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N-Phenyl-1,2,4-triazoline-3,5-dione (PTAD) as a Dienophilic Dinitrogen Equivalent: A Simple Synthesis of 3-Amino-1,2,4-benzotriazines from Arylcarbodiimides

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Dedicated to Professor Benito Alcaide on the occasion of his 60th anniversary

Keywords: Cycloaddition / Nitrogen heterocycles / Synthetic methods / Transition states

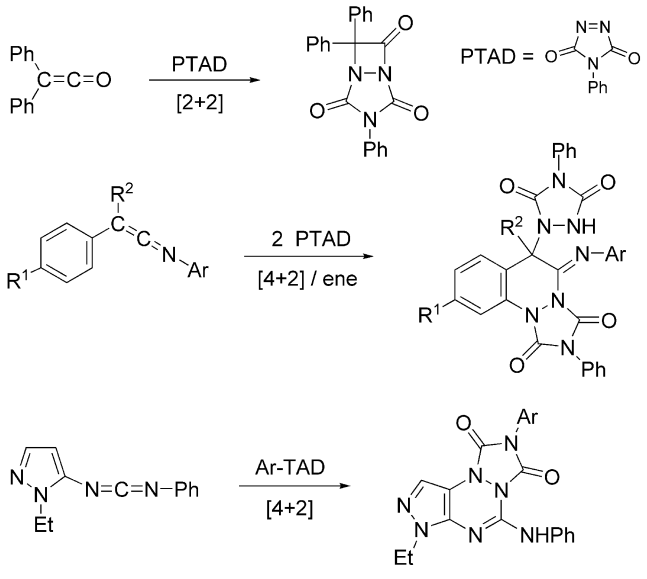
N-Arylcarbodiimides react with PTAD to provide [1,2,4]triazolo[1,2-*a*][1,2,4]benzotriazines by a [4+2] cycloaddition reaction. When asymmetrically substituted diarylcarbodiimides are used, the cycloaddition proceeds with total chemoselectivity because only the more electron-rich aryl nucleus is involved. This observation has been rationalized by a computational study using DFT methods that shows that, in the reaction of HTAD with arylcarbodiimides, the magnitude of the energy barriers depend on the electronic features of the substituents at the aryl nucleus; the calculations also indicate that the reaction proceeds through asynchronous states with polar characteristics. The treatment of the final cycloadducts with potassium hydroxide affords 3-aryl(alkyl)amino-1,2,4-benzotriazines.

Introduction

The chemistry of the most common five-membered cyclic azodicarbonyl compounds, 1,2,4-triazoline-3,5-diones (TADs), has been thoroughly reviewed.[1] These strong electron-acceptors have often been deployed in organic synthesis as enophiles[2] and dienophiles,[3] affording *N*-substituted urazoles (ene products) and/or [2+2] cycloadducts in their reactions with alkenes, whereas they mainly undergo Diels–Alder reactions with dienes.[4] As very reactive dienophiles, TADs have found wide application in characterizing dienes,[5] protecting diene moieties,[6] and capturing unstable or volatile intermediates.[7]

Our research group has a long-standing interest in exploring the chemistry of different types of heterocumulenes such as ketenimines,[8] carbodiimides,[9] ketenes,[10] and isothiocyanates;[11] we have more commonly directed our attention toward their [2+2] and [4+2] cycloaddition reactions.[12] In general, the cycloaddition chemistry of heterocumulenes is usually dominated by the [2+2] rather than the [4+2] mode of addition.[13]

To the best of our knowledge, very few reactions between TADs and heterocumulenes have been reported (Scheme 1). PTAD (*N*-phenyl TAD) has been shown to react with the C=C double bond of diphenyl ketene in a [2+2] fashion.[14] We have recently shown that C-aryl ketenimines react with two equivalents of PTAD through a Diels–Alder/ene se-



Scheme 1. Known examples of reactions of TADs with heterocumulenes.[14–16]

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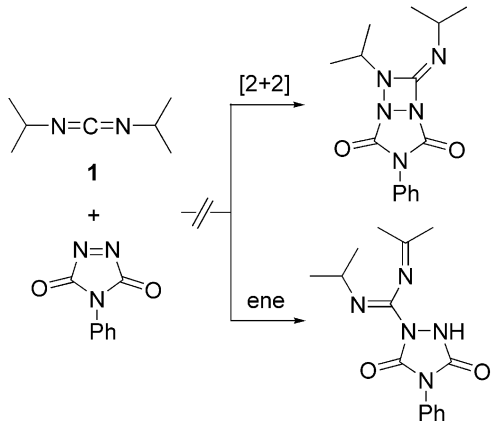
quence to yield 1,2,4-triazolo[1,2-*a*]cinnolines with a pendant triazolidinedione group.[15] Finally, *N*-phenyl-*N*′-(pyrazol-5-yl)carbodiimide has been reacted with two different *N*-aryl TADs to give very low yields (about 10%) of the [4+2] cycloadducts resulting from the participation of the C4=C5 double bond of the pyrazole nucleus and its vicinal cumulated N=C bond in a reactive 2-azadiene fragment.[16]

Following these two latter reports, we reasoned that simple arylcarbodiimides could behave as reactive 2-azadienes in Diels–Alder reactions with the dienophilic N=N bond of TADs, providing that the dearomatization of the aryl ring was not too costly on energetic grounds. Here we show that this new type of [4+2] cycloaddition is, in fact, easily feasible. Furthermore, differing electronic effects of the substituents can cause the addition to occur with complete regioselectivity when diarylcarbodiimides bearing two well-differentiated aryl groups are used.

Results and Discussion

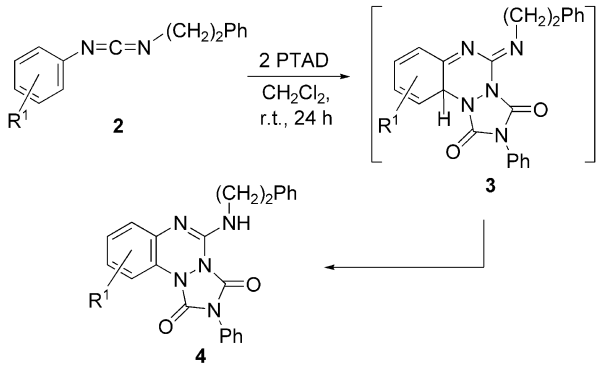
Because the reactions of carbodiimides with TADs are almost completely unexplored, we first checked the reaction of a simple dialkylcarbodiimide – commercially available *N*,*N*′-diisopropylcarbodiimide (**1**) – with PTAD to evaluate if any reaction occurred in the absence of aryl or alkenyl substituents linked to the nitrogen atoms of the heterocumulenic function, i.e. whether either a [2+2] cycloaddition or an ene-process took place between the reagents (Scheme 2).



Scheme 2. Unsuccessful reaction of *N*,*N*′-diisopropylcarbodiimide (**1**) with PTAD.

Unfortunately, all the attempts at reacting PTAD with *N*,*N*′-diisopropylcarbodiimide (**1**) were unsuccessful; when the reactions were performed in either dichloromethane or acetonitrile at room temperature, compound **1** was recovered unaltered. When the reaction of **1** with PTAD was carried out in either acetonitrile or toluene at reflux, only very complex reaction mixtures were obtained, probably as consequence of decomposition of PTAD.

Our second approach involved the reaction of the alkyl arylcarbodiimide **2a** [R^1 = 4-$(CH_3)_2CH$], which was prepared by reacting *N*-(4-isopropylphenyl)triphenyliminophosphorane and phenethyl isocyanate with PTAD (Scheme 3). It was found that, after the addition of two equivalents of the enophile to a solution of **2a** in anhydrous dichloromethane, and stirring at room temperature for 24 h, this carbodiimide was totally consumed. 9-Isopropyl-2-phenyl-5-[(2-phenylethyl)amino]-1*H*-[1,2,4]triazolo[1,2-*a*][1,2,4]benzotriazine-1,3(2*H*)-dione (**4a**) was isolated from the reaction mixture, which was easily identified from its spectroscopic and exact mass data. This product should reasonably result from a sequence of two consecutive processes: a Diels–Alder reaction of PTAD with the 2-azadiene fragment formed by a cumulated N=C bond and the adjacent C=C bond of its *N*-bonded aryl group, followed by a rapid rearomatization of the intermediate cycloadduct **3** through a prototropic equilibrium (formally a 1,5-proton shift; Scheme 3).



Scheme 3. Reactions of *N*-aryl-*N*′-phenethylcarbodiimides **2** with PTAD.

Several other aryl phenethylcarbodiimides **2b**–**d** behaved similarly and yielded the new triazolo-benzotriazines **4b**–**d** in moderate to good yields (Scheme 3, Table 1). As expected, when the aryl nucleus was *ortho*-monosubstituted, as in carbodiimide **2d** (entry 4), only the unsubstituted *ortho*-position was involved in the cycloaddition.

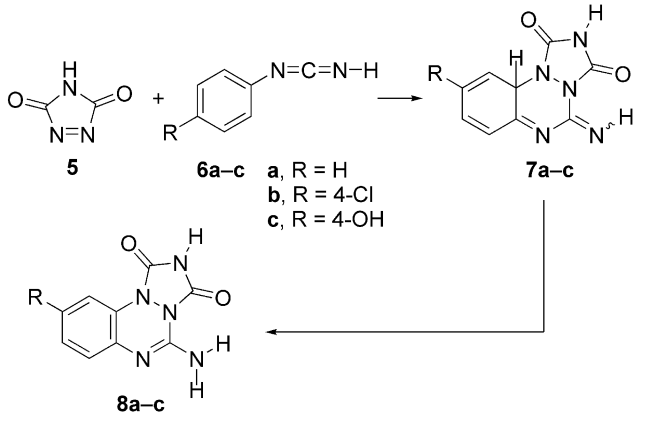
Table 1. 1*H*-[1,2,4]Triazolo[1,2-*a*][1,2,4]benzotriazine-1,3(2*H*)-dione derivatives **4**.

Entry	**2**	R^1	Yield [%] of **4**
1	**2a**	4-$(CH_3)_2CH$	50
2	**2b**	4-CH_3O	58
3	**2c**	4-Br	48
4	**2d**	2-CH_3	48

Having thus demonstrated that both *ortho*-unsubstituted and *ortho*-monosubstituted *N*-arylcarbodiimide fragments were reactive enough to accomplish [4+2] cycloadditions with PTAD under mild conditions, we next tested the use of diarylcarbodiimides to address the question of chemoselectivity in cases where asymmetrical reactants were used.

