Synthetic Applications of Bis(iminophosphoranes). One-Pot Preparation of Rigid Bicyclic Guanidines

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A one-pot synthesis of [6 + 6], [6 + 7], and [6 + 8] bicyclic guanidines based on a new method of dihydropyrimido annelation, which involves reaction of bis(iminophosphoranes) with aryl isocyanates or isothiocyanates is described. The method is also applicable for the preparation of chiral bicyclic guanidines.

Compounds containing a cyclic guanidine moiety are of considerable interest because of a range of biological activities, as versatile very strong organic bases,[1] and because they serve as binding sites for anionic functional groups.[2] In this context, rigid bicyclic guanidines have been utilized as enantioselective and/or substrate specific oxoanion hosts.[3] The cyclic guanidines saxitoxin, ptilocaulin, and tetrodotoxin are potent ion-channel blockers, and the polycyclic marine-derived guanidine ptilomycalin A has been reported to exhibit remarkable antitumor, antiviral, and antifungal activities.[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 open-chain triamine precursor[5] or an intramolecular cyclization of alkenylated monocyclic guanidines via aminomercuration.[6]

Continuing our interest on the preparation and synthetic applications of bis(iminophosphoranes), we have shown that *C,N*-bis(iminophosphoranes) are useful building blocks for the one-pot preparation of fused benzotriazepines.[7] In addition, *C,C*-bis(iminophosphoranes), in which one iminophosphorane group is directly linked to an aromatic or heteroaromatic ring and the other is on a vinyl side chain, undergo a plethora of heterocyclization reactions via multistep processes to give complex nitrogen-containing heterocyclic systems.[8]

In this paper, we describe a new one-pot preparation of bicyclic guanidines starting from appropriate *C,C*-bis(iminophosphoranes) in which both iminophosphorane groups are directly linked to different aromatic or heteroaromatic rings. This new annelation approach, which involves as the key step a consecutive aza Wittig-type reaction/[2 + 2] cycloaddition/transannular dihydropyrimido annelation process, has surprisingly been found to be useful in the simultaneous formation of two fused dihydropyrimidine rings in the synthesis of bicyclic guanidines.

Results and Discussion

The key intermediates bis(iminophosphoranes) **4** were easily prepared in 60–90% overall yields by condensation of the appropriate *o*-azidobenzylamines **1** with *o*-azidocarbonyl compounds **2** to give the bis(azides) **3**, which by sequential treatment with triphenylphosphine and reduction with sodium borohydride led to **4**. The bis(iminophosphorane) **4a** was prepared in 90% yield by Staudinger reaction of bis(*o*-azidobenzyl)amine, available from *o*-azidobenzyl chloride and ammonia, with triphenylphosphine in ether at room temperature.

Reaction of bis(iminophosphoranes) **4** with 2 equiv of aryl isocyanate (*p*-tolyl, *p*-fluoro, *p*-chloro, or *p*-methoxyphenyl) in benzene at room temperature for a short period of time gave directly the bicyclic guanidines **5**, which were isolated as crystalline solids in 43–68% yields (Scheme I, Table I), the corresponding diarylcarbodiimide, and triphenylphosphine oxide. Similar results were achieved when aryl isothiocyanates were used instead of aryl isocyanates. However, when aliphatic (e.g., ethyl, isopropyl) or electron-withdrawing substituted isocyanates or isothiocyanates (e.g., benzoyl, benzenesulfonyl, or ethoxycarbonyl) were used a complex mixture was obtained in which the bicyclic guanidine **5** could not be detected.

In an analogous reaction sequence the related bis(azides) **6** and **9**, readily available from *o*-azidobenzylamines **1** and 5-azido-4-formyl-3-methyl-1-phenyl-1*H*-pyrazole or 4-azido-5-formyl-2-phenylthiazole,[9] respectively, also resulted in the smooth formation of the bis(iminophosphoranes) **7** and **10**, which were converted into the previously unreported bicyclic guanidines **8** and **11** in 41–77% yields (Scheme II, Table I) by treatment with 2 equiv of aryl isocyanate or isothiocyanate.

^{1}H and ^{13}C NMR spectra of **8** and **11** exhibited signals very similar to those of compounds **5**. Likewise, microanalytical and spectral data confirmed the structure shown (see Experimental Section). In the ^{1}H NMR spectra of

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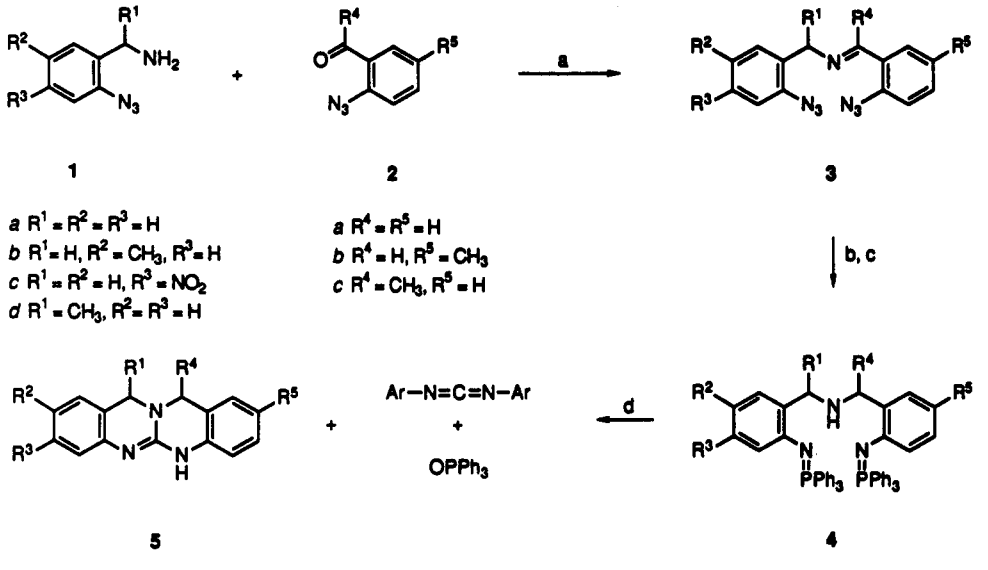
(9) Molina, P.; Arques, A.; Vinader, M. V.; Becher, J.; Brondum, K. *J. Org. Chem.* **1988**, *53*, 4654.

0022-3263/93/1958-1687$04.00/0

Scheme I[a]



1

a $R^1 = R^2 = R^3 = H$
b $R^1 = H, R^2 = CH_3, R^3 = H$
c $R^1 = R^2 = H, R^3 = NO_2$
d $R^1 = CH_3, R^2 = R^3 = H$

2

a $R^4 = R^5 = H$
b $R^4 = H, R^5 = CH_3$
c $R^4 = CH_3, R^5 = H$

3

b, c

4

5

a $R^1 = R^2 = R^3 = R^4 = R^5 = H$
b $R^1 = CH_3, R^2 = R^3 = R^4 = H, R^5 = CH_3$
c $R^1 = CH_3, R^2 = R^3 = H, R^4 = CH_3, R^5 = H$
d $R^1 = R^2 = R^3 = R^4 = H, R^5 = CH_3$
e $R^1 = H, R^2 = CH_3, R^3 = R^4 = H, R^5 = CH_3$
f $R^1 = R^2 = R^3 = H, R^4 = CH_3, R^5 = H$

[a]Reagents: (a) EtOH, cat. AcOH, r.t. for $R^4 = H$; Et_2O, Na_2SO_4 / $MgSO_4$, r.t. for $R^4 = CH_3$; (b) Triphenylphosphine, CH_2Cl_2 / Et_2O, r.t.; (c) $NaBH_4$, CH_2Cl_2 / MeOH, 0 °C; (d) 2 equiv. Ar-NCO, C_6H_6, r.t.

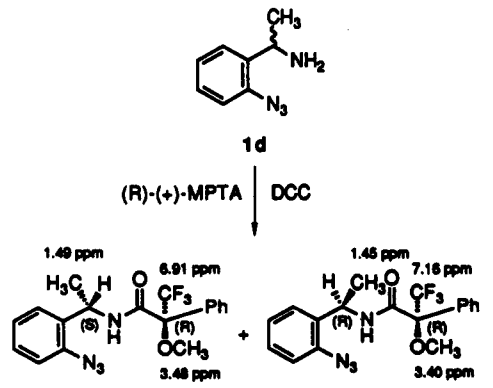
Table I. Bicyclic Guanidines 5, 8, 11, 21, and 23

compd	R^1	R^2	R^3	R^4	R^5	yield, %	mp, °C
5a	H	H	H	H	H	45	229–231
5b	CH_3	H	H	H	CH_3	68	218–220
5c	CH_3	H	H	CH_3	H	68	87–89
5d	H	H	H	H	CH_3	43	235–236
5e	H	CH_3	H	H	CH_3	58	263–265
5f	H	H	H	CH_3	H	57	105–106
8a	H	H	H			45	306–307
8b	H	CH_3	H			53	246–248
8c	H	H	NO_2			77	242–244
8d	CH_3	H	H			65	220–222
11a	H	H	H			57	250–251
11b	H	CH_3	H			41	247–248
21a				H	H	61	161–162
21b				H	CH_3	63	105–106
21c				CH_3	H	59	97–98
23a				H	H	33	289–290
23b				H	CH_3	42	298–299

the guanidines the NH proton appears as only one signal in the range 8.68–9.99 ppm; this means that either only one tautomer exists in solution or the tautomeric equilibrium is so fast that it is not observable in the NMR time scale. In spite of the moderate yields, this experimentally convenient sequence provides direct access to bicyclic guanidines in a one-step process. In almost all cases the conversion 1 + 2 → 5 was performed as a one-flask reaction without isolation of the intermediates 3 and 4.

In general, this annelation reaction proceeded without complications in a range of substrates. Table I presents some of the bicyclic guanidines rendered readily available via this methodology.

