Chemical Reactions of the Stable Carbene 1,3,4-Triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene

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The title compound 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene (**1**), a stable carbene, is chemically characterized via its reactivity towards a multitude of organic substrates. Its behaviour in insertion, addition and cycloaddition reactions allows its classification as a typical representative of nucleophilic carbenes.

Introduction

Carbenes belong to the most important reactive species in organic synthesis. A multitude of useful and well-established organic reactions proceed via the intermediate formation of carbenes or carbenoids. However, for more than a century chemists have been unsuccessful in their quest to isolate representatives of these species[1]. The first attempts date back to the early works of Dumas and Regnault[2], who tried to dehydrate methanol by means of conc. sulphuric acid or phosphoric pentoxide. Many attempts followed, until finally it was generally accepted that carbenes are notoriously evasive due to their pronounced reactivity.

Recently, a few groups have reported the preparation of carbenes that are stable in the absence of humidity and oxygen[3,4,5]. Among these, the reactivity of Arduengo-type carbenes, which are closely related to Wanzlick carbenes, has been intensively investigated during the last three years[6]. However, the reactivity of Wanzlick carbenes with regard to classical organic substrates, allowing an empirical classification of their character, has never been thoroughly and comprehensively investigated.

We recently described the preparation of a new heterocyclic carbene **1**, 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazol-5-ylidene, which is stable up to 150 °C in the absence of oxygen[7]. Ab initio calculations on the parent heterocyclic system suggest that the π-donation from the adjacent nitrogen atoms leads to a significant transfer of electron density into the formally vacant *p*-orbital at the carbenic carbon atom[8]. This should result in a strong decrease in electrophilicity of the carbenic centre. In contrast, the nucleophilic character of the carbene should be strongly enhanced because of the accumulation of electron density at the carbene carbon atom. The reactivity pattern proposed by the aforementioned theoretical considerations is shown by so-called nucleophilic carbenes (e.g. Wanzlick carbenes)[9].

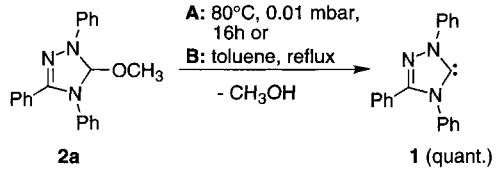
We now wish to report on a comprehensive study of the reactivity of the triazolylidene **1** regarding classical carbene reactions towards a variety of organic substrates, thus providing a detailed impression of its chemical nature.

Results and Discussion

Preparation of the Carbene

Triazolylidene **1** is readily available by thermal decomposition of the methoxytriazoline **2a** (**A**, Scheme 1), which can be easily prepared in large amounts from cheap starting materials[10]. For some applications it proved to be more efficient and comfortable to generate the carbene **1** in situ by refluxing methoxytriazoline **2a** in toluene in the presence of the respective substrate (**B**, Scheme 1). Generally, pathway **B** is recommended for all transformations requiring elevated temperatures.

Scheme 1. Preparation of carbene **1** via α-elimination



2a **1** (quant.)

Insertion Reactions

The carbene **1** readily reacts with alcohols, amines and thiols via insertion into the O–H, N–H or S–H bond, respectively (Scheme 2). The reaction proceeds at ambient temperature within 10 min, affording the analytically pure alkoxytriazolines **2**, aminotriazolines **3** and alkylthiotriazoline **4**[11] in very good yields. The mechanism probably in-

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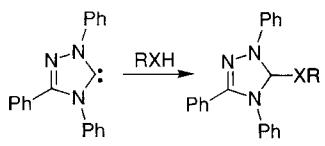
volves protonation of the carbene with subsequent nucleophilic attack of the respective anion (i.e. alkoxide, sulphide or amide), which then leads to the formation of the corresponding orthoformic amide derivatives. However, mechanisms involving ylide formation or direct concerted insertion are also conceivable[12].

Scheme 2. Insertion of carbene **1** into the X–H bond



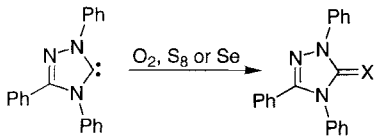
2a RX = OMe (99%)
2b RX = OEt (98%)
2c RX = O-*n*Pr (98%)
2d RX = (4-pyridyl)methyloxy (95%)
3a RXH = morpholine (98%)
3b RXH = pyrrolidine (96%)
3c RXH = benzylamine (97%)
4 RX = S-*n*Pr (98%)

Attempts to isolate insertion products of carbene **1** into a C–H bond have so far proved to be unsuccessful. Insertion into activated C–H bonds as in nitromethane or ketones possibly requires temperatures exceeding the stability of the carbene (>150 °C)[13].

Addition Reactions

Carbene **1** readily reacts with chalcogens such as oxygen, sulphur and selenium to afford the corresponding triazolinone **5**, triazolinthione **6** and triazolinselenone **7** with good yields (Scheme 3). This kind of reactivity was earlier described for nucleophilic carbenes[9,13,14]. The resulting products show spectroscopic properties typical of cyclic ureas, as can be readily seen from the chemical shifts of the carbonyl-analogous carbon atoms in the ^{13}C-NMR spectra [δ(C=O) = 151.9, δ(C=S) = 168.5, δ(C=Se) = 164.2].

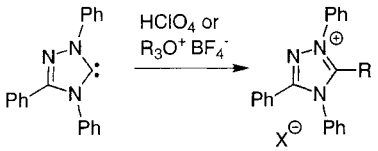
Scheme 3. Chalcogenation of carbene **1**



5 X = O (54%)
6 X = S (98%)
7 X = Se (88%)

Since **1** behaves like a fairly strong base[15], it can be easily protonated by treatment with perchloric acid to afford the corresponding triazolium salt **8** (Scheme 4). As was previously reported by us[8], the calculated proton affinity of the parent heterocyclic system of **1** is very high (1027 kJ/mol, MP2 + ZPE/6-31G**//RHF/6-31G**). Accordingly, the protonation proceeds very quickly and smoothly. Similarly, **1** can be alkylated using standard alkylating reagents such as trialkyloxonium salts, yielding the 5-alkyltriazolium salts **9a,b** in very good yields (Scheme 4). These reactions amply exemplify the strong nucleophilic character of carbene **1**.

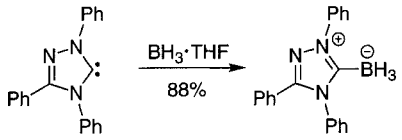
Scheme 4. Protonation and alkylation of carbene **1**



8 R = H, X = ClO_4 (96%)
9a R = Me, X = BF_4 (93%)
9b R = Et, X = BF_4 (95%)

Another type of reactivity closely related to nucleophilicity is the Lewis basicity. Due to its lone electron pair, carbene **1** is also well-suited to functioning as a Lewis base. Accordingly, it readily adds to typical Lewis acids such as $BH_3 \cdot THF$, yielding the corresponding triazoline–borane **10** (Scheme 5). In the ^{13}C-NMR spectrum a chemical shift of δ = 177.5 was found for the carbenic carbon atom. The boron atom gives rise to a signal at δ = −35.4 in the ^{11}B-NMR spectrum ($^1J_{BH}$ = 88 Hz), which is typical of tetrahedrally coordinated boron[16]. Similar data were found by Kuhn et al. for BH_3 adducts with Arduengo-type carbenes[17].

Scheme 5. Lewis base-type addition of carbene **1** to $BH_3 \cdot THF$



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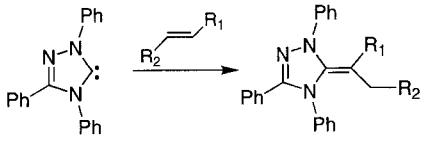
[2 + 1] Cycloaddition Reactions

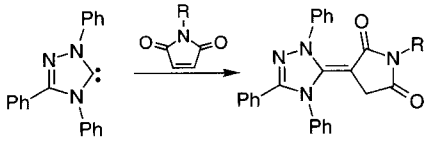
Triazolylidene **1** readily reacts with a number of electron-deficient alkenes, leading to formation of the 5-methylene-triazolines **11**. The reaction was carried out with methyl fumarate and maleate to give compound **11a**, with fumaric dinitrile to yield **11b**, with nitrostyrene to give **11c**[18] (Scheme 6) and with *N*-substituted maleic imides to afford compounds **11d–f** and **11g**, **h**, respectively (Scheme 7).

Scheme 6. Addition of carbene **1** to activated double bonds (I)



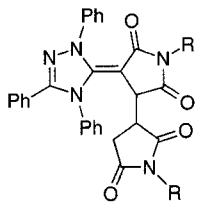
11a R_1, R_2 = CO_2Me (68%)
11b R_1, R_2 = CN (56%)
11c R_1 = Ph, R_2 = NO_2 (25%)

Scheme 7. Addition of carbene **1** to activated double bonds (II)



11d R = Me (80%)
11e R = *n*Bu (84%)
11f R = Ph (47%)

and / or

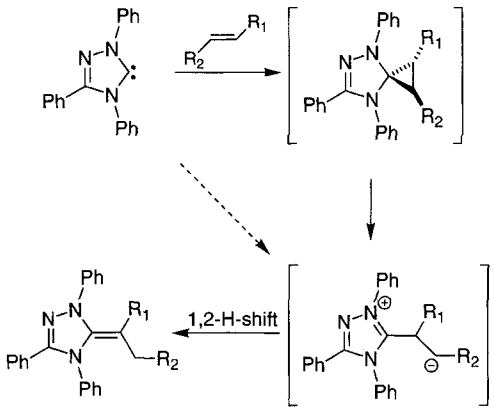


11g R = Me (54%)
11h R = Ph (56%)

The following mechanistic proposal rationalizes the formation of these compounds (Scheme 8). First, the respective cyclopropane system is formed via a [2 + 1] cycloaddition, then it subsequently rearranges to the open-chain products **11** due to the considerable ring strain inherent to the spirocyclic system. The barrier to the ring opening in-

volved should be very low because of the push-pull substitution pattern of the three-membered ring. The intermediately formed dipole then undergoes a 1,2-proton shift, providing further stabilization of the system via formation of the corresponding methylenetriazolines. A simple AM1 calculation[19] yielded a considerable negative reaction enthalpy of $\Delta H = -76$ kJ/mol for the rearrangement of the bismethoxycarbonyl-substituted cyclopropane system to methylenetriazoline **11a**[7,20,21].