Previously, we carried out a computational study using DFT methods at the B3LYP/6-31+G** theoretical level with the aim of addressing this question and gaining an insight into the mechanism of the hetero-Diels–Alder reactions of PTAD with *N*-arylcarbodiimides. For this study we selected the structurally simpler 1,2,4-triazoline-3,5-dione

(HTAD; **5**) and the monoarylcarbodiimides **6a**–**c** as reactants (Scheme 4). These carbodiimides were selected to compare the influence of electron-withdrawing and -donating substituents at the aryl nucleus on the energy barriers associated with their hetero-Diels–Alder reactions with HTAD.



Scheme 4. Hetero-Diels–Alder reaction of HTAD with monoarylcarbodiimides used in the computational study.

Figure 1 displays the calculated lowest energy transition-states and cycloadduct structures, optimized at the B3LYP/6-31+G** theoretical level, for the Diels–Alder reactions of HTAD with phenylcarbodiimide (**6a**). Table 2 contains the calculated low frequencies and the relative electronic and free energies calculated at the B3LYP/6-31+G** theoretical level for the stationary points found in the Diels–Alder reaction of HTAD with the arylcarbodiimides **6a**–**c**. Here, we will comment only on the calculated electronic energies, unless otherwise stated.

We explored the potential energy surface of the Diels–Alder reaction of HTAD with phenylcarbodiimide by searching both the *endo* and the *exo* approachs. Two *endo* (**TSa**$_{endo\text{-}anti}$ and **TSa**$_{endo\text{-}syn}$) and two *exo* (**TSa**$_{exo\text{-}anti}$ and **TSa**$_{exo\text{-}syn}$) transition structures were located, which are shown in Figure 1.

The difference between the two *endo* transition structures comes from the position of the lone pair at the unsubstituted nitrogen atom of the heterocumulenic moiety. Thus, whereas in **TSa**$_{endo\text{-}anti}$ this lone pair is positioned *anti* to the adjacent C–N forming bond, in the **TSa**$_{endo\text{-}syn}$ conformation it is located in the *syn* position. Analogously, the difference between **TSa**$_{exo\text{-}anti}$ and **TSa**$_{exo\text{-}syn}$ also depends on the *anti* or *syn* orientation of the lone pair at the same nitrogen atom. In other words, two different orientations, *anti* and *syn*, are conceivable for each *endo* or *exo* mode of approach to the HTAD dienophile; one approach to each stereoface of the diene in the axially-chiral phenylcarbodiimide, as depicted for the *endo* mode in Figure 2.

The relative energies of the four transition structures are shown in Table 2. Their differing values can be rationalized on the basis of the *exo*-lone-pair effect.[17] Accordingly, in the *exo* transition structures, the lone pairs at the two double bonded nitrogen atoms of HTAD induce a massive destabilizing effect by their proximity to the dienic π-system.[18] On the other hand, it is reasonable that the *anti* transition states are stabilized in relation to their *syn* analogous because in the latter cases the nitrogen lone pair at the unsubstituted nitrogen atom of the original carbodiimide function is placed synperiplanar to the adjacent forming C–N bond, thus electronically disturbing its formation.[19] The combination of these two stereoelectronic effects makes

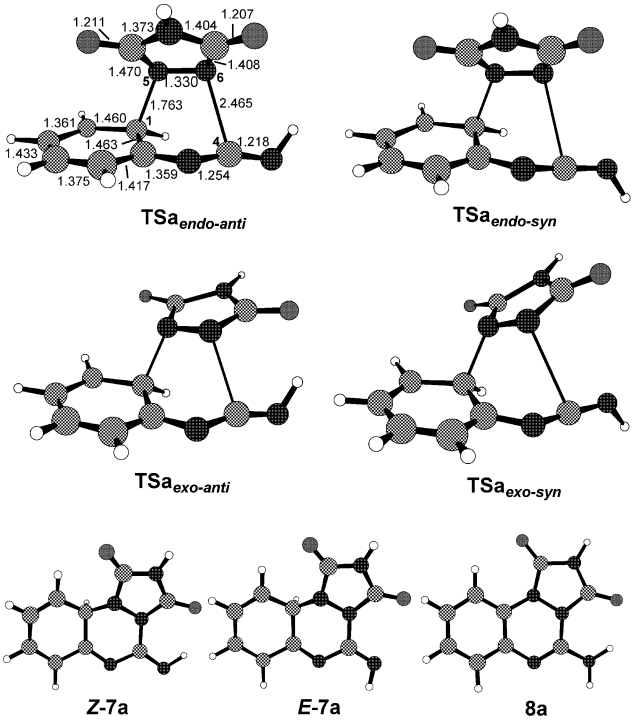


Figure 1. Transition states and cycloadducts, optimized at the B3LYP/6-31+G** theoretical level, located for the Diels–Alder reaction of HTAD with phenylcarbodiimide (**6a**).

Table 2. Relative energies with zero-point vibrational energy corrections, relative free energies, and low frequencies calculated at the B3LYP/6-31+G**//B3LYP/6-31+G** theoretical level for the stationary found in the Diels–Alder reaction of HTAD (**5**) with arylcarbodiimides **6a**–**c**.

Structure	Relative energy [kcal mol^{-1}]	Relative free energy [kcal mol^{-1}]	Low frequencies [cm^{-1}]
5 + **6a**	0.00	0.00	139.5/54.6
TSa$_{endo\text{-}anti}$	21.11	35.12	–372.2
TSa$_{endo\text{-}syn}$	26.86	40.64	–293.6
TSa$_{exo\text{-}anti}$	25.75	39.97	–432.0
TSa$_{exo\text{-}syn}$	33.04	46.33	–339.9
(*Z*)-**7a**	–9.71	4.85	54.7
(*E*)-**7a**	–8.09	6.27	42.7
8a	–52.96	–38.44	46.8
5 + **6b**	0.00	0.00	139.5/45.9
TSb$_{endo\text{-}anti}$	21.94	36.04	–362.5
(*Z*)-**7b**	–9.37	6.24	42.2
8b	–52.48	–37.88	40.7
5 + **6c**	0.00	0.00	139.5/52.9
TSc$_{endo\text{-}anti}$	19.26	33.38	–361.7
(*Z*)-**7c**	–11.01	3.61	46.3
8c	–52.95	–38.35	44.9

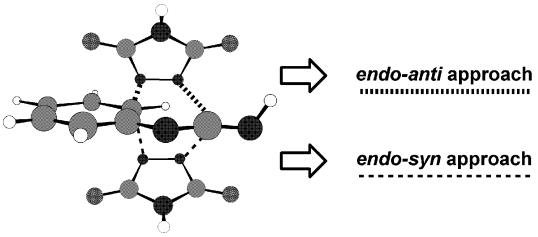


Figure 2. The two possible *endo* approachs, *endo–anti* and *endo–syn*, of HTAD to phenylcarbodiimide.

clear why the transition structure $\mathbf{TSa}_{endo\text{-}anti}$ is the lowest in energy (21.1 kcal/mol up to reactants, or 35.1 kcal/mol after including the entropy correction) of the four located transition states (Table 2). The reaction of HTAD with phenylcarbodiimide through either $\mathbf{TSa}_{endo\text{-}anti}$ or $\mathbf{TSa}_{exo\text{-}anti}$ leads to the cycloadduct (*Z*)-**7a**, whereas transitions structures $\mathbf{TSa}_{endo\text{-}syn}$ and $\mathbf{TSa}_{exo\text{-}syn}$ lead to (*E*)-**7a**. However, because both isomeric structures are finally converted into the cycloadduct **8a** as a result of hydrogen shifts, this aspect of the reaction was not analyzed in this study.

We have analyzed in more detail the transition structure $\mathbf{TSa}_{endo\text{-}anti}$. Concerning its geometry, it is worth pointing out the significant twisting between the HTAD ring and the carbodiimide diene fragment in which the HTAD ring is tilted 55.4° relative to the plane containing the diene fragment.[20] This transition structure is highly asynchronous because the formation of the bond between the aryl carbon atom of the diene fragment and the corresponding nitrogen atom (C1–N5) is notably more advanced than that between the central carbon atom of the carbodiimide and the second nitrogen atom (C4–N6); the measured bond lengths being 1.76 and 2.46 Å, respectively (see numbering in Figure 1). We have also computed the Wiberg bond indexes by using the NBO method, indicating that the C1–N5 bond is partially formed; the calculated bond order value of 0.61 is notably higher than that for the C4–N6 bond (0.11). We have also calculated a synchronicity value of 0.74 for the transformation **5** + **6a**→(*Z*)-**7a** via $\mathbf{TSa}_{endo\text{-}anti}$, confirming that this process takes place asynchronously. The natural population analysis also allowed to us to evaluate the charge-transfer along this conversion. The B3LYP/6-31+G** natural atomic charges at the transition-state $\mathbf{TSa}_{endo\text{-}anti}$ showed that the phenylcarbodiimide is acting as an electron-donor and that the HTAD acts as an electron-acceptor as the charge-transfer fluxes from the diene to the dienophile,[21] the value of the charge transferred being 0.46e.

These data clearly show that the reaction of HTAD with phenylcarbodiimide can be considered to be a polar process that is characterized by nucleophilic attack of the diene fragment on the N=N double bond of HTAD.[22] This is in accord with the fact that the 1,2,4-triazolidin-3,5-diones are among the most reactive dienophiles due to their low LUMO energies.[1]

Because the calculations predict that the preferred channel for the Diels–Alder reaction of HTAD with phenylcarbodiimide is through $\mathbf{TSa}_{endo\text{-}anti}$, for the other transformations studied (**5** + **6b**,**c**→**7b**,**c**), we only considered the approach through the corresponding $\mathbf{TSb,c}_{endo\text{-}anti}$ transition states (Figure 2). All these transformations were calculated to involve exothermic processes, their reaction energies being in the range of –53.0 to –52.5 kcal mol^{-1}, by considering the compounds **8a**–**c** as the final cycloadducts (Table 2).

Substitution of the hydrogen atom at the *para* position of the benzene ring by either a chlorine atom or a hydroxy group caused divergent effects in the magnitude of their respective energy barriers when compared with that involving **6a**. Thus, in the conversion **5** + **6b**→(*Z*)-**7b**, the chlorine atom provokes a slight increase in the value of the energy barrier when compared to the unsubstituted case, **5** + **6a**→(*Z*)-**7a** (21.9 vs. 21.1 kcal mol^{-1}); the energy barrier found when the arylcarbodiimide bears a hydroxy group at the *para* position is 19.3 kcal mol^{-1} (see Table 2 and Figure 3).

