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PAPER

Unprecedented intramolecular [3 + 2] cycloadditions of azido-ketenimines and azido-carbodiimides. Synthesis of indolo[1,2-*a*]quinazolines and tetrazolo[5,1-*b*]quinazolines†

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N-(2-Azidomethyl)phenyl ketenimines and *N*-(2-azidomethyl)phenyl-*N*′-alkyl(aryl) carbodiimides undergo, under mild thermal conditions, intramolecular [3 + 2] cycloaddition reactions between the azido group and either the C=C or the distal C=N double bonds of the ketenimine and carbodiimide functions respectively. The reaction products are indolo[1,2-*a*]quinazolines and/or indolo[2,1-*b*]-quinazolines in the case of azido-ketenimines, and tetrazolo[5,1-*b*]quinazolines in the case of azido-carbodiimides. The formation of the two classes of indoloquinazolines implies the ulterior dinitrogen extrusion from the non-isolated, putative [3 + 2] cycloadducts between the azide and ketenimine functions, whereas in the case of azido-carbodiimides the initial cycloadducts, tetrazoloquinazolines, were cleanly isolated and further converted into 2-aminoquinazolines by thermally induced dinitrogen extrusion.

Introduction

Cycloaddition reactions are an important class of chemical transformations having found extensive use in the construction of structurally simple molecules as well of elaborated molecular frameworks.[1] In this context, dipolar [3 + 2] cycloaddition reactions (1,3-dipolar cycloadditions) have become an appreciated method for the preparation of a great variety of heterocyclic compounds bearing a five-membered ring embedded into their structures.[2]

Ketenimines are nitrogenated heterocumulenes showing a very rich and diverse chemistry prone to participate in pericyclic processes such as electrocyclic ring closures, [*n* + 2] cycloadditions and sigmatropic rearrangements.[3] Whereas no intramolecular examples of dipolar [3 + 2] cycloadditions of ketenimines have been disclosed up to now, a few examples of the intermolecular version are known. In most of such cases, the ketenimine plays the role of the dipolarophile contributing with two atoms to the resulting five-membered ring. The reactive double bond can be either its cumulated C=C or C=N double bond. In these reactions the 1,3-dipolar reagents are *N*-aminopyridininium ylides,[4] diazo compounds,[5] azides,[6] acylnitrenes,[7] aziridines,[8] tiiranes,[9] oxaziridines[10] or heterocyclic carbine-derived 1,3-dipoles.[11] Interestingly, the presence of phosphanyl groups at the terminal carbon atom of ketenimines promotes new reactivity patterns, these species being able of behaving as 1,3-dipoles towards alkynes, isocyanates or isothiocyanates.[12]

Carbodiimides are another class of nitrogenated heterocumulenes with a versatile chemical behaviour,[13] also participating in cycloaddition reactions. Several articles dealing with intermolecular [3 + 2] cycloadditions of carbodiimides can be found in the chemical literature. In these reports, carbodiimides usually act as the two-electron component when reacting with 1,3-dipolar reagents such as 1-aza-[14] and 1,3-diaza-2-azoniallenes,[15] or with nitrile oxides and imines.[16] However, examples of intramolecular [3 + 2] cycloadditions involving carbodiimides have not yet been reported.

For years we have been involved in studying the chemistry of heterocumulenes, especially that of ketenimines and carbodiimides.[17] A recent publication of Feldman, Lopez and co-workers summarizing their works on the intramolecular [3 + 2] cycloaddition reactions between allenes and azides[18] captured our attention and directed our interest to testing comparable intramolecular reactions between azides and heterocumulenes such as ketenimines or carbodiimides. In a first approach we targeted the preparation of a series of azido-ketenimines and azido-carbodiimides with their two functionalities built up on an *ortho*-benzylic scaffold, more specifically the azido group placed at the benzylic carbon atom whereas the heterocumulene function is *N*-linked to the *ortho* position of the aromatic nucleus. We here disclose the results of our experimental study showing that such azido-heterocumulenes

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† Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR spectra of compounds **2**, **4**, **5**, **12**, **14** and **15**. ^{31}P NMR spectra of compounds **2**. Cif files of **4a** and **12**. CCDC reference numbers 824784 and 824785. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1ob05745f

Table 1 Azido-ketenimines **3**, indolo[1,2-*a*]quinazolines **4** and indolo[2,1-*b*]quinazolines **5**

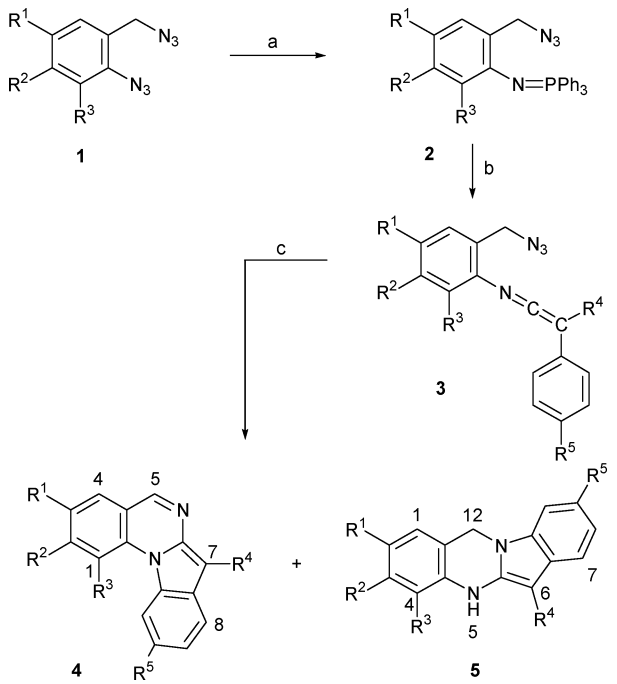
Entry	R^1	R^2	R^3	R^4	R^5	**3** Yield (%)	**4** Yield (%)	**5** Yield (%)
a	H	H	H	Ph	H	99	61	—
b	H	H	Me	Ph	H	57	—	66
c	Br	H	H	Ph	H	99	45	—
d	Cl	H	H	Ph	H	98	69	—
e	Cl	H	H	Me	H	92	16	—
f	Cl	H	H	Et	H	80	20	—
g	C_4H_4		H	Ph	H	97	40	—
h	H	H	H	4-Cl-C_6H_4	Cl	92	50	—
i	H	H	Me	4-Cl-C_6H_4	Cl	96	25	40
j	Cl	H	H	4-Cl-C_6H_4	Cl	95	35	—
k	Me	H	H	4-Cl-C_6H_4	Cl	89	51	—
l	C_4H_4		H	4-Cl-C_6H_4	Cl	78	55	—

undergo, under mild thermal conditions, the presumed [3 + 2] cycloaddition reactions converting into fused heterocyclic systems, either indolo[1,2-*a*]quinazolines and indolo[2,1-*b*]quinazolines. Both these products are formed following the N_2 extrusion in the presumed primary cycloadducts between the azide and ketenimine functions, or tetrazolo[5,1-*b*]quinazolines in the case of azido-carbodiimides, in which a further N_2 extrusion yielding 2-aminoquinolines took place.

Results and discussion

The slow addition of one equivalent of triphenylphosphine, dissolved in anhydrous diethyl ether, to a solution of bis(azides) **1** in the same solvent at room temperature provided the azido-iminophosphoranes **2**, through a chemoselective Staudinger reaction of the phosphine with the more electrophilic azido group, the one *N*-linked to the benzene ring. The aza-Wittig reaction of azido-iminophosphoranes **2** with ketenes, in dichloromethane solution at room temperature, yielded the azido-ketenimines **3** (Table 1), which were separated from the triphenylphosphine oxide by short column chromatography on silica gel and immediately submitted to the next reaction step for avoiding its partial hydrolysis. Although compounds **3** were not fully characterized, their formation was guaranteed by recording an IR spectrum of each one after the purification step. These spectra showed two very strong absorption bands around 2100 and 2000 cm^{-1}, respectively, attributable to the azide and ketenimine functional groups. The heating at reflux temperature of toluene solutions of azido-ketenimines **3** afforded, in most of the studied cases, indolo[1,2-*a*]quinazolines **4** as the unique reaction products (Scheme 1), isolated from the reaction mixture in low to moderate yields (Table 1). Interestingly, the thermal treatment of azido-ketenimines **3b** and **3i**, in which R^3 = Me, provided the isomeric fused systems indolo[2,1-*b*]quinazolines **5** as the unique or major products.

