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C–H Activation*

Synthesis of 3-Amino-1-benzothiophene-1,1-diones by Alkyne Directed Hydroarylation and 1/N→3/C-Sulfonyl Migration


Abstract: A completely regioselective and highly stereoselective palladium-catalyzed intramolecular hydroarylation of arnesulfonyl ynamines to benzothiazoles was developed. The presence of an electron-withdrawing group on the triple bond of the sulfonyl yamine was crucial for the success of the reaction and our mechanistic studies suggest an alkyne-directed 5-exo-dig cyclization pathway. The products easily underwent photoinduced rearrangement to 3-amino-1-benzothiophene-1,1-diones (up to 35 % yields after two steps).

Introduction

Sulfonyl ynamines have recently emerged as a privileged class of ynamides.[1] They are stable compounds, readily prepared[2] and easy to handle. In addition, the polarized alkyne system of sulfonyl ynamines shows excellent reactivity in a wide variety of reactions featuring π-acid catalysis,[3] metal-catalyzed cyclizations,[4] cycloadditions[5] and rearrangements[6] for the synthesis of complex nitrogen-containing heterocycles and natural products. With the idea of extending the chemistry of these ynamines, we envisioned that arenesulfonyl ynamines 1 could be used as simple precursors for a single step, atom-efficient synthesis of 1,2-benzothiazole-1,1-diones, key elements of diverse biologically active compounds and useful reagents in organic synthesis (Scheme 1).[7]

Considering that compounds 1 react in the presence of alkynophilic transition metals usually through π-activation of the triple bond, we anticipated that initial alkyne coordination might direct an aromatic ortho-C–H activation followed by a stereocontrolled intramolecular hydroarylation (pathway A, Scheme 1), similar to that of N-alkynyl indoles developed by Park et al.[8] or alkynyl aryl ethers developed by Hiyama et al.[9] Moreover, excitation of the obtained benzothiazolediones 2 with light could trigger a [1,3]sigmatropic rearrangement of the sulfonyl group by S–N bond cleavage[10] followed by colig- gation to 3-amino-1-benzothiophene-1,1-diones 3 (pathway B, Scheme 1).[11] In particular, our interest in these compounds was awakened because they are potential crop protecting agents, and therefore beneficial for the ECHONET program we are part of.[12] To the best of our knowledge, alkyne-directed 5-exo-dig cyclizations of arenesulfonyl ynamines to 1,2-benzothiazole-1,1-diones and its following rearrangement to 3-amino-1-benzothiophene-1,1-diones have not been yet explored.

Results and Discussion

We initially investigated the behavior of sulfonyl yamine 1a in the presence of alkynophilic transition metals and Brensted acids (Table 1; for detailed information on the reaction optimization, see the Supporting Information). The reaction took place only with palladium-based catalysts. Thus, sulfonyl yamine 1a was converted to products (E/Z)-2a, 3, 4 and 5 in the presence of Pd(OAc)2 (5 mol-%) in toluene at 100 °C for 18 h (Table 1, entry 1). The (E)-exo-cyclic alkyldiene product 2a was isolated in
Table 1. Reaction optimization.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Additive</th>
<th>Ratio of products [%][a]</th>
<th>Yield (E)-2a [%][b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd(OAc)$_2$</td>
<td></td>
<td>27 35 33 3 2</td>
<td>82:18 21</td>
</tr>
<tr>
<td>2</td>
<td>Pd(PPh$_3$)$_4$</td>
<td>HOAc</td>
<td>30 10 58 2 0</td>
<td>90:10 7</td>
</tr>
<tr>
<td>3</td>
<td>Pd(PPh$_3$)$_4$</td>
<td>Zn</td>
<td>43 23 17 3 14</td>
<td>92:8 14</td>
</tr>
<tr>
<td>4</td>
<td>Pd(OAc)$_2$</td>
<td>NaOAc</td>
<td>23 37 38 2 0</td>
<td>85:15 20</td>
</tr>
<tr>
<td>5</td>
<td>Pd(OAc)$_2$</td>
<td>P(0-tol)$_3$</td>
<td>28 14 58 0 0</td>
<td>85:15 8</td>
</tr>
</tbody>
</table>

[a] Reaction conditions: 1a (1.0 mmol), Pd catalyst (5 mol-%), phosphine ligand (10 mol-%), additive (10 mol-%), PhMe (10.0 mL), 100 °C for 18 h. [b] Based on the $^1$H NMR spectrum of the crude. [c] NaOAc (2.0 equiv.).

21 % yield after purification of the crude mixture by neutral silica-gel column chromatography.

The structure of (E)-2a was unambiguously determined by NMR spectroscopy and X-ray crystallography. This reaction also showed degradation of sulfonyl ynamine 1a under the reaction conditions forming N-phenyl sulfonamide 3, which was the main byproduct of the ynamide cyclization. Compound 3 reacted further with 1a to form Michael adduct 4, which was successfully isolated after purification. Furthermore, sulfonyl ynamine 1a underwent partial hydrogenation of the triple bond to yield sulfonyl enamine 5 in a trace amount.[13] The reaction also took place in the presence of palladium(0), albeit in a much lower conversion compared to Pd(OAc)$_2$ (entries 2 and 3). The use of Pd(OAc)$_2$ and Zn, a catalytic system developed by Hiyama et al. for the cyclization of alkynyl aryl ethers,[9] had no influence on the yield of 2a (entry 4). These initial studies showed that formation of benzothiazoledione 2a took place without any further additives (e.g., NaOAc, entry 5). Finally, addition of phosphine ligands promoted the cyclization. Bulky ligands led in general to higher yields and better ratios of the stereoisomers (entries 6 and 7).

