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Nitrogen Heterocycles

# A Synthetic Route Toward Tetrazoles: The Thermolysis of Geminal Diazides

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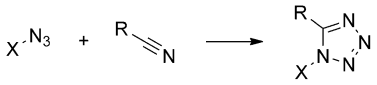
**Abstract:** A new synthetic route toward the tetrazole core is described, which is based on a general fragmentation pattern that was found in a range of compounds featuring geminal diazido units. Through a simple two-step procedure, the synthesis of structurally diverse target compounds containing a tetrazole, such as tetrazoloquinoxalinones, benzoylaryltetrazoles, tetrazolotriazinones, and tetrazoloazepinones, was easily accomplished, starting from broadly accessible substrates (i.e., oxindoles, diarylethanones, pyrazolones, and phenanthrols). The initial oxidative diazidation reaction with iodine and sodium azide under mild conditions is followed by the thermal fragmentation under microwave irradiation, leading to the tetrazole products. Noteworthy, an experimental solution is presented in which the potentially hazardous diazide intermediates are not isolated and the concentration of crude reaction mixtures containing diazides is not required to achieve the tetrazoles in good yields.

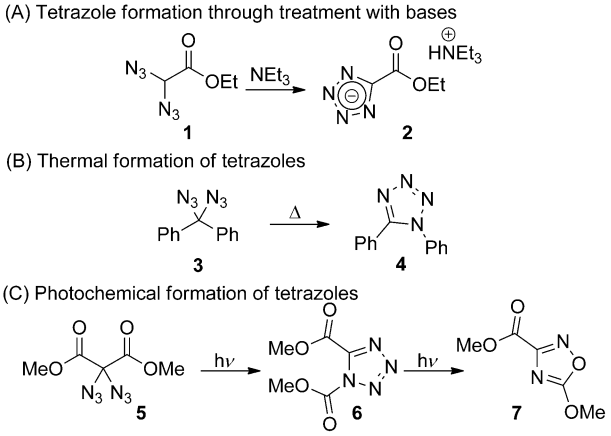
## Introduction

Tetrazoles, with a particularly high percentage of nitrogen atoms in a stable cyclic compound, are nitrogen-containing heterocycles of overwhelming interest, and they were heavily researched since their first appearance in the scientific literature in 1885.[1] Even though tetrazoles are not produced by nature, the tetrazole scaffold has been useful in a plethora of applications and fields including, amongst others, medicinal chemistry,[2] biochemistry,[3] high-energetic materials,[4] and nanomaterials.[5] The importance of tetrazoles was extensively reviewed,[6] and the synthetic strategies for their synthesis are manifold.[7] However, the main approach to tetrazoles relies on the 1,3-dipolar cycloaddition between nitriles and (organic) azides; numerous detailed variations of the reactions conditions have been reported (Scheme 1).[8] In many cases, the regioselectivity of the cycloaddition becomes a challenging issue, and variants were developed in which the nitriles were generated in the course of the reaction, by starting from alcohols and aldehydes,[9] or by using oximes for the tetrazole formation.[10]



**Scheme 1.** Cycloaddition strategy for the synthesis of tetrazoles.

During our ongoing studies on the synthesis[11] and reactivity[12] of compounds with geminal diazido units, we observed that tetrazole formation can be easily triggered with this still barely known compound class:[13,14] Diazido esters (e.g., **1**) were smoothly converted into the corresponding tetrazoles through simple treatment with triethylamine as base additive (Scheme 2 A).[15] We then questioned whether a universal approach to the tetrazole core may exist, starting from geminal diazide substrates, and deliberately different from the classical cycloaddition with nitriles and azides. Indeed, our literature search




**Scheme 2.** Syntheses of tetrazoles starting from geminal diazides.

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revealed that a few examples for the conversion of diazido compounds into tetrazoles were reported: For example, the thermal decomposition of diazidodiphenylmethane **3** into tetrazole **4** was shown in 1909 by Schroeter, and later confirmed by Götzky (Scheme 2B).[16] Subsequent studies on the thermolysis of geminal diazides by Moriarty and co-workers described tetrazole formation with a few diazidomalonic acid derivatives.[17] This compound class was also prone to deliver tetrazoles through photochemical decomposition. As exemplified for methyl 2,2-diazidomalonate **5** in Scheme 2C, tetrazole **6** underwent further loss of nitrogen under prolonged irradiation to yield **7**, and a partially characterized dimeric compound was also formed.[18] However, the synthetic scope of the diazide-tetrazole conversion was hardly addressed, with only singular examples, and the method still lacks applications to other diazido substrates.

In this paper, we now disclose our full results on the synthesis of tetrazole heterocycles, starting from geminal diazides and using simple thermolysis conditions. As summarized in Figure 1, the reaction is applied to four principal scaffolds, and the tetrazole-containing compound classes **A**, **B**, **C**, and **D** are presented. The 1,5-disubstituted tetrazoles were achieved with complete control of the regioisomer formation, a known challenge with other strategies for the synthesis of 1,5-disubstituted tetrazoles.[7] We also address safety concerns regarding the handling of organic diazides: An experimental variant is outlined that does not require the isolation of azide-containing organic compounds, thus offering a unique method for tetrazole synthesis directly from nitrogen-free starting substrates.

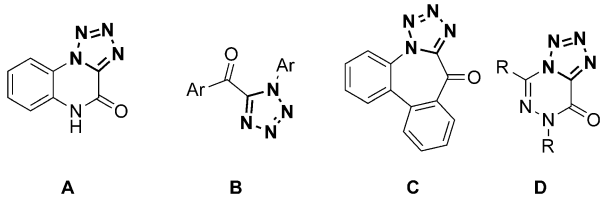
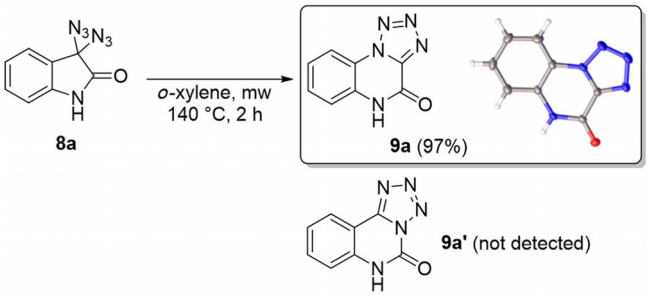



**Figure 1.** Structures of tetrazoloquinoxalinone **A**, benzoylaryltetrazole **B**, tetrazoloazepinone **C**, and tetrazolotriazinone **D**.

## Results and Discussion

We began our studies with the thermal conversion of the 3,3-diazidooxindoles **8**, a class of diazide compounds that was recently demonstrated to be easily accessible.[19] As shown in Scheme 3, microwave heating in *o*-xylene resulted in the transformation of 3,3-diazidoindolin-2-one (**8a**) into tetrazolo[1,5-*a*]quinoxalin-4(5*H*)-one (**9a**) in an excellent yield of 97% without further optimization. After two hours at 140 °C, complete consumption of the starting material was observed and the product precipitated as a colorless solid, which was then isolated through simple filtration. We note that classical heating conditions provide nearly identical results, albeit with elongated reaction times. The structure of tetrazole **9a** was unequivocally evidenced by X-ray crystallography: A suitable single crystal of **9a** was grown from DMSO and demonstrated that the carbonyl group was connected to the tetrazole carbon atom, whereas the aryl group was migrated onto the nitrogen atom.




**Scheme 3.** Synthesis and X-ray crystal structure of tetrazolo[1,5-*a*]quinoxalin-4(5*H*)-one **9a**.

We were not able to detect even traces of the isomeric tetrazole **9a′**, which shows that the diazide fragmentation proceeds with excellent regioselectivity. The thermal properties of **9a** were studied by differential scanning calorimetric analysis (DSC) and thermogravimetric analysis (TGA; see Supporting Information). TGA curves show that decomposition of the tetrazole starts at 280 °C. Drop hammer experiments proved that **9a** is not sensitive to impact (>20 J).

