# 1,3-Dipolar Cycloaddition Reactions of Organic Azides with Morpholinobuta-1,3-dienes and with an $\alpha$-Ethynyl-enamine

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Dedicated to Professor *Rolf Huisgen* on the occasion of his 85th birthday

The cycloaddition of organic azides with some conjugated enamines of the 2-amino-1,3-diene, 1-amino-1,3-diene, and 2-aminobut-1-en-3-yne type is investigated. The 2-morpholinobuta-1,3-diene **1** undergoes regioselective [3+2] cycloaddition with several electrophilic azides $RN_3$ **2** (**a**, R = 4-nitrophenyl; **b**, R = ethoxycarbonyl; **c**, R = tosyl; **d**, R = phenyl) to form 5-alkenyl-4,5-dihydro-5-morpholino-1*H*-1,2,3-triazoles **3** which are transformed into 1,5-disubstituted 1*H*-triazoles **4a**,**d** or $\alpha,\beta$-unsaturated carboximidamide **5** (*Scheme 1*). The cycloaddition reaction of 4-[(1*E*,3*Z*)-3-morpholino-4-phenylbuta-1,3-dienyl]morpholine (**7**) with azide **2a** occurs at the less-substituted enamine function and yields the 4-(1-morpholino-2-phenylethenyl)-1*H*-1,2,3-triazole **8** (*Scheme 2*). The 1,3-dipolar cycloaddition reaction of azides **2a**–**d** with 4-(1-methylene-3-phenylprop-2-ynyl)morpholine (**9**) is accelerated at high pressure (*ca.* 7–10 kbar) and gives 1,5-disubstituted dihydro-1*H*-triazoles **10a**,**b** and 1-phenyl-5-(phenylethynyl)-1*H*-1,2,3-triazole (**11d**) in significantly improved yields (*Schemes 3* and *4*). The formation of **11d** is also facilitated in the presence of an equimolar quantity of *t*BuOH. The three-component reaction between enamine **9**, phenyl azide, and phenol affords the 5-(2-phenoxy-2-phenylethenyl)-1*H*-1,2,3-triazole **14d**.

**1. Introduction.** – Organic azides undergo [3+2] cycloaddition with a wide range of C–C, C–heteroatom, and heteroatom–heteroatom multiple bonds [1][2]. With olefinic and acetylenic dipolarophiles, dihydro-1,2,3-triazoles and 1,2,3-triazoles are obtained which are not only synthetic targets in their own right but are prone to more or less facile transformations depending on the substitution pattern. For example, dihydro-1,2,3-triazoles can yield 1,2,3-triazoles by $\beta$-elimination or dehydrogenation, imines + diazoalkanes by a formal [3+2] cycloreversion, and aziridines by elimination of dinitrogen [1–3]. Certain dihydro-1,2,3-triazoles undergo ring-opening to form $\alpha$-aminodiazoalkanes and $\beta$-amino-$\alpha$-diazo esters [3], and some 1-acceptor-5-donor-substituted 1,2,3-triazoles undergo isomerization to form $\alpha$-diazoimines [1][4]. Inter- and intramolecular cycloaddition reactions of azides and subsequent transformations of the cycloadducts have been used quite frequently in the synthesis of alkaloid-type natural products and related compounds [5].

The mechanistic aspects of azide cycloadditions have been studied above all by *Huisgen* and co-workers [3][6][7]. It was found that phenyl azide reacts with both electron-rich and electron-deficient olefinic $\pi$ bonds, but the former are by far more reactive. Thus, 1-pyrrolidinocyclopentene reacts with phenyl azide by a factor of 48000 more rapidly than ethene at 25°, while the rate enhancement with ethyl acrylate is only 40-fold compared with hept-1-ene [6]. A rationalization of this dual reactivity has been

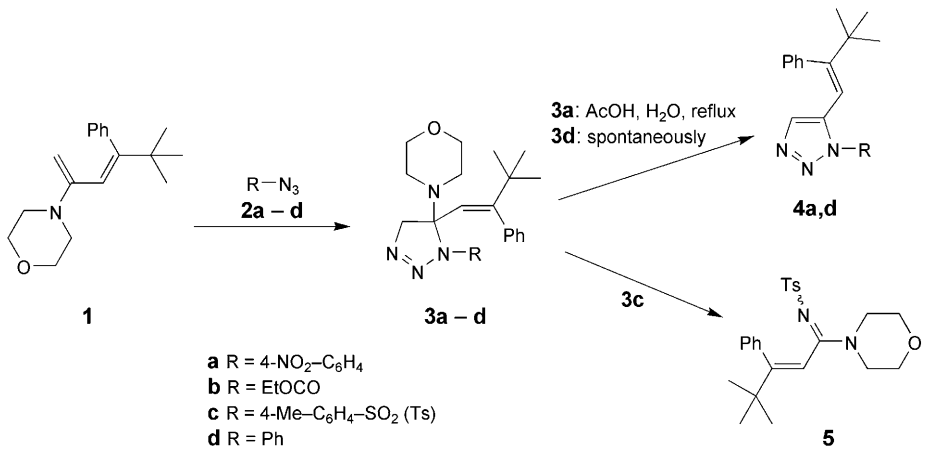
given in the framework of FMO theory by *Sustmann et al.* [8] who showed that azide cycloadditions can be both HOMO(dipole) and LUMO(dipole) controlled, depending on the electron demand of the reactants.

While enamines have been recognized as dipolarophiles par excellence for [3 + 2] cycloadditions with aryl and arylsulfonyl azides since the early investigations of *Fusco et al.* [9] and the kinetic studies of *Huisgen et al.* [6], conjugated enamines, *i. e.*, 1-amino- and 2-amino-1,3-dienes, have been somewhat neglected in this respect. *Bianchetti et al.* have reported that 1,4-dialkyl-substitued 2-morpholinobuta-1,3-dienes [10] and a 2-morpholinocyclohexa-1,3-diene derivative [11] react with 4-nitrophenyl azide and *p*-toluenesulfonyl azide in much the same manner as simple enamines. The 2-alkylidene-1,2-dihydroquinolines, which may be considered a particular type of 2-aminodienes, also undergo cycloaddition with phenyl azide, ethyl carbonazidate, and various sulfonyl azides. These reactions as well as the subsequent chemistry of the cycloadducts were investigated by several groups [12 – 14].

The present study was undertaken to expand our understanding of the reactivity of electrophilic azides with enamines that are in conjugation with an additional olefinic or acetylenic $\pi$ bond. To this end, we employed a 2-morpholinobuta-1,3-diene, a 1,3-dimorpholinobuta-1,3-diene, and an $\alpha$-ethynyl-enamine.

**2. Results and Discussion.** – 2.1. *Cycloadditions with a 2-Morpholinobuta-1,3-diene.* We have chosen the 2-morpholinobuta-1,3-diene **1** as an example of substituted 2-aminodienes which can be prepared conveniently by conjugate organocuprate addition to propyneiminium salts followed by spontaneous tautomerization of the initially formed allenamines [15]. Azides **2a – d** react smoothly with aminodiene **1** in a [3 + 2] cycloaddition which takes place exclusively at the enamine C=C bond. The final result, however, depends on the nature of the organic azide (*Scheme 1* and *Table 1*). The dihydro-1,2,3-triazoles **3a**,**b** were isolated from the reaction with 4-nitrophenyl azide

*Scheme 1*[a])




[a]) See *Table 1* for reaction conditions and products.

(**2a**) and ethyl carbonazidate (**2b**), respectively. On the other hand, the reaction with *p*-toluenesulfonyl azide (**2c**) yielded the $\alpha,\beta$-unsaturated carboximidamide **5**. Evidently, the primary [3+2] cycloadduct, the dihydrotriazole **3c**, underwent a spontaneous cycloreversion under the condition of reaction to furnish diazomethane and the carboximidamide **5**. This behavior, which is attributed to the strongly electron-withdrawing character of the tosyl group, is well known from the reaction of simple enamines with arenesulfonyl azides, and the mechanism has been studied [9]. In the reaction of phenyl azide (**2d**) with **1**, dihydrotriazole **3d** could not be isolated either because it underwent spontaneous elimination of morpholine producing triazole **4d**. In the case of the more-stable dihydrotriazole **3a**, a proton-catalyzed elimination of morpholine furnished triazole **4a**.

