126.32, 120.74 (^3J_P = 9.5 Hz), 118.74 (^3J_P = 9.5 Hz), 118.41, 117.27, 115.40, 109.19, 46.08 (CH_2). – MS, *m/z* (%): 473 (11), 382 (43), 368 (59), 277 (100), 262 (53), 183 (87). – $C_{49}H_{41}N_3P_2$ (733.8): calcd. C 80.20, H 5.63, N 5.73; found C 80.39, H 5.56, N 5.61.

Bis(azide) **4**: To a mixture of *o*-azidobenzoic acid (1.50 g, 9.20 mmol), *o*-azidoaniline (1.12 g, 8.36 mmol), 4-(dimethylamino)pyridine (1.12 g, 9.20 mmol), and dry dichloromethane (10 ml), a solution of *N*-[3-(dimethylamino)propyl]-*N'*-ethylcarbodiimide hydrochloride (1.75 g, 9.20 mmol) in the same solvent (10 ml) was added at 0°C. The resultant mixture was stirred at room temp. under N_2 for 16 h and then concentrated to dryness. Subsequently, 1 N HCl (25 ml) was added, and the mixture was extracted with ethyl acetate (2 × 25 ml). The combined organic layers were washed with a 5% aqueous solution of $NaHCO_3$ (2 × 25 ml), a saturated solution of NaCl (25 ml), water (2 × 25 ml), and dried with Na_2SO_4. The

solvent was removed under reduced pressure and the residual material chromatographed on a silica gel column using ethyl acetate/*n*-hexane as eluent (1:3) to give **4**: Yield 1.54 g (60%), m.p. 103–104°C, brown prisms. – IR: $\tilde{\nu}$ = 3284, 2135, 2116, 1660, 1534, 1452, 1300, 1178, 1079, 895, 760, 741, 672, 660 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 9.71 (s, 1H, NH), 8.55 (dd, ^3J = 8.1, ^4J = 1.8 Hz, 1H), 8.21 (dd, ^3J = 7.7, ^4J = 1.5 Hz, 1H), 7.45 (td, ^3J = 7.6, ^4J = 1.5 Hz, 1H), 7.32–7.12 (m, 5H). – ^{13}C NMR ($CDCl_3$): δ = 162.42 (CO), 137.02 (q), 132.80, 132.44, 129.84 (q), 128.53 (q), 125.56, 125.28, 125.01 (q), 124.54, 121.57, 118.53, 117.63. – MS, *m/z* (%): 279 (26) [M^+], 251 (9), 222 (6), 146 (66), 140 (3), 91 (35), 90 (100). – $C_{13}H_9N_7O$ (279.3): calcd. C 55.91, H 3.25, N 35.11; found C 56.07, H 3.20, N 35.30.

Bis(iminophosphorane) **5**: To a cooled solution of triphenylphosphane (1.12 g, 4.30 mmol) in dry dichloromethane (10 ml) was added dropwise under N_2 a solution of the bis(azide) **4** (0.60 g, 2.15 mmol) in the same solvent. The reaction mixture was stirred at room temp. for 16 h, and the solvent was removed under reduced pressure. The crude product was recrystallized from *n*-hexane to give **5**: Yield 1.41 g (88%), m.p. 188–190°C, white prisms. – IR: $\tilde{\nu}$ = 3223, 1688, 1647, 1600, 1527, 1300, 1230, 1112, 891, 721, 691 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 12.03 (s, 1H, NH), 8.21 (br. s, 1H), 8.02 (td, ^3J = 7.8, ^4J = 2.0 Hz, 1H), 7.63–7.48 (m, 14H), 7.37–7.30 (m, 7H), 7.18–7.07 (m, 9H), 6.95 (td, ^3J = 7.7, ^4J = 1.6 Hz, 1H), 6.78–6.61 (m, 3H), 6.52 (d, ^3J = 8.0 Hz, 1H), 6.38 (d, ^3J = 7.5 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ = 166.92 (C=O), 149.34 (q), 140.12 (q), 133.61 (^3J_P = 20.1 Hz), 133.37 (q, ^3J_P = 16.8 Hz), 132.56 (^2J_P = 9.9 Hz), 132.53 (^2J_P = 9.9 Hz), 132.03 (^4J_P = 1.5 Hz), 131.80 (^4J_P = 2.0 Hz), 130.84, 130.45, 129.67 (q, ^1J_P = 99.5 Hz), 129.60 (q, ^1J_P = 100.1 Hz), 128.55 (^3J_P = 12.1 Hz), 128.48 (^3J_P = 12.1 Hz), 123.58, 122.81 (^3J_P = 10.5 Hz), 122.02, 120.97, 117.58. – MS, *m/z* (%): 368 (2), 277 (8), 183 (100), 149 (25). – $C_{49}H_{39}N_3OP_2$ (747.8): calcd. C 78.70, H 5.26, N 5.62; found C 78.91, H 5.20, N 5.78.

Preparation of Guanidines **6**. – *General Procedure:* To a solution of the bis(iminophosphorane) **3** (0.50 g, 0.68 mmol) in dry dichloromethane (10 ml) was added the appropriate isocyanate (1.36 mmol). The reaction mixture was stirred at room temp. The separated solid was collected by filtration and recrystallized from ethanol to give the guanidines **6**.

6a (Ar = C_6H_5): Yield 0.15 g (55%), m.p. 184–185°C, white prisms. – IR: $\tilde{\nu}$ = 1658, 1597, 1578, 1554, 1496, 1453, 1291, 825, 764, 731 cm^{-1}. – ^1H NMR ([D_6]DMSO): δ = 10.25 (s, 1H, NH), 7.86 (t, ^3J = 7.9 Hz, 1H), 7.80 (d, ^3J = 7.7 Hz, 1H), 7.56 (t, ^3J = 7.9 Hz, 2H), 7.40–7.19 (m, 4H), 7.12–6.95 (m, 6H), 6.91 (d, ^3J = 7.1 Hz, 1H), 6.81 (t, ^3J = 6.8 Hz, 1H), 6.73–6.56 (m, 2H), 5.15 (br. s, 2H, CH_2). – ^{13}C NMR ([D_6]DMSO): δ = 149.78 (q), 146.41 (q), 144.62 (q), 142.28 (q), 140.96 (q), 139.95 (q), 134.33 (q), 130.54, 129.12, 128.56 (2 CH), 124.18 (q), 123.27, 122.91, 122.05, 121.91, 121.76, 121.69, 119.32, 118.16, 116.86, 110.18, 45.45 (CH_2). – MS, *m/z* (%): 415 (2) [M^+], 221 (94), 194 (100). – $C_{27}H_{21}N_5$ (415.5): calcd. C 78.05, H 5.09, N 16.86; found C 78.24, H 5.04, N 16.70.

6b (Ar = 4-$CH_3C_6H_4$): Yield 0.12 g (42%), m.p. 220–221°C, brown prisms. – IR: $\tilde{\nu}$ = 3200, 1634, 1616, 1594, 1515, 1432, 1342, 1281, 1223, 817, 807, 733, 719 cm^{-1}. – ^1H NMR ([D_6]DMSO): δ = 9.83 (s, 1H, NH), 7.74–7.46 (m, 5H), 7.30–7.17 (m, 3H), 7.05 (d, ^3J = 7.8 Hz, 2H), 6.99 (td, ^3J = 5.7 Hz, 1H), 6.96–6.80 (m, 3H), 6.61 (d, ^3J = 8.4 Hz, 2H), 5.07 (br. s, 2H, CH_2), 2.61 (s, 3H, CH_3), 2.51 (s, 3H, CH_3). – ^{13}C NMR ([D_6]DMSO): δ = 149.45 (q), 147.02 (q), 144.80 (q), 140.99 (q), 139.99 (q), 137.99 (q), 134.22 (q), 133.14 (2 × q), 130.82, 128.94, 128.73 (2 CH), 124.15 (q), 122.91, 121.70, 121.67, 121.40, 119.19, 117.89, 117.44, 109.69, 45.42 (CH_2), 20.35 (CH_3), 20.12 (CH_3). – MS, *m/z* (%): 443 (2) [M^+], 222 (41), 221 (100), 220 (36). – $C_{29}H_{25}N_5$ (443.6): calcd. C 78.53, H 5.68, N 15.79; found C 78.69, H 5.72, N 15.61.

