Tripod – Tripod Coupling of Triazides with Triphosphanes. The Synthesis, Characterization, and Stability in Solution of New Cage Compounds: Chiral Macrobicyclic Triphosphazides

Mateo Alajarín,* Antonia López-Lázaro, Angel Vidal, and José Berná

Dedicated to the memory of Derek H. R. Barton

Abstract: Several examples of a new type of cage compound, chiral macrobicyclic triphosphazides **15**, have been prepared by tripod – tripod coupling of tris(2-azidobenzyl)amines with 1,1,1-tris[(diphenylphosphino)methyl]ethane (triphos). The structure determination of C_3 or pseudo-C_3-symmetric compounds **15** revealed their propellerlike topology, which accounted for their chirality, the rare *Z* configuration of the three phosphazide units, and a new conformation of the triphos fragment. Compounds **15** decomposed in solution with a phosphane arm-off mechanism, to give rise to complex mixtures instead of the expected tri-λ^5-phosphazenes. The stability of **15** in solution was enhanced by the quaternization of the bridgehead nitrogen atom in the form of an *N*-oxide. Substituents either in the *ortho* position to the *N* termini of the phosphazide units or on the benzylic carbon atoms contributed to a decrease in the stability of macrobicycles **15**, and in some cases even prevented their preparation.

Keywords: azides · cage compounds · chirality · macrocycles · phosphazides

Introduction

Control of self-organization at the molecular level is a field of major interest in molecular design and engineering. Molecular self-assembly, defined as *the evolution towards spatial confinement through spontaneous connection of a few components, resulting in the formation of discrete entities at the molecular, covalent level*,[1] is in fact a special type of synthetic procedure in which several reactions between several reagents occur in one experimental operation to yield the final covalent structure. Molecular self-assembly requires firstly complementary components containing two or more interaction sites capable of establishing multiple connections, and secondly the reversibility of the connecting events in order to allow the full exploration of the energy hypersurface of the system.[2]

Several synthetic strategies may be devised for the construction of macrobicyclic systems. The more direct one is tripod – tripod coupling, a molecular self-assembly process that requires the formation of three bonds in a single step.[3] A major drawback of tripod – tripod coupling is the occurrence of extensive side reactions which minimize the yield of the expected bicyclic product. Only in limited cases[4] have such processes been carried out in synthetically useful yields, provided that a fine tuning of reagents, reactions, and conditions could be achieved.

The imination reaction of tervalent phosphorus derivatives with organic azides is known as the Staudinger reaction.[5] In its classical form, the Staudinger reaction is a two-step process involving the initial electrophilic addition of an azide to a P^{III} center followed by dinitrogen elimination from the intermediate phosphazide $(R^1)_3PN_3R^2$ giving the λ^5-phosphazene $(R^1)_3P{=}NR^2$. The primary imination products, phosphazides, have only been isolated in a few instances.[5b] The X-ray structural data of seven phosphazides[6] revealed the essentially zwitterionic character of the PN_3 framework ($P^+{-}N{=}N{-}N^-$) and the almost exclusive *E* configuration of the central N=N bond.

In a previous communication[7] we reported the preparation of the first two examples of chiral C_3-symmetric, macrobicyclic triphosphazides by a coupling reaction between two tripodal subunits by means of triple P – N bond formation in a Staudinger reaction, and without recourse to high-dilution conditions. Such an unprecedented type of cage compound[8] was shown to possess very rare, intracyclic PN_3 units of *Z* configuration, propellerlike topology, and a new conformation of the tripodal phosphane fragment.

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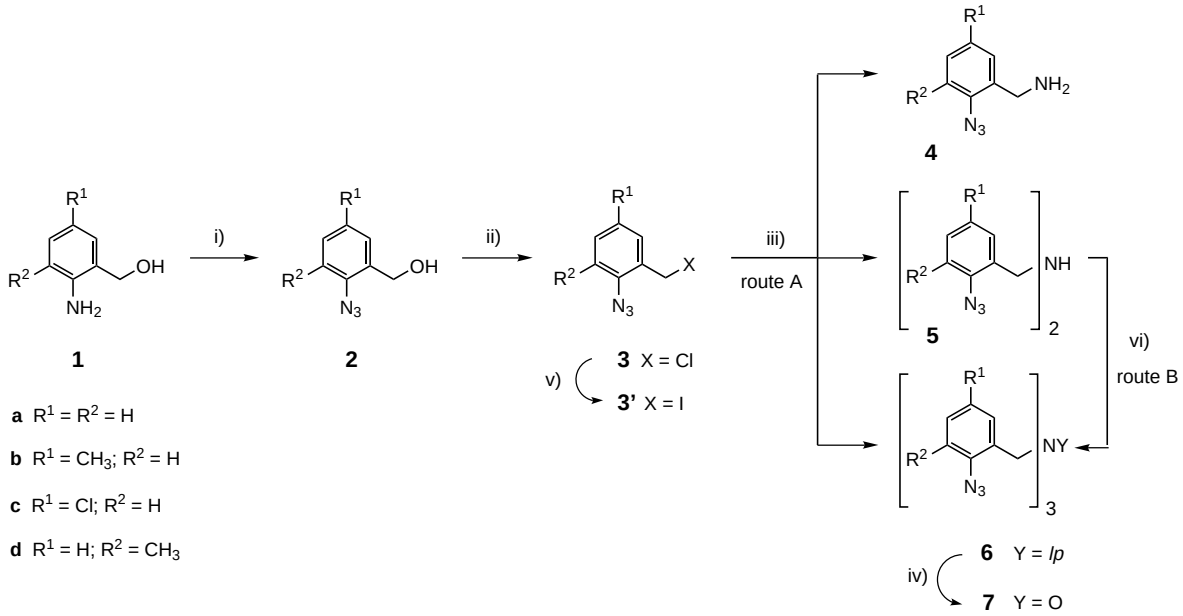


Scheme 1. Synthesis of C_3-symmetric triazides **6** and **7**. Reagents and conditions: i) $NaNO_2$, dil. H_2SO_4, 0 °C, 30 min, then NaN_3, 25 °C, 16 h; ii) $SOCl_2$, CH_2Cl_2, 0 °C, 3 h; iii) liq. NH_3, sealed tube, 25 °C, 48 h; iv) *m*CPBA, $CHCl_3$, 25 °C, 4 h; v) NaI, acetone, 25 °C, 12 h; vi) **3′**, dioxane, reflux, 4 h, then Et_3N, 25 °C, 2 h.

Here we report on the preparation and spectroscopic characterization of a variety of C_3 and pseudo-C_3-symmetric macrobicyclic triphosphazides, along with the discussion of the structural facts that determine their availability and stability in solution. Attempts to explore the dynamic control of the topological asymmetry of these species by the absolute configuration of a stereogenic carbon atom in one of the arms of the bicyclic skeleton are also reported.

Results and Discussion

C_3-Symmetric triazides **6** were prepared by standard procedures, as outlined in Scheme 1, starting from the commercially available 2-aminobenzyl alcohols **1a–d**, which were converted into the 2-azidobenzyl chlorides **3** and iodides **3′** by well-known methods. The alkylation of ammonia by the chlorides **3** gave rise to mixtures of primary, secondary, and tertiary 2-azidobenzyl amines **4**, **5**, and **6**, respectively, in variable yields, from which the pure components could be easily separated by column chromatography. Although the desired tertiary amines **6** were not obtained in high yields (Table 1), the simplicity of the method allowed their preparation in multigram amounts (with the exception of **6c**), and the major components of the reaction mixtures, secondary amines **5**, could be either efficiently converted into **6** by reaction with iodides **3′** or used for the preparation of other triazides (e.g. **8**, Scheme 2). Subsequent oxidation of **6** with *m*CPBA yielded *N*-oxides **7** in good yields.

Table 1. Synthesis of tris(2-azidobenzyl)amines **6** and their *N*-oxides **7**.

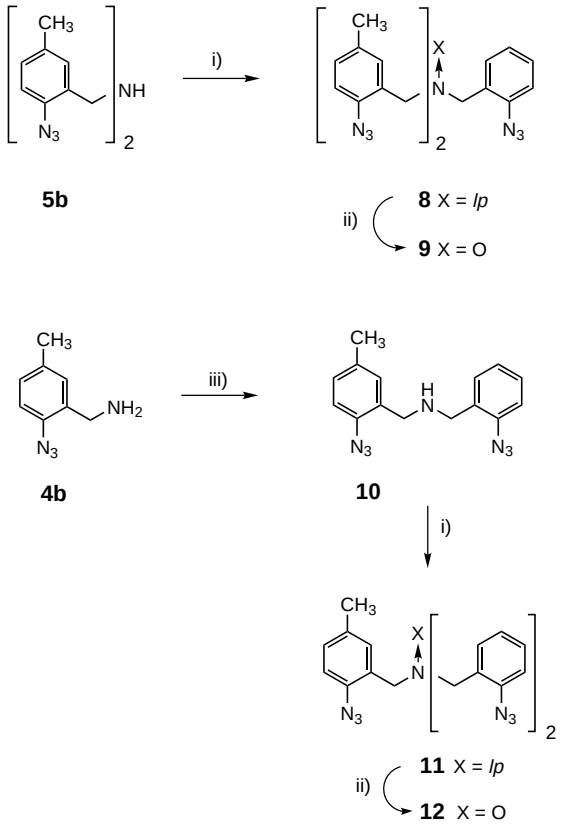
Compound	Route[a]	Yield [%][b]
6a	A	37
	B	59
6b	A	40
6c	A	0
	B	27
6d	A	21
7a		68
7b		87
7c		63
7d		80

[a] For an explanation of routes A and B see Scheme 1. [b] Yield of the last step in the reaction sequence.

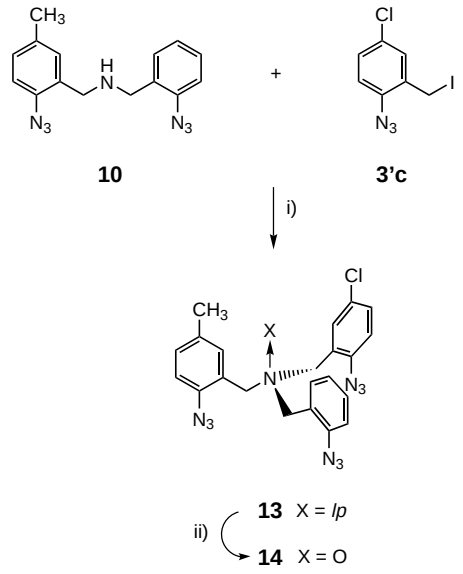
C_S-Symmetric triazides **8** and **11**, and their respective *N*-oxides **9** and **12**, were obtained following similar methodologies (Scheme 2). Thus, alkylation of **5b** with iodide **3′a** yielded **8** (77% yield), which was then oxidized to **9**. The amine **4b**[9] was monoalkylated with 2-azidobenzyl bromide[10] to give **10** (also used in the synthesis of **13**, vide infra), which reacted with **3′a** to give **11** and then **12** by subsequent oxidation.

Asymmetric triazides **13** and **14** were prepared similarly starting from the secondary amine **10** (Scheme 3).

Abstract in Spanish: *En este trabajo se describe la preparación de varios ejemplos de trifosfazidas macrobicíclicas quirales **15** por acoplamiento de especies de estructura tipo trípode: tris(2-azidobencil)aminas y la trifosfina 1,1,1-[tris(difenilfosfino)metil]etano. La determinación estructural de estos compuestos pone de manifiesto su topología helicoidal, responsable de su quiralidad, su simetría local C_3* o pseudo-*C_3, la configuración Z de sus tres unidades fosfazida y un nuevo tipo de conformación del fragmento trifosfina. Se discuten algunos factores estructurales que determinan su estabilidad en disolución.*

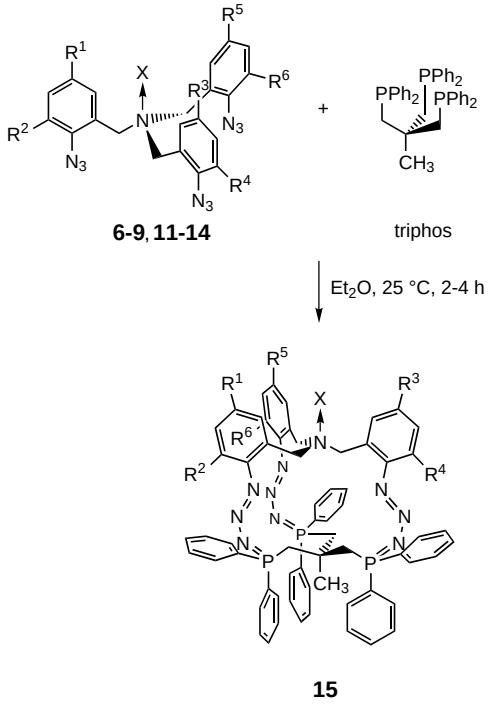


Scheme 2. Synthesis of C_S-symmetric triazides **8** , **9**, **11**, and **12**. Reagents and conditions: i) **3′a**, dioxane, reflux, 4 h, then Et_3N, 25 °C, 2 h; ii) *m*CPBA, $CHCl_3$, 25 °C, 4 h; iii) 2-azidobenzyl bromide, dioxane, reflux, 3 h, then Et_3N, 25 °C, 2 h.



Scheme 3. Synthesis of asymmetric triazides **13** and **14**. Reagents and conditions: i) dioxane, reflux, 4 h, then Et_3N, 25 °C, 2 h; ii) *m*CPBA, $CHCl_3$, 25 °C, 4 h.

The self-assembly of triazides **6–9** and **11–14** with 1,1,1-tris[(diphenylphosphino)methyl]ethane (triphos) was carried out in diethyl ether solution at room temperature. The resulting macrobicyclic triphosphazides **15** (Scheme 4) precipitated from the reaction medium as yellow solids and



Scheme 4. Synthesis of macrobicyclic triphosphazides **15**.

were prepared in good yields, with the exception of **15g** which could not be obtained (Table 2). In this case, the material isolated from the reaction corresponding to entry 7 of Table 2 seemed to be oligomeric, as indicated by its ^1H, ^{13}C, and $^{31}P\{^1H\}$ NMR spectra.