Although the yields are relatively low, this unprecedented intramolecular hydroarylation reaction is completely regioselective and highly stereoselective: (E)-exocyclic 1,2-benzothiazole-1,1-dione 2a is the major isomer with an E/Z-ratio of up to 98:2, confirmed by NOE studies in all cases.

With these results in hand, we focused our attention on the scope and limitations of the reaction varying the substituents on the alkyne terminus (R$^1$), on the aromatic ring of the sulfonamide group (R$^3$) and on the nitrogen (R$^2$) for the hydroarylation of sulfonyl ynamines 1a–k (Scheme 2). Notably, the presence of an electron-withdrawing group on the triple bond, e.g., ester or ketone, was essential for the success of the hydroarylation. Thus, sulfonyl ynamines with a ketone showed similar reactivity to sulfonyl ynamine 1a proceeding with exclusive regioselectivity and excellent stereoselectivity (2b–2c). In stark contrast, when the reaction was performed with sulfonyl ynamines 1d–1f (R = H, SiMe$_3$, Ph) no cyclization was detected and only decomposition to 3 was observed. Changing the conditions (solvent, temperature, Pd catalyst, addition of base) did not lead to products 2d–2f either.
Next, a series of electronically different sulfonyl ynamines were employed for this transformation. To our delight, we observed no significant difference in the reaction efficiency when changing the substituents at the aryl group of the sulfonamide. 1,2-Benzothiazole-1,1-diones (2g–i) were obtained in comparable yields and also with complete regioselectivity and with excellent stereoselectivity. Finally, sulfonyl ynamines 1j and 1k were subjected to the reaction conditions to compare the reactivity of compounds with different substitution on the nitrogen. Compound 1j formed product 2j in 31 % yield and compound 1k resulted in a formation of a mixture of 2k (>99:1 E/Z ratio) and 6 in 26 and 10 % yield, respectively.[14]

For a better understanding of the reaction mechanism, we investigated the reaction pathway with DFT calculations (Figure 1). The most logical mechanistic scenario for the reaction of sulfonyl ynamine 1l and Pd(OAc)₂ would involve coordination of the Pd⁰ species to the substrate, as in 7, followed by an alkynedirected concerted deprotonation-metalation sequence (CDM).[15] Thus, calculations indicate transition state TS1 in which one of the acetate groups is acting both as a κ² ligand and as a base. The proton abstraction presents the highest activation barrier within the catalytic cycle (22.6 kcal/mol), and therefore should be considered as the rate-determining step of the reaction. Additionally, ortho-C–H activation in TS1 proceeds much slower for the alkyné–H and alkyné–SiMe₃ substructures (24.5 and 24.6 kcal/mol, for 1d and 1e, respectively) compared to the corresponding alkyné–CO₂Me substructure 1l. The difference between these barrier values is >2.5 kcal/mol corresponding to more than 100 times slower reaction rate, which is in agreement with the experimental results. Consequently, the intermediate 8 performs a carboxyadation to the CC triple bond through TS2, leading to intermediate 9. Also, this step was predicted to be a few kcal/mol higher for sulfonyl ynamines 1d and 1e (16.0 and 14.2 kcal/mol respectively) than for sulfonyl ynamine 1l (11.2 kcal/mol). Further protonation of the “push-pull” alkyné–Pd⁰ species 9 with acetic acid forms an enol intermediate 10, with almost free rotation around the exocyclic C–C bond. We found that the enol structure 10 lies 12.9 kcal/mol higher in energy than palladium species 9, confirming the feasibility of this or related isomerization processes. The final protodemetalation with acetic acid renders the major product (E)-2a and recovers the active Pd-áacetate species.

Our DFT calculations further reveal that the (E)-isomer is the most stable isomer [2.5 kcal/mol Lower in energy than the (Z)-isomer, Scheme 3]. To validate this result, (E)-2a and (Z)-2a were subjected independently to the same experimental conditions. We observed the formation of an 85:15 E/Z mixture of isomers after 18 h of reaction time. These results suggest that the cyclization of 1a might proceed in an exceptional stereoselective manner (as proposed in Scheme 2), however the major product further undergoes partial isomerization under the reaction conditions.

Finally, 1,2-benzothiazole-1,1-diones 2 underwent a previously unexplored photoinduced rearrangement to 3-amino-1-benzothiophene-1,1-diones 12 while being irradiated with UV light (300 nm; Scheme 4).