6c (Ar = 4-FC_6H_4): Yield 0.12 g (40%), m.p. 245–246°C, white prisms. – IR: $\tilde{\nu}$ = 3216, 1640, 1612, 1591, 1488, 1341, 1421, 812, 786, 667 cm^{-1}. – ^1H NMR ([D_6]DMSO): δ = 10.33 (s, 1H, NH), 7.93–7.77 (m, 3H), 7.65–6.80 (m, 10H), 6.72–6.60 (m, 3H), 5.13 (s, 2H, CH_2). – ^{13}C NMR ([D_6]DMSO): δ = 158.15 (q, ^1J_F = 239.8 Hz), 157.75 (^1J_F = 239.1 Hz), 149.96 (q), 146.95 (q), 145.20 (q), 141.20 (q), 139.15 (q, ^4J_F = 2.4 Hz), 136.53 (q, ^4J_F = 2.5 Hz), 134.62 (q), 130.88, 129.46, 124.63 (q), 123.69, 122.32, 122.09, 121.98, 121.32 (^3J_F = 7.5 Hz), 119.33 (^3J_F = 8.2 Hz), 118.43, 115.47 (^2J_F = 22.7 Hz), 115.40 (^2J_F = 22.5 Hz), 110.47, 45.68 (CH_2). – MS, *m/z* (%): 230 (100), 220 (13), 149 (41). – $C_{27}H_{19}F_2N_5$ (451.5): calcd. C 71.83, H 4.24, N 15.51; found C 71.98, H 4.20, N 15.42.

6d (Ar = 4-ClC_6H_4): Yield 0.18 g (60%), m.p. 215–216°C, white prisms. – IR: $\tilde{\nu}$ = 3233, 1636, 1590, 1562, 1490, 1452, 1225, 819, 756, 726, 629 cm^{-1}. – ^1H NMR ([D_6]DMSO): δ = 10.35 (s, 1H, NH), 7.90–7.79 (m, 3H), 7.55 (d, ^3J = 8.0 Hz, 1H), 7.37–7.20 (m, 5H), 7.13–6.88 (m, 5H), 6.68 (t, ^3J = 6.0 Hz, 2H), 5.29 (s, 2H, CH_2). – ^{13}C NMR ([D_6]DMSO): δ = 150.06 (q), 145.75 (q), 144.14 (q), 141.18 (q), 139.90 (2 q), 134.34 (q), 130.24 (2 q), 130.72, 128.39 (2 CH), 128.24, 124.27 (q), 122.90, 121.71, 121.56, 121.24, 120.13 (2 CH), 118.24, 110.41, 45.41 (CH_2). – MS, *m/z* (%): 264 (57), 262 (85), 221 (85), 220 (100). – $C_{27}H_{19}Cl_2N_5$ (484.4): calcd. C 66.95, H 3.95, N 14.46; found C 67.10, H 4.02, N 14.31.

Benzimidazole **7**: To a solution of **3** (0.50 g, 0.68 mmol) in dry dichloromethane (10 ml) was added dropwise at 0°C 4-fluorophenyl isocyanate (0.09 g, 0.68 mmol). The mixture was stirred at that temp. for 2 h. The solvent was removed under reduced pressure, and the residual material was chromatographed on a silica gel column by using ethyl acetate/*n*-hexane (1:1) as eluent to give **7**: Yield 0.16 g (40%), m.p. 174–175°C, white prisms. – IR: $\tilde{\nu}$ = 3210, 1624, 1590, 1574, 1320, 1217, 1205, 748, 718, 691 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 9.83 (s, 1H, NH), 7.65 (ddd, ^3J_P = 12.2, ^3J = 7.5, ^4J = 0.9 Hz, 6H), 7.54–7.06 (m, 18H), 6.83 (td, ^3J = 7.3, ^4J = 1.3 Hz, 1H), 6.73–6.54 (m, 2H), 5.53 (s, 2H, CH_2). – ^{13}C NMR ($CDCl_3$): δ = 157.90 (q, ^1J_F = 255.0 Hz), 151.37 (q), 147.50 (q), 142.89 (q), 136.20 (q), 134.00 (q), 132.70 (^2J_P = 9.8 Hz), 132.12 (^4J_F = 1.5 Hz), 131.95, 130.99, 129.05 (^3J_P = 12.1 Hz), 128.62, 128.35 (q), 122.60 (^3J_P = 9.5 Hz), 121.50 (^3J_F = 7.8 Hz), 121.01, 119.71, 116.64, 114.36 (^2J_F = 22.3 Hz), 107.32, 40.75 (CH_2). – MS, *m/z* (%): 380 (100), 352 (20), 226 (30), 183 (8). – $C_{38}H_{30}FN_4P$ (592.2): calcd. C 77.01, H 5.10, N 9.45; found C 77.21, H 5.14, N 9.36.

To a solution of compound **7** (0.50 g, 0.84 mmol) in dry dichloromethane (10 ml) was added 4-fluorophenyl isocyanate (0.11 g, 0.84 mmol). The mixture was stirred at room temp. for 24 h. The precipitated solid was collected by filtration and recrystallized from ethanol to give **6c** (40%).

Thermolysis of the Bicyclic Guanidines **6**: 1.10 mmol of **6** was heated at a temp. slightly above its melting point (300–325°C) under reduced pressure. The destillate was collected, and it was found to be the corresponding diarylcarbodiimide. After cooling, the residue was recrystallized from ethanol to give **8**: Yield 53–60%, m.p. 312–313°C, white prisms. – IR: $\tilde{\nu}$ = 3261, 1632, 1605, 1594, 1573, 1307, 1270, 1170, 882, 729, 669 cm^{-1}. – ^1H NMR ([D_6]DMSO): δ = 10.31 (s, 1H, NH), 7.31–7.17 (m, 3H), 7.08–6.91 (m, 5H), 5.29 (s, 2H, CH_2). – ^{13}C NMR ([D_6]DMSO): δ = 147.70 (q), 142.59 (q), 136.09 (q), 133.05 (q), 128.17, 127.12, 121.31, 120.97, 119.10, 115.66, 114.89, 114.62 (q), 108.01, 42.89 (CH_2). – MS, *m/z* (%): 221 (77) [M^+ + 1], 220 (100) [M^+]. – $C_{14}H_{11}N_3$ (221.1): calcd. C 75.99, H 5.01, N 19.00; found C 75.87, H 4.96, N 19.09.

Reaction of Iminophosphoranes **12** *and* **14** *with Isocyanates:* To a solution of **12** or **14** (2.18 mmol) in dry dichloromethane (10 ml) was added the appropriate isocyanate (2.18 mmol). The mixture was stirred at room temp. for 5 h (for **12**) or 16 h (for **14**). The reaction product was isolated from the reaction mixture by using one of the following methods.

Method A: The separated solid was collected by filtration and recrystallized from dichloromethane to give **13**.