The structure determination of compounds **15** was accomplished by means of their analytical and spectral data. Full characterization of **15a** and **15b** was discussed in our previous communication,[7] and the X-ray structure analysis of **15b** was described; it is shown here for convenience (Figure 1).

Selected physical data of the new triphosphazides **15c**, **15e**, **15i**, **15k**, and **15m/15m′**, as well as the triphosphazide *N*-oxides **15d**, **15f**, **15h**, **15j**, **15l**, and **15n/15n′** were essentially coincident with those of the previously reported **15a** and **15b**, respectively (Table 3). For this reason, tridimensional arrangements of the new compounds **15** prepared here were assumed to be similar to that of **15b**, which has been unequivocally determined by X-ray analysis: a propellerlike shape, with the X, oxygen, or lone pair (*lp*), and CH_3 groups on the bridgehead atoms directed away from the bicyclic cavity, and with three zwitterionic phosphazide units $P^+-N{=}N-N^-$ of *Z* configuration around the central N=N bond, which is *s-cis* in the $P{=}N-N{=}N$ canonical form.

The simplicity of the NMR data of C_3-symmetric **15a–f** and **15h** indicates high symmetry. The $^{31}P\{^1H\}$ NMR spectra of these compounds show only one singlet at $\delta = -2.56$ to 1.34, shifted 25–30 ppm downfield relative to that of the phosphane triphos $\delta = -27.3$,[11] in accordance with previous reports on acyclic phosphazides.[12] In the ^1H and ^{13}C NMR spectra only one set of signals is observed for the three equivalent arms of the bicyclic structure. The methylene protons of the CH_2N and CH_2P groups are magnetically inequivalent in the ^1H NMR spectra, as a consequence of their

0947-6539/98/0412-2560 $ 17.50+.50/0 *Chem. Eur. J.* **1998**, *4*, No. 12

Table 2. Synthesis of macrobicyclic triphosphazides **15**.

Entry	Triazide	R^1	R^2	R^3	R^4	R^5	R^6	X	Product	Yield [%]
1	**6a**	H	H	H	H	H	H	*lp*	**15a**	66
2	**7a**	H	H	H	H	H	H	O	**15b**	85
3	**6b**	CH_3	H	CH_3	H	CH_3	H	*lp*	**15c**	98
4	**7b**	CH_3	H	CH_3	H	CH_3	H	O	**15d**	95
5	**6c**	Cl	H	Cl	H	Cl	H	*lp*	**15e**	42
6	**7c**	Cl	H	Cl	H	Cl	H	O	**15f**	73
7	**6d**	H	CH_3	H	CH_3	H	CH_3	*lp*	**15g**	0
8	**7d**	H	CH_3	H	CH_3	H	CH_3	O	**15h**	27
9	**8**	CH_3	H	CH_3	H	H	H	*lp*	**15i**	41
10	**9**	CH_3	H	CH_3	H	H	H	O	**15j**	88
11	**11**	CH_3	H	H	H	H	H	*lp*	**15k**	57
12	**12**	CH_3	H	H	H	H	H	O	**15l**	75
13	**13**	Cl	H	CH_3	H	H	H	*lp*	**15m/15m′**	60
14	**14**	Cl	H	CH_3	H	H	H	O	**15n/15n′**	93

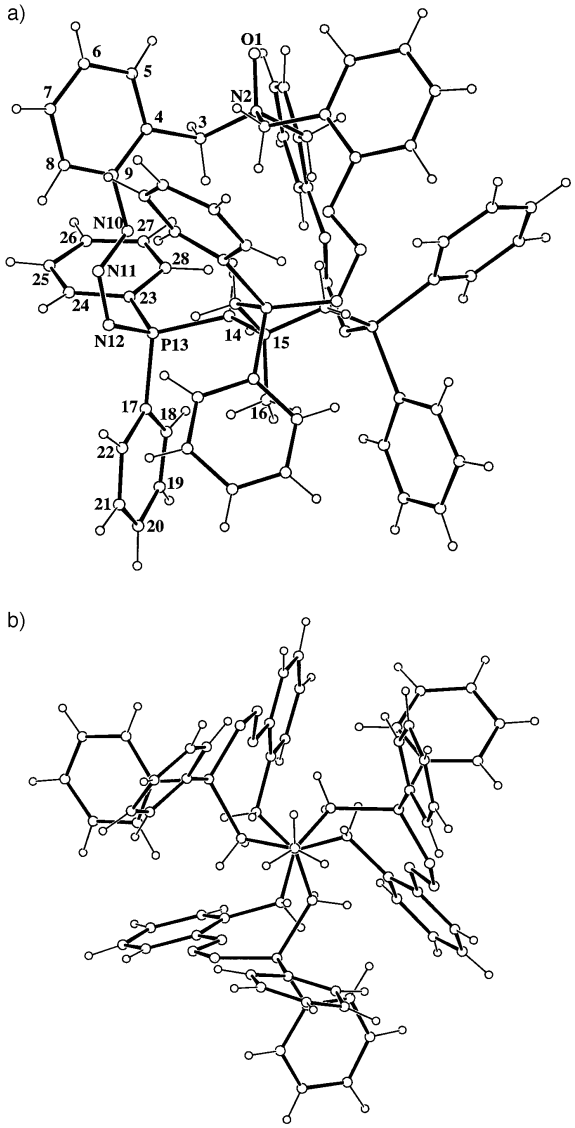


Figure 1. a) Molecular structure of compound **15b;** b) a perspective view as projected along the threefold axis.

Table 3. Selected NMR data of compounds **15**.

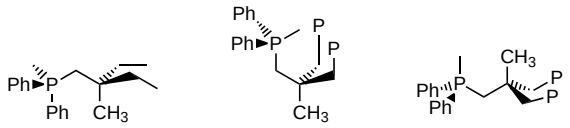
Compound	^{1}H NMR CH_3C	CH_2N	CH_2P	^{13}C NMR CH_3C	CH_3C	CH_2N	CH_2P	^{31}P{^{1}H} NMR *P*
15a	−0.13	3.66 3.88	3.92 4.24	26.36	40.64	55.61	36.51	1.34
15b	−0.03	4.18 4.96	3.85 4.10	25.66	40.33	66.74	37.10	−1.41
15c	−0.13	3.66 3.86	3.92 4.23	26.43	40.70	55.62	36.60	−0.01
15d	−0.06	4.14 4.89	3.80 4.07	25.79	40.39	66.69	37.40	−1.44
15e	−0.15	3.59 3.82	3.92 4.14	26.41	40.69	54.75	36.90	0.44
15f	−0.06	4.85 4.16–3.96	3.75	25.81	40.38	65.13	37.50	−1.22
15h	−0.26	3.93 5.12	4.25[a]	26.21	39.80	64.94	37.15	−2.56
15i	−0.12	4.25–3.65		26.38	40.64	55.46 55.54 55.77	36.56	0.01[a] 0.39
15j	−0.04	4.93–3.76		25.73	40.34	66.58 66.70 66.78	37.28	−1.46[a] −1.36
15k	−0.12	4.32–3.59		26.44	40.72	55.50 55.72[a]	36.60	0.03 0.36[a]
15l	−0.03	4.95–3.79		25.67	40.31	66.62 66.68 66.80	37.11	−1.49 −1.40[a]
15m/15m′	−0.13	4.25–3.50		26.43	40.69	54.98 55.17 55.19 55.35[a] 55.66	36.62	−0.27 −0.21 0.14[a] 0.90 1.04
15n/15n′	−0.05	5.00–3.60		25.77	40.37	67.00–66.00	37.40	−1.73 −1.63 −1.50 −1.37 −0.93 −0.91

[a] Signals of double intensity.

diastereotopic nature, and accounting for the chirality of these propeller-shaped compounds (see Figure 1 b).

In the ^{1}H NMR spectra of compounds **15** described here, the protons of the pivotal CH_3 group appear as a broad singlet at $\delta = -0.26$ to -0.03, notably shifted upfield relative to those in the phosphane ($\delta = 0.95$[11]), contrary to the diastereotopic CH_2P protons appearing at $\delta = 3.50-4.25$, which are shifted downfield from those in the phosphane ($\delta = 2.48$[11]). This data differs from that of most known triphos–transition metal complexes, where these protons appear in the ranges $\delta = 1.12-2.09$ (CH_3) and $\delta = 2.06-2.78$ (CH_2P).[13] The explan-

ation for the peculiar chemical shifts of the protons belonging to the triphos fragment of compounds **15** stems from the unusual conformation of this subunit in the macrobicyclic triphosphazides, which resembles a normal umbrella instead of the characteristic inverted umbrella conformation found in all the known triphos complexes in which the ligand is coordinated in a η^3-fashion.



To the best of our knowledge, this normal umbrella conformation has no precedents and thus accounts for the shielding of the CH_3 protons by the three pseudoapical (vide infra) *Ph*P groups (C17 – C22, Figure 1 a) and the deshielding of the CH_2P protons by the remaining three pseudoequatorial *Ph*P rings (C23 – C28). In this context, the CH_3 carbon atom of **15** is also shielded in the ^{13}C NMR spectra ($\delta = 25.66 - 26.44$, $\delta = 29.5$ and $36 - 40$ in the phosphane and its complexes, respectively).[11, 13] Those relevant NMR shifts may be of diagnostic value for this new type of conformation of the triphos fragment.

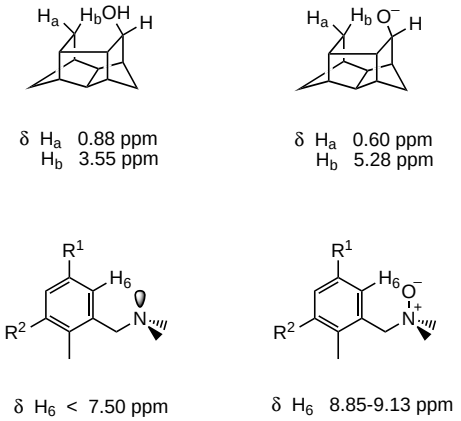
Neither bicyclic compounds incorporating a triphos fragment nor η^3-monometallic triphos complexes showing a CH_3-*in* conformation have been reported to date. An open-chain trimetallic complex incorporating a CH_3-*in* triphos unit has recently been characterized.[14]

With respect to the conformation of the triphos fragment, the inspection of the X-ray crystallographic data of **15b**[7] reveals short atomic contacts H – C(sp^2) (2.95 and 3.01 Å) between the pivotal methyl hydrogen atoms and the π-face of the pseudoapical phenyl groups. These values are in the range of interatomic distances that give rise to stabilizing [CH ··· π] interactions,[15] which probably play a role in the preorganization of triphos in the self-assembly process leading to **15,** as well as in the stability of the resulting products.

In the ^1H NMR spectra of triphosphazide *N*-oxides **15** (X = O) the aromatic protons in the *ortho* position to the CH_2N sidechain appear with considerable downfield shifts ($\delta \approx 9.0$), as a result of the through-space deshielding effect of the oxygen atom. Similar effects have been reported before, as is the case of the half-cage alcohol and the corresponding alkoxide[16] represented in Scheme 5.

In the ^{13}C NMR spectra of compounds **15**, the two phenyl rings linked to each phosphorus atom are magnetically inequivalent, and show notable differences in the $^1J(C,P)$ coupling constants for their two *ipso* carbons (see Experimental Section). This fact is a consequence of the environment of the phosphorus atoms,[7] which causes the differentiation of the two *Ph*P rings: one pseudoapical (C17 – C22, Figure 1 a) and the other pseudoequatorial (C23 – C28).

As expected, the NMR data of triphosphazides **15i – n**, which lack the C_3 symmetry axis, are more complex than those of the C_3-symmetric **15a – f** and **15h**. Compounds **15i – l**, with



Scheme 5. Downfield shifts of protons resulting from through-space deshielding effects of oxygen atoms in ^1H NMR spectroscopy.

only two chemically identical arms, exhibit two singlets in a 2:1 intensity ratio in their $^{31}P\{^1H\}$ NMR spectra. The ^1H and ^{13}C spectra of these bicyclic compounds disclose the diastereotopicity of the two chemically equivalent arms, and there are separate signals for some of their atoms (see Table 3 and Experimental Section).

Entries 13 and 14 of Table 2 merit special consideration. The triphosphazides derived from the constitutionally chiral, racemic amine **13** and *N*-oxide **14**, like the rest of the chiral **15** prepared in this work, have been obtained in racemic form but, in these two last cases, as an approximately equimolecular mixture of two diastereoisomers in each case, **15m/15m′** and **15n/15n′**, respectively. The two diastereoisomers were not separated from their mixtures but analyzed as such, and the diastereomeric composition of the product mixtures (1:1) was deduced by NMR spectroscopy. Their $^{31}P\{^1H\}$ NMR spectra show six singlets of equal intensity which correspond to the three inequivalent phosphorus atoms of each diastereoisomer. The equimolecular diastereomeric composition of the mixtures could also be inferred from some regions of their ^1H and ^{13}C NMR spectra, such as the CH_2N signals in the ^{13}C spectrum of **15m/15m′** and in the range $\delta = 8.7 - 9.2$ in the ^1H spectrum of **15n/15n′**.

From a dynamic stereochemical point of view, the transformations **13** → **15m/15m′** and **14** → **15n/15n′** took place without any diastereoselectivity. This was not unexpected, as one could hardly imagine how the chirality of the benzyl amines **13** and **14**, which results from the different substituents Cl, CH_3, and H at the 5, 5′, and 5″ positions (far away from the cavity of the macrocyclic products), would influence the helicity of the self-assembled products.