Scheme 8. Proposed mechanism for the formation of the methylenetriazolines **11**

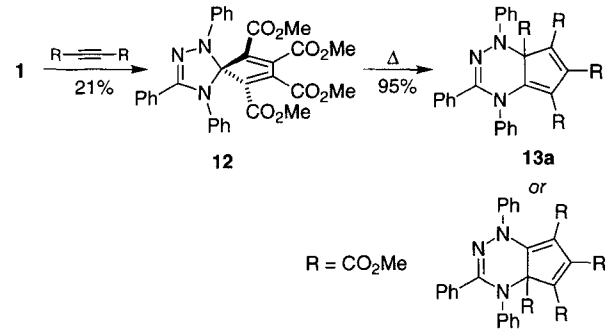


However, a slightly different mechanism is also conceivable. The reaction could also proceed via the attack of carbene **1** at the double bond in a Michael-type manner, directly leading to the dipole, which then spontaneously rearranges to the methylenetriazolines **11** without previous formation of the cyclopropane system[22,23]. Interestingly, depending on the reaction conditions, the formation of the adducts **11g**, **h** (1:2) was sometimes observed on the addition of carbene **1** to *N*-phenyl and *N*-methyl maleic imide (use of any excess of the imide led to the preferential formation of the bis-adducts) (Scheme 7). These somewhat unexpected products are obviously formed via nucleophilic attack of the intermediate dipole at a second maleic imide molecule, affording a new dipole which is then stabilized by 1,4-proton migration. This side reaction can be taken as strong evidence for the intermediate formation of the dipole in the course of the reaction, and supports the mechanistic suggestions.

A feature common to all methylenetriazolines described here is the low rotational barrier of the C=C double bond, which leads to virtually free rotation around this bond at ambient temperature[24]. Thus a single set of signals is found in both the ^{1}H- and ^{13}C-NMR spectra. As expected, significant broadening of the signals was observed on cooling the samples. The extremely low rotational barrier can be explained by the push-pull substitution pattern of the double bond, allowing a highly efficient charge stabilization in the transition state of the rotation (dihedral angle 90°), which leads to a strongly facilitated heterolytic opening of the double bond in the course of this process[25].

The reaction of triazol-ylidene **1** with methyl acetylenedicarboxylate leads to the spirocyclic compound **12**, formed via addition of the carbene to the triple bond with subsequent 1,3-dipolar cycloaddition of the intermediate dipole to a second molecule of methyl acetylenedicarboxylate (Scheme 9).

Scheme 9. Addition of carbene **1** to activated triple bonds



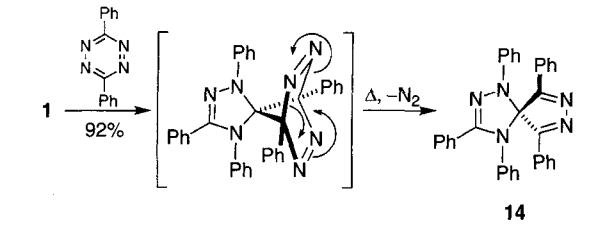
The spiro system **12** proved to be thermally unstable, readily rearranging upon heating to give the annulated bicyclic compound **13** via a 1,5-*N* shift (Scheme 9). However, the direction of the shift could not be determined, because all attempts to obtain crystals suitable for X-ray structure determination were unsuccessful. Distinction between the bicyclic systems **13a** and **13b** by NMR methods proved impossible. Nevertheless, other theoretically conceivable structures could be excluded for symmetry reasons[20].

Attempts to react triazol-ylidene **1** with nonactivated alkenes, e.g. cyclohexene, were unsuccessful. As was suggested by our theoretical investigations[7,8], **1** is virtually void of any electrophilic properties, which accounts for its lack of reactivity towards nonactivated olefines[26].

[4 + 1] Cycloaddition Reactions

Since the isolation of [2 + 1] cycloadducts turned out to be unsuccessful, an attempt was undertaken to effect an electronically inverse [4 + 1] cycloaddition with an electron-deficient diene-type system, e.g. 3,6-diphenyl-1,2,4,5-tetrazine. Möhrle et al. reacted a Wanzlick olefin with the aforementioned tetrazine and obtained a spirocyclic system after formation of the 1,4-adduct and subsequent extrusion of nitrogen[27]. The same reaction pattern was observed upon reaction of carbene **1** with the tetrazine, affording the spirocyclic compound **14** in excellent yield (Scheme 10).

Scheme 10. Proposed mechanism for the [4 + 1] cycloaddition of carbene **1** to 3,6-diphenyl-1,2,4,5-tetrazine

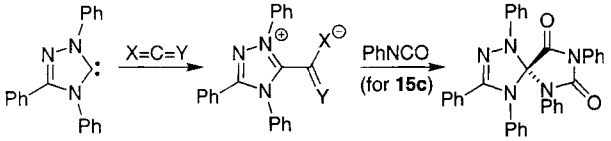


Reactions with Heterocumulenes

Heterocumulenes are known to react with nucleophilic carbenes, e.g. Wanzlick carbenes, to give dipolar adducts or spirocyclic compounds[28]. Accordingly, carbene **1** readily reacts with heterocumulenes such as carbondisulphide,

phenyl isothiocyanate and phenyl isocyanate to afford the betaines **15a–c** (Scheme 11). In the case of phenyl isocyanate the reaction does not stop at the dipole stage. Instead, the betaine engages in a [3 + 2] dipolar cycloaddition, reacting further with residual phenyl isocyanate to give the corresponding spirocyclic hydantoin **16** (Scheme 11).

Scheme 11. Addition of carbene **1** to heterocumulenes



15a X,Y = S (90%)
15b X = S, Y = NPh (71%)
(**15c** X = O, Y = NPh)

16 (92%)

Isolation of the betaine **15c** proved impossible, even at low temperatures using an excess of carbene **1**. Thus the second step, i.e. the dipolar cycloaddition, is probably much faster than the primary attack of the carbene at the first phenyl isocyanate molecule. The difference between the reactivities of the dipoles **15b** and **15c** is due to the higher activity of phenyl isocyanate as dipolarophile because of the stronger activation of the C=N bond by the electronegative oxygen. Furthermore, the charge stabilization in the anionic part of the sulphur-containing dipoles should be more efficient due to the higher polarizability of sulphur and should therefore decrease the reactivity of the corresponding dipoles. However, upon extensive refluxing of the carbene with phenyl isothiocyanate in toluene, some spirocyclic [3 + 2] cycloaddition product was found. The dipole **15a** is characterized by the strong low-field shift of the carbodithioate carbon in the ^{13}C-NMR spectrum [$\delta(CS_2^-)$ = 220.5], in compliance with expectations[29]. The ^{13}C-NMR spectrum of compound **15b** also shows a low-field-shifted signal for the corresponding carbon atom {δ[C(NPh)S$^-$] = 164.9}. The spirocyclic compound **16** shows spectroscopic data typical of a hydantoin [δ(C=O) = 165.1, 152.0; ν(C=O) = 1794, 1739 cm^{-1}].

Conclusion

The study carried out proves that the reactivity of the title compound **1** towards a multitude of organic substrates is closely related to that observed for the most prominent nucleophilic carbenes, i.e. the Wanzlick carbenes. Its carbenic character manifests itself in its insertion and cycloaddition reactions. However, the stabilization of the carbene takes its toll in that it does not insert into C–H bonds. As was expected from ab initio calculations, the carbene is virtually void of electrophilic properties, which is reflected by the absence of any reactivity towards nonactivated olefines. The strong nucleophilic character is shown by its reactivity towards typical electrophilic reagents, i.e. protic acids, alkylating reagents and Lewis acids. In summary, the reactivity study allows an unequivocal classification of carbene **1** as a typical nucleophilic carbene.

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Experimental

All reactions were carried out using standard Schlenk techniques under argon atmosphere. Solvents were dried and purified by conventional methods prior to use. THF (with potassium), toluene (with sodium) and dichloromethane (with CaH_2) were distilled under argon. All reagents were distilled and stored under argon. – Column chromatography: Merck silica gel 60, 0.040–0.063 mm (230–400 mesh). – Preparative HPLC: Gilson with a Merck, Packed column RT, 25 × 250 mm, LiChrosorb, Si60 (7 µm), Ethyl acetate/ether (1:5), UV detector. – IR spectra: Perkin Elmer FT/IR 1750. – ^{1}H and ^{13}C-NMR spectra: Varian VXR 300, Varian Gemini 300, Varian Unity 500. – Mass spectra: Varian MAT 212 (EI), Finnigan MAT 95 (FAB, HRMS). – Microanalyses: Heraeus CHN-O-Rapid.

General Procedure 1 (GP 1): The alcohol or amine (5 mmol) was added to 0.297 g (1 mmol) **1** at ambient temperature under argon. The resultant solution was stirred for 1 h, then the excess alcohol or amine was removed in vacuo.

General Procedure 2 (GP 2): Compound **2a** (0.329 g, 1 mmol) and 1.1 mmol of the chalcogen were dissolved or suspended in 20 ml toluene and heated to reflux for 3 h under argon. A precipitate was formed upon cooling. Pentane (10 ml) was added to complete the crystallization. The crystals were collected by filtration, washed with some diethyl ether and dried in vacuo.

