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 yname 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 $\pi$-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 alkylnophilic transition metals usually through $\pi$-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 colligation 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 yname 1a in the presence of alkylnophilic 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 yname 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>1a</th>
<th>2a</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>E/Z-ratio</th>
<th>Yield (E)-2a [%]</th>
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<tr>
<td>1</td>
<td>Pd(OAc)₂</td>
<td></td>
<td>27</td>
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<td>HOAc</td>
<td>30</td>
<td>10</td>
<td>58</td>
<td>2</td>
<td>0</td>
<td>90:10</td>
<td>7</td>
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<tr>
<td>3</td>
<td>Pd(PPh₃)₄</td>
<td>Zn</td>
<td>23</td>
<td>37</td>
<td>38</td>
<td>2</td>
<td>0</td>
<td>85:15</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>Pd(OAc)₂</td>
<td>NaOAc</td>
<td>28</td>
<td>14</td>
<td>58</td>
<td>0</td>
<td>0</td>
<td>85:15</td>
<td>6</td>
</tr>
<tr>
<td>5</td>
<td>Pd(OAc)₂</td>
<td>P(p-tol)₃</td>
<td>13</td>
<td>48</td>
<td>36</td>
<td>0</td>
<td>3</td>
<td>90:10</td>
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<td>Pd(OAc)₂</td>
<td>P(2-tol)₃</td>
<td>10</td>
<td>51</td>
<td>35</td>
<td>0</td>
<td>4</td>
<td>98:2</td>
<td>37</td>
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</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] Isolated yield. [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. 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, had no influence on the yield of 2a (entry 4). These initial studies showed that formation of benzo[b]thiazole-1,1-dione 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 (R¹), on the aromatic ring of the sulfonamide group (R²) and on the nitrogen (R³) 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, SiMe₃, 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.

Scheme 2. Scope of sulfonyl ynamines for intramolecular hydroarylation. Reaction conditions: 1 (1.0 mmol), Pd(OAc)₂ (5 mol-%), P(p-tol)₃ (10 mol-%), PhMe (10.0 mL), 100 °C for 18 h. [a] Isolated yield. [b] Based on the ¹H NMR spectrum of the crude mixture.
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 the 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 sulfonyl ynamine 1l and Pd(OAc)2 would involve coordination of the Pd2 species to the substrate, as in 7, followed by an alkyn-directed 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 alkyne–H and alkyne–SiMe3 substructures (24.5 and 24.6 kcal/mol, for 1d and 1e, respectively) compared to the corresponding alkyne–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 carboxypalladation 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” alkenyl–Pd2 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 Pd2-acetate 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-benzothiazole-dione 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 1H and 13C NMR spectroscopy and X-ray crystallography of 12a and 12d.

Scheme 3. Equilibration between (E)- and (Z)-isomers of 2a. Free energies (298 K) are shown in kcal/mol.

The structure of the products was confirmed by 1H and 13C NMR 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.[7] This [1,3]sigmatropic rearrangement entails a homolytic cleavage of the sulfonamide...
under a nitrogen atmosphere. 1H and 13C NMR spectra were recorded on a JEOL AccuTOF CS JMS-T100CS (ESI) mass spectrometer. Automatic flash column chromatography was performed using Biotage Isolera Spektra One, using SNAP cartridges (Biotage, 30–100 μm, 60 Å), 10–50 g. Analysis by TLC was conducted on Silica gel F254 (Merck KGaA) plates with detection by UV absorption (254 nm) where applicable, and by dipping into a solution of aqueous KMnO4/Na2CO3/NaOH solution followed by charring at ca. 150 °C. IR spectra were recorded on a Bruker Tensor 27 FTIR spectrometer.

**General Procedure for the Synthesis of Sulfonylamides:** Sulfonylamides 3 and 51–55 were prepared by the literature procedure reported by Murphy et al. The sulfonyl chloride (11 mmol, 1.1 equiv.) was added to a solution of the amine (10 mmol, 1 equiv.) and pyridine (950 mg, 12 mmol, 1.2 equiv.) in CH2Cl2 (30 mL) portion-wise with stirring. The reaction mixture was then stirred at 23 °C for 12 h before evaporation of CH2Cl2 and quenching with an aqueous NaOH solution (2 N, 100 mL). The aqueous solution was rinsed with diethyl ether (2 × 50 mL) and acidified with concentrated HCl extracted with CH2Cl2 (3 × 50 mL). The combined organic washings were dried with sodium sulfate and concentrated in vacuo. The obtained crude product was used directly in the next step without further purification.