Thus, when either stereoisomer of 2a or the mixture of both was exposed to irradiation at 50 °C for 24 h, a complete photochemical conversion to 3-amino-1-benzothiophene-1,1-dione 12a was observed. Furthermore, to show the scope of this transformation, several 1,2-benzothiazoledione derivatives were subjected to the same reaction conditions. The corresponding products 12b–12d were obtained in excellent yields in all cases. The structure of the products was confirmed by selfNOE spectroscopy and X-ray crystallography of 12a and 12d. We also propose a plausible mechanism on the basis of previously reported photoinduced cleavage of sulfonamides.[27] This [1,3]sigmatropic rearrangement entails a homolytic cleavage of the sulfonamide

![Figure 1. Computed pathway for cyclization of 1l. Free energies (298 K) with respect to starting materials are shown in kcal/mol.](image-url)
S–N bond of 1,2-benzothiazole-1,1-diones 2, followed by recombination of the resulting sulfinate radical with the C-terminus of the enamyl radical (13). Subsequent tautomerization of the formed imine 14 results in 3-amino-1-benzothiophene-1,1-dione 12.

Conclusions

In summary, we have demonstrated a completely regioselective and highly stereoselective intramolecular hydroarylation of sulfonamides. This method opens an easy access to benzothiazole heterocycles, valuable scaffolds in medicinal and organic synthesis. Our mechanistic studies suggest an alkyne-directed 5-exo-dig intramolecular cyclization pathway, where the presence of an electron-withdrawing group at the triple bond was key for the success of the reaction. Moreover, we have discovered the first example of photoinduced rearrangement of 1,2-benzothiazole-1,1-diones to form 3-amino-1-benzothiophene-1,1-dione derivatives in excellent yields. Optimization studies that broaden the synthetic scope and applications of the reaction are currently under investigation.

Experimental Section

General Information: Reagents were obtained from commercial suppliers and were used without purification. Standard syringe techniques were applied for the transfer of dry solvents and air- or moisture-sensitive reagents. All inert reactions were carried out under a nitrogen atmosphere using flame-dried flasks. If stated, moisture-sensitive reagents.

Scheme 4. Photochemical rearrangement of 1,2-benzothiazole-1,1-diones 2 to 3-amino-1-benzothiophene-1,1-diones 12. Reaction conditions: 2 (0.1 mmol), MeCN (10.0 mL), hv (300 nm), 24 h. [a] Isolated yield.

Sulfonamide 3 was prepared from aniline (0.9 g, 10 mmol) and benzenesulfonyl chloride (1.9 g, 11 mmol) according to the general procedure and obtained in 11% yield as a white solid. 1H NMR [400 MHz, CDCl3]: δ = 6.58 (br. s, 1 H); δ = 7.02–7.09 (m, 2 H), 7.09–7.18 (m, 1 H), 7.20–7.29 (m, 2 H), 7.40–7.48 (m, 2 H), 7.50–7.58 (m, 1 H), 7.72–7.79 (m, 2 H) ppm. 13C NMR [101 MHz, CDCl3]: δ = 121.6, 125.4, 127.3, 129.3, 129.7, 133.0, 136.5, 139.0 ppm. These data were in accordance to those reported in the literature.[17]

4-Methyl-N-phenylbenzenesulfonamide (3): Sulfonamide 3 was prepared from aniline (0.9 g, 10 mmol) and 4-methylbenzenesulfonfonyl chloride (2.1 g, 11 mmol) according to the general procedure and obtained in 92% yield as a white solid. 1H NMR [400 MHz, CDCl3]: δ = 2.35 (s, 3 H), 6.61 (br. s, 1 H), 7.02–7.10 (m, 2 H), 7.12–7.25 (m, 5 H), 7.62–7.68 (m, 2 H) ppm. 13C NMR [101 MHz, CDCl3]: δ = 21.6, 121.5, 125.1, 127.5, 129.2, 129.6, 136.0, 136.4, 143.9 ppm. These data were in accordance to those reported in the literature.[17]

4-Methoxy-N-phenylbenzenesulfonamide (52): Sulfonamide 52 was prepared from aniline (0.9 g, 10 mmol) and 4-methoxybenzenesulfonyl chloride (2.3 g, 11 mmol) according to the general procedure and obtained in 81% yield as a white solid. 1H NMR [400 MHz, CDCl3]: δ = 3.82 (s, 3 H), 6.70 (br. s, 1 H), 6.81–6.96 (m, 2 H), 7.03–7.15 (m, 3 H), 7.18–7.31 (m, 2 H), 7.59–7.78 (m, 2 H) ppm. 13C NMR [101 MHz, CDCl3]: δ = 55.7, 114.3, 121.6, 125.2, 129.4, 129.5, 130.7, 136.9, 163.2 ppm. These data were in accordance to those reported in the literature.[17]

4-Nitro-N-phenylbenzenesulfonamide (53): Sulfonamide 53 was prepared from aniline (0.9 g, 10 mmol) and 4-nitrobenzenesulfonyl chloride (2.4 g, 11 mmol) according to the general procedure and obtained in 94% yield as a light yellow solid. 1H NMR [400 MHz, CDCl3]: δ = 6.02 (br. s, 1 H), 7.07–7.32 (m, 5 H), 7.89–7.93 (m, 2 H), 8.22–8.30 (m, 2 H) ppm. 13C NMR [101 MHz, CDCl3]: δ = 122.4, 124.3, 126.6, 128.7, 129.9, 135.2, 144.5, 150.3 ppm. These data were in accordance to those reported in the literature.[18]

