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# Thiazolo[3,4-*b*]indazole-2,2-dioxides as Masked Extended Dipoles: Pericyclic Reactions of Benzodiazafulvenium Methides

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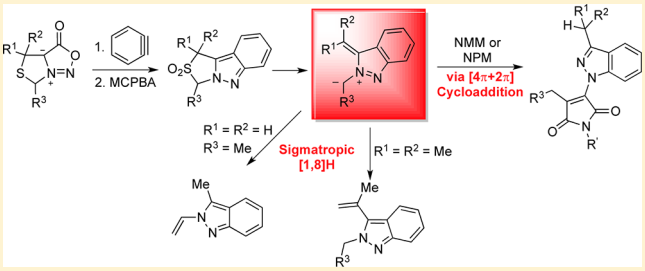
Supporting Information

**ABSTRACT:** Herein we report the first examples of 1,3-dipolar cycloadditions of thiazolidine-derived sydnones with benzyne leading to 1,3-dihydrothiazolo[3,4-*b*]indazoles. These heterocycles were converted into the corresponding sulfones which were used as precursors of novel benzo-2,3-diazafulvenium methides. These reactive intermediates reacted with *N*-substituted maleimides affording new 1*H*-indazoles characterized by an intense yellow color, a property that gives them a potential application as dyes. The synthesis of these heterocycles was rationalized considering the initial 1,3-cycloaddition of benzodiazafulvenium methides to maleimides. This chemical behavior is in contrast with the previously observed reactivity for 4,5-(methoxycarbonyl)diazafulvenium methides, which participate exclusively in [8$\pi$ + 2$\pi$] cycloadditions to give 1,7-cycloadducts. Quantum chemical calculations, carried out at the DFT level of theory, were in agreement with the rationalization of the observed reactivity. Under flash vacuum pyrolysis or under microwave irradiation, 1-methyl- and 7,7-dimethylbenzo-2,3-diazafulvenium methides undergo sigmatropic [1,8]H shifts allowing the efficient synthesis of *N*-vinyl- and *C*-vinyl-2*H*-indazoles.




## 1. INTRODUCTION

The study of pericyclic reactions of aza- and diazafulvenium methide systems **1** and **2** is one of our current research interests.[1] After the pioneering work of Storr and co-workers[2] describing the first evidence for trapping of these transient dipolar systems in pericyclic reactions, we further explored this chemistry and demonstrated their versatility as building blocks for the synthesis of heterocyclic compounds. Aza- and diazafulvenium methides are generated from 1*H*,3*H*-pyrrolo-[1,2-*c*]thiazole-2,2-dioxides and 1*H*,3*H*-pyrazolo[1,5-*c*]thiazole-2,2-dioxides, respectively, by thermal extrusion of sulfur dioxide. These "higher-order" azomethine ylides and azomethine imines can act as 4$\pi$ 1,3-dipoles or as 8$\pi$ 1,7-dipoles although the typical reactivity pattern is that expected for 1,7-dipoles. In fact, only with 5-(trifluoromethyl)azafulvenium methides did we observe evidence of azafulvenium methides acting as a 1,3-dipole.[1f] Thus, 1,7-dipoles **3**-**6** participate in sigmatropic [1,8]H shifts giving vinylpyrroles and vinylpyrazoles (Scheme 1).

Azafulvenium methides **7** can be intercepted in microwave-induced [8$\pi$ + 2$\pi$] cycloadditions affording 1,7-cycloadducts.[1e] Diazafulvenium methides **8** also behave as 8$\pi$ 1,7-dipoles either under microwave irradiation or conventional heating giving pyrazolo-annulated heterocycles.[1g−j] This synthetic methodology was used to obtain a new type of stable 4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyridine-fused chlorines **10** and bacteriochlorins **11**, macrocycles with potential for various biomedical applications (Scheme 2).[1i,j]

Our goal is to broaden the study to new extended dipolar systems capable of participating in pericyclic reactions, as a way of developing new synthetic routes to heterocycles. Indazoles were selected as our target scaffold, a class of compounds displaying a wide variety of biological activities but rare in nature, making the chemistry of indazoles of considerable interest.[3] In recent years, significant efforts have been made to find synthetic strategies to avoid harsh reaction conditions of some of the known methods and to widen the diversity of substituted indazole derivatives. Several synthetic approaches involve the construction of the pyrazole ring from suitable 1,2-substituted benzene derivatives.[3a,b] More recently, the syntheses of indazoles based on addition reactions to arynes have been reported.[4] These include [3 + 2] cycloaddition of arynes with diazo compounds,[4a−c] with nitrile imines,[4d] and with sydnones[4e,f] and [3 + 2] annulation of arynes with *N*-tosylhydrazones.[4g,h] The synthesis of pyridino[1,2-*b*]indazoles via 1,3-dipolar cycloaddition of arynes has also been described.[5] In this context, we envisaged that thiazolo[3,4-*b*]indazoles **13** could be obtained by the cycloaddition of benzyne with sydnones **12** and converted into the corresponding sulfones **14**. Pericyclic reactions of the novel reactive species derived from thiazolo[3,4-*b*]indazole-2,2-dioxides **14** and benzo-2,3-diazafulvenium methides **15** would give access to functionalized indazoles (Scheme 3).

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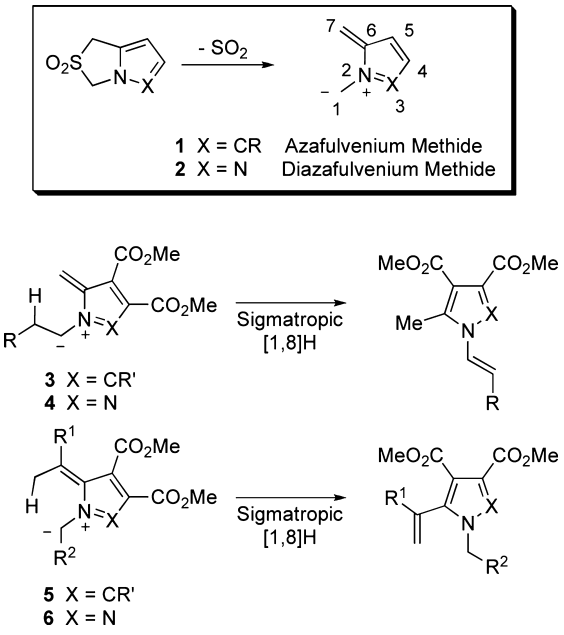
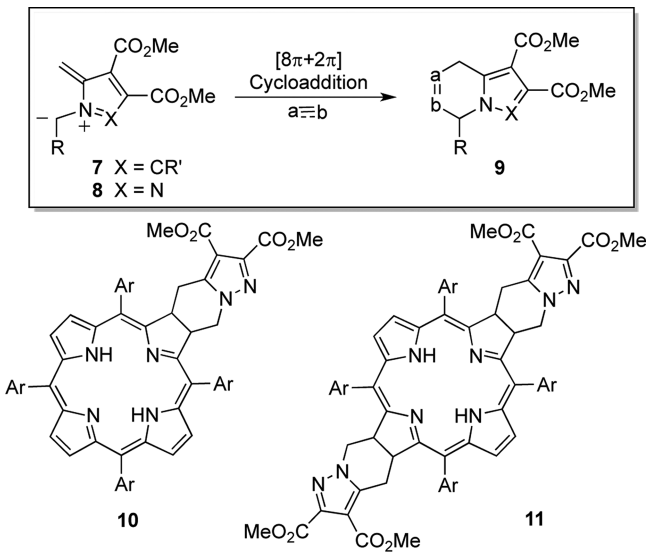
**Scheme 1. Pericyclic Reactions of Aza- and Diazafulvenium Methides**



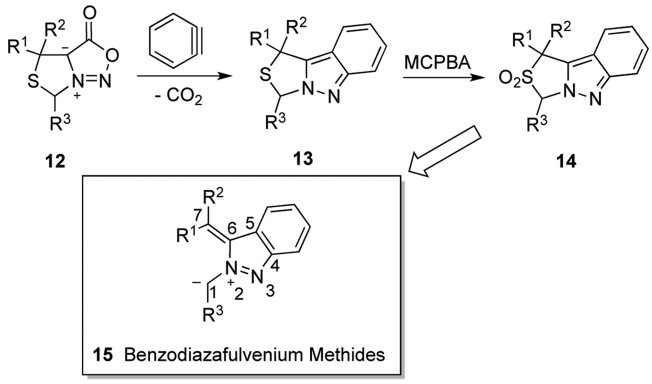

**Scheme 2. [8π + 2π] Cycloaddition of Aza- and Diazafulvenium Methides**




## 2. RESULTS AND DISCUSSION

**Synthesis of Thiazolo[3,4-*b*]indazole-2,2-dioxides.** The approach for the synthesis of thiazolo[3,4-*b*]indazole-2,2-dioxides is outlined in Scheme 4. Thiazolidine-derived sydnones **12** are stable mesoionic species which can be isolated and undergo 1,3-dipolar cycloaddition with dipolarophiles such as acetylene dicarboxylates giving 1*H*,3*H*-pyrazolo[1,5-*c*]-thiazole derivatives.[1,6] On the other hand, arynes have demonstrated good reactivity as dipolarophiles in several 1,3-dipolar cycloaddition reactions leading to 2*H*-indazole, including in the reaction with a proline-derived sydnone.[4e,f] Thus, dihydrothiazolo[3,4-*b*]indazoles **13a** and **13b** were prepared by 1,3-dipolar cycloaddition of the corresponding thiazolidine-derived sydnones **12** with benzyne, generated either from *o*-(trimethylsilyl)phenyl triflate[7] in the presence