Indoloquinazolines **4** and **5** were characterized according to their spectral data (IR, ^{1}H and ^{13}C NMR) and high-resolution mass spectra. In the ^{1}H NMR spectra of indolo[1,2-*a*]quinazolines **4** the C(5)H proton resonates as a singlet at δ = 8.31–8.96 ppm, and their ^{13}C NMR spectra show the signal of the methine carbon C5 at δ = 148.1–152.1 ppm. Relevant ^{1}H and ^{13}C NMR data of the indolo[2,1-*b*]quinazolines **5** are the chemical shifts of the C(12)H protons appearing at δ = 5.18–5.25 ppm, of the methylene carbon C12 at δ = 42.9–43.0 ppm and that of the quaternary carbon

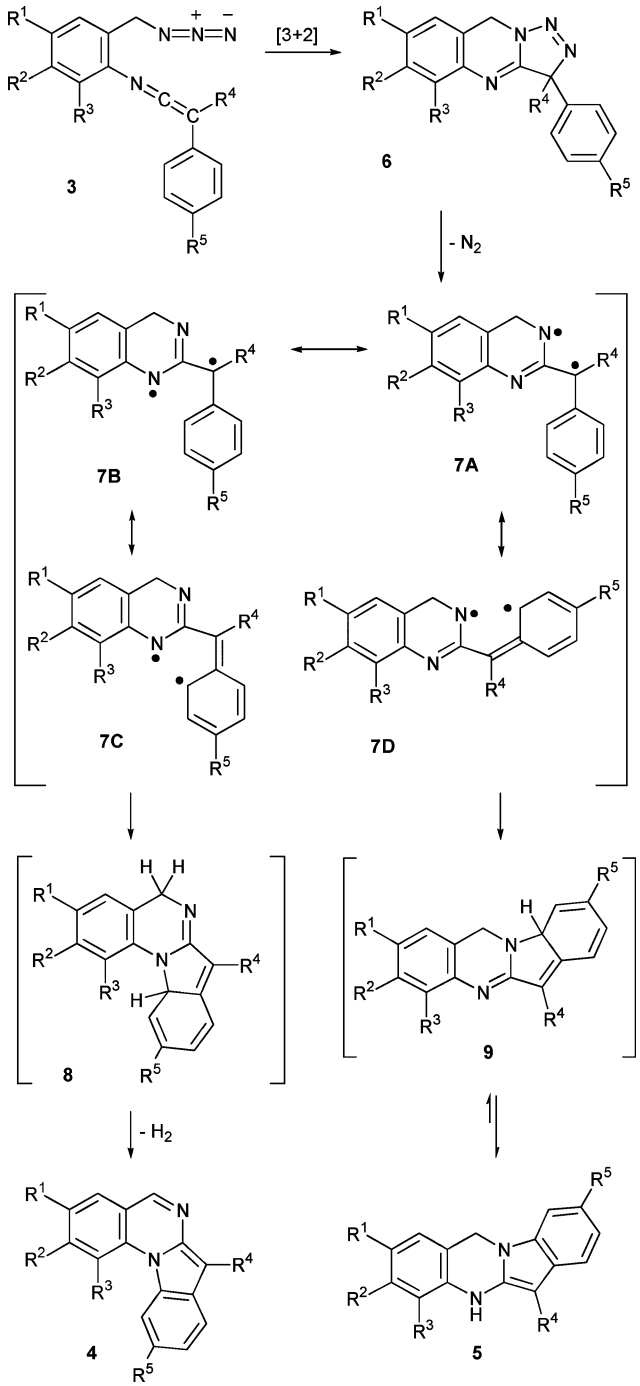


Scheme 1 *Reagents and conditions*: (a) PPh_3, Et_2O, r.t., 12 h; (b) R^4(4-R^5-C_6H_4)C═C═O, CH_2Cl_2, r.t., 15 min; (c) Toluene, reflux, 2–4 h.

C6 resonating at δ = 92.7–93.7 ppm. Moreover, the structure of compound **4a** ($R^1 = R^2 = R^3$ = H; R^4 = Ph; R^5 = H) was determined by X-ray crystal diffraction (see Fig. S1 in the ESI†).

The transformation **3** → **4** and/or **5** most probably proceeds through an intramolecular [3 + 2] cycloaddition of the azido moiety with the carbon–carbon double bond of the ketenimine function to give the respective [1,2,3]triazolo[5,1-*b*]quinazoline **6** (Scheme 2). Following this, dinitrogen extrusion from the triazoloquinazoline **6** would afford the diradical **7**, which is resonance stabilized. Cyclization of the diradical **7** through the canonical structure **7C**, forming a C–N bond, should lead to the tetracyclic intermediate **8**, which, after a final dehydrogenation step, would yield the fully aromatic indoloquinazoline **4**. Ring-closure of the canonical structure **7D** should give compound **9**, which after prototropic equilibration should convert into the indoloquinazoline **5**.

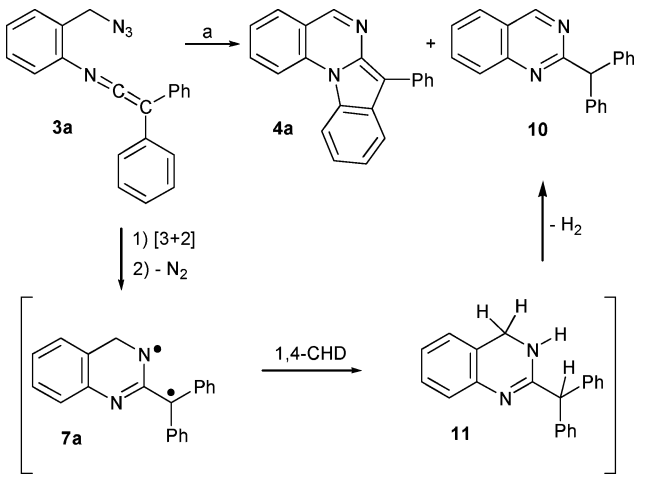
The experimental data presented in Table 1 indicate that, in most cases, the cyclization of the diyl intermediates **7** occur



Scheme 2 Proposed mechanism for the conversion **3** → **4** + **5**.

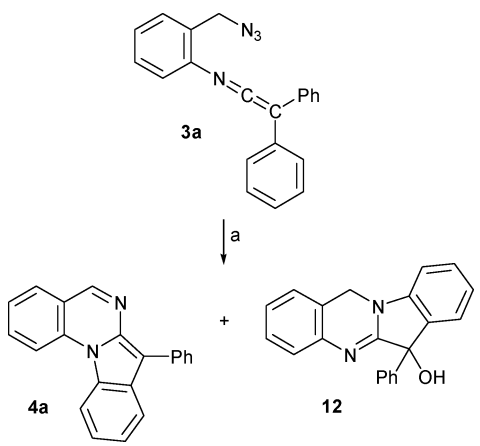
regioselectively to furnish the angular heterocyclic system **4**, except for diradicals **7b** and **7i**, which rather undergo cyclization to the linearly fused indoloquinazoline system **5**. It seems that the presence of a methyl substituent (R^3 = Me) at the *ortho* position of the keteniminic nitrogen in the azido-ketenimines leading to **7b** and **7i** has a significant influence on directing the product selectivity toward compounds **5**. Probably, there are repulsive steric interactions originated by such Me group in the transition states of the cyclizations of the biradical intermediates **7b** and **7i** *via* the resonance structure C. These repulsions increase the preference for its cyclization *via* the canonical form D leading to the linear indoloquinazolines **5**.

Evidences for the intermediacy of the biradicals **7** in the formation of indoloquinazolines **4** and **5** were then sought by trapping experiments with 1,4-cyclohexadiene. When azido-ketenimine **3a** was heated at 88–89 °C for 5 h in 1,4-cyclohexadiene as solvent, the indolo[1,2-*a*]quinazoline **4a** (40% yield) and 2-(diphenylmethyl)quinazoline **10** (20% yield) were isolated from the final reaction mixture (Scheme 3). The abstraction of two hydrogen atoms from 1,4-cyclohexadiene by the biradical **7a** would afford the 3,4-dihydroquinazoline **11**, which under the thermal reaction conditions seems to convert into the aromatic quinazoline **10** by a subsequent 3,4-dehydrogenation.



Scheme 3 *Reagents and conditions*: (a) 1,4-Cyclohexadiene, reflux, 5 h.