N-Benzyl-4-methylbenzenesulfonamide (54): Sulfonamide 54 was prepared from benzylamine (1.07 g, 10 mmol) and 4-methyl-
benzenesulfonyl chloride (2.1 g, 11 mmol) according to the general procedure and obtained in 91 % yield as a white solid. 1H NMR [400 MHz, CDCl3]: δ = 2.32 (s, 3 H), 4.02 (d, J = 6.5 Hz, 2 H), 6.74 (br. t, J = 6.5 Hz, 1 H), 7.05–7.21 (m, 5 H), 7.22–7.31 (m, 2 H), 7.64–7.71 (m, 2 H) ppm. 13C NMR [101 MHz, CDCl3]: δ = 21.7, 48.3, 128.3, 128.4, 129.1, 129.5, 130.9, 139.1, 139.2, 144.3 ppm. These data were in accordance to those reported in the literature.[19]

N,4-Dimethylbenzenesulfonamide (S5): Sulfonamide S5 was prepared from methylvamine hydrochloride (0.68 g, 10 mmol) and 4-methylbenzenesulfonyl chloride (2.1 g, 11 mmol) according to the general procedure and obtained in 89 % yield as brown oil. 1H NMR [400 MHz, CDCl3]: δ = 2.42 (s, 3 H), 2.62 (d, J = 5.5 Hz, 3 H), 4.45 (br. s, 1 H), 7.29–7.33 (m, 2 H), 7.70–7.76 (m, 2 H) ppm. 13C NMR [101 MHz, CDCl3]: δ = 21.2, 29.5, 127.3, 129.8, 135.7, 143.3 ppm. These data were in accordance to those reported in the literature.[20]

General Procedure for the Synthesis of 1,2-Dichlorovinyl Sulfonanides: 1,2-Dichlorovinyl sulfonamides S6–S11 were prepared from the literature procedure reported by Anderson et al.[21] The sulfonamide (8 mmol, 1.0 equiv.) was added dropwise to a suspension of sodium hydride (670 mg, 60 % dispersion in mineral oil, 16.8 mmol, 2.1 equiv.) in DMP (30 mL) and the reaction mixture was warmed to 23° C in 2 h. Trichloroethene (800 mL, 8.8 mmol, 1.1 equiv.) was slowly added to this solution, which was after stirred at 50 °C for 16 h. After cooling to 23° C, the reaction mixture was quenched with water (300 mL) and extracted with AcOEt (3 × 50 mL). The combined organic washings were dried with sodium sulfate, concentrated in vacuo and the crude residue was purified by column chromatography as indicated. The E-configuration of the obtained products including the new compounds was assigned by the literature procedure reported by Davies et al.[23] 1H NMR spectra and X-ray crystallography data known from the literature.[24]

N-(E)-1,2-Dichlorovinyl)-N-phenylbenzenesulfonamide (S6): Column chromatography (heptane/AcOEt, 40:1 → 10:1) afforded the product S6 as a yellow oil (72 %). Rf (silica gel, heptane/AcOEt, 10:1): 0.34 (UV, KMN04 solution). 1H NMR [400 MHz, CDCl3]: δ = 6.46 (s, 1 H), 7.30–7.39 (m, 5 H), 7.43–7.50 (m, 2 H), 7.58–7.63 (m, 1 H), 7.75–7.80 (m, 2 H) ppm. 13C NMR [101 MHz, CDCl3]: δ = 120.7, 128.6, 128.78, 128.79, 129.2, 129.4, 130.6, 133.6, 137.6, 138.5 ppm. FTIR: ν = 811, 819, 1089, 1163, 1469, 2934, 3086 cm–1. HRMS (ESI-TOF) m/z: [M + H]+ calcd. for C15H15Cl2NO3S 372.9966, found 372.9954.

N-(E)-1,2-Dichlorovinyl)-4-methylphenylbenzenesulfonamide (S7): Column chromatography (heptane/AcOEt, 40:1 → 10:1) afforded the product S7 as a white solid (91 %). Rf (silica gel, heptane/AcOEt, 10:1): 0.70 (UV, KMN04 solution). 1H NMR [400 MHz, CDCl3]: δ = 2.31 (s, 3 H), 2.64 (s, 1 H), 2.67–2.81 (br. s, 2 H), 6.27 (s, 1 H), 2.78–2.84 (m, 5 H), 7.32–7.37 (m, 2 H), 7.80–7.86 (m, 2 H) ppm. 13C NMR [101 MHz, CDCl3]: δ = 21.7, 52.0, 121.7, 128.6, 128.78, 128.79, 129.2, 129.4, 130.6, 133.6, 137.6, 138.5 ppm. FTIR: ν = 811, 819, 1089, 1163, 1469, 2934, 3086 cm–1. HRMS (ESI-TOF) m/z: [M + H]+ calcd. for C15H13Cl2NO2S 279.9966, found 279.9983.

