EtOH) λ max (nm) 210, 263; R_f 0.29 in solvent A).

Compound **6c** was obtained in 54% yield after flash chromatography using 4% methanol in CH_2Cl_2 (mp 115–117 °C; UV (95% EtOH) λ max (nm) 210, 263; R_f 0.26 in solvent A).

Compound **5d** was obtained in 66% yield after flash chromatography using successively 2%, 3%, and 4% methanol in CH_2Cl_2 (mp 103–106 °C; UV (95% EtOH) λ max (nm) 208, 264; R_f 0.37 in solvent A).

Compound **6d** was obtained in 76% yield in the same manner as for **5d** (mp 120–123 °C; UV (95% EtOH) λ max (nm) 208, 263; R_f 0.27 in solvent A).

Preparation of Detritylated Dinucleotides (7a–d, 8a–d). A standard procedure was used for the detritylation reactions and is illustrated for **7a**. A solution of trichloroacetic acid in CH_2Cl_2 (5%, 25 mL) was transferred to a round-bottom flask containing **5a** (300 mg). After stirring for 20 min at room temperature the solution was poured into CH_2Cl_2 (25 mL). The organic solution was then extracted with 5% aqueous sodium bicarbonate solution (2 × 50 mL) and dried over Na_2SO_4, and the solvents were removed at reduced pressure. The residue was redissolved in minimum amount of CH_2Cl_2 and precipitated in Et_2O (50 mL) to give pure **7a** as a white powder in 61% yield (140 mg; mp 130–133 °C; UV (95% EtOH) λ max (nm) 210, 278; R_f 0.65 in solvent B).

Compound **8a** (52% yield; mp 126–129 °C; UV (95% EtOH) λ max (nm) 210, 278; R_f 0.65 in solvent B).

Compound **7b** (precipitated in hexane/Et_2O (2/1, 30 mL); 55% yield, mp 130–133 °C; UV (95% EtOH) λ max (nm) 208, 263, 306; R_f 0.59 in solvent B).

Compound **8b** (precipitated in hexane/Et_2O (1/1, 30 mL); 60% yield; mp 132–135 °C; UV (95% EtOH) λmax (nm) 206, 263, 306; R_f 0.65 in solvent B).

Compound **7c** (isolated by silica gel column chromatography using 5% methanol in CH_2Cl_2; 65% yield; mp 119–121 °C; UV (95% EtOH) λ max (nm) 210, 263; R_f 0.59 in solvent B).

Compound **8c** (precipitated in Et_2O (50 mL); 51%; mp 117–120 °C; UV (95% EtOH) λ max (nm) 210, 278; R_f 0.55 in solvent B).

Compound **7d** (isolated by silica gel column chromatography eluting first with EtOAc/Et_2O/CH_2Cl_2 (4/1/2) followed by 5% methanol in CH_2Cl_2; 82%; mp 122–125 °C; UV (95% EtOH) λ max (nm) 208, 264; R_f 0.59 in solvent B).

Compound **8d** (isolated by silica gel chromatography using 4% methanol in CH_2Cl_2; 87%; mp 108–110 °C; UV (95% EtOH) λ max (nm) 208, 264; R_f 0.59 in solvent B).

HPLC Analysis of Intermediates during the Deprotection. The general procedure is illustrated by the deprotection of **7a** to give **13a**.

(a) Removal of Methyl Phosphate Protection (Preparation of 9a–d, 10a–d). A solution of thiophenoxide (dioxane/Et_3N/thiophenol, 2/2/1, 1.2 mL) was transferred to an Eppendorf tube containing **7a** (45 mg). After the solution was allowed to stand for 1 h at room temperature, TLC indicated that a very polar compound had formed (R_f 0.11 in 20% methanol in CH_2Cl_2). The reaction was quenched by the addition of 95% ethanol (1 mL). The solution was then concentrated under the reduced pressure, and the residue was redissolved in a minimum amount of CH_2Cl_2 and precipitated in hexane (50 mL). The precipitate was filtered to give **9a** (35 mg) as a white powder. This was used directly for ^{31}P measurement, HPLC analysis, and the next deprotection step without further purification. A portion (0.2 mg) of the sample was dissolved in 50% CH_3CN in triethylammonium acetate (100 μL, 0.1 M, pH 7) and used for HPLC analysis (10 μL was used for each analysis; HPLC conditions: column, Whatman C8 Partisil 5 (4.6 × 250 mm); solvent, isocratic or gradient CH_3CN in TEAA (0.1 M, pH 7); flow = 1 mL/min (Table V)). For ^{31}P NMR measurement, the sample (ca. 15 mg) was dissolved in $CDCl_3$ (see Table V).

(b) Removal of the *N*-Acyl Protecting Group (Preparation of 11a–c, 12a–c). Compound **9** (ca. 0.5 mg) was weighed into a 5-mL plastic tube. Methanolic ammonia (4 mL) was introduced to the tube. The tube was then capped with rubber septum (Aldrich) and sealed tightly with tape. After the mixture was allowed to stand at room temperature for 12 h, a needle was inserted to release the pressure inside the tube before it was exposed to the air. The solvent was evaporated by blowing Argon over it and then further lyophilized on a Speed-Vac concentrator. The residue was redissolved in water (1 mL) and divided into two Eppendorf tubes (0.5 mL each). Part of these was used for the next step. Another part was further diluted with water to 1 mL to give a solution of **11** for HPLC analysis. HPLC conditions: column, Whatman C8 Partisil 5 (4.6 × 250 mm); solvent, isocratic CH_3CN in TEAA (0.1 M, pH 7); flow = 1 mL/min (see Table VI).

(c) Removal of the 2'-Silyl Protecting Group (Preparation of 13a–d, 14a–d). A solution of **11** in one of the Eppendorf tubes described above was lyophilized on Speed-Vac. TBAF (100 μL) was added. After the solution was allowed to stand at room temperature for 4 h, the reaction was quenched with sterile water (0.5 mL). The solution was lyophilized and then redissolved in water (1 mL) to give a solution of **13** for HPLC analysis (10 μL was used for each injection; HPLC conditions: column, Whatman C8 Partisil 5 (4.6 × 250 mm); solvent, isocratic CH_3CN in TEAA (0.1 M, pH 7); flow = 1 mL/min (see Table VII)).

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Iminophosphorane-Mediated Synthesis of 2*H*-Indazole Derivatives: Preparation of 2,3-Diamino-2*H*-indazoles by Intramolecular Trapping of Phosphazides and 1*H*-1,2,4-Triazolo[2,3-*b*]indazoles by a Tandem Aza-Wittig/Heterocumulene-Mediated Strategy

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Treatment of *o*-azidobenzaldimines **2** with tertiary phosphines in methylene chloride at 0 °C leads to the corresponding 2,3-diamino-2*H*-indazole derivatives **3** by cyclization of the intermediate phosphazide. Compounds **3** react with isocyanates, carbon dioxide, and carbon disulfide to give the 1*H*-1,2,4-triazolo[2,3-*b*]indazoles **8**, **9**, and **10**, respectively. Compounds **8** can also be prepared from **2** in a one-pot reaction by sequential treatment with polystyryldiphenylphosphine and isocyanates. In tetrahydrofuran at room temperature, iminophosphoranes **3** react with acyl chlorides to form *N*-acyliminophosphoranes **11**, which, under acid catalysis, undergo cyclization to yield the fused indazoles **12**.

The reaction of a tertiary phosphine with an organic azide to produce an iminophosphorane after nitrogen evolution is known as the Staudinger reaction.[1] The primary imination products, phosphazides, are sometimes isolable

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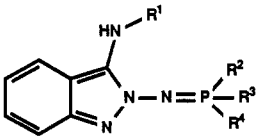
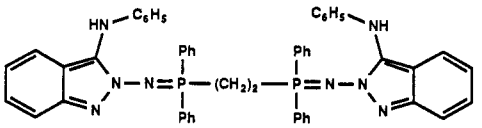
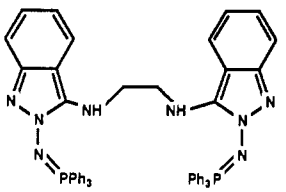
Table I. 2,3-Diamino-2*H*-indazoles



compd	R^1	R^2	R^3	R^4	yield, %	mp, °C
3a	C_6H_5	C_6H_5	C_6H_5	C_6H_5	75	215–216
3b	4-H_3CO-C_6H_4	C_6H_5	C_6H_5	C_6H_5	60	192–193
3c	*n*-C_3H_7	C_6H_5	C_6H_5	C_6H_5	60	175–176
3d	$C_6H_5CH_2$	C_6H_5	C_6H_5	C_6H_5	68	99–100
3e	C_6H_5	$N(CH_3)_2$	$N(CH_3)_2$	$N(CH_3)_2$	74	134–135
3f	C_6H_5	C_6H_5	CH_3	CH_3	60	160–161
3g	C_6H_5	C_6H_5	C_6H_5	CH_3	67	200–202
3h					56	249–250
3i					55	165–167

and stable,[2] but as a rule they lose nitrogen at room temperature or even at lower temperature to give the corresponding iminophosphorane compound in practically quantitative yields. The mechanism of the Staudinger reaction seems to proceed without either free radicals or nitrene participation and for the decomposition of the phosphazide it has been postulated, as a result of kinetic measurements,[3] a four-membered ring transition state in which the phosphorus atom is loosely connected to the nitrogen atom attached to the carbon atom. In spite of the important role of iminophosphoranes in organic synthesis, the chemistry of the phosphazides has been much less investigated; in fact, while relevant examples involving iminophosphoranes have been reported,[4] there have been no reports dealing with general synthetic applications of phosphazides, to the best of our knowledge.

The Staudinger reaction is a very useful reaction in synthetic organic chemistry.[5] Consequently, improvements that increase the efficiency or enlarge its applicability are desirable, and the discovery of novel functionalized azides bearing a moiety able to react either with the phosphazide or the iminophosphorane moiety is important in this respect.