**Conclusions**

In summary, we have demonstrated a completely regioselective and highly stereoselective intramolecular hydroarylation of sulfonaryl ynamines. This method opens an easy access to benzothiazole heterocycles, valuable scaffolds in medicinal and organic chemistry. Our mechanistic studies suggest an alkyne-directed S–N bond of 1,2-benzothiazole-1,1-diones to form 3-amino-1-benzothiophene-1,1-diones.

**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, reactions were performed in Biotage Initiator+ Microwave Synthesizer under a nitrogen atmosphere. 1H and 13C NMR spectra were recorded at 298 K on a Varian Inova 400 MHz or Bruker 500 MHz spectrometer in the solvent indicated. Chemical shifts are given in parts per million (ppm) with respect to tetramethylsilane (δ = 0.00 ppm) as internal standard for 1H NMR; and CDCl3 (δ = 77.16 ppm) as internal standard for 13C NMR spectroscopy. Coupling constants are reported as J values in Hertz (Hz). 1H NMR spectroscopic data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, quint = quintet, t = triplet and combination of them), coupling constants (Hz) and integration. All NMR signals were assigned on the basis of 1H NMR, 13C NMR, gCOSY, gHSQC, gHMBC and NOESY experiments.

**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), CH3CN (10.0 mL), hv (300 nm), 24 h. [a] Isolated yield.

[S–N bond of 1,2-benzothiazole-1,1-diones, followed by recombination of the resulting sulfonate radical with the C-terminus of the enaminal radical] Subsequent tautomerization of the formed imine results in 3-amino-1-benzothiophene-1,1-dione.

**5-Methyl-1-[1-phenyl]benzenesulfonamide (S1):** Sulfonamide S1 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 90 % 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), 7.70–7.84 (m, 1 H), 7.72–8.64 (m, 2 H) ppm. 13C NMR [101 MHz, CDCl3]: δ = 121.6, 125.4, 127.3, 129.3, 129.7, 135.8, 136.5, 139.0 ppm. These data were in accordance to those reported in the literature.

**4-Methyl-N-phenylbenzenesulfonamide (S2):** Sulfonamide S2 was prepared from aniline (0.9 g, 10 mmol) and 4-methylbenzenesulfonyl 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 [400 MHz, CDCl3]: δ = 121.6, 125.1, 127.5, 129.2, 130.7, 136.9, 143.9 ppm. These data were in accordance to those reported in the literature.

**4-Methoxy-N-phenylbenzenesulfonamide (S3):** Sulfonamide S3 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 = 3.32 (s, 3 H), 6.70 (br. s, 1 H), 6.81–6.96 (m, 2 H), 7.03–7.15 (m, 2 H), 7.18–7.23 (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, 130.7, 136.6, 163.2 ppm. These data were in accordance to those reported in the literature.

**4-Nitro-N-phenylbenzenesulfonamide (S4):** Sulfonamide S4 was prepared from benzylamine (1.07 g, 10 mmol) and 4-nitrobenzenesulfonyl chloride (2.4 g, 11 mmol) according to the general procedure and obtained crude product was used directly in the next step without further purification.
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. s, 1H), 7.05–7.21 (m, 5 H), 7.27–7.31 (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-[E]-1,2-Dichlorovinyl]-N-phenylbenzenesulfonamide (S5): Sulfonamide S5 was prepared from methylamine 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 = 2.41 (s, 3 H), 2.62 (d, J = 5.5 Hz, 3 H), 4.45 (br. s, 1H), 7.29–7.33 (m, 2 H), 7.70–7.76 (m, 2 H) ppm. 13C NMR (101 MHz, CDCl3): δ = 120.7, 128.6, 129.72, 129.77, 129.83, 137.6, 138.5 ppm. FTIR: ν = 809, 1089, 1160, 1261, 1361, 1489, 1594, 2945 cm–1. HRMS (ESI-TOF): m/z: [M + H]+ calcd. for C14H12Cl2N2O4S 372.9966, found 372.9983.