General Procedure 3 (GP 3): Trialkyloxonium tetrafluoroborate (1 mmol) was slowly added at ambient temperature under argon to a cooled solution of 0.297 g (1 mmol) **1** in 10 ml CH_2Cl_2. The solution was stirred for 1 h, then 1 ml ethanol was added and the solvent was evaporated. The residue was digested with diethyl ether, the formed crystals collected by filtration, thoroughly washed with ether and finally dried in vacuo.

General Procedure 4 (GP 4): The Michael acceptor (1 mmol) in 5 ml THF was added dropwise to a solution of 1 mmol **1** in 15 ml THF at ambient temperature under argon. The reaction mixture was stirred for 2 h, then the solvent was evaporated and the residue was purified by column chromatography.

General Procedure 5 (GP 5): The Michael acceptor (1 mmol) was added to a solution of 1 mmol **2a** in 20 ml toluene at ambient temperature under argon. The mixture was heated to reflux for 3 h, then it was allowed to cool to ambient temperature. Pentane (20 ml) was added to complete crystallization, the crystals were filtered off, washed with pentane and dried in vacuo.

1,3,4-Triphenyl-4,5-dihydro-1H-1,2,4-triazol-5-ylidene (**1**): Compound **1** was prepared according to a literature procedure. The analytical data were in compliance with those previously published[7].

5-Methoxy-1,3,4-triphenyl-4,5-dihydro-1H-1,2,4-triazol (**2a**): Compound **2a** was prepared according to a literature procedure. The analytical data were in compliance with those previously published[7].

5-Ethoxy-1,3,4-triphenyl-4,5-dihydro-1H-1,2,4-triazol (**2b**): Ethanol (0.230 g, 5 mmol) and 0.297 g (1 mmol) **1** were reacted according to GP 1, yielding 0.336 g **2b** (98%) as almost colourless crystals. – M.p. 82 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 3050 (w, CH), 2980 (m, CH), 2925 (m, CH), 2880 (m, CH), 1595 (s, C=C), 1560 (m), 1492 (s, C=C), 1460 (m, CH_2), 1450 (m), 1415 (m), 1380 (m), 1360 (s), 1260

(s), 1175 (m), 1120 (w), 1070 (m), 1040 (s), 915 (m), 880 (w), 765 (s), 745 (s), 695 (s) cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.21 (t, *J* = 7.0 Hz, 3H, OCHHC*H*$_3$), 3.35 (dq, *J* = 7 Hz, *J* = 7 Hz, 1H, OC*H*HCH$_3$), 3.57 (dq, *J* = 7 Hz, *J* = 7 Hz, 1H, OCH*H*CH$_3$), 6.72 [s, 1H, NC(H)N], 6.84–7.60 (m, 15H, arom. H). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 14.99 (CH_3), 55.42 (OCH_2), 100.57 [NC(H)N], 112.82, 120.01, 122.78, 124.98, 127.44, 128.45, 128.91, 129.08, 129.28 (arom. C), 127.85, 140.12, 142.17 (*ipso*-C), 145.42 (C=N). – MS (70 eV); *m/z* (%): 329 (1) [M^+], 313 (8) [$C_{20}H_{15}N_3O$], 296 (19) [$C_{20}H_{14}N_3$], 194 (100) [PhNCNPh], 180 (7) [$C_{13}H_{10}N$], 166 (5) [$C_{13}H_{10}$], 91 (68) [C_6H_5N], 77 (86) [C_6H_5], 64 (19) [C_5H_4], 51 (43) [C_4H_3]. – $C_{22}H_{21}N_3O$ (357.5): calcd. C 76.88, H 6.16, N 12.24; found C 76.45, H 6.18, N 12.33.

1,3,4-Triphenyl-5-propoxy-4,5-dihydro-1H-1,2,4-triazol (**2c**): *n*-Propanol (0.300 g, 5 mmol) and 0.297 g (1 mmol) **1** were reacted according to GP 1, yielding 0.340 g **2c** (98%) as almost colourless crystals. – M.p. 85°C (dec.). – IR (KBr): ṽ = 3040 (w, CH), 2980 (m, CH), 2930 (m, CH), 2860 (m, CH), 1600 (s, C=C), 1560 (m), 1490 (s, C=C), 1460 (m, CH_2), 1450 (m), 1410 (m), 1390 (s), 1370 (s), 1300 (w), 1260 (s), 1170 (m), 1120 (w), 1070 (m), 1040 (s), 1010 (s), 930 (m), 880 (w), 770 (s), 750 (s), 690 (s), 550 (w) cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.82 (t, *J* = 7.4 Hz, 3H, CH_2CH_3), 1.53 (ddq, *J* = 7 Hz, 2H, CH_2CH_3), 3.17 (dt, *J* = 9.1 Hz, *J* = 6.8 Hz, 1H, OC*H*HCH$_2$), 3.38 (dt, *J* = 9.1 Hz, *J* = 6.6 Hz, 1H, OCH*H*CH$_2$), 6.64 [s, 1H, NC(H)N], 6.78–7.54 (m, 15H, arom. H). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 11.15 (CH_3), 22.83 (CH_2), 61.66 (OCH_2), 100.81 [NC(H)N], 113.00, 120.15, 122.86, 125.08, 127.61, 128.62, 129.05, 129.22, 129.43 (arom. C), 128.05, 140.35, 142.34 (*ipso*-C), 145.59 (C=N). – MS (70 eV); *m/z* (%): 313 (18) [$C_{20}H_{15}N_3O$], 296 (27) [$C_{20}H_{14}N_3$], 194 (58) [PhNCNPh], 180 (7) [$C_{13}H_{10}N$], 166 (4) [$C_{13}H_{10}$], 151 (2) [$C_{12}H_7$], 91 (44) [C_6H_5N], 77 (47) [C_6H_5], 64 (12) [C_5H_4], 51 (26) [C_4H_3], 44 (100) [C_2H_4O]. – $C_{23}H_{23}N_3O$ (357.5): calcd. C 77.28, H 6.49, N 11.76; found C 77.53, H 6.52, N 11.91.

1,3,4-Triphenyl-5-(4-pyridylmethoxy)-4,5-dihydro-1H-1,2,4-triazol (**2d**): 4-Pyridylmethanol (0.109 g, 1 mmol) dissolved in 10 ml THF and 0.297 g (1 mmol) **1** in 10 ml THF were reacted according to GP 1, yielding 0.386 g **2d** (95%) as an orange viscous oil. – IR (KBr): ṽ = 3040 (m), 3025 (m), 2930 (s, CH), 2850 (s, CH), 1650 (m), 1600 (s, C=C), 1560 (s), 1490 (s, C=C), 1460 (w, CH_2), 1450 (m), 1410 (s), 1360 (m), 1290 (m), 1260 (s), 1150 (m, COC), 1040 (s), 910 (m), 800 (m), 750 (s), 695 (s), 500 (w) cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 4.32 (d, *J* = 13.1 Hz, 1H, OC*H*HPyr), 4.44 (d, *J* = 12.8 Hz, 1H, OCH*H*Pyr), 6.81 [s, 1H, NC(H)N], 6.98–7.50 (m, 17H, arom. H), 8.40 (d, *J* = 5.7 Hz, 2H, HC=N_{pyr}). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS):δ = 60.86 (CH_2), 101.23 [NC(H)N], 113.08, 120.74, 122.29, 123.09, 125.60, 127.61, 128.70, 129.23, 129.39, 129.74 (arom. C), 140.02, 142.00, 145.87 (*ipso*-C), 147.00 (C=$N_{triazol}$), 149.74 (C=N_{pyr}). – MS (70 eV); *m/z* (%): 296 (44) [$C_{20}H_{14}N_3$], 194 (100) [PhNCNPh], 180 (8) [$C_{13}H_{10}N$], 166 (6) [$C_{13}H_{10}$], 151 (4) [$C_{12}H_7$], 109 (10) [C_9H_4], 91 (40) [C_6H_5N], 77 (58) [C_6H_5], 64 (12) [C_5H_4], 51 (35) [C_4H_3], 44 (50) [C_2H_4O]. – $C_{26}H_{22}N_4O$ (406.5): calcd. C 76.83, H 5.46, N 13.78; found C 75.69, H 5.67, N 13.33. – HRMS ($C_{20}H_{15}N_3$): calcd. 297.1266; found 297.1259.

5-(N-Morpholino)-1,3,4-triphenyl-4,5-dihydro-1H-1,2,4-triazol (**3a**): Morpholine (0.435 g, 5 mmol) and 0.297 g (1 mmol) **1** were reacted according to GP 1, yielding 0.376 g **3a** (98%) as almost colourless crystals. – M.p. 84°C. – IR (KBr): ṽ = 3060 (m, CH), 2950 (m, CH), 2910 (m, CH), 2860 (m, CH), 2835 (m), 1595 (s), 1564 (s), 1505 (s), 1495 (s), 1450 (s, CH_2), 1400 (m), 1340 (w), 1285 (m), 1260 (s), 1160 (m), 1140 (s), 1120 (s), 1070 (s), 1004 (s), 864 (m), 765 (s), 745 (s), 690 (s), 660 (m) cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.84 (q, *J* = 4.6 Hz, 4H, NCH_2CH_2O), 3.66 (q, *J* = 5 Hz, 4H, NCH_2CH_2O), 6.05 [s, 1H, NC(H)N], 6.75–7.70 (m, 15H, arom. H). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 45.66 (NCH_2), 66.98 (OCH_2), 98.10 [NC(H)N], 113.50, 119.54, 125.22, 125.52, 127.42, 128.36, 128.88, 129.14, 129.21 (arom. C), 128.28, 143.29, 144.40 (*ipso*-C), 147.79 (C=N). – MS (70 eV); *m/z* (%): 384 (0.8) [M^+], 297 (66) [$C_{20}H_{15}N_3$], 296 (70) [$C_{20}H_{14}N_3$], 194 (100) [PhNCNPh], 180 (6) [$C_{13}H_{10}N$], 148 (4) [$C_{13}H_{10}$], 103 (5) [C_7H_5N], 91 (18) [C_6H_5N], 77 (29) [C_6H_5], 57 (12) [C_5H_4], 51 (10) [C_4H_3]. – $C_{24}H_{24}N_4$ (368.5): calcd. C 74.97, H 6.29, N 14.57; found C 74.04, H 6.39, N 14.46. – HRMS ($C_{20}H_{15}N_3$): calcd. 297.1266; found 297.1267.

