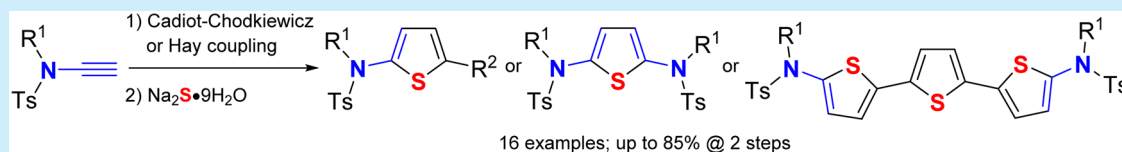


## Application of Ynamides in the Synthesis of 2-(Tosylamido)- and 2,5-Bis(tosylamido)thiophenes

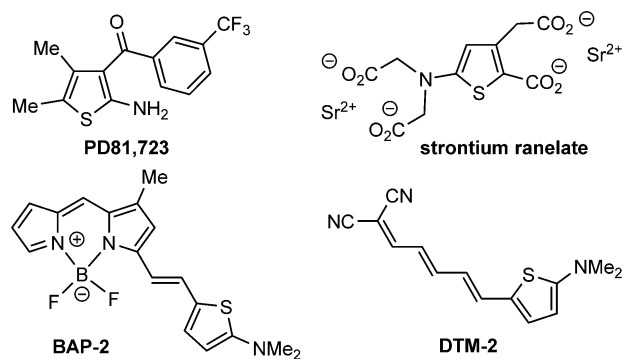
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## S Supporting Information



**ABSTRACT:** A step-economic and metal-catalyst-free synthesis of 2-(tosylamido)- and 2,5-bis(tosylamido)-thiophenes from nonsymmetrical 1,3-butadiynamides and symmetrical 1,3-butadiyne-1,4-diamides is reported. The reaction proceeds in the presence of Na<sub>2</sub>S·9H<sub>2</sub>O (2–3 equiv) under mild reaction conditions (50 °C) and is facilitated by polarized carbon–carbon triple bonds in ynamides. This new approach to thiophenes based on the chemistry of ynamides was applied to the synthesis of a bis(tosylamido)-capped terthiophene having a string of N,S-heteroatoms embedded in a highly  $\pi$ -conjugated molecular frame.

Functionalized thiophenes are an important class of molecules with applications in both medicinal<sup>1</sup> and material science.<sup>2</sup> In particular, 2-aminothiophenes display interesting biological activities and have been noted as structural motifs in sensors and optoelectronic materials.<sup>3</sup> For example, PD81,723<sup>4</sup> is an allosteric modulator of the adenosine A1 receptor, and the strontium salt of ranelic acid is able to reduce the risk of vertebral fracture in women with osteoporosis (Figure 1).<sup>5</sup>



**Figure 1.** Examples of biologically active 2-aminothiophenes and 2-aminothiophene-based fluorescent biomarkers.

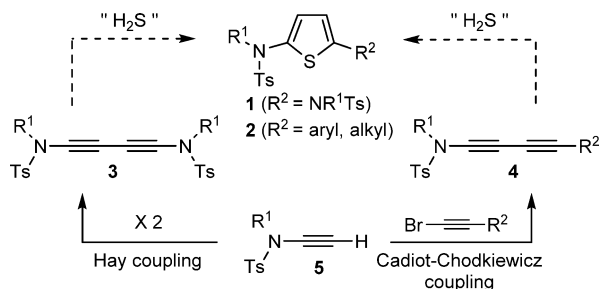
Push–pull 2-aminothiophene derivatives such as BAP-2 and DTM-2 serve as *in vivo* fluorescence imaging probes of  $\beta$ -amyloid (A $\beta$ ) plaques for the detection of Alzheimer's disease.<sup>6</sup> Notably, 2-aminothiophene moieties have also been embedded into push–pull systems for optoelectronic applications and solar cells,<sup>7</sup> and they resemble the electron donor part in  $\pi$ -conjugated chromophores displaying excellent nonlinear optical (NLO) responses.<sup>8</sup> Bis(bis(4-alkoxyphenyl)amino) derivatives of oligo-

thiophenes exhibit high charge delocalizations of their radical cations, which makes them attractive as a hole-transporting layer in organic electronics.<sup>9</sup>