Having established that the reaction of bis(iminophosphoranes) type 4 with aryl isocyanates provides bicyclic guanidines, we considered the suitability of this reaction for the synthesis of chiral bicyclic guanidines. To this end the previously unreported (*S*)-(−)-1-(*o*-azidophenyl)-ethylamine (**12**) was prepared from *o*-azidobenzaldehyde **2a**. Reaction of aldehyde **2a** with methylmagnesium iodide at 0 °C produced 1-(*o*-azidophenyl)ethanol in a yield of 49%. Mitsunobu reaction[10] of the carbinol with PPh_3–diethyl azodicarboxylate (DEAD)–phthalimide (63%) followed by hydrazinolysis (93%) afforded 1-(*o*-azidophenyl)ethylamine (**1d**). The amine was then converted to its mandelate salt with (*R*)-(−)-mandelic acid. Three recrystallizations followed by liberation of the free base with 1 N NaOH afforded (*S*)-(−)-1-(*o*-azidophenyl)ethylamine (**12**) of 97% ee. The enantiomeric excess and configuration of the chiral amine were determined by conversion of **1d** and **12** to the corresponding Mosher amines with (*R*)-(+)-MPTA and DCC. Comparison of the ^1H and ^{19}F NMR spectra of the diastereomeric amides derived from the racemic amide **1d** revealed the following chemical shifts.



The relative shift patterns are consistent with the configurations assigned to the structures shown above.[11] The Mosher amide derived from (*R*)-(+)-MPTA and the optically active amine **12** showed only one set of signals, those corresponding to the (*S*,*R*) diastereomer, so we assign the (*S*)-configuration to the chiral amine **12**. The experimental setup would have allowed to us to see less than

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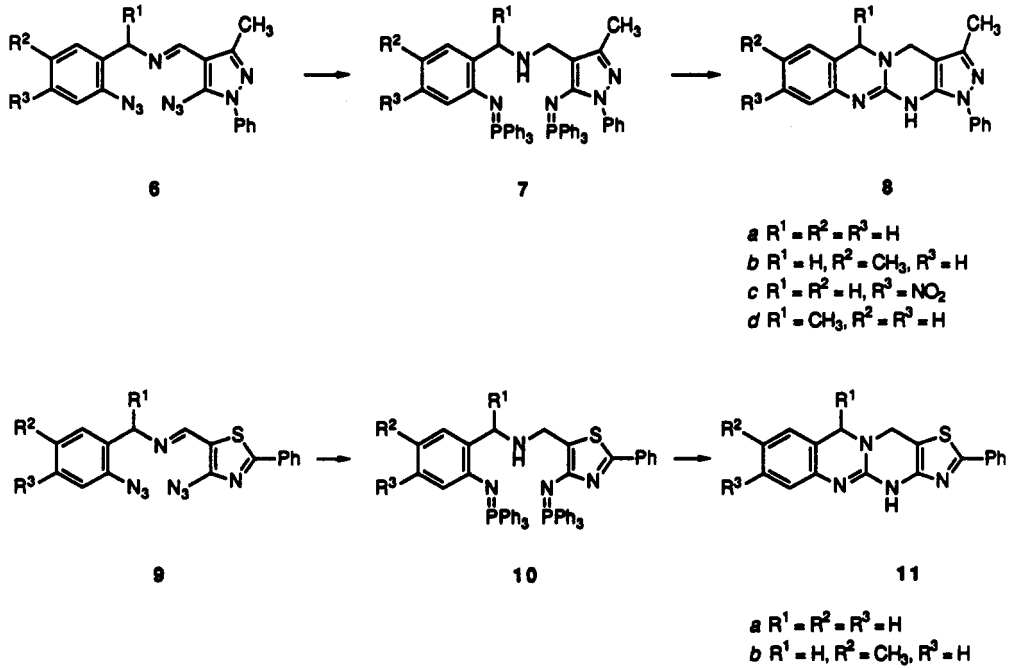
(11) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543.

Scheme II



6 7 8

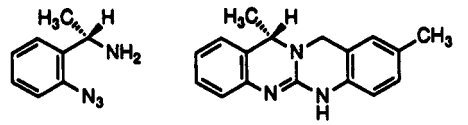
a $R^1 = R^2 = R^3 = H$
b $R^1 = H, R^2 = CH_3, R^3 = H$
c $R^1 = R^2 = H, R^3 = NO_2$
d $R^1 = CH_3, R^2 = R^3 = H$

9 10 11

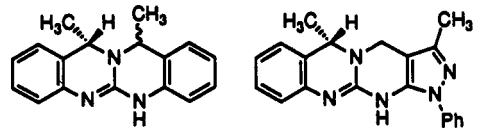
a $R^1 = R^2 = R^3 = H$
b $R^1 = H, R^2 = CH_3, R^3 = H$

3% of the other diastereomer, so that the lower limit of the enantiomeric purity of 12 can be set to ee > 97%.

Condensation of the amine 12 with the benzaldehyde derivative 2b followed by Staudinger reaction with triphenylphosphine, reduction with sodium borohydride, and finally reaction with 2 equiv of aryl isocyanate afforded the bicyclic guanidine 13 in an overall yield of 45%. In a similar way, using *o*-azidoacetophenone 2c or 4-formyl-3-methyl-1-phenyl-1*H*-pyrazole as the carbonyl component, the bicyclic guanidines 14 and 15 were obtained in an overall yield of 44% and 48%, respectively.



12 13



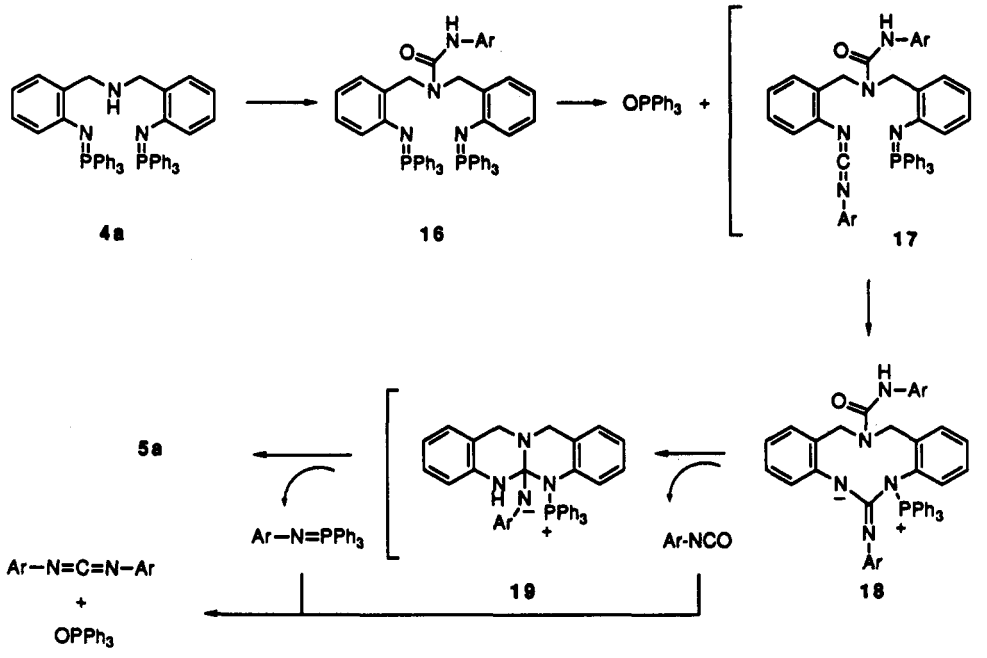
14 15

Since the chiral quaternary carbon center remained unaffected from 12 (ee > 97%) throughout all stages leading to 13–15, it is reasonable to assume this minimum value for the enantiomeric purity of guanidines 13–15 as well. Supplementary evidence is provided from the inspection of the ^1H NMR data of the complexation of racemic 5b and optically active 13 with (*R*)-(+)-MPTA. Carboxylates that are chiral at the α-carbon atom form diastereomeric host–guest complexes with chiral bicyclic guanidines,[3] which are readily distinguishable by NMR. Accordingly, our racemic target guanidine 5b furnished two well-separated doublets for the CH_3 group on mixing the respective solutions of host and guest in $CDCl_3$, whereas only one doublet was detected when optically active guanidine 13 was used as the host.

The ^1H NMR spectra of guanidines 5b, 5f, 8d, 13, and 15, which possess an asymmetric carbon atom, merit some comments. The proton spectra of guanidines 5b, 5f, and 13 recorded at 298 K show the geminal protons of the methylene group as a singlet: the two protons are magnetically equivalent, and they would be expected to appear as two doublets corresponding to a AB system because these protons occupy diastereotopic positions. However, for the guanidines 8d and 15 these protons appear as two doublets with a geminal coupling constant of 11.2 Hz at the same temperature. ^1H NMR spectra of 13 at low temperature (223 K) show the expected multiplicity for the protons of the methylene group with a coupling constant of 14.3 Hz. In this spectrum on going from 223 to 298 K an increase in the central bands at the expense of the outer components in the two doublets was observed, and they coalesce to a singlet at 298 K. On the other hand, the ^1H NMR spectrum of 15 at high temperature (433 K) still shows the methylene protons as two doublets.

Bis(iminophosphorane) 4a was reacted with 1 equiv of *p*-tolylisocyanate to give 16, which can be alternatively prepared from bis(*o*-azidobenzyl)amine by reaction with *p*-tolylisocyanate at room temperature and further Staudinger reaction with triphenylphosphine. Compound 16 was recovered unchanged after heating in benzene at reflux temperature for 2 h; however, it does react with 1 equiv of *p*-tolylisocyanate at room temperature to give the bicyclic guanidine 5a and bis(*p*-tolyl)carbodiimide. The same bicyclic guanidine and *N*-(*p*-tolyl)-*N'*-(*p*-methoxyphenyl)carbodiimide were obtained when compound 16 was treated with *p*-methoxyphenyl isocyanate. These observations suggest a probable mechanism for the conversion 4 → 5, 7 → 8, and 10 → 11 involving initial addition of 1 equiv of the isocyanate on the secondary amino group of 4a to give 16. An aza Wittig-type reaction between one iminophosphorane group of 16 and the second equivalent of the isocyanate leads to 17 and intramolecular [2 + 2] cycloaddition between the carbodiimide and the iminophosphorane moieties, and further P–N bond cleavage