Table 1. *Reaction of 2-Morpholinobuta-1,3-diene* **1** *with Azides* **2a–d** (see *Scheme 1*)

| Azide | R | Conditions | Product | Yield [%] |
|---|---|---|---|---|
| **2a** | 4-$NO_2$–$C_6H_4$ | benzene, 40°, 3.5 h | **3a** | 76 |
| **b** | $CO_2Et$ | $CHCl_3$, r.t., 16 h | **3b** | 45 |
| **c** | 4-Me–$C_6H_4$–$SO_2$ | benzene, r.t. 15 h | **5** | 56 |
| **d** | Ph | $CHCl_3$, r.t. 24 h | **4d** | 63 |

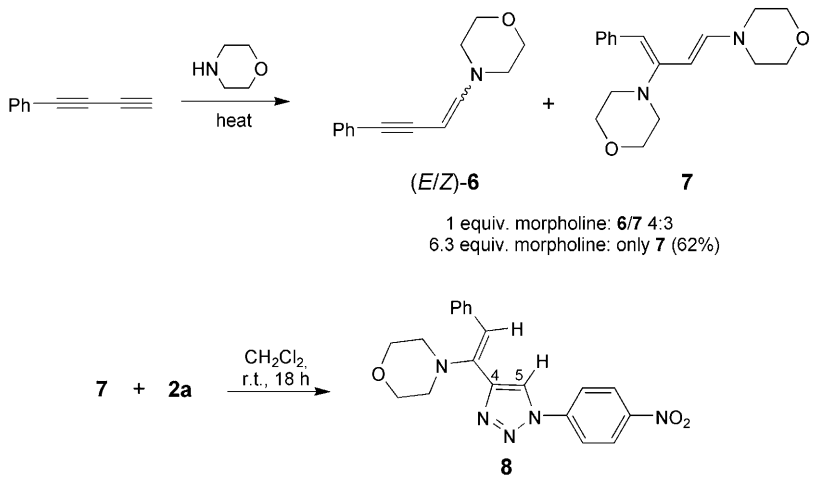
The constitution and configuration of the heterocycles **3a**,**b** and **4a**,**d** can be derived from their $^1$H-and $^{13}$C-NMR spectra. For the Ph substituent at the side chain of dihydrotriazole **3a**, hindered rotation is indicated by the $^1$H-NMR spectrum (observation of five clearly separated signals for the Ph protons) and the $^{13}$C-NMR spectrum as well (two magnetically nonequivalent $C_o$ and $C_m$ signals). The rotation of this Ph substituent is only hindered when this group is in close distance to the 4-nitrophenyl substituent at N(1). A significant steric interaction between the Ph and the 4-nitrophenyl group is expected only for the case where the two substituents of the heterocyclic ring are in 1,5 rather than in 1,4 positions. Further evidence for the regiochemical assignment of structure **3a** comes from the high-field shift of one of the $H_o$ of the Ph group ($\delta$ 6.26 *vs.* 6.90 for the other $H_o$), indicating that this proton is positioned in the shielding cone of the 4-nitrophenyl ring. For triazoles **4a** and **4d**, the triazole-ring C-atoms give rise to $^{13}$C-NMR signals at $\delta$ 132.0–132.7 ($^1J$(C,H) = 197–198 Hz, C(4)) and 132.6–134.7 ($^2J$(C,H) = 15 Hz, C(5)). These values indicate the 5-substitution of the triazole ring because, compared with 1-phenyl- and 1-(4-nitrophenyl)-1*H*-1,2,3-triazole [16], the C(5) resonance exhibits a low-field shift of 11–13 ppm, while C(4) is affected only by a small high-field shift of 2–3 ppm. NOE Experiments establish the *cis*-relationship between the olefinic proton and the *t*-Bu group of **3**–**5**, and thus confirm the original assignment [15] of the (*Z*)-configuration at the olefinic bond of **1**. The triazole-ring proton H–C(4) of **4d** gives rise to an NMR signal at $\delta$ 6.16, *ca.* 1.2 ppm upfield compared to 5-methyl-1-phenyl-1*H*-1,2,3-triazole [2]. This significant difference suggests that H–C(4) is magnetically shielded by the Ph substituent at the olefinic side chain which is possible only for a conformation close to s-*cis* at the $C(5)_{triazole}$–$C_{olef.}$ bond, as shown in *Scheme 1*.

It is worth mentioning that all azides **2a–d** studied here are regioselectively added to the enamine C=C bond of aminodiene **1** to give the dihydro-5-morpholino-1,2,3-triazoles **3a–d** as primary cycloadducts. Thus, the reliable regiochemistry, well known for the cycloadditions of simple enamines with electrophilic azides [1][2][10], is not altered by the conjugation with a second C=C bond. In summary, the results described here confirm the findings obtained by *Bianchetti et al.* for an acyclic 2-morpholinodiene substituted with less-bulky groups at the olefinic C(4) position [11].

2.2. *Cycloaddition with 1,3-Dimorpholinobuta-1,3-diene* **7**. Butadiene **7** was prepared from phenylbutadiyne and morpholine analogously to 1,3-bis(dimethylami-

no)buta-1,3-diene [17] (*Scheme 2*). When the two components were heated in an equimolar mixture, a mixture of 4-(4-phenylbut-1-en-3-ynyl)morpholine (**6**; (*E*/*Z*) mixture) and of 1,3-dimorpholinobuta-1,3-diene **7** was obtained. The two products could be separated, but (*E*/*Z*)-**6** could not be isolated in pure form. On the other hand, heating of phenylbutadiyne with a large excess of morpholine furnished 1:2 adduct **7** as the sole product in acceptable yield (62%), and notably, only the (*E*) configuration at the disubstituted enamine C=C bond was found – in contrast to the formation of the two diastereoisomers in the 1:1 adduct **6**. While the configuration at the disubstituted enamine C=C bond of **7** is derived from the vicinal coupling constant ($^3J$(H,H) = 13.8 Hz *vs.* 13.8 and 9.6 Hz in (*E*)- and (*Z*)-**6**, resp.), the configuration at the trisubstituted C=C bond could not be firmly established based on NMR data. It could be derived, however, from NMR spectra of cycloaddition product **8**, as described below.

*Scheme 2*

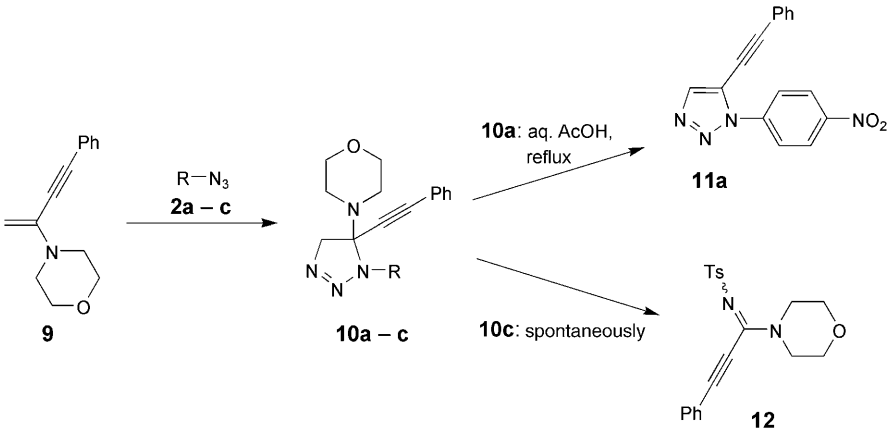



Dimorpholinobutadiene **7** reacted with 4-nitrophenyl azide (**2a**) smoothly at room temperature to furnish the 4-(1-morpholinoethenyl)triazole **8** as violet crystals in 61% yield. Cycloaddition at the other, more highly substituted enamine bond was not observed, even when 2 equiv. of the azide were supplied. Thus, diene **7** reacts as a 1- rather than a 2-aminodiene and yields a 1,4-disubstituted triazole, *i.e.* **8**, chemo- and regioselectively.