1,3,4-Triphenyl-5-(N-pyrrolidino)-4,5-dihydro-1H-1,2,4-triazol (**3b**): Pyrrolidine (0.355 g, 5 mmol) and 0.297 g (1 mmol) **1** were reacted according to GP 1, yielding 0.354 g **3b** (96%) as almost colourless crystals. – M.p. 125°C. – IR (KBr): ṽ = 3060 (m, CH), 2960 (m, CH), 2920 (m, CH), 2870 (m, CH), 2830 (m), 1600 (s), 1560 (s), 1490 (s), 1460 (s, CH_2), 1400 (m), 1380 (w), 1280 (m), 1250 (s), 1180 (m), 1140 (s), 1120 (s), 1090 (s), 1060 (s), 1030 (s), 880 (s), 770 (s), 750 (s), 690 (s), 650 (m), 550 (w) cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.67 (m, 2H, CH_2), 2.85 (m, 2H, NCH_2), 6.34 [s, 1H, NC(H)N], 6.75–7.53 (m, 15H, arom. H). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 24.43 (CH_2), 45.58 (NCH_2), 94.17 [NC(H)N], 113.52, 119.23, 124.04, 124.73, 127.60, 128.45, 128.97, 129.06, 129.11 (arom. C), 128.82, 142.98, 144.91 (*ipso*-C), 147.03 (C=N). – MS (70 eV); *m/z* (%): 297 (41) [$C_{20}H_{15}N_3$], 296 (54) [$C_{20}H_{14}N_3$], 194 (100) [PhNCNPh], 180 (8) [$C_{13}H_{10}N$], 166 (4) [$C_{13}H_{10}$], 103 (9) [C_7H_3N], 91 (38) [C_6H_5N], 77 (54) [C_6H_5], 64 (14) [C_5H_4], 51 (29) [C_4H_3], 43 (34) [C_2H_5N]. – $C_{24}H_{24}N_4$ (368.5): calcd. C 78.23, H 6.57, N 15.20; found C 78.32, H 6.59, N 15.23.

5-(N-Benzylamino)-1,3,4-triphenyl-4,5-dihydro-1H-1,2,4-triazol (**3c**): Benzylamine (0.553 g, 5 mmol) and 0.297 g (1 mmol) **1** were reacted according to GP 1, yielding 0.392 g **3c** (97%) as almost colourless crystals. – M.p. 117°C. – IR (KBr): ṽ = 3300 (s, NH), 3050 (m, CH), 2900 (m, CH), 2840 (m, CH), 1600 (s), 1550 (s), 1490 (s), 1460 (s, CH_3), 1410 (s), 1350 (s, CH_2), 1250 (s), 1215 (m), 1180 (m), 1150 (m), 1100 (s), 1070 (m), 1030 (m), 890 (m), 770 (s), 750 (s), 740 (s), 700 (s), 640 (m), 530 (m), 510 (m) cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.72 (ddd, *J* = 2.7 Hz, *J* = 7.0 Hz, *J* = 7.0 Hz, 1H, NH), 3.66 (dd, *J* = 13.1 Hz, *J* = 6.4 Hz, 1H, NC*H*HPh), 3.79 (dd, *J* = 13.1 Hz, *J* = 7.1 Hz, 1H, NCH*H*Ph), 6.37 [d, *J* = 3 Hz, 1H, NC(H)N], 7.00–7.46 (m, 20H, arom. H). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 44.22 (CH_2), 92.35 [NC(H)N], 113.09, 119.49, 123.88, 125.09, 127.00, 127.59, 128.30, 128.42, 129.12, 129.22 (arom. C), 140.00, 141.69, 143.83 (*ipso*-C), 146.75 (C=N). – MS (70 eV); *m/z* (%): 296 (60) [$C_{20}H_{14}N_3$], 194 (100) [PhNCNPh], 180 (7) [$C_{13}H_{10}N$], 166 (3) [$C_{13}H_{10}$], 106 (95) [C_7H_8N], 91 (31) [C_6H_5N], 77 (55) [C_6H_5], 65 (8) [C_5H_5], 51 (33) [C_4H_3], 39 (12) [C_3H_3]. – $C_{27}H_{24}N_4$ (404.5): calcd. C 80.17, H 5.98, N 13.85; found C 80.12, H 6.04, N 13.92.

1,3,4-Triphenyl-5-(n-Propylthio)-4,5-dihydro-1H-1,2,4-triazol (**4**): *n*-Propanethiol (0.375 g) and 0.297 g (1 mmol) **1** were reacted according to GP 1, yielding 0.365 g **4** (98%) as a colourless oil. – IR (KBr): ṽ = 3055 (m), 3041 (m), 3026 (m, CH), 2984 (m), 2962 (m), 2924 (m), 2904 (m), 2869 (m, CH), 1704 (m), 1595 (m), 1554 (m), 1492 (m, C=C), 1458 (m), 1362 (m), 1337 (m), 1315 (m), 1287 (m), 1249 (s), 1149 (s), 1124 (m), 899 (m), 762 (s), 745 (s), 693 (s) cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$, TMS): 0.74 (t, *J* = 7.3 Hz, 3H, $CH_2CH_2CH_3$), 1.43 (sext, *J* = 7.2 Hz, 2H, $CH_2CH_2CH_3$), 2.47 (t, *J* = 7.1 Hz, 3H, $CH_2CH_2CH_3$), 5.85 [s (br), 1H, NC(H)N],

6.75–7.46 (m, 15H, arom. H). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): 14.33 ($CH_2CH_2CH_3$), 24.50 ($CH_2CH_2CH_3$), 29.32 ($CH_2CH_2CH_3$), 98.1 [br., NC(H)N], 115.01, 120.99, 124.68, 126.35, 128.26, 129.18, 129.59, 129.73, 130.23 (arom. C), 128.06, 140.95, 142.05 (*ipso*-C), 148.40 (C=N). – MS (70 eV); *m/z* (%): 329 (3) [M – C_3H_8], 298 (16) [$C_{20}H_{15}N_3$], 194 (100) [PhNCNPh], 129 (4), 103 (89), 91 (30), 77 (37), 65 (6), 51 (12). – $C_{22}H_{21}N_3S$ (373.5): calcd. C 73.96, H 6.21, N 11.25; found C 73.93, H 5.80, N 12.03.

1,3,4-Triphenyl-4,5-dihydro-1H-1,2,4-triazol-5-one (**5**): Compound **2a** (0.329 g, 1 mmol) was dissolved in 10 ml toluene and heated to reflux for 24 h under air. Then 30 ml pentane was added and the precipitate was filtered off, washed with pentane and dried in vacuo, yielding 0.169 g **5** (54%) as cream-coloured crystals. – M.p. 217°C. – IR (KBr): $\tilde{\nu}$ = 3045 (m, CH), 1705 (s, C=O), 1595 (s, C=C), 1551 (s), 1495 (s, C=C), 1450 (m), 1415 (s), 1375 (s), 1315 (m), 1150 (m), 965 (s), 760 (s), 705 (s), 695 (s) cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 7.14–7.45 (m, 13H, arom. H), 8.06 (m, 2H, arom. H). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 118.97, 125.62, 127.44, 128.14, 128.68, 128.95, 129.10, 129.64, 130.40 (arom. C), 126.46, 133.57, 137.94 (*ipso*-C), 145.30 (C=O), 151.93 (C=N). – MS (70 eV); *m/z* (%): 313 (58) [M$^+$], 194 (16) [PhNCNPh], 91 (100) [C_6H_5N], 77 (21) [C_6H_5], 64 (22) [C_5H_4], 51 (15) [C_4H_3]. – $C_{20}H_{15}N_3O$ (313.4): calcd. C 76.66, H 4.82, N 13.41; found C 76.77, H 4.87, N 13.20.

1,3,4-Triphenyl-4,5-dihydro-1H-1,2,4-triazol-5-thione (**6**): Compound **2a** (0.329 g, 1 mmol) and 0.035 g (1.1 mmol) sulphur were reacted according to GP 2, yielding 0.322 g **6** (98%) as cream-coloured crystals. – M.p. 178°C. – IR (KBr): $\tilde{\nu}$ = 3065 (m, CH), 3040 (m, CH), 3015 (m, CH), 1590 (s, C=C), 1550 (s), 1490 (s, C=C), 1450 (s), 1400 (s), 1370 (s), 1340 (s), 1300 (s), 1280 (s), 1100 (m, C=S), 1060 (m), 1020 (m), 970 (s), 940 (m), 910 (w), 780 (s), 760 (s), 740 (s), 710 (s), 700 (s), 580 (w), 510 (m) cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 7.25–7.55 (m, 13H, arom. H), 8.15 (m, 2H, arom. H). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 124.34, 128.16, 128.34, 128.60, 128.66, 128.76, 129.71, 129.84, 130.73 (arom. C), 125.19, 135.04, 138.25 (*ipso*-C), 150.03 (C=N), 168.46 (C=S). – MS (70 eV); *m/z* (%): 329 (80) [M$^+$], 194 (15) [PhNCNPh], 166 (5) [$C_{13}H_{10}$], 91 (100) [C_6H_5N], 77 (35) [C_6H_5], 64 (35) [C_5H_4], 51 (23) [C_4H_3]. – $C_{20}H_{15}N_3S$ (329.4): calcd. C 72.92, H 4.59, N 12.76; found C 72.61, H 4.51, N 12.46.