In the course of our studies directed toward the synthesis of fused heterocycles, we had occasion to explore heterocyclization reactions of iminophosphoranes derived from *o*-azidoformilazoles by a tandem aza-Wittig/electrocyclic ring closure strategy.[6] We now report a fundamentally new approach to the synthesis of 2-amino-3-(alkyl(aryl)-amino)-2*H*-indazoles and fused indazoles. Our approach is based on the reaction of aryl azides bearing an imine group at the ortho position with tertiary phosphines to give a 1,2,6-triazahexatriene moiety containing a nitrogen atom at one end and a phosphazide group at the other, which subsequently undergoes ring closure to give the five-membered ring instead of the expected iminophosphorane by loss of nitrogen.

2*H*-Indazole (isoindazole) derivatives are an interesting class of heterocyclic compounds from both theoretical and synthetic points of view. In particular, 2-amino-2*H*-indazoles are considered as a source of indalolyl nitrenes, thus the iminophosphorane derived from 2-amino-2*H*-indazole by flash thermolysis expels nitrogen to form cyanodienynes,[7] whereas the oxidation of 2-amino-2*H*-indazoles with lead tetraacetate provides an efficient general route to 1,2,3-benzotriazines[8] which by flash thermolysis are converted into benzazates.[9] The two most important approaches for the synthesis of 2-amino-2*H*-indazole derivatives involve either amination of the indazole ring with hydroxylamine-*O*-sulfonic acid,[8,10] thermal decomposition of hydrazone derivatives,[11] or semicarbazone derived from *o*-azidobenzaldehyde.[12] Both of these methods are somewhat tedious, particularly the former,

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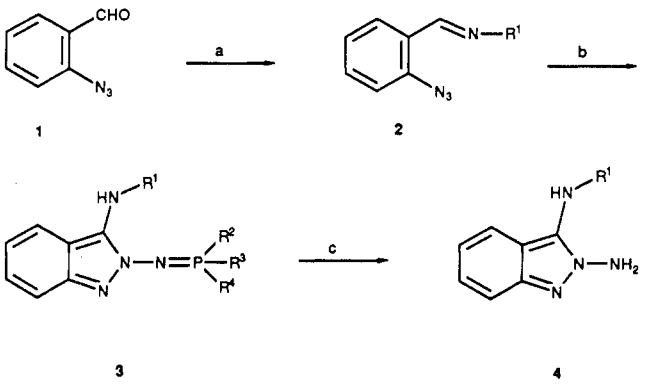
Scheme I[a]



[a] (a) R^1NH_2, EtOH, room temperature; (b) $R^2R^3R^4P$, CH_2Cl_2, 0 °C 1 h/room temperature 4 h; (c) HCl, H_2O, room temperature.

which leads to a mixture of 1- and 2-amino-2*H*-indazoles.

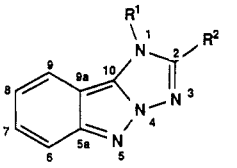
Results and Discussion

A. Preparation of 2-Amino-3-(alkyl(aryl)amino)-2*H*-indazoles. The *o*-azidobenzaldehyde 1 was prepared by a previously reported procedure.[12] The preparation of the desired *o*-azidobenzaldimines 2 was accomplished very easily by reaction of 1 with primary amines in ethanol at room temperature (Scheme I). When a methylene chloride solution of **2a** was treated with triphenylphosphine at 0 °C for 1 h the indazole derivative **3a** was obtained in almost pure form, instead of the expected *o*-(triphenylphosphoranylidene)aminobenzaldimine. Reaction of the related *o*-azidobenzaldimines **2b**, **2c**, and **2d** also resulted in smooth formation of the 2,3-diamino-2*H*-indazole derivatives **3b**, **3c**, and **3d**, respectively, in good yields (Table I). In addition, compound **2a** reacted with several tertiary phosphines to give the corresponding iminophosphoranes derived from 2-amino-3-(phenylamino)-2*H*-indazole **3e–g**, confirming the generality of the reaction. Bis(iminophosphoranes) **3h** and **3i** were also obtained either from **2a** and 1,2-bis(diphenylphosphino)ethane or from the bis(aldimine) derived from ethylenediamine and triphenylphosphine.

Acid hydrolysis of **3** led to 2-amino-2*H*-indazoles **4** in 70–75% yields. The structure **3** is derivable from mass and IR spectral data and from NMR absorption as summarized in the Experimental Section.

It is significant that aldimines derived from *o*-azidoformilazoles react with triphenylphosphine in a completely "normal" fashion to give the triphenylphosphoranylideneamino compounds[6] with no evidence of indazole formation.

Table II. 1*H*-1,2,4-Triazolo[2,3-*b*]indazoles

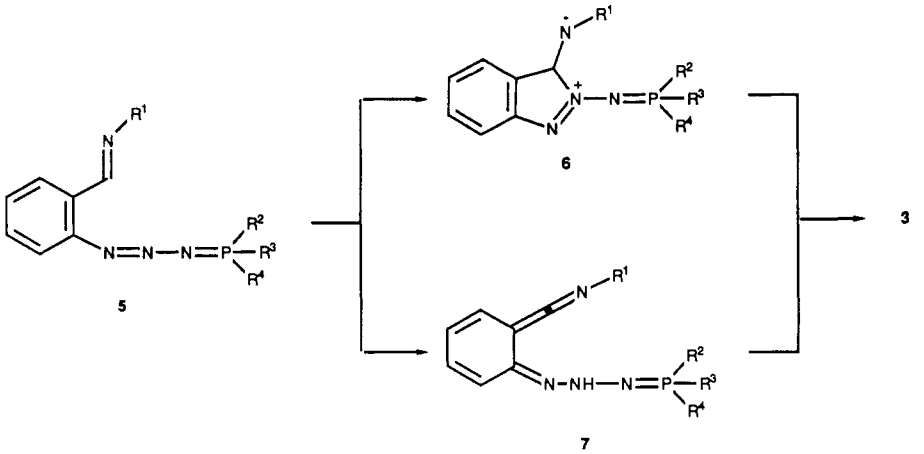


compd	R^1	R^2	yield, %	mp, °C
8a	C_6H_5	C_6H_5NH	60	288–289
8b	C_6H_5	4-F-C_6H_4NH	59	278–279
8c	C_6H_5	4-CH_3-C_6H_4NH	56	218–219
8d	C_6H_5	C_2H_5NH	69	224–225
8e	C_6H_5	CH_3NH	76	245–246
8f	4-H_3CO-C_6H_4	C_6H_5NH	47	290–291
8g	4-H_3CO-C_6H_4	4-F-C_6H_4NH	53	299–300
8h	4-H_3CO-C_6H_4	CH_3NH	67	233–234
8i	*n*-C_3H_7	4-F-C_6H_4NH	59	200–201
8j	*n*-C_3H_7	CH_3NH	88	203–204
9	C_6H_5	OH	50	234–235
10	C_6H_5	SH	58	205–206
12a	$C_6H_5CH_2$	*i*-C_3H_7	45	149–150
12b	$C_6H_5CH_2$	C_2H_5	42	157–158
12c	$C_6H_5CH_2$	CH_3	40	193–194

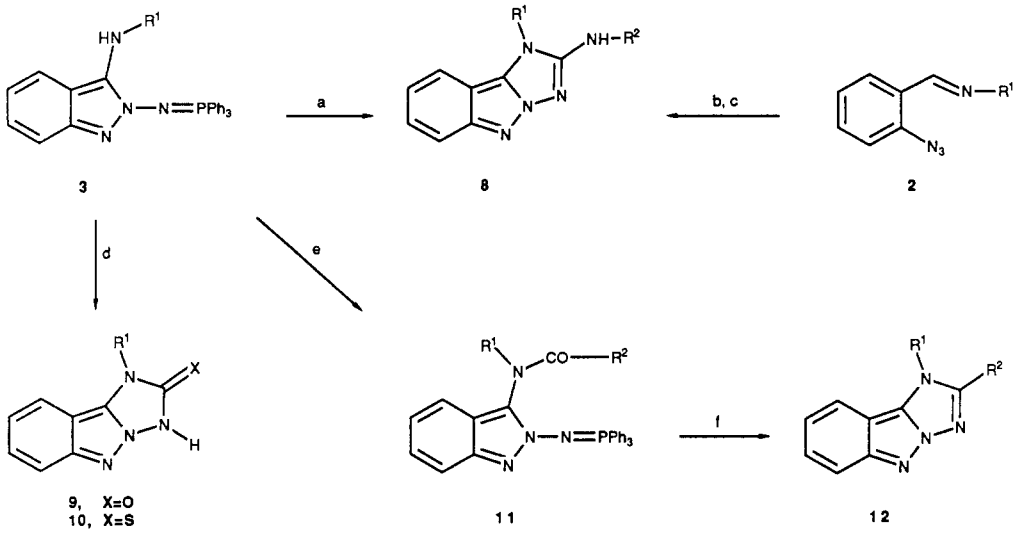
Thus, it is clear that the benzene ring plays a key role in the selective formation of indazole compounds. A tentative mechanism for the conversion **2** → **3** involves an initial Staudinger reaction to give a phosphazide **5** as a highly reactive intermediate which clearly undergoes cyclization by nucleophilic attack of the central nitrogen atom of the phosphazide moiety on the carbon atom of the azomethine group leading to the zwitterionic intermediate **6**, and further transformation of **6** will lead to the indazoles **3** (Scheme II). Another plausible pathway would involve the conversion of **5** to the ketenimine **7** through [1,5] sigmatropic shifts and subsequent ring closure by nucleophilic attack of the amino group on the central sp hybridized carbon atom of the ketenimine moiety. To the best of our knowledge the reaction of *o*-azidobenzaldimines with tertiary phosphines represents the first example reported of an intramolecular trapping of a phosphazide by an imine function and constitutes a new and general entry to a variety of iminophosphoranes derived from the otherwise not readily available 2-amino-3-(alkyl(aryl)-amino)-2*H*-indazoles ring system. Due to the the easy access of the starting materials, good yields, mild reaction conditions, and simplicity of the experimental one-pot procedure, this synthetic approach compares favorably with other synthetic methods.[10–12]

B. Preparation of 1*H*-1,2,4-Triazolo[2,3-*b*]-indazoles. The previously unreported 1*H*-1,2,4-triazolo-

Scheme II



Scheme III[a]

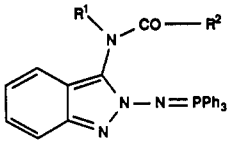


[a] (a) R^2-NCO, toluene, reflux; (b) ⓟ-PPh_2, CH_2Cl_2 room temperature; (c) R^2-NCO, toluene, reflux; (d) CO_2, toluene, sealed tube, 120 °C for 9, CS_2, toluene, reflux for 10 h; (e) R^2-COCl, Et_3N, THF, room temperature; (f) HCl(c), ethanol, reflux.