We then turned our attention to the substrate scope and found that a good variety of oxindole derivatives were smoothly transformed into the corresponding tetrazoloquinoxalinones in good to excellent yields, employing the conditions detailed in Scheme 3. As Figure 2 shows, several substituents at the aromatic core were well tolerated. For example, 7-chlorotetrazolo[1,5-*a*]quinoxalin-4(5*H*)-one (**9b**) and its trifluoromethyl derivative **9c** were isolated in 86 and 87% yield, respectively. With the 6-chloro substituent, the reaction furnished product **9g** in 90% yield. Regarding the substituents at the 8-position, bromo (**9f**), nitro (**9h**), methoxy (**9j**), and *tert*-butyldimethylsilyloxy (**9k**) substituents were successfully used and gave the products with yields ranging from 76 to 97%. The structure of **9f** was supported by X-ray crystallography, revealing the connectivity of the quinoxalinone core. As demonstrated by the formation of **9d** in 96% and **9e** in 82%, *N*-substituted diazidooxindoles were also transformed. Furthermore, the two structurally interesting pyrido derivatives **9i** and **9l** were obtained in high yields, by using diazidopyrrolopyridinone starting materials. We note that all products were easily isolated in pure form after cooling the reaction mixture to room temperature followed by filtration.

The tricyclic scaffold of the product compounds **9** represents an interesting system, having potential applications in medicinal chemistry and crop protection.[20] The few previous efforts regarding their synthesis were based on a different strategy: Rather than ring-expanding the oxindole framework, the modification of the already existing quinoxalinone framework was the main approach. For example, 3-chloroquinoxalin-2(1*H*)-ones were converted into the desired tetrazoloquinoxalin-4(5*H*)-ones through nucleophilic substitution with sodium azide[21] or through treatment with hydrazine followed by nitrous acid.[22] Alternatively, the cycloaddition of azidotrimethylsilane with quinoxalin-2(1*H*)-ones under metal-catalyzed and oxidative conditions was employed to construct this kind of tetrazoles.[23]

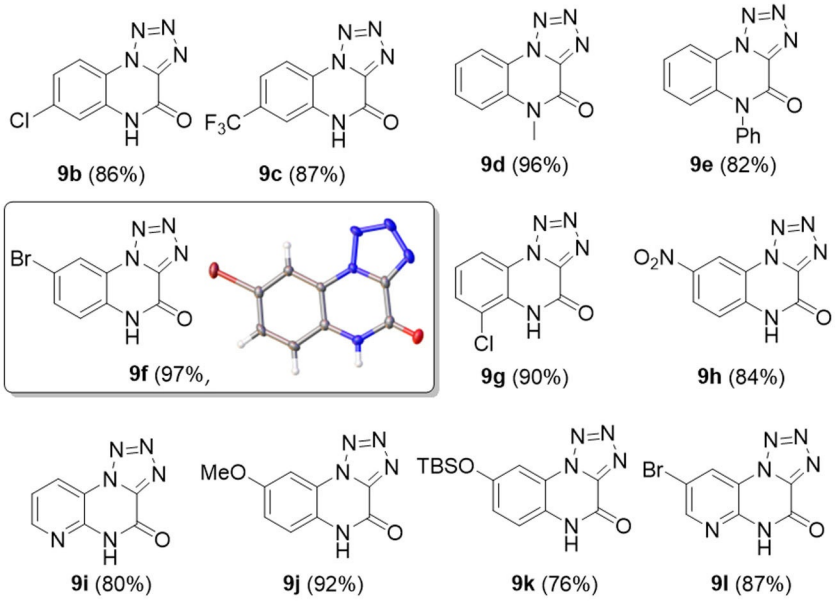


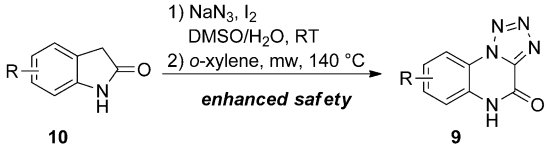

**Figure 2.** Scope of the formation of tetrazolo[1,5-*a*]quinoxalin-4(5*H*)-ones **9**.

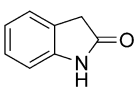
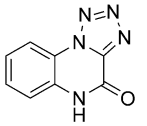
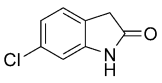
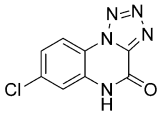
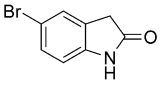
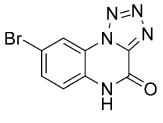
Despite the obvious disadvantages of the preceding approaches to tetrazoloquinoxalinones **9**, such as the use of toxic and explosive reagents or prefunctionalized starting compounds, we felt that practicing chemists may be somewhat reluctant to use our method because diazidooxindoles **8** appear to be potentially hazardous compounds. To increase the attraction of our oxindole-based synthetic strategy, we decided to develop an experimental variant that provides the tetrazoloquinoxalinones **9** directly from the simplest oxindoles **10**. With the new protocol used for the examples in Table 1, we aimed to prevent the isolation of the potentially unsafe diazidooxindole key intermediates **8**. The other goal was to make sure that dilute reaction mixtures containing crude organic diazides were not concentrated, at any stage. To this end, the oxindoles **10** were converted under our standard diazidation conditions, by using sodium azide and iodine in aqueous DMSO at room temperature, as published before.[19] After the complete consumption of the oxindole, the reaction was stopped through the addition of sodium thiosulfate and water to reduce the remaining iodine oxidant. The reaction mixture was then extracted with *o*-xylene, thus removing azide and iodide ions with the aqueous phase. The organic layer containing the diazidooxindoles was then submitted to the thermolysis conditions. After the indicated heating time at 140 °C and subsequent cooling to room temperature, the desired tetrazoloquinoxalinones precipitated in pure form. This safety-optimized protocol allowed for the tetrazoloquinoxalinone synthesis in good overall yields, in a pretty general way.

Next, we sought to expand the tetrazole-forming method to other classes of easily accessible diazides. To our delight, the conversion of diazidodiarylethanones[24] **11a** and **11b** furnished the corresponding benzoylaryltetrazoles **12**, under the straightforward thermolysis conditions, after a slightly elongated reaction time (Scheme 4). The yields were excellent, and the 5-aroyl-1-aryltetrazoles were the only products obtained, whereas the isomeric 1-aroyl-5-aryltetrazoles were not formed. Surprisingly, synthetic routes toward 5-aroyl-1-aryltetrazoles are rare, consisting of low-yielding multistep sequences.[25] Consequently, only a limited number of examples belonging to this interesting compound class were reported in the literature before, most of which were accessed through an Ugi-type four-component reaction and subsequent modifications.[26]

We also applied the safety-optimized protocol to the benzoylaryltetrazole synthesis: The 1,2-diarylethanones **13** were di-

**Table 1.** *Safety-optimized* formation of tetrazolo[1,5-*a*]quinoxalin-4(5*H*)-ones **9**.



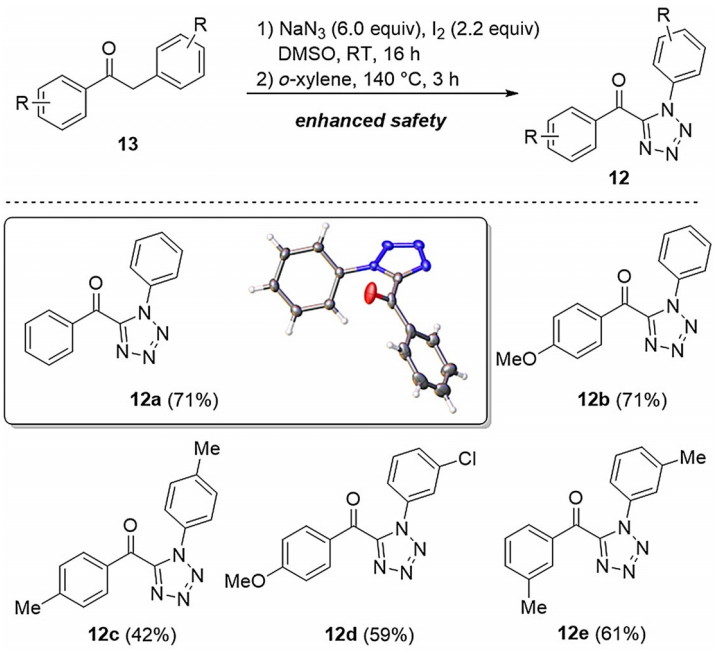

| Compound | Substrate | Product[a] | Yield[b] [%] |
|---|---|---|---|
| **9a** |  |  | 77 |
| **9b** |  |  | 61 |
| **9f** |  |  | 70 |

[a] Conditions: 1) $NaN_3$ (10.0 equiv), $I_2$ (2.2 equiv), DMSO/$H_2O$ (2:1), RT, 2–16 h; 2) *o*-xylene, mw, 140 °C, 2 h. [b] Isolated yield of pure compound after filtration.