The identification of **8** as a 4- rather than 5-substituted triazole is based on the chemical shifts of pyrrole-ring atoms C(4) ($\delta$ 121.3) and C(5) ($\delta$ 108.7, $^1J$(C,H) = 196 Hz), which are found at significantly higher field ($\Delta\delta = -10.4$ and $-26.0$ ppm, resp.) than in the 5-substituted triazole **4a**. The protons H–C(5) and PhC*H*=C must be in close proximity, as indicated by a rather large NOE effect (15% intensity enhancement of the H–C(5) signal upon irradiation at the resonance of PhC*H*=C), a $^5J$(H,H) coupling constant of 3.8 Hz, and a $^4J$(C,H) coupling constant of 7.1 Hz observed for C(5) and PhC*H*=C. These observations allow the conclusion that the enamine C=C bond has the (*Z*) configuration and that a s-*cis* conformation of the exocyclic C(4)–C single bond prevails.

2.3. *Cycloadditions with 2-Morpholinobut-1-en-3-yne* **9**. No cycloadditions of azides to $\alpha$-alkynyl-enamines have been reported so far. Here, we describe the reaction of $\alpha$-ethynyl-enamine **9** [18] with electron-deficient azides **2a – c**. The reaction with **2a** yielded dihydro-5-morpholino-5-(phenylethynyl)triazole **10a** which under proton catalysis was readily converted into 5-(phenylethynyl)triazole **11a** (*Scheme 3* and *Table 2*). In the reaction of **9** with *p*-toluenesulfonyl azide (**2c**), only alkynimidamide **12** was isolated. Evidently, these results are in full accord with those obtained with morpholinodiene **1** as described above. However, the product yields are markedly lower, and the reaction of **9** with ethyl carbonazidate (**2b**) did not lead to a defined product at all. Since 1,3-dipolar cycloaddition reactions are associated with a negative volume of activation, $\Delta V^{\#} < 0$, application of high pressure should result in a rate enhancement [19–21]. In fact, some azide cycloadditions have been found to occur at lower temperature, shorter reaction time, and with significantly higher yields under high-pressure conditions (15 kbar) [22]. We were pleased to find that pressure increased the rates of the reactions investigated here. At a pressure of 7–8 kbar, the yield of dihydrotriazole **10a** could be improved and dihydrotriazole **10b**, not observed in the reaction of **9** with **2b** at atmospheric pressure, was now formed in high yield (see *Table 2*).

*Scheme 3*[a])




[a]) See *Table 2* for reaction conditions and products.

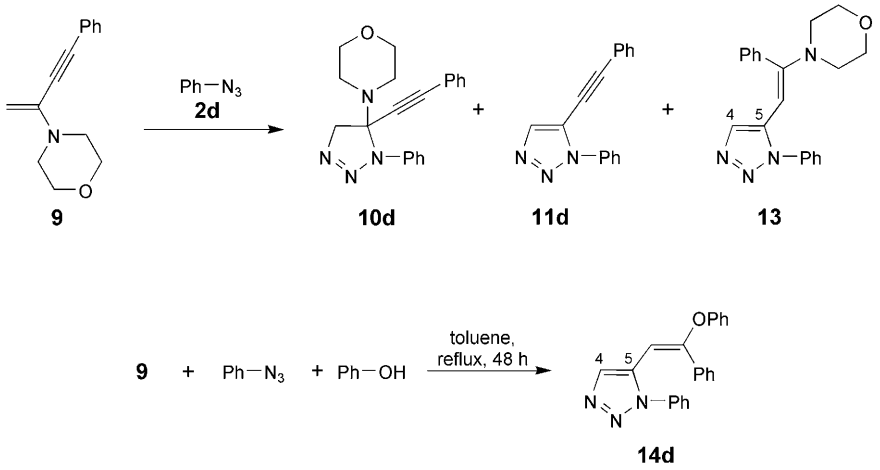
Table 2. *Reaction of 2-Morpholinobut-1-en-3-yne* **9** *with Azides* **2a – c** (see *Scheme 3*)

| Azide | R | Conditions | Product | Yield [%] |
|---|---|---|---|---|
| **2a** | 4-$NO_2$–$C_6H_4$ | $CH_2Cl_2$, 1 bar, r.t., 10 h | **10a** | 37 |
| | | toluene, 7.25 kbar, 22°, 10 h | **10a** | 54 |
| **b** | EtOCO | toluene, 1 bar, r.t., 48 h | – | |
| | | toluene, 7.85 kbar, 22°, 10 h | **10b** | 85 |
| **c** | 4-Me–$C_6H_4$–$SO_2$ | $CH_2Cl_2$, 1 bar, r.t., 1.5 h | **12** | 47 |

The reaction of phenyl azide (**2d**) with **9** showed remarkable dependence on the reaction conditions. At room temperature, the reaction did not proceed at an

appreciable rate. On heating in boiling toluene, 5-(2-morpholino-2-phenylethenyl)-triazole **13** was isolated in very low yield as the sole product (*Scheme 4* and *Table 3*). Under high-pressure conditions (10 kbar), however, the expected 5-(phenylethynyl)-triazole **11d** was obtained in 54% yield under mild conditions (22°, 6 h). The primary cycloadduct, dihydrotriazole **10d**, was isolated when the reaction was carried out at a pressure of 6.7 kbar and stopped before conversion of the starting materials was complete.

*Scheme 4*[a])




[a]) See *Table 3* for reaction conditions and products.

Table 3. *Reaction of 2-Morpholinobut-1-en-3-yne* **9** *with Phenyl Azide* (**2d**) *in Toluene* (see *Scheme 4*)

| Conditions | Additive | Yield of product(s) [%] | | | |
|---|---|---|---|---|---|
| | | **10d** | **11d** | **13** | **14d** |
| 1 bar, 110°, 48 h | | | | 8 | |
| 10 kbar, 22°, 6 h | | | 54 | | |
| 6.70 kbar, 22°, 10 h | | 31[a]) | | | |
| 1 bar, 110°, 48 h | PhOH | | trace | | 46 |
| 1 bar, 110°, 24 h | *t*-BuOH | | 47 | | |

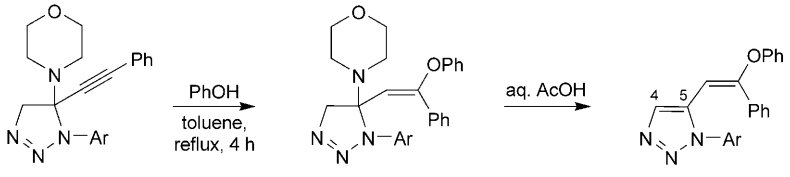
[a]) 58% of enamine **9** was recovered.

Triazole **13** represents a constitutional isomer of dihydrotriazole **10d** and may have been formed by elimination of morpholine from **10d** and re-addition of morpholine to the C≡C bond of triazole **11d**. To check this hypothesis, we wanted to know whether an alcohol added to the mixture of the starting materials can compete with the addition of morpholine to the C≡C bond present in **10d** and **11d** which were assumed to be the intermediates in the reaction of **9** with **2d** yielding **13**. No such reaction occurred when phenyl azide **2d** was heated with equimolar amounts of enamine **9** and *t*-BuOH in toluene, but gratifyingly, triazole **11d** was now isolated in 47% yield (*Table 3*).

We propose that triazole **11d** is formed by elimination of morpholine from the primary cycloadduct, dihydrotriazole **10d**, catalyzed by *t*-BuOH; this $\beta$-elimination may proceed through a six-membered transition state in which *t*-BuOH is H-bonded to the morpholine N-atom of **10d** and accepts a H–C(4) proton of **10d** at the O-atom. On the other hand, acceleration of the cycloaddition step **9** + **2d** → **10d** by added *t*-BuOH is not expected because only very small solvent effects have been observed for cycloadditions of phenyl azide in organic solvents [23].

When equimolar quantities of enamine **9**, phenyl azide (**2d**), and phenol were heated in boiling toluene, the 5-(2-phenoxy-2-phenylethenyl)triazole **14d** was obtained in 46% yield besides traces of triazole **11d**. A few experiments were made to clarify the course of this novel three-component reaction and gave the following results: no reaction was observed when either enamine **9** or triazole **11d** is heated in toluene for 24 h in the presence of phenol. Thus, addition of phenol at the C≡C bond is likely to take place at the dihydrotriazole stage. In fact, the reaction of dihydrotriazole **10a** with phenol in boiling toluene produced dihydro-5-morpholino-5-(2-phenoxy-2-phenylethenyl)-1,2,3-triazole **15a** besides a trace of triazole **11a** (*Scheme 5*). The dihydrotriazole **15a** was identified by its NMR spectra and directly converted into triazole **14a** by $H^+$-catalyzed elimination of morpholine.