From these calculations it is expected that electron-withdrawing groups at the aryl ring of the carbodiimide will retard the Diels–Alder reaction with HTAD, whereas electron-donor substituents will accelerate it. These electronic effects are characteristic of a Diels–Alder reaction with normal electronic demands, whereby the electron-donor substituents at the aryl ring decrease the $HOMO_{diene}$–$LUMO_{HTAD}$ energy gap and facilitate the electron flux from the diene to HTAD. Therefore, similar chemoselective processes can be reasonably expected when using diarylcarbodiimide reactants whose two aryl nuclei are electronically differentiated by appropriate substituents. We confirmed this assumption with the following experiments.

A series of diarylcarbodiimides **9**, prepared by treatment of *N*-aryltriphenyliminophosphoranes with aryl isocyanates, was treated with PTAD in dicloromethane solution at room temperature for 24 hours. These reactions smoothly provided the 1*H*-[1,2,4]triazolo[1,2-*a*][1,2,4]benzotriazine-1,3(2*H*)-diones **10**, in moderate to good yields (Scheme 5, Table 3).

As summarized in Table 3, seven symmetrically substituted (entries 1–3, 8, 9, 12, and 13) and six asymmetrically substituted (entries 4–7, 10, and 11) diarylcarbodiimides were assayed. In the symmetrical cases, the reactions gave a single product when the aryl nuclei were *ortho*- or *para*-monosubstituted, whereas when only one of the *meta*-positions was substituted at each moiety (entry 13) the reaction with PTAD yielded a mixture of the two triazolo-benzotriazines **10**, resulting from the occurrence of two Diels–Alder reactions involving the two different *ortho*-positions of the aryl ring participating in the cycloaddition. It is worth noting the large influence of the electronic effects of the substituents. Thus, with electron-donor groups (alkyl, alkoxy) at the aryl nuclei, the reactions resulted in good yields of **10** (entries 1–3, 12, and 13), whereas an electron-withdrawing group either considerably reduced the yield (Br, entry 8) or even prevented the reaction (NO_2, entry 9). This electronic bias perturbs the otherwise expected normal electronic demand of these $HOMO_{diene}$–$LUMO_{PTAD}$ Diels–Alder reaction.

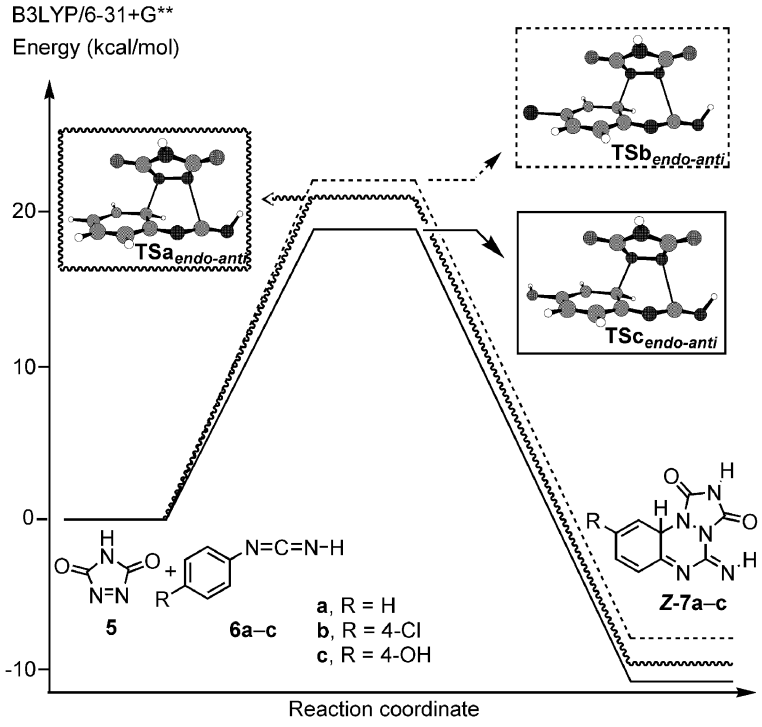
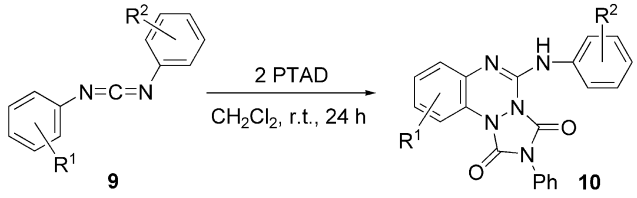


Figure 3. Qualitative reaction profiles of the reactions between HTAD and the arylcarbodiimides **6a**–**c** leading to the cycloadducts **7a**–**c**$_{anti}$ through transition structures **TSa**–**c**$_{endo\text{-}anti}$ calculated at the B3LYP/6-31+G** level.

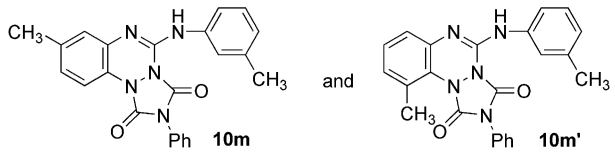


Scheme 5. Reactions of diarylcarbodiimides **9** with PTAD.

Table 3. 1*H*-[1,2,4]Triazolo[1,2-*a*][1,2,4]benzotriazine-1,3(2*H*)-dione derivatives **10**.

Entry	**9**	R^1	R^2	Yield [%] of **10**
1	**9a**	4-CH_3	4-CH_3	93
2	**9b**	4-$(CH_3)_2CH$	4-$(CH_3)_2CH$	53
3	**9c**	4-CH_3O	4-CH_3O	75
4	**9d**	4-CH_3O	4-Br	72
5	**9e**	4-$(CH_3)_2CH$	4-Br	63
6	**9f**	4-$(CH_3)_2CH$	4-Cl	65
7	**9g**	4-CH_3	4-NO_2	67
8	**9h**	4-Br	4-Br	36
9	**9i**	4-NO_2	4-NO_2	0
10	**9j**	4-CH_3O	4-CH_3	80
11	**9k**	4-CH_3O	2,6-$(CH_3)_2$	61
12	**9l**	2-CH_3	2-CH_3	53
13	**9m**	3-CH_3	3-CH_3	51[a]

[a] Inseparable mixture of

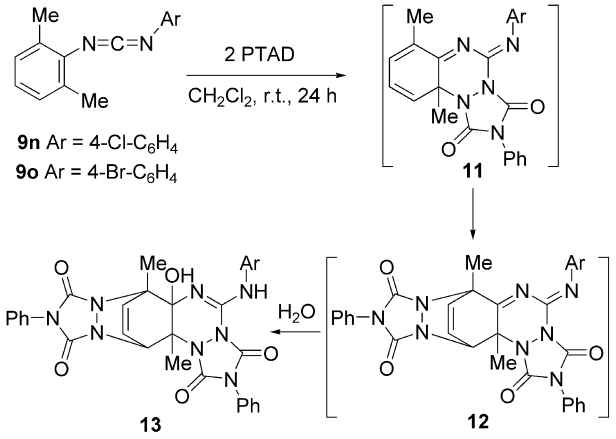


In general, when the reactions involved an aryl fragment that was strongly activated by a methoxy substituent, only one equivalent of PTAD was necessary for the reactions to go to completion (entries 3, 4, 10 and 11), while in the other cases two equivalents of dienophile were required.

As far as the asymmetrically substituted diarylcarbodiimides **9** are concerned, the chemoselectivity was complete, yielding the triazolo-benzotriazine **10** from the exclusive participation of the more activated aryl nucleus (electron-donor vs. electron-withdrawing groups, entries 4–7, and alkoxy vs. alkyl, entries 10 and 11).

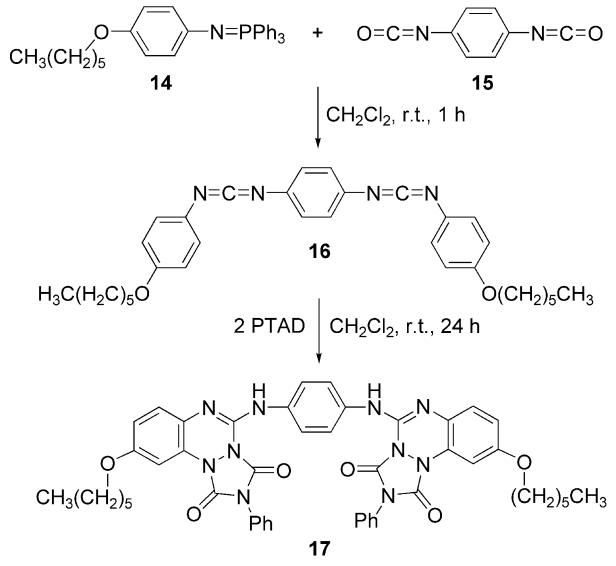
We attempted to force the reversal of such normal electronic bias by placing two methyl substituents at both *ortho* positions of one ring to give an activated, but sterically congested, aryl fragment, and included deactivating 4-halo substituents on the second phenyl ring, as in carbodiimides **9n** and **9o** (Scheme 6). However, the reactions of these two asymmetrically substituted carbodiimides with PTAD still resulted in the exclusive participation of the activated 2,6-dimethylphenyl ring. The analytical data of the products revealed that two units of the dienophilic reactant plus a water molecule were incorporated into the structure of the final adducts. Following a detailed analysis of their spectroscopic data, these adducts were tentatively identified as species **13**, which could be formed as a result of a tandem [4+2]/[4+2] process, leading from **9n** or **9o** to the first and second cycloadducts **11** and **12**, followed by the final addition of water to the 1,4-diazabutadiene fragment of **12**.

This new reaction between carbodiimides and PTAD was also applied to the preparation of a bis(triazolo-benzotriazine). The reaction of iminophosphorane **14** with 1,4-



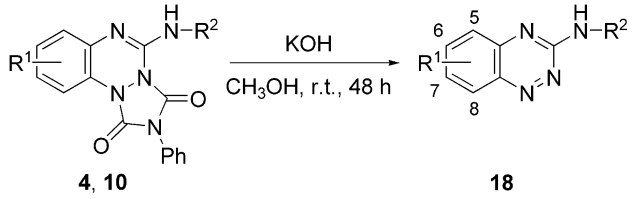
Scheme 6. Reactions of carbodiimides **9n** and **9o** with PTAD.

phenylene diisocyanate **15** yielded bis(carbodiimide) **16**, which was converted into bis(triazolo-benzotriazine) **17**. In the latter compound the two [1,2,4]triazolo[1,2-*a*][1,2,4]-benzotriazine-1,3-dione rings are linked through their respective C4 atoms by a 1,4-diaminophenylene chain (Scheme 7).



Scheme 7. Preparation of bis(triazolo-benzotriazine) **17**.