The conformational rigidity and stability in solution of compounds **15a** and **15b** were discussed in the communication preceding this paper.[7] The new compounds **15** prepared here have similar properties: i) they do not experience significant, dynamic processes in $CDCl_3$ solution at room temperature, as their ^1H NMR spectra did not change on cooling to 203 K; ii) triphosphazides **15** (X = *lp*) are instable in $CDCl_3$ solutions at room temperature; they totally decompose in less than 24 h (as monitored by NMR) to give intractable mixtures, and iii) triphosphazides **15**

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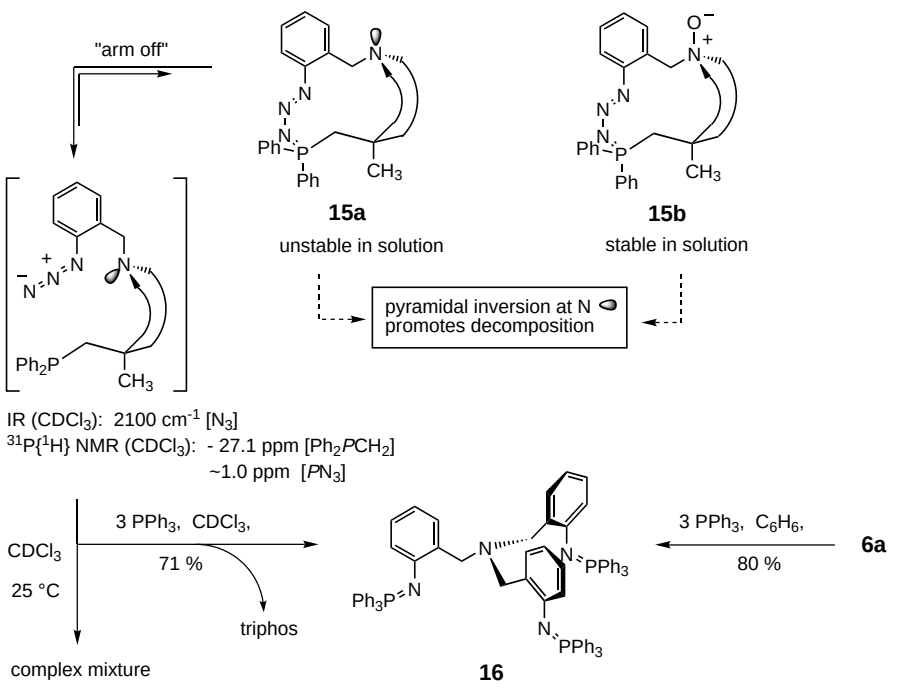


Scheme 6. Mechanistic proposal for the decomposition of compounds **15** (X = *lp*) in $CDCl_3$ solution, and for the preparation of tri-λ^5-phosphazene **16**.

(X = O) are notably more stable; they remain unchanged in $CDCl_3$ solution at room temperature after several weeks; high-temperature ^1H NMR experiments ($CDCl_3$, from 298 to 330 K) showed no changes in their normal spectra.

From this data, as well as from the spectral characteristics of **15**, two consequences could be concluded. Firstly, the propellerlike shape of the chiral macrobicycles is retained in solution in the range of temperatures studied, and enantiomerization processes via labile conformations with local C_1 symmetry could be discarded. Secondly, the lability of **15** (X = *lp*) in solution could be favored by the pyramidal inversion of the bridgehead nitrogen atom, given that its quaternization in the form of the *N*-oxides **15** (X = O) resulted in greater stability.

We reasoned that the lability of **15** (X = *lp*) in solution could result from the initial dissociation of one phosphazide function into phosphane and azide, promoted by the simultaneous inversion of the pivotal nitrogen atom (Scheme 6). This step is slightly reminiscent of the phosphane arm-off mechanism operative in some η^3-triphos–metal complexes by which one phosphane arm temporarily detaches from the metal.[17] Moreover, some phosphazides have been reported to equilibrate in solution with their phosphane and azide counterparts.[18] We have obtained some experimental evidence that support, although not conclusively, the proposed mechanism.

FT-IR experiments on aliquots of a $CDCl_3$ solution of **15a** at room temperature after one hour displayed absorptions near $\tilde{\nu} = 2100\ cm^{-1}$, which may be attributed to the N_3 group of the split PN_3 unit. Similarly, $^{31}P\{^1H\}$ NMR spectra contained one singlet at $\delta = -27.1$, which is in the range of the phosphane P atoms, along with some others signals at $\delta \approx 1.0$, close to the one of pure **15a**, which we attributed to the non-dissociated phosphazide functions. After 10 h both regions of the spectrum contained plenty of signals.

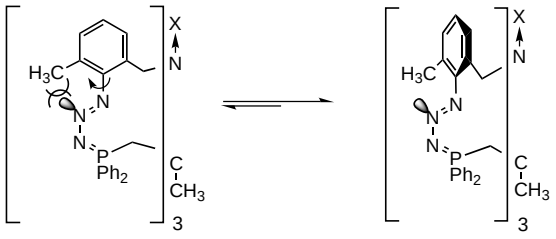
The addition of 3 equivalents of triphenylphosphane to a solution of triphosphazide **15a** in $CDCl_3$ under gentle refluxing led to the quantitative formation of tri-λ^5-phosphazene **16**, which was identical to a sample prepared by reaction of triazide **6a** and PPh_3, along with an equivalent amount of triphos (Scheme 6).

This result accounted for the dissociation, in solution, of the phosphazide functions of **15a**, thus allowing the Staudinger reaction[5] of the so-formed azido groups with the externally added phosphane PPh_3, and the extrusion of dinitrogen from the new phosphazide units to complete the formation of **16**. To our knowledge, such interchange of phosphane fragments in phosphazides has no precedent in the chemical literature.

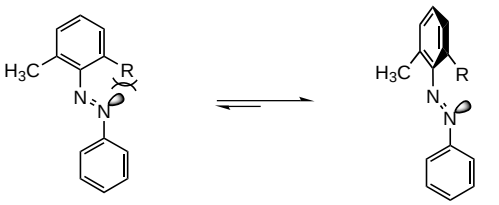
With regard to the factors that govern the stability of **15** in solution, the unsuccessful attempt to prepare triphosphazide **15g** was illustrative. We rationalized this failure to be a consequence, presumably, of the instability of the expected product **15g**, and taking account of the low stability of its *N*-oxide analogue **15h**. Unlike the rest of the triphosphazide *N*-oxides **15** (X = O) in Table 2, which were stable in solution, compound **15h** decomposed in $CDCl_3$ solution at room temperature in less than 6 h. These particular properties of **15g** and **15h** when compared with the other compounds **15** (X = *lp*) and **15** (X = O), respectively, may be due to the presence of three CH_3 groups in the 3, 3′, and 3″ positions of the tribenzylamine fragment, which flank the azido groups. This might cause a twisting of the trisubstituted aromatic rings out of the phosphazide planes, in order to avoid the steric interference of the methyl hydrogens with the lone pair on the central nitrogen of the PN_3 units, thus preventing the effective conjugation of both π-systems and so enhancing the instability of **15g** and **15h**. The effect of substituents R of increasing bulkiness (H < CH_3 < I) at the 6-position in the upfield shifting of the methyl protons in the ^1H NMR spectra of 2-methyl-6-R-substituted azobenzenes[19] has been rationalized in similar terms (*N*-aryl twisting), as summarized in Scheme 7.

In this context, the observed chemical shift of the 3,3′,3″-$(CH_3)_3$ protons in the ^1H NMR spectrum of **15h**, $\delta = 1.71$, may be indicative of the *N*-aryl twisting proposed above to explain its instability in solution.

With the aim of obtaining more information on the effect that substituents in the *ortho* position to the -N_3P groups have on the stability of triphosphazides **15**, we synthesized triazides



15g (X = *lp*)
15h (X = O)



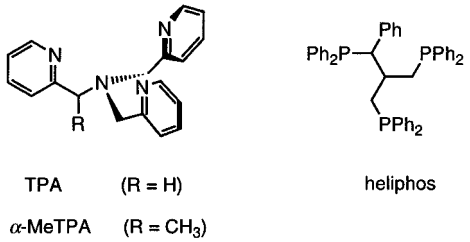
R	δ CH_3
H	2.68
Me	2.38
I	2.20

Scheme 7. *N*-Aryl twisting in triphosphazides **15g**, **15h**, and azobenzenes caused by the steric interference of *ortho* substituents.

18 and **19** by standard methods, starting from the azidobenzyl chloride **3d** (Scheme 8). Both triazides, possessing only one methyl group in the *ortho* position to the azido groups, coupled efficiently with triphos to yield the new macrobicycles **20** and **21**.

The stability in solution of these two triphosphazides was studied by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy in $CDCl_3$ at room temperature. The stability of compound **20** is similar to all the previously described **15** (X = *lp*); it totally decomposed in less than 24 h. In contrast, **21** is approximately as stable as the other **15** (X = O) compounds discussed above, with the exception of **15h**. These qualitative results indicate the negligible effect of one methyl group *ortho* to the -N_3P functions on the stability in solution of the macrobicyclic tris(phosphazide)s.

On the other hand, Canary et al. recently reported the preparation of coordination complexes with propellerlike chirality and C_3-symmetrical arrangements, derived from the tripodal ligand tris(2-pyridylmethyl)amine (TPA).[20] Surprisingly, they found that the presence of an alkyl substituent on the sp^3 carbon atom of one arm of the ligand, in for example amine α-MeTPA, gave rise to coordination complexes in which the sense of twist (Λ or Δ) of their helical asymmetry was dictated by the configuration of the chiral carbon atom (*R* or *S*, respectively). A similar effect has been observed in the preparation of a helical Rh^I complex of the new tripodal ligand 1,3-bis(diphenylphosphino)-2-[(diphenylphosphino)-methyl]-1-phenylpropane (heliphos).[21]

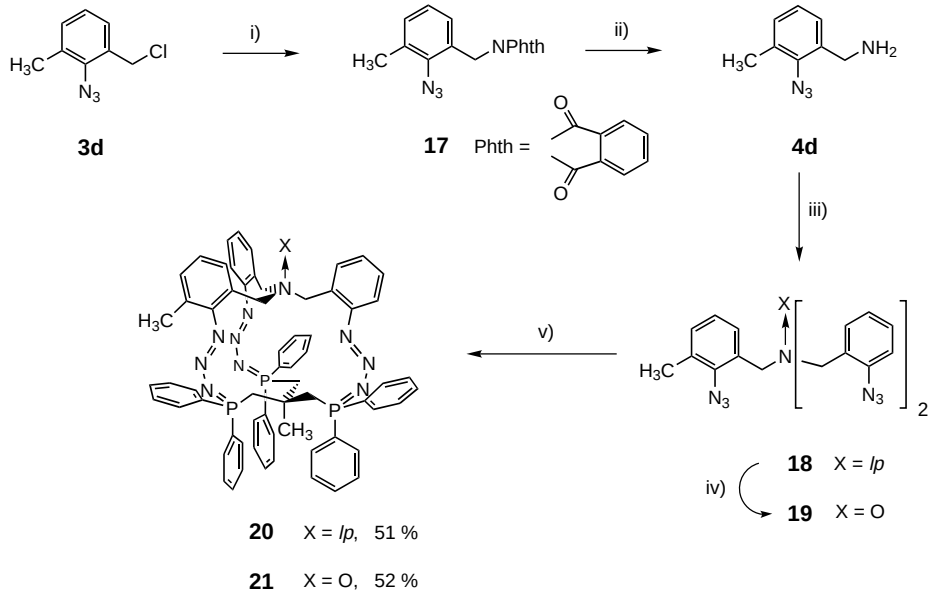


TPA (R = H)
α-MeTPA (R = CH_3)
heliphos

With these results in mind, we prepared racemic triazide **23**, which bears a methyl substituent on a benzylic carbon, by dialkylation of the known amine **22**[9](Scheme 9).

We hoped that the methyl group of triazide **23** would control the topological asymmetry of the triphosphazide, which would result from its self-assembly with triphos, to give rise to predominantly one of the two possible diastereoisomeric macrobicycles. Unfortunately, **23** did not couple efficiently with triphos either under standard conditions (room temperature, diethyl ether) or at lower temperatures; these reactions always yielded uncharacterized oligomers. This failure, obviously associated with the presence of the methyl substituent, may be caused either by the thermodynamic instability of the putative triphosphazide, due to the methyl group placed in the sterically congested interior of the cavity, or by the lower population of the optimally reactive conformer of **23** for the self-assembly reaction when compared with the unsubstituted tribenzylamine **6a**.[22]

In contrast to all phosphazides reported hitherto, the macrobicyclic triphosphazides **15**, **20**, and **21** did not extrude dinitrogen to give



3d **17** Pht = **4d**

20 X = *lp*, 51 %
21 X = O, 52 %
18 X = *lp**
19 X = O

Scheme 8. Synthesis of triphosphazides **20** and **21**. Reagents and conditions: i) Potassium phthalimide (KNPht), DMF, 80 °C, 12 h; ii) $N_2H_4 \cdot H_2O$, EtOH, reflux, 3 h; iii) **3′a**, dioxane, reflux, 4 h, then Et_3N, 25 °C, 2 h; iv) *m*CPBA, $CHCl_3$, 25 °C, 4 h; v) triphos, Et_2O, 25 °C, 2 h.