Despite their relevance, the number of syntheses of 2-amino- and 2-amidothiophenes is quite limited, and reported methods can be classified by (i) assembly of two to three acyclic components by condensation reactions (e.g., Gewald reaction)<sup>3,10</sup> and (ii) C–N bond-forming reaction with appropriately functionalized thiophenes comprising S<sub>N</sub>Ar<sup>11</sup> and transition-metal-catalyzed aryl amination and amidation reactions.<sup>12,13</sup> Regarding 2,5-bis-aminothiophenes, the unsubstituted derivative is very labile and decomposes at room temperature.<sup>14</sup> Notably, only a few examples of *N*-substituted analogues such as 2,5-bis(diarylamino)thiophenes<sup>12c,15</sup> and 2,5-bis(acetylamido)-thiophenes<sup>16</sup> have been described.

Within our ongoing interest in the synthesis and use of ynamides as versatile building blocks in natural product and electronic materials synthesis,<sup>17,18</sup> we reasoned that treatment of ynamide-derived buta-1,3-diyne by a sulfur reagent would allow a straightforward approach to unprecedented 2,5-bis-(tosylamido)thiophenes 1 as well as 2-(tosylamido)thiophenes 2 (Scheme 1). Both envisaged precursors 3 and 4 are readily available from terminal ynamide 5<sup>19,20</sup> via Hay or Cadiot–Chodkiewicz cross-coupling reactions. To the best of our knowledge, ynamide to thiophene transformations have no precedent in the literature, whereas 2,5-bis(amido)pyrroles and furans were obtained from buta-1,3-diyne-1,4-diamides under Au(I) catalysis.<sup>21</sup> For thiophene syntheses based on buta-1,3-diyne, various sulfur sources (elemental sulfur,<sup>22</sup> sodium

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**Scheme 1. Synthetic Strategy for 2,5-Bis(tosylamido)- (1) and 2-(Tosylamido)thiophenes (2)**


hydrosulfide,<sup>23</sup> or sodium sulfide<sup>23,24</sup>) with or without additional base or metal catalysts have been used. With respect to the inherent polarization of the carbon–carbon triple bond in ynamides, we chose a transition-metal-free approach for the transformation of ynamide-derived buta-1,3-diyne to the corresponding thiophenes as the ynamide triple bond is activated enough to interact with a sulfur nucleophile. Notably, sodium sulfide hydrate, a very mild and readily available reagent, was selected for initial studies.

The conversion of diyne **3a**<sup>25</sup> ( $R^1 = \text{Bn}$ ) to the corresponding 2,5-bis(tosylamido)thiophene **1a** using 3 equiv of  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  served for optimization studies including different solvents, reaction temperatures, and times (Table 1).

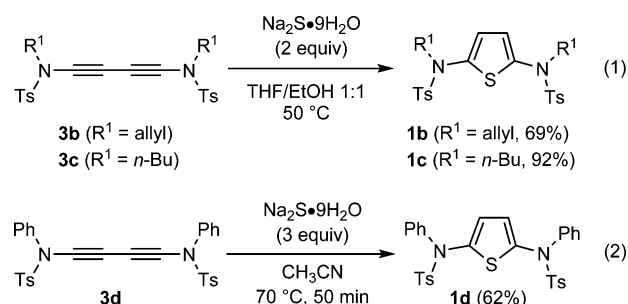
**Table 1. Optimization of the Reaction Conditions**

entry	solvent	temp (°C)	time (min)	$\text{Na}_2\text{S}^a$ (equiv)	yield <sup>b</sup> (%)
1	DMF	20	40	3	45
2	MeCN	50	120	3	47
3	THF	66	120	3	0
4	$\text{CH}_2\text{Cl}_2$	40	180	3	0
5	MeOH	65	120	3	3
6	THF/EtOH (1:1)	50	50	3	90
7	THF/EtOH (1:1)	50	70	2	89
8	THF/EtOH (1:1)	50	120	1	21

<sup>a</sup> $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  was used. <sup>b</sup>Yield refers to isolated **1a**.