13b (Ar = 4-$CH_3C_6H_4$): Yield 0.17 g (25%), m.p. 191−192°C, white prisms. − IR: $\tilde{\nu}$ = 3250, 1638, 1616, 1556, 1525, 1512, 1353, 1247, 823, 741, 717, 695 cm^{-1}. − ^1H NMR ([D$_6$]DMSO): δ = 9.32 (s, 1H, NH), 8.14−7.30 (m, 13H), 5.87 (s, 2H, CH_2), 2.60 (s, 3H, CH_3). − ^{13}C NMR ([D$_6$]DMSO): δ = 150.43 (q), 142.05 (q), 138.30 (q), 137.02 (q), 133.55 (q), 129.85 (q), 128.97, 128.59, 127.29, 126.64, 120.94, 119.65, 118.10, 116.12, 108.50, 44.97 (CH_2). − MS, *m/z* (%): 313 (8) [M^+], 181 (15), 117 (100). − $C_{21}H_{19}N_3$ (313.4): calcd. C 80.48, H 6.11, N 13.41; found C 80.60, H 6.06, N 13.55.

13c (Ar = 4-FC_6H_4): Yield 0.23 g (33%), m.p. 189−190°C, white prisms. − IR: $\tilde{\nu}$ = 1639, 1620, 1568, 1558, 1505, 1348, 1220, 1100, 823, 791, 771, 722 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 9.30 (s, 1H, NH), 7.45−6.85 (m, 13H), 5.23 (s, 2H, CH_3). − ^{13}C NMR ($CDCl_3$): δ = 157.15 (q, ^1J_F = 237.4 Hz), 150.49 (q), 142.03 (q), 137.38 (q), 137.13 (q), 133.71 (q), 128.84, 127.54, 126.83, 121.25, 120.02, 119.72 (^3J_F = 7.5 Hz), 116.41, 115.27 (^2J_F = 22.0 Hz), 108.81, 45.01 (CH_2). − MS, *m/z* (%): 318 (7) [M^+ + 1], 317 (27) [M^+], 91 (100). − $C_{20}H_{16}FN_3$ (317.4): calcd. C 75.69, H 5.08, N 13.24; found C 75.80, H 5.12, N 13.15.

Method B: The solvent was removed under reduced pressure, and the residual material was chromatographed on a silica gel column by using ethyl acetate/*n*-hexane (1:1) as eluent to give **15**: Yield 0.54 g (40%), m.p. 115−116°C, brown prisms. − IR: $\tilde{\nu}$ = 3284, 1649, 1620, 1594, 1509, 1316, 1107, 1028, 747, 718, 693 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.62 (ddd, ^3J_P = 12.3, ^3J = 7.0, ^4J = 1.7 Hz, 6H), 7.51−7.36 (m, 9H), 7.26−7.23 (m, 2H), 7.20 (d, ^3J = 8.0 Hz, 2H), 7.14 (d, ^3J = 8.0 Hz, 2H), 6.79−6.73 (m, 3H), 6.60 (td, ^3J = 7.5, ^4J = 1.0 Hz, 1H), 6.42 (d, ^3J = 8.0 Hz, 2H), 5.27 (CH_2), 3.71 (OCH_3), 2.20 (CH_3). − ^{13}C NMR ($CDCl_3$): δ = 158.06 (CO), 155.45 (q), 148.67 (q), 136.97 (q), 135.89 (q), 132.51 (^2J_P = 9.7 Hz), 131.68 (^4J_P = 1.2 Hz), 131.62 (q), 131.44 (q), 131.14 (q, ^1J_P = 98.9 Hz), 129.60, 128.90, 128.55 (^3J_P = 11.8 Hz), 127.25, 121.30 (^3J_P = 7.3 Hz), 119.94, 117.64, 114.45, 55.32 (OCH_3), 49.64 (CH_2), 20.66 (CH_3). − MS, *m/z* (%): 621 (2) [M^+], 183 (100). − $C_{40}H_{36}N_3O_2P$ (621.7): calcd. C 77.28, H 5.84, N 6.76; found C 77.37, H 5.80, N 6.90.

Preparation of Benzimidazoles **16**

Method A: To a solution of **5** (0.50 g, 0.66 mmol) in dry dichloromethane (10 ml) the appropriate isocyanate (0.66 mmol) was added dropwise at 0°C. The reaction mixture was stirred at that temp. for 3 h. The solvent was removed under reduced pressure, and the crude product was chromatographed on a silica gel column by using ethyl acetate/*n*-hexane (1:1) as eluent to give:

16a (R = C_6H_5): Yield 0.18 g (48%), m.p. 177−178°C, brown prisms. − IR: $\tilde{\nu}$ = 3128, 1665, 1590, 1564, 1360, 1170, 1108, 744, 721, 691 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 10.29 (s, 1H, NH), 7.95 (d, ^3J = 7.7 Hz, 1H), 7.45−7.01 (m, 23H), 6.80 (t, ^3J = 7.2 Hz, 1H), 6.62 (t, ^3J = 7.2 Hz, 1H), 6.35 (d, ^3J = 8.2 Hz, 1H), 6.17 (d, ^3J = 8.0 Hz, 1H). − ^{13}C NMR ($CDCl_3$): δ = 173.92 (CO), 150.43 (q), 149.63 (q), 143.06 (q), 139.33 (q), 132.30 (^2J_P = 9.9 Hz), 132.26 (q), 131.86, 131.79 (q, ^1J_P = 98.6 Hz), 131.75 (^4J_P = 2.8 Hz), 130.73 (q), 129.19, 128.58 (^3J_P = 12.2 Hz), 127.81 (^4J_P = 3.0 Hz), 124.09, 122.62, 121.44 (^3J_P = 10.6 Hz), 121.05, 119.21, 117.17, 117.08, 113.01. − MS, *m/z* (%). 589 (15) [M^+ + 1], 588 (4) [M^+], 497 (25), 380 (100). − $C_{38}H_{29}N_4OP$ (588.6): calcd. C 77.54, H 4.97, N 9.52; found C 77.70, H 5.07, N 9.63.

16b (R = 4-$CH_3C_6H_4$): Yield 0.20 g (50%), m.p. 112−113°C, white prisms. − IR: $\tilde{\nu}$ = 3220, 1695, 1610, 1555, 1511, 1411, 1247, 1024, 757, 740, 694 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 10.19 (s, 1H, NH), 7.73 (d, ^3J = 8.3 Hz, 2H), 7.38−7.25 (m, 8H), 7.22−7.13 (m, 11H), 7.03 (td, ^3J = 7.3, ^4J = 1.8 Hz, 1H), 6.98 (td, ^3J = 7.6, ^4J = 1.3 Hz, 1H), 6.74 (td, ^3J = 7.3, ^4J = 1.0 Hz, 1H), 6.55 (td, ^3J = 7.8, ^4J = 1.3 Hz, 1H), 6.31 (d, ^3J = 8.1 Hz, 1H), 6.10 (d, ^3J = 8.1 Hz, 1H), 2.31 (s, 3H, CH_3). − ^{13}C NMR ($CDCl_3$): δ = 173.86 (CO), 150.68 (q), 149.54 (q), 143.15 (q), 136.72 (q), 132.27 (^2J_P = 9.9 Hz), 132.07 (q), 132.06, 131.80, 131.73 (^4J_P = 2.5 Hz), 130.42 (q, ^3J_P = 25.5 Hz), 129.68 (q, ^1J_P = 99.3 Hz), 129.65, 128.65 (^3J_P = 12.0 Hz), 127.72 (^4J_P = 3.0 Hz), 124.03, 121.40 (^3J_P = 10.5 Hz), 120.85, 119.32, 117.05, 117.01, 112.93, 20.95 (CH_3). − MS, *m/z* (%): 602 (5) [M^+], 496 (12), 380 (100). − $C_{39}H_{31}N_4OP$ (602.7): calcd. C 77.73, H 5.18, N 9.30; found C 77.83, H 5.24, N 9.44.