N-Benzyl-[E]-1,2-dichlorovinyl]-4-methylbenzenesulfonamide (S10): Column chromatography (heptane/AcOEt, 40:1 → 4:1) afforded the product S10 as a white solid (73 %). Rf (silica gel, heptane/AcOEt, 10:1): 0.23 (UV, K MnO4 solution). 1H NMR (400 MHz, CDCl3): δ = 2.47 (s, 3 H), 3.72–4.81 (br. s, 2 H), 6.27 (s, 1 H), 7.28–7.34 (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, 128.23, 128.28, 129.3, 129.8, 133.5, 135.3, 144.7 ppm. These data were in accordance to those reported in the literature.[21]

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**Full Paper**


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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 chloroformate (714 µL, 7.5 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 % Et$_3$N in heptane before being used for column chromatography) afforded the product 1a as a white solid (82 %). R$_f$ (silica gel, heptane/AcOEt, 10:1): 0.11 (UV, KMnO$_4$ solution). $^1$H NMR [400 MHz, CDCl$_3$]: δ = 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 (m, 2 H), 7.29–7.34 (m, 2 H), 7.34–7.38 (m, 3 H), 7.58–7.67 (m, 2 H) ppm. $^{13}$C NMR [101 MHz, CDCl$_3$]: δ = 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-oxopropyl-1-ynyl-1-yl)-4-methyl-phenylbenzenesulfonamide (1b): Sulfonil ynamine 1b was prepared according to general procedure B. The reaction with pivaloyl chloride (767 µL, 6.6 mmol) was performed at 30 °C for 18 h. Column chromatography (toluene; silica gel was washed with 1 % Et$_3$N in heptane before being used for column chromatography) afforded the product 1b as a light yellow oil (79 %). R$_f$ (silica gel, heptane/AcOEt, 10:1): 0.25 (UV, KMnO$_4$ solution). 1H NMR [400 MHz, CDCl$_3$]: δ = 2.42 (s, 3 H), 7.25–7.29 (m, 4 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. $^{13}$C NMR [101 MHz, CDCl$_3$]: δ = 21.7, 74.9, 90.2, 126.4, 128.7, 129.2, 129.9, 132.9, 133.5, 136.9, 137.1, 145.9, 145.6, 193.2 ppm. These data were in accordance to those reported in the literature.[24]

4-Methyl-N-(3-oxo-3-phenylprop-1-ynyl)-N-phenylbenzenesulfonamide (1c): Sulfonil ynamine 1c 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 chloroformate (714 µL, 7.5 mmol) at –78 °C for 15 min and at 23 °C for 3 h. Column chromatography (toluene; silica gel was washed with 1 % Et$_3$N in heptane before being used for column chromatography) afforded the product 1c as a white solid (82 %). R$_f$ (silica gel, heptane/AcOEt, 10:1): 0.27 (UV, KMnO$_4$ solution). 1H NMR [400 MHz, CDCl$_3$]: δ = 21.7, 70.6, 83.2, 122.7, 126.5, 126.8, 128.1, 128.3, 128.4, 129.0, 129.5, 131.4, 132.9, 139.0, 145.1 ppm. These data were in accordance to those reported in the literature.[25]

Ethyl 3-(4-Methyl-N-phenylbenzenesulfonamido)propanoate (1g): Sulfonil ynamine 1g was prepared according to general procedure A using 1,2-dichlorovinyl sulfonamide S6 (1.6 g, 5.0 mmol). The lithium acetylide was treated with freshly distilled ethyl chloroformate (714 µL, 7.5 mmol) at –78 °C for 15 min and at 23 °C for 2 h. Column chromatography (toluene; silica gel was washed with 1 % Et$_3$N in heptane before being used for column chromatography) afforded the product 1g as a white solid (74 %). R$_f$ (silica gel, heptane/AcOEt, 10:1): 0.35 (UV, KMnO$_4$ solution). $^1$H NMR [400 MHz, CDCl$_3$]: δ = 1.31 (t, J = 7.1 Hz, 3 H), 4.24 (q, J = 7.1 Hz, 2 H), 7.14–7.22 (m, 2 H), 7.30–7.41 (m, 3 H), 7.49–7.58 (m, 2 H), 7.64–7.73 (m, 1 H), 7.74–7.80 (m, 2 H) ppm. $^{13}$C NMR [101 MHz, CDCl$_3$]: δ = 21.6, 26.3, 44.3, 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.[26]