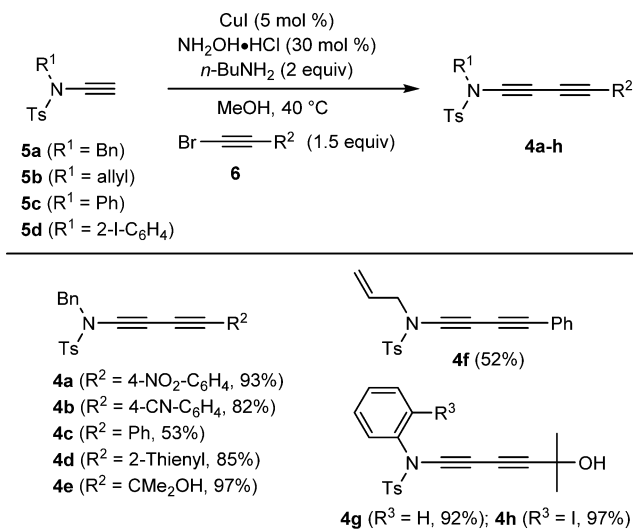
Moderate yields of 45% and 47% were obtained when the reaction was carried out in DMF or acetonitrile, respectively. However, no reaction took place in THF or dichloromethane, probably due to the poor solubility of  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  in these solvents. Switching to methanol brought no improvement and only provided trace amounts of **1a**. Finally, combining ethanol with THF (1:1) allowed the reaction to proceed efficiently and afforded **1a** in 90% isolated yield after 50 min at 50 °C. The yield was not affected when the amount of  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  was reduced to 2 equiv. However, the conversion of **3a** to **1a** was slow when 1 equiv of sulfur reagent was used, and **1a** was isolated in only 21% yield. The optimized reaction conditions involving the use of  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  (2 equiv) in a 1:1 mixture of THF/EtOH at 50 °C were also successfully applied to diynes **3b**<sup>25</sup> and **3c**<sup>18b</sup> bearing, respectively, an allyl and *n*-butyl group on the nitrogen atom. These mild reaction conditions for a thiophene synthesis based on 1,3-diyne underline the improved reactivity of polarized ynamide carbon–carbon triple bonds. In analogy, the corre-

sponding thiophenes **1b** and **1c** were obtained in, respectively, 69 and 92% yield (Scheme 2). On the other hand, these conditions

**Scheme 2. Synthesis of 2,5-Bis(tosylamido)thiophenes**


were not suitable for the *N*-phenyl-substituted diyne **3d**<sup>25</sup> and delivered only minor amounts of the thiophene **1d** (7%). Probably the addition of ethanol to the more reactive carbon–carbon triple bonds of **3d**, whose electrophilic character is now enhanced by conjugation with the *N*-phenyl group, is responsible for these nonselective reaction paths. However, these side reactions vanished when acetonitrile was used as the solvent, and the yield of **1d** increased to 62% (Scheme 2).

2-(Tosylamido)thiophenes **2** are likewise accessible by starting from nonsymmetrical 1,3-butadiynamides (Scheme 3).