[2,3-*b*]indazole ring system was prepared by the following approaches: (a) Reaction of iminophosphoranes **3** (R^1 = R^2 = R^3 = Ph) with several aliphatic or aromatic isocyanates in dry toluene at reflux temperature resulted in the formation of the corresponding 1-substituted 2-(alkyl(aryl)amino)-1*H*-1,2,4-triazolo[2,3-*b*]indazoles **8** directly in moderate yields (Table II).

The conversion **3** → **8** involves initial aza-Wittig type reaction between iminophosphorane **3** and isocyanate to give a carbodiimide as intermediate (as evidenced by IR) which undergoes ring closure by nucleophilic attack of the adjacent amino group to give the corresponding fused indazole derivatives. Although reaction of carbodiimides with compounds containing amino groups have been reported,[13] to our knowledge this is the first example reported to triazolo annelation based on the reaction of carbodiimides with secondary amino groups. (b) Indazoles **8** were also obtained by a one-pot reaction from *o*-azidobenzaldimines **2** by sequential treatment with polystyryldiphenylphosphine in methylene chloride at room temperature and the appropriate isocyanate in toluene at reflux temperature (Scheme III), the yield of the isolated product being higher than 60%. (c) When iminophosphorane **3a** was treated with carbon dioxide at 120 °C in a sealed glass tube or with carbon disulfide in dry toluene at reflux temperature, fused indazoles **9** and **10**, respectively, were formed in moderate yields (Table II). Finally, iminophosphoranes **3** react with acyl chlorides in the presence of triethylamine in tetrahydrofuran at room temperature to give the corresponding *N*-acyl derivatives **11** instead of the expected imidoyl chlorides[14] (Table III). This conversion shows the preferential reactivity of the amino group of compound **3** with respect to the iminophosphorane moiety toward electrophilic reagents. It seemed likely that *N*-acyl derivatives **11** could be useful precursors of 1*H*-1,2,4-triazolo[2,3-*b*]indazoles bearing an alkyl or aryl substituent in the 2-position via an intramolecular version of the aza-Wittig reaction. Despite its apparent simplicity, intramolecular aza-Wittig reaction involving an amide carbonyl group is rare; in this context some examples of this type of reactions have been recently reported.[4b,e,15]

Table III. (*N*-Acylimino)phosphoranes



compd	R^1	R^2	yield, %	mp, °C
11a	$C_6H_5CH_2$	CH_3	71	158–159
11b	$C_6H_5CH_2$	C_2H_5	73	165–166
11c	$C_6H_5CH_2$	*i*-C_3H_7	88	204–205
11d	*n*-C_3H_7	C_2H_5	68	140–141
11e	*n*-C_3H_7	C_6H_5	79	208–209
11f	C_6H_5	C_2H_5	52	162–164
11g	C_6H_5	*i*-C_3H_7	54	210–211

When *N*-acyl derivatives **11** were heated in toluene solutions at reflux temperature for 24 h or even at temperatures slightly higher than their melting points, the starting materials were recovered inalterated. This could be ascribable to the restricted conformation of the side chain at position 3 that could be entropically unfavorable for the cyclization. For this reason, in the ^1H NMR spectra of **11a–c** the *N*-methylene protons appear as diastereotopic as two double doublets whereas in **11d–e** they appear as two complex multiplets. This phenomenon was previously observed[16] in N,N-disubstituted acetamides when one N-substituent was an ortho-substituted aryl group and the other contained an α-methylene group, and it was interpreted in terms of restricted rotation about the aryl–nitrogen bond.[17]

Iminophosphoranes **11**, however, undergo ring closure in ethanolic solutions under acid catalysis to give the desired fused indazoles **12** in moderate yields (Table II). This conversion involves initial hydrolysis of the iminophosphorane group and subsequent cyclization to **12**. This assumption is supported by the isolation in some cases of the corresponding 2-amino-3-(*N*-alkyl(*N*-acyl)amino)-2*H*-indazoles.

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Table IV. ^{13}C Chemical Shifts (ppm) for Carbon Atoms in the Heteroaromatic Ring of Several 1,3-Disubstituted 1*H*-1,2,4-Triazolo[2,3-*b*]indazoles (*J*, Hz)

compd	C_2	C_{5a}	C_6	C_7	C_8	C_9	C_{9a}	C_{10}
8h	155.72 (d), J = 3.9	148.39 (dd), J = 10.6, J = 6.8	116.46[a]	124.44 (ddd), J = 156.4, J = 7.9, J = 3.1	117.88 (ddd), J = 161.6, J = 7.7, J = 3.0	116.50[a]	102.85 (dd), J = 9.2, J = 5.9	128.84
8j	155.10 (d), J = 2.8	148.14 (dd), J = 10.0, J = 6.5	115.65 (dd), J = 163.2, J = 7.4	124.56 (dd), J = 160.7, J = 8.1	117.85 (dd), J = 161.0, J = 7.1	116.63 (dd), J = 159.6, J = 8.0	103.28 (dd), J = 89.5, J = 6.4	129.50
9	158.99 (s)	130.79 (m)	112.60 (dd), J = 169.8, J = 7.9	132.10 (dd), J = 155.6, J = 7.8	124.68 (dd), J = 168.5	119.34 (dd), J = 168.5, J = 5.8	107.12 (ddd), J = 10.3, J = 4.3, J = 1.6	133.37 (d), J = 2.2
10	153.12 (s)	130.77 (m)	112.93 (dd), J = 172.1, J = 6.8	133.22 (dd), J = 165.6, J = 6.7	124.78 (dd), J = 164.4, J = 6.4	119.25 (dd), J = 168.8, J = 6.5	105.13 (ddd), J = 10.8, J = 5.0, J = 2.0	136.97 (s)
12b	154.15 (m)	150.08 (dd), J = 9.8, J = 6.3	116.45 (dd), J = 160.0, J = 7.2	125.63	118.06 (dd), J = 162.4, J = 7.6	117.32 (dd), J = 161.8, J = 7.9	102.57 (dd), J = 9.8, J = 5.5	131.64 (m)

[a] Interchangeables.

All analytical and spectroscopic data are in best agreement with the constitution of compounds **8–12**. The ^1H NMR spectra of compounds **8** suggest the exocyclic N-H, e.g. for **8e**, **8h**, and **8j** as the methyl signal appeared as a doublet (J = 5 Hz) and for **8d** the methylene signal appeared as a quintuplet. ^{13}C chemical shifts for representative 1*H*-1,2,4-triazolo[2,3-*b*]indazoles are shown in Table IV (values were assigned by decoupling methods and 2D H–C correlation techniques).

Concluding Remarks

The work described in this paper shows for the first time that the easily available hetero 1,3,5-hexatrienes bearing a phosphazide moiety at one end and an azomethine group at the other clearly undergo heterocyclization to give directly iminophosphoranes derived from 2-amino-3-(alkyl(aryl)amino)-2*H*-indazoles, which have been shown to be useful precursors for the preparation of the unknown 1*H*-1,2,4-triazolo[2,3-*b*]indazole ring system via a tandem aza-Wittig/heterocumulene-mediated annelation strategy. It should be noted that the prepared 2*H*-indazole derivatives represent variations in structural diversity not accessible by other routes.

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 chemical shifts are expressed in parts per million (δ) relative to internal Me_4Si. Two-dimensional spectra were recorded using standard conditions. Electron-impact mass spectra were carried out on a Hewlett-Packard 5993C spectrometer at an ionization potential of 70 eV. Microanalysis were performed on a Perkin-Elmer 240C instrument.

Materials. *o*-Azidobenzaldehyde[12] **1** and *o*-azidobenzaldimines[18] **2** were prepared as described in the literature. The methylene chloride was dried over calcium chloride and then stored on molecular sieves, 4-Å.

General Procedure for the Preparation of 3-(Alkyl(aryl)amino)-2-((triphenylphosphoranylidene)amino)-2*H*-indazoles (3). A solution of *o*-azidobenzaldimine (3 mmol) in 20 mL of dry methylene chloride was added dropwise under nitrogen to a well-stirred solution of the appropriate phosphine (3 mmol) in 15 mL of the same solvent at 0 °C. After the stirring was continued for 1 h at the same temperature, the mixture was slowly warmed to room temperature while the stirring was continued for 4 h, and then the solvent was removed under reduced pressure. The resultant crude product was purified by recrystallization from the appropriate solvent to give **3** as crystalline solids.

3a: yield 75%; mp 215–216 °C; white prisms (from toluene/*n*-hexane); IR (Nujol) 3165, 1596, 1115, 1036 cm^{-1}; ^1H NMR (DMSO-d_6) δ 6.62–6.72 (m, 3 H), 6.76 (t, ^3J = 7.4 Hz, 1 H, H-5), 6.97 (t, ^3J = 6.5 Hz, 1 H, H-6), 7.02–7.25 (m, 4 H), 7.42–7.62 (m, 9 H), 7.72 (ddd, J_{H-P} = 12.0, J_o = 8.2, J_m = 1.5 Hz, 6 H), 8.07 (s, 1 H, NH); ^{13}C NMR (DMSO-d_6) δ 114.43, 114.81 (C-5 and C-7), 118.00 (C-4), 118.05, 122.98 (C-6), 126.08 (J = 12.2 Hz, C-3), 128.38 (J = 98.0 Hz, C_i), 128.55 (J = 12.1 Hz, C_m), 128.63, 132.27 (J = 2.9 Hz, C_p), 132.90 (J = 10.0 Hz, C_o), 141.67 (C-7a), 145.24 (C-3a was unobserved); mass spectrum, m/e (relative intensity) 484 (M^+, 5), 277 (12), 276 (49), 209 (33), 208 (24), 198 (12), 183 (75), 152 (32), 122 (35), 108 (27), 107 (26), 77 (100). Anal. Calcd for $C_{31}H_{25}N_4P$: C, 76.84; H, 5.20; N, 11.56. Found: C, 76.62; H, 5.31; N, 11.41.