In the course of our previous work on the reaction of *C*-aryl ketenimines with PTAD,[15] we developed a simple and high-yielding method of removing the O=C–N(Ph)–C=O moiety that was introduced by the PTAD molecule in the [4+2] cycloaddition, and which finally forms part of the fused triazolinedione ring in the resulting cycloadducts. The removal was accomplished by treatment of the cycloadducts with methanolic KOH at room temperature; the reaction occurred with subsequent oxidation in situ of the remaining cyclic system bearing the two adjacent nitrogen atoms (cinnoline in that work). In this way, at the end of the sequence of three consecutive chemical steps, Diels–Alder reaction/removal of the O=C–N(Ph)–C=O fragment/oxidation, the dienophilic PTAD molecule served as a synthetic equivalent of molecular dinitrogen. We attempted a similar degradation of the cycloadducts from the new Diels–Alder reactions and were pleased to find that triazolo-benzotriazines **4** and **10** were cleanly converted into the respective 3-alkyl(aryl)amino-1,2,4-benzotriazines **18** upon treatment with methanolic KOH (Scheme 8, Table 4). A simple work-up allowed the isolation of pure **18**.



Scheme 8. Preparation of 3-alkyl(aryl)amino-1,2,4-benzotriazines **18**.

Table 4. 3-Alkyl(aryl)amino-1,2,4-benzotriazines **18**.

Entry	**18**	R^1	R^2	Yield [%]
1	**18a**	7-CH_3	4-CH_3-C_6H_4	59
2	**18b**	7-$(CH_3)_2CH$	4-$(CH_3)_2CH$-C_6H_4	83
3	**18c**	7-CH_3O	4-CH_3O-C_6H_4	80
4	**18d**	7-CH_3O	4-Br-C_6H_4	80
5	**18e**	7-$(CH_3)_2CH$	4-Br-C_6H_4	97
6	**18f**	7-$(CH_3)_2CH$	4-Cl-C_6H_4	86
7	**18g**	7-CH_3	4-NO_2-C_6H_4	66
8	**18h**	7-Br	4-Br-C_6H_4	66
9	**18i**	7-CH_3O	4-CH_3-C_6H_4	86
10	**18j**	7-CH_3O	2,6-$(CH_3)_2$-C_6H_3	98
11	**18k**	5-CH_3	2-CH_3-C_6H_4	77
12	**18l**	7-$(CH_3)_2CH$	$PhCH_2CH_2$	83
13	**18m**	7-Br	$PhCH_2CH_2$	93
14	**18n**	5-CH_3	$PhCH_2CH_2$	86
15	**18o**	7-CH_3O	$PhCH_2CH_2$	95

Conclusions

The sequential treatment of arylcarbodiimides with PTAD and methanolic KOH emerges from this work as a new and valuable synthetic approach to 3-amino-1,2,4-benzotriazines. The global sequence can be viewed as a [4+2] cycloaddition between the arylcarbodiimide moiety and molecular dinitrogen, this latter, inert reactant being contributed in a "protected" and very reactive form by the dienophilic PTAD molecule.

Experimental Section

General: All melting points are uncorrected. Infrared (IR) spectra were recorded as Nujol emulsions. NMR spectra were recorded in CD_2Cl_2, $CDCl_3$, $C_2D_2Cl_4$, CF_3CO_2D or [D_6]DMSO, at 300 or 400 MHz for ^1H and at 75 or 100 MHz for ^{13}C NMR. The chemical shifts are expressed in ppm relative to Me_4Si (δ = 0.00 ppm) for ^1H NMR, while the chemical shifts for ^{13}C are reported relative to the resonance of CD_2Cl_2 (δ = 54.0 ppm), $CDCl_3$ (δ = 77.1 ppm), $C_2D_2Cl_4$ (δ = 74.2 ppm), CF_3CO_2D (δ = 164.4, 116.5 ppm) or [D_6]-DMSO (δ = 39.5 ppm).

General Procedure for the Preparation of Triazolo-benzotriazine Derivatives 4 and 10: To a solution of the corresponding carbodiimide **2** or **9** (1 mmol) in anhydrous dichloromethane (15 mL), was added solid PTAD (1 or 2 mmol) in several batches. The reaction mixture was stirred at r.t. for 24 h. The precipitated solid was filtered and air-dried for compounds **4a**, **10a**–**d**, and **10f**–**j**. For compounds **4b**–**d**, **10e**, and **10k**–**m**, the solvent was removed under reduced pressure and the resulting material was purified by column chromatography on silica gel.

4a [R^1 = 9-$(CH_3)_2$-CH]: Yield 50% (0.22 g); colorless prisms; m.p. 108–109 °C (diethyl ether). IR (Nujol): $\tilde{\nu}$ = 3340 (m), 1762 (s), 1708 (vs), 1636 (s), 1598 (s), 1502 (vs), 1439 (vs), 1360 (m) cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 1.23 [d, J = 6.8 Hz, 6 H, 9-CH(CH_3)$_2$], 2.88 [sept, J = 6.8 Hz, 1 H, 9-CH(CH_3)$_2$], 2.98 (t, J = 7.2 Hz, 2 H, CH_2CH_2Ph), 3.69–3.74 (m, 2 H, C$H_2$$CH_2$Ph), 6.97 (dd, J = 8.4, 2 Hz, 1 H, 8-H), 7.02 (d, J = 8.4 Hz, 1 H, 7-H), 7.22–7.35 (m, 6 H), 7.46–7.57 (m, 5 H), 7.94 (d, J = 2 Hz, 1 H, 10-H) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): δ = 24.0, 34.2, 35.6, 42.5, 112.9, 124.0, 124.3, 124.8 (s), 126.6, 126.8, 128.9, 129.1, 129.4, 129.7, 130.6 (s), 131.5 (s), 139.2 (s), 142.0 (s), 143.7 (s), 145.2 (s), 145.5 (s) ppm. HRMS (ESI): calcd. for $C_{26}H_{26}N_5O_2$ [M + H]$^+$ 440.2086; found 440.2084.

4b (R^1 = 9-CH_3O): Eluent for column chromatography: dichloromethane; yield 58% (0.25 g); colorless prisms; m.p. 200–201 °C (diethyl ether). IR (Nujol): $\tilde{\nu}$ = 3337 (vs), 1769 (s), 1721 (vs), 1638 (vs), 1548 (s), 1503 (vs), 1416 (vs), 1311 (vs) cm^{-1}. ^1H NMR (300 MHz, [D_6]DMSO, 25 °C): δ = 2.90 (t, J = 7.2 Hz, 2 H, CH_2CH_2Ph), 3.55–3.62 (m, 2 H, C$H_2$$CH_2$Ph), 3.70 (s, 3 H, 9-$OCH_3$), 6.64 (dd, J = 8.7, 2.7 Hz, 1 H, 8-H), 6.95 (d, J = 8.7 Hz, 1 H, 7-H), 7.18–7.23 (m, 1 H), 7.27–7.33 (m, 5 H), 7.47–7.57 (m, 6 H) ppm. ^{13}C NMR (75 MHz, [D_6]DMSO, 25 °C): δ = 34.1, 41.7, 55.4, 100.4, 110.1, 124.0, 125.2 (s), 126.3, 126.6, 127.1, 128.5, 128.7, 128.9, 129.1 (s), 130.4 (s), 139.1 (s), 141.1 (s), 143.9 (s), 145.1 (s), 154.9 (s) ppm. HRMS (ESI): calcd. for $C_{24}H_{22}N_5O_3$ [M + H]$^+$ 428.1717; found 428.1713.

4c (R^1 = 9-Br): Eluent for column chromatography: dichloromethane; yield 48% (0.23 g); colorless prisms; m.p. 178–180 °C (diethyl ether). IR (Nujol): $\tilde{\nu}$ = 3343 (vs), 1772 (s), 1722 (vs), 1634 (vs), 1537 (s), 1494 (vs), 1407 (s), 1303 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.89 (t, J = 7.2 Hz, 2 H, CH_2CH_2Ph), 3.65 (m, 2 H, C$H_2$$CH_2$Ph), 6.88 (d, J = 8.4 Hz, 1 H, 7-H), 7.11 (dd, J = 8.4, 2.4 Hz, 1 H, 8-H), 7.16–7.19 (m, 3 H), 7.24–7.27 (m, 3 H), 7.38–7.45 (m, 5 H), 8.13 (d, J = 2.4 Hz, 1 H, 10-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 35.3, 42.4, 115.7 (s), 117.4, 125.3, 125.4 (s), 126.0, 126.8, 128.8, 129.3, 129.4, 129.5, 129.9 (s), 132.6 (s), 138.4 (s), 142.0 (s), 143.3 (s), 145.0 (s) ppm. HRMS (ESI): calcd. for $C_{23}H_{19}BrN_5O_2$ [M + H]$^+$ 476.0717; found 476.0719.

4d (R^1 = 7-CH_3): Eluent for column chromatography: dichloromethane; yield 48% (0.20 g); colorless prisms; m.p. 150–152 °C (diethyl ether). IR (Nujol): $\tilde{\nu}$ = 3351 (vs), 1767 (vs), 1706 (vs), 1638 (vs), 1596 (s), 1488 (vs), 1412 (vs), 1358 (s) cm^{-1}. ^1H NMR (300 MHz, [D_6]DMSO, 25 °C): δ = 2.27 (s, 3 H, 7-CH_3), 2.91 (t, J = 7.2 Hz, 2 H, CH_2CH_2Ph), 3.55–3.62 (m, 2 H, C$H_2$$CH_2$Ph), 6.81 (t, J = 7.5 Hz, 1 H), 6.91 (d, J = 7.5 Hz, 1 H), 7.17–7.31 (m, 5 H), 7.41–7.54 (m, 6 H), 7.71 (d, J = 8.1 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D_6]DMSO, 25 °C): δ = 17.1, 34.5, 42.1, 111.5, 122.1, 124.6 (s), 126.2, 126.8, 127.0, 128.4, 128.6, 128.8, 129.0, 130.5 (s), 131.1 (s), 131.5 (s), 139.1 (s), 141.7 (s), 143.8 (s), 145.1 (s) ppm. HRMS (ESI): calcd. for $C_{24}H_{22}N_5O_2$ [M + H]$^+$ 412.1768; found 412.1767.