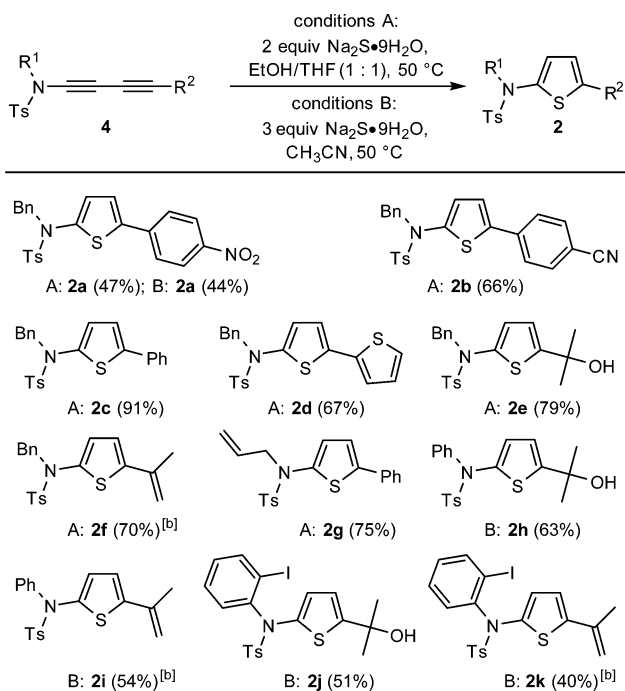
**Scheme 3. Synthesis of Diynes 4 via Cadiot–Chodkiewicz Coupling between Ynamides 5 and 1-Bromoalkynes 6**


The therefore needed 1,3-butadiynamides **4** are readily available through a Cadiot–Chodkiewicz coupling between terminal ynamides **5** and 1-bromoalkynes **6** according to our previously described method for the synthesis of push–pull ynamides, i.e., diyne **4a** ( $R^2 = 4\text{-NO}_2\text{C}_6\text{H}_4$ ) in 93% yield.<sup>18a</sup>

Thus, the conversion of *N*-benzyl-, *N*-allyl-, and *N*-arylynamides **5** into various diynes **4** was performed with various bromoalkynes **6** at 40 °C in oxygen-free methanol in the presence of *n*-butylamine (2 equiv) and hydroxylamine hydrochloride (30 mol %) with copper iodide (5 mol %) as the catalyst. The diynes **4b–h** were obtained in isolated yields ranging from 52 to 97% yield. With the exception of compounds **4a**,<sup>18a</sup> and **4f**,<sup>26</sup> the synthesized ynamide-derived buta-1,3-diyne **4** are unprecedented. It is worth noting that 1,3-butadiynamides are air stable and storable at room temperature over several months.

With a set of various functionalized 1,3-butadiynamides **4** in hand, we investigated their conversion into the corresponding 2-(tosylamido)thiophenes **2** (Scheme 4).

#### Scheme 4. Scope of 2-(Tosylamido)thiophenes<sup>a</sup>



<sup>a</sup>Yields refer to isolated compounds. <sup>b</sup>Yield over two steps through treatment of **2** ( $\text{R}^2 = \text{CMe}_2\text{OH}$ ) with cat. HCl.

The reaction of *N*-benzyl derivatives **4a–e** with  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  (2 equiv) readily proceeded in 1:1 EtOH/THF at 50 °C (conditions A) and was completed during 1 h. Because of their enhanced electrophilic character, the 1,3-butadiynamides **4a** and **4b** bearing either a *p*-NO<sub>2</sub> or *p*-CN substituent were consumed in less than 30 min at 50 °C, and the thiophenes **2a** and **2b** were isolated in 47 and 66% yield, respectively. The reaction of **4a** in acetonitrile at 50 °C gave **2a** in a comparable yield of 44% (conditions B). Worthy of note is that **2a** and **2b** are new specimens of push–pull thiophenes. The best yield (91%) was obtained with the phenyl derivative **2c**, but heteroaryl substituents and free hydroxy function were also tolerated as illustrated by the 2-thienyl-substituted thiophene **2d** and the (1-methyl-1-hydroxy)ethyl derivative **2e**, which were obtained in 67 and 79% respective yield. The *N*-allyl derivative **4f** successfully underwent the reaction with  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  (2 equiv) to give thiophene **2g** in 75% yield. By analogy to the synthesis of 2,5-bis(tosylamido)thiophene **3d** (Scheme 2), the conversion of *N*-phenyl diyne **4g** was performed with  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  (3 equiv) in acetonitrile at 50 °C (conditions B), and 2-(tosylamido)-thiophene **2h** was obtained in 63% yield. Diyne **4h** bearing a 2-iodoaryl substituent on the nitrogen atom delivered thiophene **2j** in 51% isolated yield when reaction conditions B were applied.