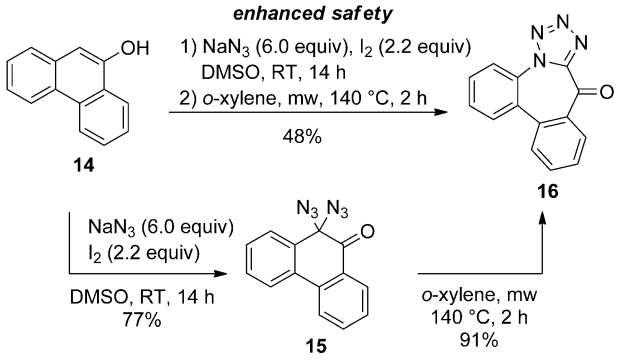

**Scheme 4.** Reaction of diazidodiarylethanones **11** to tetrazoles **12**.

azidated under standard conditions, and the work-up procedure with *o*-xylene was utilized as described above. The subsequent thermal fragmentation was carried out by using an oil bath at 140 °C, and purification by column chromatography gave the tetrazole products. As summarized in Scheme 5, several benzoylaryltetrazoles **12** were obtained in moderate to good yields, ranging from 42 to 71%. Methyl, methoxy, and chloro substituents were easily installed at the aromatic cores. The structure of tetrazole **12a** was verified by X-ray crystallography; a suitable single crystal was grown from chloroform-$d_1$. The benzoyl group was attached to the carbon atom of the tetrazole nucleus, whereas the phenyl group migrated onto the neighboring nitrogen.

The method was further extended to the aromatic core of 9-phenanthrol (**14**) (Scheme 6). The diazidation conditions[24] led to the formation of diazidocarbonyl compound **15** in 77% yield, and the aromaticity of the central ring was abolished. Under microwave irradiation at 140 °C, fragmentation of the diazido unit occurred, providing the 9*H*-dibenzo[*d*,*f*]-tetrazolo[1,5-*a*]azepin-9-one (**16**) in 91% yield. The safety-optimized protocol gave azepinone **16** in a moderate yield of 48%. We point out that our literature search did not reveal any previous reports on the synthesis and chemistry of dibenzotetrazoloazepinones similar to **16**.




**Scheme 5.** *Safety-optimized* formation of benzoylaryltetrazoles **12**.

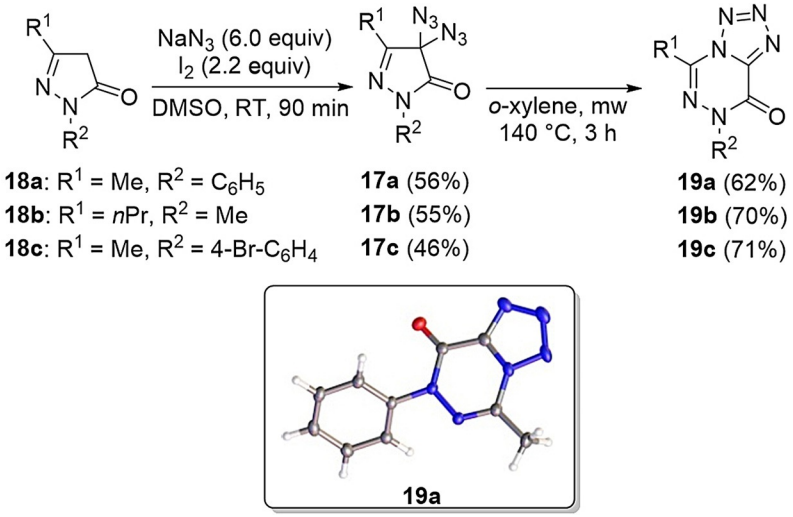



**Scheme 6.** Diazidation of 9-phenanthrol **14** and formation of 9*H*-dibenzo[*d*,*f*]tetrazolo[1,5-*a*]azepin-9-one **16**.

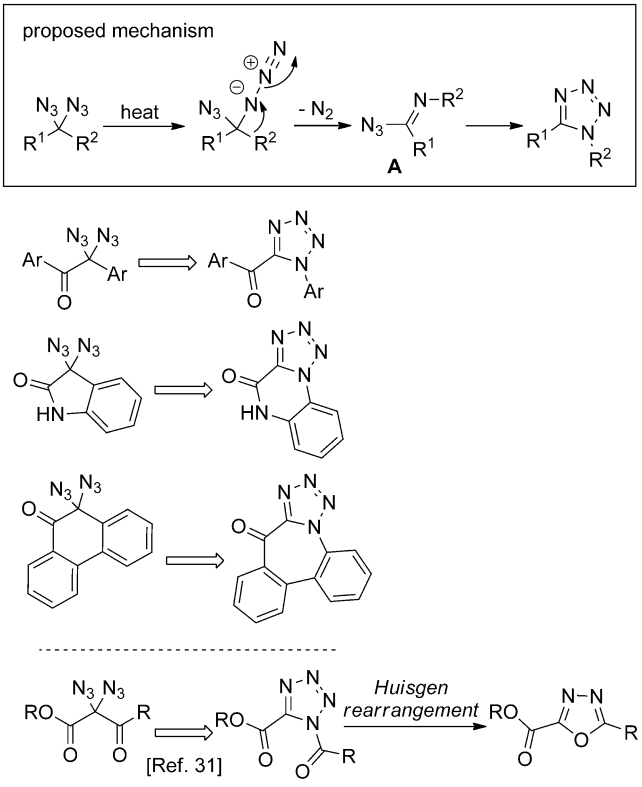
Finally, we studied the fragmentation of diazides **17** derived from pyrazolones under thermolysis conditions (Scheme 7). We had a straightforward entry to diazides **17** by using our oxidative diazidation method[11c] with iodine and sodium azide in DMSO at room temperature. The 4,4-diazidopyrazolones **17a–c** were obtained in moderate yields, for example. Notably, a few previous studies by others were able to provide similar 4,4-diazidopyrazolones starting from the corresponding dibromo pyrazolones and through substitution with azide anions.[27] When submitting the diazides **17a–c** to thermolysis at 140 °C under microwave irradiation, tetrazolotriazinones **19a–c** were obtained in good yields between 62 and 71%. The structure of **19a** was confirmed with X-ray crystallography. Tetrazolo[1,5-*d*][1,2,4]triazin-8(7*H*)-ones **19** belong to a class of compounds that was barely synthesized prior to this work.[28] We realized that the extremely uncommon heterocyclic core of those tetrazolotriazinones **19** possesses a high degree of nitrogen atoms and, therefore, holds potential as energetic compounds. Preliminary impact sensitivity measurements with tetrazole **19b** by using drop hammer tests showed that the compound is relatively stable (> 20 J). TGA-DSC curves show that the decomposition of tetrazole **19b** starts at around 173 °C (see Supporting Information).

Our results clearly demonstrate the ease of accessing various kinds of tetrazoles through the thermolysis of geminal diazides. As presented in Scheme 8, it is assumed that the fragmentation starts with the loss of dinitrogen and concomitant [1,2] shift of one of the groups attached to the diazido unit, upon heating. This leads to the formation of a key imidoyl azide intermediate **A** that undergoes direct cyclization to the tetrazole product.[29] The diazide fragmentations discussed in this paper had a uniform migratory aptitude with the relative tendency of aryl > carbonyl. In a recent report on the thermolysis of geminal diazides derived from acylacetate compounds, we found that the migration of the carbonyl groups is favored over the migration of esters and amides; in this particular case, however, the initially formed tetrazole intermediate undergoes a further Huisgen rearrangement[30] that results in the construction of the 1,3,4-oxadiazole core.[31] Future studies will test the




**Scheme 7.** Synthesis of tetrazolotriazinones **19**.




**Scheme 8.** Mechanistic proposal for tetrazole formation.

migration tendencies of other groups, with the goal to fully understand the synthetic potential of thermolysis reactions with geminal diazides.