10a (R^1 = 9-CH_3; R^2 = 4-CH_3): Yield 93% (0.37 g); colorless prisms; m.p. 276–277 °C (dichloromethane). IR (Nujol): $\tilde{\nu}$ = 3281 (m), 1764 (vs), 1713 (vs), 1644 (s), 1612 (s), 1561 (s), 1506 (vs), 1309 (s) cm^{-1}. ^1H NMR (300 MHz, [D_6]DMSO, 100 °C): δ = 2.28 (s, 3 H, 9-CH_3), 2.30 (s, 3 H, 5-NH-Ar-CH_3), 6.91 (dd, J = 7.6, 1.6 Hz, 1 H, 8-H), 6.98 (d, J = 7.6 Hz, 1 H, 7-H), 7.17 (d, J = 8.8 Hz, 2 H, 5-NH-ArH), 7.47–7.62 (m, 7 H, 5-NH-ArH + 2-Ph), 7.80 (d, J = 1.6 Hz, 1 H, 10-H), 9.21 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, [D_6]DMSO, 100 °C): δ = 19.6, 20.1, 113.8, 120.1, 123.3, 124.8 (s), 125.6, 126.2, 128.3, 128.4, 128.7, 129.7 (s), 132.4 (s), 133.1 (s), 134.4 (s), 138.7 (s), 143.4 (s), 144.4 (s), 145.2 (s) ppm. HRMS (ESI): calcd. for $C_{23}H_{20}N_5O_2$ [M + H]$^+$ 398.1612; found 398.1595.

10b [R^1 = 9-$(CH_3)_2$CH; R^2 = 4-$(CH_3)_2$CH]: Yield 53% (0.24 g); colorless prisms; m.p. 151–152 °C (dichloromethane). IR (Nujol): $\tilde{\nu}$ = 2960 (vs), 1767 (vs), 1716 (vs), 1643 (vs), 1502 (vs), 1407 (vs), 1304 (s), 1228 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.24 [d, J = 6.8 Hz, 6 H, 9-CH(CH_3)$_2$], 1.26 [d, J = 6.8 Hz, 6 H, 5-NH-Ar-CH(CH_3)$_2$], 2.86–2.95 [m, 2 H, 9-CH(CH_3)$_2$ + 5-NH-Ar-CH(CH_3)$_2$], 6.98 (dd, J = 8.1, 2.1 Hz, 1 H, 8-H), 7.13 (d, J = 8.4 Hz, 1 H, 7-H), 7.23 (d, J = 8.4 Hz, 2 H, 5-NH-ArH), 7.46–7.50 (m, 1 H, 2-Ph), 7.53–7.61 (m, 6 H, 2-Ph + 5-NH-ArH), 8.01 (d, J = 2 Hz, 1 H, 10-H), 9.34 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 23.9, 24.1, 33.7, 34.0, 112.8, 120.8, 124.4, 124.7, 124.9 (s), 126.0, 127.0, 129.3, 129.5, 130.0 (s), 130.2 (s), 134.9 (s), 138.4 (s), 143.3 (s), 145.0 (s), 145.4 (s), 146.1 (s) ppm. HRMS (ESI): calcd. for $C_{27}H_{28}N_5O_2$ [M + H]$^+$ 454.2238; found 454.2228.

10c (R^1 = 9-CH_3O; R^2 = 4-CH_3O): Yield 75% (0.32 g); colorless prisms; m.p. 223–225 °C (dichloromethane). IR (Nujol): $\tilde{\nu}$ = 3351 (vs), 1767 (vs), 1706 (vs), 1638 (vs), 1596 (s), 1488 (vs), 1412 (vs), 1358 (s) cm^{-1}. ^1H NMR (300 MHz, $C_2D_2Cl_4$, 25 °C): δ = 3.71 (s, 3 H), 3.75 (s, 3 H), 6.59 (dd, J = 8.7, 2.7 Hz, 1 H, 8-H), 6.83 (d, J = 9 Hz, 2 H, 5-NH-ArH), 7.02 (d, J = 8.7 Hz, 1 H, 7-H), 7.40–7.52 (m, 7 H, 2-Ph + 5-NH-ArH), 7.63 (d, J = 2.7 Hz, 1 H, 10-H), 9.02 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 25 °C): δ = 56.0, 56.1, 73.3 (s), 101.0, 112.1, 114.5, 122.5, 125.4 (s), 125.8, 126.4, 129.7, 129.9, 130.5 (s), 137.6 (s), 143.4 (s), 145.2 (s), 156.4 (s), 156.7 (s) ppm. HRMS (ESI): calcd. for $C_{23}H_{20}N_5O_4$ [M + H]$^+$ 430.1515; found 430.1505.

10d (R^1 = 9-CH_3O; R^2 = 4-Br): Yield 72% (0.34 g); colorless prisms; m.p. 244–246 °C (dichloromethane). IR (Nujol): $\tilde{\nu}$ = 1766 (vs), 1715 (vs), 1642 (vs), 1601 (vs), 1552 (vs), 1505 (vs), 1411 (vs), 1295 (vs) cm^{-1}. ^1H NMR (400 MHz, [D_6]DMSO, 25 °C): δ = 3.71 (s, 3 H, 9-OCH_3), 6.67 (dd, J = 8.8, 2.4 Hz, 1 H, 8-H), 7.04 (d, J = 8.4 Hz, 1 H, 7-H), 7.49–7.56 (m, 8 H, 10-H, + 5-NH-ArH + 2-Ph), 7.66 (d, J = 8.4 Hz, 2 H, 5-NH-ArH), 9.36 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D_6]DMSO, 25 °C): δ = 55.4, 100.6, 110.2, 115.1 (s), 121.9, 125.0, 125.1 (s), 125.9 (s), 126.9, 129.1, 129.2, 130.2 (s), 131.7, 137.0 (s), 137.7 (s), 143.8 (s), 145.5 (s), 156.1 (s) ppm. HRMS (ESI): calcd. for $C_{22}H_{17}BrN_5O_3$ [M + H]$^+$ 478.0509; found 478.0497.

10e [R^1 = 9-$(CH_3)_2$CH; R^2 = 4-Br]: Eluent for column chromatography: hexanes/diethyl ether (9:1, v/v); yield 63% (0.31 g); colorless prisms; m.p. 178–180 °C (diethyl ether). IR (Nujol): $\tilde{\nu}$ = 1758 (vs), 1713 (vs), 1642 (vs), 1608 (vs), 1555 (vs), 1504 (vs), 1488 (s), 1310 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.22 [d, J = 7.2 Hz, 6 H, 9-CH(CH_3)$_2$], 2.29 [sept, J = 7.2 Hz, 1 H, 9-CH(CH_3)$_2$], 6.95 (d, J = 8.4, 2 Hz, 1 H, 8-H), 6.97 (d, J = 2 Hz, 1 H, 7-H), 7.42–7.57 (m, 9 H, 2-Ph + 5-NH-ArH), 7.97 (d, J = 2 Hz, 1 H, 10-H), 9.40 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 23.8, 33.9, 112.7, 116.5 (s), 121.8, 124.4, 124.7, 124.8 (s), 125.9, 129.2, 129.5, 129.7 (s), 129.8 (s), 131.9, 136.4 (s), 137.8 (s), 143.1 (s), 145.2 (s), 146.5 (s) ppm. HRMS (ESI): calcd. for $C_{24}H_{21}BrN_5O_2$ [M + H]$^+$ 490.0873; found 490.0863.

10f [R^1 = 9-$(CH_3)_2CH$; R^2 = 4-Cl]: Yield 65% (0.29 g); colorless prisms; m.p. 175–176 °C (dichloromethane). IR (Nujol): $\tilde{\nu}$ = 1759 (vs), 1713 (vs), 1641 (vs), 1609 (vs), 1558 (vs), 1504 (vs), 1490 (vs), 1311 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.22 [d, J = 6.9 Hz, 6 H, 9-CH(CH_3)$_2$], 2.85 [sept, J = 6.9 Hz, 1 H, 9-CH(CH_3)$_2$], 6.96 (dd, J = 8.4, 1.8 Hz, 1 H, 8-H), 7.07 (d, J = 8.1 Hz, 1 H, 7-H), 7.24–7.28 (m, 2 H, 5-NH-ArH), 7.42–7.55 (m, 5 H, 2-Ph), 7.58–7.62 (m, 2 H, 5-NH-ArH), 7.96 (d, J = 1.8 Hz, 1 H, 10-H), 9.37 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 23.8, 34.0, 112.8, 121.5, 124.5, 124.7, 124.8 (s), 125.9, 129.0 (s), 129.1, 129.3, 129.5, 129.8 (s), 129.9 (s), 136.0 (s), 137.9 (s), 143.1 (s), 145.2 (s), 146.5 (s) ppm. HRMS (ESI): calcd. for $C_{24}H_{21}ClN_5O_2$ [M + H]$^+$ 446.1378; found 446.1639.

10g (R^1 = 9-CH_3; R^2 = 4-NO_2): Yield 67% (0.28 g); yellow prisms; m.p. 250–252 °C (dichloromethane). IR (Nujol): $\tilde{\nu}$ = 1788 (vs), 1757 (vs), 1716 (vs), 1646 (vs), 1582 (s), 1505 (vs), 1399 (s), 1170 (m) cm^{-1}. ^1H NMR (300 MHz, [D_6]DMSO, 60 °C): δ = 2.28 (s, 3 H, 9-CH_3), 6.95 (d, J = 7.8 Hz, 1 H, 8-H), 7.08 (d, J = 8.1 Hz, 1 H, 7-H), 7.45–7.60 (m, 5 H, 2-Ph), 7.78 (s, 1 H, 10-H), 7.95 (d, J = 9 Hz, 2 H, 5-NH-ArH), 8.21 (d, J = 9 Hz, 2 H, 5-NH-ArH), 9.89 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, [D_6]DMSO, 60 °C): δ = 20.5, 114.4, 119.4, 124.5, 125.3 (s), 126.0, 126.5, 128.7, 128.8, 129.0, 129.9 (s), 134.7 (s), 138.1 (s), 142.2 (s), 143.6 (s), 144.9 (s), 145.3 (s) ppm. HRMS (ESI): calcd. for $C_{22}H_{17}N_6O_4$ [M + H]$^+$ 429.1306; found 429.1301.

10h (R^1 = 9-Br; R^2 = 4-Br): Yield 36% (0.19 g); colorless prisms; m.p. 283–285 °C (dichloromethane). IR (Nujol): $\tilde{\nu}$ = 1769 (vs), 1755 (vs), 1717 (vs), 1634 (s), 1606 (s), 1554 (vs), 1488 (vs), 1301 (m) cm^{-1}. ^1H NMR (400 MHz, $C_2D_2Cl_4$, 25 °C): δ = 6.98 (d, J = 8.4 Hz, 1 H, 7-H), 7.17 (dd, J = 8.4, 2 Hz, 1 H, 8-H), 7.40–7.51 (m, 9 H, 2-Ph + 5-NH-ArH), 8.13 (d, J = 1.6 Hz, 1 H, 10-H), 9.30 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $C_2D_2Cl_4$, 25 °C): δ = 117.4 (s), 117.6 (s), 117.7, 122.5, 125.8 (s), 126.2, 126.5, 129.6 (s), 129.8, 130.0, 131.5 (s), 132.4, 136.2 (s), 138.7 (s), 143.3 (s), 145.3 (s) ppm. HRMS (ESI): calcd. for $C_{21}H_{14}Br_2N_5O_2$ [M + H]$^+$ 525.9509; found 525.9509.