N-(E)-1,2-Dichlorovinyl)-4-methylphenylbenzenesulfonamide (S11): Column chromatography (heptane/AcOEt, 40:1 → 10:1) afforded the product S11 as brown oil (64 %). Rf (silica gel, heptane/AcOEt, 10:1): 0.13 (UV, KMN04 solution). 1H NMR [400 MHz, CDCl3]: δ = 2.45 (s, 3 H), 2.94 (s, 3 H), 6.39 (s, 1 H), 7.31–7.37 (m, 2 H), 7.79–7.85 (m, 2 H) ppm. 13C NMR [101 MHz, CDCl3]: δ = 21.7, 37.9, 121.4, 127.8, 129.2, 129.5, 132.4, 143.2 ppm. FTIR: ν = 693, 722, 1084, 1160, 1333, 1498, 2986, 3012 cm–1. HRMS (ESI-TOF) m/z: [M + H]+ calcd. for C15H13Cl2NO2S 279.9966, found 279.9983.

General Procedure A for the Syntheses of Sulfonyl Ynamines: Sulfonyl Ynamines 1a, 1d, 1e, 1g, 1h, 1i, 1j and 1k were prepared by the literature procedure reported by Davies et al.[23] n-Butylthium (3.8 mL, 1.6 M in THF, 6 mmol, 2.1 equiv.) was slowly added to a stirred solution of 1,2-dichlorovinyl sulfonamide (5 mmol, 1.0 equiv.) in THF (30 mL) under an argon atmosphere at –78 °C. After stirring for 1 h, the lithium acetylide was treated with the corresponding electrophile and stirred for 1 h at –78 °C. The mixture was warmed to 23 °C and stirred for 2–3 h. The reaction mixture was quenched with brine (100 mL) and extracted with EtO (2 × 50 mL). The combined organic washings were dried with sodium sulfate, concentrated in vacuo and the crude residue was purified by column chromatography as indicated.

General Procedure B for the Syntheses of Sulfonyl Ynamines: Sulfonyl Ynamines 1b and 1c were prepared by the literature procedure reported by Wolf et al.[24] Sulfonyl ynamine 1d (1.0 g, 3.7 mmol, 1.0 equiv.), Cul (70 mg, 0.37 mmol, 0.1 equiv.) and N,N-diisopropylethylamine (1.5 mL, 7.4 mmol, 2.0 equiv.) were dissolved in chloroform (20 mL) under a nitrogen atmosphere. After 30 min, the acyl chloride (5.6 mmol, 1.5 equiv.) was added, and the mixture was stirred until completion as determined by TLC. Solvent was removed in vacuo and the crude residue was purified by column chromatography as indicated.

General Procedure C for the Syntheses of Sulfonyl Ynamines: Sulfonyl Ynamine 1f was prepared by the literature procedure reported by Hsung et al.[25] Sulfonyl ynamine 1d (1.0 g, 3.7 mmol, 1.0 equiv.), iodosbenzene (830 mg, 4.1 mmol, 1.1 equiv.) and Pd(PPh3)4 (214 mg, 0.185 mmol, 0.05 equiv.) were dissolved in Et3N/toluene mixture (2:1, 36 mL) under a nitrogen atmosphere. The solution was stirred at 23 °C for 10 min, and Cul (11 mg, 0.06 mmol, 0.015 equiv.) was then added. After heating the reaction mixture at 60 °C for 12 h, the mixture was diluted with AcOEt, filtered through a diatomaceous earth pad, and concentrated in vacuo. The resulting crude residue was purified by silica gel flash column chromatography as indicated.
Ethyl 3-(4-Methyl-N-phenylbenzenesulfonamido)propanoate (1a): Sulfonyl ynamine 1a was prepared according to general procedure A using 1,2-dichlorovinyl sulfonamide S7 (1.7 g, 5.0 mmol). The lithium acetylide was treated with freshly distilled ethyl chlorofluoride (714 µL, 7.5 mmol) at −78 °C for 15 min and at 23 °C for 2 h. Column chromatography (heptane/AcOEt, 20:1) afforded the product 1a as a white solid (82 %). \( R_\text{f} \) (silica gel, heptane/AcOEt, 10:1): 0.11 (UV, KMnO4 solution). \( H \) NMR [400 MHz, CDCl3]: \( \delta = 1.31 \) (t, J = 7.1 Hz, 3 H), 2.46 (s, 3 H), 4.24 (q, J = 7.1 Hz, 2 H), 7.16–7.23 (2 m, H), 7.29–7.34 (m, 2 H), 7.34–7.38 (m, 3 H), 7.58–7.67 (m, 2 H) ppm. \( 1^C \) NMR [101 MHz, CDCl3]: \( \delta = 14.2, 21.7, 61.7, 66.2, 82.2, 126.5, 128.4, 129.3, 129.6, 130.0, 133.1, 137.5, 145.9, 154.8 \) ppm. These data were in accordance to those reported in the literature.[23]