3b: yield 60%; mp 192–193 °C; light green prisms (from methylene chloride/*n*-hexane); IR (Nujol) 3171, 1608, 1558, 1109, 1049 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.75 (s, 3 H, CH_3O), 6.23 (s, 1 H, NH), 6.70–6.82 (m, 5 H), 7.03 (ddd, ^3J = 8.5, ^3J = 6.5, ^4J = 1.0 Hz, 1 H, H-6), 7.18 (dd, ^3J = 8.0, ^4J = 1.0 Hz, 1 H, H-4), 7.30 (d, ^3J = 8.5 Hz, 1 H, H-7), 7.37–7.55 (m, 9 H), 7.75 (ddd, J_{H-P} = 12.1, J_o = 7.9, J_m = 1.5 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 55.57 (CH_3O), 111.67 (C-3a), 114.31, 115.37 (C-7), 117.31 (C-5), 118.27, 118.95 (C-4), 123.25 (C-6), 128.39 (J = 98.0 Hz, C_i), 128.85 (J = 11.0 Hz, C-3), 128.41 (J = 12.0 Hz, C_m), 132.02 (J = 3.0 Hz, C_p), 133.18 (J = 10.0 Hz, C_o), 137.03, 142.50 (C-7a), 154.00; mass spectrum, m/e (relative intensity) 514 (M^+, 2), 276 (29), 262 (19), 239 (16), 224 (31), 184 (18), 183 (100), 152 (21), 122 (29), 108 (48), 107 (35), 106 (10), 92 (10). Anal. Calcd for $C_{32}H_{27}N_4OP$: C, 74.69; H, 5.29; N, 10.89. Found: C, 74.41; H, 5.17; N, 10.93.

3c: yield 60%; mp 175–176 °C; yellow prisms (from methylene chloride/*n*-hexane); IR (Nujol) 3347, 1613, 1562, 1115, 1041 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (t, J = 7.3 Hz, 3 H), 1.56 (st, 2 H), 3.37 (t, J = 7 Hz, 2 H), 4.65 (s, br, 1 H, NH), 6.67 (ddd, ^3J = 8.1, ^3J = 6.6, ^4J = 0.8 Hz, 1 H, H-5), 6.96 (t, ^3J = 6.6 Hz, 1 H, H-6), 7.18 (d, ^3J = 8.3 Hz, 1 H, H-7), 7.30–7.53 (m, 10 H), 7.72 (ddd, J_{H-P} = 11.9, J_o = 8.2, J_m = 1.6 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 11.23 (CH_3), 23.82 (CH_2), 47.74 (CH_2), 108.67 (C-3a), 114.97 (C-7), 115.91 (C-5), 118.94 (C-4), 123.28 (C-6), 128.44 (J = 12 Hz, C_m), 128.78 (J = 98.1 Hz, C_i), 132.01 (J = 3.0 Hz, C_p), 133.13 (J = 9.5 Hz, C_o), 142.62 (C-7a), (C-3 was unobserved); mass spectrum, m/e (relative intensity) 450 (M^+, 19), 227 (27), 276 (98), 183 (100), 152 (16), 146 (15), 118 (22), 117 (67), 108 (35), 103 (80), 102 (28), 90 (24), 77 (26). Anal. Calcd for $C_{28}H_{27}N_4P$: C, 74.65; H, 6.04; N, 12.44. Found: C, 74.81; H, 5.92; N, 12.28.

3d: yield 68%; mp 99–100 °C; yellow prisms (from methylene chloride/diethyl ether); IR (Nujol) 1613, 1574, 1155, 1041 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.62 (s, 2 H, CH_2N), 5.30 (s, br, 1 H, NH),

(18) Krbechek, L.; Takimoto, H. *J. Org. Chem.* **1964**, *29*, 1150.

6.63 (ddd, ^3J = 8.0, ^3J = 6.4, ^4J = 0.8 Hz, 1 H, H-5), 6.96 (ddd, ^3J = 7.7, ^3J = 6.4, ^4J = 0.7 Hz, 1 H, H-6), 7.17–7.50 (m, 16 H), 7.75 (ddd, J_{P-H} = 12.0, J_o = 8.5, J_m = 1.7 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 49.98 (CH_2), 108.79 (C-3a), 115.05 (C-7), 116.18 (C-5), 118.82 (C-4), 123.31 (C-6), 126.96, 127.12, 128.42, 128.47 (J = 12.0 Hz, C_m), 128.76 (J = 98.1 Hz, C_i), 132.03 (J = 3.0 Hz, C_p), 133.19 (J = 9.5 Hz, C_o), 140.24, 142.60 (C-7a), (C-3 was unobserved); mass spectrum, m/e (relative intensity) 498 (M^+, 2), 277 (28), 276 (100), 262 (15), 222 (10), 221 (58), 220 (78), 183 (62), 118 (29), 108 (17), 107 (17), 91 (50), 77 (30). Anal. Calcd for $C_{32}H_{27}N_4P$: C, 77.09; H, 5.46; N, 11.24. Found: C, 76.87; H, 5.58; N, 10.98.

3e: yield 74%; mp 134–135 °C; white prisms (from benzene-/n-hexane); IR (Nujol) 3205, 1630, 1608, 1189, 1070 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.55 (d, J_{P-H} = 8.9 Hz, 18 H, 6 CH_3N), 6.53 (s, broad, 1 H, NH), 6.73–6.87 (m, 4 H), 7.04–7.19 (m, 3 H), 7.32 (d, ^3J = 8.1 Hz, 1 H, H-4), 7.46 (d, ^3J = 9.0 Hz, 1 H, H-7); ^{13}C NMR ($CDCl_3$) δ 37.19 (J = 3.0 Hz, CH_3), 112.58 (C-3a), 115.13 (C_o), 115.88 (C-7), 117.86 (C-5), 119.16 (C-4), 119.44 (C_p), 123.30 (C-6), 127.94 (J = 11.1 Hz, C-3), 129.00 (C_m), 143.02 (C_i), 143.99 (C-7a); mass spectrum, m/e (relative intensity) 385 (M^+, 2), 209 (5), 179 (11), 178 (8), 135 (61), 134 (14), 119 (15), 91 (100), 77 (19). Anal. Calcd for $C_{19}H_{28}N_7P$: C, 59.21; H, 7.32; N, 25.44. Found: C, 59.13; H, 7.47; N, 25.31.

3f: yield 60%; mp 160–161 °C; yellow prisms (from methylene chloride/diethyl ether); IR (Nujol) 1619, 1602, 1115, 1047 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.97 (d, J = 13.0 Hz, 6 H, 2 CH_3P), 6.72 (s, 1 H, NH), 6.76–6.88 (m, 4 H), 7.05–7.20 (m, 3 H), 7.26–7.42 (m, 5 H), 7.58 (ddd, J_{P-H} = 12.0, J_o = 8.3, J_m = 1.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.70 (J = 68.1 Hz, CH_3), 112.86 (C-3a), 115.16 (C-7), 115.51, 117.86 (C-5), 119.00 (C-4), 119.58, 123.37 (C-6), 126.54 (J = 11.0 Hz, C-3), 128.70 (J = 12.0 Hz, C_m), 128.93, 130.00 (J = 98.0 Hz, C_i), 130.28 (J = 9.5 Hz, C_o), 131.89 (J = 3.0 Hz, C_p), 142.76 (C-7a), 143.86; mass spectrum, m/e (relative intensity) 360 (M^+, 3), 209 (10), 208 (7), 180 (11), 179 (46), 178 (19), 153 (47), 152 (11), 139 (10), 138 (36), 123 (15), 121 (18), 109 (12), 91 (19), 62 (100). Anal. Calcd for $C_{21}H_{21}N_4P$: C, 69.99; H, 5.87; N, 15.55. Found: C, 70.16; H, 5.73; N, 15.41.

3g: yield 67%; mp 200–202 °C; white prisms (from toluene-/n-hexane); IR (Nujol) 3194, 1625, 1596, 1041 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 2.35 (d, J_{P-H} = 14.0 Hz, 3 H, CH_3P), 6.51–6.65 (m, 4 H), 6.81 (ddd, ^3J = 7.0, ^3J = 8.3, ^4J = 1.6 Hz, 1 H, H-6), 6.94–7.04 (m, 4 H), 7.23–7.35 (m, 6 H), 7.65 (ddd, J_{H-P} = 12.0, J_o = 7.2, J_m = 1.6 Hz, 4 H), 7.86 (s, 1 H, NH); ^{13}C NMR (DMSO-d_6) δ 13.76 (J = 63.6 Hz, CH_3P), 114.14 (C-3a), 114.71 (C-7), 114.74, 117.82 (C-5), 118.07 (C-4), 118.61, 122.84 (C-6), 125.86 (J = 12.0 Hz, C-3), 128.62 (J = 11.7 Hz, C_m), 128.74, 130.08 (J = 98.0 Hz, C_i), 131.38 (J = 9.5 Hz, C_o), 131.94 (J = 3 Hz, C_p), 141.94 (C-7a), 145.27; mass spectrum, m/e (relative intensity) 422 (M^+, 4), 215 (21), 214 (100), 200 (16), 183 (16), 179 (19), 178 (10), 152 (8), 122 (13), 77 (43). Anal. Calcd for $C_{26}H_{23}N_4P$: C, 73.92; H, 5.49; N, 13.26. Found: C, 74.13; H, 5.31; N, 13.37.

3h: yield 56%; mp 249–250 °C; white prisms (from methylene chloride/n-hexane); IR (Nujol) 3211, 1625, 1602, 1115, 1049 cm^{-1}; ^{1}H NMR ($CDCl_3$ + TFA) δ 3.90 (s, broad, 2 H, CH_2P), 6.52 (d, ^3J = 8.4 Hz, 1 H), 6.67–6.75 (m, 2 H), 7.06 (t, ^3J = 7.6 Hz, 1 H), 7.37–7.44 (m, 4 H), 7.58–7.95 (m, 11 H), 9.70 (s, broad, 1 H, NH); mass spectrum, m/e (relative intensity) 434 (2), 405 (3), 393 (10), 209 (100), 208 (82), 201 (10), 200 (6), 185 (11), 180 (17), 179 (23), 152 (23), 124 (10), 108 (7), 104 (15), 91 (14), 90 (8), 77 (67). Anal. Calcd for $C_{52}H_{44}N_8P$: C, 74.10; H, 5.26; N, 13.29. Found: C, 73.94; H, 5.16; N, 13.38.