## Conclusions

In conclusion, we have reported a new and general synthetic approach toward tetrazole heterocycles. Through a simple two-step procedure consisting of oxidative diazidation and subsequent thermolysis, simple starting compounds were easily transformed into several barely known classes of tetrazoles, including tetrazoloquinoxalinones, benzoylaryltetrazoles, dibenzotetrazoloazepinones, and tetrazolotriazinones. We also addressed safety issues regarding the potentially hazardous character of diazido intermediates with the goal to render the method more attractive to practitioners and to trigger its use in all fields of chemistry. In upcoming studies, we will expand this thermolysis approach to other compounds bearing the geminal diazido motif, in order to complete our understanding of the key aspects of this thermal fragmentation and to grasp the full capability of transforming this still neglected compound class.

## Experimental Section

*Caution!* We accentuate that geminal diazides are potentially hazardous compounds and should be handled with suitable care and safety equipment.

### General procedures

**General procedure A for the synthesis of tetrazolo[1,5-*a*]quinoxalin-4(5*H*)-ones 9**: 3,3-Diazidooxindole **8** (1.0 equiv) was dissolved in *o*-xylene (0.05 M), and the reaction mixture was heated at 140 °C under microwave irradiation for 2 h. The solid was filtered off and washed with $CH_2Cl_2$.

**General procedure B for the *safety-optimized* formation of tetrazolo[1,5-*a*]quinoxalin-4(5*H*)-ones 9**: Oxindole **10** (1.0 equiv) was dissolved in a mixture of DMSO (0.15 M) and water (0.30 M), and sodium azide (10.0 equiv) and iodine (2.2 equiv) were added. The reaction mixture was stirred at RT until thin layer chromatography indicated complete consumption of the starting material. A saturated aqueous solution of sodium thiosulfate and water was added (approx. 10 mL), and the mixture was extracted with *o*-xylene (approx. 0.05 M with regard to **10**). The combined organic phases were washed with a saturated aqueous solution of sodium bicarbonate and brine and dried with magnesium sulfate. The solution was transferred to a microwave tube and stirred for 2 h at 140 °C

under microwave irradiation. The precipitate was filtered off after cooling to RT and washed with ethyl acetate (EtOAc), dichloromethane ($CH_2Cl_2$) and *n*-pentane.

**General procedure C for the synthesis of tetrazoles 12 and 19**: The diazide **11** or **17** (1.0 equiv) was dissolved in *o*-xylene (0.05 M) and the reaction mixture was heated at 140 °C under microwave irradiation for 3 h. The mixture was allowed to cool to RT and the solution was concentrated in vacuo. Flash chromatography on silica gel afforded the corresponding tetrazoles.

**General procedure D for the *safety-optimized* formation of tetrazoles 12**: 1,2-Diarylethanone **13** (1.0 equiv) was dissolved in DMSO (0.10 M), and sodium azide (6.0 equiv) and iodine (2.2 equiv) were added. The suspension was stirred for 16 h at RT. The mixture was diluted with ice-cold water and a small amount of a saturated aqueous solution of sodium thiosulfate (until decoloration) and extracted with *o*-xylene (approx. 0.05 M with regard to **13**). The combined organic phases were washed with a saturated aqueous solution of sodium bicarbonate and brine and dried with magnesium sulfate. The solution was transferred to a flask and stirred for 3 h at 140 °C in an oil bath. The solution was concentrated in vacuo, and flash chromatography on silica gel afforded the corresponding tetrazoles **12**.

**General procedure E for the synthesis of diazidopyrazolones 17**: Pyrazolone **18** (1.0 equiv) was dissolved in DMSO (0.15 M), and sodium azide (6.0 equiv) and iodine (2.2 equiv) were added. The reaction mixture was stirred for 90 min at RT. Some drops of a saturated aqueous solution of sodium thiosulfate were added and the mixture was extracted with dichloromethane. The combined organic phases were washed with brine and dried with magnesium sulfate. The solution was concentrated in vacuo, and flash chromatography on silica gel afforded the corresponding 4,4-diazido-pyrazol-5-ones **17**.

## Syntheses

**Tetrazolo[1,5-*a*]quinoxalin-4(5*H*)-one (9a)**: According to the *general procedure A* using 3,3-diazidooxindole (**8a**, 50 mg, 0.23 mmol, 1.0 equiv), tetrazolo[1,5-*a*]quinoxalin-4(5*H*)-one (**9a**, 42 mg, 0.22 mmol, 97%) was obtained as a white solid. T (decomp./TGA) 287.9 °C; $^1$H NMR (400 MHz, DMSO): $\delta = 12.54$ (s, 1H), 8.24 (dd, $J =$ 8.2, 1.0 Hz, 1H), 7.65–7.58 (m, 1H), 7.51–7.47 (m, 1H), 7.46–7.4 ppm (m, 1H); $^{13}$C NMR (101 MHz, DMSO): $\delta = 151.2$, 144.3, 129.9, 129.6, 123.9, 119.9, 116.9, 116.4 ppm; IR (ATR): $\tilde{\nu} = 1710$, 1665, 1620, 1517, 1472, 1451, 1418, 1069, 758, 704, 676 cm$^{-1}$; HRMS (ESI-TOF): *m/z* calcd for $C_8H_5N_5O^+$: 187.0494; found: 187.0465. The analytical data are in agreement with previously reported ones.[32]

**7-Chlorotetrazolo[1,5-*a*]quinoxalin-4(5*H*)-one (9b)**: According to the *general procedure A* using 3,3-diazido-6-chloroindolin-2-one (**8b**, 50 mg, 0.20 mmol, 1.0 equiv), 7-chlorotetrazolo[1,5-*a*]quinoxalin-4(5*H*)-one (**9b**, 38 mg, 0.17 mmol, 86%) was obtained as a white solid. T (decomp.) > 260 °C; $^1$H NMR (600 MHz, DMSO): $\delta =$ 12.63 (s, 1H), 8.34–8.20 (m, 1H), 7.57–7.43 ppm (m, 2H); $^{13}$C NMR (151 MHz, DMSO): $\delta = 151.2$, 144.3, 133.8, 130.9, 123.8, 119.1, 118.2, 116.2 ppm; IR (ATR): $\tilde{\nu} = 1716$, 1698, 1615, 1599, 1386, 1312, 1203, 869, 82, 706, 452 cm$^{-1}$; HRMS (ESI-TOF): *m/z* calcd for $C_8H_4N_5O^+$: 221.0104; found: 221.0109.

**7-(Trifluoromethyl)tetrazolo[1,5-*a*]quinoxalin-4(5*H*)-one (9c)**: According to the *general procedure A* using 3,3-diazido-6-(trifluoromethyl)indolin-2-one (**8c**, 50 mg, 0.18 mmol, 1.0 equiv.), 7-(trifluoromethyl)tetrazolo[1,5-*a*]quinoxalin-4(5*H*)-one (**9c**, 39 mg, 0.15 mmol, 87%) was obtained as white solid. T (m.p.) 198 °C; $^1$H NMR (400 MHz, DMSO): $\delta = 12.76$ (s, 1H), 8.48 (d, $J = 8.6$ Hz, 1H), 7.83–7.76 ppm (m, 2H); $^{13}$C NMR (101 MHz, DMSO): $\delta = 151.2$, 144.9, 130.2, 129.7 (q, $J = 32.7$ Hz), 123.4 (q, $J = 272.6$ Hz), 122.0, 120.4 (q, $J = 3.6$ Hz), 117.9, 113.7 ppm (q, $J = 4.1$ Hz); $^{19}$F NMR (376 MHz, DMSO): $\delta = -61.4$ ppm; IR (ATR): $\tilde{\nu} = 3194$, 3134, 1696, 1635, 1459, 1401, 1299, 1176, 1074, 882, 664 cm$^{-1}$; HRMS (FD): *m/z* calcd for $C_9H_4N_5OF_3^+$: 255.0368; found: 255.0383.