1,3,4-Triphenyl-4,5-dihydro-1H-1,2,4-triazol-5-selenone (**7**): Compound **2a** (0.329 g, 1 mmol) and 0.088 g (1.1 mmol) red selenium were reacted according to GP 2, yielding 0.331 g **7** (88%) as colourless crystals. – M.p. 212°C. – IR (KBr): $\tilde{\nu}$ = 3047 (m, CH), 1595 (m, C=C), 1537 (m), 1497 (s, C=C), 1446 (m), 1407 (s), 1322 (s), 1299 (s), 1288 (s), 1155 (m), 1073 (m), 977 (s), 775 (s), 767 (s), 704 (s), 694 (s) cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 7.27–7.58 (m, 13H, arom. H), 8.15 (m, 2H, arom. H). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 125.35, 128.60, 128.83, 128.86, 128.92, 128.93, 129.85, 130.21, 131.06 (arom. C), 124.90, 135.87, 138.77 (*ipso*-C), 152.11 (C=N), 164.25 (C=S). – MS (70 eV); *m/z* (%): 380 (4), 379 (20), 378 (30), 377 (93) [M$^+$], 376 (66), 375 (46), 374 (46), 373 (24), 372 (10), 371 (2), 296 (14) [$C_{20}H_{15}N_3$], 194 (25) [PhNCNPh], 166 (9) [$C_{13}H_{10}$], 91 (100) [C_6H_5N], 77 (43) [C_6H_5], 64 (25) [C_5H_4], 51 (20) [C_4H_3]. – $C_{20}H_{15}N_3Se$ (376.3): calcd. C 63.83, H 4.02, N 11.17; found C 63.72, H 4.04, N 11.17.

1,3,4-Triphenyl-4H-1,2,4-triazol-1-ium Perchlorate (**8**): Perchloric acid (70%, 0.5 ml) was added to a solution of 0.297 g (1 mmol) **1** in 5 ml THF at ambient temperature. After 5 min 5 ml water was added and the formed precipitate was stirred for another 15 min. Then the crystals were collected by filtration, washed with ether and dried under air, yielding 0.381 g **8** (96%) as colourless crystals. The analytical data were in compliance with those previously published[10].

5-Methyl-1,3,4-triphenyl-4H-1,2,4-triazol-1-ium Tetrafluoroborate (**9a**): Trimethyloxonium tetrafluoroborate (0.222 g, 1.5 mmol) and 0.297 g (1 mmol) **1** were reacted according to GP 3, yielding 0.374 g **9a** (94%) as almost colourless crystals. – M.p. 178°C. – IR (KBr): $\tilde{\nu}$ = 3067 (m, CH), 2975 (m, CH), 1596 (m, C=C), 1562 (m), 1508 (m, C=C), 1459 (m, CH_3), 1386 (m, CH_3), 1060 (s), 1035 (s), 770 (s), 753 (s), 694 (s) cm^{-1}. – ^{1}H NMR (300 MHz, [D$_6$]DMSO, TMS): δ = 2.59 (s, 3H, CH_3), 7.44–7.92 (m, 15H, arom. H). – ^{13}C NMR (75 MHz, [D$_6$]DMSO, TMS): δ = 11.62 (CH_3), 125.19, 127.42, 128.85, 129.10, 130.11, 130.53, 131.59, 131.70, 131.98 (arom. C), 122.72, 131.29, 134.62 (*ipso*-C), 152.37 (NN*C*CH$_3$), 153.40 (C=N). – MS (FAB): pos. ions 312 (100) [$C_{21}H_{18}N_3$]; neg. ions 87 (100) [BF_4]. – $C_{21}H_{18}N_3BF_4$ (399.2): calcd. C 63.18, H 4.54, N 10.53; found C 62.68, H 4.68, N 10.45.

5-Ethyl-1,3,4-triphenyl-4H-1,2,4-triazol-1-ium Tetrafluroborate (**9b**): Triethyloxonium tetrafluoroborate (0.285 g, 1.5 mmol) and 0.297 g (1 mmol) **1** were reacted according to GP 3, yielding 0.395 g **9b** (96%) as almost colourless crystals. – M.p. 206°C. – IR (KBr): $\tilde{\nu}$ = 3069 (m, CH), 2989 (m, CH), 2945 (m, CH), 1595 (m, C=C), 1549 (m), 1504 (m, C=C), 1459, 1383 (m, CH_2), 1100 (s), 1058 (s), 774 (s), 756 (s), 693 (s) cm^{-1}. – ^{1}H NMR (300 MHz, [D$_6$]DMSO, TMS): δ = 0.97 (q, *J* = 7.5 Hz, 3H, CH_2CH_3), 2.93 (t, *J* = 7.5 Hz, 2H, CH_2CH_3), 7.44–7.92 (m, 15H, arom. H). – ^{13}C NMR (75 MHz, [D$_6$]DMSO, TMS): δ = 9.82 (CH_2CH_3), 17.92 (CH_2CH_3), 125.57, 127.55, 128.95, 129.00, 130.51, 130.25, 131.58, 131.80, 131.90 (arom. C), 122.77, 131.46, 134.64 (*ipso*-C), 152.58 (C=N), 156.04 (NN*C*CH$_2$CH$_3$). – MS (FAB): pos. ions 326 (100) [$C_{22}H_{20}N_3$]; neg. ions 87 (100) [BF_4]. – $C_{22}H_{20}N_3BF_4$ (413.2): calcd. C 63.95, H 4.88, N 10.17; found C 63.76, H 4.87, N 10.22.

1,3,4-Triphenyl-4,5-dihydro-1H-1,2,4-triazoline(C^5–B)borane (**10**): BH_3 · THF (1 ml, 1 M solution in THF) was added dropwise to a solution of 0.297 g (1 mmol) **1** in 5 ml THF at ambient temperature. The solution was stirred for 2 h, then the solvent was evaporated. The residue was washed with pentane and dried in vacuo, yielding 0.274 g **10** (88%) as cream-coloured crystals. – M.p. 198°C. – IR (KBr): $\tilde{\nu}$ = 3066 (m, CH), 2359 (s, BH_3), 2295 (s, BH_3), 1595 (m, C=C), 1496 (m, C=C), 1459 (m), 1446 (s), 1404 (s), 1354 (s), 1157 (m), 1116 (m), 1073 (m), 765 (s), 690 (s) cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.04 (q, 3H, *J* = 88 Hz, BH_3), 7.21–7.50 (m, 15H, arom. H). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 124.19, 127.70, 126.84, 127.73, 127.83, 128.51, 128.03, 128.91, 129.98 (arom. C), 123.44, 134.29, 137.21 (*ipso*-C), 151.12 (C=N), 177.49 (NNCBH_3). – ^{11}B NMR (160 MHz, $CDCl_3$, TMS): δ = –35.38 (q, *J* = 88 Hz, 3H, BH_3). – MS (70 eV); *m/z* (%): 311 (0.3) [M$^+$], 298 (41) [M – BH_3], 194 (87) [PhNCNPh], 121 (54), 103 (90), 91 (48), 77 (100), 66 (42), 56 (69), 51 (41). – HRMS ($C_{20}H_{15}BN_3$): calcd. 308.1359; found 308.1364.

Methyl 2-(1,3,4-Triphenyl-4,5-dihydro-1H-1,2,4-triazol-5-ylidene)succinate (**11a**): Methyl fumarate (0.144 g, 1 mmol) and 0.297 g (1 mmol) **1** were reacted according to GP 4, yielding after column chromatography (silica gel, ethyl acetate) 0.300 g **11a** (68%) as yellow crystals. – R_f = 0.64 (ethyl acetate). – M.p. 76°C. – IR (KBr): $\tilde{\nu}$ = 3059 (m, CH), 2945 (m, CH), 1730 (s, C=O), 1640 (s, C=CC=O), 1595 (s, C=C), 1527 (s), 1496 (s, C=C), 1435 (s, CH_2), 1403 (s), 1295 (s), 1170 (s), 1130 (s), 1104 (s), 763 (s), 695 (s) cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.93 (s, 2H, NNC=CCH_2), 2.97 (s, 3H, COOCH_3), 3.56 (s, 3H, COOCH_3), 7.21–7.80 (m, 15H, arom. H). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 33.07 (NNC=*C*CH$_2$), 49.37 (COO*C*H$_3$), 51.51 (COO*C*H$_3$), 123.10, 127.56, 127.76, 128.43, 129.26, 129.28, 129.39,

129.70, 130.55 (arom. C), 125.20, 135.62, 140.44 (*ipso*-C), 150.41 (NN*C*=CCH$_2$), 156.00 (C=N), 167.60 (C=C*C*OOCH$_3$), 174.43 (*C*OOCH$_3$). – MS (70 eV); *m/z* (%): 441 (20) [M$^+$], 382 (100) [M – COOCH$_3$], 322 (19) [M – 2 COOCH$_3$], 91 (5), 77 (17), 51 (5). – $C_{26}H_{23}N_3O_4$ (441.5): calcd. C 70.74, H 5.25, N 9.52; found C 71.08, H 5.39, N 9.18. – HRMS ($C_{26}H_{23}N_3O_4$): calcd. 441.1689; found 441.1700.