*Scheme 5*




It should be noted that the reaction conditions given in *Table 3* are not optimized. It is likely that higher yields of triazoles **11d** and **14d** can be achieved when the reaction parameters (temperature, amount of aliphatic alcohol or phenol) are modified. For example, it is known that, due to the thermal lability of dihydro-1,2,3-triazoles in general, high reaction temperatures may not be the best choice for a high-yielding triazole synthesis. On the other hand, very extended reaction times at room temperature may be 'somewhat deterring', as *Huisgen* once put it [24].

The constitution and configuration of triazole **13** was established by single-crystal X-ray-diffraction analysis (*Fig. 1*)[1]). The compound has the (*E*)-configuration at the olefinic C=C bond (corresponding to a *cis*-addition of morpholine at the former C≡C bond) and an approximate s-*trans* conformation at the $C(5)_{triazole}–C_{olef.}$ bond. This

[1]) Crystal data: $C_{20}H_{20}N_4O$, $M = 332.31$, crystal dimensions $0.55 \times 0.35 \times 0.45$ mm; triclinic, space group *P*-1; $a = 13.301(8)$, $b = 19.685(12)$, $c = 10.838(5)$ Å, $\alpha = 94.44(4)$, $\beta = 101.18(5)$, $\gamma = 72.86(6)°$; $Z = 6$, $D_{calc} = 1.25$ Mg/m$^3$; $R$ ($wR$) = 0.056 (0.076) for all reflections with $I > 2.2\sigma(I)$. CCDC-264912 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre*, *via* www.ccdc.cam.ac.uk/data_request/cif.

conformation explains again (see **4d**, *Sect. 2.1.*) the observation of the triazole proton H–C(4) at relatively high field in the $^1$H-NMR spectrum, because it is magnetically shielded by the Ph substituent at the olefinic side chain. In contrast, the corresponding signal in 5-(phenylethynyl)triazole **11d** and 5-(2-phenoxy-2-phenylethenyl)triazole **14d** is found at much lower field (*Fig. 2*) because of the absence of a similar shielding effect. Based on this reasoning and an NOE experiment, the s-*trans* conformation at the 5-exocyclic single bond can be assumed for triazole **14d**.

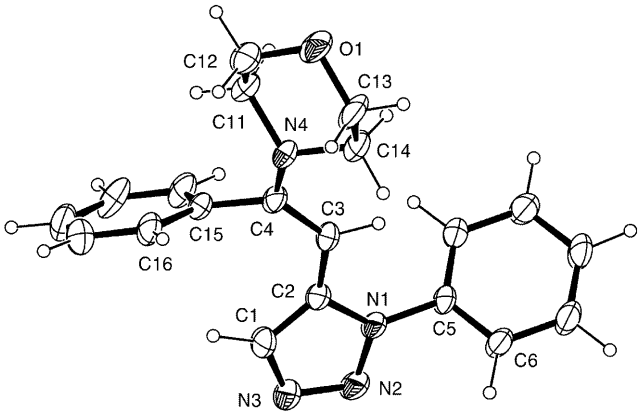



Fig. 1. *Molecular structure of triazole* **13** *in the crystal*. Ellipsoids of thermal vibration are drawn at the 30% probability level. Three independent molecules are found in the asymmetric unit of the triclinic space group *P*-1, of which only one is shown here. Some conformational differences exist between the three independent molecules, in particular: torsion angle C(1)–C(2)–C(3)–C(4) –17.8, 15.0, and 26.6°, resp. interplanar angle between least-squares plane of the triazole ring and the phenyl ring at N(1) 58.1, 57.9, and 39.9°, resp. Arbitrary numbering.

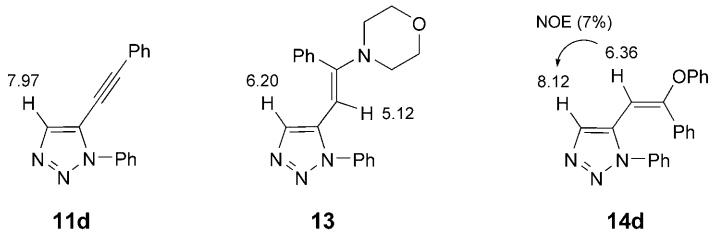



Fig. 2. *$^1$H-NMR Shifts* ($CDCl_3$) *of triazole-ring protons and olefinic protons in* **11d**, **13**, *and* **14d**. $\delta$ in ppm.

**3. Conclusions.** – This study has shown that conjugated enamines of the 2-aminodiene, 1-aminodiene, and 2-aminobut-1-en-3-yne type readily accept electrophilic azides at the enamine C=C bond. Furthermore, the [3 + 2] cycloaddition yields the 5-amino-dihydro-1,2,3-triazoles regioselectively, in full agreement with the behavior of simple enamines and a few 2-aminodienes that have been investigated earlier. Application of high pressure (*ca.* 7–10 kbar) results in an acceleration of the reaction rates and in significantly improved yields. The cycloaddition reactions described here provide access to novel 5-amino-dihydro-1,2,3-triazoles and 1,5-

disubstituted 1,2,3-triazoles, both of which bear alkenyl or alkynyl groups at C(5) of the triazole ring. It should be recalled that, for the synthesis of 1,2,3-triazoles, an enamine represents a synthetic equivalent of an alkyne, due to the sequence of 1,3-dipolar cycloaddition and amine elimination. The advantage of enamines, in addition to their high reactivity towards electrophilic azides compared to alkynes, rests on the reliable regiochemistry of the cycloaddition step, yielding 1,5-disubstituted triazoles. In contrast, the cycloaddition of azides and alkynes, in general, yields mixtures of 1,4- and 1,5-disubstituted triazoles [1][2], while the copper(I)-assisted reaction between azides and terminal alkynes affords only 1,4-disubstituted 1,2,3-triazoles [25]. Another interesting aspect of the present study is provided by the synthesis of a 1-aryl-5-(2-phenoxy-2-phenylethenyl)-1,2,3-triazole from an $\alpha$-ethynyl-enamine, an aryl azide, and phenol. This novel three-component reaction deserves further investigation because it may be useful for a diversity-oriented synthesis of functionalized 1,5-disubstituted triazoles.

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## Experimental Part

1. *General*. Solvents were dried by standard procedures and stored under Ar. Reactions were routinely performed under Ar. The petroleum ether used had a boiling point range of 40–60°. High-pressure reactions were carried out in 14-kbar systems containing either a 30-ml vessel manufactured by *A. W. Birks*, Queen's University of Belfast, Northern Ireland, Department of Mechanical and Manufacturing Engineering, or a 100-ml vessel manufactured by *Hofer Hochdrucktechnik*, Mülheim/Ruhr; the reaction solns. were sealed in PTFE (poly(tetrafluoroethene)) tubes to separate them from the hydraulic oil which was used to transduce the pressure. The following compounds were prepared by literature procedures: Morpholinodiene **1** [15], azides **2a** [26], **2b** [27], **2c** [28], **2d** [26], and 4-(1-methylene-3-phenylprop-2-ynyl)morpholine (**9**) [18]. Chromatography (CC): under hydrostatic pressure (silica gel, *Macherey-Nagel*, 0.063–0.2 mm) or under elevated pressure (*Merck Lobar* columns, *Lichroprep Si60*, particle size 40–63 μm). M.p.: copper block; not calibrated. IR Spectra: *Perkin-Elmer IR 1310*; in $cm^{-1}$. NMR Spectra: *Bruker AMX-400*; $^1H$ at 400.1 MHz with $SiMe_4$ as internal standard; $^{13}C$ at 100.6 MHz with residual solvent signal as standard ($\delta(CHCl_3)$ 77.0); $\delta$ in ppm, $J$ in Hz. Elemental analyses: *Perkin-Elmer EA CHN 2400*.