**5-Methyltetrazolo[1,5-*a*]quinoxalin-4(5*H*)-one (9d)**: According to the *general procedure A* using 3,3-diazido-1-methylindolin-2-one (**8d**, 50 mg, 0.22 mmol, 1.0 equiv), 5-methyltetrazolo[1,5-*a*]quinoxalin-4(5*H*)-one (**9d**, 42 mg, 0.21 mmol, 96%) was obtained as a white solid. T (decomp.) 234 °C; $^1$H NMR (400 MHz, DMSO): $\delta = 8.35$ (dd, $J = 8.1$, 1.2 Hz, 1H), 7.82–7.71 (m, 2H), 7.54 (ddd, $J = 8.3$, 7.2, 1.4 Hz, 1H), 3.70 ppm (s, 3H); $^{13}$C NMR (101 MHz, DMSO): $\delta = 151.0$, 143.5, 130.7, 130.2, 124.4, 120.1, 116.9, 116.6, 29.5 ppm; IR (ATR): $\tilde{\nu} = 3079$, 1680, 1615, 1341, 1259, 1132, 764, 654 cm$^{-1}$; HRMS (FD): *m/z* calcd for $C_9H_7N_5O^+$: 201.0651; found: 201.0623. The analytical data are in agreement with previously reported ones.[33]

**5-Phenyltetrazolo[1,5-*a*]quinoxalin-4(5*H*)-one (9e)**: According to the *general procedure A* using 3,3-diazido-1-phenylindolin-2-one (**8e**, 50 mg, 0.17 mmol, 1.0 equiv), 5-phenyltetrazolo[1,5-*a*]quinoxalin-4(5*H*)-one (**9e**, 37 mg, 0.14 mmol, 82%) was obtained as a white solid. T (decomp.) 256 °C; $^1$H NMR (600 MHz, DMSO): $\delta =$ 8.45–8.42 (m, 1H), 7.74–7.70 (m, 2H), 7.67–7.63 (m, 1H), 7.57–7.51 (m, 2H), 7.49–7.46 (m, 2H), 6.72–6.69 ppm (m, 1H); $^{13}$C NMR (151 MHz, DMSO): $\delta = 151.1$, 144.2, 135.6, 132.2, 130.4, 129.9, 129.7, 128.8, 124.4, 120.1, 117.2, 116.7 ppm; IR (ATR): $\tilde{\nu} = 3089$, 1694, 1587, 1486, 1335, 1243, 757, 713 cm$^{-1}$; HRMS (FD): *m/z* calcd for: $C_{14}H_9N_5O^+$ 263.0807; found: 263.0803.

**8-Bromotetrazolo[1,5-*a*]quinoxalin-4(5*H*)-one (9f)**: According to the *general procedure A* using 3,3-diazido-5-bromoindolin-2-one (**8f**, 50 mg, 0.17 mmol, 1.0 equiv), 8-bromotetrazolo[1,5-*a*]quinoxalin-4(5*H*)-one (**9f**, 44 mg, 0.17 mmol, 97%) was obtained as a white solid; T (decomp.) 244 °C; $^1$H NMR (600 MHz, DMSO): $\delta = 12.66$ (s, 1H), 8.41 (d, $J = 2.1$ Hz, 1H), 7.80 (dd, $J = 8.7$, 2.1 Hz, 1H), 7.43 ppm (d, $J = 8.7$ Hz, 1H); $^{13}$C NMR (151 MHz, DMSO): $\delta = 151.1$, 144.5, 132.7, 129.0, 121.0, 118.8, 118.8, 115.1 ppm; IR (ATR): $\tilde{\nu} = 3099$, 2941, 1713, 1667, 1521, 1470, 1309, 870, 693, 455 cm$^{-1}$; HRMS (FD): *m/z* calcd for $C_8H_4N_5OBr^+$: 264.9599; found: 264.9568.

**6-Chlorotetrazolo[1,5-*a*]quinoxalin-4(5*H*)-one (9g)**: According to the *general procedure A* using 3,3-diazido-7-chloroindolin-2-one (**8g**, 50 mg, 0.20 mmol, 1.0 equiv), 6-chlorotetrazolo[1,5-*a*]quinoxalin-4(5*H*)-one (**9g**, 40 mg, 0.18 mmol, 90%) was obtained as a white solid. T (decomp.) > 260 °C; $^1$H NMR (400 MHz, DMSO): $\delta =$ 12.06 (s, 1H), 8.27 (dd, $J = 8.2$, 1.3 Hz, 1H), 7.77 (dd, $J = 8.1$, 1.3 Hz, 1H), 7.46 ppm (t, $J = 8.2$ Hz, 1H); $^{13}$C NMR (101 MHz, DMSO): $\delta =$ 151.4, 144.5, 130.1, 127.2, 124.4, 121.3, 120.0, 115.5 ppm; IR (ATR): $\tilde{\nu} = 3157$, 3077, 1688, 1599, 1513, 1324, 1200, 1125, 798, 470 cm$^{-1}$; HRMS (FD): *m/z* calcd for: $C_8H_4N_5OCl^+$ 221.0104; found: 221.0103.

**8-Nitrotetrazolo[1,5-*a*]quinoxalin-4(5*H*)-one (9h)**: According to the *general procedure A* using 3,3-diazido-5-nitroindolin-2-one (**8h**, 60 mg, 0.23 mmol, 1.0 equiv), 8-nitrotetrazolo[1,5-*a*]quinoxalin-4(5*H*)-one (**9h**, 45 mg, 0.19 mmol, 84%) was obtained as a white solid. T (decomp.) > 260 °C; $^1$H NMR (600 MHz, DMSO): $\delta = 13.09$ (s, 1H), 8.92 (d, $J = 2.5$ Hz, 1H), 8.47 (dd, $J = 9.1$, 2.5 Hz, 1H), 7.66 ppm (d, $J = 9.1$ Hz, 1H); $^{13}$C NMR (151 MHz, DMSO): $\delta = 151.4$, 144.7, 142.3, 134.9, 125.0, 119.8, 117.8, 112.2 ppm; IR (ATR): $\tilde{\nu} = 3066$, 1678, 1620, 1540, 1454, 1302, 841, 694, 460 cm$^{-1}$; HRMS (FD): *m/z* calcd for $C_8H_4N_6O_3^+$: 232.0345; found: 232.0334.

**Pyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrazine-4(5*H*)-one (9i)**: According to the *general procedure A* using 3,3-diazido-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (**8i**, 50 mg, 0.23 mmol, 1.0 equiv), pyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrazine-4(5*H*)-one (**9i**, 35 mg, 0.19 mmol, 80%) was obtained as a white solid. T (decomp.) > 260 °C; $^1$H NMR (600 MHz,

DMSO): $\delta = 13.05$ (s, 1H), 8.69 (dd, $J = 8.1$, 1.5 Hz, 1H), 8.62 (dd, $J = 4.8$, 1.5 Hz, 1H), 7.50 ppm (dd, $J = 8.1$, 4.8 Hz, 1H); $^{13}$C NMR (151 MHz, DMSO): $\delta = 151.7$, 149.4, 144.7, 142.4, 125.0, 119.6, 116.5 ppm; IR (ATR): $\tilde{\nu} = 2702$, 1702, 1688, 1419, 1327, 823, 645, 439 cm$^{-1}$; HRMS (FD): *m/z* calcd for $C_7H_4N_6O^+$: 188.0447; found: 188.0467.

**8-Methoxytetrazolo[1,5-*a*]quinoxalin-4(5*H*)-one (9j)**: According to the *general procedure A* using 3,3-diazido-5-methoxyindolin-2-one (**8j**, 60 mg, 0.24 mmol, 1.0 equiv), 8-methoxytetrazolo[1,5-*a*]quinoxalin-4(5*H*)-one (**9j**, 49 mg, 0.23 mmol, 92%) was obtained as a white solid. T (decomp.) $> 260\,^{\circ}$C; $^1$H NMR (600 MHz, DMSO): $\delta =$ 12.45 (s, 1H), 7.74 (d, $J = 2.7$ Hz, 1H), 7.45 (d, $J = 9.0$ Hz, 1H), 7.27 (dd, $J = 9.0$, 2.8 Hz, 1H), 3.91 ppm (s, 3H); $^{13}$C NMR (151 MHz, DMSO): $\delta = 155.7$, 150.6, 144.5, 123.3, 120.3, 118.2, 117.9, 99.9, 56.0 ppm; IR (ATR): $\tilde{\nu} = 3173$, 3109, 3085, 2961, 1699, 1662, 1607, 1354 1246, 1139, 1139, 832, 710 cm$^{-1}$; HRMS (FD): *m/z* calcd for $C_9H_7N_5O_2^+$: 217.0599; found: 217.0589.