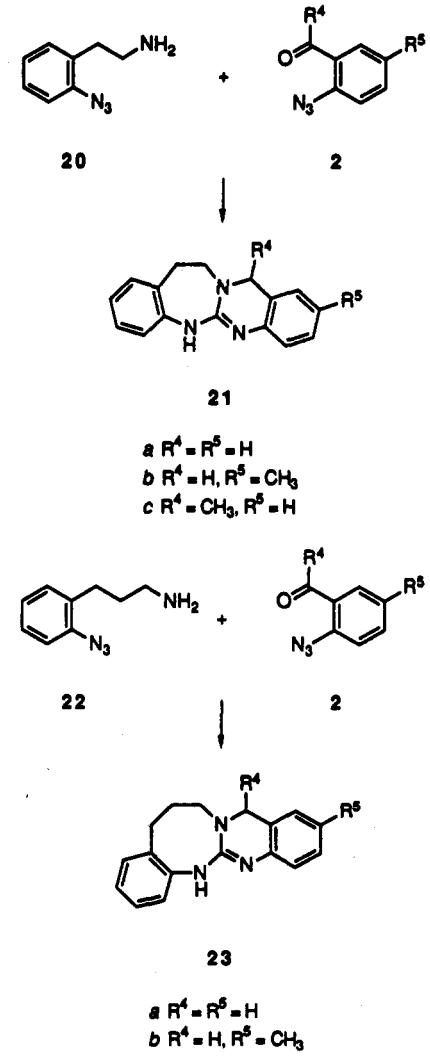
Scheme III



affords the intermediate betaine 18.[12] Molecular models of compound 18 revealed that the amino group of the carbamoyl function and the negative nitrogen atom of the guanidine portion are very close. As a consequence, elimination from 18 of 1 equiv of isocyanate, promoted by the negative nitrogen atom of the guanidine portion, with concomitant transannular nucleophilic attack of the nitrogen atom of the amino group on the central carbon atom of the guanidine portion takes place to give 19, which by loss of (*N*-arylimino)phosphorane leads to **5a**. Further reaction of the aryl isocyanate with the (*N*-arylimino)-phosphorane yields the diarylcarbodiimide[13] (Scheme III).

Varying the length of the amino-bearing side chain in the component 1 was effective in producing bicyclic guanidines of varying ring size and complexity (Scheme IV). The 2-(*o*-azidophenyl)ethylamine (**20**) was successfully employed in the preparation of [6 + 7] bicyclic guanidines **21**. The amine **20** was prepared from 2-(*o*-azidophenyl)ethanol[14] by reaction with PPh_3–DEAD–phthalimide (64%) and further hydrazinolysis (83%). Starting from the amine **20** and the corresponding carbonyl compound **2** the [6 + 7] bicyclic guanidines **21** were obtained, albeit in moderate yields (Table I), in one-flask reactions using the methodology described for the conversion **1** + **2** → **5**. Similarly, the [6 + 8] bicyclic guanidines **23** were obtained in moderate yields (Table I) from 3-(*o*-azidophenyl)propylamine **22**, available from 3-(*o*-aminophenyl)propanol[15] by standard chemistry: diazotization followed by azidation (45%), reaction with PPh_3–DEAD–phthalimide (74%), and finally hydrazinolysis (92%).

Scheme IV



a $R^4 = R^5 = H$
b $R^4 = H$, $R^5 = CH_3$
c $R^4 = CH_3$, $R^5 = H$

a $R^4 = R^5 = H$
b $R^4 = H$, $R^5 = CH_3$

Concluding Remarks

The methodology described in this paper affords a simple but effective new and general route to bicyclic

(12) It has been described that the reaction between iminophosphoranes and carbodiimides yields 1,2,4-phosphadiazetidines as intermediates, which undergo reactions to give different products depending on the nature of the starting materials: Huisgen, R.; Wulff, J. *Chem. Ber.* **1969**, *102*, 1948. Bödeker, J.; Köckritz, P.; Courault, K. *Z. Chem.* **1979**, *19*, 59. Molina, P.; Alajarín, M.; López-Leonardo, C.; Claramunt, R. M.; Foces-Foces, M. C.; Cano, F. H.; Catalán, J.; de Paz, J. L. G.; Elguero, J. *J. Am. Chem. Soc.* **1989**, *111*, 355.

(13) Molina, P.; Alajarín, M.; Arques, A.; Saez, J. *Synth. Commun.* **1982**, *12*, 573.

(14) Smith, P. A. S.; Shang-Shing, P. C. *J. Org. Chem.* **1981**, *46*, 3970.

(15) Kao, Y. S.; Lee, M. K. *Hua Hsüeh Hüeh Pao* **1956**, *22*, 32; *Chem. Abstr.* **1958**, *52*, 6251h.

guanidines with variable substituents and ring size forming part of new tetracyclic ring systems. These relatively complex structures, which would be difficult to prepare by classical synthetic routes, are assembled in a simple one-pot procedure in moderate yields and mild reaction conditions and from readily available starting materials. We are continuing to explore the scope and generality of this strategy, and we hope that it would find further useful applications to produce compounds of demonstrated utility in complexation studies.

Experimental Section

General Methods. All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. IR spectra were obtained as Nujol emulsions on a Nicolet FT-5DX spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 and on a Varian Unity-300, and chemical shifts are expressed in parts per million (δ) relative to tetramethylsilane. ^{31}P NMR spectra were observed at 121.42 MHz, and chemical shifts are referenced to 85% H_3PO_4. ^{19}F NMR spectra were observed at 282.20 MHz, and chemical shifts are referenced to CF_3COOH. Electron-impact mass spectra were carried out on a Hewlett-Packard 5993C spectrometer at an ionization potential of 70 eV. Microanalyses were performed on a Perkin-Elmer 240C instrument. Optical rotations were recorded on a Perkin-Elmer 241 polarimeter.

Materials. *o*-Azidobenzylamine[16] (**1a**), *o*-azidobenzaldehyde[17] (**2a**), 2-azido-5-methylbenzaldehyde[18] (**2b**), *o*-azidoacetophenone[19] (**2c**), 5-azido-4-formyl-3-methyl-1-phenyl-1*H*-pyrazole,[9] and 4-azido-5-formyl-2-phenylthiazole[9] were prepared as described in the literature.

Preparation of 2-Azido-5-methylbenzylamine (1b). To an ice-cooled solution of 2-azido-5-methylbenzyl alcohol[18] (4.89 g, 30 mmol) in 40 mL of dry dichloromethane was added thionyl chloride (4.16 g, 35 mmol) dropwise. The reaction mixture was stirred at 0 °C for 3 h, the solvent was removed, and the residue was purified by column chromatography (silica gel; benzene/n-hexane (1:1)) to give **2-azido-5-methylbenzyl chloride**: yield 82%; oil; IR 2128, 2086, 1501, 1299 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.31 (s, 3 H), 4.51 (s, 2 H), 7.03 (d, 1 H, J = 7.8 Hz), 7.15 (d, 1 H, J = 7.8 Hz), 7.17 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.7, 41.5, 118.3, 128.2 (s), 130.7, 131.6, 134.9 (s), 135.7 (s); mass spectrum m/z (relative intensity) 183 (M^+ + 2, 21), 181 (M^+, 72), 153 (100). Anal. Calcd for $C_8H_8ClN_3$: C, 52.90; H, 4.44; N, 23.13. Found: C, 52.84; H, 4.37; N, 23.05.

A mixture of 2-azido-5-methylbenzyl chloride (4.54 g, 25 mmol) and potassium phthalimide (5.55 g, 30 mmol) in 30 mL of dimethylformamide was heated at 80 °C for 12 h, with vigorous stirring. The cooled mixture was poured into ice/water, and the resulting precipitate was collected, washed with water, dried, and recrystallized from chloroform/ether to give ***N*-(2-azido-5-methylbenzyl)phthalimide** (4.31 g, 59%) as white needles of mp 173–174 °C.

N-(2-Azido-5-methylbenzyl)phthalimide was dissolved in 75 mL of ethanol, and 85% aqueous hydrazine (5 mL) was added. The mixture was stirred at reflux temperature for 3 h. After cooling, the precipitate that formed was dissolved by adding 50 mL of 10% sodium hydroxide solution. The resulting solution was extracted with dichloromethane (3 × 50 mL), and the extracts were dried over Na_2SO_4. The solvent was removed under reduced pressure and the resulting oil purified by column chromatography (silica gel; ethanol) to give 2-azido-5-methylbenzylamine (**1b**): yield 98%; oil; IR 3375, 3233, 2123, 2076, 1483, 1293 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.78 (s, 2 H), 2.30 (s, 3 H), 3.71 (s, 2 H), 6.98–7.08 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 20.6, 42.5, 117.8, 128.6, 129.7, 133.9 (s), 134.5 (s), 134.8 (s); mass spectrum m/z (relative intensity) 162 (M^+, 35), 134 (100). Anal. Calcd for $C_8H_{10}N_4$: C, 59.24; H, 6.21; N, 34.54. Found: C, 59.13; H, 6.10; N, 34.60.

Preparation of 2-Azido-4-nitrobenzylamine (1c). A mixture of 2-azido-1-methylnitrobenzene[20] (5.34 g, 30 mmol), *N*-bromosuccinimide (5.34 g, 30 mmol), and benzoyl peroxide (2.42 g, 10 mmo) in 50 mL of dry benzene was heated at reflux temperature for 4 h. After cooling, the mixture was poured into ether/water. The organic layer was separated, washed with water, and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the material was chromatographed (silica gel; benzene/n-hexane (1:4)) to give **2-azido-4-nitrobenzyl bromide**: yield 48%; mp 100–101 °C; colorless prisms; IR (Nujol) 2129, 1521, 1349 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.48 (s, 2 H), 7.57 (d, 1 H, J = 8.4 Hz), 7.96 (dd, 1 H, J = 2.2, 8.4 Hz), 8.01 (d, 1 H, J = 2.2 Hz), ^{13}C NMR ($CDCl_3$) δ 26.2, 113.5, 119.8, 132.0, 135.4 (s), 140.2 (s), 148.5 (s); mass spectrum m/z (relative intensity) 258 (M^+ + 2, 21), 256 (M^+, 23), 228 (100). Anal. Calcd for $C_7H_5BrN_4O_2$: C, 32.71; H, 1.96; N, 21.79. Found: C, 32.65; H, 1.91; N, 21.64.

2-Azido-4-nitrobenzyl bromide was treated in the same way as 2-azido-5-methylbenzyl chloride to give 2-azido-4-nitrobenzylamine (**1c**): overall yield 55%; oil; IR 2129, 1517, 1347 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.06 (s, 2 H), 3.88 (s, 2 H), 7.54 (d, 1 H, J = 7.8 Hz), 7.97 (d, 1 H, J = 7.8 Hz), 7.92 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 42.0, 113.0, 119.9, 129.5, 139.4 (s), 141.2 (s), 147.6 (s); mass spectrum m/z (relative intensity) 193 (M^+, 11), 175 (100).