Interestingly, during NMR analysis of thiophene **2e**, which bears a heteroaryl tertiary hydroxy function, the spontaneous conversion into thiophene **2f** substituted by an isopropenyl group was observed (Scheme 4 and see the <sup>1</sup>H NMR spectra in the Supporting Information). This dehydration was probably catalyzed by trace amounts of HCl contaminating the used  $\text{CDCl}_3$ . Indeed, the acid-catalyzed dehydration could be

reproduced by stirring a diluted solution ( $10^{-3}$  M) of **2e** in  $\text{CHCl}_3$  in the presence of one drop of 37% aq HCl at room temperature for 1 h, and thiophene **2f** was thereafter isolated in 88% yield. In analogy, acid treatment of **2h** and **2j** delivered thiophenes **2i** and **2k** in 86 and 79% respective yields. It should be pointed out that thiophenes **2f,i,k** would have been difficult to access from the corresponding highly conjugated isopropenyl-substituted 1,3-butadiynamides.

Single-crystal molecular structures of the thiophenes **1b** and **2g** were obtained by slow diffusion of pentane into a  $\text{CHCl}_3$ –**1b** or  $\text{CHCl}_3$ –**2g** solution, respectively, and were analyzed by X-ray diffraction (Figure 2).<sup>27</sup>

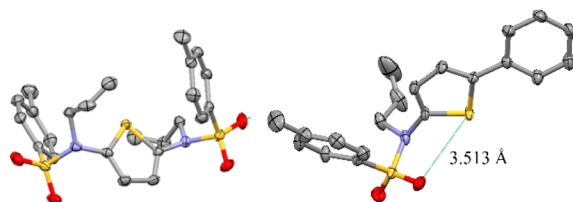


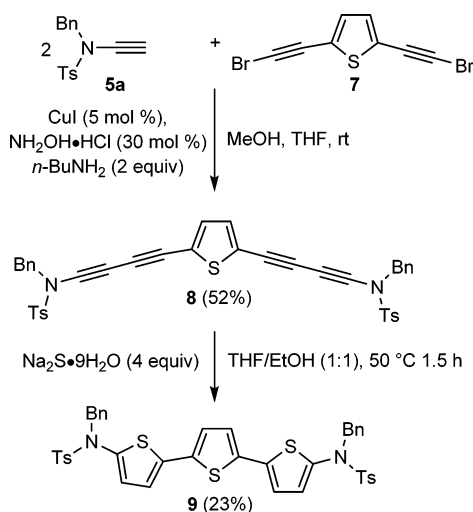
Figure 2. Crystal structures of **1b** (left) and **2g** (right). 50% ellipsoids; hydrogen atoms omitted for clarity.

Unlike the crystallographic structure of 2,5-bis(acetamido)-thiophene,<sup>16</sup> where close contact between the S and the two carbonyl O atoms was noticed ( $\text{S}\cdots\text{O}$  2.82, 2.86 Å), no intramolecular interaction between the tosyl O atoms and the S atom was observed. In the case of **2g**, the tosyl group is located on the side of the S atom but the distance  $\text{S}\cdots\text{O}$  (3.51 Å) is longer than the sum of their van der Waals radii (3.25 Å).

To further extend the scope of this new method for the synthesis of 2-(tosylamido)- and 2,5-bis(tosylamido)thiophenes, we applied it for the construct of the terthiophene **9** that is end-capped with two tosylamido groups and displays a string of mixed N,S-heteroatoms embedded into a  $\pi$ -extended molecular framework (Scheme 5).