**8-[(*tert*-Butyldimethylsilyl)oxy]tetrazolo[1,5-*a*]quinoxalin-4(5*H*)-one (9k)**: According to the *general procedure A* using 3,3-diazido-5-(*tert*-butyldimethylsilyl)oxy)indolin-2-one (**8k**, 70 mg, 0.20 mmol, 1.0 equiv), 8-((*tert*-butyldimethylsilyl)oxy)tetrazolo[1,5-*a*]quinoxalin-4(5*H*)-one (**9k**, 49 mg, 0.15 mmol, 76%) was obtained as a white solid. T (decomp.) 225 °C; $^1$H NMR (600 MHz, DMSO): $\delta = 12.45$ (s, 1H), 7.60 (d, $J = 2.6$ Hz, 1H), 7.41 (d, $J = 8.9$ Hz, 1H), 7.18 (dd, $J = 8.9$, 2.6 Hz, 1H), 0.98 (s, 9H), 0.25 ppm (s, 6H); $^{13}$C NMR (151 MHz, DMSO): $\delta = 151.2$, 150.6, 144.4, 124.0, 122.4, 120.3, 118.3, 106.6, 25.5, 17.9, −4.7 ppm; IR (ATR): $\tilde{\nu} = 2959$, 2894, 2856, 1715, 1670, 1630, 1526, 1311, 1197, 940, 779, 740 cm$^{-1}$; HRMS (FD): *m/z* calcd for $C_{14}H_{19}N_5O_2Si^+$: 317.1308; found: 317.1304.

**8-Bromopyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrazine-4(5*H*)-one (9l)**: According to the *general procedure A* using 3,3-diazido-5-bromo-1*H*-pyrrolo[2,3-*b*]pyridin-2(3*H*)-one (**8l**, 60 mg, 0.20 mmol, 1.0 equiv), 8-bromopyrido[2,3-*e*]tetrazolo[1,5-*a*]pyrazine-4(5*H*)-one (**9l**, 47 mg, 0.18 mmol, 87%) was obtained as a white solid. T (decomp.) 252 °C; $^1$H NMR (400 MHz, DMSO): $\delta = 13.22$ (s, 1H), 8.98 (d, $J = 2.2$ Hz, 1H), 8.76 ppm (d, $J = 2.2$ Hz, 1H); $^{13}$C NMR (101 MHz, DMSO): $\delta = 151.5$, 149.9, 144.8, 141.6, 126.9, 117.2, 113.2 ppm; IR (ATR): $\tilde{\nu} = 1703$, 1598, 1527, 1469, 1301, 1205, 900, 700, 667 cm$^{-1}$; HRMS (FD): *m/z* calcd for $C_7H_3N_6OBr^+$: 265.9552; found: 265.9527.

**Tetrazolo[1,5-*a*]quinoxalin-4(5*H*)-one (9a)**: According to the *general procedure B* using 2-indolone (**10a**, 100 mg, 0.73 mmol, 1.0 equiv), tetrazolo[1,5-*a*]quinoxalin-4(5*H*)-one (**9a**, 105 mg, 0.56 mmol, 77%) was obtained as a white solid. T (decomp./TGA) 287.9 °C; $^1$H NMR (400 MHz, DMSO): $\delta = 12.55$ (s, 1H), 8.26 (dd, $J = 8.2$, 1.0 Hz, 1H), 7.65–7.59 (m, 1H), 7.50 (dd $J = 8.3$, 0.9 Hz, 1H), 7.48–7.41 ppm (m, 1H); $^{13}$C NMR (101 MHz, DMSO): $\delta = 151.2$, 144.3, 129.9, 129.6, 123.9, 119.9, 116.9, 116.4 ppm. The analytical data are in agreement with those reported above.

**7-Chlorotetrazolo[1,5-*a*]quinoxalin-4(5*H*)-one (9b)**: According to the *general procedure B* using 6-chloroindolin-2-one (**10b**, 100 mg, 0.60 mmol, 1.0 equiv), 7-chlorotetrazolo[1,5-*a*]quinoxalin-4(5*H*)-one (**9b**, 81 mg, 0.37 mmol, 61%) was obtained as a white solid. T (decomp.) $> 260\,^{\circ}$C; $^1$H NMR (400 MHz, DMSO): $\delta = 12.62$ (s, 1H), 8.34–8.18 (m, 1H), 7.73–7.26 ppm (m, 2H); $^{13}$C NMR (101 MHz, DMSO): $\delta = 151.2$, 144.3, 133.8, 130.9, 123.8, 119.0, 118.2, 116.1 ppm. The analytical data are in agreement with those reported above.

**8-Bromotetrazolo[1,5-*a*]quinoxalin-4(5*H*)-one (9f)**: According to the *general procedure B* using 5-bromoindolin-2-one (**10f**, 100 mg, 0.47 mmol, 1.0 equiv), 8-bromotetrazolo[1,5-*a*]quinoxalin-4(5*H*)-one (**9f**, 88 mg, 0.33 mmol, 70%) was obtained as a white solid. T (decomp.) 244 °C; $^1$H NMR (400 MHz, DMSO): $\delta = 12.65$ (s, 1H), 8.41 (d, $J = 2.1$ Hz, 1H), 7.80 (dd, $J = 8.8$, 2.2 Hz, 1H), 7.43 ppm (d, $J = 8.8$ Hz, 1H); $^{13}$C NMR (101 MHz, DMSO): $\delta = 151.1$, 144.5, 132.7, 129.0, 120.9, 118.8, 118.8, 115.1 ppm. The analytical data are in agreement with those reported above.

**Phenyl(1-phenyl-1*H*-tetrazol-5-yl)methanone (12a)**: According to the *general procedure C* using 2,2-diazido-1,2-diphenylethanone (**11a**, 65 mg, 0.23 mmol, 1.0 equiv), phenyl(1-phenyl-1*H*-tetrazol-5-yl)methanone (**12a**, 54 mg, 0.22 mmol, 92%) was obtained as a white solid after chromatography (*n*-pentane/EtOAc 95:5→8:2). T (m.p.) 89 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 8.28$–8.22 (m, 2H), 7.76–7.67 (m, 1H), 7.59–7.47 ppm (m, 7H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta = 181.6$, 150.1, 135.6, 134.9, 134.3, 131.0, 130.8, 129.7, 129.2, 125.1 ppm; IR (ATR): $\tilde{\nu} = 1674$, 1593, 1302, 1212, 1179, 916, 710 cm$^{-1}$; HRMS (ESI-TOF): *m/z* calcd for $C_{14}H_{10}N_4NaO^+$: 273.0733; found: 273.0747.

**(4-Methoxyphenyl)(1-phenyl-1*H*-tetrazol-5-yl)methanone (12b)**: According to the *general procedure C* using 2,2-diazido-1-(4-methoxyphenyl)-2-phenylethanone (**11b**, 50 mg, 0.16 mmol, 1.0 equiv), (4-methoxyphenyl)(1-phenyl-1*H*-tetrazol-5-yl)methanone (**12b**, 42 mg, 0.15 mmol, 92%) was obtained as a white solid after chromatography (*n*-pentane/EtOAc 95:5→8:2). T (m.p.) 108 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 8.30$–8.15 (m, 2H), 7.62–7.43 (m, 5H), 7.08–6.86 (m, 2H), 3.91 ppm (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta =$ 179.8, 165.7, 150.3, 134.3, 133.7, 130.7, 129.8, 128.0, 125.0, 114.5, 55.9 ppm; IR (ATR): $\tilde{\nu} = 3065$, 3007, 2923, 2849, 1646, 1598, 1566, 1305, 1171, 705, 668 cm$^{-1}$; HRMS (FD): *m/z* calcd for $C_{15}H_{12}N_4NaO_2^+$ : 303.0852; found: 303.0854.

**Phenyl(1-phenyl-1*H*-tetrazol-5-yl)methanone (12a)**: According to the *general procedure D* using 1,2-diphenylethanone (**13a**, 80 mg, 0.41 mmol, 1.0 equiv), phenyl(1-phenyl-1*H*-tetrazol-5-yl)methanone (**12a**, 72 mg, 0.29 mmol, 71%) was obtained as a white solid after chromatography (*n*-pentane/EtOAc 95:5→8:2). T (m.p.) 89 °C; $^1$H NMR (600 MHz, $CDCl_3$): $\delta = 8.26$–8.23 (m, 2H), 7.74–7.69 (m, 1H), 7.58–7.52 (m, 5H), 7.51–7.48 ppm (m, 2H); $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta = 181.6$, 150.1, 135.6, 134.9, 134.2, 131.0, 130.8, 129.7, 129.1, 125.1 ppm. The analytical data are in agreement with those reported above.