16c (R = 4-FC_6H_4): Yield 0.31 g (77%), m.p. 180°C, yellow prisms. − IR: $\tilde{\nu}$ = 3128, 1687, 1611, 1591, 1574, 1140, 1110, 1046, 846, 757, 746, 691 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 10.22 (s, 1H, NH), 7.86 (dd, ^3J = 9.0, ^4J_F = 4.8 Hz, 2H), 7.44−7.21 (m, 17H), 7.13−7.03 (m, 4H), 6.82 (t, ^3J = 7.2 Hz, 1H), 6.64 (td, ^3J = 8.1, ^4J = 1.2 Hz, 1H), 6.39 (d, ^3J = 7.8 Hz, 1H), 6.19 (d, ^3J = 8.4 Hz, 1H). − ^{13}C NMR ($CDCl_3$): δ = 173.87 (CO), 158.59 (q, ^1J_F = 239.8 Hz), 150.55 (q), 149.36 (q), 142.89 (q), 135.46 (q, ^4J_F = 2.4 Hz), 132.37 (^2J_P = 9.5 Hz), 132.24, 132.06 (q), 131.94, 131.49 (q, ^1J_P = 96.6 Hz), 130.39 (q, ^3J_P = 25.0 Hz), 128.64 (^3J_P = 12.0), 127.89, 124.18, 121.58 (^3J_P = 8.5 Hz), 121.15, 120.72 (^3J_F = 7.5 Hz), 117.30, 117.13, 115.74 (^2J_F = 22.0 Hz), 113.05. − MS, *m/z* (%): 497 (2), 381 (27), 380 (100), 226 (17). − $C_{38}H_{28}FN_4OP$ (606.6): calcd. C 75.24, H 4.65, N 9.24; found C 75.38, H 4.72, N 9.37.

16d (R = *n*Pr): Yield 0.11 g (30%), m.p. 95−96°C, yellow prisms. − IR: $\tilde{\nu}$ = 3200, 1679, 1628, 1574, 1500, 1320, 1268, 1109, 744, 721, 693 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 9.50 (br. s, 1H, NH), 7.96 (dd, ^3J = 7.0, ^3J = 6.0 Hz, 1H), 7.48−7.25 (m, 16H), 7.06 (t, ^3J = 6.3 Hz, 1H), 6.99 (t, ^3J = 7.3 Hz, 1H), 6.77 (t, ^3J = 7.4 Hz, 1H), 6.54 (t, ^3J = 7.7 Hz, 1H), 6.36 (d, ^3J = 8.0 Hz, 1H), 6.10 (d, ^3J = 8.0 Hz, 1H), 3.65 (m, 2H, CH_2N), 1.79 (sext, ^3J = 7.4 Hz, 2H, CH_2), 1.05 (t, ^3J = 7.4 Hz, 3H, CH_3). − ^{13}C NMR ($CDCl_3$): δ = 173.29 (CO), 154.82 (q), 149.20 (q), 142.03 (q), 132.26 (^2J_P = 9.9 Hz), 131.65 (^4J_P = 2.4 Hz), 131.44, 131.20 (q), 130.56 (q, ^3J_P = 24.6 Hz), 129.74 (q, ^1J_P = 99.6 Hz), 128.43 (^3J_P = 12.0 Hz), 127.50 (^4J_P = 3.0 Hz), 123.82, 121.26 (^3J_P = 11.0 Hz), 119.85, 116.94, 115.75, 112.73, 44.72 (CH_2N), 22.74 (CH_2), 11.51 (CH_3). − MS, *m/z* (%): 555 (4) [M^+ + 1], 554 (2) [M^+], 380 (100). − $C_{35}H_{31}N_4OP$ (554.2): calcd. C 75.78, H 5.64, N 10.11; found C 75.62, H 5.57, N 10.23.

Method B: A mixture of the iminophosphorane **17** (1.0 g, 1.94 mmol), the appropriate isocyanate (1.94 mmol), and dry dichloromethane (15 ml) was stirred at room temp. for 12 h. The solvent was removed under reduced pressure, and the residue was chromatographed on a silica gel column by using ethyl acetate/*n*-hexane as eluent to give **18**; Yield 0.54 g (76%), m.p. 160−161°C, brown prisms. − IR: $\tilde{\nu}$ = 3230, 2140, 2109, 1686, 1636, 1571, 1350, 1340, 1300, 815, 754, 740, 722 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 10.07 (s, 1H, NH), 7.68−7.59 (m, 3H), 7.46−7.37 (m, 2H), 7.34−7.26 (m, 2H), 7.16−7.07 (m, 3H), 6.69 (td, ^3J = 7.7, ^4J = 0.9 Hz, 1H), 5.80 (d, ^3J = 8.2 Hz, 1H), 2.23 (s, 3H, CH_3). − ^{13}C NMR ($CDCl_3$): δ = 168.40 (CO), 150.51 (q), 142.43 (q), 138.38 (q), 135.92 (q), 133.65 (q), 133.43, 130.12, 129.87 (q), 128.95, 126.76 (q), 125.94, 125.61, 121.65, 120.29, 119.53, 117.99, 112.39, 21.24 (CH_3). − MS, *m/z* (%): 368 (57) [M^+], 340 (30), 207 (56), 90 (100). − $C_{21}H_{16}N_6O$

(368.4): calcd. C 68.47, H 4.38, N 22.81; found C 68.55, H 4.47, N 22.60.

To a cooled solution of triphenylphosphane (0.31 g, 1.20 mmol) in dry dichloromethane (10 ml) was added a solution of **18** (0.44 g, 1.20 mmol) in the same solvent. The mixture was stirred at 0°C for 1 h and then allowed to warm at room temp. Stirring was continued for 6 h. The solvent was removed under reduced pressure, and the residual material was recrystallized from ethanol to give **16**.

Preparation of the Bicyclic Guanidines **19**. – *General Procedure:* A mixture of **5** (0.50 g, 0.66 mmol), the appropriate isocyanate (1.33 mmol), and dry dichloromethane (10 ml) was stirred at room temp. for 16 h. The solution was concentrated to dryness, and the residual material was chromatographed on a silica gel column eluting by using ethyl acetate/*n*-hexane (1:1) as eluent to give **19**.

19a (R = 4-$CH_3OC_6H_4$): Yield 0.21 g (65%), yellow prisms, m.p. 197–198°C. – IR: $\tilde{\nu}$ = 3153, 1692, 1630, 1604, 1580, 1536, 1247, 1036, 817, 751, 689 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 9.75 (s, 1H, NH), 8.61 (d, ^3J = 8.2 Hz, 1H), 8.30 (d, ^3J = 8.0 Hz, 1H), 7.89 (t, ^3J = 8.0 Hz, 1H), 7.82–7.77 (m, 5H), 7.70–7.59 (m, 3H), 7.47 (t, ^3J = 7.7 Hz, 1H), 6.98 (d, ^3J = 8.9 Hz, 4H), 3.83 (s, 6H, 2 OCH_3). – ^{13}C NMR ($CDCl_3$): δ = 161.01 (CO), 155.98 (2 q), 150.52 (q), 147.10 (q), 146.12 (q), 141.32 (q), 135.25 (2 q), 134.18, 131.24 (q), 129.47, 128.10, 125.62, 123.08, 120.82 (2 CH), 120.75, 117.45, 115.27 (q), 114.64, 114.50 (2 CH), 55.54 (2 OCH_3). – MS, *m/z* (%): 489 (3) [M^+], 341 (100), 326 (84). – $C_{29}H_{23}N_5O_3$ (489.5): calcd. C 71.15, H 4.74, N 14.31; found C 69.84, H 6.47, N 19.20.