3i: yield 55%; mp 165–167 °C; orange prisms (from methylene chloride/n-hexane); IR (Nujol) 3279, 1619, 1557, 1109, 1047 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.50 (s, broad, 2 H, CH_2N), 5.11 (s, broad, 1 H, NH), 6.67 (t, ^3J = 7.3 Hz, 1 H, H-5), 7.00 (t, ^3J = 7.3 Hz, 1 H, H-6), 7.22–7.50 (m, 11 H), 7.44 (ddd, J_{P-H} = 12.0, J_o = 6.9, J_m = 1.3 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 46.90 (CH_2), 109.68 (C-3a), 115.12 (C-7), 116.50 (C-5), 118.70 (C-4), 123.34 (C-6), 128.47 (J = 12.0 Hz, C_m), 128.76 (J = 98.0 Hz, C_i), 132.00 (J = 3.0 Hz, C_p), 133.26 (J = 9.6 Hz, C_o), 142.65 (C-7a), (C-3 was unobserved); mass spectrum, m/e (relative intensity) 309 (2), 277 (27), 262 (21), 198 (10), 185 (13), 184 (19), 183 (100), 133 (44), 116 (4), 108 (41), 107 (39), 77 (28). Anal. Calcd for $C_{52}H_{44}N_8P_2$: C, 74.10; H, 5.26; N, 13.29. Found: C, 74.19; H, 5.08; N, 13.47.

Preparation of 2-Amino-3-(phenylamino)-2H-indazole (4). To a stirred suspension of iminophosphorane **3a** (0.5 g, 1 mmol) in 20 mL of water was added 3 mL of concentrated hydrochloric acid. After the stirring was continued for 16 h at room temperature, the solid triphenylphosphine oxide was removed by filtration. To the filtrate was added 6 mL of concentrated ammonium hydroxide solution, and the mixture was extracted with ethyl ether (3 × 10 mL). The combined extracts were dried (Na_2SO_4) and evaporated under reduced pressure. The obtained residue was recrystallized from diethyl ether/n-hexane (1:1, v/v) to give **4** (R^1 = C_6H_5): 0.16 g (70%); mp 161–162 °C; white crystals; IR (Nujol) 3301, 3216, 1653, 1625 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 6.60 (s, 2 H, NH_2), 6.70–6.86 (m, 4 H), 7.09–7.20 (m, 3 H), 7.27 (d, ^3J = 8.3 Hz, 1 H, H-4), 7.42 (dd, ^3J = 8.6, ^4J = 0.7 Hz, 1 H, H-7), 8.07 (s, 1 H, NH); ^{13}C NMR (DMSO-d_6) δ 112.58 (C-3a), 114.82 (C_o), 116.30 (C-7), 118.72 (C-5), 119.12 (C_p), 119.67 (C-4), 124.78 (C-6), 128.74 (C_m), 129.44 (C-3), 143.35 (C-7a), 144.00 (C_i); mass spectrum, m/e (relative intensity) 225 (M^+ + 1, 5), 224 (M^+, 39), 208 (10), 180 (19), 179 (100), 178 (30), 152 (27), 102 (15), 77 (67). Anal. Calcd for $C_{13}H_{12}N_4$: C, 69.62; H, 5.39; N, 24.98. Found: C, 69.51; H, 5.43; N, 25.17.

General Procedure for the Preparation of 1-Substituted 2-(Alkyl(aryl)amino)-1H-1,2,4-triazolo[2,3-b]indazoles (8). To a well-stirred suspension of the appropriate iminophosphorane **3** (1 mmol) in 10 mL of dry toluene was added the isocyanate (1 mmol). The resultant mixture was stirred at reflux temperature for 4 h. After cooling, the separated solid was collected by filtration and recrystallized from toluene to give **8** as a crystalline solid.

8a: yield 60%; mp 288–289 °C; white prisms; IR (Nujol) 3364, 1636, 1608, cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 6.87 (t, ^3J = 7.2 Hz, 1 H, H-8), 6.99 (t, ^3J = 7.2 Hz, 1 H), 7.18–7.36 (m, 4 H), 7.55–7.63 (m, 4 H), 7.70 (t, ^3J = 7.0 Hz, 2 H), 7.84 (d, ^3J = 7.3 Hz, 2 H), 9.31 (s, 1 H, NH); ^{13}C NMR (DMSO-d_6) δ 102.39 (C-9a), 115.77 (C-6), 116.82 (C-9), 117.66 (C-8), 118.21, 121.90, 124.57 (C-7), 125.91, 128.28 (C-10), 128.73, 129.21, 130.21, 133.06, 139.84, 147.92 (C-5a), 149.09 (C-2); mass spectrum, m/e (relative intensity) 326 (M^+ + 1, 9), 325 (M^+, 42), 208 (5), 194 (7), 179 (100), 178 (37), 152 (18), 118 (10), 91 (8), 77 (82). Anal. Calcd for $C_{20}H_{15}N_5$: C, 73.83; H, 4.65; N, 21.52. Found: C, 74.07; H, 4.74; N, 21.69.

8b: yield 59%; mp 278–279 °C; white prisms; IR (Nujol) 3211, 1635, 1620, 1585 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 6.82 (t, ^3J = 7.6 Hz, 1 H, H-8), 6.97 (t, ^3J = 8.7 Hz, 2 H), 7.16 (dd, ^3J = 8.6, ^3J = 7.6 Hz, 1 H, H-7), 7.22 (d, ^3J = 8.6 Hz, 1 H, H-9), 7.48–7.74 (m, 8 H), 9.08 (s, 1 H, NH); ^{13}C NMR (DMSO-d_6) δ 101.16 (C-9a), 113.68 (J = 22.3 Hz, C_o), 114.46 (C-6), 115.38 (C-9), 116.40 (C-8), 118.84 (J = 7.7 Hz, C_m), 123.17 (C-7), 124.31, 126.81 (C-10), 127.71, 128.77, 131.72, 134.35 (J = 2.6 Hz, C_p), 146.77 (C-5a), 147.90 (C-2), 156.41 (J = 240.0 Hz, C_i); mass spectrum, m/e (relative intensity) 344 (M^+ + 1, 4), 343 (M^+, 20), 194 (8), 179 (100), 178 (40), 152 (17), 151 (9), 136 (13), 109 (7), 102 (11), 77 (73). Anal. Calcd for $C_{20}H_{14}FN_5$: C, 69.96; H, 4.11; N, 20.40. Found: C, 70.18; H, 4.25; N, 20.30.

8c: yield 56%; mp 218–219 °C; white prisms; IR (Nujol) 3245, 1630, 1613 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 3 H, CH_3-Ar), 6.84–6.91 (m, 2 H, H-8 and NH), 7.05 (d, ^3J = 8.4 Hz, 2 H), 7.19–7.26 (m, 2 H), 7.42 (d, ^3J = 8.4 Hz, 2 H), 7.50–7.67 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 20.67 (CH_3), 102.78 (C-9a), 116.58 (C-6), 116.69 (C-9), 118.20, 118.28 (C-8), 124.97 (C-7), 125.43, 127.97 (C-10), 129.65, 129.68, 130.80, 132.67, 132.69, 135.53, 148.35 (C-5a), 148.78 (C-2); mass spectrum, m/e (relative intensity) 340 (M^+ + 1, 25), 339 (M^+, 100), 179 (29), 178 (10), 152 (5), 132 (6), 102 (3), 91 (6), 77 (30). Anal. Calcd for $C_{21}H_{17}N_5$: C, 74.32; H, 5.05; N, 20.63. Found: C, 74.19; H, 4.87; N, 20.52.

8d: yield 69%; mp 224–225 °C; white prisms; IR (Nujol) 3154, 1630, 1599 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 1.25 (t, J = 7.0 Hz, 3 H, CH_3), 3.39 (quint, 2 H, CH_2), 6.18 (t, J = 5.6 Hz, 1 H, NH), 6.84 (m, 1 H, H-8), 7.17 (ddd, ^3J = 8.3, ^3J = 6.7, ^4J = 1.1 Hz, 1 H, H-7), 7.25 (dd, ^3J = 8.1, ^4J = 1.1 Hz, 1 H, H-9), 7.50–7.70 (m, 6 H); ^{13}C NMR (DMSO-d_6) δ 13.46 (CH_3), 37.23 (CH_2), 101.88 (C-9a), 114.94 (C-6), 115.65 (C-9), 116.67 (C-8), 123.15 (C-7), 124.04 (C_o), 127.24 (C-10), 127.81 (C_p), 129.30 (C_m), 132.21 (C_i), 146.93 (C-5a), 152.16 (C-2); mass spectrum, m/e (relative intensity) 278 (M^+ + 1, 17), 277 (M^+, 89), 220 (5), 194 (6), 179 (100), 178 (36), 152 (15), 77 (44). Anal. Calcd for $C_{16}H_{15}N_5$: C, 69.30; H, 5.45; N, 25.25. Found: C, 69.10; H, 5.68; N, 25.31.

8e: yield 76%; mp 245–246 °C; white prisms; IR (Nujol) 3160, 1608, 1562 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 2.91 (d, J = 4.6 Hz, 3 H,

CH_3N), 6.76–6.84 (m, 2 H, H-8 and NH), 7.08–7.21 (m, 2 H), 7.45–7.72 (m, 6 H); ^{13}C NMR (DMSO-d_6) δ 29.42 (CH_3), 102.42 (C-9a), 115.57 (C-6), 116.44 (C-9), 117.27 (C-8), 123.74 (C-7), 124.97 (C_o), 128.00 (C-10), 128.58 (C_p), 130.06 (C_m), 132.87 (C_i), 147.33 (C-5a), 153.86 (C-2); mass spectrum, m/e (relative intensity) 264 ($M^+ + 1$, 6), 263 (M^+, 31), 234 (5), 193 (5), 179 (100), 178 (41), 152 (17), 151 (10), 102 (15), 77 (78). Anal. Calcd for $C_{15}H_{13}N_5$: C, 68.43; H, 4.98; N, 26.60. Found: C, 69.19; H, 4.72; N, 26.33.