**(4-Methoxyphenyl)(1-phenyl-1*H*-tetrazol-5-yl)methanone (12b)**: According to the *general procedure D* using 1-(4-methoxyphenyl)-2-phenylethanone (**13b**, 50 mg, 0.22 mmol, 1.0 equiv), (4-methoxyphenyl)(1-phenyl-1*H*-tetrazol-5-yl)methanone (**12b**, 44 mg, 0.16 mmol, 71%) was obtained as a white solid after chromatography (cyclohexane/EtOAc 95:5→8:2). T (m.p.) 108 °C; $^1$H NMR (400 MHz, DMSO): $\delta = 8.30$–8.19 (m, 2H), 7.59–7.46 (m, 5H), 7.06–6.97 (m, 2H), 3.92 ppm (s, 3H); $^{13}$C NMR (101 MHz, DMSO): $\delta =$ 179.8, 165.7, 150.3, 134.3, 133.7, 130.7, 129.7, 128.0, 125.0, 114.5, 55.9 ppm. The analytical data are in agreement with those reported above.

***p*-Tolyl[1-(*p*-tolyl)-1*H*-tetrazol-5-yl]methanone (12c)**: According to the *general procedure D* using 1,2-di-*p*-tolylethanone (**13c**, 100 mg, 0.45 mmol, 1.0 equiv), *p*-tolyl[1-(*p*-tolyl)-1*H*-tetrazol-5-yl]methanone (**12c**, 52 mg, 0.19 mmol, 42%) was obtained as a white solid after chromatography (*n*-pentane/EtOAc 95:5→8:2). T (m.p.) 115 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta = 8.19$–8.07 (m, 2H), 7.40–7.28 (m, 6H), 2.46 (s, 3H), 2.43 ppm (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta = 181.3$, 150.2, 147.1, 141.1, 132.6, 131.8, 131.1, 130.3, 129.9, 124.8, 22.1, 21.4 ppm; IR (ATR): $\tilde{\nu} = 2924$, 1653, 1601, 1515, 1302, 916, 821, 770 cm$^{-1}$; HRMS (ESI-TOF): *m/z* calcd for $C_{16}H_{14}N_4NaO$: 301.1060; found: 301.1062.

**[1-(3-Chlorophenyl)-1*H*-tetrazol-5-yl](4-methoxyphenyl)methanone (12d)**: According to the *general procedure D* using 2-(3-chlorophenyl)-1-(4-methoxyphenyl)ethanone (**13d**, 110 mg, 0.42 mmol,

1.0 equiv), [1-(3-chlorophenyl)-1*H*-tetrazol-5-yl](4-methoxyphenyl)-methanone (**12d**, 78 mg, 0.25 mmol, 59%) was obtained as a white solid after chromatography (*n*-pentane/EtOAc 95:5→8:2). T (m.p.) 120 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.35–8.22 (m, 2H), 7.57–7.52 (m, 2H), 7.50–7.45 (m, 1H), 7.40 (ddd, $J$ = 7.9, 1.9, 1.3 Hz, 1H), 7.08–6.97 (m, 2H), 3.93 ppm (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 179.4, 165.9, 150.3, 135.5, 135.3, 133.8, 131.0, 130.6, 127.9, 125.5, 123.4, 114.6, 55.9 ppm; IR (ATR): $\tilde{\nu}$ = 3071, 2940, 2844, 1640, 1592, 1566, 1476, 1266, 1173, 793, 645 cm$^{-1}$; HRMS (ESI-TOF): *m/z* calcd for $C_{15}H_{11}ClN_4NaO_2^+$: 337.0463; found: 337.0451.

***m*-Tolyl[1-(*m*-tolyl)-1*H*-tetrazol-5-yl]methanone (12e)**: According to the *general procedure D* using 1,2-di-*m*-tolylethanone (**13e**, 140 mg, 0.56 mmol, 1.0 equiv), *m*-tolyl[1-(*m*-tolyl)-1*H*-tetrazol-5-yl]-methanone (**12e**, 96 mg, 0.34 mmol, 61%) was obtained as a white solid after chromatography (*n*-pentane/EtOAc 95:5→8:2). T (m.p.) 119 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.03–7.98 (m, 1H), 7.54–7.49 (m, 1H), 7.45–7.30 (m, 2H), 7.26–7.22 (m, 1H), 2.42 (s, 2H), 2.41 ppm (s, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 181.9, 150.2, 140.1, 139.1, 136.4, 134.9, 134.1, 131.5, 131.2, 129.4, 129.0, 128.3, 125.5, 122.0, 21.4, 21.3 cm$^{-1}$; IR (ATR): $\tilde{\nu}$ = 2924, 1654, 1601, 1472, 1207, 1173, 916, 821, 770 522 cm$^{-1}$; HRMS (ESI-TOF): *m/z* calcd for $C_{16}H_{14}N_4NaO^+$: 301.1060; found: 301.1057.

**10,10-Diazidophenanthren-9(10*H*)-one (15)**: 9-Phenanthrol (**14**, 400 mg, 2.06 mmol, 1.0 equiv) was dissolved in DMSO (21 mL, 0.1 M), and sodium azide (807 mg, 12.36 mmol, 6.0 equiv) and iodine (1.16 g, 4.53 mmol, 2.2 equiv) were added. The reaction mixture was stirred for 14 h at RT. The mixture was diluted with ice-cold water and some drops of a saturated aqueous solution of sodium thiosulfate and extracted with ethyl acetate. The combined organic phases were washed with brine and dried with magnesium sulfate. Evaporation of the solvent in vacuo and flash chromatography on silica gel (*n*-pentane→*n*-pentane/EtOAc 9:1) afforded the 10,10-diazidophenanthren-9(10*H*)-one (**15**, 437 mg, 1.58 mmol, 77%) as a white solid. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.09–8.04 (m, 1H), 7.99–7.95 (m, 2H), 7.81 (dd, $J$ = 7.8, 1.2 Hz, 1H), 7.77–7.71 (m, 1H), 7.56 (td, $J$ = 7.7, 1.5 Hz, 1H), 7.51–7.45 ppm (m, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 190.6, 136.4, 135.9, 131.3, 130.9, 130.6, 129.7, 129.4, 129.0, 128.3, 127.6, 124.9, 123.7, 80.5 ppm; IR (ATR): $\tilde{\nu}$ = 2013, 1702, 1596, 1448, 1261, 1224, 727 cm$^{-1}$; HRMS (FD): *m/z* calcd for $C_{14}H_8N_6O^+$: 276.0759; found: 276.0736.

**9*H*-Dibenzo[*d*,*f*]tetrazolo[1,5-*a*]azepin-9-one (16)**: 10,10-Diazidophenanthren-9(10*H*)-one (**15**, 70 mg, 0.25 mmol, 1.0 equiv) was dissolved in *o*-xylene (6 mL, 0.04 M) and the reaction mixture was heated at 140 °C under microwave irradiation for 2 h. The mixture was cooled down to 5 °C and the solid was filtered off and washed with a small amount of cold *o*-xylene. 9*H*-Dibenzo[*d*,*f*]tetrazolo[1,5-*a*]azepin-9-one (**16**, 57 mg, 0.23 mmol, 91%) was obtained as a white solid. T (decomp.) 234 °C; $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 8.20–8.18 (m, 1H), 8.02 (dd, $J$ = 7.8, 1.3 Hz, 1H), 7.88–7.83 (m, 2H), 7.80 (td, $J$ = 7.7, 1.4 Hz, 1H), 7.72–7.64 ppm (m, 3H); $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ = 180.5, 153.6, 138.6, 135.2, 134.3, 132.7, 131.1, 131.0, 130.7, 130.5, 130.0, 129.5, 129.4, 123.9 ppm; IR (ATR): $\tilde{\nu}$ = 1679, 1593, 1293, 1216, 925, 756, 736 cm$^{-1}$; HRMS (ESI-TOF): *m/z* calcd for $C_{14}H_8N_4NaO^+$: 271.0590; found: 271.0595.