19b (R = 4-$CH_3C_6H_4$): Yield 0.11 g (38%), m.p. 159–160°C, white prisms. – IR: $\tilde{\nu}$ = 3210, 1705, 1594, 1569, 1511, 1241, 1117, 782, 743, 694 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 9.82 (s, 1H, NH), 8.25 (dd, ^3J = 7.8, ^4J = 1.2 Hz, 1H), 7.70 (td, ^3J = 8.1, ^4J = 1.5 Hz, 1H), 7.57–7.47 (m, 3H), 7.36 (dd, ^3J = 8.1, ^4J = 1.0 Hz, 1H), 7.29–7.20 (m, 4H), 7.11 (d, ^3J = 8.4 Hz, 2H), 7.06 (d, ^3J = 7.8 Hz, 2H), 6.76 (d, ^3J = 7.8 Hz, 2H), 1.96 (s, 6H, 2 CH_3). – ^{13}C NMR ($CDCl_3$): δ = 162.05 (CO), 150.35 (q), 147.74 (q), 145.38 (q), 139.42 (q), 137.71 (q), 135.45 (q), 134.62 (q + CH), 133.07, 131.35 (q), 129.44, 129.32, 128.30, 127.88, 127.55, 127.34, 124.12, 124.01, 120.68 (q), 119.79, 118.92, 110.00, 20.79 (CH_3), 20.63 (CH_3). – MS, *m/z* (%): 457 (22) [M^+], 235 (40), 222 (21), 91 (100). – $C_{29}H_{23}N_5O$ (457.5): calcd. C 76.13, H 5.07, N 15.31; found C 76.24, H 4.93, N 15.42.

19c (R = 4-FC_6H_4): Yield 0.10 g (35%), m.p. 142–143°C, white prisms. – IR: $\tilde{\nu}$ = 3300, 1700, 1673, 1605, 1506, 1212, 1157, 1017, 833, 773, 756, 738, 696 cm^{-1}. – ^1H NMR ([D_6]DMSO): δ = 8.15 (dd, ^3J = 7.2, ^4J = 0.9 Hz, 1H), 7.71 (td, ^3J = 8.1, ^4J = 1.5 Hz, 1H), 7.65 (t, ^3J = ^3J_F = 7.8 Hz, 2H), 7.46 (td, ^3J = 7.5, ^4J = 1.2 Hz, 1H), 7.05–6.66 (m, 11H). – ^{13}C NMR ([D_6]DMSO): δ = 162.40 (CO), 162.36 (q, ^1J_F = 248.7 Hz), 158.73 (q, ^1J_F = 240.3 Hz), 148.38 (q), 145.83 (q), 142.03 (q), 140.87 (q), 135.46, 131.70 (q), 130.42 (2 q, ^4J_F = 2.5 Hz), 128.67, 127.72, 127.55, 123.43, 121.32, 120.90 (q), 120.58 (2 CH, ^3J_F = 7.9 Hz), 117.48, 115.81 (2 CH, ^2J_F = 22.5 Hz), 109.36. – MS, *m/z* (%): 465 (5) [M^+], 230 (100), 227 (77), 226 (86). – $C_{27}H_{17}F_2N_5O$ (465.5): calcd. C 69.67, H 3.68, N 15.05; found C 69.83, H 3.74, N 14.92.

19d (R = *i*Pr): Yield 0.09 g (40%), m.p. 90–91°C, yellow prisms. – IR: $\tilde{\nu}$ = 3227, 1688, 1622, 1603, 1572, 1567, 1270, 1215, 1170, 738, 723, 697 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 8.31 (d, ^3J = 7.8 Hz, 1H), 7.88–7.43 (m, 4H), 7.36–6.91 (m, 4H), 4.29 (m, CH, 1H), 4.00 (m, CH, 1H), 1.57 (d, ^3J = 6.9 Hz, 3H), 1.52 (d, ^3J = 6.9 Hz, 3H), 1.32 (d, ^3J = 6.3 Hz, 3H), 1.29 (d, ^3J = 6.3 Hz, 3H). – ^{13}C NMR ($CDCl_3$): δ = 163.11 (CO), 152.27 (q), 150.09 (q), 146.02 (q), 142.52 (q), 134.73, 133.49 (q), 128.29, 127.36, 127.01, 123.26, 123.10 (q), 120.86, 117.06, 108.27, 53.34 [*C*H(CH_3)$_2$], 45.94 [*C*H(CH_3)$_2$], 23.26 (CH_3), 22.96 (CH_3), 20.21 (CH_3), 19.92 (CH_3). – MS, *m/z* (%): 361 (60) [M^+], 304 (36), 236 (100), 235 (43). – $C_{21}H_{23}N_5O$ (361.4): calcd. C 69.78, H 6.41, N 19.38; found C 69.84, H 6.47, N 19.20.

Preparation of Bis(iminophosphoranes) **20** *and* **22**. – *General Procedure:* To a cooled mixture of *o*-azidobenzoic acid (1.10 g, 6.70 mmol), dicyclohexylcarbodiimide (1.80 g, 6.70 mmol), and dry dichloromethane (25 ml) was added *o*-azidobenzylamine (0.99 g, 6.70 mmol) or (*o*-azidophenyl)ethylamine (1.08 g, 6.70 mmol). The resultant mixture was stirred at 0°C for 30 min, allowed to warm to room temp. and further stirred for 16 h. The precipitated dicyclohexylurea was separated by filtration, and the filtrate was concentrated to dryness. The residue was chromatographed on a silica gel column eluting by using ethyl acetate/*n*-hexane (1:1) as eluent.

2-Azido-N-(2-azidobenzyl)benzamide: Yield 0.80 g (41%), white prisms, m.p. 61–63°C. – IR: $\tilde{\nu}$ = 3392, 2123, 2086, 1632, 1549, 1290, 1164, 1090, 989, 839, 753 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 8.14 (dd, ^3J = 7.7, ^4J = 1.5 Hz, 1H), 7.96 (t, ^3J = 6.0 Hz, 1H, NH), 7.48 (td, ^3J = 7.7, ^4J = 1.5 Hz, 1H), 7.41 (d, ^3J = 7.5 Hz, 1H), 7.33 (td, ^3J = 7.7, ^4J = 1.5 Hz, 1H), 7.25–7.16 (m, 3H), 7.11 (t, ^3J = 7.5 Hz, 1H), 4.59 (d, ^3J = 6.0 Hz, 2H, CH_2). – ^{13}C NMR ($CDCl_3$): δ = 164.50 (CO), 138.68 (q), 137.04 (q), 132.41, 132.35, 130.74 (q), 130.18, 129.42 (q), 128.91, 125.19, 125.03, 118.41, 118.15, 39.95 (CH_2). – MS, *m/z* (%): 265 (2) [M^+ – 28], 147 (21), 146 (14), 119 (77), 118 (26), 90 (100). – $C_{14}H_{11}N_7O$ (293.3): calcd. C 57.33, H 3.78, N 33.43; found C 57.50, H 3.76, N 33.33.