**Scheme 3. Synthetic Strategy for the Generation of Benzo-2,3-diazafulvenium Methides**




of fluoride ion (method A and B) or from the reaction of anthranilic acid with isoamyl nitrite (method C) (Table 1). Dihydrothiazolo[3,4-*b*]indazole **13a** was obtained in moderate yield from the fluoride-induced 1,2-elimination of *o*-trimethylsilyltriflate using CsF in acetonitrile (method A, entry 1). Attempts to improve the efficiency of this synthesis, either by increasing the number of equivalents of the benzyne precursor or by carrying out the reaction at various reaction temperatures, were unsuccessful. Changing the fluoride source from CsF to tetra-*n*-butylamonium fluoride (TBAF) also did not lead to any improvement (method B, entry 2). When benzyne was generated from anthranilic acid in the presence of isoamyl nitrite, by decomposition of the internal benzenediazonium-2-carboxylate, the target compound **13a** was obtained in 31% yield (method C, entry 3). Dihydrothiazolo[3,4-*b*]indazole **13b** was obtained in moderate yields by using either *o*-(trimethylsilyl)phenyl triflate or anthranilic acid as benzyne precursor (entries 4 and 5). Since compounds **13a** and **13b** were obtained in moderate yields regardless of the methodology used to generate benzyne and considering that anthranilic acid is an easily available reagent, the synthesis of dihydrothiazolo[3,4-*b*]indazoles **13c** and **13d** was carried out using only method C. We were pleased to observed that starting from sydnones **12c** and **12d** the corresponding 1,1-dimethyl-dihydrothiazolo[3,4-*b*]indazoles **13c** and **13d** could be obtained in 66% and 62% yield, respectively (entries 6 and 7). It is worth noting that the synthesis of this new type of indazole-annulated system represents the first examples of 1,3-dipolar cycloaddition of thiazolidine-derived sydnones with benzyne acting as dipolarophile.

1,3-Dihydrothiazolo[3,4-*b*]indazole-2,2-dioxides **14** were obtained in good yield from the oxidation of thiazolo[3,4-*b*]indazole derivatives **13** with *m*-chloroperoxybenzoic acid (MCPBA) (Scheme 4, Table 2).

**Generation and Reactivity of Benzo-2,3-diazafulvenium Methides.** The first evidence for the generation of benzo-2,3-diazafulvenium methides **15** came from the extrusion of $SO_2$ from sulfones **14** in presence of maleimides under conventional thermolysis or under microwave irradiation (Table 3). The expected 1,7-cycloadducts were not formed, and 4-(1*H*-indazol-1-yl)-1*H*-pyrrole-2,5-dione derivatives **18** were isolated instead.

In fact, the reaction of unsubstituted 1,3-dihydrothiazolo[3,4-*b*]indazole-2,2-dioxide (**14a**) and *N*-methylmaleimide (NMM) in boiling 1,2,4-trichlorobenzene (1,2,4-TCB) afforded one product in 27% yield isolated as a solid (Table 3, entry 1). The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**Scheme 4. Synthesis of 1,3-Dihydrothiazolo[3,4-*b*]indazoles 13 and 1,3-Dihydrothiazolo[3,4-*b*]indazole-2,2-dioxides 14**

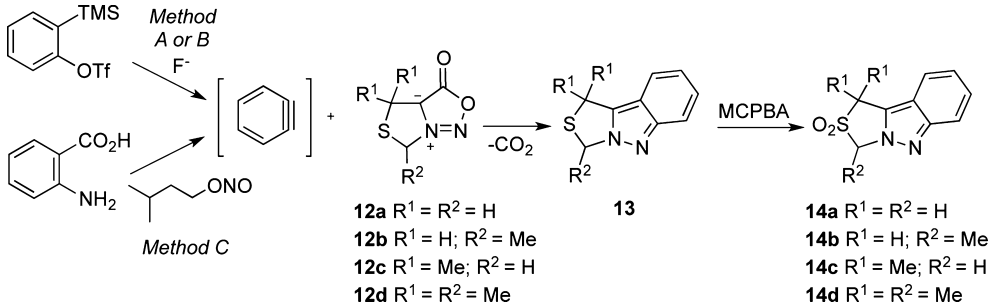


**Table 1. Synthesis of 1,3-Dihydrothiazolo[3,4-*b*]indazoles 13**

| entry | sydnone | method | reaction conditions | **13**, isolated yield (%) |
|---|---|---|---|---|
| 1 | **12a** | A | CsF, $CH_3CN$, 80 °C, 24 h | **13a**, 29 |
| 2 | **12a** | B | TBAF, THF, r.t., 19 h | **13a**, 28 |
| 3 | **12a** | C | DCM, reflux[a] | **13a**, 31 |
| 4 | **12b** | B | TBAF, THF, r.t., 12 h | **13b**, 26 |
| 5 | **12b** | C | DCM, reflux[a] | **13b**, 40 |
| 6 | **12c** | C | DCM, reflux, 1 h | **13c**, 66 |
| 7 | **12d** | C | DCM, reflux[a] | **13d**, 62 |

[a]The reaction was complete after finishing the addition of the anthranilic acid solution.

**Table 2. Synthesis of 1,3-Dihydrothiazolo[3,4-*b*]indazole-2,2-dioxides 14**

| entry | substrate | reaction time (h) | **14**, isolated yield (%) |
|---|---|---|---|
| 1 | **13a** | 1.5 | **14a**, 74 |
| 2 | **13b** | 2 | **14b**, 53 |
| 3 | **13c** | 4 | **14c**, 66 |
| 4 | **13d** | 2 | **14d**, 74 |

same product was obtained in 35% yield when the reaction was carried out under microwave irradiation (MW) at 230 °C for 10 min (Table 3, entry 2). The structure of this heterocycle could only be unambiguously established by X-ray crystallography as being 4-(1*H*-indazol-1-yl)-1*H*-pyrrole-2,5-dione **18a** (Figure S52).

The reaction of **14a** and *N*-phenylmaleimide (NPM) under conventional thermolysis or under microwave irradiation also afforded the corresponding indazole derivative **18b** in yields ranging from 20% to 40% (Table 3, entries 3−10).

The chemical behavior of 1,3-dihydrothiazolo[3,4-*b*]-indazole-2,2-dioxides **14b−d** under microwave-induced thermolysis in 1,2,4-trichlorobenzene in the presence of *N*-substituted maleimides was similar to the one observed for sulfone **14a**, giving the corresponding indazole derivatives **18** in moderate yield (Table 3, entries 11−16). However, in the case of the reaction of maleimides with benzo-2,3-diazafulvenium methide **15b**, the indazoles **18c** and **18d** could only be obtained in low yield (Table 3, entries 11 and 12).

The synthesis of 1*H*-indazoles **18** can be rationalized considering that initially benzodiazafulvenium methides **15** react with maleimides affording cycloadducts **16**, resulting from the addition across the 1,3-position. Cycloadducts **16** undergo pyrazolidine ring-opening, followed by a sigmatropic H-shift giving the more stable 1*H*-indazoles **18**. It is noteworthy that the new 1*H*-indazoles **18**, with an unusual substitution pattern, are characterized by an intense yellow color, a property that gives them a potential application as dyes.

We have previously observed that diazafulvenium methides with the general structure **8** participate in [8π + 2π] cycloadditions, and addition to 1,3-positions was never observed.[1g,h,e] The [8π + 2π] cycloadditions of dipole **8** (R = H) was observed to occur with both electron-rich and electron-deficient dipolarophiles, whereas 1,7-dipole **8** (R = Me) only reacts with electron-deficient dipolarophiles. An illustrative example of the typical reactivity of diazafulvenium methides **8** is shown in Scheme 5. The thermolysis of 1*H*,3*H*-pyrazolo[1,5-*c*][1,3]thiazole-2,2-dioxide **19** in refluxing 1,2,4-trichlorobenzene for 7 h in the presence of *N*-phenylmaleimide gives hexahydro-5*H*-pyrrolo[3′,4′:5,6]pyrazolo[1,5-*a*]pyridine **20** in high yield via [8π + 2π] cycloaddition of diazafulvenium methide **8a**.[1h] Carrying out the microwave irradiation of sulfone **19** at 260 °C for 20 min in the presence of *N*-phenylmaleimide affords heterocycle **20** in 44% yield.

In contrast with these observations, here it was reported that benzodiazafulvenium methides **15** behave as 1,3-dipoles on reacting with maleimides. On the other hand, attempts to intercept dipole **15** by carrying out thermolysis (MW, 230 °C, 10 min) in the presence of bis(trimethylsilyl)acetylene, furan-2,5-dione, and 2,3-dihydrofuran were unsuccessful. Thus, the reactivity of benzodiazafulvenium methides **15** toward dipolarophiles is quite distinct from diazafulvenium methides **8**, since they could only be intercepted with *N*-substituted maleimides via [4π + 2π] cycloaddition.