Preparation of Racemic 1-(*o*-Azidophenyl)ethylamine (1d). *o*-Azidobenzaldehyde (5.88 g, 40 mmol) was dissolved in 100 mL of dry ether and cooled to 0 °C. A solution of methylmagnesium iodide (80 mmol) was added dropwise, under nitrogen. The reaction mixture was stirred at 0 °C for 1 h and then 1 h at room temperature. After the mixture was recooled to 0 °C, the reaction was quenched by addition of 1 N HCl (100 mL) and then water (100 mL). The organic layer was separated, the aqueous layer was extracted two more lines (CH_2Cl_2, 100 mL), and the combined organics were dried over $MgSO_4$. The solvent was concentrated to dryness, and the residue was chromatographed (silica gel, ether/n-hexane (1:)) to give **1-(*o*-azidophenyl)ethanol**: yield 49%; oil; IR 3455, 2129, 1297 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.44 (d, 3 H, J = 6.5 Hz), 2.44 (s, 1 H), 5.05 (q, 1 H, J = 6.5 Hz), 7.14 (t, 2 H, J = 7.6 Hz), 7.28 (d, 1 H, J = 7.6 Hz), 7.45 (d, 1 H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$) δ 23.7, 65.7, 117.9, 125.1, 126.5, 128.4, 136.3 (s), 136.8 (s); mass spectrum m/z (relative intensity) 163 (M^+, 29), 120 (100), 106 (46). Anal. Calcd for $C_8H_9N_3O$: C, 58.88; H, 5.56; N, 25.75. Found: C, 58.75; H, 5.50; N, 25.63.

To a solution of triphenylphospine (5.90 g, 22.5 mmol) in 50 mL of dry tetrahydrofuran at 0 °C was added diethyl azodicarboxylate (3.91 g, 22.5 mmol). This mixture was stirred 30 min at that temperature, and then 1-(*o*-azidophenyl)ethanol (2.44 g, 15 mmol) and phthalimide (3.31 g, 22.5 mmol) were added. The reaction mixture was stirred 1 h at 0 °C and 24 h at room temperature. The solvent was removed, and the residue was chromatographed (silica gel; ethyl acetate/n-hexane (1:4)) to obtain ***N*-[1-(*o*-azidophenyl)ethyl]phthalimide**: yield 63%; mp 129–130 °C; colorless prisms (ethyl acetate/n-hexane); IR (Nujol) 2137, 2112, 1711 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.81 (d, 3 H, J = 7.2 Hz), 5.72 (q, 1 H, J = 7.2 Hz), 7.06–7.19 (m, 2 H), 7.26–7.35 (m, 1 H), 7.65–7.81 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 17.6, 44.5, 118.0, 123.2, 124.6, 129.0, 129.1, 130.7 (s), 131.9 (s), 133.9, 137.7 (s), 167.9 (s); mass spectrum m/z (relative intensity) 292 (M^+, 5), 97 (35), 69 (100). Anal. Calcd for $C_{16}H_{12}N_4O_2$: C, 65.75; H, 4.14; N, 19.16. Found: C, 65.71; H, 4.11; N, 19.03.

Hydrazine hydrate (7.5 equiv) was added to a solution of *N*-[1-(*o*-azidophenyl)ethyl]phthalimide (2.92 g, 10 mmol) in 100 mL of tetrahydrofuran and 16 mL of ethanol. After 16 h at room temperature the suspension was heated at 70 °C for 8 h. After cooling, the mixture was filtered, the solid was washed with tetrahydrofuran, and the solvent was removed from the filtrate. The resulting material was purified by chromatography (silica gel; ethyl acetate/methanol (1:1)) to afford racemic 1-(*o*-azidophenyl)ethylamine (**1d**): yield 93%; oil; IR 3381, 3279, 2128 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (d, 3 H, J = 6.6 Hz), 2.15 (s, 2 H),

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4.30 (q, 1 H, J = 6.6 Hz), 7.12 (t, 2 H, J = 7.5 Hz), 7.26 (t, 1 H, J = 7.5 Hz), 7.41 (d, 1 H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 23.6, 46.1, 118.0, 124.9, 126.2, 127.8, 136.7 (s), 138.3 (s); mass spectrum m/z (relative intensity) 162 (M^+, 5), 149 (33), 119 (100). Anal. Calcd for $C_8H_{10}N_4$: C, 59.24; H, 6.21; N, 34.54. Found: C, 59.15; H, 6.12; N, 34.50.

Mosher amide of **1d**: ^{1}H NMR ($CDCl_3$) δ 1.45 (d, 3 H, J = 6.9 Hz), 1.49 (d, 3 H, J = 6.9 Hz), 3.40 (s, 3 H), 3.48 (s, 3 H), 5.22–5.28 (m, 2 H), 7.05–7.56 (m, 20 H); ^{19}F NMR ($CDCl_3$) δ 6.91, 7.16.

Preparation of (*S*)-(−)-1-(*o*-Azidophenyl)ethylamine (12). The amine **1d** (1.05 g and (*R*)-(−)-mandelic acid (0.99 g) were dissolved in a hot mixture of ethyl acetate (100 mL) and methanol (2 mL). The solution was cooled to room temperature. After 3 h the supernatant liquid was separated and the white solid was recrystallized from ethyl acetate (60 mL) and methanol (1 mL). After 4 h at room temperature the separated solid was filtered and dried to give 0.90 g of the amine–mandelate salt. The salt was suspended in 40 mL of dichloromethane, 1 N NaOH (40 mL) was added, and the mixture was stirred for 35 min. The organic layer was separated, the aqueous layer was extracted two more times (CH_2Cl_2, 20 mL), and the combined organic extracts were dried over $MgSO_4$. The solvent was removed to give (*S*)-1-(*o*-azidophenyl)ethylamine (0.42 g, 90%). The α-methoxy-α-phenyl-α-(trifluoromethyl)acetamide of this material was prepared from (*R*)-(+)-MPTA and DCC and analyzed by ^{1}H NMR to reveal a diastereomeric ratio of 90:10, the major isomer corresponding to the (*S*)-1-(*o*-azidophenyl)ethylamine. A third recrystallization of the amine mandelate from ethyl acetate (50 mL) and methanol (0.5 mL) afforded 0.54 g of the salt, which upon basification provided (*S*)-(−)-1-(*o*-azidophenyl)ethylamine (**12**): $[\alpha]^{20}_D$ −15.9° [*c* 6.66 10^{-3} g/mL (CH_2Cl_2), 97% ee].

Mosher amide of **12**: ^{1}H NMR ($CDCl_3$) δ 1.49 (d, 3 H, J = 6.9 Hz), 3.48 (s, 3 H), 5.20–5.29 (m, 1 H), 7.07–7.42 (m, 10 H); ^{19}F NMR ($CDCl_3$) δ 6.91.

Preparation of Bis(*o*-azidobenzyl)amine. A mixture of *o*-azidobenzyl chloride (6.70 g, 40 mmol) and liquid ammonia was kept 48 h in a sealed tube stored at room temperature. The excess of ammonia was removed by evaporation, water (100 mL) was added, and the organic layers were extracted with dichloromethane (3 × 30 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was chromatographed (silica gel; ethyl acetate/n-hexane (1:1) and then ethanol) to give tris(*o*-azidobenzyl)amine (27%), bis(*o*-azidobenzyl)amine (37%), and *o*-azidobenzylamine (**1a**) (25%).

Bis(*o*-azidobenzyl)amine: yield 37%; mp 42–43 °C; colorless needles (ether); IR (Nujol) 3324, 2133 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.99 (s, 1 H), 3.70 (s, 4 H), 7.04–7.13 (m, 4 H), 7.23–7.33 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 48.9, 118.1, 124.7, 128.4, 130.3, 131.4 (s), 138.2 (s); mass spectrum m/z (relative intensity) 279 (M^+, 5), 106 (100), 91 (63). Anal. Calcd for $C_{14}H_{13}N_7$: C, 60.20; H, 4.69; N, 35.10. Found: C, 60.09; H, 4.65; N, 34.99.

General Procedure for the Preparation of the Imines 3, 6, and 9. Method A. To a solution of the corresponding aldehyde **2a**, **2b**, 5-azido-4-formyl-3-methyl-1-phenyl-1*H*-pyrazole, or 4-azido-5-formyl-2-phenylthiazole (10 mmol) in 25 mL of dry ethanol was added the corresponding benzylamine **1** (10 mmol) and a catalytic amount of acetic acid. The reaction mixture was stirred at room temperature for 12 h, and the separated solid was collected and crystallized.

Method B. A mixture of *o*-azidoacetophenone **2c** (0.80 g, 5 mmol) and the corresponding benzylamine **1** (5 mmol) was kept at room temperature, in the presence of 4Å molecular sieves and $MgSO_4$, until the band corresponding to the carbonyl group disappeared in the IR of the mixture. The ketimines prepared by this method (**3c**, **3f**) were used without purification in the next step.

3b: yield 82%; mp 59–60 °C; colorless prisms (ethanol); IR (Nujol) 2129, 1640 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.50 (d, 3 H, J = 6.6 Hz), 2.33 (s, 3 H), 4.85 (q, 1 H, J = 6.6 Hz), 7.03 (d, 1 H, J = 8.2 Hz), 7.11–7.29 (m, 4 H), 7.68 (dd, 1 H, J = 1.6, 7.7 Hz), 7.86 (d, 1 H, J = 1.6 Hz), 8.66 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.8, 23.8, 63.7, 118.1, 118.3, 125.1, 127.1 (s), 127.9, 128.0, 128.1, 132.6, 134.7 (s), 136.4 (s), 136.8 (s), 137.1 (s), 155.7; mass spectrum m/z (relative intensity) 305 (M^+, 7), 234 (100), 91 (89). Anal. Calcd for $C_{16}H_{15}N_7$: C, 62.94; H, 4.95; N, 32.11. Found: C, 62.80; H, 4.89; N, 32.03.