On the other hand, in attempts to improve the yield of conversion **3** → **4** we assayed the thermal treatment of **3** under deoxygenated reaction conditions, in order to avoid the association of the putative biradical intermediates with oxygen. In these experiments we obtained an unexpected, worthy of mentioning, result. When a strictly deoxygenated toluene solution of azido-ketenimine **3a** was heated at reflux temperature for 2 h the indoloquinazoline **4a** (20% yield) and 6-phenyl-6-hydroxy-6,12-dihydroindolo[2,1-*b*]quinazoline **12** (50% yield) were obtained (Scheme 4). It seems reasonable to postulate that the 6-hydroxy



Scheme 4 *Reagents and conditions*: (a) Toluene (deoxygenated), reflux, 2 h.

derivative **12** should form during the purification stage by oxidation of the corresponding indolo[2,1-*b*]quinazoline **5a** by the action of atmospheric oxygen. In fact, in the ^{1}H NMR and ^{13}C NMR spectra of the crude material obtained after this thermal treatment of the azido-ketenimine **3a** we observed, besides others, the signals expected for **5a** [C(12)H singlet at $\delta = 5.28$ ppm; C2 $\delta =$ 42.9 ppm], whereas those corresponding to compound **12** did not appear.

A single-crystal X-ray analysis of compound **12** shows that its tetracyclic fused system presents a planar geometry, the main deviation from plane being 0.0512 Å (see Fig. S2 in the ESI†), and the angle between the mean planes of the indoloquinazoline system and that of the benzene ring attached to C9 (crystallographic numbering) is 79.9°. The main feature of this structure is that the molecules of **12** in the crystal are linked by two intermolecular O1–H1 ··· N2 (crystallographic numbering) hydrogen bonds, thus resulting in the formation of dimers (see Fig. S3 in the ESI†). Although the overlapping of the benzene rings of the two molecules forming each dimer is not complete, it may be stabilized by pi ··· pi stacking interactions, the distance between the centroids of the two benzene rings being 3.637 Å. The dimers are further interconnected through C24–H24 ··· O1 (crystallographic numbering) contacts, giving rise to the formation of ribbons along the *c* axis (see Fig. S4 in the ESI†).

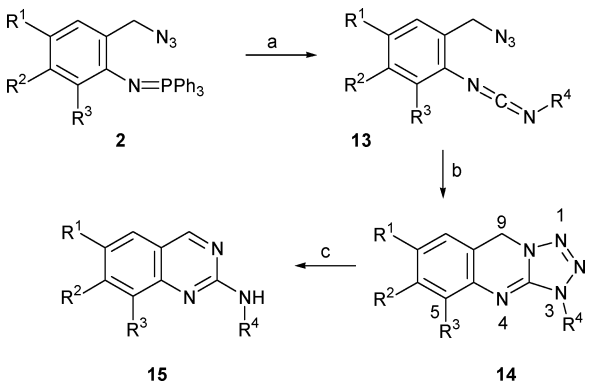
For the study of the azide-carbodiimide intramolecular [3 + 2] cycloaddition, the aza-Wittig reaction of azido-iminophosphoranes **2** with alkyl and aryl isocyanates easily allowed us the synthesis of a series of the appropriate starting materials. Thus, treatment of **2**, with phenethyl isocyanate, benzyl isocyanate and several aryl isocyanates, in dichloromethane solution at room temperature, provided azido-carbodiimides **13**, isolated in moderated yields after a short column chromatography on silica gel (Table 2). The heating at reflux temperature during 2–5 h of toluene solutions of heterocumulenes **13** gave good yields of the tetrazolo[5,1-*b*]quinazolines **14** (Scheme 5 and Table 2)

The determination of the structure of the tetrazoloquinazolines **14** was essentially based on their ^{1}H and ^{13}C NMR spectroscopic data and high-resolution mass spectra. In their ^{1}H NMR spectra the C(9)H benzylic protons appear at $\delta = 5.50$–5.66 ppm. Their ^{13}C NMR spectra show the signal due to the C9 carbon atom at $\delta =$ 56.7–48.0 ppm. In their mass spectra the peak due to the losing of dinitrogen was observed, in addition to the expected molecular ion.

It seems obvious that the more plausible mechanism explaining the formation of the tetrazolo[5,1-*b*]quinazolines **14** is the intramolecular [3 + 2] cycloaddition between the azido group and the distal carbon–nitrogen double bond of the carbodiimide function, C═NR.[4]

Table 2 Azido-carbodiimides **13** and tetrazolo[5,1-*b*]quinazolines **14**

Entry	R^1	R^2	R^3	R^4	**13** Yield (%)	**14** Yield (%)
a	H	H	H	4-Me-C_6H_4	75	63
b	H	H	H	$PhCH_2CH_2$	50	93
c	H	H	Me	4-Br-C_6H_4	54	98
d	Cl	H	H	4-Me-C_6H_4	75	67
e	Me	H	H	4-Cl-C_6H_4	57	95
f	Me	H	H	3-MeO-C_6H_4	74	99
g	Me	H	H	$PhCH_2$	87	99
h	C_4H_4		H	4-MeO-C_6H_4	61	99



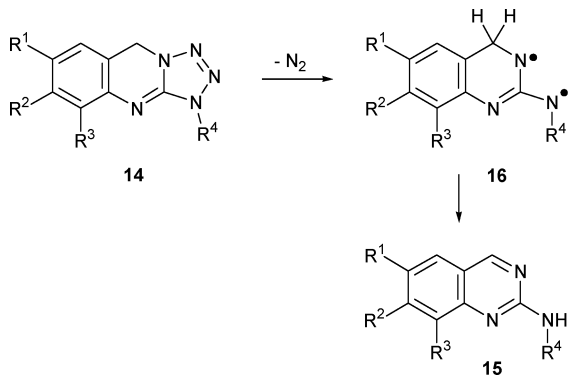
Scheme 5 *Reagent and conditions*: (a) R^4-N═C═O, CH_2Cl_2, r.t., 30 min; (b) Toluene, reflux, 2–5 h; (c) Toluene, sealed tube, 150–180 °C, 5–12 d.

Table 3 2-Aminoquinazolines **15**

Compound	R^1	R^2	R^3	R^4	Yield (%)
15a	H	H	H	$PhCH_2CH_2$	70
15b	H	H	Me	4-Br-C_6H_4	63
15c	Cl	H	H	4-Me-C_6H_4	40
15d	Me	H	H	$PhCH_2$	95

The tetrazolo[5,1-*b*]quinazolines **14** are thermally stable in refluxing toluene solutions. Nevertheless, under harsher reaction conditions (heating of their toluene solutions at 150–180 °C in a sealed tube for long periods of time ranging from 5 to 12 days) the tetrazoloquinazolines **14** converted into the 2-aminoquinazolines **15** with concomitant dinitrogen extrusion (Scheme 5 and Table 3).

It is reasonable to assume that such extrusion of dinitrogen from compounds **14** gives, in the first instance, the aminyl biradicals **16**, which would then undergo a subsequent hydrogen transfer from C4 to the exocyclic aminyl center ultimately providing the 2-aminoquinazolines **15** (Scheme 6).



Scheme 6 Proposed mechanism for the conversion **14** → **15**.

Conclusions

We have experimentally scrutinized two new types of intramolecular [3 + 2] cycloadditions between an azido group (3-atom component) and ketenimine and carbodiimide functions (as 2-atom components). Appropriate substrates for these tests were *N*-aryl heterocumulenes bearing a 2-azidomethyl lateral chain at the aryl nucleus. These species were easily available by applying

aza-Wittig chemistry on an azido-iminophosphorane, prepared in turn by a chemoselective Staudinger Ph_3P-azidation reaction of the adequate bisazide. The [3 + 2] cyloaddition reactions of the azido-ketenimines occurred in refluxing toluene solution, but the initial cycloadducts underwent *in situ* dinitrogen extrusion converting into members of two isomeric (linear and angular) heterocyclic systems, indolo[1,2-*a*]quinazolines and indolo[2,1-*b*]quinazolines. One of the presumable biradical intermediates of these extrusion reactions could be captured, before its final cyclization, by double H abstraction from 1,4-cyclohexadiene. Whereas the angular isomers are commonly the products of these tandem cycloaddition/dinitrogen extrusion/cyclization sequences, a methyl group placed at the *ortho* position to the *N*-linked aryl carbon plays a fundamental role in promoting the appearance of the linear isomer in the reaction mixture. This effect is rationalized by a presumable steric biasing at the cyclization step. In contrast to these results, the [3 + 2] cycloadducts resulting from the azido-carbodiimides, tetrazolo[5,1-*b*]quinazolines, proved to be stable under similar reaction conditions, in refluxing toluene solutions, and could be thus isolated and characterized. Only under harsh thermal activation (150–180 °C, days) they extruded dinitrogen for converting into 2-aminoquinazolines. These results are useful for confirming that the *ortho*-benzylic scaffolding is an adequate tether in this type of [3 + 2] cycloaddition reaction, and also disclosed the relative thermal stability of the respective cycloadducts resulting from azido-ketenimines and -carbodiimides.