In order to be able to rationalize the different chemical behavior of benzodiazafulvenium methides **15** and diazafulvenium methides **8** toward dipolarophiles, quantum chemical calculations were carried out at the DFT level of theory (see Supporting Information). The B3LYP functional, selected for this task, has been shown to be an effective method for modeling dipolar cycloadditions.[8] Cycloadditions of benzodiazafulvenium methide **15a** and diazafulvenium methide **8a** with *N*-phenylmaleimide (NPM) were selected as the model reactions. Full geometry optimizations were performed, followed by harmonic frequency calculations, at the same level of theory, which also allowed characterization of the nature of the stationary points. For the dipole diazafulvenium **8a**, four different conformers were found by performing a systematic variation of the two relevant torsion angles [τCC−C═O) and τNC−C═O)], from 0° to 360°, with increments of 90° (Figure S49). Nonetheless, only the two lower energy conformers **8a**C1 and **8a**C2 were used in the cycloaddition reaction modeling studies. The dipole benzodiazafulvenium methide **15a** was found to be planar, and only this structure was used in the cycloaddition calculations (Figure S50). For the dipolarophile *N*-phenylmaleimide, it was found that the phenyl


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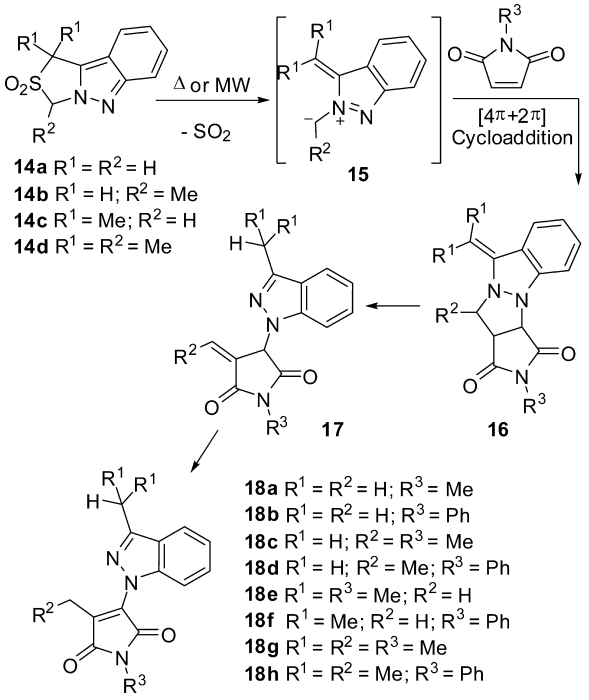
**Table 3. Reaction of Benzo-2,3-diazafulvenium Methides 15 with *N*-Substituted Maleimides**

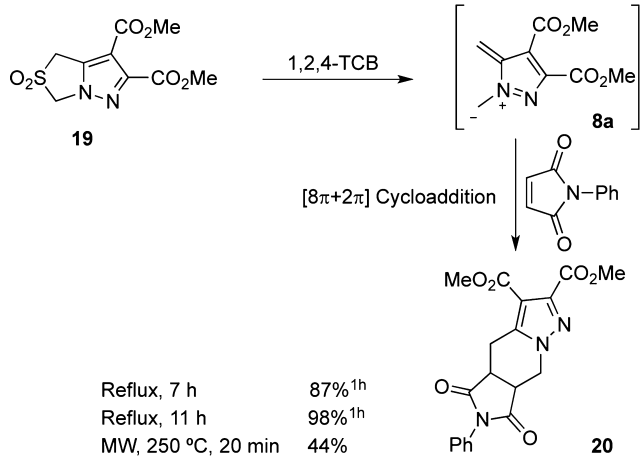



| entry | substrate | dipolarophile | reaction conditions | **18**, isolated yield (%) |
|---|---|---|---|---|
| 1 | **14a** | NMM | Δ, 1,2,4-TCB, reflux, 2 h | **18a**, 27 |
| 2 | **14a** | NMM | MW, 1,2,4-TCB, 230 °C, 10 min | **18a**, 35 |
| 3 | **14a** | NPM | Δ, 1,2,4-TCB, reflux, 2 h | **18b**, 36 |
| 4 | **14a** | NPM | Δ, 1,2,4-TCB, reflux, 6 h | **18b**, 23 |
| 5 | **14a** | NPM | MW, 1,2,4-TCB, 150 °C, 10 min | **18b**, 30 |
| 6 | **14a** | NPM | MW, 1,2,4-TCB, 200 °C, 5 min | **18b**, 39 |
| 7 | **14a** | NPM | MW, 1,2,4-TCB, 200 °C, 10 min | **18b**, 40 |
| 8 | **14a** | NPM | MW, 1,2,4-TCB, 200 °C, 20 min | **18b**, 20 |
| 9 | **14a** | NPM | MW, 1,2,4-TCB, 230 °C, 10 min | **18b**, 31 |
| 10 | **14a** | NPM | MW, 1,2,4-TCB, 250 °C, 20 min | **18b**, 27 |
| 11 | **14b** | NMM | MW, 1,2,4-TCB, 230 °C, 15 min | **18c**, 8 |
| 12 | **14b** | NPM | MW, 1,2,4-TCB, 230 °C, 15 min | **18d**, 13 |
| 13 | **14c** | NMM | MW, 1,2,4-TCB, 230 °C, 10 min | **18e**, 38 |
| 14 | **14c** | NPM | MW, 1,2,4-TCB, 230 °C, 10 min | **18f**, 45 |
| 15 | **14d** | NMM | MW, 1,2,4-TCB, 230 °C, 15 min | **18g**, 22 |
| 16 | **14d** | NPM | MW, 1,2,4-TCB, 230 °C, 15 min | **18h**, 30 |

ring rotation leads to four symmetric minor-image equivalent forms. Nevertheless, two of these forms were not equivalent in the transition states of the cycloaddition reactions, and for this reason the two forms **NPM**C1 and **NPM**C2 were used in the modeling studies (Figure S51).

In the study of cycloaddition reactions of diazafulvenium **8a** and benzodiazafulvenium methide **15a** with *N*-phenylmaleimide, transition states resulting from the following reactions

**Scheme 5. Cycloadddition of Diazafulvenium Methide 8a with *N*-Phenylmaleimide**




were considered: (i) *exo*-1,3-cycloaddition; (ii) *endo*-1,3-cycloaddition; (iii) *exo*-1,7-cycloaddition, and (iv) *endo*-1,7-cycloaddition. The activation energies corresponding to these transitions states are reported in Tables 4 and 5. The results

**Table 4. Relative Energy of the Transition States for the Cycloaddition of Diazafulvenium 8a with NPM, Calculated at the B3LYP/6-31G* Level of Theory**

| transition state | relative energy (kJ mol$^{-1}$) B3LYP/6-31G* |
|---|---|
| TS[*Exo*-1,3-(**8a**C1-**NPM**C1)] | 22.1 |
| TS[*Exo*-1,3-(**8a**C1-**NPM**C2)] | 24.3 |
| TS[*Exo*-1,3-(**8a**C2-**NPM**C1)] | 23.3 |
| TS[*Exo*-1,3-(**8a**C2-**NPM**C2)] | 24.7 |
| TS[*Endo*-1,3-(**8a**C1-**NPM**C1)] | 23.2 |
| TS[*Endo*-1,3-(**8a**C1-**NPM**C2)] | 20.6 |
| TS[*Endo*-1,3-(**8a**C2-**NPM**C1)] | 26.7 |
| TS[*Endo*-1,3-(**8a**C2-**NPM**C2)] | 22.7 |
| TS[*Exo*-1,7-(**8a**C1-**NPM**C1)] | 8.8 |
| TS[*Exo*-1,7-(**8a**C1-**NPM**C2)] | 8.5 |
| TS[*Exo*-1,7-(**8a**C2-**NPM**C1)] | 8.4 |
| TS[*Exo*-1,7-(**8a**C2-**NPM**C2)] | 8.2 |
| TS[*Endo*-1,7-(**8a**C1-**NPM**C1)] | 13.5 |
| TS[*Endo*-1,7-(**8a**C1-**NPM**C2)] | 12.4 |
| TS[*Endo*-1,7-(**8a**C2-**NPM**C1)] | 12.2 |
| TS[*Endo*-1,7-(**8a**C2-**NPM**C2)] | 9.3 |

**Table 5. Relative Energy of the Transition States for the Cycloaddition of Benzodiazafulvenium Methide 15a with NPM, Calculated at the B3LYP/6-31G* Level of Theory**

| transition state | relative energy (kJ mol$^{-1}$) B3LYP/6-31G* |
|---|---|
| TS[*Exo*-1,3-(**15a**-**NPM**C1)] | 5.9 |
| TS[*Exo*-1,3-(**15a**-**NPM**C2)] | 8.1 |
| TS[*Endo*-1,3-(**15a**-**NPM**C1)] | 4.4 |
| TS[*Endo*-1,3(**15a**-**NPM**C2)] | 2.4 |
| TS[*Exo*-1,7-(**15a**-**NPM**C1)] | 12.3 |
| TS[*Exo*-1,7-(**15a**-**NPM**C2)] | 12.0 |
| TS[*Endo*-1,7-(**15a**-**NPM**C1)] | 17.4 |
| TS[*Endo*-1,7-(**15a**-**NPM**C2)] | 16.1 |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include zero-point-energy (ZPE) correction, but no thermal correction; they are $\Delta H_{(0K)}$. The optimized geometries of the more relevant transition structures for the cycloaddition of diazafulvenium **8a** and benzodiazafulvenium methide **15a** with *N*-phenylmaleimide are presented in Figures 1 and 2, respectively.