2. *Cycloaddition Reactions with 2-Morpholino-1,3-diene* **1**. 2.1. *4-[5-(3,3-Dimethyl-2-phenylbut-1-enyl)-4,5-dihydro-1-(4-nitrophenyl)-1*H*-1,2,3-triazol-5-yl]morpholine* (**3a**). To a soln. of **1** (620 mg, 2.28 mmol) in benzene (10 ml), a suspension of 4-nitrophenyl azide (**2a**; 370 mg, 2.25 mmol) in benzene (25 ml) was added within a few minutes. The mixture was heated at 40° and stirred for 3.5 h. After cooling the homogeneous soln. to r.t., a yellow powder was precipitated by addition of $Et_2O$ (35 ml). Recrystallization from benzene/$Et_2O$ 1:2 furnished **3a** (750 mg, 76%). Yellow crystals. M.p. 144°. IR (KBr): 1585*s*, 1515(sh), 1490*s*, 1315*vs*, 1115*s*, 1010*s*, 845*s*. $^1H$-NMR ($CDCl_3$): 0.97 (*s*, *t*-Bu); 2.21 (*m*, 2 H, $CH_2N$); 2.39 (*m*, 2 H, $CH_2N$); 3.69 ('*t*', $J = 4.6$, 4 H, $CH_2O$); 4.18, 4.39 (*AB*, $|^2J| = 18.9$, 2 H, $CH_2$); 6.14 (*s*, CH=C); 6.26 (*d*, $J = 7.2$, 1 $H_o$ (Ph)); 6.90 (*d*, $J = 7.4$, 1 $H_o$ (Ph)); 7.14 (*t*, $J = 7.2$, 1 H, Ph); 7.24 (*t*, $J = 7.5$, 1 H, Ph); 7.32 (*t*, $J = 7.4$, 1 H, Ph); 7.67, 8.25 (*AA'BB'*, $^3J = 9.1$, $NO_2-C_6H_4$). $^{13}C$-NMR ($CDCl_3$): 29.3 (*q*); 37.4 (*s*); 45.3 (*t*); 66.6 (*t*); 70.3 (*t*); 79.3 (*s*); 114.9 (*d*); 123.5 (*d*); 125.0 (*d*); 127.1 (*d*); 127.5 (*d*); 127.7 (*d*); 128.0 (*d*); 128.6 (*d*); 135.9 (*s*); 142.2 (*s*); 144.4 (*s*); 156.7 (*s*). Anal. calc. for $C_{24}H_{29}N_5O_3$ (435.53): C 66.19, H 6.71, N 16.08; found: C 65.9, H 6.8, N 15.9.

2.2. *Ethyl 5-(3,3-Dimethyl-2-phenylbut-1-enyl)-4,5-dihydro-5-morpholino-1*H*-1,2,3-triazole-1-carboxylate* (**3b**). A soln. of **1** (400 mg, 1.47 mmol) and ethyl carbonazidate (**2b**; 170 mg, 1.48 mmol) in $CHCl_3$ (2 ml) was stirred at r.t. for 16 h. The solvent was evaporated, and the residue was recrystallized from $Et_2O$/petroleum ether 1:1: **3b** (255 mg, 45%). Pale-yellow crystals. M.p. 94°. IR (KBr): 1715*vs*, 1500*w*, 1370*s*, 1325*vs*, 1290*m*, 1260*m*, 1195*s*, 1110*vs*, 1055*s*, 1030*s*, 950*s*. $^1H$-NMR ($CDCl_3$): 1.10 (*s*, *t*-Bu); 1.41 (*t*, $J = 7.1$, *Me*$CH_2O$); 2.22 (*m*, 2 H, $CH_2N$); 2.57 (*m*, 2 H, $CH_2N$); 3.52 ('*t*', $J = 4.7$, 4 H, $CH_2O$); 3.56, 4.01 (*AB*, $|^2J| = 18.6$, 2 H, $CH_2$); 4.38 (*m*, Me*CH*$_2$O); 6.46 (*s*, CH=C); 7.02 (*m*, 3 arom. H); 7.30 (*m*, 2 arom. H). $^{13}C$-NMR ($CDCl_3$): 14.2 (*q*); 29.5 (*q*); 37.0

(*s*); 47.2 (*t*); 62.6 (*t*); 66.8 (*t*); 77.1 (*t*); 80.4 (*s*); 122.4 (*d*); 126.9 (*d*); 127.0 (*d*); 129.4 (br. *d*); 137.8 (*s*); 152.5 (*s*); 153.7 (*s*). Anal. calc. for $C_{21}H_{30}N_4O_3$ (386.49): C 65.25, H 7.82, N 14.50; found: C 65.5, H 7.9, N 14.3.

2.3. *5-(3,3-Dimethyl-2-phenylbut-1-enyl)-1-(4-nitrophenyl)-1*H*-1,2,3-triazole* (**4a**). A soln. of **3a** (340 mg, 0.78 mmol) in 50% aq. AcOH (40 ml) was heated under reflux. When a homogeneous soln. had formed, it was cooled to 0° whereupon an orange solid appeared. Precipitation was completed by addition of $H_2O$ (10 ml), and the solid was filtered off. Recrystallization from MeCN gave **4a** (220 mg, 81%). Deep-red needles. M.p. 117°. IR (KBr): 1590*s*, 1485*s*, 1340v*s*, 1255*m*, 1070*s*, 965*s*, 850v*s*. $^1$H-NMR ($CDCl_3$): 1.16 (*s*, *t*-Bu); 6.28 (*s*, 1 H, CH=); 6.36 (*s*, 1 H, CH=); 7.08 (*m*, 3 arom. H); 7.41 (*m*, 2 arom. H); 7.76, 8.45 (*AA′BB′*, $^3J = 8.9$, $NO_2-C_6H_4$). $^{13}$C-NMR ($CDCl_3$): 29.0 (*q*); 37.2 (*s*); 108.3 (*d*); 124.7 (*d*); 125.7 (*d*); 127.6 (*d*); 128.3 (*d*); 128.5 (*d*); 132.7 (*d*, $J = 198$, C(4)); 134.7 (*d*, $J = 15$, C(5)); 138.6 (*s*); 141.1 (*s*); 147.5 (*s*); 159.4 (*s*). Anal. calc. for $C_{20}H_{20}N_4O_2$ (348.40): C 68.95, H 5.79, N 16.08; found: C 69.0, H 5.9, N 16.3.

2.4. *5-(3,3-Dimethyl-2-phenylbut-1-enyl)-1-phenyl-1*H*-1,2,3-triazole* (**4d**). A soln. of **1** (361 mg, 1.33 mmol) and phenyl azide (**2d**; 159 mg, 1.33 mmol) in $CHCl_3$ (2 ml) was stirred at r.t. for 24 h. The solvent was evaporated and the residue purified by CC (*Lobar* column, $Et_2O$/petroleum ether 6:4). Crystallization from $Et_2O$ yielded **4d** (255 mg, 63%). Colorless needles. M.p. 101°. IR (KBr): 2950*s*, 1590*s*, 1490v*s*, 1450*m*, 1350*s*, 1255*s*, 1200*s*, 1125*m*, 1090*s*, 1065*s*, 970*s*, 835*s*. $^1$H-NMR ($CDCl_3$): 1.11 (*s*, *t*-Bu); 6.16 (*s*, 1 H, CH=); 6.33 (*s*, 1 H, CH=); 7.07 (*m*, 2 arom. H); 7.39–7.58 (*m*, 8 arom. H). $^{13}$C-NMR ($CDCl_3$): 29.1 (*q*); 37.1 (*s*); 109.2 (*d*); 125.5 (*d*); 127.6 (*d*); 128.6 (*d*, 2 coinciding signals); 129.3 (*d*, 2 coinciding signals); 132.0 (*d*, $J = 197$, C(4)); 132.6 (*d*, $J = 15$, C(5)); 136.2 (*s*); 139.2 (*s*); 157.7 (*s*). Anal. calc. for $C_{20}H_{21}N_3$ (303.41): C 79.17, H 6.98, N 13.85; found: C 79.3, H 7.1, N 13.7.