2-Azido-N-[(2-azidophenyl)ethyl]benzamide: Yield 1.07 g (52%), white prisms, m.p. 83–85°C. – IR: $\tilde{\nu}$ = 3313, 2125, 2095, 1636, 1550, 1303, 1282, 752, 746 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 8.05 (dd, ^3J = 7.8, ^4J = 1.5 Hz, 1H), 7.42–7.36 (m, 2H), 7.22 (dt, ^3J = 7.8, ^4J = 1.5 Hz, 1H), 7.18–6.99 (m, 4H), 3.62 (dt, ^3J = 7.0, ^3J = 5.7 Hz, 2H), 2.84 (t, ^3J = 7.0 Hz, 2H). – ^{13}C NMR ($CDCl_3$): δ = 164.55 (CO), 138.40 (q), 136.80 (q), 132.37, 132.21, 131.40, 130.36 (q), 128.25 (q), 128.14, 125.17, 124.70, 118.39, 118.14, 40.27 (CH_2), 31.10 (CH_2). – MS, *m/z* (%): 307 (1) [M^+], 147 (37), 146 (36), 119 (26), 118 (57), 117 (100). – $C_{15}H_{13}N_7O$ (307.3): calcd. C 58.63, H 4.26, N 31.90; found C 58.44, H 4.27, N 31.81.

To a solution of the above-described *N*-substituted *o*-azidobenzamides (3.20 mmol) in dry dichloromethane (30 ml) a solution of triphenylphosphane (1.68 g, 6.40 mmol) in the same solvent (20 ml) was added. The mixture was stirred at 0°C under N_2 for 1 h and then at room temp. for 16 h. The solvent was removed under reduced pressure, and the residual material was either chromatographed on a silica gel column by using ethyl acetate/*n*-hexane as eluent (for compound **20**) or recrystallized from diethyl ether (compound **22**).

Bis(iminophoshorane) **20**: Yield 2.07 g (85%), white prisms, m.p. 143–145°C. – IR: $\tilde{\nu}$ = 3358, 1638, 1591, 1438, 1327, 1112, 999, 740, 717, 693 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 11.46 (br. s, 1H, NH), 8.40 (d, ^3J = 6.8 Hz, 1H), 7.68 (dd, ^3J_P = 11.7, ^3J = 7.8 Hz, 6H), 7.56 (dd, ^3J_P = 11.7, ^3J = 7.8 Hz, 6H), 7.41–7.34 (m, 7H), 7.26–7.14 (m, 12H), 6.78–6.73 (m, 2H), 6.88 (t, ^3J = 7.2 Hz, 1H), 6.53 (t, ^3J = 7.2 Hz, 1H), 6.45–6.37 (m, 2H), 4.99 (br. s, 2H, CH_2). – ^{13}C NMR ($CDCl_3$): δ = 168.30 (CO), 150.21 (q), 150.17 (q), 132.20 (q, ^1J_P = 99.0 Hz), 132.59 (^2J_P = 9.9 Hz), 132.43 (^2J_P = 9.9 Hz), 131.94 (^4J_P = 2.5 Hz), 131.75, 131.74, 131.55, 130.44, 130.80 (q, ^1J_P = 98.0 Hz), 128.78 (^3J_P = 12.0 Hz), 128.50 (^3J_P = 12.1 Hz), 126.85, 122.69 (^3J_P = 12.5 Hz), 120.61 (^3J_P = 10.0 Hz), 117.33 (2 CH), 42.28 (CH_2). – MS, *m/z* (%): 277 (92), 199 (100), 183 (62). – $C_{50}H_{41}N_3OP_2$ (761.8): calcd. C 78.83, H 5.42, N 5.51; found C 79.05, H 5.40, N 5.39.

Bis(iminophosphorane) **22**: Yield 2.41 g (97%), white prisms, m.p. 224–226°C. – IR: $\tilde{\nu}$ = 3239, 1638, 1589, 1544, 1482, 1437, 1348,

1333, 1269, 1109, 755, 721, 695 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 11.2 (br. s, 1H, NH), 8.27 (dd, ^3J = 7.5, ^4J = 1.5 Hz, 1H), 7.71 (dd, ^3J_P = 12.0, ^3J = 7.8 Hz, 6H), 7.54 (dd, ^3J_P = 12.2, ^3J = 7.9 Hz, 6H), 7.38–7.28 (m, 18H), 6.94 (d, ^3J = 7.5 Hz, 1H), 6.82 (t, ^3J = 7.5 Hz, 1H), 6.67 (t, ^3J = 7.5 Hz, 1H), 6.56 (t, ^3J = 7.5, 1H), 6.40–6.35 (m, 2H), 6.27 (t, ^3J = 7.5 Hz, 1H), 3.80 (dt, ^3J = 7.0, ^3J = 6.3 Hz, 2H), 3.07 (t, ^3J = 7.0 Hz, 2H). – ^{13}C NMR ($CDCl_3$): δ = 167.90 (CO), 150.09 (q), 148.79 (q), 134.45 (q, ^3J_P = 22.0 Hz), 132.68 (^2J_P = 9.9 Hz), 132.52 (^2J_P = 10.5 Hz), 132.20 (^4J_P = 2.5 Hz), 131.60, 131.58 (^4J_P = 2.5 Hz), 131.41 (q, ^1J_P = 98.6 Hz), 130.92 (q, ^1J_P = 98.6 Hz), 130.48, 129.95 (^4J_P = 2.5 Hz), 129.01 (^3J_P = 12.0 Hz), 128.63 (^3J_P = 12.0 Hz), 126.27, 125.60 (q, ^3J_P = 21.0 Hz), 122.59 (^3J_P = 12.0 Hz), 120.85 (^3J_P = 9.9 Hz), 117.45, 117.25, 40.16 (CH_2), 33.22 (CH_2). – MS, *m/z* (%): 277 (6), 183 (41), 108 (33), 77 (100). – $C_{51}H_{43}N_3OP_2$ (775.9): calcd. C 78.95, H 5.59, N 5.42; found C 79.15, H 5.58, N 5.40.

Preparation of the Bicyclic Guanidines **21** *and* **23**. – *General Procedure:* A mixture of **20** or **22** (0.66 mmol), the appropriate isocyanate (1.30 mmol), and dry toluene (15 ml) was stirred under N_2 at room temp. for 12 h. The solution was concentrated to dryness, and the crude product was chromatographed on a silica gel column by using ethyl acetate/*n*-hexane (1:1) as eluent to give **21** or **23**, respectively, which were recrystallized from *n*-hexane.

21a (R = C_6H_5): Yield 0.15 g (51%), white prisms, m.p. 154–156°C. – IR: ṽ = 3222, 1686, 1646, 1615, 1593, 1571, 1538, 1495, 1391, 1305, 1211, 1100, 980, 778, 760, 725, 691 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 7.59–7.55 (m, 2H), 7.36–7.28 (m, 2H), 7.25–6.92 (m, 13H), 6.55 (dd, ^3J = 7.8, ^4J = 0.9 Hz, 1H), 5.55 (d, ^2J = 15.1 Hz, 1H), 3.30 (d, ^2J = 15.1 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ = 168.29 (CO), 147.32 (q), 146.92 (q), 146.12 (q), 141.71 (q), 138.87 (q), 138.44 (q), 131.02, 129.06, 128.96 (2 CH), 128.67, 128.09 (q), 126.32 (q), 125.67, 125.48, 125.12, 124.28, 123.40, 123.26, 122.74, 121.53, 120.27, 42.80 (CH_2). – MS, *m/z* (%): 443 (3) [M^+], 298 (3), 194 (100). – $C_{28}H_{21}N_5O$ (443.5): calcd. C 75.83, H 4.77, N 15.79; found C 75.77, H 4.79, N 15.83.