N-(4,4-Dimethyl-3-oxoprop-1-yn-1-yl)-4-methylbenzenesulfonamide (1b): Sulfonyl ynamine 1b was prepared according to general procedure B. The reaction with pivaloyl chloride (767 mg, 20.0 mmol) in heptane before being used for column chromatography afforded the product 1b as a light yellow oil (79 %). \( R_\text{f} \) (silica gel, heptane/AcOEt, 10:1): 0.09 (UV, KMnO4 solution). \( H \) NMR [400 MHz, CDCl3]: \( \delta = 1.20 \) (s, 9 H), 2.40 (s, 3 H), 7.16–7.20 (2 m, H), 7.24–7.28 (2 m, H), 7.30–7.34 (m, 3 H), 7.53–7.59 (m, 2 H) ppm. \( 1^C \) NMR [101 MHz, CDCl3]: \( \delta = 21.6, 26.3, 44.5, 73.6, 89.1, 126.3, 128.3, 129.1, 129.3, 132.7, 132.4, 145.6, 193.2 \) ppm. These data were in accordance to those reported in the literature.[24]

Ethyl 3-(4-Methyl-N-phenylbenzenesulfonamido)propanoate (1c): Sulfonyl ynamine 1c was prepared according to general procedure B. The reaction with benzyol chloride (767 mg, 20.0 mmol) in heptane before being used for column chromatography afforded the product 1c as a light yellow oil (81 %). \( R_\text{f} \) (silica gel, heptane/AcOEt, 10:1): 0.33 (UV, KMnO4 solution). \( H \) NMR [400 MHz, CDCl3]: \( \delta = 2.44 \) (s, 3 H), 7.25–7.29 (2 m, H), 7.36–7.41 (m, 3 H), 7.47–7.55 (m, 2 H), 7.60–7.65 (m, 3 H), 8.14–8.26 (m, 2 H) ppm. \( 1^C \) NMR [101 MHz, CDCl3]: \( \delta = 121.7, 174.9, 90.2, 126.4, 128.2, 128.7, 129.2, 129.2, 129.5, 129.9, 132.3, 135.6, 136.9, 137.1, 145.9, 176.8 \) ppm. These data were in accordance to those reported in the literature.[24]

Ethyl 3-(4-Methyl-N-phenylbenzenesulfonamido)propanoate (1f): Sulfonyl ynamine 1f was prepared according to general procedure B. The reaction with pivaloyl chloride (767 mg, 20.0 mmol) in heptane before being used for column chromatography afforded the product 1f as a light yellow solid (80 %). \( R_\text{f} \) (silica gel, heptane/AcOEt, 10:1): 0.27 (UV, KMnO4 solution). \( H \) NMR [400 MHz, CDCl3]: \( \delta = 2.45 \) (s, 3 H), 7.27–7.36 (m, 9 H), 7.36–7.42 (m, 3 H), 7.61–7.65 (m, 2 H) ppm. \( 1^C \) NMR [101 MHz, CDCl3]: \( \delta = 21.7, 70.6, 83.2, 122.7, 126.5, 126.8, 128.1, 128.3, 129.0, 129.5, 131.4, 132.9, 139.0, 145.1 \) ppm. These data were in accordance to those reported in the literature.[27]
uct during the course of the reaction.\[26\] Compound 1i: R₆ (silica gel, toluene): 0.33 (UV, KMnO₄ solution). ¹H NMR (400 MHz, CDCl₃): δ = 1.32, (t, J = 7.1 Hz, 3 H), 4.25 (q, J = 7.1 Hz, 2 H), 7.17–7.23 (m, 2 H), 7.36–7.46 (m, 3 H), 7.92–8.00 (m, 2 H), 8.33–8.42 (m, 2 H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 14.1, 62.0, 66.7, 80.4, 124.5, 126.5, 129.7, 129.81, 129.84, 136.5, 140.9, 150.7, 153.6 ppm. FTIR: ν = 690, 740, 854, 1086, 1126, 1206, 1348, 1533, 1593, 1706, 2223, 2925, 3107 cm⁻¹. HRMS (ESI-TOF) m/z: [M + H]⁺ calcd. for C₁₇H₁₆N₂O₆S: 375.0651, found 375.0659.

**Column chromatography**

R₆ Column chromatography (heptane/AcOEt, 20:1)

R₆ Column chromatography (heptane/AcOEt, 40:1

R₆ A using 1,2-dichlorovinyl sulfonamide

R₆ The lithium acetylide was treated with freshly distilled ethyl chloroformate (714 mg, 7.1 mmol) at –78 °C for 15 min and at 23 °C for 2 h. Column chromatography (heptane/AcOEt, 20:1 → 10:1; silica gel was washed with 1 % Et₃N in heptane before being used for column chromatography).

**Ethyl (E)-2-[5-Methyl-1,1-dioxo-2-phenyl-1,2-benzothiazol-3(2H)-ylidene]acetate ([E]-2a): R₆ (silica gel, toluene): 0.28 (UV, KMnO₄ solution).** ¹H NMR (400 MHz, CDCl₃): δ = 1.01 (t, J = 7.1 Hz, 3 H), 2.54 (s, 3 H), 3.66 (q, J = 7.1 Hz, 2 H), 5.83 (s, 1 H), 7.36–7.49 (m, 5 H), 7.55 (m, J = 8.0, 1.2, 0.6 Hz, 1 H), 7.62 (quint, J = 0.6 Hz, 1 H), 7.79 (d, J = 8.0 Hz, 1 H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 13.9, 22.0, 60.4, 93.0, 121.5, 122.0, 126.9, 128.6, 129.5, 130.2, 131.3, 134.9, 140.2, 144.9, 164.0 ppm. FTIR: ν = 693, 907, 1012, 1145, 1626, 1372, 1494, 1635, 1708, 3029 cm⁻¹. HRMS (ESI-TOF) m/z: [M + H]⁺ calcd. for C₁₉H₁₈N₂O₄S: 434.0957, found 344.0966.