2.5. N-*(4,4-Dimethyl-1-morpholino-3-phenylpent-2-enylidene)-4-methylbenzenesulfonamide* (**5**). A soln. of 4-methylbenzenesulfonyl azide (**2c**; 350 mg, 1.77 mmol) in benzene (20 ml) was added dropwise into a soln. of **1** (480 mg, 1.77 mmol) in benzene (20 ml). After keeping the stirred mixture at r.t. for 15 h, the solvent was evaporated and the residue crystallized from $Et_2O$: **5** (425 mg, 56%). Pale-yellow microcrystals. M.p. 183°. IR (KBr): 2950*s*, 1620*m*, 1590*m*, 1455*s* (br.), 1420*s*, 1270v*s*, 1255*s*, 1135v*s*, 1105*s*, 1080v*s*, 860v*s*. $^1$H-NMR ($CDCl_3$): 1.22 (*s*, *t*-Bu); 2.41 (*s*, *Me*$C_6H_4$); 3.27–3.35 (*m*, 8 H, $CH_2N$, $CH_2O$); 6.43 (*s*, CH=); 7.24–7.30 (*m*, 7 H, Ph, Ts); 7.85 (*AA′* of *AA′BB′*, $^3J = 8.1$, 2 $H_{tosyl}$, Ts). $^{13}$C-NMR ($CDCl_3$): 21.4 (*q*); 29.3 (*q*); 37.3 (*s*); 44.1 (*t*, $CH_2N$); 47.6 (*t*, $CH_2N$); 65.8 (*t*, $CH_2O$); 66.4 (*t*, $CH_2O$); 116.0 (*d*); 126.3 (*d*); 127.6 (*d*); 127.7 (*d*); 128.5 (*d*); 129.0 (*d*); 138.1 (*s*); 141.2 (*s*); 141.8 (*s*); 157.3 (*s*); 163.9 (*s*). Anal. calc. for $C_{24}H_{30}N_2O_3S$ (426.58): C 67.58, H 7.09, N 6.57; found: C 67.1, H 7.1, N 6.4.

3. *Cycloaddition with Dimorpholinobutadiene* **7**. 3.1. *[(1*E*,3*Z*)-3-(Phenylmethylene)prop-1-ene-1,3-diyl]-bis[morpholine]* (**7**). a) A mixture of phenylbuta-1,3-diyne [29] (1.02 g, 8.09 mmol) and morpholine (710 mg, 8.15 mmol) was heated under reflux during 7 h. The product mixture was extracted with $Et_2O$ (5 × 25 ml), and the combined extract was evaporated: orange oil, which was identified as a 4:3 mixture of (*E*/*Z*)-**6** ((*E*)/(*Z*) 1:1.17) and **7** by $^1$H-NMR. Bulb-to-bulb distillation at 160°/0.002 mbar furnished rather impure (*E*/*Z*)-**6** (725 mg, 42%) which could not be purified further. The residue of the distillation consisted of **7** (435 mg, 18%).

*Data of 4-[(1*E*)- and (1*Z*)-4-Phenylbut-1-en-3-ynyl)morpholine* ((*Z*)/(*E*)-**6**): $^1$H-NMR ($CDCl_3$): 2.91 ('*t*', 4 H, $CH_2N$); 3.61 (*m*, 4 H, $CH_2O$); 4.21 (*d*, $^3J = 9.6$, H–C(2) of (*Z*)-**6**); 4.47 (*d*, $^3J = 13.8$, H–C(2) of (*E*)-**6**); 5.77 (*d*, $^3J = 9.6$, H–C(1) of (*Z*)-**6**); 6.49 (*d*, $^3J = 13.8$, H–C(1) of (*E*)-**6**); 7.10–7.52 (*m*, 5 H). $^{13}$C-NMR: 48.1, 49.7 (2*t*, $CH_2N$); 66.0, 66.6 (2*t*, $CH_2O$); 77.6, 74.8 (2*d*, C(2)); 86.4, 89.9, 89.8 (3*s*, C(3), C(4)); 149.3, 144.5 (2*d*, C(1)).

b) A mixture of phenylbuta-1,3-diyne [29] (1.15 g, 9.12 mmol) and morpholine (5.04 g, 57.8 mmol) was heated at 100° during 15 h. The excess of morpholine was evaporated at 0.005 mbar, the residue extracted with $Et_2O$ (4 × 25 ml), the combined extract evaporated, and the residue crystallized from $Et_2O$/pentane 1:1: **7** (1.70 g, 62%). Yellow crystals. M.p. 94°. IR (KBr): 2835*s*, 1620v*s*, 1580*s*, 1435*s*, 1370*s*, 1245*s*, 1205*s*, 110v*s*, 1005*s*, 965*s*. $^1$H-NMR ($CDCl_3$): 2.99 (*m*, 8 H, $CH_2N$), 3.72 ('*t*', $J = 4.8$, 4 H, $CH_2O$); 3.78 ('*t*', $J = 4.6$, $CH_2O$); 5.25 (*d*, $^3J = 13.8$, H–C(2)); 5.44 (*s*, PhC*H*=C); 6.50 (*d*, $^3J = 13.8$, H–C(1)); 7.06 (*t*, $^3J = 7.4$, 1 H); 7.24 (*t*, $^3J = 7.5$, 2 H); 7.31 (*d*, $^3J = 7.4$, 2 H). $^{13}$C-NMR ($CDCl_3$): 49.0 (*t*, $CH_2N$); 51.5 (*t*, $CH_2N$); 66.4 (*t*, $CH_2O$); 67.5 (*t*, $CH_2O$); 96.0 (*dd*, $J = 154$, $J = 7.8$, C(2)); 106.3 (*d*, $J = 152$, Ph*C*H=C); 124.4 (*d*); 127.9 (*d*); 128.4 (*d*); 139.6 (*s*); 143.1 (*d*, $J = 165$, C(1)); 149.5 (*s*, C(3)). Anal. calc. for $C_{18}H_{24}N_2O_2$ (300.40): C 71.97, H 8.05, N 9.33; found: C 71.8, H 7.7, N 9.0.

3.2. *4-{(1*Z*)-1-[1-(4-Nitrophenyl)-1*H*-1,2,3-triazol-4-yl]-2-phenylethenyl}morpholine* (**8**). A soln. of **2a** (355 mg, 2.17 mmol) in $CH_2Cl_2$ (35 ml) was added dropwise to a soln. of **7** (320 mg, 1.07 mmol) in $CH_2Cl_2$ (25 ml). After 18 h, the solvent was evaporated, and the residue was filtered through a short column (silica gel (20 g), $Et_2O$/petroleum ether 8:2). Evaporation and recrystallization from $CH_2Cl_2$/$Et_2O$ 2:1 yielded **8** (245 mg, 61%). Violet crystals. M.p. 143°. IR (KBr): 1575*m*, 1505*s*, 1330v*s*, 1300*s*, 1265*s*, 1215v*s*, 1115*s*, 1055*s*, 1010*s*, 850*s*.

$^1$H-NMR ($CDCl_3$): 2.89 (*t*, 4 H, $CH_2N$); 3.72 (*t*, 4 H, $CH_2O$); 6.35 (*d*, $^5J = 3.8$, 1 H, PhC*H*=C); 7.33 (*t*, $J = 7.4$, 1 H, Ph); 7.43 (*t*, $J = 7.6$, 2 $H_m$ (Ph)); 7.66 (*d*, $J = 7.6$, 2 $H_o$ (Ph)); 7.68, 8.24 (*AA′BB′*, $NO_2-C_6H_4$); 7.70 (*s*, $^5J = 3.9$, H–(5) (triazole)). $^{13}$C-NMR ($CDCl_3$): 51.5 (*t*, $CH_2N$); 67.0 (*t*, $CH_2O$); 106.3 (*dd*, $J = 173$, PhCH=C); 108.7 (*dd*, $J = 196$, 7.1, C(5)); 121.3 (*s*, C(4)); 123.0 (*d*); 124.8 (*d*); 127.2 (*d*); 127.9 (*d*); 130.5 (*s*); 130.6 (*d*); 138.6 (*d*, $J = 9.2$, PhCH=*C*); 147.5 (*s*); 152.9 (*s*). Anal. calc. for $C_{20}H_{19}N_5O_3$ (377.40): C 63.65, H 5.07, N 18.56; found: C 63.3, H 5.2, N 18.4.