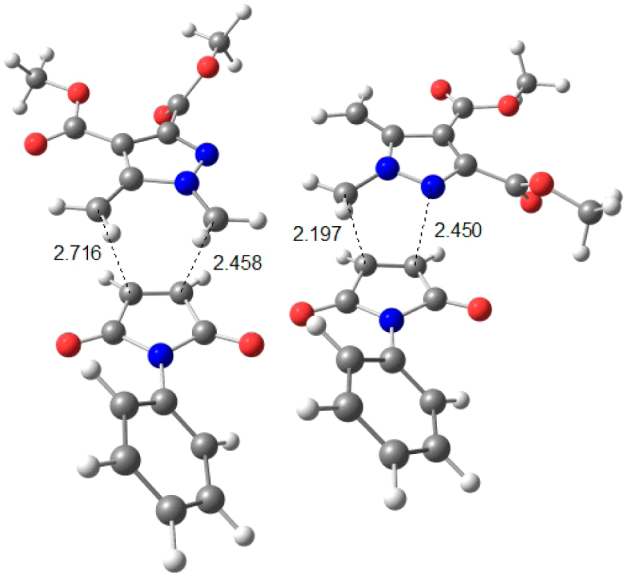



**Figure 1.** Geometries of transition states for the cycloaddition of diazafulvenium **8a** with *N*-phenylmaleimide, TS[*Exo*-1,7-(**8a**C2-**NPM**C2)] and TS[*Exo*-1,3-(**8a**C2-**NPM**C2)], calculated at the B3LYP/6-31G* level of theory.

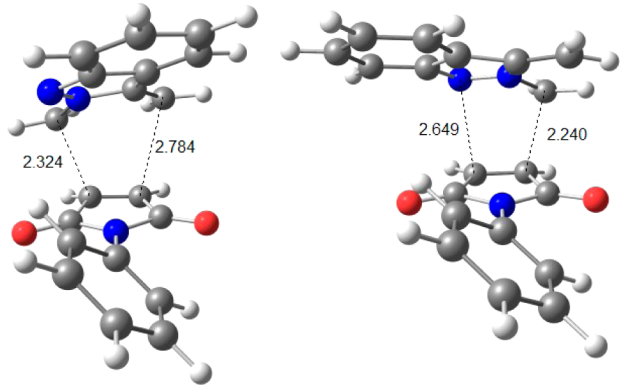


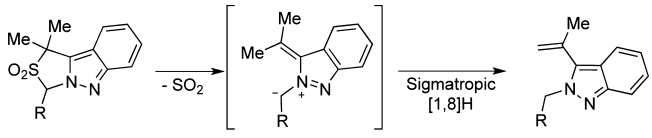

**Figure 2.** Geometries of transition states for the cycloaddition of benzodiazafulvenium methide **15a** with *N*-phenylmaleimide, TS[*Endo*-1,7-(**15a**-**NPM**C2)] and TS[*Endo*-1,3(**15a**-**NPM**C2)], calculated at the B3LYP/6-31G* level of theory.

The results of the quantum chemical calculations demonstrate that transition states of the addition of *N*-phenylmaleimide to the 1,7-positions of diazafulvenium methide **8a** are significantly more stable than transition states resulting from the addition across the 1,3-positions, which is consistent with the experimentally observed exclusive formation of the corresponding [$8\pi + 2\pi$] cycloadduct. Furthermore, the *exo*-addition is predicted to be favored over the *endo*-approach of this 1,7-dipole and *N*-phenylmaleimide (Table 4 and Figure 1).

Interestingly, the computational results on the cycloaddition reaction of benzodiazafulvenium methide **15a** with *N*-phenylmaleimide indicate that this reactive intermediate should react as a 1,3-dipole, which corroborates the rationalization of the synthesis of 1*H*-indazoles **18** from 1,3-dihydrothiazolo[3,4-*b*]indazole-2,2-dioxides **14** via the initial 1,3-cycloaddition of benzodiazafulvenium methides **15** to maleimides (Table 3). The *endo*-[$4\pi + 2\pi$] cycloaddition of benzodiazafulvenium methide **15a** with *N*-phenylmaleimide is predicted to be favored (Table 5 and Figure 2).

Sigmatropic [1,8]H shifts of the new benzo-2,3-diazafulvenium methide derivatives were also explored (Scheme 6, Table 6). 1,3-Dihydrothiazolo[3,4-*b*]indazole-2,2-dioxides **14b**–**14d**, having hydrogen atoms in the appropriate position to undergo sigmatropic shifts, were selected for this study. As expected, when carrying out the flash vacuum pyrolysis (FVP), at 500 °C, of the unsubstituted 1,3-dihydrothiazolo[3,4-*b*]indazole-2,2-dioxide **14a**, no products could be detected. However, under FVP reaction conditions (500 °C, 2.0 × $10^{-5}$ mbar), compound **14b**, bearing one methyl group at C-3, afforded 3-methyl-2-vinyl-2*H*-indazole (**21**) in 69% yield (Scheme 6). The structural assignment of 2-vinyl-2*H*-indazole **21** was based on a NOESY experiment. In the NOESY spectrum, methyl protons at C-3

**Table 6. Sigmatropic [1,8]H Shift of Benzo-2,3-diazafulvenium Methides 15c and 15d**

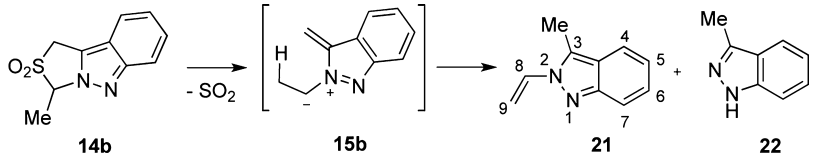



**14c** R = H **14d** R = Me | **15c** R = H **15d** R = Me | **23a** R = H **23b** R = Me

| entry | substrate | reaction conditions | **23**, isolated yield (%) |
|---|---|---|---|
| 1 | **14c** | FVP (600 °C, 2.0 × $10^{-5}$ mbar) | **23a**, 61 |
| 2 | **14c** | FVP (500 °C, 2.0 × $10^{-5}$ mbar) | **23a**, 73 |
| 3 | **14c** | MW (1,2,4-TCB, 230 °C, 10 min) | **23a**, 58 |
| 4 | **14d** | FVP (500 °C, 2.0 × $10^{-5}$ mbar) | **23b**, 92 |
| 5 | **14d** | MW (1,2,4-TCB, 230 °C, 10 min) | **23b**, 71[a] |

[a]Compound **24** was also isolated in 23% yield.

**Scheme 6. Chemical Behavior of Benzo-2,3-diazafulvenium Methide 15b under Thermolysis**




**14b** **15b** **21** **22**

| | | | |
|---|---|---|---|
| **FVP** | (500 °C, 2.0 x $10^{-5}$ mbar) | 69% | --- |
| **MW** | (1,2,4-TCB, 230 °C, 15 min) | 32% | 16% |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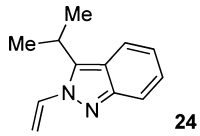
show connectivity with the vinyl proton at C-8 and with the aromatic proton at C-4, thus confirming that the vinyl group is attached to the nitrogen in position 2. Under microwave irradiation (230 °C, 15 min) sulfone **14b** affords the expected *N*-vinyl-indazole **21** (32%) together with the formation of 3-methyl-1*H*-indazole (**22**) (16%).

Flash vacuum pyrolysis of 1,1-dimethyl-1,3-dihydrothiazolo-[3,4-*b*]indazole-2,2-dioxide (**14c**) carried out at 600 °C gave 3-vinyl-2*H*-indazole **23a** exclusively in 61% yield (Table 6, entry 1). Decreasing the temperature to 500 °C allowed the isolation of vinylindazole **23a** in higher yield (73%) (Table 6, entry 2). The same indazole **23a** was also obtained from sulfone **14c** under MW irradiation in 58% yield (Table 6, entry 3). The structural assignment of 2*H*-indazole **23a** was supported by a NOESY experiment, since connectivity was observed between methyl protons at N-2 and the two vinyl proton at position 3.

Under FVP conditions (500 °C, 2.0 × $10^{-5}$ mbar), 1,1,3-trimethyl-1,3-dihydrothiazolo[3,4-*b*]indazole-2,2-dioxide (**14d**) was converted exclusively into 3-vinyl-2*H*-indazole **23b** in high yield (92%) (Table 6, entry 4). It is worth noticing that in this particular case, the $SO_2$ extrusion from indazole **14d** leads to benzodiazafulvenium methide **15d** where two potential sigmatropic [1,8]H shifts could in principle take place. In fact, microwave-induced thermolysis of sulfone **14d** afforded *C*-vinyl-2*H*-indazole **23b** in 71% yield together with *N*-vinyl-2*H*-indazole **24** in 23% yield (Table 6, Entry 5).




**24**

These results have shown that 1,3-dihydrothiazolo[3,4-*b*]indazole-2,2-dioxides **14b**−**14d** are efficiently converted into vinyl-2*H*-indazoles via sigmatropic [1,8]H shifts of the in situ generated benzo-2,3-diazafulvenium methides. Moreover, when flash vacuum pyrolysis was used, higher yields and higher selectivity were observed than in the microwave-induced thermolysis due to the milder gas-phase thermolysis conditions.

## 3. CONCLUSION

The generation and reactivity of benzo-2,3-diazafulvenium methides derived from thiazolo[3,4-*b*]indazole-2,2-dioxides are described for the first time. The new dipoles could be trapped in the presence of *N*-substituted maleimides, giving new indazole derivatives characterized by an intense yellow color, a property that gives them a potential application as dyes.

The reported results gave an insight into the chemistry of a new type of extended dipolar systems. The studied benzodiazafulvenium methides participated in 1,3-cycloaddition with maleimides in contrast with the previously observed reactivity for 4,5-(methoxycarbonyl)diazafulvenium methides, which participate exclusively in 1,7-cycloadditions. Quantum chemical calculations were in agreement with this finding.