**Ethyl (Z)-2-[5-Methyl-1,1-dioxo-2-phenyl-1,2-benzothiazol-3(2H)-ylidene]acetate ([Z]-2a): R₆ (silica gel, toluene): 0.28 (UV, KMnO₄ solution).** ¹H NMR (400 MHz, CDCl₃): δ = 1.01 (t, J = 7.1 Hz, 3 H), 2.54 (s, 3 H), 3.66 (q, J = 7.1 Hz, 2 H), 5.83 (s, 1 H), 7.36–7.49 (m, 5 H), 7.55 (m, J = 8.0, 1.2, 0.6 Hz, 1 H), 7.62 (quint, J = 0.6 Hz, 1 H), 7.79 (d, J = 8.0 Hz, 1 H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 13.9, 22.0, 60.4, 93.0, 121.5, 122.0, 126.9, 128.6, 129.5, 130.2, 131.3, 134.9, 140.2, 144.9, 164.0 ppm. FTIR: ν = 693, 907, 1012, 1145, 1626, 1372, 1494, 1635, 1708, 3029 cm⁻¹. HRMS (ESI-TOF) m/z: [M + H]⁺ calcd. for C₁₉H₁₈N₂O₄S: 434.0957, found 344.0943.

**Ethyl (Z)-2-[5-Methyl-1,1-dioxo-2-phenyl-1,2-benzothiazol-3(2H)-ylidene]acetate ([Z]-2a):**
prepared according to general procedure using sulfonyl ynamine 1a (343 mg, 1.0 mmol). Ratio E/Z = 98:2 was determined by 1H NMR spectroscopy. Column chromatography (toluene; silica gel was washed with 1% Et3N in heptane before being used for column chromatography) afforded product (E)-2a as a white solid (127 mg, 37%). The spectroscopic data were identical to those reported above.

(E)-3,3-Dimethyl-1-(5-methyl-1,1-dioxo-2 phenyl-1,2-benzo thiadiazol-3(2H)-ylidene)butan-2-one (E)-1b was prepared according to general procedure using sulfonyl ynamine 1b (355 mg, 1.0 mmol). Ratio E/Z > 99:1 was determined by 1H NMR spectroscopy. Column chromatography (toluene; silica gel was washed with 1% Et3N in heptane before being used for column chromatography) afforded the product (E)-2b as a white solid (121 mg, 34%). Rf (silica gel, toluene): 0.28 (UV, KMnO4 solution).

1H NMR [400 MHz, CDCl3]: δ = 1.05 (t, J = 7.1 Hz, 8 H), 2.87–2.88 (m, 1 H), 2.95, 3.68 (m, 6 H, 7.1 Hz, 2 H), 3.69, 6.62 (m, 6 H, 7.8 Hz, 2 H), 8.09 (q, J = 1.2 Hz, 1 H). HRMS (ESI-TOF) m/z: [M + H]+ calcd for C18H19NO5S 356.1320, found 356.1334.

(E)-2-[5-(Methyl-1,1-dioxo-2 phenyl-1,2-benzo thiadiazol-3(2H)-ylidene)-1 phenylethan-1-one (E)-2c was prepared according to general procedure used sulfonyl ynamine 1c (375 mg, 1.0 mmol). Ratio E/Z = 98:2 was determined by 1H NMR spectroscopy. Column chromatography (toluene; silica gel was washed with 1% Et3N in heptane before being used for column chromatography) afforded the product (E)-2c as a white solid (116 mg, 31%). Rf (silica gel, toluene): 0.31 (UV, KMnO4 solution).

1H NMR [400 MHz, CDCl3]: δ = 2.57 (s, 3 H), 6.59 (s, 1 H), 7.37–7.45 (m, 2 H), 7.48–7.55 (m, 1 H), 7.56–7.66 (m, 6 H, 7.1 Hz, 2 H), 7.72–7.79 (m, 2 H), 7.85 (d, J = 8.0 Hz, 1 H), 9.00 (quint, J = 0.5 Hz, 1 H) ppm. 13C NMR [101 MHz, CDCl3]: δ = 22.2, 23.6, 44.7, 101.5, 121.0, 127.8, 129.4, 130.4, 130.5, 130.6, 130.8, 133.4, 145.1, 145.6, 204.3 ppm. FTIR: ν = 995, 966, 1078, 1183, 1322, 1566, 1673, 2965 cm–1. HRMS (ESI-TOF) m/z: [M + H]+ calcd for C18H19NO5S 356.1320, found 356.1334.

Ethyl (E)-2-[1-(1,1-Dioxo-2 phenyl-1,2-benzo thiadiazol-3(2H)-ylidene)acetate (E)-2g was prepared according to general procedure used sulfonyl ynamine 1g (330 mg, 1.0 mmol). Ratio E/Z = 98:2 was determined by 1H NMR spectroscopy. Column chromatography (toluene; silica gel was washed with 1% Et3N in heptane before being used for column chromatography) afforded product (E)-2g as a white solid (112 mg, 34%). Rf (silica gel, toluene): 0.31 (UV, KMnO4 solution).