N-Ethyl-4-methyl-N-phenylbenzenesulfonamide (1d): Sulfonil ynamine 1d 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 water (10 mL) and the resulting mixture was stirred at 23 °C for 2 h. Column chromatography (heptane/AcOEt, 20:1 → 10:1; silica gel was washed with 1 % Et$_3$N in heptane before being used for column chromatography) afforded the product 1d as a light yellow oil (81 %). R$_f$ (silica gel, heptane/AcOEt, 10:1): 0.18 (UV, KMnO$_4$ solution). $^1$H NMR [400 MHz, CDCl$_3$]: δ = 2.44 (s, 3 H), 2.83 (s, 1 H), 7.23–7.34 (m, 7 H), 7.56–7.61 (m, 2 H) ppm. $^{13}$C NMR [101 MHz, CDCl$_3$]: δ = 21.7, 59.1, 75.8, 126.2, 128.2, 128.3, 129.0, 129.4, 132.7, 138.4, 145.0 ppm. These data were in accordance to those reported in the literature.[27]

4-Methyl-N-phenyl-N-(phenylethynyl)benzenesulfonamide (1f): Sulfonil ynamine 1f was prepared according to general procedure C. Column chromatography (heptane/AcOEt, 20:1 → 10:1; silica gel was washed with 1 % Et$_3$N in heptane before being used for column chromatography) afforded the product 1f as a light yellow solid (80 %). R$_f$ (silica gel, heptane/AcOEt, 10:1): 0.27 (UV, KMnO$_4$ solution). $^1$H NMR [400 MHz, CDCl$_3$]: δ = 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. $^{13}$C NMR [101 MHz, CDCl$_3$]: δ = 127.6, 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: \(R_c\) (silica gel, toluene): 0.33 (UV, KMO\(_3\) solution). \(^1H\) NMR (400 MHz, CDCl\(_3\)): \(\delta = 1.32, (t, J = 7.1 Hz, 3 H), 4.25, (q, J = 7.1 Hz, 2 H), 7.17–7.23\) (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, CDCl\(_3\)): \(\delta = 14.1, 62.0, 66.7, 80.4, 124.5, 126.5, 129.7, 129.81, 129.84, 136.5, 140.9, 150.7, 153.6\) ppm. FTIR: \(\tilde{\nu} = 690, 740, 854, 1086, 1126, 1206, 1348, 1533, 1593, 1706, 2223, 2925, 3107\) cm\(^{-1}\). HRMS (ESI-TOF) \(m/z:\) [M + H]\(^+\) calcld. for \(C_{10}H_{12}N_2O_3\): 275.0861, found 275.0860. Compound 1J: \(R_c\) (silica gel, toluene): 0.07 (UV, KMO\(_3\) solution). \(^1H\) NMR (400 MHz, CDCl\(_3\)): \(\delta = 1.41, (t, J = 7.1 Hz, 3 H), 4.33, (q, J = 7.1 Hz, 2 H), 6.14, (s, 1 H), 7.11–7.16 (m, 2 H), 7.20–7.23 (m, 2 H), 7.24–7.27 (m, 2 H), 7.33–7.38 (m, 2 H), 7.40–7.45 (m, 2 H), 7.45–7.50 (m, 3 H), 7.52–7.57 (m, 1 H), 7.93–8.00 (m, 2 H), 8.09–8.18 (m, 2 H) ppm. \(^13C\) NMR (101 MHz, CDCl\(_3\)): \(\delta = 14.1, 61.6, 110.0, 117.5, 123.4, 124.1, 129.4, 129.6, 129.93, 129.97, 129.99, 130.0, 136.0, 136.3, 139.9, 143.4, 144.2, 149.9, 150.4, 163.9 ppm. FTIR: \(\tilde{\nu} = 694, 740, 855, 1086, 1139, 1172, 1202, 1530, 1531, 1720, 3106\) cm\(^{-1}\). HRMS (ESI-TOF) \(m/z:\) [M + H]\(^+\) calcld. for \(C_{29}H_{34}N_2O_5\): 563.1012, found 653.1034.