3d: yield 85%; mp 58 °C; colorless prisms (ethanol); IR (Nujol) 2129, 2084, 1641 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.29 (s, 3 H), 4.69 (s, 2 H), 7.00–7.17 (m, 5 H), 7.41 (dt, 1 H, J = 1.6, 8.3 Hz), 8.03 (d, 1 H, J = 7.8 Hz), 8.67 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.9, 60.4, 118.0, 118.4, 124.9, 127.3 (s), 128.1, 129.0, 130.1 (s), 130.7, 131.8, 134.6 (s), 135.1 (s), 139.7 (s), 157.8; mass spectrum m/z (relative intensity) 291 (M^+, 5), 234 (100), 91 (65). Anal. Calcd for $C_{15}H_{13}N_7$: C, 61.85; H, 4.50; N, 33.66. Found: C, 61.78; H, 4.40; N, 33.74.

3e: yield 83%; mp 78 °C; colorless prisms (ethanol); IR (Nujol) 2129, 2095, 1643 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 6 H), 4.68 (s, 2 H), 7.00–7.24 (m, 5 H), 7.84 (d, 1 H, J = 2.2 Hz), 8.65 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.7, 20.9, 60.5, 118.0, 118.3, 126.9 (s), 128.2, 129.0, 130.1 (s), 130.8, 132.7, 134.6 (s), 134.7 (s), 135.2 (s), 137.1 (s), 158.0; mass spectrum m/z (relative intensity) 305 (M^+, 7), 248 (100), 91 (80). Anal. Calcd for $C_{16}H_{15}N_7$: C, 62.94; H, 4.95; N, 32.11. Found: C, 62.81; H, 4.89; N, 32.07.

6a: yield 81%; mp 97–98 °C; colorless needles (ethanol); IR (Nujol) 2194, 1649 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.42 (s, 3 H), 4.71 (s, 2 H), 7.07–7.59 (m, 9 H), 8.36 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.0, 60.8, 110.1 (s), 118.0, 124.0, 124.8, 127.7, 128.3, 128.9, 130.1, 130.8 (s), 136.5 (s), 137.8 (s), 149.7 (s), 153.3, one quaternary carbon was not observed; mass spectrum m/z (relative intensity) 357 (M^+, 7), 329 (86), 77 (100). Anal. Calcd for $C_{18}H_{15}N_9$: C, 60.50; H, 4.23; N, 35.27. Found: C, 60.47; H, 4.15; N, 35.19.

6b: yield 76%; mp 98 °C; colorless prisms (ethanol); IR (Nujol) 2135, 1652 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.26 (s, 3 H), 2.37 (s, 3 H), 4.63 (s, 2 H), 6.96–7.54 (m, 8 H), 8.32 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.1, 20.9, 61.0, 110.2 (s), 118.0, 124.1, 127.8, 129.0, 130.5 (s), 130.9, 134.6 (s), 135.1 (s), 136.6 (s), 137.9 (s), 149.8 (s), 153.2 (s), one aromatic CH was not observed; mass spectrum m/z (relative intensity) 371 (M^+, 5), 149 (100), 77 (91). Anal. Calcd for $C_{19}H_{17}N_9$: C, 61.45; H, 4.61; N, 33.94. Found: C, 61.34; H, 4.49; N, 33.85.

6c: yield 83%; mp 113–114 °C; colorless prisms (ethanol); IR (Nujol) 2146, 1644, 1290 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.44 (s, 3 H), 4.75 (s, 2 H), 7.32–7.65 (m, 6 H), 7.93–7.99 (m, 2 H), 8.42 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.1, 60.3, 109.9 (s), 112.8, 119.7, 124.1, 127.9, 129.0, 130.3, 136.7 (s), 137.7 (s), 138.3 (s), 139.1 (s), 147.6 (s), 149.9 (s), 154.6; mass spectrum m/z (relative intensity) 402 (M^+, 7), 183 (100), 163 (44). Anal. Calcd for $C_{18}H_{14}N_{10}O_2$: C, 53.73; H, 3.51; N, 34.81. Found: C, 53.61; H, 3.47; N, 34.70.

6d: yield 75%; mp 67–68 °C; colorless prisms (ethanol); IR (Nujol) 2130, 1639 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.51 (d, 3 H, J = 6.6 Hz), 2.40 (s, 3 H), 4.77 (q, 1 H, J = 6.6 Hz), 7.14 (t, 2 H, J = 7.9 Hz), 7.26 (td, 1 H, J = 1.6, 7.7 Hz), 7.33 (d, 1 H, J = 7.1 Hz), 7.43 (t, 2 H, J = 7.8 Hz), 7.56 (d, 2 H, J = 8.8 Hz), 7.72 (d, 1 H, J = 7.9 Hz), 8.37 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.0, 24.7, 64.9, 110.2 (s), 117.9, 124.1, 125.1, 127.7, 127.9, 128.2, 128.9, 136.3 (s), 136.5 (s), 136.6 (s), 137.9 (s), 149.9 (s), 151.1; mass spectrum m/z (relative intensity) 371 (M^+, 6), 118 (89), 91 (100). Anal. Calcd for $C_{19}H_{17}N_9$: C, 61.44; H, 4.61; N, 33.94. Found: C, 61.38; H, 4.50; N, 33.85.

9a: yield 93%; mp 114 °C; yellow needles (ethanol); IR (Nujol) 2121, 1623, 1284 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.68 (s, 2 H), 7.09–7.16 (m, 2 H), 7.29–7.33 (m, 2 H), 7.39–7.45 (m, 3 H), 7.91–7.94 (m, 2 H), 8.32 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 59.9, 118.1, 118.7 (s), 125.0, 126.5, 128.6, 129.1, 130.1, 131.3, 132.7 (s), 138.0 (s), 138.3 (s), 149.3 (s), 151.8, 168.8 (s); mass spectrum m/z (relative intensity) 360 (M^+, 5), 84 (100), 77 (87). Anal. Calcd for $C_{17}H_{12}N_8S$: C, 56.66; H, 3.36; N, 31.09. Found: C, 56.54; H, 3.29; N, 31.00.

9b: yield 86%; mp 131 °C; yellow prisms (ethanol); IR (Nujol) 2129, 1622, 1238 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 3 H), 4.64 (s, 2 H), 6.99–7.09 (m, 3 H), 7.37–7.47 (m, 3 H), 7.89–7.94 (m, 2 H), 8.31 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.9, 59.9, 118.0, 118.8 (s), 126.5, 129.1, 129.2, 129.7 (s), 130.8, 131.2, 132.6 (s), 134.7 (s), 135.2 (s), 149.3 (s), 151.6, 168.7 (s); mass spectrum m/z (relative intensity) 374 (M^+, 6), 145 (94), 83 (100). Anal. Calcd for $C_{18}H_{14}N_8S$: C, 57.74; H, 3.77; N, 29.93. Found: C, 57.65; H, 3.71; N, 29.87.

General Procedure for the Preparation of the Bis(iminophosphoranes) 4, 7, and 10. Method A. To a solution of triphenylphosphine (2.62 g, 10 mmol) in 25 mL of dry ether was added bis(*o*-azidobenzyl)amine (1.39 g, 5 mmol) in the same solvent. The reaction mixture was stirred at room temperature for 12 h, and the separated solid was filtered and crystallized. Only **4a** was prepared following this method.

Method B. To a solution of triphenylphosphine (2.62 g, 10 mmol) in 25 mL of dry ether was added the corresponding imine **3**, **6**, or **9** (5 mmol) in dichloromethane (10 mL). The reaction mixture was stirred at room temperature for 12 h. The solvent was removed to dryness and the resulting material was dissolved in a mixture of dry dichloromethane (20 mL) and dry methanol (20 mL). After cooling at 0 °C sodium borohydride (1.51 g, 40 mmol) was added. After 30 min a second batch of sodium borohydride (1.51 g, 40 mmol) was added, and stirring was continued 1 h. The solvent was removed under reduced pressure, and the residue was treated with cold water, filtered, and dried, initially at room temperature and then at 70 °C. Except for **4a** all the bis(iminophosphoranes) were prepared by this method.

4a: yield 90%; mp 115–117 °C; colorless prisms (benzene/n-hexane); IR (Nujol) 3296, 1438, 1109 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.11 (s, 1 H), 4.18 (s, 4 H), 6.42 (d, 2 H, J = 7.3 Hz), 6.55 (t, 2 H, J = 7.4 Hz), 6.74 (t, 2 H, J = 7.5 Hz), 7.17–7.43 (m, 20 H), 7.65–7.75 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 51.6, 117.1, 120.7 (d, J_{P-C} = 9.9 Hz), 126.3, 128.5 (d, J_{P-C} = 2.3 Hz), 128.5 (d, J_{P-C} = 11.9 Hz), 130.6 (one of the signals corresponding to the doublet of the C_i over the triphenylphosphine group, the other one was not observed), 131.4 (d, J_{P-C} = 2.8 Hz), 132.5 (d, J_{P-C} = 9.6 Hz), 134.9 (s, d, J_{P-C} = 21.4 Hz), 149.0 (s, d, J_{P-C} = 1.5 Hz); ^{31}P NMR ($CDCl_3$) δ 0.44; mass spectrum m/z (relative intensity) 199 (43), 183 (48), 152 (34), 133 (100), 91 (50). Anal. Calcd for $C_{50}H_{43}N_3P_2$: C, 80.30; H, 5.80; N, 5.62. Found: C, 80.17; H, 5.73; N, 5.56.

7a: yield 96%; mp 178–179 °C; colorless prisms (benzene/n-hexane); IR (Nujol) 3267, 1437, 1204, 1112 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.99 (s, 3 H), 3.21 (s, 2 H), 3.71 (s, 2 H), 6.42 (d, 1 H, J = 7.7 Hz), 6.55 (t, 1 H, J = 7.2 Hz), 6.75 (t, 1 H, J = 7.2 Hz), 6.94 (d, 1 H, J = 7.1 Hz), 7.05–7.57 (m, 29 H), 7.67–7.77 (m, 6 H), the NH was not observed clearly; ^{13}C NMR ($CDCl_3$) δ 13.0, 42.8, 51.6, 106.6 (s, d, J_{P-C} = 4.6 Hz), 116.8, 120.6 (d, J_{P-C} = 10.1 Hz), 125.3, 125.4, 126.4, 127.9, 128.3 (d, J_{P-C} = 12.1 Hz), 128.8 (d, J_{P-C} = 11.7 Hz), 128.8 (d, J_{P-C} = 2.6 Hz), 130.4 (one of the signals corresponding to the doublet of a C_i over the triphenylphosphine group, the other one was not observed), 130.6 (one of the signals corresponding to the doublet of a C_i over the triphenylphosphine group, the other one was not observed), 131.5 (d, J_{P-C} = 2.3 Hz, this signal include both C_P of the two triphenylphosphine groups), 132.5 (d, J_{P-C} = 9.2 Hz), 132.5 (d, J_{P-C} = 9.9 Hz), 134.5 (s, d, J_{P-C} = 22.1 Hz), 140.8 (s), 146.0 (s, d, J_{P-C} = 3.1 Hz), 148.1 (s, d, J_{P-C} = 2.2 Hz), 149.1 (s); mass spectrum m/z (relative intensity) 433 (20), 183 (62), 152 (23), 77 (92), 51 (100). Anal. Calcd for $C_{54}H_{47}N_5P_2$: C, 78.34; H, 5.72; N, 8.46. Found: C, 78.21; H, 5.63; N, 8.51.