21b (R = 4-$CH_3OC_6H_4$): Yield 0.23 g (70%), white prisms, m.p. 127–129°C. – IR: ṽ = 3222, 1689, 1648, 1592, 1573, 1509, 1307, 1249, 1036, 978, 832, 763, 726 cm^{-1}. – ^1H NMR ([D_6]DMSO): δ = 9.98 (br. s, 1H, NH), 7.71–7.66 (m, 2H), 7.38 (t, ^3J = 6.8 Hz, 1H), 7.29 (d, ^3J = 6.9 Hz, 1H), 7.21–6.79 (m, 12H), 5.63 (d, ^2J = 15.0 Hz, 1H), 4.16 (d, ^2J = 15.0 Hz, 1H), 3.70 (s, 6H, 2 CH_3O). – ^{13}C NMR ([D_6]DMSO): δ = 168.11 (CO), 157.60 (q), 155.32 (q), 147.13 (q), 146.20 (q), 145.52 (q), 142.53 (q), 132.63 (q), 131.46, 131.06 (q), 128.91, 128.37, 127.70 (q), 126.18 (q + CH), 127.73, 124.03, 123.28, 123.09, 122.91, 120.85, 114.85, 113.97, 55.28 (2 OCH_3), 43.10 (CH_2). – MS, *m/z* (%): 503 (34) [M^+], 248 (18), 196 (100). – $C_{30}H_{25}N_5O_3$ (503.6): calcd. C 71.56, H 5.00, N 13.91; found C 71.75, H 4.98, N 13.88.

21c (R = 4-FC_6H_4): Yield 0.16 g (51%), white prisms, m.p. 137–139°C. – IR: ṽ = 3222, 1680, 1628, 1608, 1564, 1509, 1406, 1211, 1152, 831, 730 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 7.54–7.52 (m, 2H), 7.26–6.82 (m, 13H), 6.64 (d, ^3J = 7.9 Hz, 1H), 5.65 (d, ^2J = 15.3 Hz, 1H), 3.57 (d, ^2J = 15.3 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ = 168.32 (CO), 160.04 (q, ^1J_F = 245.4 Hz), 159.45 (q, ^1J_F = 242.8 Hz), 147.28 (q), 146.50 (q), 145.82 (q), 141.76 (q), 134.85 (q, ^4J_F = 3.0 Hz), 134.47 (q, ^4J_F = 3.0 Hz), 131.39, 129.32, 128.74, 127.91 (q), 126.13 (q), 125.78, 125.59, 123.86 (^3J_F = 8.4 Hz), 123.78, 123.36, 122.79, 121.89 (^3J_F = 8.0 Hz), 115.89 (^2J_F = 22.6 Hz), 115.80 (^2J_F = 22.5 Hz), 43.26 (CH_2). – MS *m/z* (%): 479 (1) [M^+], 248 (100), 230 (12). – $C_{28}H_{19}F_2N_5O$ (479.5): calcd. C 70.14, H 3.99, N 14.61; found C 69.94, H 4.00, N 14.64.

21d (R = *i*Pr): Yield 0.08 g (31%), white prisms, m.p. 142–144°C. – IR: ṽ = 3302, 3222, 1634, 1612, 1586, 1573, 1368, 1220, 1102, 985, 760, 734, 723 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 7.33 (td, ^3J = 8.1, ^4J = 1.3 Hz, 1H), 7.26–6.98 (m, 5H), 6.88 (d, ^3J = 8.4 Hz, 1H), 5.76 (d, ^2J = 14.7 Hz, 1H), 4.45 (br. s, 1H), 4.42–4.28 [m, 1H, C*H*(CH_3)$_2$], 4.14–4.11 [m, 1H, C*H*(CH_3)$_2$], 3.95 (d, ^2J = 14.7 Hz, 1H), 1.32–1.30 [m, 6H, 2 CH_3), 1.23 (d, ^3J = 6.3 Hz, 3H, CH_3), 0.88 (d, ^3J = 6.9 Hz, 3H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 168.25 (CO), 147.39 (q), 146.63 (q), 146.30 (q), 143.18 (q), 131.07, 129.66, 128.40, 127.99 (q), 125.95 (q), 125.51, 123.81, 123.19, 123.08, 123.03, 48.34 (CHN), 44.08 (CHN), 43.50 (CH_2), 22.29 (2 CH_3), 20.83 (CH_3), 20.11 (CH_3). – MS, *m/z* (%): 375 (3) [M^+], 249 (100), 248 (97). – $C_{22}H_{25}N_5O$ (375.5): calcd. C 70.38, H 6.71, N 18.65; found C 70.57, H 6.69, N 18.59.

23a (R = 4-$CH_3C_6H_4$): Yield 0.24 g (74%), colorless prisms, m.p. 238–239°C. – IR: ṽ = 3279, 1666, 1652, 1634, 1596, 1511, 1364, 1338, 1324, 1209, 820, 757 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 9.56 (s, 1H, NH), 7.56 (d, ^3J = 8.4 Hz, 2H), 7.44 (td, ^3J = 7.5, ^4J = 1.2 Hz, 1H), 7.32–7.26 (m, 3H), 7.19–7.09 (m, 6H), 7.03 (dt, ^3J = 7.5, ^4J = 1.2 Hz, 1H), 6.99 (dt, ^3J = 7.5, ^4J = 1.2 Hz, 1H), 6.82 (dd, ^3J = 7.5, ^4J = 1.2 Hz, 1H), 6.42 (dd, ^3J = 7.5, ^4J = 1.2 Hz, 1H), 4.92 (ddd, ^2J = 13.0, ^3J = 13.0, ^3J = 5.4 Hz, 1H, CH_2N), 3.83 (dd, ^2J = 13.0, ^3J = 6.6 Hz, 1H, CH_2N), 3.19 (ddd, ^2J = 13.0, ^3J = 13.0, ^3J = 6.6 Hz, 1H, C*H*$_2CH_2$), 2.93 (dd, ^2J = 13.0, ^3J = 5.4 Hz, 1H, C*H*$_2CH_2$), 2.26 (s, 3H, CH_3), 2.44 (s, 3H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 166.25 (CO), 146.75 (q), 146.26 (q), 145.26 (q), 143.25 (q), 137.20 (q), 136.17 (q), 135.66 (q), 131.73, 131.28 (q), 130.19 (q), 129.34, 129.11, 128.75, 128.69 (q), 127.61, 126.79, 125.13, 123.67, 123.08, 122.82, 122.43, 119.17, 51.96 (CH_2), 29.46 (CH_2), 20.46 (CH_3), 20.34 (CH_3). – MS, *m/z* (%): 485 (2) [M^+], 263 (85), 222 (100). – $C_{31}H_{27}N_5O$ (485.6): calcd. C 76.68, H 5.60, N 14.42; found C 76.46, H 5.62, N 14.45.

23b (R = 4-$CH_3OC_6H_4$): Yield 0.21 g (62%), colorless prisms, m.p. 146–148°C. – IR: ṽ = 3285, 1659, 1649, 1636, 1595, 1510, 1296, 1246, 1211, 1030, 832, 764 cm^{-1}. – ^1H NMR ([D_6]DMSO): δ = 9.48 (s, 1H, NH); 7.59 (d, ^3J = 8.4 Hz, 2H), 7.45 (t, ^3J = 7.5 Hz, 1H), 7.36–7.12 (m, 5H), 7.06–6.82 (m, 7H), 6.43 (d, ^3J = 8.1 Hz, 1H), 4.93–4.82 (m, 1H, CH_2), 3.73–3.71 (m, 7H, 2 CH_3O + CH_2), 3.21–3.09 (m, 1H), 2.85–2.77 (m, 1H). – ^{13}C NMR ([D_6]DMSO): δ = 166.28 (CO); 157.51 (q), 155.02 (q), 146.85 (q), 146.51 (q), 145.43 (q), 143.54 (q), 132.80 (q), 131.56, 131.27 (q), 130.19 (q), 128.83, 128.80 (q), 127.61, 126.91, 126.79, 123.55, 122.99 (2 CH), 122.43, 119.84, 113.88, 113.82, 55.25 (OCH_3), 55.17 (OCH_3), 52.01 (CH_2), 29.51 (CH_2). – MS, *m/z* (%): 517 (2) [M^+], 263 (26), 254 (44), 77 (100). – $C_{31}H_{27}N_5O_3$ (517.6): calcd. C 71.94, H 5.26, N 13.53; found C 72.14, H 5.24, N 13.49.