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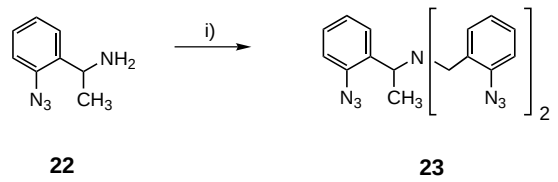
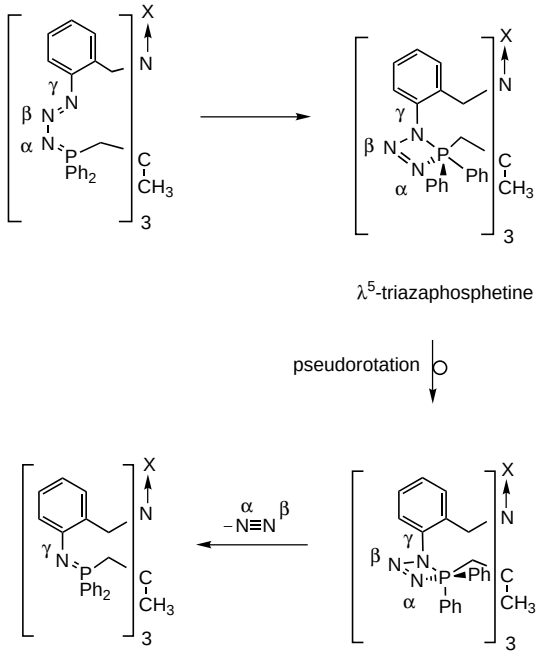


22 **23**

Scheme 9. Synthesis of triazide **23**. Reagents and conditions: i) **3′a**, dioxane, reflux, 4 h, then Et_3N, 25 °C, 2 h.

the corresponding tri-λ^5-phosphazenes upon heating in solution.[5] Instead, such attempts gave only intractable mixtures in which the corresponding tri-λ^5-phosphazenes could neither be isolated nor spectroscopically detected, under a variety of experimental conditions (solvent, temperature). In some way not yet fully understood, the conformational constraints imposed on these triphosphazides by their bicyclic skeletons render difficult either the collapsing of the phosphazide units to four-membered λ^5-triazaphosphetine rings or the Berry pseudorotation[23] at the bipyramidal phosphorus atoms of these phosphacycles, mechanistically mandatory to translate the N_α atom from equatorial to apical position, a prerequisite to the fragmentation of the P–N_α bond that would achieve the extrusion of dinitrogen (Scheme 10).



Scheme 10. Mechanistic pathway for the conversion of macrobicyclic triphosphazides into tri-λ^5-phosphazenes.

The inspection of molecular models of the species represented in Scheme 10 showed severe steric constraints in the structure of the λ^5-triazaphosphetine initially formed, particularly that caused by the apical Ph groups and the methyl hydrogen atoms, as well that caused by the proximity of both methylene groups in each arm of the macrobicyclic skeleton. The less constrained pseudorotation process at the phosphorus appeared to be that which involves the equatorial P–CH_2 bond as a pivot, so that the resulting structure seemed more sterically congested than the former, with severe interactions between the above-mentioned methylene groups (as a result of the shortening of the P–N_γ bond), and also of the new apical Ph groups with several atoms of the arm in their vicinity. In the model of the final λ^5-phosphazene, only the zone between the methylene carbons remained sterically congested.

We are currently investigating which of the above constraints determine the inability of compounds **15** to yield tri-λ^5-phosphazenes by the study of new macrobicyclic triphosphazides less sterically congested than **15**.

Conclusions

A wide range of examples of a new type of cage compound, chiral macrobicyclic triphosphazides, has been prepared. The relevant structural characteristics common to these compounds are:

- their propellerlike topology;
- the rare *s-cis* configuration of their PN_3 units (*Z* configuration of the $P^+–N{=}N–N^-$ canonical form),
- and the unusual conformation of their triphos fragments.

The stability in solution of these species has been qualitatively evaluated and found to be related to the following structural factors:

- the quaternization of the pivotal nitrogen atom, in the form of an *N*-oxide, increased their stability;
- the presence of substituents flanking the *N* termini of the phosphazide functions decreased their stability.

The reported method is not suitable for the synthesis of macrobicyclic tri-phosphazides substituted at the benzylic carbon atoms. These macrobicycles did not collapse to the corresponding tri-λ^5-phosphazenes in the usual way following the Staudinger reaction; instead they decompose in solution, through an arm-off mechanism, to give complex mixtures.

Experimental Section

All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. IR spectra were obtained as Nujol emulsions or films on a Nicolet Impact 400 spectrophotometer. NMR spectra were recorded on a Bruker AC 200 or a Varian Unity 300. Chemical shifts are given relative to tetramethylsilane (TMS) in the case of ^1H and ^{13}C spectra and to 85% aqueous phosphoric acid in the case of ^{31}P. Abbreviations of coupling patterns are as follows: s, singlet; d, doublet; t, triplet; q, quadruplet. Mass spectra were recorded on a Hewlett-Packard 5993C spectrometer (EI) or on a VG-Autospec spectrometer (FAB+). Microanalyses were performed on a Carlo Erba EA-1108 instrument.

Materials: Compounds 2-azidobenzyl alcohol (**2a**),[24] 2-azido-5-methylbenzyl alcohol (**2b**),[25] 2-azido-3-methylbenzyl alcohol (**2d**),[25] 2-azidobenzyl chloride (**3a**),[26] 2-azido-5-methylbenzyl chloride (**3b**),[9] and 2-azido-α-methylbenzylamine (**23**)[9] were prepared following previously reported procedures.

Preparation of 2-azido-5-chlorobenzyl alcohol (2c): A solution of sodium nitrite (3.30 g, 48 mmol) in H_2O (30 mL) was added dropwise to an ice-cooled solution of 2-amino-5-chlorobenzyl alcohol (5.20 g, 33 mmol) in H_2O (40 mL) and concentrated sulfuric acid (7.3 mL). The mixture was stirred at that temperature for 30 min. A solution of sodium azide (4.42 g, 68 mmol) in H_2O (25 mL) was then added dropwise. After stirring for 16 h

at room temperature, the precipitated solid was isolated by filtration, washed with H_2O (100 mL), air dried, and recrystallized from abs. EtOH to give **2c**. Yield: 80%, colorless prisms. M.p. 61–62°C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.61$ (br s, 1H; OH), 4.55 (s, 2H; CH_2), 7.04 (d, J(H,H) = 8.4 Hz, 1H; H3), 7.25 (dd, J(H,H) = 8.4, 2.4 Hz, 1H; H4), 7.35 (d, J(H,H) = 2.4 Hz, 1H; H6); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 60.66$ (CH_2), 119.16, 128.65, 128.72, 130.31 (s), 133.57 (s), 136.03 (s); IR (Nujol): $\tilde{\nu} = 3211$ (OH), 2123 (N_3) cm^{-1}; MS (70 eV, EI): m/z (%) = 185 (7) [M^++2], 183 (22) [M^+], 129 (31), 127 (100); $C_7H_6ClN_3O$ (183.60): calcd C 45.79, H 3.29, N 22.89; found C 45.41, H 3.65, N 23.09.

General procedure for the preparation of the 2-azidobenzyl chlorides (3): Thionyl chloride (4.16 g, 35 mmol) was added dropwise to an ice-cooled solution of the corresponding 2-azidobenzyl alcohol **2** (30 mmol) in dry CH_2Cl_2 (40 mL) and the reaction mixture was stirred at 0°C for 3 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel; diethyl ether/*n*-hexane 1:1), to give compounds **3** as yellow oils.

2-Azido-5-chlorobenzyl chloride (3c): Yield: 91%; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 4.45$ (s, 2H; CH_2), 7.00 (d, J(H,H) = 8.5 Hz, 1H; H3), 7.26 (dd, J(H,H) = 8.5, 2.5 Hz, 1H; H4), 7.33 (d, J(H,H) = 2.5 Hz, 1H; H6); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 40.55$ (CH_2), 119.44, 129.73, 129.94 (s), 130.02 (s), 130.60, 136.89 (s); IR (film): $\tilde{\nu} = 2128$ (N_3) cm^{-1}; MS (70 eV, EI): m/z (%) = 206 (5) [M^++4], 204 (9) [M^++2], 202 (18) [M^+], 88 (100); $C_7H_5Cl_2N_3$ (202.04): calcd C 41.61, H 2.49, N 20.80; found C 41.29, H 2.22, N 21.04.

2-Azido-3-methylbenzyl chloride (3d): Yield: 78%; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.42$ (s, 3H; CH_3), 4.63 (s, 2H; CH_2), 7.00–7.24 (m, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 17.92$ (CH_3), 42.82 (CH_2), 126.16, 128.53, 131.25 (s), 132.02, 133.21 (s), 136.98 (s); IR (film): $\tilde{\nu} = 2130$ (N_3) cm^{-1}; MS (70 eV, EI): m/z (%) = 183 (61) [M^++2], 181 (15) [M^+], 153 (100); $C_8H_8ClN_3$ (181.62): calcd C 52.90, H 4.44, N 23.14; found C 53.13, H 4.81, N 22.81.

General procedure for the preparation of the 2-azidobenzyl iodides (3′): Sodium iodide (2.85 g, 19 mmol) was added in one go to a solution of the corresponding 2-azidobenzyl chloride **3** (13 mmol) in dry acetone (25 mL). The reaction mixture was stirred at room temperature for 12 h. The precipitated solid was separated by filtration. From the filtrate, the solvent was removed under reduced pressure and the resulting material was chromatographed (silica gel; diethyl ether/*n*-hexane 1:1).

2-Azidobenzyl iodide (3′a): Yield: 83%; m.p. 85–87°C (colorless prisms from *n*-hexane); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 4.39$ (s, 2H; CH_2), 7.06 (m, 2H), 7.29 (m, 2H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 0.33$ (CH_2), 118.68, 125.07, 129.52, 130.28, 130.64 (s), 138.16 (s); IR (Nujol): $\tilde{\nu} = 2120$ (N_3) cm^{-1}; MS (70 eV, EI): m/z (%) = 259 (3) [M^+], 132 (100); $C_7H_6IN_3$ (259.05): calcd C 32.45, H 2.33, N 16.22; found C 32.31, H 2.24, N 16.37.

2-Azido-5-chlorobenzyl iodide (3′c): Yield: 86%; m.p. 45–46°C (yellow prisms from diethyl ether); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 4.32$ (s, 2H; CH_2), 7.04 (d, J(H,H) = 8.4 Hz, 1H; H3), 7.25 (dd, J(H,H) = 8.4, 2.4 Hz, 1H; H4), 7.32 (d, J(H,H) = 2.4 Hz, 1H; H6); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = -1.44$ (CH_2), 119.93, 129.48, 130.12 (s), 130.45, 131.96 (s), 136.82 (s); IR (Nujol): $\tilde{\nu} = 2125$ (N_3) cm^{-1}; MS (70 eV, EI): m/z (%) = 166 (18) [$M^+ - I$], 102 (100); $C_7H_5ClIN_3$ (293.49): calcd C 28.65, H 1.72, N 14.32; found C 28.86, H 2.05, N 14.57.

General procedure for the preparation of tris(2-azidobenzyl)amines (6):

Route A: A mixture of the corresponding 2-azidobenzyl chloride **3** (40 mmol) and liquid ammonia (50 mL) was kept 48 h at room temperature in a sealed tube. The excess ammonia was removed by evaporation, followed by the addition of H_2O (100 mL) and NaOH (20 mL, 2N). The mixture was extracted with CH_2Cl_2 (3 × 40 mL), and the organic extracts were combined and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the residue, a mixture of amines **4**, **5**, and **6**, was separated by chromatography [silica gel; 1) ethyl acetate/*n*-hexane 1:1, 2) ethanol].

2-Azidobenzylamine (4a):[27] Yield: 25%.

Bis(2-azidobenzyl)amine (5a):[9] Yield: 37%.

Tris(2-azidobenzyl)amine (6a): Yield: 37%; m.p. 64–66°C (colorless prisms from diethyl ether); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 3.55$ (s, 6H; CH_2), 7.09 (m, 6H), 7.23 (t, J(H,H) = 7.6 Hz, 3H), 7.57 (d, J(H,H) = 7.7 Hz, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 52.94$ (CH_2), 118.04, 124.74, 128.14, 130.40, 130.86 (s), 138.40 (s); IR (Nujol): $\tilde{\nu} = 2128$ (N_3) cm^{-1}; MS (70 eV, EI): m/z (%) = 410 (4) [M^+], 77 (100); $C_{21}H_{18}N_{10}$ (410.44): calcd C 61.45, H 4.42, N 34.12; found C 61.30, H 4.51, N 34.02.

2-Azido-5-methylbenzylamine (4b):[9] Yield: 20%.

Bis(2-azido-5-methylbenzyl)amine (5b): Yield: 35%; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.95$ (br s, 1H; NH), 2.29 (s, 6H; CH_3), 3.65 (s, 4H; CH_2), 6.96–7.21 (m, 6H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 20.67$ (CH_3), 48.85 (CH_2), 117.78, 128.77, 130.91, 130.95 (s), 134.24 (s), 135.19 (s); IR (film): $\tilde{\nu} = 3343$ (NH), 2121 (N_3) cm^{-1}; MS (70 eV, EI): m/z (%) = 307 (5) [M^+], 133 (100); $C_{16}H_{17}N_7$ (307.36): calcd C 62.52, H 5.57, N 31.90; found C 62.38, H 5.45, N 32.00.

Tris(2-azido-5-methylbenzyl)amine (6b): Yield 40%; m.p. 113–115°C (colorless prisms from diethyl ether); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.31$ (s, 9H; CH_3), 3.50 (s, 6H; CH_2), 6.97 (d, J(H,H) = 8.1 Hz, 3H), 7.03 (d, J(H,H) = 8.1 Hz, 3H), 7.33 (s, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 20.95$ (CH_3), 53.04 (CH_2), 117.80, 128.63, 130.44 (s), 131.51, 134.07 (s), 135.55 (s); IR (Nujol): $\tilde{\nu} = 2122$ (N_3) cm^{-1}; MS (70 eV, EI): m/z (%) = 452 (6) [M^+], 91 (100); $C_{24}H_{24}N_{10}$ (452.52): calcd C 63.70, H 5.34, N 30.95; found C 63.51, H 5.23, N 30.90.