8f: yield 47%; mp 290–291 °C; white prisms; IR (Nujol) 3369, 1602, 1574 cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.85 (s, 3 H, CH_3O), 6.60 (t, ^3J = 7.9 Hz, 1 H), 6.92 (t, ^3J = 6.7 Hz, 1 H), 7.11–7.27 (m, 6 H), 7.47–7.64 (m, 5 H), 8.91 (s, 1 H, NH); ^{13}C NMR (DMSO-d_6) δ 54.96 (CH_3O), 101.99 (C-9a), 114.75, 115.21 (C-6), 116.26 (C-9), 117.07 (C-8), 117.72, 121.41, 123.99 (C-7), 124.90, 127.03, 128.00 (C-10), 128.06, 139.14, 147.59 (C-5a), 148.86 (C-2), 159.37; mass spectrum, m/e (relative intensity) 356 ($M^+ + 1$, 15), 355 (M^+, 72), 209 (53), 194 (14), 180 (8), 179 (8), 166 (22), 118 (20), 107 (10), 106 (100), 104 (16), 92 (53), 91 (47), 77 (48). Anal. Calcd for $C_{21}H_{17}N_5O$: C, 70.97; H, 4.82; N, 19.71. Found: C, 71.17; H, 4.77; N, 19.58.

8g: yield 53%; mp 299–300 °C; white prisms; IR (Nujol) 3381, 1619, 1574 cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.87 (s, 3 H, CH_3O), 6.85 (t, ^3J = 7.7 Hz, 1 H, H-7), 7.13–7.26 (m, 6 H), 7.52–7.66 (m, 3 H), 7.75 (d, ^3J = 8.8 Hz, 2 H), 9.18 (s, 1 H, NH); ^{13}C NMR (DMSO-d_6) δ 55.58 (CH_3O), 102.36 (C-9a), 115.28 (J = 22.5 Hz, C_o), 115.39, 115.71 (C-6), 116.74 (C-9), 117.55 (C-8), 120.18 (J = 7.7 Hz, C_m), 124.51 (C-7), 125.28, 127.98, 128.68 (C-10), 136.10 (J = 2.4 Hz, C_p), 147.83 (C-5a), 149.72 (C-2), 157.45 (J = 238.8 Hz, C_i), 159.86; mass spectrum, m/e (relative intensity) 374 ($M^+ + 1$, 15), 373 (M^+, 59), 210 (10), 209 (63), 194 (12), 180 (10), 179 (9), 166 (24), 136 (18), 107 (12), 106 (100), 104 (21), 102 (10), 95 (12), 92 (44), 91 (31), 77 (31). Anal. Calcd for $C_{21}H_{16}FN_5O$: C, 67.55; H, 4.32; N, 18.76. Found: C, 67.38; H, 4.51; N, 18.63.

8h: yield 67%; mp 233–234 °C; white crystals; IR (Nujol) 3171, 1633, 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.07 (d, J = 5.1 Hz, 3 H, CH_3N), 3.85 (s, 3 H, CH_3O), 4.60 (q, J = 5.1 Hz, 1 H, NH), 6.86 (m, 1 H, H-8), 7.04 (d, ^3J = 9.0 Hz, 2 H, H_m), 7.21 (ddd, ^3J = 9.1, ^3J = 7.0, ^4J = 1.5 Hz, 1 H, H-7), 7.24 (dd, ^3J = 8.0, ^4J = 1.5 Hz, 1 H, H-9), 7.47 (d, ^3J = 9.0 Hz, 2 H, H_o), 7.63 (dd, ^3J = 9.1, ^4J = 1.0 Hz, 1 H, H-6); ^{13}C NMR ($CDCl_3$) δ 29.97 (CH_3N), 55.64 (CH_3O), 102.85 (C-9a), 115.66 (C_m), 116.46 (C-6), 116.50 (C-9), 117.86 (C-8), 124.44 (C-7), 125.22 (C_i), 126.77 (C_o), 128.84 (C-10), 148.39 (C-5a), 153.72 (C-2), 160.15 (C_p); mass spectrum, m/e (relative intensity) 294 ($M^+ + 1$, 21), 293 (M^+, 98), 209 (52), 208 (5), 194 (15), 121 (10), 116 (5), 107 (10), 106 (100), 102 (16), 77 (28). Anal. Calcd for $C_{16}N_{15}N_5O$: C, 65.52; H, 5.15; N, 23.88. Found: C, 65.70; H, 5.28; N, 23.60.

8i: yield 59%; mp 200–201 °C; colorless crystals; IR (Nujol) 3177, 1637, 1616 cm^{-1}; ^1H NMR ($CDCl_3$ + DMSO-d_6) δ 1.01 (t, J = 7.3 Hz, 3 H, CH_3), 1.97 (st, 2 H, CCH_2C), 4.35 (t, J = 7.1 Hz, 2 H, CH_2N), 6.94–7.07 (m, 3 H), 7.24 (t, ^3J = 8.6 Hz, 1 H), 7.54–7.68 (m, 4 H), 9.04 (s, 1 H, NH); ^{13}C NMR ($CDCl_3$ + DMSO-d_6) δ 10.44 (CH_3), 22.13 (CH_2), 45.03 (CH_2), 102.42 (C-9a), 114.80 (J = 22.4 Hz, C_o), 115.39 (C-6), 116.46 (C-9), 117.33 (C-8), 119.48 (J = 7.6 Hz, C_m), 124.07 (C-7), 128.17 (C-10), 135.59 (J = 2.5 Hz, C_p), 147.85 (C-5a), 149.62 (C-2), 157.44 (J = 240.5 Hz, C_i); mass spectrum, m/e (relative intensity) 310 ($M^+ + 1$, 18), 309 (M^+, 93), 266 (39), 199 (11), 137 (81) 136 (24), 118 (20), 117 (47), 110 (17), 103 (79), 102 (100), 95 (23), 77 (18). Anal. Calcd for $C_{17}H_{16}FN_5$: C, 66.01; H, 5.21; N, 22.64. Found: C, 65.82; H, 5.39; N, 22.81.

8j: yield 88%; mp 203–204 °C; white prisms; IR (Nujol) 3205, 1637, 1614 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (t, J = 7.0 Hz, 3 H, CH_3C), 1.92 (quint, 2 H, CCH_2C), 3.07 (d, J = 4.8 Hz, 3 H, CH_3N), 4.16 (t, J = 7.0 Hz, 2 H, CH_2N), 6.47 (q, J = 4.8 Hz, 1 H, NH), 6.99 (m, 1 H, H-8), 7.27 (ddd, ^3J = 8.2, ^3J = 6.5, ^4J = 0.9 Hz, 1 H, H-7), 7.58 (dd, ^3J = 7.3, ^4J = 0.9 Hz, 1 H, H-9), 7.62 (dd, ^3J = 8.2, ^4J = 0.7 Hz, 1 H, H-6); ^{13}C NMR ($CDCl_3$) δ 11.00 (CH_3), 22.52 (CH_2), 29.85 (CH_3N), 45.57 (CH_2N), 103.28 (C-9a), 115.65 (C-6), 116.63 (C-9), 117.85 (C-8), 124.56 (C-7), 129.50 (C-10), 148.14 (C-5a), 155.10 (C-2); mass spectrum, m/e (relative intensity) 230 ($M^+ + 1$, 13), 229 (M^+, 100), 187 (22), 186 (79), 118 (16), 117 (38), 116 (10), 103 (76), 102 (92), 90 (15), 76 (24). Anal. Calcd for $C_{12}H_{15}N_5$: C, 62.86; H, 6.59; N, 30.54. Found: C, 63.07; H, 6.44; N, 30.67.

Preparation of 1-Phenyl-2-oxo-2,3-dihydro-1*H*-1,2,4-triazolo[2,3-*b*]indazole (9). The iminophosphorane **3a** (0.96 g, 2 mmol) in dry toluene (40 mL) and an excess of solid carbon dioxide were heated in a sealed tube at 120 °C for 8 h. After cooling, the solvent was removed under reduced pressure, and the crude product was slurried with diethyl ether (15 mL), filtered, and recrystallized from toluene to give **9**: 0.25 g (50%); mp 234–235 °C; brown prisms; IR (Nujol) 1636 cm^{-1}; ^1H NMR ($CDCl_3$ + TFA) δ 7.40–7.48 (m, 1 H), 7.56–7.79 (m, 8 H); ^{13}C NMR ($CDCl_3$ + TFA) δ 107.24 (C-9a), 112.84, 119.60, 125.07, 125.20, 130.57, 130.82, 132.68, 134.68, 142.21, 158.91 (C-10 was unobserved); mass spectrum, m/e (relative intensity) 250 (M^+, 5), 209 (100), 208 (60), 193 (5), 179 (23), 178 (12), 119 (13), 118 (12), 91 (23). Anal. Calcd for $C_{14}H_{10}N_4O$: C, 67.19; H, 4.03; N, 22.39. Found: C, 66.92; H, 3.97; N, 22.48.

Preparation of 1-Phenyl-2-thioxo-2,3-dihydro-1*H*-1,2,4-triazolo[2,3-*b*]indazole (10). A solution of iminophosphorane **3a** (0.96 g, 2 mmol) in dry toluene (30 mL) and an excess of carbon disulfide (15 mL) was stirred under nitrogen at reflux temperature for 8 h. After cooling, the precipitated solid was collected by filtration and recrystallized from toluene to give **10**: 0.3 g (58%); mp 205–206 °C; light yellow prisms; IR (Nujol) 1240 cm^{-1}; ^1H NMR ($CDCl_3$ + TFA) δ 7.41–7.46 (m, 1 H), 7.64–7.71 (m, 3 H), 7.75–7.84 (m, 5 H); ^{13}C NMR ($CDCl_3$ + TFA) δ 105.12, 113.06, 119.08, 124.78, 125.61, 130.82, 131.32, 132.39, 133.15, 133.77, 143.30, 153.90; mass spectrum, m/e (relative intensity) 266 (M^+, 9), 234 (98), 233 (43), 208 (23), 207 (11), 206 (27), 205 (13), 179 (32), 178 (16), 118 (12), 117 (19), 103 (21), 102 (22), 90 (24), 77 (100). Anal. Calcd for $C_{14}H_{10}N_4S$: C, 63.14; H, 3.78; N, 21.04. Found: C, 62.97; H, 3.95; N, 20.93.