Furthermore, 1-methyl- and 7,7-dimethylbenzo-2,3-diazafulvenium methides undergo sigmatropic [1,8]H shifts under flash vacuum pyrolysis or under microwave irradiation allowing the efficient synthesis of *N*-vinyl- and *C*-vinyl-2*H*-indazoles, respectively.

## 4. EXPERIMENTAL SECTION

Microwave reactions were carried out in a microwave reactor CEM Focused Synthesis System Discover S-Class using 10 mL microwave tubes. The reaction temperatures were measured by infrared surface detector during microwave heating. Thin-layer chromatography (TLC) analyses were performed using precoated silica gel plates. Flash column chromatography was performed with silica gel 60 as the stationary phase. $^1$H NMR spectra were recorded on an instrument operating at 400 MHz. $^{13}$C NMR spectra were recorded on an instrument operating at 100 MHz. Chemical shifts are expressed in parts per million relatively to internal tetramethylsilane (TMS), and coupling constants (*J*) are in hertz. Infrared spectra (IR) were recorded on a Fourier transform spectrometer. Mass spectra were recorded under electron impact (EI) or electrospray ionization (ESI). High-resolution mass spectra (HRMS) spectra were obtained on an electron impact (EI) or electrospray (ESI) TOF mass spectrometer. Melting points were determined in open glass capillaries and are uncorrected. 4*H*,6*H*-Thiazolo[3,4-*c*][1,2,3]oxadiazol-7-ium-3-oxides **1a**[6] and **1b**−**d**[1h] were prepared as described in the literature.

**General Procedure for the Synthesis of 1,3-Dihydrothiazolo-[3,4-*b*]indazoles.** *Method A.* To a mixture of the appropriate sydnone **12** (4.50 mmol) and the benzyne precursor (5.40 mmol) in acetonitrile (38 mL) was added cesium fluoride (11.25 mmol). The resulting mixture was stirred at 80 °C under $N_2$ over a period of 24 h. After cooling to room temperature the reaction mixture was quenched with saturated $NaHCO_3$ solution (20 mL), the organic fraction was extracted with ethyl acetate and dried over anhydrous $Na_2SO_4$, and the solvent was evaporated off. The products were isolated by flash chromatography.

*Method B.* To a mixture of the appropriate sydnone **12** (1.00 mmol) and the benzyne precursor (1.60 mmol) in tetrahydrofuran (10 mL) was added TBAF, 1 M in THF solution (1.6 mmol, 1.6 mL). The resulting mixture was stirred under $N_2$ at room temperature for the time indicated in each case. After cooling to room temperature the reaction mixture was treated with saturated aqueous sodium bicarbonate solution (20 mL), the organic fraction was extracted with ethyl acetate and dried over anhydrous $Na_2SO_4$, and the solvent was evaporated off. The products were isolated by flash chromatography.

*Method C.* A solution of anthranilic acid (5.50 mmol) in acetone (25 mL) was added dropwise over 45−60 min to a refluxing mixture of the appropriate sydnone **12** (5.00 mmol) and isoamyl nitrite (10.00 mmol) in dichloromethane (50 mL) under $N_2$. The resulting solution was isolated immediately after finishing the addition of the solution of anthranilic acid or refluxed for an additional time. After cooling to room temperature the reaction mixture was quenched with 3 M KOH (20 mL), the organic fraction was extracted with ethyl acetate and dried over anhydrous $Na_2SO_4$, and the solvent was evaporated off. The residue was purified by flash chromatography.

**1,3-Dihydrothiazolo[3,4-*b*]indazole (13a).** *Method A.* Obtained from compound **12a**[6] (650 mg, 4.50 mmol) as described in the general procedure. Purification of the crude product by flash chromatography [hexanes/EtOAc (2:1)] gave compound **13a** as a solid (230 mg, 29%).

*Method B.* Obtained from compound **12a**[6] (148 mg, 1.03 mmol) as described in the general procedure (reaction time: 19 h). Purification by flash chromatography [hexanes/EtOAc (2:1)] gave compound **13a** (50 mg, 28%).

*Method C.* Obtained from compound **12a**[6] (288 mg, 1.03 mmol) as described in the general procedure (the reaction was complete after finishing the addition of the solution of anthranilic acid). Purification by flash chromatography [hexanes/EtOAc (2:1)] gave compound **13a** (108 mg, 31%).

White needles; mp 134−136 °C (from hexanes/diethyl ether); IR (KBr) 1627, 1376, 1275, 1222, 1160 $cm^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 4.40 (s, 2H), 5.50 (s, 2H), 7.09 (pseudo-t, $J$ = 7.4 Hz, 1H), 7.30 (pseudo-t, $J$ = 7.6 Hz, 1H), 7.54 (d, $J$ = 8.4 Hz, 1H), 7.65 (d, $J$ = 8.8 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 27.2, 50.9, 116.2, 118.0, 119.4, 121.5, 126.4, 135.9, 154.5; MS (EI) $m/z$: 176 (100) $[M]^+$, 148 (5), 131 (31), 102 (38); HRMS (EI) $m/z$: calcd for $C_9H_8N_2S$ $[M]^+$ 176.0408, found 176.0412.

**3-Methyl-1,3-dihydrothiazolo[3,4-*b*]indazole (13b).** *Method B.* Obtained from compound **12b**[1h] (108 mg, 0.68 mmol) as described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in the general procedure (reaction time: 12 h). Purification by flash chromatography [hexanes/EtOAc (2:1)] gave compound **13b** as a low melting solid (35 mg, 26%).

*Method C.* Obtained from compound **12b**[1h] (1.16 g, 7.34 mmol) as described in the general procedure (the reaction was completed after finishing the addition of the solution of anthranilic acid). Purification by flash chromatography [hexanes/EtOAc (2:1)] gave compound **13b** as a low melting solid (0.56 g, 40%).

IR (film) 1742, 1629, 1400, 1333, 1270, 1211, 1092 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.98 (d, $J$ = 6.2 Hz, 3H), 4.35−4.44 (m, 2H), 5.85−5.89 (m, 1H), 7.09 (pseudo-t, $J$ = 7.6 Hz, 1H), 7.30 (pseudo-t, $J$ = 7.8 Hz, 1H), 7.55 (d, $J$ = 8.4 Hz, 1H), 7.67 (d, $J$ = 8.8 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 23.6, 26.3, 61.4, 116.3, 118.1, 119.4, 121.4, 126.3, 135.1, 154.2; MS (EI) $m/z$: 190 (100) $[M]^+$, 178 (26), 158 (26), 145 (21), 131 (82), 102 (37); HRMS (EI) $m/z$: calcd for $C_{10}H_{10}N_2S$ $[M]^+$ 190.0565, found 190.0571.

**1,1-Dimethyl-1,3-dihydrothiazolo[3,4-*b*]indazole (13c).** Obtained from compound **12c**[1h] (0.99 g, 5.76 mmol) as described in the general procedure for method C (reaction time: 1 h). Purification by flash chromatography [hexanes/EtOAc (3:1), then hexanes/EtOAc (2:1)] gave compound **13c** as a yellowish solid (0.77 g, 66%). mp 93−95 °C (from hexanes/diethyl ether); IR (KBr) 1398, 1367, 1317, 1245, 1123, 1075 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.95 (s, 6H), 5.57 (s, 2H), 7.07 (pseudo-t, $J$ = 7.4 Hz, 1H), 7.29 (pseudo-t, $J$ = 7.8 Hz, 1H), 7.61 (d, $J$ = 8.4 Hz, 1H), 7.65 (d, $J$ = 8.8 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 31.2, 51.0, 51.2, 114.5, 118.2, 118.6, 121.2, 126.3, 143.9, 154.2; MS (EI) $m/z$: 204 (41) $[M]^+$, 189 (100), 158 (29), 128 (11), 115 (16); HRMS (EI) $m/z$: calcd for $C_{11}H_{12}N_2S$ $[M]^+$ 204.0721, found 204.0724.

**1,1,3-Trimethyl-1,3-dihydrothiazolo[3,4-*b*]indazole (13d).** Obtained from compound **12d**[1h] (0.64 g, 3.44 mmol) as described in the general procedure for method C (the reaction was completed after finishing the addition of the solution of anthranilic acid). Purification by flash chromatography [hexanes/EtOAc (3:1)] gave compound **13d** as a yellowish oil (0.47 g, 62%); IR (film) 1627, 1456, 1384, 1334, 1270, 1214, 1123 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.92 (s, 3H), 1.98 (s, 3H), 1.99 (d, $J$ = 6.4 Hz, 3H), 5.93 (q, $J$ = 6.4 Hz, 1H), 7.07 (pseudo-t, $J$ = 7.6 Hz, 1H), 7.29 (pseudo-t, $J$ = 7.6 Hz, 1H), 7.61 (d, $J$ = 8.4 Hz, 1H), 7.68 (d, $J$ = 8.8 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 24.1, 31.8, 32.0, 49.8, 61.8, 114.6, 118.2, 118.8, 121.1, 126.2, 143.2, 154.1; MS (EI) $m/z$: 218 (41) $[M]^+$, 203 (100), 188 (17), 159 (16), 129 (10), 115 (15); HRMS (EI) $m/z$: calcd for $C_{12}H_{14}N_2S$ $[M]^+$ 218.0878, found 218.0880.