23c (R = 4-ClC_6H_4): Yield 0.29 g (83%), colorless prisms, m.p. 212–213°C. – IR: ṽ = 3279, 1666, 1652, 1632, 1596, 1492, 1392, 1337, 1322, 1210, 1094, 822, 764 cm^{-1}. – ^1H NMR ([D_6]DMSO): δ = 9.92 (s, 1H, NH), 7.71 (d, ^3J = 8.6 Hz, 2H), 7.49–7.02 (m, 12H), 6.82 (d, ^3J = 7.3 Hz, 1H), 6.44 (d, ^3J = 7.3 Hz, 1H), 4.92–4.87 (m, CH_2, 1H), 3.81–3.75 (m, CH_2, 1H), 3.20–3.13 (m, CH_2, 1H), 2.85–2.75 (m, CH_2, 1H). – ^{13}C NMR ([D_6]DMSO): δ = 166.27 (CO), 146.44 (q), 146.17 (q), 144.77 (q), 142.93 (q), 138.70 (q), 137.49 (q), 131.73, 130.58 (q), 130.39 (q), 129.14, 129.00, 128.76, 128.55 (q), 127.88, 126.99, 126.94, 126.71 (q), 124.22, 123.68, 122.91, 122.68, 120.73, 52.37 (CH_2), 29.62 (CH_2). – MS, *m/z* (%): 528 (3) [M^+ + 2], 526 (5) [M^+], 262 (19), 263 (59). – $C_{29}H_{21}Cl_2N_5O$ (526.4): calcd. C 66.17, H 4.02, N 13.30; found C 65.98, H 4.04, N 13.27.

N-Substituted 2-Azidobenzamide **25**: A solution of 4-aminobutyric acid (0.60 g, 6.00 mmol) in 2 N NaOH (10 ml) was cooled to 0°C, then *o*-azidobenzoyl chloride (1.10 g, 6.00 mmol) was added dropwise with stirring. The resultant mixture was stirred at 0°C for 1 h. 1 N HCl was added until pH = 6, and then the mixture was

extracted with dichloromethane (3 × 20 ml). The combined organic layers were dried with Na_2SO_4. The solvent was removed, and the residue was recrystallized from diethyl ether/*n*-hexane to give **25**: Yield 0.80 g (54%), colorless prisms, m.p. 79–81°C. – IR: $\tilde{\nu}$ = 3290, 2124, 2081, 1701, 1639, 1543, 1325, 1290, 1220, 1103, 934, 752, 700, 689 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 9.50 (br. s, 1H, CO_2H), 8.07 (dd, ^3J = 7.8, ^4J = 1.5 Hz, 1H), 7.66 (br. s, 1H, NH), 7.46 (dt, ^3J = 7.8, ^4J = 1.5 Hz, 1H), 7.22–7.14 (m, 2H), 3.53–3.47 (m, 2H), 2.43 (t, ^3J = 6.9 Hz, 2H), 1.94 (t, ^3J = 6.9 Hz, 2H). – ^{13}C NMR ($CDCl_3$): δ = 177.95 (q, CO_2H), 165.25 (q, CONH), 137.04 (q), 132.57, 132.20, 125.19, 124.73 (q), 118.39, 39.36 (CH_2NH), 31.53 (CH_2CO_2H), 24.64 ($CH_2CH_2CH_2$). – MS, *m/z* (%): 248 (2) [M^+], 220 (100), 146 (89), 118 (41). – $C_{11}H_{12}N_4O_3$ (248.2): calcd. C 53.22, H 4.87, N 22.57; found C 53.07, H 4.97, N 22.68.

Iminophosphorane **26** was prepared from **25** and triphenylphosphane by the method used for the preparation of **20** and **22**: Yield 1.31 g (85%), colorless crystals, m.p. 144–146°C. – IR: $\tilde{\nu}$ = 3256, 1726, 1580, 1546, 1345, 1274, 1159, 1109, 1011, 997, 758, 722, 694 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 10.80 (s, 1H), 8.22 (d, ^3J = 7.8 Hz, 1H), 7.78–7.46 (m, 15H), 6.93 (t, ^3J = 7.8 Hz, 1H), 6.75 (t, ^3J = 7.8 Hz, 1H), 6.46 (d, ^3J = 7.8 Hz, 1H), 3.44 (t, ^3J = 6.6 Hz, 2H), 2.33 (t, ^3J = 6.6 Hz, 2H), 1.76 (t, ^3J = 6.6 Hz, 2H). – ^{13}C NMR ($CDCl_3$): δ = 176.36 (q) (CO_2H), 169.46 (q, CONH), 149.49 (q), 132.86 (^4J_P = 2.5 Hz), 132.49 (^2J_P = 10.0 Hz), 131.45, 129.48 (^3J_P = 12.4 Hz), 127.76, 122.37 (^3J_P = 11.0 Hz), 118.26, 38.68 (CH_2NH), 32.55 (CH_2CO_2H), 26.24 ($CH_2CH_2CH_2$). – MS, *m/z* (%): 380 (2), 277 (81), 185 (100), 183 (71). – $C_{29}H_{27}N_2O_3P$ (482.5): calcd. C 72.19, H 5.64, N 5.81; found C 71.96, H 5.66, N 5.84.

Preparation of Acyl Azide **27**: A mixture of **26** (0.72 g, 1.50 mmol) diphenylphosphoryl azide (6.10 g, 22.50 mmol), triethylamine (2.27 g), and dry benzene (40 ml) was stirred at room temp. for 24 h. The solution was concentrated to dryness, and the residual material was chromatographed on a silica gel column by using ethyl acetate/*n*-hexane (3:1) as eluent to give **27**: Yield 0.36 g (48%), yellow prisms, m.p. 107–109°C. – IR: $\tilde{\nu}$ = 3284, 2136, 1716, 1617, 1544, 1350, 1275, 1230, 1110, 926, 759, 722, 692 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 11.55 (s, 1H, NH), 8.23 (d, ^3J = 7.6 Hz, 1H), 7.73–7.36 (m, 15H), 6.92 (t, ^3J = 7.6 Hz, 1H), 6.75 (t, ^3J = 7.6 Hz, 1H), 6.45 (d, ^3J = 7.6 Hz, 1H), 3.42 (t, ^3J = 6.1 Hz, 2H), 3.20 (t, ^3J = 6.1 Hz, 2H), 1.56 (quint, ^3J = 6.1 Hz, 2H). – ^{13}C NMR ($CDCl_3$): δ = 169.16 (q, CONH), 156.35 (q, CON_3), 149.79 (q), 132.46, 132.36 (^2J_P = 9.8 Hz), 131.34 (^4J_P = 1.5 Hz), 131.04, 129.31 (^1J_P = 99.3 Hz), 129.02 (^3J_P = 12.1 Hz), 122.53 (^3J_P = 11.8 Hz), 117.75, 37.40 (CH_2NH), 35.57 (CH_2CO_2H), 29.97 ($CH_2CH_2CH_2$). – MS, *m/z* (%): 507 (2) [M^+], 277 (75), 183 (40), 77 (100). – $C_{29}H_{26}N_5O_2P$ (507.5): calcd. C 68.63, H 5.16, N 13.8, found C 68.44, H 5.17, N 13.83.

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[75/93]