10j (R^1 = 9-CH_3O; R^2 = 4-CH_3): Yield 80% (0.33 g); colorless prisms; m.p. 238–239 °C (dichloromethane). IR (Nujol): $\tilde{\nu}$ = 1763 (vs), 1721 (vs), 1645 (vs), 1613 (vs), 1561 (vs), 1508 (vs), 1413 (vs), 1270 (vs) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.30 (s, 3 H, 5-NH-ArH-CH_3), 3.74 (s, 3 H, 9-OCH_3), 6.61 (dd, J = 8.8, 2.8 Hz, 1 H, 8-H), 7.06 (d, J = 8.4 Hz, 1 H, 7-H), 7.11 (d, J = 8.4 Hz, 2 H, 5-NH-ArH), 7.42–7.55 (m, 7 H, 2-Ph + 5-NH-ArH), 7.70 (d, J = 2.8 Hz, 1 H, 10-H), 9.20 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 20.8, 55.6, 100.4, 111.8, 120.2, 125.2 (s), 125.4 (s), 125.5, 125.8, 129.1, 129.4, 129.5, 129.9 (s), 133.5 (s), 134.7 (s), 137.1 (s), 143.0 (s), 144.9 (s), 156.5 (s) ppm. HRMS (ESI): calcd. for $C_{23}H_{20}N_5O_3$ [M + H]$^+$ 414.1561; found 414.1557.

10k [R^1 = 9-CH_3O; R^2 = 2,6-$(CH_3)_2$]: Eluent for column chromatography: diethyl ether/hexanes (4:1, v/v); yield 61% (0.26 g); colorless prisms; m.p. 214–215 °C (diethyl ether). IR (Nujol): $\tilde{\nu}$ = 3314 (vs), 1766 (vs), 1717 (vs), 1642 (vs), 1529 (vs), 1506 (vs), 1411 (vs), 1306 (vs) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.35 (s, 6 H, 5-NH-Ar-CH_3), 3.77 (s, 3 H, 9-OCH_3), 6.58 (dd, J = 8.8, 2.8 Hz, 1 H, 8-H), 6.92 (d, J = 8.8 Hz, 1 H, 7-H), 7.10–7.18 (m, 3 H, 5-NH-ArH), 7.44–7.48 (m, 1 H, 2-Ph), 7.52–7.60 (m, 4 H, 2-Ph), 7.76 (d, J = 2.8 Hz, 1 H, 10-H), 8.50 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 18.8, 55.7, 100.5, 111.8, 125.3 (s), 125.5, 126.1, 127.4, 128.4, 129.2, 129.5, 130.0 (s), 133.3 (s), 135.9 (s), 138.3 (s), 143.4 (s), 145.2 (s), 156.4 (s) ppm. HRMS (ESI): calcd. for $C_{24}H_{22}N_5O_3$ [M + H]$^+$ 428.1717; found 428.1716.

10l (R^1 = 7-CH_3; R^2 = 2-CH_3): Eluent for column chromatography: diethyl ether/hexanes (4:1, v/v); yield 53% (0.21 g); colorless prisms; m.p. 232–234 °C (diethyl ether). IR (Nujol): $\tilde{\nu}$ = 1787 (vs), 1716 (vs), 1637 (vs), 1596 (vs), 1567 (s), 1413 (vs), 1333 (s), 1268 (s) cm^{-1}. ^1H NMR (300 MHz, [D_6]DMSO, 115 °C): δ = 2.26 (s, 3 H), 2.29 (s, 3 H), 6.89–6.97 (m, 2 H), 7.03 (td, J = 7.5, 0.9 Hz, 1 H), 7.20–7.24 (m, 2 H), 7.42–7.60 (m, 5 H), 7.80 (dd, J = 8.9, 1.5 Hz, 1 H), 8.24 (d, J = 8.1 Hz, 1 H), 9.20 (s, 1 H) ppm. ^{13}C NMR (75 MHz, [D_6]DMSO, 115 °C): δ = 16.1, 16.4, 111.1, 121.0, 122.8, 123.2, 124.9 (s), 125.5, 125.8 (s), 126.1, 126.4, 127.8 (s), 128.1, 128.3, 128.6, 129.5, 131.5 (s), 135.3 (s), 138.5 (s), 145.3 (s) ppm. HRMS (ESI): calcd. for $C_{23}H_{20}N_5O_2$ [M + H]$^+$ 398.1612; found 398.1612.

10m and 10m′ (R^2 = 3-CH_3): Eluent for column chromatography: hexanes/diethyl ether (4:1, v/v); yield 51% (0.20 g). IR (Nujol): $\tilde{\nu}$ = 1763 (vs), 1720 (vs), 1646 (vs), 1617 (vs), 1578 (s), 1493 (vs), 1328 (s), 1287 (s) cm^{-1}. ^1H NMR (400 MHz, [D_6]DMSO, 25 °C): δ = 2.24 (s, 3 H), 2.31 (s, 6 H), 2.32 (s, 3 H), 6.87 (dd, J = 8.4, 1.2 Hz, 1 H), 6.91–6.97 (m, 5 H), 7.13 (t, J = 7.6 Hz, 2 H), 7.25 (t, J = 7.6 Hz, 2 H), 7.46–7.62 (m, 13 H), 7.78 (d, J = 8 Hz, 1 H), 9.27 (s, 1 H), 9.40 (s, 1 H) ppm. ^{13}C NMR (100 MHz, [D_6]DMSO, 25 °C): δ = 19.9, 20.4, 21.1, 133.6, 117.2, 120.5, 120.6, 121.1, 122.8 (s), 122.9 (s), 124.3, 124.4, 124.6, 124.7, 126.9, 127.0, 127.2, 127.4, 128.7, 128.8, 129.0, 129.1, 130.0 (s), 130.6 (s), 132.2 (s), 135.2 (s), 136.2 (s), 137.3 (s), 137.5 (s), 138.2 (s), 138.4 (s), 139.5 (s), 142.3 (s), 143.6 (s), 145.3 (s), 145.8 (s), 150.3 (s) ppm. HRMS (ESI): calcd. for $C_{23}H_{20}N_5O_2$ [M + H]$^+$ 398.1612; found 398.1605.

General Procedure for the Preparation of Compounds 13: To a solution of carbodiimides **9n** or **9o** (2 mmol) in anhydrous dichloromethane (15 mL), solid PTAD (0.73 g, 4.2 mmol) was added in several batches. The reaction mixture was stirred at r.t. for 48 h. The solvent was removed under reduced pressure and the resulting material was purified by column chromatography on silica gel using dichloromethane/diethyl ether (4:1, v/v) as eluent.

13a (Ar = 4-Cl-C_6H_4): Yield 30% (0.37 g); colorless prisms; m.p. 200–202 °C (diethyl ether). IR (Nujol): $\tilde{\nu}$ = 3467 (m), 3302 (m), 1777 (s), 1713 (vs), 1666 (s), 1606 (vs), 1559 (s), 1502 (s), 1405 (vs), 1329 (s) cm^{-1}. ^1H NMR (300 MHz, [D_6]DMSO, 25 °C): δ = 1.54 (s, 3 H), 1.93 (s, 3 H), 5.55 (d, J = 6 Hz, 1 H), 6.43 (d, J = 6 Hz, 1 H), 6.48 (s, 1 H), 6.64 (t, J = 6 Hz, 1 H), 7.26 (d, J = 8.4 Hz, 2 H), 7.28–7.52 (m, 10 H), 7.71 (d, J = 8.4 Hz, 2 H), 8.98 (s, 1 H) ppm. ^{13}C NMR (75 MHz, [D_6]DMSO, 25 °C): δ = 15.5, 19.4, 54.1, 66.5 (s), 66.9 (s), 84.4 (s), 121.8, 126.4, 127.0 (s), 127.1, 127.3, 128.4, 128.7, 129.0, 129.2, 130.1 (s), 131.2 (s), 136.9 (s), 137.2, 137.8 (s), 147.2 (s), 148.7 (s), 151.2 (s), 151.3 (s) ppm. HRMS (ESI): calcd. for $C_{31}H_{26}ClN_8O_5$ [M + H]$^+$ 625.1709; found 625.1707.

13b (Ar = 4-Br-C_6H_4): Yield 30% (0.42 g); colorless prisms; m.p. 177–178 °C (diethyl ether). IR (Nujol): $\tilde{\nu}$ = 3469 (m), 3302 (m), 1777 (s), 1765 (vs), 1714 (vs), 1668 (s), 1605 (vs), 1556 (vs), 1502 (vs), 1405 (vs) cm^{-1}. ^1H NMR (300 MHz, [D_6]DMSO, 25 °C): δ = 1.57 (s, 3 H), 1.95 (s, 3 H), 5.56 (d, J = 6 Hz, 1 H), 6.45 (d, J = 6 Hz, 1 H), 6.51 (s, 1 H), 6.65 (t, J = 6 Hz, 1 H), 7.27 (d, J = 9 Hz, 2 H), 7.33–7.56 (m, 10 H), 7.67 (d, J = 9 Hz, 2 H), 9.00 (s, 1 H) ppm. ^{13}C NMR (75 MHz, [D_6]DMSO, 25 °C): δ = 15.6, 19.6, 54.2, 66.7 (s), 67.1 (s), 84.6 (s), 115.2 (s), 122.3, 126.5, 127.2, 127.5, 128.5, 129.2, 129.4, 130.2 (s), 131.3 (s), 131.7, 137.3, 137.4 (s), 137.8 (s), 147.3 (s), 148.8 (s), 151.2 (s), 151.3 (s) ppm. HRMS (ESI): calcd. for $C_{31}H_{26}BrN_8O_5$ [M + H]$^+$ 699.1204; found 699.1193.

Procedure for the Preparation of Bis(triazolo-benzotriazine) Derivative 17: To a solution of bis(carbodiimide) **16** (1 mmol) in anhydrous dichloromethane (15 mL), solid PTAD (0.38 g, 2.2 mmol) was added. The reaction mixture was stirred at r.t. for 24 h. The solvent was removed under reduced pressure and the resulting ma-

terial was purified by column chromatography on silica gel using diethyl ether/dichloromethane (7:3, v/v) as eluent.