2-Azido-5-chlorobenzylamine (4c): Yield: 14%; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.71$ (br s, 2H; NH_2), 3.74 (s, 2H; CH_2), 7.04 (d, J(H,H) = 8.4 Hz, 1H; H3), 7.24 (dd, J(H,H) = 8.4, 2.4 Hz, 1H; H4), 7.29 (d, J(H,H) = 2.4 Hz, 1H; H6); ^{13}C (NMR (50.4 MHz, $CDCl_3$): $\delta = 42.17$ (CH_2), 119.24, 127.94, 128.93, 130.09 (s), 136.04 (s), 136.30 (s); IR (film): $\tilde{\nu} = 3375$ (NH_2), 3278 (NH_2), 2121 (N_3) cm^{-1}; MS (70 eV, EI): m/z (%) = 184 (2) [M^++2], 182 (6) [M^+], 153 (100); $C_7H_7ClN_4$ (182.61): calcd C 46.04, H 3.86, N 30.68; found C 45.89, H 3.59, N 30.83.

Bis(2-azido-5-chlorobenzyl)amine (5c): Yield: 73%; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 3.68$ (s, 4H; CH_2), 7.06 (d, J(H,H) = 8.4 Hz, 2H; H3), 7.27 (dd, J(H,H) = 8.4, 2.3 Hz, 2H; H4), 7.35 (d, J(H,H) = 2.3 Hz, 2H; H6), the NH proton was not observed; ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 48.47$ (CH_2), 119.34, 128.40, 130.19, 132.94 (s), 136.83 (s), a (s) carbon was not observed; IR (film): $\tilde{\nu} = 3290$ (NH), 2133 (N_3) cm^{-1}; MS (70 eV, EI): m/z (%) = 348 (26) [M^+], 140 (100); $C_{14}H_{11}Cl_2N_7$ (348.19): calcd C 48.29, H 3.18, N 28.16; found: 48.45, H 3.23, N 28.31.

Tris(2-azido-5-chlorobenzyl)amine (6c): Yield: 0%.

2-Azido-3-methylbenzylamine (4d): Yield: 12%; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.74$ (br s, 2H; NH_2), 2.30 (s, 3H; CH_3), 3.70 (s, 2H; CH_2), 6.90–7.10 (m, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 24.86$ (CH_3), 42.99 (CH_2), 126.01, 126.67, 130.34, 132.64 (s), 136.08 (s), 149.72 (s); IR (film): $\tilde{\nu} =$ 3375 (NH_2), 3286 (NH_2), 2130 (N_3) cm^{-1}; MS (70 eV, EI): m/z (%) = 162 (21) [M^+]; $C_8H_{10}N_4$ (162.19): calcd C 59.24, H 6.21, N 34.54; found C 59.46, H 6.02, N 34.31.

Bis(2-azido-3-methylbenzyl)amine (5d): Yield: 51%; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.40$ (s, 6H; CH_3), 3.85 (s, 4H; CH_2), 7.05–7.07 (m, 4H), 7.18–7.20 (m, 2H), the NH proton was not observed; ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 18.11$ (CH_3), 49.85 (CH_2), 125.82, 128.00, 130.38, 132.64 (s), 133.81 (s), 136.76 (s); IR (film): $\tilde{\nu} = 3150$ (NH), 2116 (N_3) cm^{-1}; MS (70 eV, EI): m/z (%) = 307 (10) [M^+], 133 (100); $C_{16}H_{17}N_7$ (307.36): calcd C 62.52, H 5.57, N 31.90; found C 62.26, H 5.60, N 31.73.

Tris(2-azido-3-methylbenzyl)amine (6d): Yield: 21%; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.37$ (s, 9H; CH_3), 3.67 (s, 6H; CH_2), 7.05 (m, 6H), 7.41 (dd, J(H,H) = 7.2, 2.1 Hz, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 17.98$ (CH_3), 54.40 (CH_2), 125.68, 128.22, 130.00, 132.50 (s), 132.91 (s), 136.99 (s); IR (film): $\tilde{\nu} = 2114$ (N_3) cm^{-1}; MS (70 eV, EI): m/z (%) = 452 (8) [M^+], 132 (100); $C_{24}H_{24}N_{10}$ (452.52): calcd C 63.70, H 5.34, N 30.95; found C 63.49, H 5.20, N 31.13.

Preparation of (2-azidobenzyl)(2-azido-5-methylbenzyl)amine (10): 2-Azidobenzyl bromide[10] (0.57 g, 3 mmol) was added to a solution of 2-azido-5-methylbenzylamine (**4b**, 0.65 g, 4 mmol) in dry dioxane (20 mL). The mixture was heated at reflux temperature for 3 h. After cooling to room temperature, triethylamine (0.40 g, 4 mmol) was added, and the mixture then stirred for 2 h. The triethylammonium bromide was separated by filtration, and the solvent removed under reduced pressure. The resulting material was chromatographed (silica gel; ethyl acetate/*n*-hexane 2:3), to give **10** as a pale oil.

(2-Azidobenzyl)(2-azido-5-methylbenzyl)amine (10): Yield: 39%; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.26$ (s, 1H; NH), 2.31 (s, 3H; CH_3), 3.68 (s, 2H; CH_2), 3.72 (s, 2H; CH_2), 7.00–7.15 (m, 4H), 7.27–7.34 (m, 3H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 20.86$ (CH_3), 48.97 (CH_2), 49.03 (CH_2),

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118.01, 118.13, 124.75, 128.46, 128.99, 130.44, 131.04 (s), 131.10, 131.39 (s), 134.49 (s), 135.40 (s), 138.26 (s); IR (film): $\tilde{\nu}$ = 2131 (N_3) cm^{-1}; MS (70 eV, EI): *m*/*z* (%) = 293 (5) [M^+], 133 (100); $C_{15}H_{15}N_7$ (293.33): calcd C 61.42, H 5.15, N 33.42; found C 61.27, H 4.98, N 33.58.

General procedure for the preparation of tris(2-azidobenzyl)amines:

Route B: The appropriate 2-azidobenzyl iodide (1 mmol) was added to a solution of the corresponding bis(2-azidobenzyl)amine (1 mmol) in dry dioxane (20 mL), and the mixture was stirred at reflux temperature for 8 h. After cooling to room temperature, triethylamine (0.15 g, 1.3 mmol) was added, and the mixture was stirred for 3 h. The triethylammonium iodide was separated by filtration. From the filtrate, the dioxane was evaporated to dryness and the residue was purified by column chromatography (silica gel; ethyl acetate/*n*-hexane 3:7).

Tris(2-azido-5-chlorobenzyl)amine (**6c**): Yield: 27%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.50 (s, 6H; CH_2), 7.00 (d, *J*(H,H) = 8.5 Hz, 3H; H3), 7.21 (dd, *J*(H,H) = 8.5, 2.4 Hz, 3H; H4), 7.48 (d, *J*(H,H) = 2.4 Hz, 3H; H6); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 53.34 (CH_2), 119.22, 128.38, 130.09 (s), 130.80, 131.76 (s), 137.04 (s); IR (film): $\tilde{\nu}$ = 2131 (N_3) cm^{-1}; MS (70 eV, EI): *m*/*z* (%) = 513 (13) [M^+], 102 (100); $C_{21}H_{15}Cl_3N_{10}$ (513.78): calcd C 49.09, H 2.94, N 27.26; found C 48.87, H 2.81, N 27.19.

Bis(2-azido-5-methylbenzyl)(2-azidobenzyl)amine (**8**): Yield: 77%; m.p. 82–84 °C (colorless prisms from diethyl ether); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.31 (s, 6H; CH_3), 3.50 (s, 4H; CH_2), 3.54 (s, 2H; CH_2), 6.94–7.55 (m, 10H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.05 (CH_3), 53.08 (CH_2), 117.89, 118.01, 124.62, 128.08, 128.74, 130.46 (s), 130.66, 130.97 (s), 131.42, 134.20 (s), 135.64 (s), 138.40 (s); IR (Nujol): $\tilde{\nu}$ = 2126 (N_3) cm^{-1}; MS (70 eV, EI): *m*/*z* (%) = 438 (6) [M^+], 91 (100); $C_{23}H_{22}N_{10}$ (438.50): calcd C 63.00, H 5.06, N 31.94; found C 62.86, H 4.97, N 31.99.

Bis(2-azidobenzyl)(2-azido-5-methylbenzyl)amine (**11**): Yield: 76%; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.31 (s, 3H; CH_3), 3.51 (s, 2H; CH_2), 3.54 (s, 4H; CH_2), 6.95–7.29 (m, 8H), 7.36 (s, 1H), 7.54–7.59 (m, 2H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.10 (CH_3), 52.91 (CH_2), 52.98 (CH_2), 117.88, 117.99, 124.66, 128.08, 128.74, 130.46, 130.81 (s), 130.86 (s), 131.14, 134.27 (s), 135.60 (s), 138.35 (s); IR (film): $\tilde{\nu}$ = 2136 cm^{-1}; MS (70 eV, EI): *m*/*z* (%) = 424 (6) [M^+], 77 (100); $C_{22}H_{20}N_{10}$ (424.47): calcd C 62.25, H 4.75, N 33.00; found C 62.03, H 4.61, N 33.09.

(2-Azidobenzyl)(2-azido-5-chlorobenzyl)(2-azido-5-methylbenzyl)amine (**13**): Yield: 58%; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.31 (s, 3H; CH_3), 3.49 (s, 2H; CH_2), 3.51 (s, 2H; CH_2), 3.54 (s, 2H, CH_2), 6.96–7.27 (m, 8H), 7.49 (dd, *J*(H,H) = 8.4, 1.8 Hz, 1H), 7.64 (d, *J*(H,H) = 2.4 Hz, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 19.2 (CH_3), 52.65 (CH_2), 53.28 (CH_2), 53.34 (CH_2), 117.97, 118.08, 119.04, 124.69, 127.88, 128.33, 129.00 (s), 130.15 (s), 130.46, 130.75, 131.54, 132.82 (s), 134.32 (s), 135.76 (s), 136.71 (s), 138.52 (s), one arom CH carbon and one arom (s) carbon were not observed; IR (film): $\tilde{\nu}$ = 2129 (N_3) cm^{-1}; MS (70 eV, EI): *m*/*z* (%) = 458 (21) [M^+], 104 (100); $C_{22}H_{19}ClN_{10}$ (458.92): calcd C 57.58, H 4.17, N 30.52; found C 57.63, H 4.26, N 30.41.

General procedure for the preparation of tris(2-azidobenzyl)amine *N*-oxides: A solution of *m*CPBA (0.26 g, 1.5 mmol) in $CHCl_3$ (20 mL) was added over a period of 1 h to a solution of the corresponding tris(2-azidobenzyl)amine (1.5 mmol) in $CHCl_3$ (25 mL) at 0 °C. The mixture was allowed to warm to room temperature in about 4 h with stirring. The solvent was then removed under reduced pressure and the residue purified by column chromatography (neutral alumina; $CHCl_3$).

Tris(2-azidobenzyl)amine *N*-oxide (**7a**): Yield: 68%; m.p. 113–115 °C (colorless prisms from $CHCl_3$/Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.25 (s, 6H; CH_2), 7.11–7.20 (m, 6H), 7.42 (td, *J*(H,H) = 7.7, 1.6 Hz, 3H), 7.82 (dd, *J*(H,H) = 7.7, 1.3 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 64.23 (CH_2), 117.50, 122.17 (s), 124.67, 130.64, 136.15, 139.85 (s); IR (Nujol): $\tilde{\nu}$ = 2125 (N_3) cm^{-1}; MS (70 eV, EI): *m*/*z* (%) = 426 (10) [M^+], 77 (100); $C_{21}H_{18}N_{10}O$ (426.44): calcd C 59.15, H 4.25, N 32.84; found C 58.98, H 4.12, N 32.97.

Tris(2-azido-5-methylbenzyl)amine *N*-oxide (**7b**): Yield: 87%; m.p. 134–136 °C (colorless prisms from $CHCl_3$/Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.32 (s, 9H; CH_3), 4.19 (s, 6H; CH_2), 7.06 (d, *J*(H,H) = 8.1 Hz, 3H; H3), 7.20 (dd, *J*(H,H) = 8.1, 1.9 Hz, 3H; H4), 7.68 (d, *J*(H,H) = 1.9 Hz, 3H; H6); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 20.82 (CH_3), 64.47 (CH_2), 117.29, 122.41 (s) 131.18, 134.34 (s), 136.50, 136.99 (s); IR (Nujol): $\tilde{\nu}$ = 2131 (N_3) cm^{-1}; MS (70 eV, EI): *m*/*z* (%) = 468 (11) [M^+], 91 (100); $C_{24}H_{24}N_{10}O$ (468.52): calcd C 61.53, H 5.16, N 29.89; found C 61.65, H 5.01, N 29.78.

Tris(2-azido-5-chlorobenzyl)amine *N*-oxide (**7c**): Yield: 63%; m.p. 121–122 °C (colorless prisms from $CHCl_3$/Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.17 (s, 6H; CH_2), 7.11 (d, *J*(H,H) = 8.6 Hz, 3H; H3), 7.39 (dd, *J*(H,H) = 8.6, 2.5 Hz, 3H; H4), 7.90 (d, *J*(H,H) = 2.5 Hz, 3H; H6); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 64.11 (CH_2), 118.68, 123.57 (s), 130.25 (s), 130.91, 135.82, 138.43 (s); IR (Nujol): $\tilde{\nu}$ = 2135 (N_3) cm^{-1}; MS (70 eV, EI): *m*/*z* (%) = 254 (6), 102 (100); $C_{21}H_{15}Cl_3N_{10}O$ (529.78): calcd C 47.61, H 2.85, N 26.44; found C 47.49, H 2.99, N 26.52.