1H NMR [400 MHz, CDCl3]: δ = 1.28 (t, J = 7.1 Hz, 3 H), 4.20 (q, J = 7.1 Hz, 2 H), 5.16 (s, 1 H), 7.46–7.56 (m, 2 H), 7.57–7.57 (m, 3 H), 7.76–7.85 (m, 2 H), 7.92–8.02 (m, 1 H), 9.44 (m, 1 H) ppm. 13C NMR [101 MHz, CDCl3]: δ = 14.4, 60.7, 97.2, 121.3, 127.4, 129.9, 130.5, 130.6, 130.7, 131.2, 132.5, 133.3, 133.9, 146.2, 166.3 ppm. FTIR: ν = 692, 910, 1045, 1099, 1157, 1186, 1234, 1619, 1708, 2925 cm–1. HRMS (ESI-TOF) m/z: [M + H]+ calcd for C18H17NO4S 330.0806, found 330.0827.

Ethyl (E)-2-[5-Methoxy-1,1-dioxo-2 phenyl-1,2-benzothiazol 3(2H)-ylidene)acetate (E)-2h was prepared according to general procedure used sulfonyl ynamine 1h (360 mg, 1.0 mmol). Ratio E/Z = 95:5 was determined by 1H NMR spectroscopy. Column chromatography (toluene; silica gel was washed with 1% Et3N in heptane before being used for column chromatography) afforded the product (E)-2h as a white solid (119 mg, 33%). Rf (silica gel, toluene): 0.17 (UV, KMnO4 solution).
[101 MHz, CDCl3]: \( \delta = 14.6, 21.8, 55.4, 60.1, 96.7, 121.9, 127.7, 128.4, 128.9, 130.1, 131.3, 133.0, 134.6, 138.1, 145.1, 152.0, 167.0 \) ppm.

FTIR: \( \tilde{\nu} = 667, 800, 1089, 1165, 1344, 1620, 1705, 2922 \) cm\(^{-1}\). HRMS (ESI-TOF) \( m/z: [M + H]^+ \) calcd. for \( C_{19}H_{21}NO_5S \) 358.1113, found 358.1132.

**Intramolecular Hydroxylation of 1d, 1e and 1f:** Sulfonyl ynamines 1d, 1e or 1f were submitted to the reaction conditions according to general procedure. \(^1\)H NMR spectroscopy of the crude product indicated partial degradation of the starting material to 4-methyl-N-phenylbenzenesulfonamide 3 and additional unidentified products. The formation of products 2d, 2e or 2f was not observed.

**Study of Equilibration Between E- and Z-Isomers of 2a:** E-1,2-Benzothiazole-1,1-dione 2a or (Z)-1,2-Benzothiazole-1,1-dione 2a (69 mg, 0.2 mmol, 1.0 equiv.) were independently dissolved in toluene (2 mL) under a nitrogen atmosphere in a Biotage Initiator microwave reactor at 100 °C. After cooling to 23 °C, the solvent was removed in vacuo. The reaction mixture was quenched with brine (50 mL) and extracted with AcOEt (2 × 20 mL). The combined organic washings were dried over anhydrous sodium sulfate, filtered off, and concentrated in vacuo. 

**General Procedure for Photochemical Rearrangement of 1,2-Benzothiazole-1,1-diones:** To 25 mL quartz flask was added 1,2-Benzothiazole-1,1-dione 2a, 2g, or 2k (0.1–1.0 mmol, 1.0 equiv.) in 10 mL of deoxygenated MeCN with stirring. This flask was irradiated in a Rayonet RMR-600 photochemical reactor, using eight lamps of 300 nm of wavelength for 24 h with internal temperature regulated in a Rayonet RMR-600 photochemical reactor, using eight lamps of 300 nm of wavelength for 24 h with internal temperature regulated.

**Ethyl 5-Methoxy-1,1-dioxo-3-(phenylamino)-1-benzothiophene-2-carboxylate (12c):** Amino-1-benzothiophene-1,1-dione 12c was prepared according to general procedure using 1,2-benzothiazole-1,1-dione 2h (36 mg, 0.1 mmol). Column chromatography (toluene; silica gel was washed with 1 % Et\(_3\)N in heptane before being used for column chromatography) afforded the product 12c as a white solid (31 mg, 87 %). \( R_f \) (silica gel, toluene): 0.20 (UV, KMN\(_2\)O solution).

**Ethyl 3-Benzylamino-5-methyl-1,1-dioxo-1-benzothiophene-2-carboxylate (12d):** Amino-1-benzothiophene-1,1-dione 12d was prepared according to general procedure using 1,2-benzothiazole-1,1-dione 2k (36 mg, 0.1 mmol). Column chromatography (toluene; silica gel was washed with 1 % Et\(_3\)N in heptane before being used for column chromatography) afforded the product 12d as a white solid (34 mg, 95 %). \( R_f \) (silica gel, toluene): 0.25 (UV, KMN\(_2\)O solution).

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