2-(1,3,4-Triphenyl-4,5-dihydro-1H-1,2,4-triazol-5-ylidene)-succinonitrile (**11b**): Fumaronitrile (0.080 g, 1 mmol) and 0.329 g (1 mmol) **2a** were reacted according to GP 5, yielding 0.421 g **11b** (56%) as light green crystals. – R_f = 0.51 (Et_2O/ethyl acetate, 1:1). – M.p. 76°C. – IR (KBr): $\tilde{\nu}$ = 3059 (m, CH), 2984 (m, CH), 2903 (m, CH), 2170 (s, CN), 1593 (m, C=C), 1572 (m), 1548 (m), 1496 (m, C=C), 1458 (m, CH$_2$), 1408 (m, CH$_2$), 1163 (m), 967 (m), 766 (s), 694 (s) cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.72 [s (br.), 2H, CH$_2$], 7.10–7.60 (m, 15H, arom. H). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 18.81 (NNC=C*C*H$_2$), 38.1 (NNC=*C*CH$_2$), 118.11 (CN), 121.20, 126.64, 128.33, 128.71, 129.74, 129.81, 130.23, 130.93, 131.26 (arom. C), 124.57, 133.62, 137.84 (*ipso*-C), 149.82 (NN*C*=CCH$_2$), 152.41 (C=N). – MS (70 eV); *m/z* (%): 375 (100) [M$^+$], 296 (2.47) [M – NC(H)C=C(H)CN], 259 (24), 194 (7) [PhNCNPh], 91 (31), 77 (45), 64 (10), 51 (22), 44 (42). – $C_{24}H_{17}N_5$ (375.4): calcd. C 76.78, H 4.56, N 18.65; found C 76.80, H 4.69, N 18.42.

5-(2-Nitro-1-phenylethylidene)-1,3,4-triphenyl-4,5-dihydro-1H-1,2,4-triazol (**11c**): ω-Nitrostyrene (0.149 g, 1 mmol) and 0.297 g (1 mmol) **1** were reacted according to GP 4, yielding after column chromatography (silica gel, CH_2Cl_2) 0.130 g **11c** (25%) as a viscous brown oil. – R_f = 0.21 (CH_2Cl_2). – IR ($CHCl_3$): $\tilde{\nu}$ = 3350 [w (br.), OH], 3020 (m, CH), 2960 (m, CH), 1700 (m), 1600 (m, C=C), 1490 (m), 1450 (m), 1350 (m), 1310 (m), 1260 (m), 1220 (s), 1100 (m), 1030 (m), 910 (w), 760 (s), 700 (m), 670 (m), 520 (w) cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 6.95–7.50 (m, 20H, arom. H), 7.82 [s, 1H, C(*H*)=NO$_2$H], 8.27 [s (br.), 1H, NO$_2$*H*]. – ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ = 69.40 [C=*C*(Ph)], 122.27, 123.04, 126.79, 127.00, 127.19, 127.33, 127.42, 127.54, 127.69, 127.78, 127.79 (arom. C), 131.25, 132.93, 135.80, 140.57 (*ipso*-C), 141.59 [=*C*(Ph)C(H)=], 144.81 (C=N$_{triazol}$), 147.59 [*C*(H)=NO$_2$H], 162.64 [N(N)*C*=C]. – MS (70 eV); *m/z* (%): 446 (12) [M$^+$], 341 (15) [$C_{21}H_{17}N_4O$], 180 (100) [PhNCNPh], 105 (10) [C_7H_5O], 91 (7) [C_6H_5N], 77 (87) [C_6H_5], 51 (25) [C_4H_3], 44 (60) [CH$_2$NO]. – $C_{28}H_{22}N_4O_2$ (446.2): calcd. C 75.32, H 4.97, N 12.55; found C 74.98, H 5.23, N 12.40. – HRMS ($C_{28}H_{22}N_4O_2$): calcd. 446.1743; found 446.1744.

1-Methyl-3-(2,4,5-triphenyl-2,4-dihydro-1,2,4-triazol-3-ylidene)-pyrrolidine-2,5-dione (**11d**): Compound **2a** (0.658 g, 2 mmol) and 0.222 g (2 mmol) *N*-methylmaleic imide were reacted according to GP 4, yielding 0.655 g **11d** (80%) as colourless crystals. – M.p. 185°C. – IR (KBr): $\tilde{\nu}$ = 3058 (w, CH), 2899 (w, CH), 1727 (s, C=O), 1666 (s, C=CC=O), 1602 (s, C=C), 1569 (s), 1545 (s), 1496 (s, C=C), 1457 (m, CH$_2$, CH$_3$), 1438 (m), 1384 (m, CH$_3$), 1334 (m), 1273 (s), 1254 (s), 1117 (m), 1028 (m), 1011 (s), 952 (m), 841 (m), 763 (m), 748 (s), 696 (s), 539 (m) cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.56 (s, 2H, CH$_2$), 2.78 (s, 3H, NCH$_3$), 7.10–7.61 (m, 15H, arom. H). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 24.75 (CH$_3$), 34.99 (CH$_2$), 65.30 (NNC=*C*), 123.74, 128.30, 129.15, 129.27, 129.44, 129.56, 130.54, 131.09, 131.27 (arom. C), 125.33, 135.33, 140.93 (*ipso*-C), 148.94 (NN*C*=C), 150.66 (C=N), 167.24 (C=C*C*=O), 175.83 (CH$_2$*C*O). – MS (70 eV); *m/z* (%): 409 (26) [M + 1], 408 (100) [M$^+$], 407 (92) [M – 1], 323 (12), 322 (45) [M – CONCH$_3$CO], 219 (8), 218 (6), 194 (7) [PhNCNPh], 128 (6), 91 (22) [C_7H_7], 77 (20) [C_6H_5], 51 (6) [C_4H_3], 44 (8). – $C_{25}H_{20}N_4O_2$ (408.1): calcd. C 73.53, H 4.90, N 13.73; found C 73.33, H 4.95, N 13.46.

1-Butyl-3-(2,4,5-triphenyl-2,4-dihydro-1,2,4-triazol-3-ylidene)-pyrrolidine-2,5-dione (**11e**): Compound **2a** (0.658 g, 2 mmol) and 0.306 g (2 mmol) *N*-butylmaleic imide were reacted according to GP 5, yielding 0.759 g **11e** (84%) as colourless crystals. – M.p. 197°C. – IR (KBr): $\tilde{\nu}$ = 3059 (w, CH), 2956 (m, CH), 2931 (m, CH), 2870 (w, CH), 1722 (s, C=O), 1666 (s, C=CC=O), 1603 (s, C=C), 1567 (s), 1549 (s), 1496 (s, C=C), 1456 (m, CH$_3$, CH$_2$), 1435 (m), 1407 (s), 1360 (m), 1331 (m), 1316 (m), 1275 (s), 1228 (m), 1193 (m), 1175 (m), 1153 (m), 1120 (m), 1075 (m), 1029 (m), 916 (m), 836 (m), 763 (m), 745 (m), 711 (m), 695 (s), 616 (w), 539 (m) cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.81 (t, *J* = 7.4 Hz, 3H, CH$_3$), 1.17 (sext, *J* = 7.2 Hz, 2H, C*H*$_2$CH$_3$), 1.37 (quin, *J* = 7.2 Hz, 2H, C*H*$_2$CH$_2$CH$_3$), 2.55 (s, 2H, CH$_2$C=O), 3.30 (t, *J* = 7.2 Hz, 2H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 7.22–7.60 (m, 15H, arom. H). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 13.91 (CH$_3$), 20.09 (*C*H$_2$CH$_3$), 30.52 (*C*H$_2$CH$_2$CH$_3$), 34.46 (N*C*H$_2$CH$_2$CH$_2$CH$_3$), 37.68 (NNC=C*C*H$_2$), 64.93 (NNC=*C*), 122.98, 127.64, 128.64, 128.76, 128.87, 129.06, 130.02, 130.53, 130.75 (arom. C), 124.89, 134.83, 140.43 (*ipso*-C), 148.41 (NN*C*=C), 150.16 (C=N), 166.79 (C=C*C*=O), 175.16 (C=O). – MS (70 eV); *m/z* (%): 451 (33) [M + 1], 450 (100) [M$^+$], 449 (61) [M – 1], 421 (2) [M – C_2H_5], 393 (4) [M – C_4H_9], 379 (10), 351 (3), 338 (4), 323 (16), 322 (53) [M – $C_6H_9O_2N$], 246 (7), 219 (10), 194 (8) [PhNCNPh], 128 (8), 91 (24), 77 (16) [C_6H_5], 51 (6) [C_4H_3], 44 (5). – $C_{28}H_{26}N_4O_2$ (450.5): calcd. C 74.65, H 5.82, N 12.44; found C 74.27, H 5.77, N 12.36.

1-Phenyl-3-(2,4,5-triphenyl-2,4-dihydro-1,2,4-triazol-3-ylidene)-pyrrolidine-2,5-dione (**11f**): Compound **2a** (0.658 g, 2 mmol) and 0.346 g (2 mmol) *N*-phenylmaleic imide were reacted according to GP 5, yielding after HPLC purification 0.472 g **11f** (47%) and 0.334 g **11h** (26%) as colourless crystals. – M.p. >230°C. – IR (KBr): $\tilde{\nu}$ = 3067 (m, CH), 2922 (m, CH), 1710 (s, C=O), 1674 (s, C=CC=O), 1598 (m, C=C), 1496 (m, C=C), 1541 (m), 1457 (m, CH$_2$), 1393 (m, CH$_2$), 761 (s), 751 (s), 691 (s) cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.68 (s, 2H, CH$_2$), 7.00–7.60 (m, 15H, arom. H). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 34.64 (NNC=C*C*H$_2$), 64.09 (NNC=*C*CH$_2$), 123.15, 126.67, 127.12, 127.87, 128.60, 128.68, 128.76, 128.93, 130.26, 130.54, 130.77 (arom. C), 124.73, 133.35, 134.72, 140.10 (*ipso*-C), 149.03 (NN*C*=C), 150.29 (C=N), 165.46 (C=C*C*=O), 174.23 (C=O). – MS (70 eV); *m/z* (%): 470 (12) [M$^+$], 322 (41), 296 (36) [$C_{20}H_{14}N_3$], 194 (96) [PhNCNPh], 77 (100), 64 (29), 51 (57), 44 (72). – $C_{30}H_{22}N_4O_2$ (470.2): calcd. C 76.58, H 4.71, N 11.91; found C 76.64, H 4.96, N 11.05. – HRMS ($C_{30}H_{22}N_4O_2$): calcd. 470.1743; found 470.1749.