Tris(2-azido-3-methylbenzyl)amine *N*-oxide (**7d**): Yield: 80%; m.p. 90–91 °C (colorless prisms from $CHCl_3$/Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.47 (s, 9H; CH_3), 4.40 (s, 6H; CH_2), 7.08–7.23 (m, 6H), 7.71 (dd, *J*(H,H) = 7.3, 1.4 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 18.25 (CH_3), 65.37 (CH_2), 124.51 (s), 125.84, 132.45 (s), 132.74, 133.17, 138.54 (s); IR (Nujol): $\tilde{\nu}$ = 2126 (N_3) cm^{-1}; MS (70 eV, EI): *m*/*z* (%) = 468 (23) [M^+], 235 (100); $C_{24}H_{24}N_{10}O$ (468.48): calcd C 61.53, H 5.16, N 29.89; found C 61.48, H 5.28, N 29.76.

Bis(2-azido-5-methylbenzyl)(2-azidobenzyl)amine *N*-oxide (**9**): Yield: 38%; m.p. 118–120 °C (colorless prisms from $CHCl_3$/Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.31 (s, 6H; CH_3), 4.21 (s, 4H; CH_2), 4.24 (s, 2H; CH_2), 7.04–7.86 (m, 10H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 20.76 (CH_3), 64.29 (CH_2), 64.45 (CH_2), 117.31, 117.44, 122.18 (s), 122.57 (s), 124.63, 130.48, 131.25, 134.39 (s), 136.17, 136.48, 137.02 (s), 139.79 (s); IR (Nujol): $\tilde{\nu}$ = 2131 (N_3) cm^{-1}; MS (70 eV, EI): *m*/*z* (%) = 454 (14) [M^+], 118 (100); $C_{23}H_{22}N_{10}O$ (454.50): calcd C 60.78, H 4.88, N 30.82; found C 60.59, H 4.99, N 30.77.

Bis(2-azidobenzyl)(2-azido-5-methylbenzyl)amine *N*-oxide (**12**): Yield: 26%; m.p. 117–119 °C (colorless prisms from $CHCl_3$/Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.31 (s, 3H; CH_3), 4.21 (s, 2H; CH_2), 4.24 (s, 4H; CH_2), 7.05–7.46 (m, 8H), 7.64 (s, 1H), 7.85 (d, *J*(H,H) = 7.0 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 20.74 (CH_3), 64.27 (CH_2), 64.46 (CH_2), 117.34, 117.47, 122.02 (s), 122.43 (s), 124.65, 130.54, 131.30, 134.41 (s), 136.16, 136.49, 137.03 (s), 139.82 (s); IR (Nujol): $\tilde{\nu}$ = 2131 (N_3) cm^{-1}; MS (70 eV, EI): *m*/*z* (%) = 440 (12) [M^+], 77 (100); $C_{22}H_{20}N_{10}O$ (440.47): calcd C 59.99, H 4.57, N 31.80; found C 60.11, H 4.48, N 31.67.

(2-Azidobenzyl)(2-azido-5-chlorobenzyl)(2-azido-5-methylbenzyl)amine *N*-oxide (**14**): Yield: 58%; m.p. 83–84 °C (colorless prisms from $CHCl_3$/Et_2O); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.31 (s, 3H; CH_3), 4.21 (s, 2H; CH_2), 4.23 (s, 2H; CH_2), 4.25 (s, 2H; CH_2), 7.00–7.24 (m, 5H), 7.36 (dd, *J*(H,H) = 8.5, 2.4 Hz, 1H), 7.42 (t, *J*(H,H) = 7.9 Hz, 1H), 7.63 (d, *J*(H,H) = 1.5 Hz, 1H), 7.84 (dd, *J*(H,H) = 7.8, 1.5 Hz, 1H), 7.93 (d, *J*(H,H) = 2.5 Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 20.83 (CH_3), 63.61 (CH_2), 64.55 (CH_2), 64.64 (CH_2), 117.43, 117.57, 118.62, 121.73 (s), 122.12 (s), 124.06 (s), 124.82, 130.07 (s), 130.60, 130.78, 131.51, 134.62 (s), 135.74, 136.24, 136.55, 137.08 (s), 138.42 (s), 139.88 (s); IR (Nujol): $\tilde{\nu}$ = 2129 (N_3) cm^{-1}; MS (70 eV, EI): *m*/*z* (%) = 474 (41) [M^+], 234 (100); $C_{22}H_{19}ClN_{10}O$ (474.91): calcd C 55.64, H 4.03, N 29.49; found C 55.47, H 4.19, N 29.40.

General procedure for the preparation of the triphosphazides (**15**): Two solutions of the corresponding tris(2-azidobenzyl)amine (1.5 mmol) in diethyl ether or CH_2Cl_2 (10 mL) and triphos (1.5 mmol) in diethyl ether (10 mL) were simultaneously added to a round-bottom flask containing diethyl ether (15 mL) under nitrogen at room temperature over a period of 30 min with stirring. The resulting mixture was then stirred for 2 h. The precipitated pale yellow solid was filtered, washed with diethyl ether (3 × 10 mL), and dried under vacuum.

Triphosphazide 15a: Yield: 66%; m.p. 254–256 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.13 (s, 3H; C-CH_3), 3.66 (d, *J*(H,H) = 12.9 Hz, 3H; CH_AH_BN), 3.88 (d, *J*(H,H) = 12.9 Hz, 3H; CH_AH_BN), 3.92 (m, 3H; CH_AH_BP), 4.24 (pseudo t, *J*(H,H), (H,P) = 14.1 Hz, 3H; CH_AH_BP), 6.90–7.40 (m, 30H), 7.59 (d, *J*(H,H) = 7.5 Hz, 3H), 7.90 (d, *J*(H,H) = 8.1 Hz, 3H), 8.05–8.12 (m, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 26.36 (br s; CH_3), 36.51 (m; CH_2P), 40.64 (q, ^2J(P,C) = 4.7 Hz; *C*-CH_3), 55.61 (CH_2N), 116.71, 126.27, 127.30, 128.35 (d, ^1J(P,C) = 104.5 Hz; *i*C-PhP), 128.62 (d, ^1J(P,C) = 83.2 Hz; *i*C-PhP), 128.64 (d, ^3J(P,C) = 11.2 Hz; *m*C-PhP), 128.74 (d, ^3J(P,C) = 11.8 Hz; *m*C-PhP), 130.13 (d, ^2J(P,C) = 9.0 Hz; *o*C-PhP), 130.39, 131.30 (d, ^4J(P,C) = 2.9 Hz; *p*C-PhP), 131.86 (d, ^4J(P,C) = 2.3 Hz; *p*C-PhP), 132.45 (d, ^2J(P,C) = 7.8 Hz; *o*C-PhP), 132.88 (C1), 147.78 (C2); ^{31}P (121.4 MHz, $CDCl_3$): δ = 1.34; IR (Nujol): $\tilde{\nu}$ = 1437 (C–P), 1112 (N–P) cm^{-1}; MS (FAB +): *m*/*z* = 1036 [MH^+]; $C_{62}H_{57}N_{10}P_3$ (1035.13): calcd C 71.94, H 5.55, N 13.53; found C 71.62, H 5.66, N 12.74.

Triphosphazide 15b: Yield: 85%; m.p. 270–272°C (pale yellow prisms from $CHCl_3/Et_2O$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = -0.03$ (br s, 3H, CH_3), 3.85 (pseudo t, $J(H,H)$, $(H,P) = 14.0$ Hz, 3H; CH_AH_BP), 4.10 (m, 3H; CH_AH_BP), 4.18 (d, $J(H,H) = 13.1$ Hz, 3H; CH_AH_BN), 4.96 (d, $J(H,H) = 13.1$ Hz, 3H; CH_AH_BN), 6.90–7.43 (m, 30H), 8.05 (d, $J(H,H) = 8.4$ Hz, 3H), 8.06–8.15 (m, 6H), 9.00 (d, $J(H,H) = 7.8$ Hz, 3H; H6); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 25.66$ (br s, CH_3), 37.10 (m, CH_2P), 40.33 (q, $^2J(P,C) = 3.5$ Hz, *C*-CH_3), 66.74 (CH_2N), 116.05, 126.22, 126.44 (C_1), 127.67 (d, $^1J(P,C) = 81.6$ Hz; *i*C-PhP), 127.70 (d, $^1J(P,C) = 109.3$ Hz; *i*C-PhP), 128.89 (d, $^3J(P,C) = 11.1$ Hz; *m*C-PhP), 129.01, 129.03 (d, $^3J(P,C) = 10.6$ Hz; *m*C-PhP), 129.98 (d, $^2J(P,C) = 9.5$ Hz; *o*C-PhP), 131.77 (d, $^4J(P,C) = 3.0$ Hz; *p*C-PhP), 132.15 (d, $^2J(P,C) = 7.6$ Hz; *o*C-PhP), 132.21 (d, $^4J(P,C) = 2.3$ Hz; *p*C-PhP), 132.48, 147.87 (C2); ^{31}P NMR (121.4 MHz, $CDCl_3$): $\delta = -1.41$; IR (Nujol): $\tilde{\nu} = 1444$ (C–P), 1108 (N–P) cm^{-1}; MS (FAB+): $m/z = 1052$ [MH^+]; $C_{62}H_{57}N_{10}OP_3$ (1051.13): calcd C 70.84, H 5.46, N 13.32; found C 69.84, H 5.57, N 12.72.

Triphosphazide 15c: Yield: 98%; m.p. 287–289°C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = -0.13$ (s, 3H; C-CH_3), 2.34 (s, 9H; $ArCH_3$), 3.66 (d, $J(H,H) = 12.8$ Hz, 3H; CH_AH_BN), 3.86 (d, $J(H,H) = 12.8$ Hz, 3H; CH_AH_BN), 3.92 (m, 3H; CH_AH_BP), 4.23 (pseudo t, $J(H,H)$, $(H,P) = 14.3$ Hz, 3H; CH_AH_BP), 6.96 (td, $J(H,H) = 7.6$, 3.1 Hz, 6H), 7.05 (dd, $J(H,H) = 8.4$, 1.9 Hz, 3H), 7.16 (td, $J(H,H) = 7.8$, 1.6 Hz, 3H), 7.25–7.44 (m, 18H), 7.80 (d, $J(H,H) = 8.1$ Hz, 3H), 8.00–8.20 (m, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 21.20$ ($ArCH_3$), 26.43 (C-*C*H_3), 36.60 (m, CH_2P), 40.70 (q, $^2J(P,C) = 3.5$ Hz;*C*-CH_3), 55.62 (CH_2N), 116.57, 128.00, 128.67 (d, $^3J(P,C) = 11.6$ Hz; *m*C-PhP), 128.68 (d, $^1J(P,C) = 107.8$ Hz; *i*C-PhP), 128.79 (d, $^3J(P,C) = 11.6$ Hz; *m*C-PhP), 128.92 (d, $^1J(P,C) = 80.6$ Hz; *i*C-PhP), 130.30 (d, $^2J(P,C) = 9.1$ Hz; *o*C-PhP), 130.55, 131.30 (d, $^4J(P,C) = 3.0$ Hz; *p*C-PhP), 131.84 (d, $^4J(P,C) = 2.0$ Hz; *p*C-PhP), 132.43 (d, $^2J(P,C) = 7.5$ Hz; *o*C-PhP), 132.82 (C5 or C1), 135.90 (C1 or C5), 145.73 (C2); ^{31}P NMR (121.4 MHz, $CDCl_3$): $\delta = -0.01$; IR (Nujol): $\tilde{\nu} = 1442$ (C–P), 1109 (N–P) cm^{-1}; MS (FAB+): $m/z = 1078$ [MH^+]; $C_{65}H_{63}N_{10}P_3$ (1077.21): calcd C 72.48, H 5.89, N 13.00; found C 72.01, H 5.69, N 12.63.

Triphosphazide 15d: Yield: 95%; m.p. 272–274°C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = -0.06$ (s, 3H; C-CH_3), 2.32 (s, 9H; $ArCH_3$), 3.80 (pseudo t, $J(H,H)$, $(H,P) = 14.3$ Hz, 3H; CH_AH_BP), 4.07 (m, 3H; CH_AH_BP), 4.14 (d, $J(H,H) = 13.1$ Hz, 3H; CH_AH_BN), 4.89 (d, $J(H,H) = 13.1$ Hz, 3H; CH_AH_BN), 6.96 (td, $J(H,H) = 7.7$, 3.1 Hz, 6H), 7.10–7.42 (m, 21H), 7.93 (d, $J(H,H) = 8.4$ Hz, 3H), 8.05–8.13 (m, 6H), 8.85 (s, 3H; H6); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 21.34$ ($ArCH_3$), 25.79 (C-*C*H_3), 37.40 (m, CH_2P), 40.39 (q, $^2J(P,C) = 3.5$ Hz; *C*-CH_3), 66.69 (CH_2N), 116.02, 126.58 (C5 or C1), 128.14 (d, $^1J(P,C) = 109.2$ Hz; *i*C-PhP), 128.16 (d, $^1J(P,C) = 81.0$ Hz; *i*C-PhP), 128.92 (d, $^3J(P,C) = 11.6$ Hz; *m*C-PhP), 129.10 (d, $^3J(P,C) = 12.1$ Hz; *m*C-PhP), 129.99, 130.10 (d, $^2J(P,C) = 9.1$ Hz; *o*C-PhP), 131.78 (d, $^4J(P,C) = 3.0$ Hz; *p*C-PhP), 132.16 (d, $^4J(P,C) = 2.5$ Hz; *p*C-PhP), 132.27 (d, $^2J(P,C) = 7.6$ Hz; *o*C-PhP), 132.67, 136.07 (C1 or C5), 145.91 (C2); ^{31}P NMR (121.4 MHz, $CDCl_3$): $\delta = -1.44$; IR (Nujol): $\tilde{\nu} = 1470$ (C–P), 1108 (N–P) cm^{-1}; MS (FAB+): $m/z = 1094$ [MH^+]; $C_{65}H_{63}N_{10}OP_3$ (1093.21): calcd C 71.41, H 5.81, N 12.81; found C 70.80, H 5.67, N 12.55.