10a: yield 96%; mp 132–133 °C; yellow prisms (benzene/n-hexane); IR (Nujol) 3279, 1438, 1111 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.06 (s, 1 H), 4.15 (s, 2 H), 4.16 (s, 2 H), 6.44 (d, 1 H, J = 7.8 Hz), 6.55 (t, 1 H, J = 7.3 Hz), 6.78 (t, 1 H, J = 7.6 Hz), 7.16–7.52 (m, 24 H), 7.67–7.85 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 44.6, 51.8, 117.2, 120.9 (d, J_{P-C} = 10.1 Hz), 125.2, 126.9, 128.2 (d, J_{P-C} = 12.1 Hz), 128.6 (d, J_{P-C} = 12.1 Hz), 129.9, 131.2 (d, J_{P-C} = 2.5 Hz), 131.4 (s, d, J_{P-C} = 99.2 Hz), 131.5 (d, J_{P-C} = 3.0 Hz), 131.6 (s, d, J_{P-C} = 99.7 Hz), 132.5 (d, J_{P-C} = 10.1 Hz), 133.1 (d, J_{P-C} = 9.6 Hz), 135.2 (s), 149.5 (s, d, J_{P-C} = 1.5 Hz), 157.1 (s, d, J_{P-C} = 6.0 Hz), 158.8 (s); mass spectrum m/z (relative intensity) 367 (9), 262 (100), 183 (94), 108 (24), 77 (15). Anal. Calcd for $C_{53}H_{44}N_4P_2S$: C, 76.61; H, 5.34; N, 6.74. Found: C, 76.53; H, 5.21; N, 6.59.

Bis(iminophosphoranes) **4b–4f**, **7b–7d**, and **10b** were used without purification in the next step.

General Procedure for the Preparation of Guanidines 5, 8, and 11. To a solution of the corresponding bis(iminophosphorane) **4**, **7**, or **10** (2 mmol) in 15 mL of dry benzene was added *p*-methylphenylisocyanate (4 mmol). The mixture was stirred at room temperature for 4 h. The guanidines were isolated from the reaction mixture using one of the following methods.

Method A. After the mixture was cooled, the separated solid was collected by filtration and recrystallized. This method was used for **8c**, **11a**, and **11b**.

Method B. After the mixture was cooled, the solvent was removed under reduced pressure, the resulting material was treated with *n*-hexane (3 × 25 mL), and the residue was chromatographed over silica gel using as eluent (a) ethanol for **5a**, **5d**, and **5e**, (b) ethanol/ether (1:1) for **5b**, **5c**, and **5f** and (c) ether for **8d**.

Method C. After the mixture was cooled, the solvent was removed under reduced pressure and the resulting material was treated with *n*-hexane (3 × 25 mL). The solid residue was dissolved in mixture of ethanol and ether (5/5 mL), and tetrafluoroboric acid (2 mL, 50% in water) was added. The precipitated solid was filtered and recrystallized. This method was used for **8a** and **8b**.

5a: yield 45%; mp 229–231 °C; colorless prisms (ethanol/ether); IR (Nujol) 1643, 1582, 1270 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.45 (s, 4 H), 6.75–7.09 (m, 8 H), 8.68 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 50.6, 118.1, 118.3 (s), 121.3, 125.2, 128.5, 140.4 (s), 149.9 (s); mass spectrum m/z (relative intensity) 235 (M^+, 70), 234 (100). Anal. Calcd for $C_{15}H_{13}N_3$: C, 76.57; H, 5.57; N, 17.86. Found: C, 76.67; H, 5.74; N, 17.64.

5b: yield 68%; mp 218–220 °C; colorless prisms (ethanol/ether); IR (Nujol) 1642, 1594, 1272 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.43 (d, 3 H, J = 6.6 Hz), 2.25 (s, 3 H), 4.46 (q, 1 H, J = 6.6 Hz), 4.55 (s, 2 H), 6.72 (d, 1 H, J = 8.0 Hz), 6.81 (s, 1 H), 6.85–6.89 (m, 3 H), 6.96 (d, 1 H, J = 7.7 Hz), 7.06 (t, 1 H, J = 7.3 Hz), 9.78 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.8, 21.6, 48.6, 56.2, 117.6, 118.5, 119.0 (s), 121.2, 124.4 (s), 125.1, 125.7, 128.2, 128.9, 130.5 (s), 137.4 (s), 139.9 (s), 149.0 (s); mass spectrum m/z (relative intensity) 263 (M^+, 32), 248 (100), 123 (45). Anal. Calcd for $C_{17}H_{17}H_3$: C, 77.53; H, 6.51; N, 15.95. Found: C, 77.43; H, 6.43; N, 15.83.

5c: yield 68%; mp 87–89 °C; colorless prisms; IR (Nujol) 1636, 1589, 1265 cm^{-1}; ^1H NMR ($CDCl_3$) δ diastereomer A 1.40 (d, 6 H, J = 6.6 Hz), 4.66 (q, 2 H, J = 6.6 Hz), diastereomer B 1.59 (d, 3 H, J = 6.6 Hz), 1.60 (d, 3 H, J = 6.6 Hz), 4.72 (q, 2 H, J = 6.6 Hz), for both diastereomers 6.88–7.14 (m, 16 H), 9.80 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ diastereomer A 22.7, 55.0, 118.2, 121.2, 125.0, 125.0 (s) or 126.2 (s), 128.2, 139.5 (s), 148.1 (s), diastereomer B 21.9, 22.1, 53.2, 118.0, 121.3, 125.0, 125.0 (s) or 126.2 (s), 128.1, 140.1 (s), 150.3 (s); mass spectrum m/z (relative intensity) 263 (M^+, 22), 248 (100), 77 (90). Anal. Calcd for $C_{17}H_{17}N_3$: C, 77.53; H, 6.51; N, 15.95. Found: C, 77.41; H, 6.44; N, 15.85.

5d: yield 43%; mp 235–236 °C; colorless prisms (ethanol); IR (Nujol) 1650, 1606, 1538 cm^{-1}; ^1H NMR ($CDCl_3$ + TFA) δ 2.28 (s, 3 H), 4.60 (s, 2 H), 4.63 (s, 2 H), 6.83–7.30 (m, 7 H), 9.81 (s, 1 H); ^{13}C NMR ($CDCl_3$ + TFA) δ 20.7, 49.7, 49.7, 115.3 (s), 115.5 (s), 115.9, 116.0, 125.7, 125.9, 126.3, 128.7 (s), 129.8, 130.4, 131.3 (s), 136.0 (s), 146.6 (s); mass spectrum m/z (relative intensity) 249 (M^+, 67), 248 (100). Anal. Calcd for $C_{16}H_{15}N_3$: C, 77.08; H, 6.06; N, 16.85. Found: C, 77.01; H, 5.97; N, 16.71.

5e: yield 58%; mp 263–265 °C; colorless prisms (ethanol); IR (Nujol) 1644, 1605, 1533 cm^{-1}; ^1H NMR ($CDCl_3$ + TFA) δ 2.31 (s, 6 H), 4.63 (s, 4 H), 6.81 (d, 2 H, J = 8.1 Hz), 6.91 (s, 2 H), 7.08 (d, 2 H, J = 8.1 Hz), 9.09 (s, 1 H); ^{13}C NMR ($CDCl_3$ + TFA) δ 20.6, 49.8, 115.4 (s), 115.8, 126.4, 128.6 (s), 130.5, 136.3 (s), 146.5 (s); mass spectrum m/z (relative intensity) 263 (M^+, 68), 262 (100), 145 (89). Anal. Calcd for $C_{17}H_{17}N_3$: C, 77.54; H, 6.51; N, 15.96. Found: C, 77.43; H, 6.40; N, 15.87.

5f: yield 57%; mp 105–106 °C; colorless prisms (chloroform/n-hexane); IR (Nujol) 1636, 1592 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.45 (d, 3 H, J = 6.4 Hz), 4.48 (q, 1 H, J = 6.4 Hz), 4.59 (s, 2 H), 6.80–7.13 (m, 8 H), 9.45 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 21.6, 48.5, 56.2, 117.7, 118.4, 119.0 (s), 121.2, 121.4, 124.3 (s), 125.1, 125.2, 128.2, 128.4, 139.4 (s), 139.8 (s), 149.0 (s); mass spectrum m/z (relative intensity) 249 (M^+, 25), 234 (100), 71 (41). Anal. Calcd for $C_{16}H_{15}N_3$: C, 77.08; H, 6.06; N, 16.85. Found: C, 77.00; H, 5.98; N, 16.77.

8a·HBF$_4$: yield 45%; mp 306–307 °C dec; colorless prisms (ethanol); IR (Nujol) 3228, 1623 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.18 (s, 3 H), 4.57 (s, 2 H), 4.61 (s, 2 H), 6.97–7.28 (m, 4 H), 7.41–7.66 (m, 5 H), 9.12 (s, 1 H), 10.41 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 11.4, 46.2, 49.6, 96.0 (s), 115.1, 117.2 (s), 122.6, 124.1, 125.9, 127.7, 128.7, 129.5, 132.8 (s), 136.6 (s), 139.2 (s), 143.4 (s), 148.8 (s). Anal. Calcd for $C_{19}H_{18}BF_4N_5$: C, 56.60; H, 4.50; N, 17.37. Found: C, 56.49; H, 4.39; N, 17.41.