Experimental

All melting points are uncorrected. Infrared (IR) spectra were recorded neat or as Nujol emulsions. ^{1}H NMR spectra were recorded at 200, 300 or 400 MHz. ^{13}C NMR spectra were recorded at 50, 75 or 100 MHz. The chemical shifts are expressed in ppm, relative to Me_4Si at $\delta = 0.00$ ppm in the ^{1}H NMR spectra recorded in $CDCl_3$ and DMSO-d_6 and to the signal of the solvent at δ = 11.50 ppm when recorded in CF_3CO_2D. The chemical shifts in the ^{13}C NMR spectra are reported relative to the resonance of $CDCl_3$ at δ = 77.1 ppm, DMSO-d_6 at δ = 39.5 ppm or CF_3CO_2D at δ = 165.4 ppm. *J* values are given in Hz.

2-Azidobenzylazide **1a**,[19] 2-azido-3-methylbenzylazide **1b**,[19] 2-azido-5-bromobenzylazide **1c**,[19] 2-azido-5-chlorobenzylazide **1d**,[19] 2-azido-5-methylbenzylazide **1e**,[19] 3-azido-2-azidomethylnaphthalene **1f**,[19] methylphenylketene,[20] ethylphenylketene[21] and diphenylketene[22] were prepared following published experimental procedures.

Preparation of azido-triphenyliminophosphoranes 2

To a solution of the corresponding 2-azidobenzylazide **1** (15 mmol) in anhydrous diethyl ether (60 mL), under nitrogen and at room temperature, a solution of triphenylphosphine (4.19 g, 16 mmol) in the same solvent (20 mL) was added dropwise during 6–8 h. The reaction mixture was stirred at room temperature for 12 h. Then, the solvent was removed under reduced pressure, and the crude material was purified by column chromatography on silica gel deactivated with triethylamine, using hexanes/diethyl ether (7 : 3, v/v) as eluent.

Azido-triphenyliminophosphorane 2a (R^1 = R^2 = R^3 = H). (4.28 g, 70%); mp 94–95 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 2092 (vs), 1593 (s), 1481 (vs), 1450 (s), 1437 (s), 1348 (vs), 1148 (vs), 1115 (s), 1022 (m), 752 (s), 715 (s), 694 (s); δ_H(300 MHz, $CDCl_3$) 4.66 (2 H, s), 6.46 (1 H, d, *J* 7.6), 6.64 (1 H, t, *J* 7.3), 6.86 (1 H, td, *J* 7.6, 1.7), 7.19–7.23 (1 H, m), 7.40–7.52 (9 H, m), 7.72–7.79 (6 H, m); δ_C(75 MHz, $CDCl_3$) 52.7, 117.1, 121.1 (d, *J* 10.2), 128.6, 128.7 (d, *J* 12.0), 129.4 (d, *J* 22.8) (s), 129.8 (d, *J* 2.4), 131.2 (d, *J* 99.8) (s), 131.7 (d, *J* 2.9), 132.6 (d, *J* 9.7), 150.2 (s); δ_P(121.4 MHz, $CDCl_3$, H_3PO_4) 2.8; HRMS (ESI): Calcd for $C_{25}H_{21}N_4P$ $[M]^+$ 408.1504, found 408.1517.

Azido-triphenyliminophosphorane 2b (R^1 = R^2 = H; R^3 = Me). (4.20 g, 66%); mp 92–93 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 2098 (vs), 1591 (m), 1466 (vs), 1435 (vs), 1350 (m), 1111 (s), 748 (s), 713 (vs), 694 (vs); δ_H(400 MHz, $CDCl_3$) 1.90 (3 H, s), 4.18 (2 H, s), 6.73 (1 H, td, *J* 7.2, 2.0), 7.01 (1 H, d, *J* 7.2), 7.05 (1 H, d, *J* 7.2), 7.41-7.45 (6 H, m), 7.50-7.54 (3 H, m), 7.57-7.62 (6 H, m); δ_C(100 MHz, $CDCl_3$) 21.3, 53.3, 118.9 (d, *J* 3.2), 127.0 (d, *J* 1.9), 128.5 (d, *J* 11.9), 130.2 (d, *J* 8.4) (s), 130.4 (d, *J* 2.7), 131.5 (d, *J* 2.7), 132.3 (d, *J* 9.6), 132.7 (d, *J* 100.9) (s), 133.5 (d, *J* 5.4) (s), 147.4 (s); δ_P(161.9 MHz, $CDCl_3$, H_3PO_4) –4.2; HRMS (ESI): Calcd for $C_{26}H_{23}N_4P$ $[M]^+$ 422.1660, found 422.1674.

Azido-triphenyliminophosphorane 2c (R^1 = Br; R^2 = R^3 = H). (5.10 g, 70%); mp 106–107 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 2098 (vs), 1581 (m), 1477 (vs), 1437 (s), 1404 (m), 1350 (s), 1288 (m), 1109 (m), 1022 (w), 881 (w), 759 (s), 692 (s); δ_H(300 MHz, $CDCl_3$) 4.61 (2 H, s), 6.29 (1 H, dd, *J* 8.5, 1.0), 6.91 (1 H, dd, *J* 8.5, 2.6), 7.31 (1 H, t, *J* 2.6), 7.42–7.48 (6 H, m), 7.51–7.54 (3 H, m), 7.69–7.76 (6 H, m); δ_C(75 MHz, $CDCl_3$) 52.1, 108.8 (s), 122.2 (d, J 10.3), 128.8 (d, *J* 12.1), 130.6 (d, *J* 100.1) (s), 131.2, 131.5 (d, *J* 23.1) (s), 131.9 (d, *J* 3.0), 132.0, 132.5 (d, *J* 9.7), 149.2 (s); δ_P(121.4 MHz, $CDCl_3$, H_3PO_4) 4.2; HRMS (ESI): Calcd for $C_{25}H_{20}BrN_4P$ $[M]^+$ 486.0609, found 486.0615.

Azido-triphenyliminophosphorane 2d (R^1 = Cl; R^2 = R^3 = H). (4.90 g, 74%); mp 107–108 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 2100 (vs), 1587 (m), 1473 (s), 1410 (m), 1356 (m), 1182 (w), 1034 (w), 1022 (w), 812 (w), 715 (s), 692 (vs); δ_H(400 MHz, $CDCl_3$) 4.61 (2 H, s), 6.34 (1 H, dd, *J* 8.5, 1.1), 6.78 (1 H, dd, *J* 8.5, 2.7), 7.18 (1 H, t, *J* 2.7), 7.43–7.48 (6 H, m), 7.51–7.53 (3 H, m), 7.70–7.75 (6 H, m); δ_C(100 MHz, $CDCl_3$) 52.2, 121.5 (s), 121.7 (d, *J* 10.2), 128.2, 128.8 (d, *J* 12.0), 129.2, 130.7 (d, *J* 100.1) (s), 131.0 (d, *J* 22.7) (s), 131.9 (d, *J* 2.6), 132.5 (d, *J* 9.6), 148.7; δ_P(161.9 MHz, $CDCl_3$, H_3PO_4) 3.6; HRMS (ESI): Calcd for $C_{25}H_{20}ClN_4P$ $[M]^+$ 442.1114, found 442.1118.

Azido-triphenyliminophosphorane 2e (R^1 = Me; R^2 = R^3 = H). (4.56 g, 72%); mp 114–115 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 2106 (s), 1610 (w), 1490 (vs), 1437 (s), 1348 (vs), 1107 (s), 1036 (w), 1024 (w), 814 (w), 737 (s), 715 (s), 694 (s); δ_H(300 MHz, $CDCl_3$) 2.19 (3 H, s), 4.64 (2 H, s), 6.37 (1 H, d, *J* 8.0), 6.67 (1 H, d, *J* 8.0), 7.03 (1 H, s), 7.40–7.52 (9 H, m), 7.72–7.78 (6 H, m); δ_C(75 MHz, $CDCl_3$) 20.6, 52.6, 120.8 (d, *J* 9.9), 126.1 (s), 128.6 (d, *J* 12.0), 129.1 (d, *J* 22.6) (s), 129.2, 130.4 (d, *J* 2.2), 131.3 (d, *J* 99.6) (s), 131.7 (d, *J* 2.8), 132.6 (d, *J* 9.7), 147.4 (s); δ_P(121.4 MHz, $CDCl_3$, H_3PO_4) 2.3; HRMS (ESI): Calcd for $C_{26}H_{23}N_4P$ $[M]^+$ 422.1660, found 422.1180.