General Procedure for the Preparation of 2-((Triphenylphosphoranylidene)amino)-3-(*N*-alkyl(aryl)-*N*-acylamino)-2*H*-indazoles (11). To a solution of iminophosphorane **3a** (0.96 g, 2 mmol) in 25 mL of dry tetrahydrofuran were added triethylamine (2 mmol) and the appropriate acyl chloride (2 mmol). The reaction mixture was stirred at room temperature for 16 h. The precipitated ammonium salt was separated by filtration, and the filtrate was concentrated to dryness under reduced pressure. The residual material was recrystallized from the appropriate solvent to give **11** as crystalline solids.

11a: yield 71%; mp 158–159 °C; yellow prisms (from tetrahydrofuran/diethyl ether); IR (Nujol) 1670, 1625, 1109, 1075 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.75 (s, 3 H, CH_3CO), 4.67 (d, ^2J = 14.0 Hz, 1 H, H_a, NCH_aH_b), 5.33 (d, ^2J = 14.2 Hz, 1 H, H_b, NCH_aH_b), 6.83 (t, ^3J = 8.2 Hz, 1 H), 6.87 (t, ^3J = 7.4 Hz, 1 H), 7.01–7.53 (m, 16 H), 7.72 (ddd, J_{P-H} = 13.6, J_o = 8.4, J_m = 1.4 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 22.04 (CH_3), 50.99 (CH_2), 115.68 (C-7), 116.61 (J = 0.8 Hz, C-3a), 116.77 (C-4), 120.26 (C-5), 123.34 (C-6), 125.53 (J = 11.7 Hz, C-3), 127.09, 127.94, 128.59 (J = 12.3 Hz, C_m), 129.11, 132.29 (J = 2.8 Hz, C_p), 133.31 (J = 10.0 Hz, C_o), 137.64, 142.17 (C-7a), 172.64 (C=O), (C_i was unobserved); mass spectrum, m/e (relative intensity) 540 (M^+, 5), 497 (5), 305 (8), 304 (15), 262 (14), 184 (10), 183 (40), 108 (17), 91 (100), 77 (4). Anal. Calcd for $C_{34}H_{29}N_4PO$: C, 75.54; H, 5.41; N, 10.36. Found: C, 75.38; H, 5.37; N, 10.53.

11b: yield 73%; mp 165–166 °C; colorless prisms (from ethanol); IR (Nujol) 1670, 1625, 1109, 1070, cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.96 (t, J = 7.3 Hz, 3 H), 1.90–2.05 (m, 2 H, CH_2CO), 4.68 (d, ^2J = 14.1 Hz, 1 H, H_a, NCH_aH_b), 5.23 (d, ^2J = 14.1 Hz, 1 H, H_b, NCH_aH_b), 6.78 (ddd, ^3J = 7.9, ^3J = 6.4, ^4J = 1.0 Hz, 1 H, H-5), 6.90 (dd, ^3J = 7.9, ^4J = 1.0 Hz, 1 H, H-4), 6.97–7.10 (m, 4 H), 7.15–7.20 (m, 2 H), 7.28 (d, ^3J = 8.5 Hz, 1 H, H-7), 7.36–7.52 (m, 9 H), 7.73 (ddd, J_{P-H} = 12.1, J_o = 6.7, J_m = 1.6 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 9.17 (CH_3), 27.06 (CH_2CO), 51.12 (CH_2N), 115.55 (C-7), 116.70 (C-4), 116.81 (J = 0.7 Hz, C-3a), 120.05 (C-5), 123.14 (C-6), 124.88 (J = 12.7, C-3), 127.00, 127.89, 128.46 (J = 99.0 Hz, C_i), 128.48 (J = 12.0 Hz, C_m), 129.13, 132.10 (J = 3.0 Hz, C_p), 133.23 (J = 9.6 Hz, C_o), 137.84, 142.07 (C-7a), 175.84 (C=O); mass spectrum, m/e (relative intensity) 554 (M^+, 5), 497 (5), 304 (17), 276 (21), 262 (5), 183 (29), 108 (17), 102 (19), 91 (100), 57 (20). Anal. Calcd for $C_{35}H_{31}N_4PO$: C, 75.80; H, 5.63; N, 10.10. Found: C, 75.98; H, 5.59; N, 10.27.

11c: yield 88%; mp 204–205 °C; colorless crystals (from tetrahydrofuran/diethyl ether); IR (Nujol) 1670, 1625 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (d, J = 7.0 Hz, 3 H), 1.02 (d, J = 7.0 Hz, 3 H), 2.28 (hept, 1 H, $(CH_3)_2CHN$), 4.67 (d, ^2J = 14.0 Hz, 1 H, H_a, CH_aH_bPh), 5.23 (d, ^2J = 14.0 Hz, 1 H, H_b, CH_aH_bPh), 6.80 (dd, ^3J = 6.5, ^4J = 0.8 Hz, 1 H, H-4), 6.92–7.08 (m, 5 H), 7.17–7.21 (m, 2 H), 7.25

(d, ^3J = 8.4 Hz, 1 H, H-7), 7.34–7.54 (m, 9 H), 7.73 (ddd, J_{P-H} = 12.0, J_o = 8.3, J_m = 1.6 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 19.25 (CH_3), 20.10 (CH_3), 32.09 (CH), 51.19 (CH_2), 115.42 (C-7), 116.60 (C-4), 117.01 (C-3a), 119.99 (C-5), 123.03 (C-6), 124.53 (J = 13.2 Hz, C-3), 126.96, 127.86, 128.40 (J = 12.2 Hz, C_m), 128.50 (J = 99.0, C_i), 129.12, 132.03 (J = 2.6, C_p), 133.10 (J = 9.5 Hz, C_o), 137.87, 141.98 (C-7a), 179.64 (C=O); mass spectrum, m/e (relative intensity) 568 (M^+, 5), 305 (15), 304 (50), 290 (48), 278 (19), 277 (28), 276 (28), 262 (27), 185 (10), 184 (13), 183 (81), 152 (12), 108 (14), 91 (100), 77 (12). Anal. Calcd for $C_{36}H_{33}N_4PO$: C, 76.04; H, 5.85; N, 9.05. Found: C, 75.87; H, 6.13; N, 9.19.

11d: yield 68%; mp 140–141 °C; yellow prisms (from diethyl ether); IR (Nujol) 1676, 1625, 1109, 1064 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.81 (t, J = 7.4 Hz, 3 H), 0.96 (t, J = 7.3 Hz, 3 H), 1.44–1.55 (m, 2 H), 1.65–1.96 (m, 2 H, CH_2CO), 3.47–3.61 (m, J = 13.0 Hz, 1 H, H_a, NCH_aH_b), 3.69–4.00 (m, J = 13.0 Hz, 1 H, H_b, NCH_aH_b), 6.95 (ddd, ^3J = 8.0, ^3J = 6.7, ^4J = 1.0 Hz, 1 H, H-5), 7.08 (ddd, ^3J = 8.3, ^3J = 6.7, ^4J = 1.0, Hz, 1 H, H-6), 7.30–7.58 (m, 11 H), 7.80 (ddd, J_{P-H} = 12.0, J_o = 8.2, J_m = 1.6, Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 9.22 (CH_3), 11.40 (CH_3), 21.56 (CH_2), 27.09 (CH_2), 49.14 (CH_2N), 115.79 (C-7), 116.67 (C-4), 117.03 (C-3a), 120.23 (C-5), 123.30 (C-6), 125.31 (J = 12.6 Hz, C-3), 128.49 (J = 99.0 Hz, C_i), 128.51 (J = 12.2 Hz, C_m), 132.15 (J = 3.0 Hz, C_p), 133.23 (J = 10.0 Hz, C_o), 142.22 (C-7a), 175.76 (C=O); mass spectrum, m/e (relative intensity) 506 (M^+, 5), 449 (5), 304 (15), 228 (40), 183 (38), 118 (14), 117 (100), 108 (30), 107 (14), 103 (31), 90 (38), 77 (10). Anal. Calcd for $C_{31}H_{31}N_4PO$: C, 73.50; H, 6.17; N, 11.06. Found: C, 73.35; H, 5.98; N, 11.29.

11e: yield 79%; mp 208–209 °C; white prisms (from methylene chloride/diethyl ether); IR (Nujol) 1659, 1517, 1115, 1070 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, J = 7.5 Hz, 3 H, CH_3), 1.60–1.75 (m, 2 H), 3.78–3.92 (m, ^2J = 13.0 Hz, 1 H, H_a, NCH_aH_b), 3.94–4.09 (m, ^2J = 13.0 Hz, 1 H, H_b, NCH_aH_b), 6.80–7.04 (m, 5 H), 7.17 (dd, ^3J = 8.0, ^4J = 1.3 Hz, 1 H), 7.33–7.50 (m, 12 H), 7.70 (ddd, J_{P-H} = 12.0, J_o = 8.4, J_m = 1.6 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 11.46 (CH_3), 21.26 (CH_2), 50.47 (CH_2N), 115.41 (C-7), 116.33 (C-4), 116.82 (C-3a), 119.92 (C-5), 122.87 (C-6), 125.20 (J = 13.4 Hz, C-3), 127.25, 127.53, 128.37 (J = 12.0 Hz, C_m), 128.65 (J = 99.9 Hz, C_i), 129.41, 131.91 (J = 3.0 Hz, C_p), 133.15 (J = 10.0 Hz, C_o), 136.62, 141.74 (C-7a), 172.15 (C=O); mass spectrum, m/e (relative intensity) 554 (M^+, 5), 304 (17), 277 (11), 276 (30), 185 (10), 183 (35), 118 (13), 117 (100), 108 (23), 105 (45), 103 (24), 90 (31), 77 (61). Anal. Calcd for $C_{35}H_{31}N_4PO$: C, 75.80; H, 5.63; N, 10.10. Found: C, 75.63; H, 5.84; N, 10.24.