**9*H*-Dibenzo[*d*,*f*]tetrazolo[1,5-*a*]azepin-9-one (16)**: 9-Phenanthrol (**14**, 120 mg, 0.62 mmol, 1.0 equiv) was dissolved in DMSO (6 mL, 0.1 M), and sodium azide (242 mg, 3.71 mmol, 6.0 equiv) and iodine (350 mg, 1.36 mmol, 2.2 equiv) were added. The reaction mixture was stirred for 14 h at RT. The mixture was diluted with ice-cold water and some drops of a saturated aqueous solution of sodium thiosulfate were added, and the mixture was extracted with *o*-xylene (12 mL). The combined organic phases were washed with a saturated aqueous solution of sodium bicarbonate and brine and dried with magnesium sulfate. The solution was transferred into a microwave tube and stirred for 2 h at 140 °C under microwave irradiation. The solution was concentrated in vacuo and flash chromatography on silica gel (*n*-pentane/EtOAc 95:5 → 85:15) afforded the 9*H*-dibenzo[*d*,*f*]tetrazolo[1,5-*a*]azepin-9-one (**16**, 74 mg, 0.30 mmol, 48%) as a white solid. $^1$H NMR (600 MHz, CDCl3): $\delta$ = 8.20–8.17 (m, 1H), 8.03 (dd, $J$ = 7.8, 1.2 Hz, 1H), 7.91–7.79 (m, 3H), 7.76–7.64 ppm (m, 3H); $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ = 180.5, 153.4, 138.3, 135.1, 134.5, 132.7, 131.1, 130.8, 130.7, 130.5, 130.0, 129.5, 129.2, 123.8 ppm. The analytical data are in agreement with those reported above.

**4,4-Diazido-3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one (17a)**: According to the *general procedure E* using 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one (**18a**, 100 mg, 0.574 mmol, 1.0 equiv), 4,4-diazido-3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one (**17a**, 83 mg, 0.32 mmol, 56%) was obtained as yellow solid after chromatography (*n*-pentane/$CH_2Cl_2$ 10:0→9:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.89–7.83 (m, 2H), 7.47–7.39 (m, 2H), 7.28–7.22 (m, 1H), 2.16 ppm (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 163.9, 155.6, 136.9, 129.2, 126.2, 118.9, 76.8, 13.0 ppm; IR (ATR): $\tilde{\nu}$ = 3039, 2924, 2119, 1722, 1512, 1189, 816 cm$^{-1}$; HRMS (ESI-TOF): *m/z* calcd for $C_{10}H_8N_8NaO^+$: 279.0713; found: 279.0715.

**4,4-Diazido-1-methyl-3-propyl-1*H*-pyrazol-5(4*H*)-one (17b)**: According to the *general procedure E* using 1-methyl-3-propyl-1*H*-pyrazol-5(4*H*)-one (**18b**, 830 mg, 5.74 mmol, 1.0 equiv), 4,4-diazido-1-methyl-3-propyl-1*H*-pyrazol-5(4*H*)-one (**17b**, 701 mg, 3.16 mmol, 55%) was obtained as a yellow oil after chromatography (cyclohexane/$CH_2Cl_2$ 10:0→8:2). $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 3.31 (s, 3H), 2.32 (t, $J$ = 7.5 Hz, 2H), 1.70 (h, $J$ = 7.4 Hz, 2H), 0.99 ppm (t, $J$ = 7.4 Hz, 3H); $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ = 165.8, 157.8, 75.8, 31.7, 29.2, 18.4, 13.9 ppm; IR (ATR): $\tilde{\nu}$ = 2966, 2936, 2877, 2099, 1724, 1200, 960 cm$^{-1}$; HRMS (ESI-TOF): *m/z* calcd for $C_7H_{10}N_8NaO^+$: 245.0870; found: 245.0871.

**4,4-Diazido-1-(4-bromophenyl)-3-methyl-1*H*-pyrazol-5(4*H*)-one (17c)**: According to the *general procedure E* using 1-(4-bromophenyl)-3-methyl-1*H*-pyrazol-5(4*H*)-one (**18c**, 100 mg, 0.387 mmol, 1.0 equiv), 4,4-diazido-1-(4-bromophenyl)-3-methyl-1*H*-pyrazol-5(4*H*)-one (**17c**, 60 mg, 0.18 mmol, 46%) was obtained as a white solid after chromatography ($CH_2Cl_2$/EtOAc 10:0→9:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.79–7.75 (m, 2H), 7.56–7.52 (m, 2H), 2.16 ppm (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$): $\delta$ = 163.9, 156.0, 135.9, 132.3, 120.3, 119.3, 76.8, 13.0 ppm; IR (ATR): $\tilde{\nu}$ = 3438, 3335, 3183, 2105, 1712, 1643, 1594, 1363, 1194, 964, 752 cm$^{-1}$; HRMS (ESI-TOF): *m/z* calcd for $C_{10}H_7BrN_8NaO^+$: 356.9818; found: 356.9817.

**8-Methyl-6-phenyltetrazolo[1,5-*d*][1,2,4]triazin-5(6*H*)-one (19a)**: According to the *general procedure C* using 4,4-diazido-3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one (**17a**, 39 mg, 0.15 mmol, 1.0 equiv), 8-methyl-6-phenyltetrazolo[1,5-*d*][1,2,4]triazin-5(6*H*)-one (**19a**, 2 mg, 0.095 mmol, 62%) was obtained as a white solid after chromatography ($CH_2Cl_2$/EtOAc 10:0→9:1). T (decomp.) 191 °C; $^1$H NMR (400 MHz, DMSO): $\delta$ = 7.61–7.54 (m, 4H), 7.52–7.46 (m, 1H), 2.81 ppm (s, 3H); $^{13}$C NMR (101 MHz, DMSO): $\delta$ = 150.4, 145.9, 139.4, 134.4, 129.0, 128.6, 125.7, 16.0 ppm; IR (ATR): $\tilde{\nu}$ = 3063. 2928, 1709, 1634, 1491,1354, 1194,1132, 967, 777 cm$^{-1}$; HRMS (FD): *m/z* calcd for $C_{10}H_8N_6O^+$: 228.0759; found: 228.0760.

**6-Methyl-8-propyltetrazolo[1,5-*d*][1,2,4]triazin-5(6*H*)-one (19b)**: According to the *general procedure C* using 4,4-diazido-1-methyl-3-propyl-1*H*-pyrazol-5(4*H*)-one (**17b**, 40 mg, 0.18 mmol, 1.0 equiv), 6-methyl-8-propyltetrazolo[1,5-*d*][1,2,4]triazin-5(6*H*)-one (**19b**, 25 mg, 0.13 mmol, 70%) was obtained as a colorless oil after chromatography ($CH_2Cl_2$/EtOAc 10:0→9:1). $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ = 3.80 (s, 3H), 3.17 (t, $J$ = 7.7 Hz, 2H), 1.94 (h, $J$ = 7.4 Hz, 2H), 1.09 ppm (t, $J$ = 7.4 Hz, 3H); $^{13}$C NMR (151 MHz, $CDCl_3$): $\delta$ = 150.2, 144.5, 137.1,

38.6, 32.0, 19.2, 13.6 ppm; IR (ATR): $\tilde{\nu}$ = 2967, 2935, 2877, 1696, 1622, 1455, 965 $cm^{-1}$; HRMS (FD): *m/z* calcd for $C_7H_{10}N_6O^+$: 194.0916; found: 194.0911.

**6-(4-Bromophenyl)-8-methyltetrazolo[1,5-*d*][1,2,4]triazin-5(6*H*)-one (19c)**: According to the *general procedure C* using 4,4-diazido-1-(4-bromophenyl)-3-methyl-1*H*-pyrazol-5(4*H*)-one (**17c**, 41 mg, 0.12 mmol, 1.0 equiv), 6-(4-bromophenyl)-8-methyltetrazolo[1,5-*d*][1,2,4]triazin-5(6*H*)-one (**19c**, 27 mg, 0.087 mmol, 71%) was obtained as a white solid after chromatography ($CH_2Cl_2$/EtOAc 10:0→9:1). T (decomp.) 191 °C; $^1$H NMR (400 MHz, DMSO): $\delta$ = 7.82–7.73 (m, 2H), 7.61–7.52 (m, 2H), 2.82 ppm (s, 3H); $^{13}$C NMR (101 MHz, DMSO): $\delta$ = 150.3, 145.8, 138.6, 134.7, 132.0, 127.6, 121.4, 16.0 ppm; IR (ATR): $\tilde{\nu}$ = 3097, 1713, 1632, 1458, 1404, 1346, 1289, 839 $cm^{-1}$; HRMS (FD): *m/z* calcd for $C_{10}H_7N_6O^+$: 305.9860; found: 305.9865.

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## Conflict of interest

The authors declare no conflict of interest.

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