Azido-triphenyliminophosphorane 2f (R^1-R^2 = C_6H_4; R^3 = H). (4.74 g, 69%); mp 130–131 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 2094 (vs), 1624 (m), 1595 (m), 1493 (w), 1461 (vs), 1387 (s), 1344 (s),

1279 (s), 1196 (m), 997 (w), 737 (vs), 694 (vs); δ_H(400 MHz, $CDCl_3$) 4.88 (2 H, s), 6.74 (1 H, s), 7.15 (1 H, t, J = 7.6), 7.21–7.27 (2 H, m), 7.47–7.52 (6 H, m), 7.55–7.59 (3 H, m), 7.69 (1 H, d, J 7.6 Hz), 7.75 (1 H, s), 7.83 (6 H, s); δ_C(100 MHz, $CDCl_3$) 52.9, 114.8, 121.8, 125.4 (d, J 21.1), 127.3 (s), 127.5, 128.1, 128.8 (d, J 47.6), 130.7 (d, J 97.2) (s), 131.9 (d, J 2.3), 132.2 (d, J 23.0) (s), 132.7 (d, J 9.6), 134.9 (s); δ_P(161.9 MHz, $CDCl_3$, H_3PO_4) 3.9; HRMS (ESI): Calcd for $C_{29}H_{23}N_4P$ $[M]^+$ 458.1660, found 458.1669.

Procedure for the preparation of azido-ketenimines 3a–g

To a solution of the azido-triphenyliminophosphorane **2** (1.5 mmol) in anhydrous dichloromethane (20 mL) a solution of the corresponding ketene (2 mmol) in the same solvent (5 mL) was added. The reaction mixture was stirred at room temperature under nitrogen for 30 min. Next the solvent was removed under reduced pressure and the resulting material was purified by column chromatography on silica gel, using hexanes/diethyl ether (9 : 1, v/v) as eluent, to afford the azido-ketenimine **3**.

Procedure for the preparation of azido-ketenimines 3h–l

To a solution of bis(4-chlorophenyl)acetyl chloride (0.66 g, 2.2 mmol) in anhydrous diethyl ether (30 mL), cooled at 0 °C and under nitrogen, triethylamine (0.263 g, 2.6 mmol) was added, and the reaction mixture was stirred at 0 °C for 15 min. Then, the solution containing bis(4-chlorophenyl)ketene was added *via* a canula, provided with a cotton filter, to a solution of the azido-triphenyliminophosphorane **2** (1.1 mmol) in anhydrous dichloromethane (20 mL). The new reaction mixture was stirred at room temperature under nitrogen for 30 min. Next the solvent was removed under reduced pressure and the resulting material was purified by column chromatography on silica gel, using hexanes/diethyl ether (9.5 : 0.5, v/v) as eluent, to afford the azido-ketenimine **3**.

Preparation of indolo[1,2-*a*]quinazolines 4 and indolo[2,1-*b*]quinazolines 5

A solution of the corresponding azido-ketenimine **3** (1 mmol) in anhydrous toluene (20 mL) was heated at reflux temperature under nitrogen for 2–4 h. After cooling at room temperature, the solvent was removed under reduced pressure and the resulting material was chromatographed on a silica gel column.

7-Phenylindolo[1,2-*a*]quinazoline 4a. Eluent for column chromatography: hexanes/diethyl ether (9 : 1, v/v); (0.18 g, 61%); mp 149–150 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1599; δ_H(400 MHz; $CDCl_3$) 7.30 (1 H, t, J 7.5), 7.36 (1 H, t, J 7.5), 7.41–7.49 (2 H, m), 7.50–7.56 (2 H, m), 7.68–7.72 (2 H, m), 7.87–7.89 (2 H, m), 8.14 (1 H, d, J 7.7), 8.30 (1 H, d, J 8.5), 8.35 (1 H, d, J 8.5), 8.55 (1 H, s); δ_C(100 MHz; $CDCl_3$) 109.8 (s), 114.1, 114.6, 119.1 (s), 120.6, 122.5, 123.2, 126.5, 128.3 (s), 128.6, 129.1, 129.7 (s), 130.0, 133.4, 133.7 (s), 138.1 (s), 138.8 (s), 151.4; HRMS (ESI): Calcd for $C_{21}H_{14}N_2$ $[M]^+$ 294.1157, found 294.1164.

3-Bromo-7-phenylindolo[1,2-*a*]quinazoline 4c. Eluent for column chromatography: hexanes/diethyl ether (9 : 1, v/v); (0.17 g, 45%); mp 202–204 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1597; δ_H(400 MHz; $CDCl_3$) 7.36–7.50 (3 H, m), 7.52–7.56 (2 H, m), 7.75–7.80 (2 H, m), 7.84–7.86 (2 H, m), 8.12 (1 H, d, J 7.5), 8.17–8.20 (2 H, m), 8.43 (1 H, s); δ_C(100 MHz; $CDCl_3$) 110.6 (s), 113.9, 115.7 (s), 116.2, 120.5 (s), 120.9, 122.8, 123.7, 126.8, 128.3 (s), 128.7, 129.6 (s), 130.0, 131.3, 133.3 (s), 135.9, 136.8 (s), 138.4 (s), 149.7; HRMS (ESI): Calcd for $C_{21}H_{13}BrN_2$ $[M]^+$ 372.0262, found 372.0262.

3-Chloro-7-phenylindolo[1,2-*a*]quinazoline 4d. Eluent for column chromatography: hexanes/diethyl ether (9 : 1, v/v); (0.23 g, 69%); mp 191–192 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1543; δ_H(400 MHz; $CDCl_3$) 7.36–7.40 (1 H, m), 7.43–7.56 (4 H, m), 7.65–7.69 (2 H, m), 7.84–7.87 (2 H, m), 8.13–8.15 (1 H, m), 8.23 (1 H, d, J 8.6), 8.30 (1 H, d, J 8.6), 8.47 (1 H, s); δ_C(100 MHz; $CDCl_3$) 110.6 (s), 113.9, 116.1, 120.2 (s), 120.9, 122.8, 123.7, 126.8, 128.2 (s), 128.3, 128.4 (s), 128.7, 129.6 (s), 130.0, 133.2, 133.3 (s), 136.5 (s), 138.5 (s), 149.8; HRMS (ESI): Calcd for $C_{21}H_{13}ClN_2$ $[M]^+$ 328.0767, found 328.0774.

3-Chloro-7-methylindolo[1,2-*a*]quinazoline 4e. Eluent for column chromatography: hexanes/diethyl ether (7 : 3, v/v); (0.042 g, 16%); mp 183–184 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1541; δ_H(400 MHz; $CDCl_3$) 2.64 (3 H, s), 7.43–7.52 (2 H, m), 7.65–7.70 (2 H, m), 7.90 (1 H, d, J 8.2), 8.20 (1 H, d, J 8.2), 8.26 (1 H, d, J 8.2), 8.40 (1 H, s); δ_C(100 MHz; $CDCl_3$) 7.9, 105.5 (s), 113.7, 115.7, 119.9 (s), 120.1, 122.0, 123.3, 127.9 (s), 128.4, 129.3 (s), 129.9 (s), 133.0, 136.9 (s), 138.8 (s), 148.1; HRMS (ESI): Calcd for $C_{16}H_{11}ClN_2$ $[M]^+$ 266.0611, found 266.0611.

3-Chloro-7-ethylindolo[1,2-*a*]quinazoline 4f. Eluent for column chromatography: hexanes/diethyl ether (9 : 1, v/v); (0.056 g, 20%); mp 135–136 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1542; δ_H(300 MHz; $CDCl_3$) 1.37 (3 H, t, J 7.5), 3.14 (2 H, q, J 7.5), 7.39–7.49 (2 H, m), 7.61–7.67 (2 H, m), 7.90–7.93 (1 H, m), 8.17–8.24 (2 H, m), 8.34 (1 H, s); δ_C(75 MHz; $CDCl_3$) 15.4, 16.6, 111.9 (s), 113.8, 115.6, 119.8 (s), 120.1, 121.9, 123.1, 127.8 (s), 128.2, 129.0 (s), 129.3 (s), 132.8, 136.6 (s), 138.3 (s), 148.1; HRMS (ESI): Calcd for $C_{17}H_{13}ClN_2$ $[M]^+$ 280.0767, found 280.0772.