8b·HBF$_4$: yield 53%; mp 246 °C dec; colorless prisms (ethanol); IR (Nujol) 3341, 1623, 1594 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.18 (s, 3 H), 2.24 (s, 3 H), 4.58 (s, 4 H), 5.56 (s, 1 H), 6.88 (d, 1 H, J = 8.0 Hz), 6.09–7.07 (m, 2 H), 7.38–7.67 (m, 5 H), 10.31 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 11.5, 20.3, 46.2, 49.6, 95.8 (s), 115.0, 117.0 (s), 122.4, 126.2, 127.4, 129.0, 129.4, 130.4 (s), 133.3 (s), 137.0 (s), 138.7 (s), 143.5 (s), 148:4 (s). Anal. Calcd for $C_{20}H_{20}BF_4N_5$: C, 57.58; H, 4.83; N, 16.79. Found: C, 57.49; H, 4.75; N, 16.71.

8c: yield 77%; mp 246 °C dec; orange prisms (benzene); IR (Nujol) 1634, 1589, 1579 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 2.07 (s, 3 H), 4.45 (s, 2 H), 4.53 (s, 2 H), 7.16 (t, 1 H, J = 7.4 Hz), 7.32–7.43 (m, 4 H), 7.72 (s, 1 H), 7.99 (d, 2 H, J = 8.2 Hz), 9.99 (s, 1 H); ^{13}C NMR (DMSO-d_6) δ 12.2, 47.0, 49.1, 94.2 (s), 107.8, 115.6, 120.2, 124.4, 124.6 (s), 126.8, 128.5, 137.6 (s), 139.9 (s), 142.9 (s), 146.3 (s), 147.5 (s), 148.9 (s); mass spectrum m/z (relative intensity) 360 (M$^+$, 5), 105 (46), 97 (54), 55 (100). Anal. Calcd for $C_{19}H_{16}N_6O_2$: C, 63.33; H, 4.48; N, 23.32. Found: C, 63.30; H, 4.39; N, 23.25.

8d: yield 65%; mp 220–222 °C; colorless prisms (chloroform/ether); IR (Nujol) 3216, 1632, 1576 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.39 (d, 3 H, J = 6.6 Hz), 2.25 (s, 3 H), 4.20 (q, 1 H, J = 6.6 Hz), 4.58 (d, 1 H, J = 11.2 Hz), 4.69 (d, 1 H, J = 11.2 Hz), 6.34 (d, 1 H, J = 7.9 Hz), 6.79–7.05 (m, 4 H), 7.27 (t, 2 H, J = 7.5 Hz), 7.90 (d, 2 H, J = 7.7 Hz), 9.12 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 12.6, 20.4, 46.0, 56.5, 94.5 (s), 113.8, 121.7, 121.9, 122.7 (s), 124.8, 125.2, 128.1, 128.5, 134.8 (s), 139.6 (s), 143.9 (s), 146.2 (s), 149.8 (s); mass spectrum m/z (relative intensity) 329 (M$^+$, 92), 328 (100), 77 (91). Anal. Calcd for $C_{20}H_{19}H_5$: C, 72.92; H. 5.81; N, 21.26. Found: C, 72.81; H, 5.73; N, 21.28.

11a: yield 57%; mp 250–251 °C; yellow prisms (benzene); IR (Nujol) 3250, 1624, 1603 cm^{-1}; ^{1}H NMR ($CDCl_3$ + TFA) δ 4.75 (s, 2 H), 4.91 (s, 2 H), 7.02–7.34 (m, 4 H), 7.49–7.64 (m, 3 H), 7.77 (d, 2 H, J = 7.5 Hz), 9.76 (s, 1 H); ^{13}C NMR ($CDCl_3$ + TFA) δ 48.1, 50.6, 103.1 (s), 115.5 (s), 116.3, 126.0, 126.9, 127.0, 128.8 (s), 130.0, 130.2, 130.3 (s), 133.4, 140.4 (s), 146.6 (s), 171.9 (s); mass spectrum m/z (relative intensity) 318 (M$^+$, 73), 317 (100), 91 (33). Anal. Calcd for $C_{18}H_{14}N_4S$: C, 67.90; H, 4.43; N, 17.60. Found: C, 67.75; H, 4.48; N, 17.48.

11b: yield 41%; mp 250 °C dec; yellow prisms (benzene); IR (Nujol) 3250, 1629, 1601 cm^{-1}; ^{1}H NMR ($CDCl_3$ + TFA) δ 2.31 (s, 3 H), 4.73 (s, 2 H), 4.91 (s, 2 H), 6.91–6.97 (m, 2 H), 7.13 (d, 1 H, J = 8.0 Hz), 7.51–7.67 (m, 3 H), 7.78 (d, 2 H, J = 7.7 Hz), 9.60 (s, 1 H); ^{13}C NMR ($CDCl_3$ + TFA) δ 20.6, 47.9, 50.7, 103.7 (s), 115.3 (s), 116.3, 126.4 (s), 127.1, 127.7, 128.5 (s), 130.1, 130.8, 133.7, 137.6 (s), 140.3 (s), 146.4 (s), 172.1 (s); mass spectrum m/z (relative intensity) 332 (M$^+$, 65), 331 (100). Anal. Calcd for $C_{19}H_{16}N_4S$: C, 68.65; H, 4.85; N, 16.85. Found: C, 68.54; H, 4.72; N, 16.76.

Preparation of the Chiral Guanidines 13–15. The chiral guanidines 13–15 were prepared from the (*S*)-(−)-1-(*o*-azidophenyl)ethylamine (12) following the procedure described above for the preparation of the corresponding racemic guanidine.

13: yield 62%; $[\alpha]^{20}_D$ +526.7° [*c* 4.65 10^{-3} g/mL (CH_2Cl_2)].

14: yield 65%; $[\alpha]^{20}_D$ +463.2° [*c* 4.75 10^{-3} g/mL (CH_2Cl_2)].

15: yield 60%; $[\alpha]^{20}_D$ +223.0° [*c* 4.95 10^{-3} g/mL (CH_2Cl_2)].

Preparation of the Intermediate 16. Method A. To a solution of 4a (0.75 g, 1 mmol) in 10 mL of dry dichloromethane was added *p*-methylphenyl isocyanate (0.13 g, 1 mmol). The reaction mixture was stirred at room temperature for 1 h, the solvent was removed under reduced pressure, and the resulting material was purified by column chromatography (silica gel; ethyl acetate) to give 16 as a white amorphous solid in 85% yield.

Method B. Bis(*o*-azidobenzyl)amine (0.56 g, 2 mmol) was dissolved in 10 mL of dry dichloromethane, and *p*-methylphenyl isocyanate (0.26 g, 2 mmol) was added. The mixture was stirred at room temperature for 1 h, the solvent was removed to dryness, and the residue was chromatographed (silica gel; ether/n-hexane (1:1)) to give **1,1-bis(*o*-azidobenzyl)-3-(4-methylphenyl)-urea**: yield 92%; mp 114–115 °C; colorless prisms (ether); IR (Nujol) 3358, 2129, 1662 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.26 (s, 3 H), 4.52 (s, 4 H), 6.89 (s, 1 H), 7.04 (d, 2 H, J = 8.3 Hz), 7.09–7.19 (m, 6 H), 7.30–7.35 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 20.7, 46.2, 118.2, 120.1, 125.3, 128.5 (s), 129.0, 129.4, 129.5, 132.6 (s), 136.6 (s), 137.8 (s), 155.9 (s); mass spectrum m/z (relative intensity) 412 (M$^+$, 7), 133 (49), 119 (75), 106 (100). Anal. Calcd for $C_{22}H_{20}N_8O$: C, 64.07; H, 4.88; N, 27.16. Found: C, 64.01; H, 4.73; N, 27.08.

To a solution of triphenylphosphine (0.52 g, 2 mmol) in 10 mL of dry dichloromethane was added, dropwise, a solution of 1,1-bis(2-azidobenzyl)-3-(4-methylphenyl)urea (0.41 g, 1 mmol) in the same solvent (5 mL). The solution was stirred at room temperature for 3 h, the solvent was removed under reduced pressure, and the solid was purified in the same way as in method A to afford 16: yield 85%; IR (Nujol) 3443, 1651, 1107 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.15 (s, 3 H), 5.12 (br s, 4 H), 6.44–7.72 (m, 42 H), 8.8 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.7, 46.5 (v br), 118.5 (br), 122.0, 127.6 (br), 129.2 (d, J_{P-C} = 11.5 Hz), 130.5 (br), 131.5 (s), 132.3 (d, J_{P-C} = 2.0 Hz), 132.5 (s), 132.6, 132.8, 133.2 (d, J_{P-C} = 9.4 Hz), 138.6 (s), 149.4 (s, br), 157.1 (s), C_i was not observed; ^{31}P NMR ($CDCl_3$) δ 2.06 (br), 6.46 (br); mass spectrum m/z (relative intensity) 366 (12), 183 (92), 133 (37), 108 (58), 91 (48), 77 (100). Anal. Calcd for $C_{58}H_{50}N_4OP_2$: C, 79.06; H, 5.72; N, 6.36. Found: C, 78.81; H, 7.58; N, 6.20.

Preparation of 2-(*o*-Azidophenyl)ethylamine (20). The amine 20 was prepared from 2-(*o*-azidophenyl)ethanol[14] following the method described for the preparation of 1d.

***N*-[2-(*o*-Azidophenyl)ethyl]phthalimide**: yield 64%; mp 119–120 °C; colorless prisms (ethyl acetate/n-hexane); IR (Nujol) 2129, 1772, 1358 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.96 (t, 2 H, J = 6.9 Hz), 3.92 (t, 2 H, J = 6.9 Hz), 6.96–7.29 (m, 4 H), 7.66–7.85 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 30.2, 37.9, 118.1, 123.1, 124.8, 128.2, 129.5 (s), 131.0, 132.0 (s), 133.9, 138.5 (s), 168.1 (s); mass spectrum m/z (relative intensity) 292 (M$^+$, 7), 264 (29), 117 (100). Anal. Calcd for $C_{16}H_{12}N_4O_2$: C, 65.75; H, 4.14; N, 19.16. Found: C, 65.64; H, 4.10; N, 19.08.