**General Procedure for the Synthesis of 1,3-Dihydrothiazolo-[3,4-*b*]indazole-2,2-dioxides.** To a stirred ice-cold solution of the appropriate 1,3-dihydrothiazolo[3,4-*b*]indazole **13** (1.00 mmol) in dry dichloromethane (8 mL) was added portionwise 3-chloroperoxybenzoic acid (3.00 mmol) under $N_2$ atmosphere. The cooling bath was removed, and the reaction mixture was allowed to warm to room temperature. After stirring at room temperature for the time indicated in each case, the reaction mixture was washed twice with 10% (w/v) aqueous sodium bisulfite solution (2 × 20 mL) and twice with 10% (w/v) aqueous sodium bicarbonate solution (2 × 20 mL). The organic fraction was then dried over anhydrous $Na_2SO_4$ and the solvent evaporated off.

**1,3-Dihydrothiazolo[3,4-*b*]indazole-2,2-dioxide (14a).** Obtained from compound **13a** (227 mg, 1.29 mmol) as described in the general procedure (reaction time: 1.5 h). The crude product was triturated with diethyl ether to give **14a** as a white solid (198 mg, 74%). mp 204−206 °C; IR (KBr) 1630, 1407, 1339, 1292, 1228, 1139 $cm^{-1}$; $^1H$ NMR (400 MHz, DMSO-$d_6$) $\delta$ 5.13 (s, 2H), 5.86 (s, 2H), 7.16 (pseudo-t, $J$ = 7.4 Hz, 1H), 7.36 (pseudo-t, $J$ = 7.6 Hz, 1H), 7.68−7.73 (m, 2H); $^{13}C$ NMR (100 MHz, DMSO-$d_6$) $\delta$ 51.7, 67.2, 117.3, 117.7, 120.0, 122.0, 126.8, 128.1, 149.3; MS (EI) $m/z$: 208 (11) $[M]^+$, 144 (100), 115 (28), 89 (14); HRMS (EI) $m/z$: calcd for $C_9H_8N_2SO_2$ $[M]^+$ 208.0306, found 208.0310.

**3-Methyl-1,3-dihydrothiazolo[3,4-*b*]indazole-2,2-dioxide (14b).** Obtained from compound **13b** (0.73 g, 3.84 mmol) as described in the general procedure (reaction time: 2 h). The crude product was triturated with diethyl ether to give **14b** as a solid (0.45 g, 53%). mp 158−160 °C; IR (KBr) 1630, 1400, 1326, 1133, 1108 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 2.02 (d, $J$ = 6.6 Hz, 3H), 4.73 (s, 2H), 5.44 (q, $J$ = 6.6 Hz, 1H), 7.12 (pseudo-t, $J$ = 7.6 Hz, 1H), 7.38 (pseudo-t, $J$ = 7.6 Hz, 1H), 7.56 (d, $J$ = 8.8 Hz, 1H), 7.76 (d, $J$ = 8.8 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 14.1, 50.9, 73.6, 118.2, 118.3, 119.0, 123.2, 124.4, 127.5, 150.3; MS (EI) $m/z$: 222 (13) $[M]^+$, 158 (100), 130 (38), 102 (11); HRMS (EI) $m/z$: calc for $C_{10}H_{10}N_2SO_2$ $[M]^+$ 222.0463, found 222.0465.

**1,1-Dimethyl-1,3-dihydrothiazolo[3,4-*b*]indazole-2,2-dioxide (14c).** Obtained from compound **13c** (0.77 g, 3.77 mmol) as described in the general procedure (reaction time: 4 h). The crude product was triturated with diethyl ether to give **14c** as a pale yellow solid (0.59 g, 66%). mp 169−171 °C; IR (KBr) 1402, 1387, 1330, 1320, 1180, 1132, 1117, 1080 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.92 (s, 6H), 5.48 (s, 2H), 7.17 (pseudo-t, $J$ = 7.4 Hz, 1H), 7.37 (pseudo-t, $J$ = 7.6 Hz, 1H), 7.65 (d, $J$ = 8.8 Hz, 1H), 7.74 (d, $J$ = 8.8 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 22.0, 63.4, 65.9, 117.0, 118.3, 118.3, 123.0, 127.4, 136.4, 150.7; MS (EI) $m/z$: 236 (5) $[M]^+$, 172 (100), 157 (38), 128 (7); HRMS (EI) $m/z$: calcd for $C_{11}H_{12}N_2SO_2$ $[M]^+$ 236.0619, found 236.0627.

**1,1,3-Trimethyl-1,3-dihydrothiazolo[3,4-*b*]indazole-2,2-dioxide (14d).** Obtained from compound **13d** (0.65 g, 2.98 mmol) as described in the general procedure (reaction time: 2 h). After purification by flash chromatography [hexanes/EtOAc (2:1)], compound **14d** was obtained as a pale yellow solid (0.55 g, 74%). mp 136−138 °C (from diethyl ether); IR (KBr) 1628, 1460, 1439, 1385, 1322, 1284, 1161, 1123, 1105 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.88 (s, 3H), 1.95 (s, 3H), 2.04 (d, $J$ = 6.6 Hz, 3H), 5.41 (q, $J$ = 6.6 Hz, 1H), 7.16 (pseudo-t, $J$ = 7.4 Hz, 1H), 7.37 (pseudo-t, $J$ = 7.8 Hz, 1H), 7.64 (d, $J$ = 8.4 Hz, 1H), 7.75 (d, $J$ = 8.8 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 13.5, 21.2, 23.7, 62.0, 71.7, 116.9, 118.3, 118.5, 122.8, 127.2, 135.1, 150.3; MS (EI) $m/z$: 250 (12) $[M]^+$, 186 (100), 171 (86), 158 (38), 144 (25), 115 (16); HRMS (EI) $m/z$: calcd for $C_{12}H_{14}N_2SO_2$ $[M]^+$ 250.0776, found 250.0775.

**General Procedures for Generation and Trapping of Benzo-2,3-diazafulvenium Methides.** *Method A.* A suspension of the appropriate 1,3-dihydrothiazolo[3,4-*b*]indazole-2,2-dioxide **14** (0.40 mmol) and *N*-substituted maleimide (2 equiv, 0.80 mmol) in 1,2,4-trichlorobenzene (3 mL) was heated at 230 °C under dry nitrogen for 2 h. After cooling to room temperature the product was isolated by flash chromatography.

*Method B.* A suspension of the appropriate 1,3-dihydrothiazolo[3,4-*b*]indazole-2,2-dioxide **14** (0.40 mmol) and *N*-substituted maleimide (2 equiv, 0.80 mmol) in 1,2,4-trichlorobenzene (1 mL) was irradiated in the microwave reactor at 230 °C for the time indicated in each case. After cooling to room temperature the product was isolated by flash chromatography.

**1,3-Dimethyl-4-(3-methyl-1*H*-indazol-1-yl)-1*H*-pyrrole-2,5-dione (18a).** *Method A.* Obtained from compound **14a** (49 mg, 0.24 mmol) as described in the general procedure. After purification of the crude product by flash chromatography [hexanes, then hexanes/EtOAc (2:1)], compound **18a** was obtained as an intense yellow solid (16 mg, 27%).

*Method B.* Obtained from compound **14a** (60 mg, 0.29 mmol) as described in the general procedure (reaction time: 10 min). Purification by flash chromatography [hexanes, then hexanes/EtOAc (2:1)] gave compound **18a** (26 mg, 35%).

mp 157−159 °C (from hexanes/DCM); IR (KBr) 1708, 1677, 1445, 1388, 1091, 1016 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 2.23 (s, 3H), 2.62 (s, 3H), 3.13 (s, 3H), 7.27 (pseudo-t, $J$ = 7.4 Hz, 1H), 7.46 (pseudo-t, $J$ = 7.6 Hz, 1H), 7.64 (d, $J$ = 8.8 Hz, 1H), 7.68 (d, $J$ = 8.0 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 9.5, 12.1, 24.1, 112.2, 120.3, 122.3, 125.1, 127.7, 127.8, 135.9, 140.6, 147.7, 166.8, 171.0; MS (ESI) $m/z$: 278 (100) $[M + Na]^+$, 256 (8); HRMS (ESI) $m/z$: calcd for $C_{14}H_{13}N_3O_2Na$ $[M + Na]^+$ 278.0906, found 278.0908; UV−vis ($CH_2Cl_2$) $\lambda$/nm ($\varepsilon/M^{-1}$ $cm^{-1}$) = 387 (5348).

**3-Methyl-4-(3-methyl-1*H*-indazol-1-yl)-1-phenyl-1*H*-pyrrole-2,5-dione (18b).** *Method A.* Obtained from compound **14a** (83 mg, 0.40 mmol) as described in the general procedure. After purification by


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flash chromatography [hexanes, then hexanes/EtOAc (2:1)], compound **18b** was obtained as an intense yellow solid (36%).

*Method B.* Obtained from compound **14a** (40 mg, 0.19 mmol) as described in the general procedure (reaction time: 10 min). Purification by flash chromatography [hexanes, then hexanes/EtOAc (2:1)] gave compound **18b** (19 mg, 31%).

mp 193−195 °C (from hexanes/DCM) ; IR (KBr) 1714, 1679, 1495, 1449, 1382, 1348, 1120 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 2.34 (s, 3H), 2.64 (s, 3H), 7.29 (pseudo-t, $J$ = 7.6 Hz, 1H), 7.38 (pseudo-t, $J$ = 7.0 Hz, 1H), 7.46−7.51 (m, 5H), 7.69−7.73 (m, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 9.8, 12.1, 112.5, 120.4, 122.5, 125.2, 126.1, 127.5, 127.8, 127.9, 129.1, 131.5, 135.8, 140.7, 148.0, 165.5, 169.7; MS (EI) $m/z$: 317 (39) $[M]^+$, 288 (16), 260 (10), 197 (34), 169 (100), 102 (13); HRMS (EI) $m/z$: calcd for $C_{19}H_{15}N_3O_2$ $[M]^+$ 317.1164, found 317.1163; UV−vis ($CH_2Cl_2$) $\lambda$/nm ($\varepsilon/M^{-1}$ $cm^{-1}$) = 390 (5331).