7-Phenylindolo[1,2-*a*]benzo[*g*]quinazoline 4g. Eluent for column chromatography: hexanes/diethyl ether (7 : 3, v/v); (0.14 g, 40%); mp 218–219 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1554; δ_H(400 MHz; $CDCl_3$) 7.39–7.43 (1 H, m), 7.44–7.52 (2 H, m), 7.55–7.61 (3 H, m), 7.62–7.65 (1 H, m), 7.89–7.91 (2 H, m), 7.94 (1 H, d, J 8.0), 7.98 (1 H, d, J 8.4), 8.14 (1 H, d, J 8.0), 8.18 (1 H, s), 8.46 (1 H, d, J 8.4), 8.60 (1 H, s), 8.66 (1 H, s); δ_C(100 MHz; $CDCl_3$) 110.9, 112.0 (s), 113.4, 119.6 (s), 120.9, 122.4, 124.0, 125.7, 128.6, 127.6, 128.2 (s), 128.7, 128.8, 128.9, 129.3 (s), 129.8, 130.1, 131.1 (s), 133.4 (s), 134.6 (s), 135.9 (s), 138.4 (s), 152.0; HRMS (ESI): Calcd for $C_{25}H_{16}N_2$ $[M]^+$ 344.1313, found 344.1312.

10-Chloro-7-(4-chlorophenyl)indolo[1,2-*a*]quinazoline 4h. Eluent for column chromatography: hexanes/dichloromethane (7 : 3, v/v); (0.18 g, 50%); mp 273–275 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1554; δ_H(400 MHz; CF_3CO_2D) 7.36–7.44 (5 H, m), 7.60 (1 H, t, J 7.6), 7.75 (1 H, d, J 8.0), 8.12 (1 H, d, J 8.0), 8.20 (1 H, t, J 8.0), 8.35 (1 H, s), 8.48 (1 H, d, J 8.0), 8.93 (1 H, s); δ_C(100 MHz; CF_3CO_2D) 110.5 (s), 114.2 (s), 116.4, 117.0 (s), 117.7 (s), 117.9, 124.0, 128.6, 128.7, 128.8 (s), 132.3, 132.9, 135.4 (s), 137.2, 138.6 (s), 142.5 (s), 145.1, 152.1; HRMS (ESI): Calcd for $C_{21}H_{12}Cl_2N_2$ $[M]^+$ 362.0378, found 362.0376.

10-Chloro-7-(4-chlorophenyl)-1-methylindolo[1,2-*a*]quinazoline 4i. Eluent for column chromatography: hexanes/diethyl ether

(9.5 : 0.5, v/v); (0.094 g, 25%); mp 183–184 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1545; δ_H(300 MHz; $CDCl_3$) 2.57 (3 H, s), 7.36 (1 H, dd, *J* 8.7, 1.8), 7.41 (1 H, t, *J* 8.0), 7.47–7.50 (2 H, m), 7.61–7.64 (2 H, m), 7.71 (1 H, d, *J* 1.8), 7.78–7.81 (2 H, m), 7.95 (1 H, d, *J* 8.4), 8.54 (1 H, s); δ_C(75 MHz; $CDCl_3$) 22.2, 108.5 (s), 115.6, 120.8, 121.8 (s), 123.1, 124.7, 125.7 (s), 126.1 (s), 126.3, 127.7 (s), 129.0, 131.1, 131.8 (s), 132.2 (s), 132.6 (s), 135.6 (s), 137.0, 141.1 (s), 152.0; HRMS (ESI): Calcd for $C_{22}H_{14}Cl_2N_2$ $[M]^+$ 376.0534, found 376.0538.

3,10-Dichloro-7-(4-chlorophenyl)indolo[1,2-*a*]quinazoline 4j. Eluent for column chromatography: hexanes/diethyl ether (9 : 1, v/v); (0.14 g, 35%); mp 318–319 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1551; δ_H(400 MHz; CF_3CO_2D) 7.42–7.49 (4 H, m), 7.55 (1 H, d, *J* 8.4), 7.85 (1 H, d, *J* 8.4), 8.12–8.16 (2 H, m), 8.39 (1 H, s), 8.51 (1 H, d, *J* 8.4), 8.96 (1 H, s); δ_C(100 MHz; CF_3CO_2D) 111.2 (s), 114.0 (s), 116.0, 118.6 (s), 119.0, 119.7 (s), 124.2, 128.2 (s), 128.5 (s), 128.8, 132.1, 132.8, 134.9 (s), 135.3, 135.8 (s), 138.7 (s), 140.6 (s), 144.3, 151.0; HRMS (ESI): Calcd for $C_{21}H_{11}Cl_3N_2$ $[M]^+$ 395.9988, found 396.0007.

10-Chloro-7-(4-chlorophenyl)-3-methylindolo[1,2-*a*]quinazoline 4k. Eluent for column chromatography: hexanes/diethyl ether (9 : 1, v/v); (0.19 g, 51%); mp 303–305 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1558; δ_H(300 MHz; CF_3CO_2D) 2.44 (3 H, s), 7.33–7.42 (5 H, m), 7.70 (1 H, d, *J* 8.7), 7.88 (1 H, s), 8.02 (1 H, d, *J* 8.7), 8.28 (1 H, s), 8.34 (1 H, d, *J* 8.7), 8.85 (1 H, s); δ_C(75 MHz; CF_3CO_2D) 21.1, 109.9 (s), 113.7 (s), 116.2, 117.7, 123.9, 128.4, 128.6 (s), 128.7 (s), 128.8 (s), 132.3, 132.7 (s), 132.9, 135.1 (s), 136.4, 138.5 (s), 140.3 (s), 140.5 (s), 146.5, 151.8; HRMS (ESI): Calcd for $C_{22}H_{14}Cl_2N_2$ $[M]^+$ 376.0534, found 376.0545.

10-Chloro-7-(4-chlorophenyl)indolo[1,2-*a*]benzo[*g*]quinazoline 4l. Eluent for column chromatography: hexanes/diethyl ether (9 : 1, v/v); (0.23 g, 55%); mp 314–316 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1562; δ_H(300 MHz; $CDCl_3/CF_3CO_2H$) 7.48 (1 H, dd, *J* 10.0, 5.2), 7.51–7.54 (2 H, m), 7.61–7.65 (3 H, m), 7.76–7.80 (1 H, m), 7.91 (1 H, d, *J* 8.8), 8.06 (1 H, d, *J* 7.6), 8.13 (1 H, d, *J* 7.6), 8.44 (1 H, s), 8.51 (1 H, d, *J* 1.6), 8.62 (1 H, s), 8.88 (1 H, s); δ_C(100 MHz; $CDCl_3/CF_3CO_2H$) 110.6 (s), 112.4, 113.2 (s), 114.0, 115.8 (s), 116.0 (s), 122.4, 125.5, 126.2 (s), 126.9 (s), 128.1, 128.3, 129.9, 130.0 (s), 130.6, 131.3, 131.6 (s), 132.7 (s), 133.1 (s), 133.6, 135.8 (s), 138.9, 139.2 (s), 151.6; HRMS (ESI): Calcd for $C_{25}H_{14}Cl_2N_2$ $[M]^+$ 412.0534, found 412.0550.

4-Methyl-6-phenyl-5,12-dihydroindolo[2,1-*b*]quinazoline 5b. Eluent for column chromatography: hexanes/diethyl ether (9 : 1, v/v); (0.20 g, 66%); mp 173–174 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 3456, 1579; δ_H(300 MHz; $CDCl_3$) 2.25 (3 H, s), 5.24 (2 H, s), 6.85–6.90 (2 H, m), 7.09 (2 H, t, *J* 9.2), 7.14–7.18 (2 H, m), 7.20–7.30 (2 H, m), 7.52 (2 H, t, *J* 9.2), 7.65 (2 H, d, *J* 9.2), 7.72 (1 H, d, *J* 9.2); δ_C(75 MHz; $CDCl_3$) 16.6, 42.9, 93.7 (s), 108.1, 114.6 (s), 116.8, 119.3, 120.4, 120.9, 121.6 (s), 125.1, 125.2, 127.5, 127.6 (s), 129.5, 129.6, 133.0 (s), 133.9 (s), 134.1 (s), 135.4 (s); HRMS (ESI): Calcd for $C_{22}H_{18}N_2$ $[M]^+$ 310.1470, found 310.1474.