17: Yield 62% (0.53 g); colorless prisms; m.p. 279–280 °C (diethyl ether). IR (Nujol): $\tilde{\nu}$ = 3256 (s), 1770 (vs), 1724 (vs), 1633 (vs), 1592 (vs), 1504 (vs), 1403 (vs), 1300 (vs) cm^{-1}. ^1H NMR (400 MHz, [D_6]DMSO, 120 °C): δ = 0.89 (t, J = 6.8 Hz, 6 H), 1.33–1.34 (m, 8 H), 1.42–1.46 (m, 4 H), 1.69–1.76 (m, 4 H), 3.98 (t, J = 6.4 Hz, 4 H), 6.69 (dd, J = 8.4, 2.4 Hz, 2 H), 7.05 (d, J = 8.8 Hz, 2 H), 7.47–7.61 (m, 12 H), 7.67 (m, 4 H), 9.17 (s, 2 H) ppm. ^{13}C NMR (100 MHz, [D_6]DMSO, 120 °C): δ = 12.8, 21.1, 24.3, 28.0, 30.1, 68.0, 101.2, 111.1, 120.4, 124.2 (s), 125.2 (s), 125.4, 125.8 (s), 126.1, 128.1, 128.3, 132.9 (s), 137.6 (s), 143.4 (s), 145.0 (s), 155.1 (s) ppm. HRMS (ESI): calcd. for $C_{48}H_{49}N_{10}O_6$ [M + H]$^+$ 861.3831; found 861.3834.

General Procedure for the Preparation of 1,2,4-Benzotriazine Derivatives 18: KOH (0.56 g, 10 mmol) was dissolved in methanol (15 mL) and either [1,2,4]triazolo[1,2-*a*][1,2,4]benzotriazine **4** or **10** (1 mmol) was added. The suspension was stirred at r.t. for 48 h. For compounds **18a**–**l** the solvent was removed under reduced pressure, the solid residue was triturated with water, and the precipitate was filtered and dried. For compounds **18m**–**o**, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel, using diethyl ether/hexanes (4:1, v/v) as eluent.

18a (R^1 = 7-CH_3; R^2 = 4-CH_3-C_6H_4): Yield 59% (0.15 g); orange prisms; m.p. 230–232 °C (diethyl ether). IR (Nujol): $\tilde{\nu}$ = 3256 (vs), 1607 (s), 1546 (vs), 1515 (vs), 1324 (s), 1241 (s), 1166 (m), 1098 (s) cm^{-1}. ^1H NMR (300 MHz, [D_6]DMSO, 25 °C): δ = 2.28 (s, 3 H, 3-NH-ArH-CH_3), 2.49 (s, 3 H, 7-CH_3), 7.16 (d, J = 8.1 Hz, 2 H, 3-NH-ArH), 7.62 (d, J = 8.7 Hz, 1 H, 5-H), 7.72 (dd, J = 8.7, 1.5 Hz, 1 H, 6-H), 7.80 (d, J = 8.1 Hz, 2 H, 3-NH-ArH), 8.05 (d, J = 1.5 Hz, 1 H, 8-H), 10.58 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, [D_6]DMSO, 25 °C): δ = 20.5, 20.9, 119.1, 126.2, 127.7, 129.2, 131.4 (s), 135.9 (s), 137.1 (s), 138.5, 139.1 (s), 142.5 (s), 157.5 (s) ppm. HRMS (ESI): calcd. for $C_{15}H_{15}N_4$ [M + H]$^+$ 251.1291; found 251.1282.

18b [R^1 = 7-$(CH_3)_2CH$; R^2 = 4-$(CH_3)_2CH$-C_6H_4]: Yield 83% (0.25 g); orange prisms; m.p. 209 °C (diethyl ether). IR (Nujol): $\tilde{\nu}$ = 3253 (s), 1610 (m), 1558 (vs), 1518 (m), 1464 (vs), 1377 (vs), 1105 (m), 837 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.29 [d, J = 6.8 Hz, 6 H, 7-CH(CH_3)$_2$], 1.38 [d, J = 6.8 Hz, 6 H, 3-NH-ArH-CH(CH_3)$_2$], 2.94 [sept, J = 6.8 Hz, 1 H, 3-NH-ArH-CH(CH_3)$_2$], 3.11 [sept, J = 6.8 Hz, 1 H, 7-CH(CH_3)$_2$], 7.29 (d, J = 8 Hz, 2 H, 3-NH-ArH), 7.68–7.74 (m, 2 H, 5-H + 6-H), 7.81 (d, J = 8 Hz, 2 H, 3-NH-ArH), 8.12 (s, 1 H, 8-H), 8.33 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 23.6, 24.2, 33.7, 33.9, 119.2, 125.5, 126.7, 127.0, 136.2, 136.5 (s), 140.3 (s), 143.5 (s), 143.9 (s), 147.1 (s), 157.5 (s) ppm. HRMS (ESI): calcd. for $C_{19}H_{23}N_4$ [M + H]$^+$ 307.1922; found 307.1902.

18c (R^1 = 7-CH_3O; R^2 = 4-CH_3O-C_6H_4): Yield 80% (0.22 g); red prisms; m.p. 217–219 °C (diethyl ether). IR (Nujol): $\tilde{\nu}$ = 3258 (vs), 1602 (vs), 1556 (vs), 1500 (vs), 1401 (s), 1328 (m), 1307 (m), 1236 (vs) cm^{-1}. ^1H NMR (400 MHz, $C_2D_2Cl_4$, 25 °C): δ = 3.75 (s, 3 H, 3-NH-ArH-OCH_3), 3.89 (s, 3 H, 7-OCH_3), 6.89 (d, J = 8.4 Hz, 2 H, 3-NH-ArH), 7.40–7.46 (m, 2 H, 6-H + 8-H), 7.58–7.64 (m, 3 H, 3-NH-ArH + 5-H), 7.80 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $C_2D_2Cl_4$, 25 °C): δ = 56.0, 56.3, 106.1, 121.2, 128.2, 130.2, 132.2 (s), 138.3 (s), 144.3 (s), 155.8 (s), 157.6 (s), 157.8 (s) ppm. HRMS (ESI): calcd. for $C_{15}H_{15}N_4O_2$ [M + H]$^+$ 283.1190; found 283.1183.

18d (R^1 = 7-CH_3O; R^2 = 4-Br-C_6H_4): Yield 80% (0.26 g); orange prisms; m.p. 246–247 °C (diethyl ether). IR (Nujol): $\tilde{\nu}$ = 3257 (vs), 1608 (vs), 1557 (vs), 1396 (s), 1361 (s), 1289 (m), 1199 (s), 1171 (vs) cm^{-1}. ^1H NMR (400 MHz, [D_6]DMSO, 25 °C): δ = 3.94 (s, 3 H, 7-OCH_3), 7.51 (d, J = 8.8 Hz, 2 H, 3-NH-ArH), 7.60 (dd, J = 9.2, 2.8 Hz, 1 H, 6-H), 7.68–7.72 (m, 2 H, 5-H + 8-H), 7.88 (d, J = 8.8 Hz, 2 H, 3-NH-ArH), 10.73 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D_6]DMSO, 25 °C): δ = 56.0, 106.2, 113.4 (s), 120.5, 127.8, 129.7, 131.5, 136.8 (s), 139.3 (s), 143.6 (s), 157.0 (s), 157.4 (s) ppm. HRMS (ESI): calcd. for $C_{14}H_{12}BrN_4O$ [M + H]$^+$ 331.0819; found 331.0185.

18e [R^1 = 7-$(CH_3)_2CH$; R^2 = 4-Br-C_6H_4]: Yield 97% (0.33 g); orange prisms; m.p. 190–191 °C (diethyl ether). IR (Nujol): $\tilde{\nu}$ = 3256 (vs), 1610 (s), 1553 (vs), 1491 (s), 1426 (m), 1366 (m), 1241 (m), 1103 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 58 °C): δ = 1.38 [d, J = 6.9 Hz, 6 H, 7-CH(CH_3)$_2$], 3.12 [sept, J = 6.9 Hz, 1 H, 7-CH(CH_3)$_2$], 7.50 (d, J = 8.7 Hz, 2 H, 3-NH-ArH), 7.67–7.78 (m, 4 H, 3-NH-ArH + 5-H + 6-H), 8.13 (s, 1 H, 8-H), 8.20 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 58 °C): δ = 23.6, 34.1, 115.7 (s), 120.9, 125.7, 126.9, 132.1, 136.4, 138.2 (s), 140.2 (s), 147.9 (s) ppm. HRMS (ESI): calcd. for $C_{16}H_{16}BrN_4$ [M + H]$^+$ 343.0553; found 343.0546.

18f [R^1 = 7-$(CH_3)_2CH$; R^2 = 4-Cl-C_6H_4]: Yield 86% (0.26 g); orange prisms; m.p. 231–233 °C (diethyl ether). IR (Nujol): $\tilde{\nu}$ = 3257 (vs), 1611 (s), 1555 (vs), 1494 (s), 1427 (m), 1241 (w), 1104 (m), 1092 (m) cm^{-1}. ^1H NMR (300 MHz, [D_6]DMSO, 25 °C): δ = 1.29 [d, J = 6.9 Hz, 6 H, 7-CH(CH_3)$_2$], 3.10 [sept, J = 6.9 Hz, 1 H, 7-CH(CH_3)$_2$], 7.39 (d, J = 8.7 Hz, 2 H, 3-NH-ArH), 7.79 (d, J = 8.4 Hz, 1 H, 5-H or 6-H), 7.87 (d, J = 8.7 Hz, 1 H, 5-H or 6-H), 7.97 (d, J = 8.4 Hz, 2 H, 3-NH-ArH), 8.10 (s, 1 H, 8-H), 10.90 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, [D_6]DMSO, 25 °C): δ = 23.3, 33.1, 120.2, 125.0, 125.7 (s), 126.4, 128.9, 136.3, 138.7 (s), 139.0 (s), 142.7 (s), 146.9 (s), 157.1 (s) ppm. HRMS (ESI): calcd. for $C_{16}H_{16}ClN_4$ [M + H]$^+$ 299.1058; found 299.1054.

18g (R^1 = 7-CH_3; R^2 = 4-NO_2-C_6H_4): Yield 66% (0.18 g); yellow prisms; m.p. 286–287 °C (diethyl ether). IR (Nujol): $\tilde{\nu}$ = 3253 (s), 1616 (s), 1584 (vs), 1562 (vs), 1542 (vs), 1504 (vs), 1334 (vs) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$ + CF_3COOD, 25 °C): δ = 2.47 (s, 3 H, 7-CH_3), 7.73 (d, J = 9.2 Hz, 1 H, 5-H), 7.78–7.81 (m, 3 H, 3-NH-ArH + 8-H), 7.96 (dd, J = 9.2, 2 Hz, 2 H, 6-H), 8.17–8.19 (m, 2 H, 3-NH-ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$ + CF_3COOD, 25 °C): δ = 23.5, 123.1, 127.7, 128.8, 129.3, 143.1 (s), 144.2 (s), 146.5 (s), 147.2, 150.4 (s), 150.5 (s), 153.8 (s) ppm. HRMS (ESI): calcd. for $C_{14}H_{12}N_5O_2$ [M + H]$^+$ 282.0986; found 282.0979.