The double Cadiot–Chodkiewicz reaction between ynamide **5a** and bis(bromoalkynyl)thiophene **7** was performed at room temperature and afforded the tetrayne **8** in 52% isolated yield. Treatment of the latter by  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  (4 equiv) in THF/EtOH (1:1) at 50 °C gave terthiophene **9** in 23% isolated yield. Terthiophene **9** is the first example of a highly conjugated

#### Scheme 5. Synthesis of Terthiophene 9





heteroaromatic that is bis-terminated with tosylamido groups. This molecular scaffold and related molecular structures are interesting for organic electronics.<sup>28</sup>

In conclusion, we reported a step-economic synthesis of 2-(tosylamido)thiophenes and 2,5-bis(tosylamido)thiophenes based on the chemistry of ynamides. Attractive features of the disclosed protocol are readily available starting materials and mild reaction conditions. Moreover, eagerly sought thiophenes displaying important functional groups (free hydroxy function, isopropenyl, iodoaryl, etc.) are obtained. A terthiophene with a string of N,S-heteroatoms could be synthesized within a short and efficient sequence. Applications of this methodology to the synthesis of organic electronics are underway.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.orglett.6b01101](https://doi.org/10.1021/acs.orglett.6b01101).

Experimental details; <sup>1</sup>H and <sup>13</sup>C NMR spectra for all new compounds (PDF)

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### Notes

The authors declare no competing financial interest.

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- (27) X-ray diffractions of **1b** and **2g** were performed at 150 K with graphite-monochromatized Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) on a Bruker–Nonius Kappa CCD area detector diffractometer. Crystallographic data of **1b** and **2g** can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) by their CCDC number. (a) **1b**: C<sub>24</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub>S<sub>3</sub>, formula weight 502.65, crystal system monoclinic, space group P2<sub>1</sub>/c,  $a = 10.6685(2)$  Å,  $b = 21.3127(5)$  Å,  $c = 11.2463(2)$  Å,  $\beta = 101.629(1)^\circ$ ,  $V = 2504.63(9)$  Å<sup>3</sup>,  $Z = 4$ , calculated density = 1.333 g/cm<sup>3</sup>,  $\mu = 0.329$  mm<sup>-1</sup>, 18870 measured reflections, 5056 Independent reflections,  $R_{\text{int}} = 0.0224$ ,  $R[F^2 > 2\sigma(F^2)] = 0.0312$ ,  $wR(F^2) = 0.0868$ , GOF = 1.020,  $2\theta_{\text{max}} = 52.78^\circ$ , 300 parameters, final difference map within 0.333 and  $-0.338$  e Å<sup>-3</sup>. CCDC 1473083 contains the crystallographic data of **1b**. (b) **2g**: C<sub>20</sub>H<sub>19</sub>NO<sub>2</sub>S<sub>2</sub>, formula weight 369.48, crystal system monoclinic, space group P2<sub>1</sub>,  $a = 10.0038(3)$  Å,  $b = 5.9369(2)$  Å,  $c = 16.0789(5)$  Å,  $\beta = 102.3464(14)^\circ$ ,  $V = 932.87(5)$  Å<sup>3</sup>,  $Z = 2$ , calculated density = 1.315 g/cm<sup>3</sup>,  $\mu = 0.298$  mm<sup>-1</sup>, 18750 measured reflections, 5655 independent reflections,  $R_{\text{int}} = 0.0257$ ,  $R[F^2 > 2\sigma(F^2)] = 0.0359$ ,  $wR(F^2) = 0.0853$ , GOF = 1.057,  $2\theta_{\text{max}} = 60.32^\circ$ , 227 parameters, final difference map within 0.356 and  $-0.220$  e Å<sup>-3</sup>. CCDC 1473084 contains the crystallographic data for **2g**.
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