1,1'-Dimethyl-4-(2,4,5-triphenyl-2,4-dihydro-1,2,4-triazol-3-ylidene)-3,3'-bipyrrol-idine-2,2',5,5'-tetraone (**11g**): Compound **2a** (0.658 g, 2 mmol) and 1.444 g (14 mmol) *N*-methylmaleic imide were reacted according to GP 5, yielding 0.564 g **11g** (54%) as colourless crystals. – M.p. 190°C. – IR (KBr): $\tilde{\nu}$ = 3064 (w, CH), 2933 (w, CH), 2893 (w, CH), 1777 (m), 1718 (s, CO), 1704 (s, CO), 1666 (s, C=C), 1600 (s, C=C), 1571 (s), 1548 (s), 1498 (s, C=C), 1439 (s, CH$_2$), 1414 (m), 1385 (s, CH$_3$), 1339 (m), 1323 (m), 1273 (s), 1255 (s), 1187 (m), 1163 (m), 1109 (s), 1066 (m), 1028 (m), 1014 (m), 971 (m), 950 (m), 851 (w), 828 (m), 789 (m), 779 (m), 769 (m), 749 (s), 709 (s), 699 (s), 642 (w), 586 (w), 537 (m) cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.17 (dd, *J* = 17.8 Hz, *J* = 9.4 Hz, 1H, CHC*H*HC=O), 2.53 (dd, *J* = 17.8 Hz, *J* = 5.7 Hz, 1H, CHCH*H*C=O), 2.75 (s, 3H, NCH$_3$), 2.75 (dd, *J* = 9.4 Hz, *J* = 5.7 Hz, 1H, C*H*CHHCO), 2.90 (s, 3H, NCH$_3$), 3.00 [s (br.), 1H, NNC=CC(H)CO], 7.14–7.58 (m, 15H, arom. H). – ^{13}C

NMR (75 MHz, $CDCl_3$, TMS): δ = 24.20 (NCH_3), 24.81 (NCH_3), 34.05 ($CHCH_2$), 40.98 ($CHCH_2$), 44.57 [NNC=C*C*(H)CO], 67.19 (NNC=*C*), 123.83, 128.13, 128.30, 128.71, 129.11, 129.23, 129.90, 130.11, 131.05 (arom. C), 124.66, 134.90, 139.05 (*ipso*-C), 148.53 (NN*C*=C), 151.03 (C=N), 165.67 (C=CC=O), 175.76, 175.98, 177.22 (C=O). – MS (70 eV); *m/z* (%): 520 (5) [M + 1], 519 (12) [M^+], 409 (5), 408 (34) [$C_{25}H_{20}N_4O_2$], 407 (100) [$C_{25}H_{19}N_4O_2$], 322 (3), 259 (6), 188 (5), 128 (3), 92 (16), 91 (16) [C_7H_7], 86 (10), 84 (20) [$C_5H_{10}N$], 77 (10) [C_6H_5], 65 (4) [C_5H_5], 51 (9) [C_4H_3], 49 (28). – $C_{30}H_{25}N_5O_4$ (519.2): calcd. C 69.35, H 4.85, N 13.48; found C 70.29, H 5.09, N 12.39. – HRMS ($C_{30}H_{25}N_5O_4$): calcd. 519.1907; found 519.1903.

1,1′-Diphenyl-4-(2,4,5-triphenyl-2,4-dihydro-1,2,4-triazol-3-ylidene)-3,3′-bipyrrolidine-2,2′,5,5′-tetraone (**11h**): Compound **2a** (0.658 g, 2 mmol) and 1.038 g (6 mmol) *N*-phenylmaleic imide were reacted according to GP 5, yielding 0.720 g **11h** (56%) as colourless crystals. – M.p. >230°C. – IR (KBr): $\tilde{\nu}$ = 3067 (m, CH), 2922 (m, CH), 1710 (s, C=O), 1674 (s, C=CC=O), 1598 (m, C=C), 1541 (m), 1496 (m, C=C), 1457 (m, CH_2), 1393 (m, CH_2), 1195 (m), 1124 (m), 1107 (m), 761 (s), 751 (s), 693 (s) cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$, TMS): 2.36 (dd, *J* = 9 Hz, *J* = 19 Hz, 1H, CHCHC*H*HCO), 2.65 (dd, *J* = 5 Hz, *J* = 19 Hz, 1H, CHCHCH*H*CO), 2.98 (dd, *J* = 5 Hz, *J* = 9 Hz, 1H, CHC*H*CHHCO), 3.28 [s (br.), 1H, C*H*CHCHHCO], 7.01–7.90 (m, 15H, arom. H). – ^{13}C NMR (300 MHz, $CDCl_3$, TMS): 34.63 ($CHCHCH_2$), 41.38 ($CHCHCH_2$), 45.34 ($CHCHCH_2$), 66.91 (NNC=*C*), 123.76, 126.91, 126.95, 127.47, 128.11, 128.42, 128.75, 128.80, 129.00, 129.31, 129.68, 130.07, 130.18, 130.41, 131.13 (arom. C), 124.58, 131.99, 133.08, 134.72, 138.99 (*ipso*-C), 148.93 (NN*C*=C), 151.14 (C=N), 164.53 (NNC=C*C*=O), 175.06 (C=O), 175.10 (C=O), 176.40 (C=O). – MS (70 eV); *m/z* (%): 643 (9) [M^+], 469 (41) [M – $C_{10}H_7N_4O_2$], 346 (6), 322 (16), 296 (3) [$C_{20}H_{14}N_3$], 219 (5), 194 (53) [PhNCNPh], 119 (22), 103 (100), 91 (25), 77 (33), 64 (12), 51 (20), 44 (88). – $C_{40}H_{29}N_5O_4$ (643.2): calcd. C 74.64, H 4.54, N 10.88; found C 74.49, H 4.36, N 10.53. – HRMS ($C_{40}H_{29}N_5O_4$): calcd. 643.2219; found 643.2217.

Tetramethyl 1,3,4-Triphenyl-1,2,4-triazaspiro[4.4]nona-2,6,8-triene-6,7,8,9-tetracarboxylate (**12**): Methyl acetylenedicarboxylate (1.420 g, 10 mmol) was added to a solution of 1.645 g (5 mmol) **1** in 30 ml THF at –78°C and stirred for 4 h under argon. The solution was evaporated and the residue was treated with diethyl ether several times. The ether fractions were combined and concentrated. Upon cooling a precipitate was formed, which was collected by filtration, yielding 0.615 g **12** (21%) as light blue crystals. – M.p. 145°C. – IR (KBr): $\tilde{\nu}$ = 3059 (w, CH), 3011 (w, CH), 2955 (m, CH), 2849 (w, CH), 1747 (s, C=O), 1718 (s, C=O), 1640 (m, C=C), 1595 (s, C=C), 1493 (s, C=C), 1435 (s), 1405 (m), 1375 (m, CH_3), 1335 (s), 1325 (s), 1267 (s, COC), 1189 (s), 1168 (s), 1141 (m), 1121 (m), 1093 (m), 1071 (m), 1027 (m), 976 (s), 756 (s), 700 (s), 694 (s) cm^{-1}. – ^1H NMR (300 MHz, [D_6]acetone, TMS): δ = 3.70 (s, 6H, $COOCH_3$), 3.81 (s, 6H, $COOCH_3$), 7.05–7.50 (m, 15H, arom. H). – ^{13}C NMR (75 MHz, [D_6]acetone, TMS): δ = 52.85, 53.29 ($COOCH_3$), 98.37 (*spiro*-C), 115.97, 121.98, 127.55, 128.34, 128.72, 129.14, 129.61, 129.82, 130.21 (arom. C), 128.86, 138.28, 140.59 (*ipso*-C), 143.79 (*C*=C), 144.96 (C=*C*), 150.16 (C=N), 161.86, 162.95 ($COOCH_3$). – MS (70 eV); *m/z* (%): 582 (9) [M + 1], 581 (29) [M^+], 523 (32), 522 (100) [M – $COOCH_3$], 194 (7) [PhNCNPh], 180 (15), 119 (9), 105 (5), 91 (20) [C_7H_7], 77 (30) [C_6H_5], 59 (18), 51 (6) [C_4H_3]. – $C_{32}H_{27}N_3O_8$ (581.6): calcd. C 66.09, H 4.68, N 7.23; found C 66.02, H 4.69, N 7.36.

Tetramethyl 1,3,4-Triphenyl-1,4-dihydrocyclopenta-4a,6-dieno[e]-[1,2,4]triazine-5,6,7,7a-tetracarboxylate (**13a**) *and Tetramethyl 1,3,4-Triphenyl-1,4-dihydrocyclopenta-5,7-dieno[e][1,2,4]triazine-4a,5,6,7-tetracarboxylate* (**13b**): (1) Compound **12** (0.291 g, 0.5 mmol) was heated to reflux in 20 ml toluene for 3 h. Then the solvent was evaporated, yielding after column chromatography (silica gel, CH_2Cl_2) 0.276 g **13** (95%) as dark-red crystals.