9-Chloro-6-(4-chlorophenyl)-4-methyl-6-phenyl-5,12-dihydroindolo[2,1-*b*]quinazoline 5i. Eluent for column chromatography: hexanes/diethyl ether (9.5 : 0.5, v/v); (0.15 g, 40%); mp 220–221 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 3398, 1573; δ_H(300 MHz; $CDCl_3$) 2.24 (3 H, s), 5.18 (2 H, s), 6.71 (1 H, s), 6.90 (1 H, t, *J* 7.5), 7.07–7.11 (3 H, m), 7.21–7.22 (1 H, m), 7.43–7.50 (5 H, m); δ_C(75 MHz; $CDCl_3$) 16.6, 43.0, 92.7 (s), 108.5, 114.3 (s), 117.2, 120.9, 121.4, 121.7 (s), 125.1 (s), 125.2, 126.0 (s), 128.6, 129.8, 131.0 (s), 133.3 (s), 133.4 (s), 133.5 (s), 134.7 (s); HRMS (ESI): Calcd for $C_{22}H_{16}Cl_2N_2$ $[M]^+$ 378.0691, found 378.0673.

Thermal treatment of azido-ketenimine 3a in 1,4-cyclohexadiene

A solution of azido-ketenimine **3a** (0.32 g, 1 mmol) in 1,4-cyclohexadiene (20 mL), under nitrogen, was heated at reflux temperature for 5 h. After cooling at room temperature, the solvent was removed under reduced pressure and the resulting material was chromatographed on a silica gel column, using hexanes/diethyl ether (9 : 1, v/v) as eluent, to give 7-phenylindolo[1,2-a]quinazoline **4a** (0.12 g, 40%) and 2-(diphenylmethyl)quinazoline **10**[23] (0.059 g, 20%).

Thermal treatment of azido-ketenimine 3a under deoxygenated conditions

A deoxygenated solution of the azido-ketenimine **3a** (0.32 g, 1 mmol) in anhydrous toluene (20 mL) was heated at reflux temperature for 2 h, under atmosphere of nitrogen. After cooling to room temperature, the solvent was removed under reduced pressure and the resulting material was chromatographed on a silica gel column, using hexanes/diethyl ether (9 : 1, v/v) as eluent.

7-phenylindolo[1,2-*a*]quinazoline 4a. (0.06 g, 20%)

6-Hydroxy-6-phenyl-6,12-dihydroindolo[2,1-*b*]quinazoline 12. (0.16 g, 50%); mp 205–206 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 3175 (m), 1643 (vs), 1597 (vs), 1573 (s), 1495 (s), 1321 (m), 1219 (m), 1174 (s), 1043 (m), 941 (w), 777 (m), 768 (m), 748 (s), 731 (m); δ_H(400 MHz, $CDCl_3$) 4.14 (1 H, d, *J* 13.6), 4.77 (1 H, d, *J* 13.6), 6.56 (1 H, d, *J* 7.6), 6.63 (1 H, d, *J* 7.6), 6.69 (1 H, s), 6.80 (1 H, t, *J* 7.2), 6.88′6.90 (1 H, m), 6.97 (1 H, t, *J* 7.2), 7.12 (1 H, t, *J* 7.6), 7.26–7.40 (5 H, m), 7.55 (2 H, d, *J* 7.2); δ_C(100 MHz, $CDCl_3$) 43.2, 79.7 (s), 107.6, 119.1 (s), 123.2, 124.9, 125.4, 125.5, 125.9, 126.0, 127.8, 128.4, 128.5, 129.4, 134.3 (s), 140.6 (s), 142.2 (s), 143.2 (s), 163.9 (s); HRMS (ESI): Calcd for $C_{21}H_{16}N_2O$ $[M]^+$ 312.1263, found 312.1272.

Procedure for the preparation of azido-carbodiimides 13

To a solution of the azido-triphenyliminophosphorane **2** (1 mmol) in anhydrous dichloromethane (20 mL) a solution of the corresponding isocyanate (1.1 mmol) in the same solvent (5 mL) was added. The reaction mixture was stirred at room temperature under nitrogen for 30 min. Next the solvent was removed under reduced pressure and the resulting material was purified by column chromatography on silica gel, using hexanes/diethyl ether (9 : 1, v/v) as eluent, to afford the azido-carbodiimide **13**.

Preparation of the tetrazolo[5,1-*b*]quinazolines 14

A solution of the azido-carbodiimide **13** (1 mmol) in anhydrous toluene (20 mL) was heated at reflux temperature under nitrogen for 2–5 h. After cooling to room temperature, the solvent was removed under reduced pressure, and the resulting material was chromatographed on a silica gel column.

3-(4-Methylphenyl)-3,9-dihydrotetrazolo[5,1-*b*]quinazoline 14a. Eluent for column chromatography: hexanes/diethyl ether (4 : 1, v/v); (0.16 g, 63%); mp 158–159 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1641, 1595; δ_H(300 MHz; $CDCl_3$) 2.38 (3 H, s), 5.53 (2 H, s), 6.95–7.00 (2 H, m), 7.11–7.14 (1 H, m), 7.16–7.21 (1 H, m), 7.27–7.30 (2 H, m), 7.96–8.00 (2 H, m); δ_C(75 MHz; $CDCl_3$) 21.2, 47.7, 115.5 (s), 119.8, 122.8, 124.7, 126.4, 129.2, 129.9, 132.7 (s), 137.4 (s), 143.5 (s), 144.0 (s); HRMS (ESI): Calcd for $C_{15}H_{13}N_5$ $[M]^+$ 263.1171, found 263.1177.

3-Phenethyl-3,9-dihydrotetrazolo[5,1-*b*]quinazoline 14b. Eluent for column chromatography: hexanes/diethyl ether (3 : 7, v/v); (0.26 g, 93%); mp 130–131 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1643, 1568; δ_H(400 MHz; $CDCl_3$) 3.24 (2 H, t, *J* 8.0), 4.34 (2 H, t, *J* 8.0), 5.50 (2 H, s), 6.93–6.96 (1 H, m), 6.99–7.01 (1 H, m), 7.11 (1 H, d, *J* 8.0), 7.20–7.34 (6 H, m); δ_C(75 MHz; $CDCl_3$) 34.1, 46.7, 47.6, 115.2 (s), 122.2, 123.9, 126.5, 127.0, 128.7, 128.9, 129.2, 136.9 (s), 143.9 (s), 145.5 (s); HRMS (ESI): Calcd for $C_{16}H_{15}N_5$ $[M]^+$ 277.1327, found 277.1334.

3-(4-Bromophenyl)-5-methyl-3,9-dihydrotetrazolo[5,1-*b*]quinazoline 14c. Eluent for column chromatography: hexanes/diethyl ether (9.5 : 0.5, v/v); (0.33 g, 98%); mp 118–119 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1647, 1604; δ_H(300 MHz; $CDCl_3$) 2.38 (3 H, s), 5.51 (2 H, s), 6.82–6.84 (1 H, m), 6.85–6.90 (1 H, m), 7.09 (1 H, d, *J* 7.2), 7.58–7.62 (2 H, m), 8.16–8.20 (2 H, m); δ_C(75 MHz; $CDCl_3$) 17.9, 48.0, 115.2 (s), 120.3, 122.9, 124.0, 130.5, 132.5, 133.0 (s), 134.9 (s), 141.5 (s), 143.1 (s); HRMS (ESI): Calcd for $C_{15}H_{12}BrN_5$ $[M]^+$ 341.0276, found 341.0276.

7-Chloro-3-(4-methylphenyl)-3,9-dihydrotetrazolo[5,1-*b*]quinazoline 14d. Eluent for column chromatography: hexanes/diethyl ether (9 : 1, v/v); (0.20 g, 67%); mp 145–146 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1673, 1593; δ_H(400 MHz; $CDCl_3$) 2.41 (3 H, m), 5.54 (2 H, m), 6.99 (1 H, s), 7.08 (1 H, d, *J* 8.8), 7.15 (1 H, dd, *J* 8.8, 1.6), 7.31 (2 H, d, *J* 8.4), 7.96 (2 H, d, *J* 8.4); δ_C(100 MHz; $CDCl_3$) 21.2, 47.5, 116.8 (s), 119.9, 125.8, 126.2, 127.6 (s), 129.3, 130.0, 132.4 (s), 137.8 (s), 142.1 (s), 144.1 (s); HRMS (ESI): Calcd for $C_{15}H_{12}ClN_5$ $[M]^+$ 297.0781, found 297.0787.