4. *Cycloaddition of* **2a**–**c** *with 2-Morpholinobut-1-en-3-yne* **9**. 4.1. *4-[4,5-Dihydro-1-(4-nitrophenyl)-5-(phenylethynyl)-1*H*-1,2,3-triazol-5-yl]morpholine* (**10a**). a) A soln. of **2a** (0.27 g, 1.66 mmol) in $CH_2Cl_2$ (10 ml) was added dropwise to a stirred soln. of **9** (0.35 g, 1.66 mmol) in $CH_2Cl_2$ (10 ml). After 10 h, the solvent was evaporated and the residue crystallized from $Et_2O/CH_2Cl_2$ 10:1: **10a** (0.23 g, 37%). Brown powder. M.p. 127°. IR (KBr): 2210*w*, 1730*m*, 1596*s*, 1263*s*, 1100*s* (br.), 1015*s*, 800*s*. $^1$H-NMR ($CDCl_3$): 2.33 (*m*, 2 H, $CH_2N$); 2.70 (*m*, 2 H, $CH_2N$); 3.68 (*m*, 4 H, $CH_2O$); 4.48, 4.93 (*AB*, $|^2J| = 18.4$, $CH_2$); 7.26–8.25 (*m*, 9 arom. H). $^{13}$C-NMR ($CDCl_3$): 45.4 (*t*), 66.5 (*t*); 72.1 (*t*); 76.2 (*s*); 84.5 (*s*); 88.9 (*s*); 115.8 (*d*); 120.8 (*s*); 125.1 (*d*); 128.5 (*d*); 129.5 (*d*); 131.7 (*d*); 143.1 (*s*); 144.1 (*s*). Anal. calc. for $C_{20}H_{19}N_5O_3$ (377.40): C 63.65, H 5.07, N 18.56; found: C 63.1, H 5.2, N 18.3.

b) A soln. of **9** (215 mg, 1.01 mmol) and **2a** (167 mg, 1.02 mmol) in toluene (5 ml) was pressurized in an autoclave at 7.25 kbar for 10 h. After decompression, the solvent was evaporated and the residue purified by CC (silica gel (30 g), $Et_2O$). Crystallization from $Et_2O/CH_2Cl_2$ 10:1 gave **10a** (204 mg, 54%). Brown powder.

4.2. *1-(4-Nitrophenyl)-5-(phenylethynyl)-1*H*-1,2,3-triazole* (**11a**). A suspension of **10a** (570 mg, 1.51 mmol) in 50% aq. AcOH (40 ml) was heated until a clear soln. had formed (10 min). The separation of a solid on cooling was completed by addition of $H_2O$ (40 ml). The solid was isolated by filtration and recrystallized from EtOH: **11a** (255 mg, 58%). Olive-green powder. M.p. 161°. IR (KBr): 2220*w*, 1610*m*, 1590*m*, 1520v*s*, 1340v*s*, 970*s*, 965v*s*. $^1$H-NMR ($CDCl_3$): 7.27–7.51 (*m*, 5 H, Ph); 8.02 (*s*, H–C(4)); 8.17, 8.43 (*AA′BB′*, $NO_2-C_6H_4$). $^{13}$C-NMR ($CDCl_3$): 73.9 (*s*); 101.5 (*s*); 120.6 (*s*); 121.0 (*s*); 123.6 (*d*); 124.8 (*d*); 128.7 (*d*); 131.5 (*d*); 138.1 (*d*); 141.0 (*s*); 147.6 (*s*). Anal. calc. for $C_{16}H_{10}N_4O_2$ (290.28): C 66.20, H 3.47, N 19.30; found: C 65.8, H 3.8, N 19.0.

4.3. *Ethyl 4,5-Dihydro-5-morpholino-5-(phenylethynyl)-1*H*-1,2,3-triazole-1-carboxylate* (**10b**). A soln. of **9** (215 mg, 1.01 mmol) and **2b** (92 mg, 0.80 mmol) in toluene (5 ml) was pressurized in an autoclave at 7.85 kbar for 10 h. After decompression, the solvent was evaporated and the residue separated by FC (silica gel, $Et_2O$) followed by CC (*Lobar* column, $Et_2O$/petroleum ether 8:2): **10b** (222 mg, 85%). Yellow oil. IR (film). 2200*m*, 1715v*s*, 1665*s* (br.), 1470*s*, 1425*s*, 1380*s*, 1360*s*, 1315v*s*, 1290*s*, 1100v*s*, 1040*s*, 1010*s*, 940*s*. $^1$H-NMR ($CDCl_3$): 1.41 (*t*, $J = 7.1$, *Me*$CH_2O$); 2.54 (*m*, 2 H, $CH_2N$); 2.84 (*m*, 4 H, $CH_2N$); 3.68 (*m*, 4 H, $CH_2O$); 4.42 (*m*, $MeCH_2O$); 4.69 (*s*, 2 H, $CH_2$); 7.29–7.56 (*m*, 5 arom. H); $^{13}$C-NMR ($CDCl_3$): 14.2 (*q*); 47.2 (*t*); 63.1 (*t*); 66.9 (*t*); 73.9 (*s*); 79.7 (*t*); 83.2 (*s*); 87.6 (*s*); 121.3 (*s*); 128.3 (*d*); 129.0 (*d*); 131.6 (*d*); 151.2 (*s*). Anal. calc. for $C_{17}H_{20}N_4O_3$ (328.37): C 62.12, H 6.14, N 17.06; found: C 62.9, H 6.2, N 16.4.

4.4. *4-Methyl*-N-*(3-phenyl-1-morpholinoprop-2-ynylidene)benzenesulfonamide* (**12**). As described in *4.1* (a) from **9** (0.58 g, 2.70 mmol) and **2c** (0.54 g, 2.73 mmol) in $CH_2Cl_2$ (90 min): **12** (0.47 g, 47%). Colorless powder. M.p. 161.5°. IR (KBr): 2200*s*, 1520*s*, 1485*m*, 1430*s*, 1260*s*, 1080*s*, 860*s*. $^1$H-NMR ($CDCl_3$): 2.37 (*s*, *Me*$C_6H_4$); 3.69–3.85 (*m*, 8 H, $CH_2N$, $CH_2O$); 7.20–7.85 (*m*, 9 arom. H). Anal. calc. for $C_{20}H_{20}N_2O_3S$ (368.40): C 65.20, H 5.47, N 7.60; found: C 64.7, H 5.2, N 7.6.

5. *Cycloaddition of Phenyl Azide* (**2d**) *with 2-Morpholinobut-1-en-3-yne* **9**. 5.1. *4-(4,5-Dihydro-1-phenyl-5-(phenylethynyl)-1*H*-1,2,3-triazol-5-yl)morpholine* (**10d**). A soln. of **9** (306 mg, 1.43 mmol) and **2d** (200 mg, 1.68 mmol) in toluene (5 ml) was pressurized in an autoclave at 6.7 kbar for 10 h. After decompression, the solvent was removed and the residue separated by CC (*Lobar* column, $Et_2O$/petroleum ether 8:2): unreacted **9** (177 mg, 58%) and **10d** (99 mg, 31%). The latter was a dark brown oil which could not be purified further (no satisfactory elemental analysis was obtained). Crude **10d**: IR (film): 2230*w*, 1590*s*, 1485v*s*, 1330*s*, 1290*s*, 1115v*s*, 1045*s*, 1015*s*. $^1$H-NMR ($CDCl_3$): 2.15 (*m*, 2 H, $CH_2N$); 2.66 (*m*, 2 H, $CH_2N$); 3.68 (*m*, 4 H, $CH_2O$); 4.45, 4.82 (*AB*, $|^2J| = 8.2$, 2 H, $CH_2$); 7.01–7.89 (*m*, 10 arom. H). $^{13}$C-NMR ($CDCl_3$): 45.8 (*t*); 66.7 (*t*); 72.0 (*t*); 77.1 (*s*); 85.4 (*s*); 88.0 (*s*); 117.4 (*d*); 121.4 (*s*); 123.8 (*d*); 128.4 (*d*); 128.9 (*d*); 129.1 (*d*); 131.7 (*d*); 139.5 (*s*).