2-(*o*-Azidophenyl)ethylamine (20): yield 83%; oil; IR 2126, 1491, 1287 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.24 (s, 2 H), 2.75 (t, 2 H, J = 6.9 Hz), 2.90 (t, 2 H, J = 6.9 Hz), 7.02–7.35 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 35.1, 42.1, 118.0, 124.6, 127.6, 130.9, 130.9 (s), 138.0 (s); mass spectrum m/z (relative intensity) 162 (M$^+$, 19), 149 (44), 117 (100). Anal. Calcd for $C_8H_{10}N_4$: C, 59.24; H, 6.21; N, 34.54. Found: C, 59.15; H, 6.12; N, 34.43.

Preparation of 3-(*o*-Azidophenyl)propylamine (22). To a solution of 3-(*o*-aminophenyl)propanol[15] (4.53 g, 30 mmol) in 180 mL of 2 N HCl cooled at −5 °C was added dropwise a solution of sodium nitrite (2.76 g, 40 mmol) in 20 mL of water. After 30 min of stirring, a solution of sodium azide (2.60 g, 40 mmol) in 20 mL of water was added dropwise, and stirring was continued for 3 h. The mixture was extracted with dichloromethane (3 × 30 mL), and the organic layers were washed with water and dried over $MgSO_4$. The solvent was removed, and the resulting oil was purified by column chromatography (silica gel, ether/n-hexane (7:3)) to give **3-(*o*-azidophenyl)propanol**: yield 45% oil; IR 2125, 1491, 1287 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.75–1.92 (m, 2 H), 2.03 (s, 1 H), 2.65 (t, 2 H, J = 7.6 Hz), 3.62 (t, 2 H, J = 6.3 Hz), 7.01–7.34 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 27.3, 33.1, 62.0, 118.1, 124.9, 127.5, 130.6, 133.3 (s), 139.5 (s); mass spectrum m/z (relative intensity) 177 (M$^+$, 32), 149 (100). Anal. Calcd for $C_9H_{11}N_3O$: C, 61.00; H, 6.26; N, 23.71. Found: C, 60.89; H, 6.30; N, 23.65.

The amine 22 was prepared from 3-(*o*-azidophenyl)propanol following the procedure described for the preparation of 1d.

***N*-[3-(*o*-Azidophenyl)propyl]phthalimide**: yield 74%; mp 88–89 °C; colorless prisms (ethyl acetate/*n*-hexane); IR (Nujol) 2118, 2094, 1714 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.92–2.02 (m, 2 H), 2.62 (t, 2 H, J = 8.2 Hz), 3.72 (t, 2 H, J = 7.1 Hz), 7.03–7.21 (m, 4 H), 7.68–7.71 (m, 2 H), 7.82–7.84 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 28.5, 28.8, 37.8, 118.1, 123.2, 124.7, 127.5, 130.2, 132.1 (s), 132.5 (s), 133.9, 137.9 (s), 168.4 (s); mass spectrum m/z (relative intensity) 306 (M$^+$, 5), 130 (67), 118 (100). Anal. Calcd for $C_{17}H_{14}N_4O_2$: C, 66.66; H, 4.60; N, 18.29. Found: C, 66.53; H, 4.51; N, 18.33.

3-(*o*-Azidophenyl)propylamine (22): yield 92%; oil; IR 3375, 3279, 2123 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.63–1.79 (m, 2 H), 2.13 (s, 2 H), 2.60 (t, 2 H, J = 7.3 Hz), 2.69 (t, 2 H, J = 7.0 Hz), 7.01–7.34 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 28.3, 34.2, 41.6, 117.9, 124.6, 127.2, 130.2, 133.4 (s), 137.8 (s); mass spectrum m/z (relative intensity) 176 (31), 148 (100). Anal. Calcd for $C_9H_{12}N_4$: C, 61.34; H, 6.86; N, 31.79. Found: C, 61.25; H, 6.77; N, 31.70.

General Procedure for the Preparation of the Guanidines 21 and 23. The corresponding carbonyl compound 2 (5 mmol) was dissolved in 20 mL of dry ether, and $MgSO_4$ (for *o*-azidoacetophenone 4-Å molecular sieves were added also) and then the adecuate amine 20 or 22 (5 mmol) was added. The mixture was kept at room temperature until the band corresponding to the carbonyl group disappeared in the IR of the mixture.

After removal the $MgSO_4$, the resulting solution of the crude imine was added dropwise to a solution of triphenylphosphine (2.62 g, 10 mmol) in 20 mL of dry ether. The new mixture was stirred at room temperature for 12 h. The separated solid was filtered and dried.

This material was dissolved in a mixture of dry dichloromethane and dry methanol (20/20 mL) and cooled at 0 °C. Then sodium borohydride (0.75 g, 20 mmol) was added. After 30 min a second batch of sodium borohydride (0.75 g, 20 mmol) was added and stirring was continued 1 h. The solvent was removed under reduced pressure, and the residue was treated with cold water, filtered, and dried, initially at room temperature and then at 70 °C to give the corresponding bis(iminophosphorane) substituted secondary amine in an overall yield of 30–81%, which was used without purification in the next step. To a solution of this bis(iminophosphorane) (1 mmol) in 20 mL of dry benzene was added *p*-methylphenyl isocyanate (2 mmol). The reaction mixture was stirred at reflux temperature for 4 h.

Guanidines **21** were isolated from the reaction mixture by the following procedure: after the mixture was cooled the solvent was removed under reduced pressure, the resulting material was treated with n-hexane (3 × 25 mL), and the residue was chromatographed over silica gel using as eluent first ethanol and then ethanol/aqueous ammonia (95:5).

Guanidines **23** were isolated from the cold reaction mixture by filtration.

21a: yield 61%; mp 161–162 °C; colorless prisms; IR (Nujol) 1632, 1585, 1570 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.12 (t, 2 H, J = 5.0 Hz), 3.68 (t, 2 H, J = 5.0 Hz), 4.43 (s, 2 H), 6.85–7.14 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 33.5, 52.4, 52.5, 119.0, 120.7 (s), 121.6, 121.7, 121.8, 124.6, 127.5, 128.3 (s), 128.4, 130.0, 141.5 (s), 142.5 (s), 152.0 (s); mass spectrum m/z (relative intensity) 249 (M^+, 100), 248 (83), 233 (29). Anal. Calcd for $C_{16}H_{15}N_3$: C, 77.08; H, 6.06; N, 16.85. Found: C, 76.97; H, 6.01; N, 16.77.

21b: yield 63%; mp 105–106 °C; colorless prisms; IR (Nujol) 1635, 1584, 1226 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.27 (s, 3 H), 3.13 (t, 2 H, J = 4.9 Hz), 3.71 (t, 2 H, J = 4.9 Hz), 4.45 (s, 2 H), 5.71 (s, 1 H), 6.80–7.07 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 20.9, 33.3, 52.5, 52.9, 117.9, 119.5 (s), 121.6, 122.7, 125.4, 127.8, 128.3 (s), 129.3, 129.9, 132.6 (s), 136.6 (s), 139.7 (s), 151.4 (s); mass spectrum m/z (relative intensity) 263 (M^+, 100), 262 (96), 91 (25). Anal. Calcd for $C_{17}H_{17}N_3$: C, 77.54; H, 6.50; N, 15.95. Found: C, 76.47; H, 6.45; N, 15.90.

21c: yield 59%; mp 97–98 °C; colorless prisms; IR (Nujol) 1632, 1584, 1569 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.37 (d, 3 H, J = 6.6 Hz), 3.10 (ddd, 1 H, J = 2.4, 9.4, 15.7 Hz), 3.26 (ddd, 1 H, J = 1.9, 6.6, 15.7 Hz), 3.54 (ddd, 1 H, J = 2.4, 6.6, 13.4 Hz), 3.89 (ddd, 1 H, J = 1.9, 9.4, 13.4 Hz), 4.45 (q, 1 H, J = 6.6 Hz), 5.40 (s, 1 H), 6.84–7.23 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 22.3, 35.8, 51.9, 60.1, 119.5, 121.4, 121.7, 124.3, 126.0 (s), 127.4, 127.7 (s), 128.2, 130.1, 141.1 (s), 141.6 (s), 150.9 (s), one aromatic CH was not observed; mass spectrum m/z (relative intensity) 263 (M^+, 30), 248 (100). Anal. Calcd for $C_{17}H_{17}N_3$: C, 77.54; H. 6.50; N, 15.95. Found: C, 77.45; H. 6.41; N, 15.91.

23a: yield 33%; mp 289–290 °C; colorless prisms (benzene); IR (Nujol) 1667, 1639 cm^{-1}; ^1H NMR ($CDCl_3$ + TFA) δ 1.77–1.86 (m, 2 H), 2.80–2.86 (m, 2 H), 3.46–3.54 (m, 2 H), 4.48 (s, 2 H), 7.08–7.35 (m, 8 H), 9.85 (s, 1 H), 10.39 (s, 1 H); ^{13}C NMR ($CDCl_3$ + TFA) δ 21.0, 27.5, 48.2, 50.9, 115.8, 117.6 (s), 121.7, 125.4, 125.6, 127.3, 128.4, 129.2 (s), 129.6, 130.9, 132.6 (s), 136.1 (s), 150.1 (s); mass spectrum m/z (relative intensity) 263 (M^+, 48), 146 (100), 106 (92). Anal. Calcd for $C_{17}H_{17}N_3$: C, 77.54; H, 6.50; N, 15.95. Found: C, 77.46; H, 6.40; N, 15.81.

23b: yield 42%; mp 298–299 °C; colorless prisms (benzene); IR (Nujol) 1666, 1638, 1611 cm^{-1}; ^1H NMR ($CDCl_3$ + TFA) δ 1.79–1.83 (m, 2 H), 2.31 (s, 3 H), 2.77–2.81 (m, 2 H), 3.42–3.51 (m, 2 H), 4.45 (s, 2 H), 6.93–7.29 (m, 7 H), 10.18 (s, 1 H), 10.57 (s, 1 H); ^{13}C NMR ($CDCl_3$ + TFA) δ 20.9, 21.0, 27.5, 48.0, 50.8, 115.7, 117.3 (s), 121.9, 125.7, 127.0, 128.3, 129.1 (s), 130.0, 130.3 (s), 130.8, 135.3 (s), 136.2 (s), 150.2 (s); mass spectrum m/z (relative intensity) 277 (M^+, 100), 149 (16), 91 (11). Anal. Calcd for $C_{18}H_{19}N_3$: C, 79.94; H, 6.90; N, 15.15. Found: C, 79.84; H, 6.83; N, 15.09.

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