11f: yield 52%; mp 162–163 °C; white prisms (from diethyl ether); IR (Nujol) 1693, 1625, 1104, 1064 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.05 (t, J = 7.4 Hz, 3 H, CH_3), 2.10–2.30 (m, 2 H, CH_2), 6.99 (t, ^3J = 7.0 Hz, 1 H, H-5), 7.08–7.23 (m, 4 H), 7.31–7.51 (m, 13 H), 7.76 (ddd, J_{P-H} = 12.0, ^3J = 7.0, ^4J = 1.5 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 9.15 (CH_3), 27.90 (CH_2), 115.79 (C-7), 116.50 (C-4), 116.93 (J = 0.8 Hz, C-3a), 120.53 (C-5), 123.39 (C-6), 124.10 (J = 13.0 Hz, C-3), 125.88, 126.12, 128.39 (J = 99.0 Hz, C_i), 128.51 (J = 12.0 Hz, C_m), 128.53, 132.15 (J = 3.0 Hz, C_p), 133.29 (J = 9.5 Hz, C_o), 141.71, 142.29 (C-7a), 175.58 (C=O); mass spectrum, m/e (relative intensity) 540 (M^+, 5), 483 (5), 304 (32), 263 (16), 262 (88), 193 (21), 192 (14), 184 (17), 183 (93), 152 (16), 108 (19), 77 (49), 57 (100). Anal. Calcd for $C_{34}H_{29}N_4PO$: C, 75.54; H, 5.41; N, 10.36. Found: C, 75.39; H, 5.68; N, 10.26.

11g: yield 54%; mp 210–211 °C; white prisms (from tetrahydrofuran/diethyl ether); IR (Nujol) 1687, 1625, 1115, 1064 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.05 (d, J = 6.7 Hz, 3 H, CH_3), 1.17 (d, J = 6.7 Hz, 3 H, CH_3), 2.48–2.62 (m, 1 H), 6.97 (t, ^3J = 7.3 Hz, 1 H, H-5), 7.05–7.25 (m, 4 H), 7.32–7.57 (m, 13 H), 7.80 (ddd, J_{P-H} = 12.2, J_o = 8.4, J_m = 1.5 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 19.20 (CH_3), 20.06 (CH_3), 32.62 (CH), 115.70 (C-7), 116.45 (C-4), 117.00 (C-3a), 120.49 (C-5), 123.34 (C-6), 124.10 (J = 13.2 Hz, C3), 125.98, 126.43, 128.35 (J = 99.5 Hz, C_i), 128.46 (J = 12.3 Hz, C_m), 128.51, 132.10 (J = 3.0 Hz, C_p), 133.23 (J = 9.6 Hz, C_o), 141.85, 142.25 (C-7a), 179.50 (C=O); mass spectrum, m/e (relative intensity) 554 (M^+, 5), 4.83 (4), 277 (15), 276 (4), 184 (5), 183 (21), 179 (29), 108 (18) 77 (100). Anal. Calcd for $C_{35}H_{31}N_4PO$: C, 75.80; H, 5.63; N, 10.10. Found: C, 76.04; H, 5.41; N, 9.93.

General Procedure for the Preparation of 2-Alkyl-1-benzyl-1*H*-1,2,4-triazolo[2,3-*b*]indazoles (12). To a well-stirred suspension of the appropriate *N*-acyliminophosphorane 11 (1.5 mmol) in 20 mL of aqueous ethanol was added 10 mL of concentrated hydrochloric acid. The resultant mixture was stirred at reflux temperature for 1 h. After cooling, the solvent was removed under reduced pressure, to the residual material was added 50 mL of water and 50 mL of concentrated ammonium hydroxide solution, and the mixture was extracted with methylene chloride (2 × 50 mL). The combined extracts were dried (Na_2SO_4) and evaporated under reduced pressure. The obtained residue was chromatographed on a silica gel column, eluting with ethyl acetate/*n*-hexane [3:1] and then recrystallized from the appropriate solvent to afford **12** as crystalline solids.

12a: yield 45%; mp 149–150 °C; yellow prisms (from methylene chloride/diethyl ether); IR (Nujol) 1636 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.41 (d, J = 7.0 Hz, 6 H, 2 CH_3), 3.18 (hept, J = 7.0 Hz, 1 H, CH), 5.33 (s, 2 H, CH_2Ph), 6.83 (ddd, ^3J = 8.3, ^3J = 6.7, ^4J = 0.7 Hz, 1 H, H-8), 7.03 (dd, ^3J = 8.3, ^4J = 0.8 Hz, 1 H, H-9), 7.13–7.34 (m, 6 H, aryl + H-7), 7.68 (dd, ^3J = 8.8, ^4J = 0.7 Hz, 1 H, H-6); ^{13}C NMR ($CDCl_3$) δ 21.11 (2 CH_3), 25.74 (CH), 48.29 (CH_2), 102.63 (C-9a), 116.34 (C-6), 117.32 (C-9), 117.94 (C-8), 125.51 (C-7), 126.45, 128.65, 129.24, 131.51 (C-10), 134.04, 150.08 (C-5a), 157.73 (C-2); mass spectrum, m/e (relative intensity) 290 (M^+, 15), 275 (5), 248 (5), 116 (6), 104 (8), 103 (13), 102 (21), 92 (21), 91 (100), 65 (30). Anal. Calcd for $C_{18}H_{18}N_4$: C, 74.46; H, 6.25; N, 19.29. Found: C, 74.58; H, 6.45; N, 18.99.

12b: yield 42%; mp 157–158 °C; white crystals (from ethanol/diethyl ether); IR (Nujol) 1625 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.40 (t, J = 7.5 Hz, 3 H, CH_3), 2.85 (q, J = 7.5 Hz, 2 H, CH_2), 5.28 (s, 2 H, CH_2-Ar), 6.85 (ddd, ^3J = 8.0, ^3J = 6.7, ^4J = 0.8 Hz, 1 H, H-8), 7.09 (d, ^3J = 8.0 Hz, 1 H, H-9), 7.15–7.20 (m, 2 H), 7.27 (ddd, ^3J = 8.7, ^3J = 6.7, ^4J = 1.2 Hz, 1 H, H-7), 7.30–7.36 (m, 3 H), 7.70 (d, ^3J = 8.7 Hz, 1 H, H-6); ^{13}C NMR ($CDCl_3$) δ 11.26 (CH_3), 19.12 (CH_2), 48.47 (CH_2-Ar), 102.57 (C-9a), 116.45 (C-6), 117.32 (C-9), 118.06 (C-8), 125.63 (C-7), 126.70, 128.78, 129.33, 131.64 (C-10), 133.98, 150.08 (C-5a), 154.15 (C-2); mass spectrum, m/e (relative intensity) 276 (M^+, 8), 185 (5), 166 (7), 102 (13), 91 (100). Anal. Calcd for $C_{17}H_{16}N_4$: C, 73.89; H, 5.84; N, 20.27. Found: C, 74.14; H, 5.72; N, 20.31.

12c: yield 40%; mp 193–194 °C; colorless crystals (from methylene chloride/diethyl ether); IR (Nujol) 1636 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.50 (s, 3 H, CH_3), 5.23 (s, 2 H, CH_2-Ph), 6.87 (t, ^3J = 6.7 Hz, 1 H, H-8), 7.12 (d, ^3J = 8.5 Hz, 1 H, H-9), 7.15–7.20 (m, 2 H), 7.25–7.40 (m, 4 H), 7.69 (d, ^3J = 8.8 Hz, 1 H, H-6); ^{13}C NMR ($CDCl_3$) δ 11.37 (CH_3), 48.67 (CH_2Ph), 102.47 (C-9a), 116.34 (C-6), 117.29 (C-9), 118.10 (C-8), 125.67 (C-7), 126.79, 128.78, 129.30, 131.48 (C-10), 133.82, 149.70 (C-5a), 149.95 (C-2); mass spectrum, m/e (relative intensity) 262 (M^+, 15), 193 (6), 116 (8), 102 (17), 91 (100). Anal. Calcd for $C_{16}H_{14}N_4$: C, 73.26; H, 5.38; H, 21.36. Found: C, 73.13; H, 5.42; N, 21.19.

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Registry No. **3a**, 126275-51-2; **3b**, 126275-52-3; **3c**, 126275-53-4; **3d**, 127358-29-6; **3e**, 126275-54-5; **3f**, 126275-55-6; **3g**, 126275-56-7; **3h**, 127358-30-9; **3i**, 127358-31-0; **4**, 126275-57-8; **8a**, 127358-32-1; **8b**, 127358-33-2; **8c**, 126275-61-4; **8d**, 126275-60-3; **8e**, 127358-34-3; **8f**, 127358-35-4; **8g**, 126275-63-6; **8h**, 126275-62-5; **8i**, 127358-36-5; **8j**, 126275-64-7; **9**, 127358-37-6; **10**, 127358-38-7; **11a**, 127358-39-8; **11b**, 127358-40-1; **11c**, 127358-41-2; **11d**, 127358-42-3; **11e**, 127358-43-4; **11f**, 127358-44-5; **11g**, 127358-45-6; **12a**, 127358-46-7; **12b**, 127358-47-8; **12c**, 127358-48-9; *o*-$N_3C_6H_4CH$=NPh, 91823-29-9; *o*-$N_3C_6H_4CH$=N-*p*-C_6H_4OMe, 126275-49-8; *o*-$N_3C_6H_4CH$=NPr, 126275-50-1; *o*-$N_3C_6H_4CH$=NCH_2Ph, 96308-06-4; *o*-$N_3C_6H_4CH$=$N(CH_2)_2N$=CH-*o*-$C_6H_4Al_3$, 127358-49-0; $P(Ph)_3$, 603-35-0; $P(NMe_2)_3$, 1608-26-0; $PhP(Me)_2$, 672-66-2; $MeP(Ph)_2$, 1486-28-8; $Ph_2P(CH_2)_2PPh_2$, 1663-45-2; PhNCO, 103-71-9; *p*-FC_6H_4NCO, 1195-45-5; *p*-MeC_6H_4NCO, 622-58-2; EtNCO, 109-90-0; MeNCO, 624-83-9.