3-(4-Chlorophenyl)-7-methyl-3,9-dihydrotetrazolo[5,1-*b*]quinazoline 14e. Eluent for column chromatography: hexanes/diethyl ether (9 : 1, v/v); (0.28 g, 95%); mp 164–165 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1647, 1606; δ_H(300 MHz; $CDCl_3$) 2.26 (3 H, s), 5.50 (2 H, s), 6.80 (1 H, s), 7.00–7.04 (2 H, m), 7.43–7.46 (2 H, m), 8.12–8.15 (2 H, m); δ_C(75 MHz; $CDCl_3$) 20.8, 47.7, 115.3 (s), 120.4, 124.7, 126.9, 129.5, 130.0, 132.6 (s), 132.9 (s), 133.9 (s), 140.5 (s), 143.3 (s); HRMS (ESI): Calcd for $C_{15}H_{12}ClN_5$ $[M]^+$ 297.0781, found 297.0793.

7-Methyl-3-(3-methoxyphenyl)-3,9-dihydrotetrazolo[5,1-*b*]quinazoline 14f. Eluent for column chromatography: hexanes/diethyl ether (9 : 1, v/v); (0.29 g, 99%); mp 187–188 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1650, 1587; δ_H(400 MHz; $CDCl_3$) 2.26 (3 H, s), 3.88 (3 H, s), 5.48 (2 H, s), 6.77 (1 H, s), 6.87 (1 H, dd, *J* 8.4, 2.0), 6.98–7.05 (2 H, m), 7.38 (1 H, t, *J* 8.4), 7.77 (1 H, d, *J* 8.4), 7.81 (1 H, s); δ_C(100 MHz; $CDCl_3$) 20.7, 47.6, 55.5, 104.8, 111.3, 113.0, 115.3 (s), 124.6, 126.8, 129.8, 130.1, 132.5 (s), 136.3 (s), 140.6 (s), 143.4 (s), 160.2 (s); HRMS (ESI): Calcd for $C_{16}H_{15}N_5O$ $[M]^+$ 293.1277, found 193.1280.

3-Benzyl-7-methyl-3,9-dihydrotetrazolo[5,1-*b*]quinazoline 14g. Eluent for column chromatography: hexanes/diethyl ether (7 : 3, v/v); (0.27 g, 99%); mp 139–140 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1643, 1603; δ_H(300 MHz; $CDCl_3$) 2.26 (3 H, s), 5.21 (2 H, s), 5.44 (2 H, s), 6.79 (1 H, s), 6.99–7.00 (2 H, m), 7.29–7.37 (3 H, m), 7.42–7.45 (2 H, m); δ_C(75 MHz; $CDCl_3$) 20.7, 47.6, 48.9, 115.0 (s), 123.8, 126.9, 128.5, 128.6, 128.9, 129.9, 131.9 (s), 134.4 (s), 141.2 (s), 145.2 (s); HRMS (ESI): Calcd for $C_{16}H_{15}N_5$ $[M]^+$ 277.1327, found 277.1328.

3-(4-Methoxyphenyl)-3,11-dihydrotetrazolo[5,1-*b*]benzo[*g*]quinazoline 14h. Eluent for column chromatography: hexanes/diethyl ether (9 : 1, v/v); (0.32 g, 99%); mp 209–210 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 1651, 1614; δ_H(400 MHz; $CDCl_3$) 3.87 (3 H, s), 5.66 (2 H, s), 7.03–7.07 (2 H, m), 7.28–7.32 (1 H, m), 7.38 (1 H, td, *J* 6.8, 1.2), 7.49 (1 H, s), 7.55 (1 H, s), 7.67 (1 H, d, *J* 8.4), 7.70 (1 H, d, *J* 8.4), 8.04–8.07 (2 H, m); δ_C(100 MHz; $CDCl_3$) 47.6, 55.7, 114.7, 117.3 (s), 120.5, 121.7, 124.4, 125.5, 126.4, 127.1, 127.3, 128.6 (s), 130.2 (s), 134.9 (s), 141.3 (s), 144.1 (s), 159.0 (s); HRMS (ESI): Calcd for $C_{19}H_{15}N_5O$ $[M]^+$ 329.1277, found 329.1290.

Preparation of 2-aminoquinazolines 15

A solution of the tetrazoloquinazoline **14** (1 mmol) in anhydrous toluene (20 mL) was heated in a sealed tube at 150–180 °C during 5–12 d. After cooling to room temperature, the solvent was removed under reduced pressure and the crude material was chromatographed on a silica gel column.

2-Phenethylaminoquinazoline 15a. Eluent for column chromatography: hexanes/ethyl acetate (7 : 3, v/v); (0.17 g, 70%); mp 123–124 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 3267 (s), 1620 (vs), 1595 (vs), 1551 (vs), 1240 (w), 1142 (w), 1113 (w), 862 (w), 796 (m), 721 (w), 700 (w); δ_H(300 MHz, $CDCl_3$) 2.97 (2 H, t, *J* 6.9), 3.82 (2 H, q, *J* 6.9), 5.51 (1 H, br s), 7.18–7.32 (6 H, m), 7.58–7.69 (3 H, m), 8.94 (1 H, s); δ_C(75 MHz, $CDCl_3$) 35.8, 42.9, 120.2 (s), 122.9, 125.3, 126.5, 127.7, 128.7, 129.0, 134.5, 139.3 (s), 159.3 (s), 162.4; HRMS (ESI): Calcd for $C_{16}H_{15}N_3$ $[M]^+$ 249.1266, found 249.1266.

2-(4-Bromophenyl)amino-8-methylquinazoline 15b. Eluent for column chromatography: hexanes/diethyl ether (1 : 1, v/v); (0.20 g, 63%); mp 221–222 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 3269 (s), 1616 (vs), 1603 (s), 1578 (s), 1549 (s), 1489 (s), 1414 (s), 1304 (m), 1254 (m), 1007 (w), 823 (m), 769 (s), 723 (m); δ_H(200 MHz, $CDCl_3$, 55 °C) 2.70 (3 H, s), 7.27 (1 H, t, *J* 7.8), 7.46–7.50 (2 H, m), 7.57–7.65 (2 H, m), 7.77–7.81 (2 H, m), 9.06 (1 H, m); δ_C(50 MHz, $CDCl_3$, 55 °C) 17.3, 114.8 (s), 120.6, 120.9 (s), 124.0, 125.3, 131.9, 134.4 (s), 134.7, 139.0 (s), 149.9 (s), 155.9 (s), 162.4; HRMS (ESI): Calcd for $C_{15}H_{12}BrN_3$ $[M]^+$ 313.0215, found 313.0218.

6-Chloro-2-(4-methylphenyl)aminoquinazoline 15c. Eluent for column chromatography: hexanes/dichloromethane (1 : 9, v/v); (0.11 g, 40%); mp 178–179 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 3253 (s), 1620 (vs), 1603 (vs), 1539 (vs), 1514 (s), 1407 (m), 1356 (s), 1174 (m), 1074 (m), 966 (w), 816 (s), 758 (w), 719 (m), 646 (w); δ_H(400 MHz, $CDCl_3$) 2.36 (3 H, s), 7.18–7.20 (2 H, m), 7.64–7.66 (3 H, m), 7.69–7.72 (3 H, m), 9.03 (1 H, s); δ_C(100 MHz, $CDCl_3$) 21.0, 120.0, 120.9 (s), 126.4, 127.1, 129.2 (s), 129.6, 133.2 (s), 135.7,

136.2 (s), 156.6 (s), 161.8; HRMS (ESI): Calcd for $C_{15}H_{12}ClN_3$ $[M]^+$ 269.0720, found 269.0710.

2-Benzylamino-6-methylquinazoline 15d. Eluent for column chromatography: dichloromethane/diethyl ether (9 : 1, v/v); (0.24 g, 95%); mp 147–148 °C (from Et_2O); ν_{max}(Nujol)/cm^{-1} 3228 (s), 1629 (m), 1599 (vs), 1544 (vs), 1311 (m), 1259 (m), 1246 (m), 1205 (w), 1143 (m), 1076 (w), 976 (w), 831 (m), 752 (m), 700 (m), 642 (m); δ_H(300 MHz, DMSO-d_6) 2.43 (3 H, s), 4.76 (2 H, d, J 5.7), 6.13 (1 H, s), 7.24–7.34 (3 H, m), 7.38–7.40 (2 H, m), 7.44 (1 H, s), 7.53–7.54 (2 H, m), 8.90 (1 H, s); δ_C(75 MHz, DMSO-d_6) 21.2, 45.8, 120.1 (s), 124.3, 126.6, 127.4, 127.8, 133.0 (s), 137.1, 138.9 (s), 158.6 (s), 162.4; HRMS (ESI): Calcd for $C_{16}H_{15}N_3$ $[M]^+$ 249.1266, found 249.1263.

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