**3-Ethyl-1-methyl-4-(3-methyl-1*H*-indazol-1-yl)-1*H*-pyrrole-2,5-dione (18c).** Obtained from compound **14b** (123 mg, 0.55 mmol) as described in the general procedure for method B (reaction time: 15 min). Purification by flash chromatography [hexanes, then hexanes/EtOAc (3:1)] gave compound **18c** as a yellow oil (12 mg, 8%). IR (film) 1709, 1654, 1443, 1386, 1074 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.17 (t, $J$ = 7.6 Hz, 3H), 2.62 (s, 3H), 2.71 (q, $J$ = 7.6 Hz, 2H), 3.12 (s, 3H), 7.25−7.28 (m, 1H), 7.46 (pseudo-t, $J$ = 7.6 Hz, 1H), 7.65−7.69 (m 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 12.1, 12.8, 17.3, 24.0, 112.2, 120.3, 122.2, 125.1, 127.8, 133.3, 135.3, 140.7, 147.6, 166.9, 170.7; MS (EI) $m/z$: 269 (10) $[M]^+$, 254 (100), 182 (28), 169 (24), 143 (5); HRMS (EI) $m/z$: calcd for $C_{15}H_{15}N_3O_2$ $[M]^+$ 269.1164, found 269.1165; UV−vis ($CH_2Cl_2$) $\lambda$/nm ($\varepsilon/M^{-1}$ $cm^{-1}$) = 386 (4329).

**3-Ethyl-4-(3-methyl-1*H*-indazol-1-yl)-1-phenyl-1*H*-pyrrole-2,5-dione (18d).** Obtained from compound **14b** (53 mg, 0.24 mmol) as described in the general procedure for method B (reaction time: 15 min). Purification by flash chromatography [hexanes, then hexanes/EtOAc (3:1)] gave compound **18d** as an intense yellow solid (10 mg, 13%). mp 118−120 °C; IR (KBr) 1714, 1670, 1503, 1374 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.24 (t, $J$ = 7.4 Hz, 3H), 2.64 (s, 3H), 2.81 (q, $J$ = 7.4 Hz, 2H), 7.26−7.30 (m, 1H), 7.38 (pseudo-t, $J$ = 6.8 Hz, 1H), 7.44−7.51 (m, 5H), 7.69 (d, $J$ = 8.0 Hz, 1H), 7.73 (d, $J$ = 8.4 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 11.1, 11.8, 16.5, 111.5, 119.3, 121.4, 124.2, 125.0, 126.8, 126.8, 128.1, 130.4, 131.9, 134.3, 139.7, 146.9, 164.6, 168.4; MS (EI) $m/z$: 331 (30) $[M]^+$, 316 (100), 211 (65), 183 (67), 169 (50), 143 (15), 102 (10); HRMS (EI) $m/z$: calcd for $C_{20}H_{17}N_3O_2$ $[M]^+$ 331.1321, found 331.1322; UV−vis ($CH_2Cl_2$) $\lambda$/nm ($\varepsilon/M^{-1}$ $cm^{-1}$) = 393 (4953).

**3-(3-Isopropyl-1*H*-indazol-1-yl)-1,4-dimethyl-1*H*-pyrrole-2,5-dione (18e).** Obtained from compound **14c** (80 mg, 0.34 mmol) as described in the general procedure for method B (reaction time: 10 min). After purification by flash chromatography [hexanes, then hexanes/EtOAc (3:1)], compound **18e** was obtained as an intense yellow solid (38 mg, 38%). mp 97−99 °C (from diethyl ether/hexanes); IR (KBr) 1705, 1651, 1387, 1074 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.47 (d, $J$ = 7.0 Hz, 6H), 2.26 (s, 3H), 3.13 (s, 3H), 3.43 (h, $J$ = 7.0 Hz, 1H), 7.24−7.27 (m, 1H), 7.45 (pseudo-t, $J$ = 7.6 Hz, 1H), 7.72 (d, $J$ = 8.8 Hz, 1H), 7.75 (d, $J$ = 8.0 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 9.5, 21.7, 24.1, 27.6, 112.6, 120.5, 122.2, 123.7, 127.6, 127.7, 136.2, 140.9, 156.3, 166.8, 171.1; MS (EI) $m/z$: 283 (100) $[M]^+$, 268 (56), 252 (36), 198 (75), 183 (49), 155 (28), 102 (26); HRMS (EI) $m/z$: calcd for $C_{16}H_{17}N_3O_2$ $[M]^+$ 283.1321, found 283.1319; UV−vis ($CH_2Cl_2$) $\lambda$/nm ($\varepsilon/M^{-1}$ $cm^{-1}$) = 388 (5845).

**3-(3-Isopropyl-1*H*-indazol-1-yl)-4-methyl-1-phenyl-1*H*-pyrrole-2,5-dione (18f).** Obtained from compound **14c** (74 mg, 0.31 mmol) as described in the general procedure for method B (reaction time: 10 min). After purification by flash chromatography [hexanes, then hexanes/EtOAc (2:1)], compound **18f** was obtained as an intense yellow solid (48 mg, 45%). mp 145−146 °C (from diethyl ether); IR (KBr) 1712, 1673, 1506, 1382, 1120 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.50 (d, $J$ = 6.9 Hz, 6H), 2.36 (s, 3H), 3.46 (h, $J$ = 6.9 Hz, 1H), 7.26−7.29 (m, 1H), 7.40 (pseudo-t, $J$ = 7.2 Hz, 1H), 7.43−7.52 (m, 5H), 7.76−7.79 (m, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 9.6, 21.5, 27.5, 112.7, 120.4, 122.2, 123.7, 126.0, 127.3, 127.6, 127.7, 129.0, 131.3, 136.0, 140.8, 156.5, 165.4, 169.6; MS (EI) $m/z$: 345 (24) $[M]^+$, 186 (51), 172 (100), 157 (82), 130 (32), 102 (19), 77 (18); HRMS (EI) $m/z$: calcd for $C_{21}H_{19}N_3O_2$ $[M]^+$ 345.1477, found 345.1477; UV−vis ($CH_2Cl_2$) $\lambda$/nm ($\varepsilon/M^{-1}$ $cm^{-1}$) = 393 (5960).

**3-Ethyl-4-(3-isopropyl-1*H*-indazol-1-yl)-1-methyl-1*H*-pyrrole-2,5-dione (18g).** Obtained from compound **14d** (66 mg, 0.26 mmol) as described in the general procedure for method B (reaction time: 15 min). Purification by flash chromatography [hexanes, then hexanes/EtOAc (3:1)] gave compound **18g** as a yellow oil (17 mg, 22%). IR (film) 1713, 1653, 1434, 1402, 1018 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.20 (t, $J$ = 7.4 Hz, 3H), 1.46 (d, $J$ = 6.8 Hz, 6H), 2.71 (q, $J$ = 7.4 Hz, 2H), 3.12 (s, 3H), 3.42 (h, $J$ = 6.8 Hz, 1H), 7.23−7.27 (m, 1H), 7.44 (pseudo-t, $J$ = 7.8 Hz, 1H), 7.73−7.76 (m, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 11.9, 16.3, 20.6, 23.0, 26.5, 111.6, 119.4, 121.1, 122.8, 126.6, 131.8, 134.7, 139.9, 155.3, 165.9, 169.8; MS (EI) $m/z$: 297 (10) $[M]^+$, 282 (100), 210 (13), 197 (17); HRMS (EI) $m/z$: calcd for $C_{17}H_{19}N_3O_2$ $[M]^+$ 297.1477, found 297.1479; UV−vis ($CH_2Cl_2$) $\lambda$/nm ($\varepsilon/M^{-1}$ $cm^{-1}$) = 390 (5538).

**3-Ethyl-4-(3-isopropyl-1*H*-indazol-1-yl)-1-phenyl-1*H*-pyrrole-2,5-dione (18h).** Obtained from compound **14d** (41 mg, 0.16 mmol) as described in the general procedure for method B (reaction time: 15 min). Purification by flash chromatography [hexanes, then hexanes/EtOAc (3:1)] gave compound **18h** as a yellow oil (18 mg, 30%). IR (film) 1716, 1656, 1502, 1386 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.26 (t, $J$ = 7.4 Hz, 3H), 1.49 (d, $J$ = 6.9 Hz, 6H), 2.81 (q, $J$ = 7.4 Hz, 2H), 3.45 (h, $J$ = 6.9 Hz, 1H), 7.24−7.28 (m, 1H), 7.38 (pseudo-t, $J$ = 7.0 Hz, 1H), 7.42−7.51 (m, 5H), 7.75 (d, $J$ = 8.0 Hz, 1H), 7.81 (d, $J$ = 8.8 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 13.0, 17.6, 21.6, 27.6, 112.9, 120.5, 122.3, 124.0, 126.1, 127.7, 127.8, 129.1, 131.5, 132.6, 135.7, 141.0, 156.7, 165.7, 169.5; MS (EI) $m/z$: 359 (27) $[M]^+$, 344 (100), 239 (51), 210 (36), 197 (31); HRMS (EI) $m/z$: calcd for $C_{22}H_{21}N_3O_2$ $[M]^+$ 359.1634, found 359.1630; UV−vis ($CH_2Cl_2$) $\lambda$/nm ($\varepsilon/M^{-1}$ $cm^{-1}$) = 395 (5391).