Triphosphazide 15e: Yield: 42%; m.p. 220–221°C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = -0.15$ (s, 3H; CH_3), 3.59 (d, $J(H,H) = 12.8$ Hz, 3H; CH_ACH_BN), 3.82 (d, $J(H,H) = 12.8$ Hz, 3H; CH_ACH_BN), 3.92 (m, 3H; CH_ACH_BP), 4.14 (pseudo t, $J(H,H)$, $(H,P) = 14.3$ Hz, 3H; CH_ACH_BP), 7.03 (td, $J(H,H) = 7.5$, 3.1 Hz, 6H), 7.18–7.42 (m, 21H), 7.55 (d, $J(H,H) = 2.2$ Hz, 3H), 7.81 (d, $J(H,H) = 8.7$ Hz, 3H), 8.00–8.10 (m, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 26.41$ (C-*C*H_3), 36.90 (m, CH_2P), 40.69 (q, $^2J(P,C) = 3.5$ Hz; *C*-CH_3), 54.75 (CH_2N), 118.11 (C4 or C6), 127.61 (C6 or C4), 127.92 (d, $^1J(P,C) = 108.3$ Hz; *i*C-PhP), 128.18 (d, $^1J(P,C) = 81.1$ Hz; *i*C-PhP), 128.90 (d, $^3J(P,C) = 11.1$ Hz; *m*C-PhP), 128.98 (d, $^3J(P,C) = 11.5$ Hz; *m*C-PhP), 129.69 (C3), 130.21 (d, $^2J(P,C) = 9.1$ Hz; *o*C-PhP), 131.83 (d, $^4J(P,C) = 3.0$ Hz; *p*C-PhP), 131.97 (C1), 132.24 (d, $^4J(P,C) = 2.8$ Hz; *p*C-PhP), 132.38 (d, $^2J(P,C) = 7.6$ Hz; *o*C-PhP), 134.01 (C5), 146.35 (d, $^4J(P,C) = 1.0$ Hz; C2); ^{31}P NMR (121.4 MHz, $CDCl_3$): $\delta = 0.44$; IR (Nujol): $\tilde{\nu} = 1465$ (C–P), 1112 (N–P) cm^{-1}; MS (FAB+): $m/z = 1138$ [MH^+]; $C_{62}H_{54}Cl_3N_{10}P_3$ (1138.47): calcd C 65.41, H 4.78, N 12.30; found C 65.40, H 4.61, N 10.97.

Triphosphazide 15f: Yield: 73%; m.p. 237–238°C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = -0.06$ (s, 3H, CH_3), 3.75 (pseudo t, $J(H,H)$, $(H,P) = 14.0$ Hz, 3H; CH_AH_BP), 3.96–4.16 (m, 6H; $CH_AH_BP + CH_AH_BN$), 4.85 (d, $J(H,H) = 12.8$ Hz, 3H; CH_AH_BN), 7.03 (td, $J(H,H) = 7.8$, 3.1 Hz, 6H), 7.25–7.44 (m, 21H), 7.96 (d, $J(H,H) = 9.0$ Hz, 3H), 8.00–8.11 (m, 6H), 9.01 (d, $J(H,H) = 2.2$ Hz, 3H; H6); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 25.81$ (C-*C*H_3), 37.50 (m; CH_2P), 40.38 (q, $^2J(P,C) = 3.5$ Hz; *C*-CH_3), 65.13 (CH_2N), 117.41, 127.36 (C1), 127.41 (d, $^1J(P,C) = 81.1$ Hz; *i*C-PhP), 127.42 (d, $^1J(P,C) = 108.7$ Hz; *i*C-PhP), 129.11 (d, $^3J(P,C) = 11.1$ Hz; *m*C-PhP), 129.26 (d, $^3J(P,C) = 12.1$ Hz; *m*C-PhP), 129.66, 129.94 (d, $^2J(P,C) = 9.1$ Hz; *o*C-PhP), 131.93 (C5), 132.15, 132.25 (d, $^4J(P,C) = 3.0$ Hz; *p*C-PhP), 132.26 (d, $^4J(P,C) = 9.1$ Hz; *o*C-PhP), 132.52 (d, $^2J(P,C) = 2.5$ Hz; *p*C-PhP), 146.61 (C2); ^{31}P NMR (121.4 MHz, $CDCl_3$): $\delta = -1.22$; IR (Nujol): $\tilde{\nu} = 1438$ (C–P), 1113 (N–P); MS (FAB+): $m/z = 1154$ [MH^+]; $C_{62}H_{54}Cl_3N_{10}OP_3$ (1154.47): C 64.51, H 4.71, N 12.14; found C 64.61, H 5.09, N 11.20.

Triphosphazide 15h: Yield: 27%; m.p. 290–291°C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = -0.26$ (s, 3H; CH_3), 1.71 (s, 9H; Ar-3-CH_3), 3.93 (d, $J(H,H) = 11.8$ Hz, 3H; CH_AH_BN), 4.25 (br d, $J(H,H) = 13.4$ Hz, 6H; $CH_AH_BP + CH_AH_BP$), 5.12 (d, $J(H,H) = 11.8$ Hz, 3H; CH_AH_BN), 7.01 (t, $J(H,H) = 7.5$ Hz, 6H), 6.98–7.47 (m, 24H), 7.59 (d, $J(H,H) = 7.8$ Hz, 3H), 8.03–8.10 (m, 6H); ^{13}C (75.4 MHz, $CDCl_3$): $\delta = 19.09$ (Ar-3-*C*H_3), 26.21 (C-*C*H_3), 37.15 (m; CH_2P), 39.80 (q, $^2J(P,C) = 3.5$ Hz;*C*-CH_3), 64.94 (CH_2N), 123.37 (s), 124.24, 127.56 (d, $^1J(P,C) = 80.1$ Hz; *i*C-PhP), 127.80 (d, $^1J(P,C) = 108.3$ Hz; *i*C-PhP), 128.80 (d, $^3J(P,C) = 11.6$ Hz; *m*C-PhP), 128.87 (d, $^3J(P,C) = 11.6$ Hz; *m*C-PhP), 130.28 (s), 130.88 (d, $^2J(P,C) = 9.6$ Hz; *o*C-PhP), 132.13 (d, $^4J(P,C) = 3.0$ Hz; *p*C-PhP), 132.32 (d, $^2J(P,C) = 8.1$ Hz; *o*C-PhP), 132.38, 132.39 (d, $^4J(P,C) = 2.5$ Hz; *p*C-PhP), 133.71, 150.96 (C2); ^{31}P (121.4 MHz, $CDCl_3$): $\delta = -2.56$; IR (Nujol): $\tilde{\nu} = 1440$ (C–P), 1110 (N–P) cm^{-1}; MS (FAB+): $m/z = 1095$ [MH^+]; $C_{65}H_{63}N_{10}OP_3$ (1093.21): calcd C 71.41, H 5.81, N 12.81; found C 70.87, H 5.26, N 11.24.

Triphosphazide 15i: Yield: 41%; m.p. 282–284°C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = -0.12$ (s, 3H; C-CH_3), 2.32 (s, 6H; $ArCH_3$), 3.65 (d, J (H,H) = 12.5 Hz, 2H; CH_AH_BN), 3.71 (d, $J(H,H) = 12.8$ Hz, 1H; CH_AH_BN), 3.82–4.02 (m, 6H), 4.25 (m, 3H), 6.88–7.43 (m, 30H), 7.63 (d, $J(H,H) = 7.5$ Hz, 1H), 7.82 (d, $J(H,H) = 8.4$ Hz, 2H), 7.90 (d, $J(H,H) = 7.8$ Hz, 1H), 8.10 (m, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 21.16$ ($ArCH_3$), 26.38 (C-*C*H_3), 36.56 (m; CH_2P), 40.64 (q, $^2J(P,C) = 3.5$ Hz; *C*-CH_3), 55.46 (CH_2N), 55.54 (CH_2N), 55.77 (CH_2N), 116.48, 116.72, 126.14, 127.03, 127.7–133.2 , 135.87 (s), 145.63 (s), 145.68 (s), 147.85 (s); ^{31}P NMR (121.4 MHz, $CDCl_3$): $\delta = 0.01, 0.39$; IR (Nujol): $\tilde{\nu} = 1438$ (C–P), 1112 (N–P) cm^{-1}; MS (FAB+): $m/z = 1064$ [MH^+]; $C_{64}H_{61}N_{10}P_3$ (1063.19): calcd C 72.30, H 5.78, N 13.17; found C 72.01, H 5.58, N 12.88.

Triphosphazide 15j: Yield: 88%; m.p. 269–270°C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = -0.04$ (s, 3H; C-CH_3), 2.36 (s, 6H; $ArCH_3$), 3.76–3.98 (m, 3H), 4.05–4.25 (m, 6H), 4.92 (d, $J(H,H) = 12.8$ Hz, 2H; CH_AH_BN), 4.93 (d, $J(H,H) = 12.8$ Hz, 1H; CH_AH_BN), 6.86–7.45 (m, 27H), 7.94 (d, $J(H,H) = 8.4$ Hz, 2H), 8.05–8.13 (m, 8H), 8.82 (s, 2H), 9.05 (d, $J(H,H) = 7.8$ Hz, 1H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 21.27$ ($ArCH_3$), 25.73 (C-*C*H_3), 37.28 (m, CH_2P), 40.34 (q, $^2J(P,C) = 3.5$ Hz; *C*-CH_3), 66.58 (CH_2N), 66.70 (CH_2N), 66.78 (CH_2N), 115.97, 116.06, 126.1–132.6, 136.05 (s), 145.74 (s), 145.86 (s), 148.00 (s); ^{31}P NMR (121.4 MHz, $CDCl_3$): $\delta = -1.36, -1.46$; IR (Nujol): $\tilde{\nu} = 1440$ (C–P), 1112 (N–P) cm^{-1}; MS (FAB+): $m/z = 1080$ [MH^+]; $C_{64}H_{61}N_{10}OP_3$ (1079.19): calcd C 71.23, H 5.70, N 12.98; found C 70.55; H 5.55, N 12.43.

Triphosphazide 15k: Yield: 57%; m.p. 280–282°C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = -0.12$ (s, 3H; C-CH_3), 2.32 (s, 3H; $ArCH_3$), 3.59–3.74 (m, 3H), 3.82–4.02 (m, 6H), 4.16–4.32 (m, 3H), 6.85–7.50 (m, 32H), 7.61 (t, $J(H,H) = 8.1$ Hz, 2H), 7.81 (d, $J(H,H) = 8.4$ Hz, 1H), 7.90 (d, $J(H,H) = 8.1$ Hz, 2H), 8.04–8.20 (m, 4H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 21.22$ ($ArCH_3$), 26.44 (C-*C*H_3), 36.60 (m; CH_2P), 40.72 (q, $^2J(P,C) = 3.5$ Hz; *C*-CH_3), 55.50 (CH_2N), 55.72 (CH_2N), 116.52, 116.74, 126.23, 127.11, 128.0–134.0, 135.96 (s), 145.70 (s), 147.85 (s), 147.91 (s); ^{31}P NMR (121.4 MHz, $CDCl_3$): $\delta = 0.03, 0.36$; IR (Nujol): $\tilde{\nu} = 1438$ (C–P), 1112 (N–P) cm^{-1}; MS (FAB+): $m/z = 1050$ [MH^+]; $C_{63}H_{59}N_{10}P_3$ (1049.16): calcd C 72.12, H 5.67, N 13.35; found C 71.33, H 5.47, N 13.00.

Triphosphazide 15l: Yield: 75%; m.p. 278–280°C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = -0.03$ (s, 3H; C-CH_3), 2.36 (s, 3H;$ArCH_3$), 3.79–3.90 (m, 3H), 4.00–4.20 (m, 6H), 4.95 (br d, $J(H,H) = 13.0$ Hz, 3H), 6.91–7.42 (m, 30H), 7.96 (d, $J(H,H) = 8.4$ Hz, 1H), 8.00–8.15 (m, 7H), 8.80 (s, 1H), 9.03 (br d, $J(H,H) = 7.2$ Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 21.24$ ($ArCH_3$), 25.67 (C-*C*H_3), 37.11 (m; CH_2P), 40.31 (q, $^2J(P,C) = 3.3$ Hz; *C*-CH_3), 66.62 (CH_2N), 66.68 (CH_2N), 66.80 (CH_2N), 116.03, 116.05, 126.0–133.0, 136.05 (s), 145.73 (s), 147.87 (s), 147.98 (s); ^{31}P NMR (121.4 MHz, $CDCl_3$): $\delta = -1.49, -1.40$; IR (Nujol); $\tilde{\nu} = 1438$ (C–P), 1109 (N–P) cm^{-1}; MS (FAB+): $m/z = 1066$ [MH^+]; $C_{63}H_{59}N_{10}OP_3$ (1065.16): calcd C 71.04, H 5.58, N 13.15; found C 71.55, H 5.37, N 12.87.

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Triphosphazide 15m/15m′: Yield: 60%; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ −0.13 (s, 3H; CH_3), 2.33 (s, 3H; Ar-5-CH_3), 3.50–4.02 (m, 9H; CH_2N + CH_AH_BP), 4.15–4.25 (m, 3H; CH_AH_BP), 6.94–7.30 (m, 29H), 7.58–7.61 (m, 2H), 7.80 (d, J(H,H) = 8.6 Hz, 2H), 7.89 (d, J(H,H) = 8.1 Hz, 1H), 8.03–8.12 (m, 6H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 21.22$ (Ar-5-CH_3), 26.43 (C-CH_3), 36.62 (m; CH_2P), 40.69 (q, ^2J(P,C) = 3.5 Hz; C-CH_3), 54.98 (CH_2N), 55.17 (CH_2N), 55.19 (CH_2N), 55.35 (CH_2N), 55.66 (CH_2N), 116.44, 116.59, 116.65, 116.85, 118.07, 118.15, 126.34, 126.37, 133.1–137.0, 134.61 (s), 134.76 (s), 136.11 (s), 136.14 (s), 145.64 (s), 146.38 (s), 146.39 (s), 146.43 (s), 146.44 (s), 147.79 (s), 147.81 (s), 147.84 (s) , 147.86 (s); ^{31}P NMR (121.4 MHz, $CDCl_3$): $\delta = -0.27$, −0.21, 0.14, 0.90, 1.04; IR (Nujol): $\tilde{\nu} = 1438$ (C–P), 1111 (N–P) cm^{-1}; MS (FAB+): $m/z = 1085$ [MH$^+$]; $C_{63}H_{58}ClN_{10}P_3$ (1083.60): calcd C 69.83, H 5.39, N 12.93; found C 66.11, H 4.51, N 11.36.