5.2. *1-Phenyl-5-(phenylethynyl)-1*H*-1,2,3-triazole* (**11d**). a) A soln. of **9** (209 mg, 0.98 mmol) and **2d** (125 mg, 1.05 mmol) in toluene (5 ml) was kept under a pressure of 10 kbar for 6 h at 22°. After decompression, the solvent was evaporated and the residue subjected to FC (silica gel (20 g), $Et_2O$). Crystallization from $Et_2O$ yielded **11d** (130 mg, 54%). Colorless crystals. M.p. 48°.

b) A soln. of **9** (340 mg, 1.49 mmol), **2d** (202 mg, 1.70 mmol), and *t*-BuOH (130 mg, 1.74 mmol) in toluene (25 ml) was heated under reflux for 8 h. The solvent was evaporated and the residue separated by CC (silica gel (50 g), $Et_2O$/petroleum ether 6:4): 185 mg (47%) of **11d**. IR (KBr): 2205*s*, 1580*m*, 1480*s*, 1215*s*, 1110v*s*, 965*s*, 905*s*, 820*s*. $^1$H-NMR ($CDCl_3$): 7.31–7.56 (*m*, 8 H); 7.83 (*d*, $J = 8.2$, 2 H); 7.97 (*s*, 1 H). $^{13}$C-NMR ($CDCl_3$): 74.5

(*s*); 100.0 (*s*); 120.7 (*s*); 121.0 (*s*); 123.4 (*d*); 128.4 (*d*); 129.1 (*d*); 129.2 (*d*); 129.5 (*d*); 131.3 (*d*); 136.2 (*s*); 137.2 (*d*, $J = 198$). Anal. calc. for $C_{16}H_{11}N_3$ (245.28): C 78.35, H 4.52, N 17.13; found: C 78.5, H 4.7, N 17.2.

5.3. *4-[(1*E*)-1-Phenyl-2-(1-phenyl-1*H*-1,2,3-triazol-5-yl)ethenyl]morpholine* (**13**). A soln. of **9** (639 mg, 2.95 mmol) and **2d** (359 mg, 2.94 mmol) in toluene (30 ml) was heated under reflux for 2 h. After cooling, the solvent was replaced by $Et_2O$ (25 ml), and charcoal (2 g) was added. After stirring for 30 min, the mixture was filtered over a pad of silica gel (20 g). From the filtered soln., the product was obtained by CC (silica gel (50 g), $Et_2O$) and crystallization from $CH_2Cl_2/Et_2O$ 1:2: **13** (75 mg, 8%). Brown-red crystals. M.p. 134°. IR (KBr): 1620*s*, 1605v*s*, 1505*s*, 1235v*s*, 1120v*s*. $^1$H-NMR ($CDCl_3$): 2.81 ('*t*', 4 H, $CH_2N$); 3.60 ('*t*', 4 H, $CH_2O$); 5.12 (*s*, PhC=C*H*); 6.20 (*s*, H–C(4)); 7.12–7.47 (*m*, 10 arom. H). $^{13}$C-NMR ($CDCl_3$): 48.4 (*t*); 66.5 (*t*); 87.8 (*d*); 125.3 (*d*); 129.3 (2 *d*); 128.9 (*d*); 130.4 (*d*, $J = 198$); 130.5 (*d*); 135.7 (*d*, $J = 15$); 135.8 (*s*); 136.0 (*s*); 136.7 (*s*); 155.0 (*s*).

5.4. *5-[(1*E*)-2-Phenoxy-2-phenylethenyl]-1-phenyl-1*H*-1,2,3-triazole* (**14d**). A soln. of **9** (229 mg, 1.07 mmol), **2d** (134 mg, 1.12 mmol), and phenol (114 mg, 1.12 mmol) in toluene (50 ml) was heated under reflux for 48 h. The solvent was evaporated, the residue dissolved in $Et_2O$ (20 ml), and charcoal (1 g) added. Filtration over silica gel (20 g) and crystallization from $Et_2O$/petroleum ether 8:2 afforded **14d** (168 mg, 46%). Beige needles. M.p. 126°. $^1$H-NMR ($CDCl_3$): 6.52 (*s*, PhC=C*H*)); 7.00–7.03 (*m*, 3 H); 7.25–7.31 (*m*, 7 H); 7.50–7.63 (*m*, 5 arom. H); 8.12 (*s*, H–C(4)). $^{13}$C-NMR ($CDCl_3$): 100.6 (*d*); 116.1 (*d*); 122.8 (*d*); 125.7 (*d*); 126.3 (*d*); 128.8 (*d*); 129.7 (*d*); 129.9 (*d*); 132.2 (*d*, $J = 15$); 133.8 (*d*, $J = 198$); 133.9 (*s*); 136.2 (*s*); 153.3 (s); 155.6 (*s*). Anal. calc. for $C_{22}H_{17}N_3O$ (339.40): C 77.86, H 5.05, N 12.4; found: C 77.2, H 5.2, N 12.3.

5.5. *4-{4,5-Dihydro-1-(4-nitrophenyl)-5-[(1*E*)-2-phenoxy-2-phenylethenyl]-1*H*-1,2,3-triazol-5-yl}morpholine* (**15a**) *and 1-(4-Nitrophenyl)-5-[(1*E*)-2-phenoxy-2-phenylethenyl]-1*H*-1,2,3-triazole* (**14a**). A soln. of **10a** (86 mg, 0.23 mmol) and phenol (24 mg, 0.26 mmol) in toluene (15 ml) was heated under reflux for 4 h, then stirred at r.t. for 12 h. The solvent was evaporated, the residue dissolved in $Et_2O$ (10 ml), and charcoal (0.5 g) added. After stirring for 15 min and filtration over silica gel (20 g), the solvent was evaporated at 0.005 mbar. According to $^1$H- and $^{13}$C-NMR the residue consisted mainly of **15a** besides traces of **14a** and minor amounts of unknown impurities. The oil was heated under reflux in 50% aq. AcOH (25 ml) for 10 min. The soln. was allowed to cool and extracted with $Et_2O$ (3 × 30 ml). The combined extract was washed with sat. aq. $NaHCO_3$ soln., dried ($Na_2SO_4$), and evaporated and the residue crystallized from $CH_2Cl_2/Et_2O$ 1:2: **14a** (76 mg, 84%). Orange crystals. M.p. 189°.

*Data of* **14a**: $^1$H-NMR ($CDCl_3$): 6.36 (*s*, PhC=C*H*); 6.84–7.42 (*m*, 10 H); 7.72, 8.39 (*AA′BB′*, $^3J = 8.8$, $NO_2-C_6H_4$); 8.01 (*s*, H–C(4)). $^{13}$C-NMR ($CDCl_3$): 99.4 (*d*); 116.3 (*d*); 123.0 (*d*); 125.2–129.9 (6*d*); 132.4 (*d*, $J = 15$); 134.2 (*d*, $J = 199$); 133.6 (*s*); 141.1 (*s*); 148.0 (*s*); 154.8 (*s*); 155.4 (*s*). Anal. calc. for $C_{22}H_{16}N_4O_3$ (384.39): C 68.74, H 4.20, N 14.58; found: C 68.8, H 4.3, N 14.0.

*Data of Crude* **15a**: $^1$H-NMR ($CDCl_3$): 2.28 (*m*, 2 H, $CH_2N$); 2.47 (*m*, 2 H, $CH_2N$); 3.66 (*m*, 4 H, $CH_2O$); 4.52, 4.69 (*AB*, $|^2J| = 18.5$, 2 H, ring-$CH_2$); 6.03 (*s*, 1 H); 6.33 (*d*, $J = 8.8$, 2 H); 6.74–7.29 (*m*, 9 H); 7.52, 8.03 (*AA′BB′*, $^3J = 9.3$, $NO_2-C_6H_4$). $^{13}$C-NMR ($CDCl_3$): 45.4 (*t*, $CH_2N$); 66.6 (*t*, $CH_2O$); 70.0 (*t*, ring-$CH_2$); 79.5 (*s*); 116.7 (*d*); 123.7 (*d*), 142.3 (*s*); 144.3 (*s*); 156.2 (*s*); further signals could not be assigned due to impurities.

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