(2) Compound **2a** (0.329 g, 1 mmol) and 0.236 g (2 mmol) methyl acetylenedicarboxylate were refluxed in toluene for 2 h. Then the solvent was evaporated and the residue purified by column chromatography (silica gel, CH_2Cl_2), yielding 0.093 g **13** (16%) as dark-red crystals. – R_f = 0.57 (CH_2Cl_2). – M.p. 105°C. – IR (KBr): $\tilde{\nu}$ = 3060 (w, CH), 3032 (w, CH), 3002 (w, CH), 2951 (m, CH), 2923 (m, CH), 2850 (m, CH), 2186 (w), 1751 (s, C=O), 1703 (s, C=O), 1595 (s, C=C), 1560 (s), 1526 (s), 1493 (s, C=C), 1436 (s), 1411 (m), 1349 (s), 1258 (s, COC), 1224 (s), 1171 (s), 1146 (s), 1100 (s), 1088 (s), 1071 (m), 1057 (m), 1027 (s), 980 (m), 867 (w), 832 (w), 796 (m), 764 (m), 753 (m), 694 (s), 526 (w) cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 3.21 (s, 3H, $COOCH_3$), 3.55 (s, 3H, $COOCH_3$), 3.72 (s, 3H, $COOCH_3$), 3.78 (s, 3H, $COOCH_3$), 7.06–7.83 (m, 15H, arom. H). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 51.15, 51.61, 52.50, 53.50 ($COOCH_3$), 71.56 (*C*$COOCH_3$), 103.40 (C=*C*$COOCH_3$), 115.69 (C=*C*$COOCH_3$), 121.75, 126.57, 128.10, 128.46, 128.62, 128.84, 129.11, 130.29, 130.64 (arom. C), 131.50, 138.79, 143.85 (*ipso*-C), 145.53 (C=*C*$COOCH_3$), 155.25 (C=N), 161.66, 161.74, 165.03, 166.02 (*C*$OOCH_3$). – MS (70 eV); *m/z* (%): 582 (12.56) [M + 1], 581 (31) [M^+], 524 (7), 523 (30), 522 (100) [M – $COOCH_3$], 180 (7), 134 (5), 119 (7), 91 (12) [C_7H_7], 77 (19) [C_6H_5], 59 (4), 58 (21), 57 (7). – $C_{32}H_{27}N_3O_8$ (581.6): calcd. C 66.09, H 4.68, N 7.23; found C 65.92, H 4.78, N 7.36.

1,3,4,6,9-Pentaphenyl-1,2,4,7,8-pentaazaspiro[4.4]nona-2,6,8-triene (**14**): 3,6-Diphenyl-1,2,4,5-tetrazine (0.234 g, 1 mmol) and 0.329 g (1 mmol) **2a** were reacted according to GP 5, yielding 0.464 g **14** (92%) as dark brown crystals. – M.p. 192°C. – IR (KBr): $\tilde{\nu}$ = 3059 (m, CH), 1594 (s, C=C), 1570 (m, C=C), 1552 (m), 1494 (s, C=C), 1457 (m), 1446 (m), 1403 (m), 1324 (s), 1200 (m), 1185 (m), 1120 (m), 1045 (m), 1025 (m), 762 (s), 750 (s), 688 (s) cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 6.71–8.10 (m, 25H, arom. H). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 99.48 (*spiro*-C), 112.83, 120.69, 126.62, 127.58, 128.02, 128.07, 128.62, 128.95, 129.18, 129.56, 130.06, 132.15 (arom. C), 126.84, 128.66, 136.06, 142.13 (*ipso*-C), 148.48 (C=N), 171.23 (*C*=NN=*C*). – MS (70 eV); *m/z* (%): 503 (0.4) [M^+], 399 (10) [M – C_6H_5CN], 296 (3) [$C_{20}H_{14}N_3$], 194 (14) [PhNCNPh], 103 (4), 91 (10), 77 (20), 51 (5), 44 (100). – $C_{34}H_{25}N_5$ (503.6): calcd. C 81.09, H 5.00, N 13.91; found C 81.34, H 5.05, N 13.81.

1,3,4-Triphenyl-4H-1,2,4-triazol-1-io-5-carbodithioat (**15a**): Carbon disulphide (1.52 g, 20 mmol) was added at room temperature to a solution of 0.297 g (1 mmol) **1** in 20 ml toluene. The resultant suspension was stirred for 2 h, then the product was collected by filtration, washed with diethyl ether and dried in vacuo, yielding 0.335 g **15a** (90%) as rose-coloured crystals. – M.p. 208°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3050 (w, CH), 1595 (w, C=C), 1540 (m), 1490 (s, C=C), 1450 (s), 1420 (m), 1370 (m), 1060 (s, C=S), 1030 (m), 985 (w), 880 (w), 760 (s), 730 (m), 700 (s), 690 (s), 550 (w) cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 7.27–7.49 (m, 13H, arom. H), 7.97 (m, 2H, arom. H). – ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 123.82, 127.60, 128.98, 129.19, 129.64, 130.05, 130.53, 131.26, 132.16 (arom. C), 122.92, 132.06, 135.61 (*ipso*-C), 151.01 [N=*C*C(S)S], 152.64 (C=N), 219.76 (SCS). – MS (70 eV); *m/z* (%): 373 (3) [M^+], 297 (5) [$C_{20}H_{15}N_3$], 194 (15) [PhNCNPh], 103 (2) [C_7H_5N], 91 (7) [C_6H_5N], 76 (100) [C_6H_4], 64 (3) [C_5H_4], 51 (5) [C_4H_3], 38 (10) [C_3H_2]. – $C_{21}H_{15}N_3S_2$ (373.5): calcd. C 67.53, H

4.05, N 11.25; found C 68.03, H 4.35, N 10.21. – HRMS ($C_{20}H_{14}N_3$): calcd. 296.1188; found 296.1188.

1,3,4-Triphenyl-α-phenylimino-4H-1,2,4-triazol-1-io-5-methanethiolate (**15b**): Phenylisothiocyanate (0.270 g, 2 mmol) was added at ambient temperature under argon to a solution of 0.594 g (2 mmol) **1** in 20 ml THF. The reaction mixture was stirred for 4 h. Then 40 ml pentane were added, the formed precipitate was filtered off, washed with pentane and dried in vacuo, yielding 0.614 g **15b** (71%) as almost colourless crystals. – M.p. 185°C. – IR (KBr): $\tilde{\nu}$ = 3049 (m, CH), 2973 (w), 2865 (w), 1593 (s, C=C), 1548 (m), 1494 (s, C=C), 1448 (s), 1433 (s), 1414 (s), 1386 (m), 1371 (s), 1319 (m), 1288 (m), 1273 (m), 1200 (m), 1186 (m), 1162 (s), 1115 (s), 1071 (m), 1052 (m), 1029 (m), 999 (m), 985 (m), 934 (s), 762 (s), 744 (s), 732 (s), 689 (s) cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 7.00–7.69 (m, 20H, arom. H). – ^{13}C NMR (300 MHz, $CDCl_3$, TMS): δ = 121.82, 123.55, 123.75, 127.42, 128.59, 129.08, 129.26, 129.60, 129.94, 130.53, 131.28, 132.18 (arom. C), 122.97, 135.80, 150.23 (*ipso*-C), 149.88 (NN*C*–C), 151.43 (C=N), 164.94 [C(NPh)S^-]. – MS (70 eV); *m/z* (%): 298 (13), 297 (56) [$C_{20}H_{15}N_3$], 296 (86), 195 (33), 194 (100) [PhNCNPh], 193 (14), 180 (12), 135 (83) [PhNCS], 91 (41) [C_7H_7], 77 (84) [C_6H_5], 65 (10), 64 (16), 63 (10), 51 (52) [C_4H_3], 50 (17). – $C_{27}H_{20}N_4S$ (432.5): calcd. C 74.97, H 4.66, N 12.95; found C 74.37, H 4.74, N 12.63.

1,3,4,6,8-Pentaphenyl-1,2,4,6,8-pentaazaspiro[4.4]non-2-ene-7,9-dione (**16**): Phenyl isocyanate (0.238 g, 2 mmol) was added at ambient temperature under argon to a solution of 0.297 g (1 mmol) **1** in 20 ml THF. The reaction mixture was stirred for 4 h. Then 40 ml pentane were added, the formed precipitate was filtered off, washed with pentane and dried in vacuo, yielding 0.492 g **16** (92%) as almost colourless crystals. – M.p. 210°C. – IR (KBr): $\tilde{\nu}$ = 3047 (w, CH), 2927 (w), 2864 (w), 1794 (s, C=O), 1739 (s, N(N)C=O), 1594 (s, C=C), 1569 (m), 1494 (s, C=C), 1448 (m), 1400 (s), 1370 (s), 1332 (s), 1291 (m), 1222 (m), 1184 (s), 1170 (s), 1155 (s), 1124 (s), 1102 (m), 1070 (m), 1058 (m), 1043 (m), 1021 (m), 1001 (m), 965 (m), 949 (m), 914 (m), 878 (m), 811 (m), 752 (s), 690 (s), 653 (m) cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 7.04–7.60 (m, 25H, arom. H). – ^{13}C NMR (300 MHz, $CDCl_3$, TMS): δ = 97.79 (*spiro*-C), 115.35, 122.36, 124.93, 126.28, 127.34, 127.43, 127.93, 128.19, 128.54, 128.95, 129.37, 129.47, 129.64, 129.72, 129.87 (arom. C), 126.70, 130.72, 134.17, 136.60, 141.56 (*ipso*-C), 147.00 (C=N), 151.96 [N(N)CO], 165.14 (CO). – MS (70 eV); *m/z* (%): 535 (0.3) [M^+], 297 (9) [$C_{20}H_{15}N_3$], 296 (9), 194 (18) [PhNCNPh], 120 (7), 119 (100) [PhNCO], 91 (41) [C_7H_7], 77 (9) [C_6H_5], 65 (7), 64 (26), 63 (10), 59 (6), 52 (5), 51 (11) [C_4H_3], 50 (7). – $C_{34}H_{25}N_5O_2$ (535.6): calcd. C 76.25, H 4.70, N 13.08; found C 76.65, H 5.14, N 12.83.

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involved in an enolate-type resonance with the adjacent ester group.

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