**Ethyl (N,4-Dimethylbenzenesulfonylamido)propanoate (1J):** Sulfonyl ynamine 1J was prepared according to general procedure A using 1,2-dichloroethyl benzenesulfonyl sulfonamide S11 (1.4 g, 5.0 mmol). The lithium acetylide was treated with freshly distilled ethyl chloroformate (714 µL, 7.5 mmol) at –78 °C for 15 min and at 23 °C for 2 h. Column chromatography (heptane/AcOEt, 20:1) was used for column chromatography before being used for column chromatography. Reduction of 1J treated with Et\(_3\)N 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):** \(R_c\) (silica gel, toluene): 0.33 (UV, KMO\(_3\) solution). \(^1H\) NMR (400 MHz, CDCl\(_3\)): \(\delta = 1.26, (t, J = 7.1 Hz, 3 H), 2.57, (s, 3 H), 4.18, (q, J = 7.1 Hz, 2 H), 5.11, (s, 1 H), 7.47–7.51 (m, 2 H), 7.54–7.62 (m, 6 H), 7.82, (d, J = 7.9 Hz, 1 H), 9.23 (quint, J = 0.8 Hz, 1 H) ppm. \(^13C\) NMR (101 MHz, CDCl\(_3\)): \(\delta = 14.2, 22.2, 60.5, 97.0, 120.9, 127.4, 129.8, 130.36, 130.39, 130.43, 130.5, 131.0, 133.1, 144.8, 146.2, 166.1 ppm. FTIR: \(\tilde{\nu} = 714, 902, 1089, 1174, 1302, 1463, 1737, 2992\) cm\(^{-1}\). HRMS (ESI-TOF) \(m/z:\) [M + H]\(^+\) calcld. for \(C_{16}H_{18}NO_3\): 244.0957, found 244.0966.

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**General Procedure for the Intramolecular Hydroarylation of Sulfonyl Ynamine 1**

Sulfonyl ynamine 1 (1.0 mmol, 1.0 equiv.) was dissolved in toluene (10 mL) under a nitrogen atmosphere in a Biotahe microwave vial (10.0–20.0 mL) equipped with a magnetic stirring bar. Pd(OAc)\(_2\) (11 mg, 0.05 mmol, 0.05 equiv.) and triop-tolyphosine (30 mg, 0.1 mmol, 0.1 equiv.) were added at 23 °C. The vial was covered with a Teflon septum and secured with a crimped aluminum cap. The reaction was irradiated in a Biotage Initiator microwave at 100 °C for 18 h (30 second prestir, Fixed Hold Time On, Low absorbance level). The reaction mixture was quenched with brine (50 mL) and extracted with AcOEt (2 × 20 mL). The resulting organic washings were dried with sodium sulfate, concentrated in vacuo and the crude residue was purified by column chromatography as indicated.

**Ethyl (E)-2-[5-Methyl-1,1-dioxo-2-phenyl-1,2-benzothiazol-3(2H)-ylidene]acetate ([E]-2a):** \(\delta\)-1,2-Benzothiazole-2a was
preparation 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 the 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-benzothiazol-3(2H)-ylidene]butan-2-one (E)-2b**: (E)-1,2-Benzothiazole-2one 2b 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, KMMoO4 solution).

1H NMR ([400 MHz, CDCl3]): δ = 1.05 (t, J = 7.1 Hz, 2 H), 2.57 (s, 3 H), 5.71 (s, 1 H), 1.74–7.53 (m, 3 H), 7.54–7.65 (m, 4 H), 7.82 (d, J = 8.6 Hz, 1 H), 10.43 (d, J = 1.6 Hz, 1 H) ppm. 13C NMR ([101 MHz, CDCl3]): δ = 14.2, 56.1, 60.5, 97.2, 113.4, 119.7, 122.4, 125.1, 129.6, 130.3, 130.5, 131.0, 146.3, 164.0, 166.2 ppm. FTRIR: ν = 1103, 1183, 1252, 1307, 1473, 1583, 1621, 1707, 2988, 3118 cm−1. HRMS (ESI-TOF): m/z: [M + H]^+ calcd. for C18H19NO3S 356.0906, found 356.0919.

**Ethyl (E)-2-[5-Nitro-1,1-dioxo-2-phenyl-1,2-benzothiazol-3(2H)-ylidene]acetate (E)-2i**: (E)-1,2-Benzothiazole-2one 2i was prepared according to general procedure using sulfonyl ynamine 1i (375 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)-2i as a white solid (113 mg, 30 %). Rf (silica gel, toluene): 0.28 (UV, KMMoO4 solution).