Triphosphazide 15n/15n′: Yield: 93%; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ −0.05 (s, 6H; CH_3), 2.36 (s, 3H; Ar-5-CH_3), 2.37 (s, 3H; Ar-5-CH_3), 3.60–3.90 (m, 6H; CH_AH_BP), 4.00–4.21 (m, 12H; CH_AH_BP + CH_AH_BN), 4.83–5.00 (m, 6H; CH_AH_BN), 6.93–7.43 (m, 56H), 7.90–8.14 (m, 18H), 8.71 (s, 1H; H6 of Ar-5-CH_3), 8.75 (s, 1H; H6 of Ar-5-CH_3), 8.94 (d, J(H,H) = 7.8 Hz, 1H; H6 of Ar-5-H), 8.99 (d, J(H,H) = 7.8 Hz, 1H; H6 of Ar-5-H), 9.13 (br s, 2H; H6 of Ar-5-Cl); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 21.30$ (Ar-5-CH_3), 25.77 (C-CH_3), 37.40 (m; CH_2P), 40.37 (q, ^2J(P,C) = 3.0 Hz; C-CH_3), 66.0–67.0 (CH_2N), 116.03, 116.12, 117.34, 125.0–133.2, 136.21 (s), 136.27 (s), 145.81 (s), 146.57 (s), 146.67 (s), 147.94 (s), 148.08 (s); ^{31}P NMR (121.4 MHz, $CDCl_3$): $\delta = -1.73$, −1.63, −1.50, −1.37, −0.93, −0.91; IR (Nujol): $\tilde{\nu} = 1438$ (C–P), 1120 (N–P) cm^{-1}; MS (FAB+): $m/z = 1100$ [MH$^+$]; $C_{63}H_{58}ClN_{10}OP_3$ (1099.60): calcd C 68.82, H 5.31, N 12.73; found C 68.23, H 5.54, N 11.42.

Reaction of triphosphazide 15a with triphenylphosphane: A solution of triphosphazide **15a** (0.20 g, 0.2 mmol) and triphenylphosphane (0.15 g, 0.6 mmol) in $CDCl_3$ (10 mL) was heated at reflux temperature for 5 h and then cooled to room temperature. The solvent was removed under reduced pressure, the resulting material was treated with diethyl ether (3 mL), and the resulting solid then isolated by filtration and recrystallized from $CHCl_3$.

Compound **16** was also prepared by reaction of tris(2-azidobenzyl)amine **6a** and triphenylphosphane (3 equiv) in benzene at reflux temperature for 3 h.

Tris[2-(triphenylphosphoranylideneamino)benzyl]amine (**16**): Yield: 71%; m.p. 343–345 °C (colorless prisms from $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.23$ (s, 6H; CH_2), 6.37 (d, J(H,H) = 7.8 Hz, 3H), 6.63 (t, J(H,H) = 7.2 Hz, 3H), 6.70 (td, J(H,H) = 7.5, 1.5 Hz, 3H), 7.21–7.27 (m, 18H), 7.31–7.37 (m, 9H), 7.75–7.78 (m, 18H), 7.86 (d, J(H,H) = 7.2 Hz, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 55.56$ (CH_2), 117.59, 120.46 (d, ^3J(P,C) = 9.9 Hz), 125.16 , 128.32 (d, ^3J(P,C) = 12.1 Hz; mC-PhP), 128.33, 131.10 (d, ^4J(P,C) = 2.0 Hz; pC-PhP), 132.05 (d, ^1J(P,C) = 98.6 Hz; iC-PhP), 132.54 (d, ^2J(P,C) = 9.5 Hz; oC-PhP), 135.47 (d, ^3J(P,C) = 20.5 Hz), 148.81 (s); ^{31}P NMR (121.4 MHz, $CDCl_3$): $\delta = -1.74$; IR (Nujol): $\tilde{\nu} = 1438$ (C–P), 1109 (N–P) cm^{-1}; MS (FAB+): $m/z = 1114$ [MH$^+$]; $C_{75}H_{63}N_4P_3$ (1113.29): calcd C 80.91, H 5.70, N 5.03; found C 81.03, H 5.54, N 4.75.

Preparation of 2-azido-3-methylbenzylamine (**4d**): A mixture of 2-azido-3-methylbenzyl chloride (4.54 g, 25 mmol) and potassium phtalimide (5.56 g, 30 mmol) in dry DMF (30 mL) was stirred at 80 °C for 12 h. After cooling to room temperature, the mixture was poured on ice/H_2O (500 mL) and the precipitated solid was isolated by filtration, washed with H_2O (2 × 100 mL), and air-dried under vacuum. The solid was then recrystallized from $CHCl_3$/Et_2O to give N-(2-azido-3-methylbenzyl)-phthalimide **17** (55%) as colorless prisms. M.p. 114–115 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.42$ (s, 3H; CH_3), 4.93 (s, 2H; CH_2), 7.04–7.10 (m, 3H), 7.69–7.72 (m, 2H), 7.82–7.87 (m, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 18.00$ (CH_3), 37.97 (CH_2), 123.47, 126.17, 126.83, 129.82 (s), 130.99, 131.74 (s), 132.13 (s), 133.10 (s), 134.12, 168.05 (s); IR (Nujol): $\tilde{\nu} = 2120$ (N_3), 1709 (C=O) cm^{-1}; MS (70 eV, EI): m/z (%) = 292 (5) [M^+], 104 (100); $C_{16}H_{12}N_4O_2$ (292.30): calcd C 65.75, H 4.14, N 19.17; found C 65.84, H 4.39, N 18.95.

$N_2H_4 \cdot H_2O$ (5 mL) was added to a solution of N-(2-azido-3-methylbenzyl)phthalimide (**17**, 5.26 g, 18 mmol) in EtOH (75 mL) in one go. The mixture was stirred at reflux temperature for 3 h. After cooling to room temperature, NaOH 10% (50 mL) was added and the resulting solution was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were washed with brine (100 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was chromatographed (silica gel; ethyl acetate/methanol 1:1) to give 2-azido-3-methylbenzylamine (**4d**). Yield: 82%.

Preparation of tris(2-azidobenzyl)amines 18 and 23: 2-Azidobenzyl iodide (1.03 g, 4 mmol) was added to a solution of the corresponding benzylamine (2 mmol) in dioxane (30 mL), and the mixture heated at reflux temperature for 4 h with stirring. After cooling to room temperature, an excess of triethylamine (0.45 g, 4.5 mmol) was added in one go, and the mixture was stirred for 2 h. The precipitated triethylammonium iodide was separated by filtration, the dioxane removed under reduced pressure and the residue was chromatographed (silica gel; ethyl acetate/n-hexane 1:4).

Bis(2-azidobenzyl)(2-azido-3-methylbenzyl)amine (**18**): Yield: 42%; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.37$ (s, 3H; CH_3), 3.56 (s, 4H; CH_2), 3.66 (s, 2H; CH_2), 7.04–7.13 (m, 6H), 7.24 (dt, J(H,H) = 6.9, 2.4 Hz, 2H), 7.40 (m, 1H), 7.56 (dd, J(H,H) = 7.8, 0.9 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 18.07$ (CH_3), 52.92 (CH_2), 54.71 (CH_2), 118.01, 124.66, 125.80, 128.16, 128.19, 130.04, 130.58, 130.70 (s), 132.65 (s), 133.32 (s), 137.15 (s), 138.42 (s); IR (film): $\tilde{\nu} = 2133$ (N_3) cm^{-1}; MS (70 eV, EI): m/z (%) = 424 (13) [M^+], 159 (100); $C_{22}H_{20}N_{10}$ (424.47): calcd C 62.25, H 4.75, N 33.00; found C 62.51, H 4.42, N 33.17.

Bis(2-azidobenzyl)(2-azido-α-methylbenzyl)amine (**23**): Yield: 67%; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.36$ (d, J(H,H) = 6.9 Hz, 3H), 3.49 (d, J(H,H) = 14.2 Hz, 2H), 3.59 (d, J(H,H) = 14.2 Hz, 2H), 4.20 (q, J(H,H) = 6.9 Hz, 1H), 7.01–7.32 (m, 10H), 7.48 (d, J(H,H) = 7.3 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 16.55$ (CH_3), 49.41 (CH_2), 53.76 (CH), 117.75, 118.34, 124.41, 124.47, 127.80, 128.13, 128.46, 130.54, 131.80 (s), 134.65 (s), 137.98 (s), 138.33 (s); IR (film): $\tilde{\nu} = 2131$ (N_3) cm^{-1}; MS (70 eV, EI): m/z (%) = 424 (12) [M^+], 77 (100); $C_{22}H_{20}N_{10}$ (424.47): calcd C 62.25, H 4.75, N 33.00; found: C 62.01, H 4.89, N 32.79.

Preparation of bis(2-azidobenzyl)(2-azido-3-methylbenzyl)amine *N*-oxide (**19**): The N-oxide **19** was prepared following the procedure described above for the preparation of the N-oxides **7**, **9**, **13**, and **15**.

Bis(2-azidobenzyl)(2-azido-3-methylbenzyl)amine *N*-oxide (**19**)**:** Yield: 83%; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.47$ (s, 3H; CH_3), 4.27 (s, 4H; CH_2), 4.36 (s, 2H; CH_2), 7.05–7.30 (m, 6H), 7.43 (td, J(H,H) = 8.6, 1.5 Hz, 2H), 7.66 (dd, J(H,H) = 7.5, 1.4 Hz, 1H), 7.85 (dd, J(H,H) = 7.5, 1.4 Hz, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 18.28$ (CH_3), 64.30 (CH_2), 65.36 (CH_2), 117.58, 122.22 (s), 124.60 (s), 124.77, 125.81, 130.73, 132.45 (s), 132.72, 133.32, 136.17, 138.60 (s), 139.90 (s); IR (film): $\tilde{\nu} = 2119$ cm^{-1}; MS (70 eV, EI): m/z (%) = 440 (52) [M^+], 160 (100); $C_{22}H_{20}N_{10}O$ (440.47): calcd C 59.99, H 4.58, N 31.80; found C 60.16, H 4.47, N 31.77.

Preparation of triphosphazides 20 and 21: These compounds were prepared following the procedure described above for the preparation of the phosphazides **15**.

Triphosphazide 20: Yield: 51%; m.p. 234–235 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -0.20$ (s, 3H; CH_3), 2.55 (s, 3H; Ar-3-CH_3), 3.58–4.01 (m, 9H; CH_AH_BN + CH_AH_BP), 4.04–4.41 (m, 3H; CH_AH_BP), 7.03–7.90 (m, 33H), 7.97–8.12 (m, 8H); ^{13}C NMR (75.4 MHz, $CDCl_3$) $\delta = 20.64$ (Ar-3-CH_3), 26.78 (C-CH_3), 36.64 (m; CH_2P), 40.80 (q, ^2J(P,C) = 3.5 Hz; C-CH_3), 53.75 (CH_2N), 54.05 (CH_2N), 58.58 (CH_2N), 116.24 (C6 of Ar-3-H), 116.31 (C6 of Ar-3-H), 117.97 (C6 of Ar-3-CH_3), 125.2–130.3, 134.12 (s), 147.46 (d, ^4J(P,C) = 1.5 Hz; C2 of Ar-3-H), 148.02 (d, ^4J(P,C) = 1.5 Hz; C2 of Ar-3-H), 148.08 (C2 of Ar-3-CH_3); ^{31}P NMR (121.4 MHz, $CDCl_3$): $\delta = -1.33$, −0.39; IR (Nujol): $\tilde{\nu} = 1438$ (C–P), 1112 (N–P) cm^{-1}; MS (FAB+): $m/z = 1050$ [MH$^+$]; $C_{63}H_{59}N_{10}P_3$ (1049.16): calcd C 72.12, H 5.67, N 13.35; found C 71.68, H 6.05, N 11.61.

Triphosphazide 21: Yield: 52%; m.p. 240–241 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -0.01$ (s, 3H; CH_3), 2.44 (br s, 3H; Ar-3-CH_3), 3.80–4.75 (m, 12H; CH_2N + CH_2P), 6.90–7.45 (m, 30H), 7.76 (br s, 3H), 8.08–8.15 (m, 6H), 8.65 (br s, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 23.02$ (Ar-3-CH_3), 25.81 (C-CH_3), 36.20–38.70 (m; CH_2P), 40.30 (q, ^2J(P,C) = 3.0 Hz; C-CH_3), 66.01 (CH_2N), 66.77 (CH_2N), 117.20, 117.50, 125.01, 125.7–133.0, 148.80 (s); ^{31}P NMR (121.4 MHz, $CDCl_3$): $\delta = -2.12$, −1.74, −1.67; IR (Nujol): $\tilde{\nu} =$ 1438 (C–P), 1109 (N–P) cm^{-1}; MS (FAB+): $m/z = 1066$ [MH$^+$]; $C_{63}H_{59}N_{10}OP_3$ (1065.16): calcd C 71.04, H 5.58, N 13.15; found C 69.52, H 5.98, N 11.52.

Acknowledgments: We gratefully acknowledge the financial support of the Dirección General de Investigación Científica y Técnica (Project no.: PB95-1019).

Received: April 29, 1998 [F1128]

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