18h (R^1 = 7-Br; R^2 = 4-Br-C_6H_4): Yield 66% (0.25 g); orange prisms; m.p. 266–267 °C (diethyl ether). IR (Nujol): $\tilde{\nu}$ = 3254 (vs), 1608 (vs), 1556 (vs), 1492 (vs), 1482 (vs), 1417 (m), 1357 (s), 1238 (s) cm^{-1}. ^1H NMR (400 MHz, [D_6]DMSO, 25 °C): δ = 7.53 (d, J = 8.8 Hz, 2 H, 3-NH-ArH), 7.69 (d, J = 8.8 Hz, 1 H, 5-H), 7.90 (d, J = 8.8 Hz, 2 H, 3-NH-ArH), 8.00 (dd, J = 9.2, 2 Hz, 1 H, 6-H), 8.55 (d, J = 2 Hz, 1 H, 8-H), 11.11 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D_6]DMSO, 25 °C): δ = 114.3 (s), 118.2 (s), 120.9, 128.8, 131.2, 131.5, 138.6 (s), 139.1, 139.3 (s), 142.7 (s), 157.1 (s) ppm. HRMS (ESI): calcd. for $C_{13}H_9Br_2N_4$ [M + H]$^+$ 378.9188; found 378.9187.

18i (R^1 = 7-CH_3O; R^2 = 4-CH_3-C_6H_4): Yield 86% (0.23 g); orange prisms; m.p. 206–207 °C (diethyl ether). IR (Nujol): $\tilde{\nu}$ = 3261 (vs), 1608 (vs), 1531 (vs), 1512 (vs), 1496 (vs), 1401 (vs), 1360 (vs), 1328 (s) cm^{-1}. ^1H NMR (400 MHz, [D_6]DMSO, 25 °C): δ = 2.26 (s, 3 H, 3-NH-ArH-CH_3), 3.92 (s, 3 H, 7-OCH_3), 7.13 (d, J = 6 Hz, 2 H, 8-H), 7.55–7.78 (m, 5 H, 3-NH-ArH + 5-H + 6-H), 10.47 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, [D_6]DMSO, 25 °C): δ = 20.5, 55.9, 106.2, 118.7, 127.7, 129.1, 129.4, 130.9 (s), 136.9 (s), 137.3 (s),

143.3 (s), 156.9 (s), 157.4 (s) ppm. HRMS (ESI): calcd. for $C_{15}H_{15}N_4O$ [M + H]$^+$ 267.1245; found 267.1237.

18j [R^1 = 7-CH_3O; R^2 = 2,6-$(CH_3)_2$-C_6H_3]: Yield 98% (0.27 g); yellow prisms; m.p. 165–166 °C (diethyl ether). IR (Nujol): $\tilde{\nu}$ = 3293 (vs), 1622 (s), 1548 (vs), 1516 (vs), 1400 (s), 1359 (vs), 1285 (s), 1202 (vs) cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 2.15 (s, 6 H), 3.91 (s, 3 H), 7.12 (br. s, 3 H), 7.47 (br. s, 2 H), 7.6 (s, 1 H), 9.52 (br., 1 H) ppm. ^{13}C NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 18.3, 55.9, 106.0, 126.4, 127.5, 128.0, 129.5, 135.9 (s), 138.2 (s), 143.3 (s), 156.5 (s), 158.7 (s) ppm. HRMS (ESI): calcd. for $C_{16}H_{17}N_4O$ [M + H]$^+$ 281.1397; found 281.1394.

18k (R^1 = 5-CH_3; R^2 = 2-CH_3-C_6H_4): Yield 77% (0.19 g); orange prisms; m.p. 202–204 °C (diethyl ether). IR (Nujol): $\tilde{\nu}$ = 3130 (vs), 1536 (vs), 1343 (m), 1307 (m), 1254 (m), 1099 (m), 1086 (m), 957 (w) cm^{-1}. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 2.30 (s, 3 H), 2.43 (s, 3 H), 7.08–7.29 (m, 1 H), 7.20–7.29 (m, 2 H), 7.42 (t, J = 9 Hz, 1 H), 7.68–7.75 (m, 2 H), 8.09 (d, J = 8.4 Hz, 1 H), 9.86 (s, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C): δ = 15.5, 18.2, 124.0, 124.8, 125.3, 125.9, 126.9, 130.5, 132.0 (s), 134.4 (s), 135.1, 137.0 (s), 140.1 (s), 142.6 (s), 157.6 (s) ppm. HRMS (ESI): calcd. for $C_{15}H_{15}N_4$ [M + H]$^+$ 251.1291; found 251.1290.

18l [R^1 = 7-$(CH_3)_2CH$; R^2 = C_6H_5-CH_2CH_2]: Yield 83% (0.24 g); yellow prisms; m.p. 120–121 °C (diethyl ether). IR (Nujol): $\tilde{\nu}$ = 3246 (vs), 1572 (vs), 1556 (vs), 1496 (m), 1333 (w), 1236 (m), 1112 (m), 1089 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.34 [d, J = 6.9 Hz, 6 H, 7-CH(C*H*$_3$)$_2$], 3.00–3.11 [m, 3 H, CH_2CH_2Ph + 7-C*H*(CH$_3$)$_2$], 3.82–3.88 (m, 2 H, C*H*$_2$CH$_2$Ph), 5.87 (br. s, 1 H, NH), 7.23–7.35 (m, 5 H, CH_2CH_2*Ph*), 7.56 (d, J = 9.1 Hz, 1 H, 5-H), 7.65 (dd, J = 9.1, 1.8 Hz, 1 H, 6-H), 8.04 (s, 1 H, 8-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 23.5, 33.7, 35.4, 42.5, 125.4, 126.2, 126.5, 128.6, 128.8, 135.8, 138.9 (s), 141.0 (s), 143.2 (s), 146.0 (s), 159.0 (s) ppm. HRMS (ESI): calcd. for $C_{18}H_{21}N_4$ [M + H]$^+$ 293.1761; found 293.1760.

18m (R^1 = 7-Br; R^2 = C_6H_5-CH_2CH_2): Yield 93% (0.30 g); yellow prisms; m.p. 156–157 °C (diethyl ether). IR (Nujol): $\tilde{\nu}$ = 3241 (vs), 1605 (vs), 1589 (vs), 1552 (vs), 1480 (vs), 1313 (m), 1109 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.95 (t, J = 6.9 Hz, 2 H, CH_2CH_2Ph), 3.76–3.78 (m, 2 H, C*H*$_2$CH$_2$Ph), 6.03 (br. s, 1 H, NH), 7.14–7.28 (m, 5 H, CH_2CH_2*Ph*), 7.43 (d, J = 8.9 Hz, 1 H, 5-H), 7.69 (dd, J = 8.9, 2.1 Hz, 1 H, 6-H), 8.33 (d, J = 2.1 Hz, 1 H, 8-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 35.4, 42.5, 117.7 (s), 126.7, 128.2, 128.8, 128.9, 131.9, 138.7 (s), 138.9, 141.1 (s), 143.2 (s), 159.4 (s) ppm. HRMS (ESI): calcd. for $C_{15}H_{14}BrN_4$ [M + H]$^+$ 329.0390; found 329.0390.

18n (R^1 = 5-CH_3; R^2 = C_6H_5-CH_2CH_2): Yield 86% (0.22 g); yellow prisms; m.p. 145–146 °C (diethyl ether). IR (Nujol): $\tilde{\nu}$ = 3240 (vs), 1586 (vs), 1568 (vs), 1533 (s), 1493 (s), 1344 (m), 1170 (m), 1111 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.51 (s, 3 H, 5-CH_3), 2.95 (t, J = 9.3 Hz, 2 H, CH_2CH_2Ph), 3.74–3.79 (m, 2 H, C*H*$_2$CH$_2$Ph), 6.02 (s, 1 H, NH), 7.12–7.16 (m, 1 H), 7.19–7.25 (m, 5 H, CH_2CH_2*Ph*), 7.46 (d, J = 7.2 Hz, 1 H), 7.99 (d, J = 8.4 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 16.1, 35.3, 42.8, 124.6, 126.5, 127.5, 128.7, 128.9, 134.8, 135.0 (s), 139.1 (s), 141.5 (s), 143.0 (s), 159.1 (s) ppm. HRMS (ESI): calcd. for $C_{16}H_{17}N_4$ [M + H]$^+$ 265.1448; found 265.1437.

18o (R^1 = 7-CH_3O; R^2 = C_6H_5-CH_2CH_2): Yield 95% (0.26 g); orange prisms; m.p. 115 °C (diethyl ether). IR (Nujol): $\tilde{\nu}$ = 3233 (vs), 1621 (s), 1576 (vs), 1559 (vs), 1496 (vs), 1237 (m), 1201 (s), 1171 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.94 (t, J = 6.7 Hz, 2 H, CH_2CH_2Ph), 3.73–3.78 (m, 2 H, C*H*$_2$CH$_2$Ph), 3.86 (s, 3 H, 7-OCH_3), 5.77 (br. s, 1 H), 7.14–7.23 (m, 5 H, CH_2CH_2*Ph*), 7.33 (dd, J = 9.1, 2.1 Hz, 1 H, 6-H), 7.41 (d, J = 1.7 Hz, 1 H, 8-H), 7.46 (d, J = 9.1 Hz, 1 H, 5-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 35.6, 42.6, 55.8, 105.9, 114.3 (s), 120.9 (s), 126.5, 127.6, 128.7, 128.9, 129.6, 139.1 (s), 156.9 (s), 159.6 (s) ppm. HRMS (ESI): calcd. for $C_{16}H_{17}N_4O$ [M + H]$^+$ 281.1397; found 281.1394.

Computational Methods: All structures were optimized by using the functional B3LYP[23] and the 6-31+G** basis set as implemented in the Gaussian03 suite of programs.[24] Density Functional Theory has been shown to reliably predict the results of [4+2] cycloadditions and other pericyclic reactions.[25] All energy minima and transition structures were characterized by frequency analysis. The energies reported in this work include the zero-point vibrational energy corrections (ZPVE) and are not scaled. Wiberg bond orders[26] and natural atomic charges were calculated within the natural bond orbital (NBO) analysis.[27] The synchronicity was determined by using a previously described approach.[28]

Supporting Information (see footnote on the first page of this article): Cartesian coordinates, electronic and free energies, and low frequencies of each stationary point optimized at the B3LYP/6-31+G** theoretical level.

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