**General Procedure for Generation and Pericyclic Reactions of Benzo-2,3-diazafulvenium Methides under MW.** A suspension of the appropriate 1,3-dihydrothiazolo[3,4-*b*]indazole-2,2-dioxide **14** (0.20 mmol) in 1,2,4-trichlorobenzene (0.5 mL) was irradiated in the microwave reactor at 230 °C for the time indicated in each case. After cooling to room temperature the product was isolated by flash chromatography.

**3-Methyl-2-vinyl-2*H*-indazole (21) and 3-methyl-1*H*-indazole (22).** Obtained from compound **14b** (62 mg, 0.28 mmol) as described in the general procedure (reaction time: 15 min). Purification of the crude product by flash chromatography [hexanes, then hexanes/EtOAc (2:1)] gave, in order of elution, 3-methyl-2-vinyl-2*H*-indazole **21** as a colorless oil (14 mg, 32%) and 3-methyl-1*H*-indazole **22** as a yellowish solid (6 mg, 16%).

**3-Methyl-2-vinyl-2*H*-indazole (21).** IR (film) 1645, 1627, 1358, 1284 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 2.66 (s, 3H), 5.18 (d, $J$ = 8.8 Hz, 1H), 6.14 (d, $J$ = 15.2 Hz, 1H), 7.04 (pseudo-t, $J$ = 7.6 Hz, 1H), 7.26−7.31 (m, 2H), 7.53 (d, $J$ = 8.8 Hz, 1H), 7.63 (d, $J$ = 8.8 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 9.8, 105.8, 117.4, 119.9, 121.1, 121.5, 127.5, 130.0, 131.4, 148.8; MS (EI) $m/z$: 158 (100) $[M]^+$, 131 (32), 102 (11), 84 (14); HRMS (EI) $m/z$: calcd for $C_{10}H_{10}N_2$ $[M]^+$ 158.0844, found 158.0849.

**3-Methyl-1*H*-indazole (22).** The indazole **22** was identified by comparison with a specimen previously described in the literature.[9] mp 102−103 °C (from hexanes/diethyl ether), lit.[9] 113 °C. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 2.60 (s, 3H), 7.15 (pseudo-t, $J$ = 7.4 Hz, 1H), 7.36−7.44 (m, 2H), 7.69 (d, $J$ = 8.0 Hz, 1H).

**2-Methyl-3-(prop-1-en-2-yl)-2*H*-indazole (23a).** Obtained from compound **14c** (50 mg, 0.21 mmol) as described in the general procedure (reaction time: 10 min). After purification by flash chromatography [hexanes, then hexanes/EtOAc (1:1)], compound **23a** was obtained as an oil (21 mg, 58%). IR (film) 1622, 1486, 1357, 1286, 1040 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 2.25 (s, 3H), 4.16 (s, 3H), 5.26 (s, 1H), 5.60 (s, 1H), 7.06 (pseudo-t, $J$ = 7.4 Hz, 1H), 7.25−7.27 (m, 1H), 7.60 (d, $J$ = 8.4 Hz, 1H), 7.65 (d, $J$ = 8.8 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 23.1, 38.6, 116.9, 120.3, 120.5, 121.3,


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126.0, 134.0, 137.2, 147.9; MS (EI) *m/z*: 172 (100) $[M]^+$, 157 (54), 128 (14), 114 (10), 103 (6), 77 (6); HRMS (EI) *m/z*: calcd for $C_{11}H_{12}N_2$ $[M]^+$ 172.1000, found 172.1001.

**2-Ethyl-3-(prop-1-en-2-yl)-2*H*-indazole (23b) and 3-Isopropyl-2-vinyl-2*H*-indazole (24).** Obtained from compound **14d** (39 mg, 0.16 mmol) as described in the general procedure (reaction time: 10 min). Purification of the crude product by flash chromatography [hexanes, then hexanes/EtOAc (3:1)] gave, in order of elution, 3-isopropyl-2-vinyl-2*H*-indazole **24** as a yellowish oil (7 mg, 23%) and 2-ethyl-3-(prop-1-en-2-yl)-2*H*-indazole **23b** as a colorless oil (20 mg, 71%).

**2-Ethyl-3-(prop-1-en-2-yl)-2*H*-indazole (23b).** IR (film) 1621, 1400, 1362, 1279, 1056 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.57 (t, $J$ = 7.2 Hz, 3H), 2.24 (s, 3H), 4.45 (q, $J$ = 7.2 Hz, 2H), 5.25 (s, 1H), 5.59 (s, 1H), 7.04 (pseudo-t, $J$ = 7.4 Hz, 1H), 7.25−7.28 (m, 1H), 7.58 (d, $J$ = 8.4 Hz, 1H), 7.66 (d, $J$ = 8.8 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 16.2, 23.4, 45.9, 117.1, 120.2, 120.3, 120.4, 121.1, 125.9, 134.2, 136.6, 147.9; MS (EI) *m/z*: 186 (100) $[M]^+$, 171 (66), 158 (36), 144 (21), 128 (24), 115 (14); HRMS (EI) *m/z*: calcd for $C_{12}H_{14}N_2$ $[M]^+$ 186.1157, found 186.1157.

**3-Isopropyl-2-vinyl-2*H*-indazole (24).** IR (film) 1400, 1261, 1096, 1017 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 1.53 (d, $J$ = 7.0 Hz, 6H), 3.54 (h, $J$ = 7.0 Hz, 1H), 5.19 (d, $J$ = 8.6 Hz, 1H), 6.16 (d, $J$ = 15.2 Hz, 1H), 6.97 (pseudo-t, $J$ = 7.6 Hz, 1H), 7.23−7.27 (m, 1H), 7.34 (dd, $J$ = 8.6 and 15.2 Hz, 1H), 7.64 (d, $J$ = 8.8 Hz, 1H), 7.73 (d, $J$ = 8.8 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 22.2, 26.6, 106.7, 117.7, 119.6, 120.9, 121.1, 127.0, 130.1, 140.6, 149.0; MS (EI) *m/z*: 186 (53) $[M]^+$, 171 (100), 156 (16), 131 (12), 115 (13); HRMS (EI) *m/z*: calcd for $C_{12}H_{14}N_2$ $[M]^+$ 186.1157, found 186.1155.

**General Procedure for Generation and Pericyclic Reactions of Benzo-2,3-diazafulvenium Methides under FVP.** Pyrolysis of the appropriate 1,3-dihydrothiazolo[3,4-*b*]indazole-2,2-dioxide (0.40 mmol) at 500 °C/2 × $10^{-5}$ mbar onto a surface cooled at −196 °C over a period of 1 h gave a yellowish pyrolysate (the rate of volatilization of the starting material was controlled by the use of a Kugelrohr oven which heated the sample at 100−250 °C). After cooling to room temperature the pyrolysate was removed from the coldfinger with dichloromethane, and the solvent was removed in vacuo. The products were isolated by flash chromatography.

**3-Methyl-2-vinyl-2*H*-indazole (21).** Obtained from compound **14b** (47 mg, 0.21 mmol) as described in the general procedure. Purification by flash chromatography [hexanes/EtOAc (2:1)] gave compound **21** (23 mg, 69%), which was identified by comparison with the specimen previously prepared.

**2-Methyl-3-(prop-1-en-2-yl)-2*H*-indazole (23a).** Obtained from compound **14c** (70 mg, 0.27 mmol) as described in the general procedure. Purification by flash chromatography [hexanes/EtOAc (2:1), then hexanes/EtOAc (1:1)] gave indazole **23a** (34 mg, 73%), which was identified by comparison with the specimen previously prepared. Compound **23a** was also obtained, although in lower yield (61%), when FVP was carried out at 600 °C.

**2-Ethyl-3-(prop-1-en-2-yl)-2*H*-indazole (23b).** Obtained from compound **14d** (95 mg, 0.38 mmol) as described in the general procedure. Purification by flash chromatography [hexanes/EtOAc (3:1)] gave compound **23b** (65 mg, 92%), which was identified by comparison with the specimen previously prepared.

**Crystallographic Data for 1,3-dimethyl-4-(3-methyl-1*H*-indazol-1-yl)-1*H*-pyrrole-2,5-dione 18a.** $C_{14}H_{13}N_3O_2$, $M$ = 255.27, monoclinic, $P2_{1/n}$ with unit cell $a$ = 11.308(2) Å, $b$ = 7.4047(15) Å, $c$ = 14.748(3) Å, $\alpha$ = 90°, $\beta$ = 101.928(12)°, $\gamma$ = 90°, $V$ = 1208.2(4) $Å^3$. It contains four molecules/unit cell. $\rho$calcd =1.403 $g{\cdot}cm^{-3}$, $Z$ = 4, $\mu$ = 0.097 $mm^{-1}$. $R$ [$I > 2\sigma(I)$] = 0.0389 and $Rw$ = 0.1082 for 2785 independent reflections.

## THEORETICAL CALCULATIONS

All calculations described were performed with Gaussian 09[10] at DFT level using the standard 6-31G* basis set. The DFT calculations were carried out with the three-parameter density functional B3LYP,[11] which includes Becke's gradient exchange correction,[12] the Lee, Young, Parr,[13] and the Vosko, Wilk, Nusair correlation functionals.[14] For more details see the Supporting Information.

## ASSOCIATED CONTENT

### Supporting Information

$^1H$ and $^{13}C$ NMR spectra for all new compounds, UV−vis spectra of compounds **18**, ORTEP, bond lengths and angles of compound **18a** determined by X-ray crystallography, and theoretical calculation results; Cartesian Coordinates (Å) obtained from the B3LYP/6-31G* calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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