1H NMR ([400 MHz, CDCl3]): δ = 1.73 (t, J = 7.1 Hz, 3 H), 2.52 (s, 1 H), 4.20 (q, J = 7.1 Hz, 2 H), 5.73–7.56 (m, 2 H), 7.58–7.69 (m, 6 H), 8.12 (d, J = 8.5 Hz, 1 H), 8.61 (dd, J = 8.5, 1.9 Hz, 1 H), 10.43 (d, J = 1.9 Hz, 1 H) ppm. 13C NMR ([101 MHz, CDCl3]): δ = 14.2, 61.2, 99.9, 122.5, 125.6, 127.3, 129.1, 129.6, 130.7, 130.9, 131.1, 137.6, 143.8, 151.2, 165.6 ppm. FTRIR: ν = 756, 1043, 1186, 1341, 1537, 1706, 2926, 3111 cm−1. HRMS (ESI-TOF): m/z: [M + H]^+ calcd. for C19H17NO4S 375.0651, found 375.0667.

**Ethyl (E)-2-[2,5-Dimethyl-1,1-dioxo-2-phenyl-1,2-benzothiazol-3(2H)-ylidene]pentan-3-one (E)-2c**: (E)-1,2-Benzothiazolinedione 2c was prepared according to general procedure using 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 (161 mg, 31 %). Rf (silica gel, toluene): 0.31 (UV, KMMoO4 solution).

1H NMR ([400 MHz, CDCl3]): δ = 2.57 (s, 3 H), 6.09 (s, 1 H), 7.37–7.45 (m, 2 H), 7.48–7.55 (m, 1 H), 7.56–7.66 (m, 6 H), 7.72–7.79 (m, 2 H), 8.75 (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, 102.4, 121.1, 124.7, 127.7, 128.2, 128.6, 129.1, 130.5, 130.6, 130.7, 130.9, 132.8, 133.6, 139.4, 145.1, 146.4, 189.7 ppm. FTRIR: ν = 696, 959, 1185, 1323, 1565, 1653, 1724, 2922, 3064 cm−1. HRMS (ESI-TOF): m/z: [M + H]^+ calcd. for C23H23NO6S 376.1037, found 376.1015.

**Ethyl (E)-2-(1,1-Dioxo-2-phenyl-1,2-benzothiazol-3(2H)-ylidene]acetate (E)-2g**: (E)-1,2-Benzothiazolinedione 2g was prepared according to general procedure using 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 the product (E)-2g as a white solid (112 mg, 34 %). Rf (silica gel, toluene): 0.31 (UV, KMMoO4 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), 7.57–7.67 (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, 97.6, 121.3, 127.4, 129.9, 130.5, 130.6, 130.7, 131.2, 132.5, 133.3, 146.2, 166.3 ppm. FTRIR: ν = 692, 910, 1045, 1099, 1157, 1186, 1234, 1619, 1708, 2925 cm−1. HRMS (ESI-TOF): m/z: [M + H]^+ calcd. for C19H17NO3S 330.0800, found 330.0827.

**Ethyl (E)-2-[5-Methoxy-1,1-dioxo-2-phenyl-1,2-benzothiazol-3(2H)-ylidene]acetate (E)-2h**: (E)-1,2-Benzothiazolinedione 2h was prepared according to general procedure using 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, KMMoO4 solution).
was prepared according to general procedure using 1,2-benzothiazole-1,1-dione and the crude residue was purified by column chromatography as a white solid (31 mg, 87 %). \( R_f \) (silica gel, toluene): 0.20 (UV, KMN-O4 solution).

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 (34 mg, 95 %). \( R_f \) (silica gel, toluene): 0.25 (UV, KMN-O4 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-O4 solution).

Acknowledgments

Financial support for this research was provided by the FP7 Marie Curie Actions of the European Commission via the ITN ECHONET (MCITN-2012-316379). Enrique Gómez-Bengoa and Lia Sotorríos thank MINECO (CTQ2016-78083-P) and IZO-SGIiker of UPV-EHU for human and technical support. Huub van Boeijen thanks the University of Groningen for a VENI grant and the Royal Netherlands Academy of Arts and Sciences (KNAW) for a fellowship.

Keywords: Ynamines · Homogeneous catalysis · Palladium · C–H activation · Synthetic methods
