Preparation of Alkyl Alkynyl Sulfones and Cyclic Vinyl Sulfones from Alkynyl(aryl)iodonium Salts

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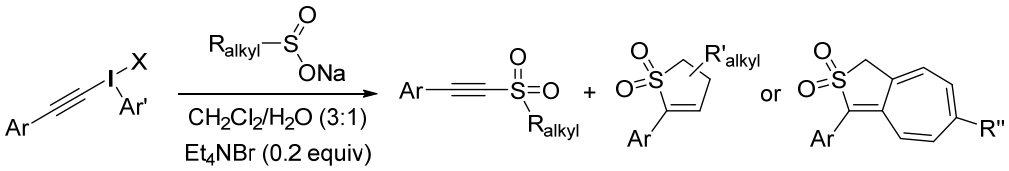
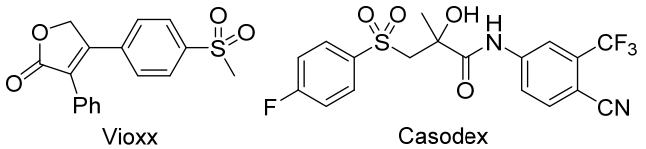


ABSTRACT: The reaction of alkyl sulfinates with alkynyl(aryl)iodonium salts provides a facile access in to otherwise difficult to obtain alkyl alkynyl sulfones and cyclic vinyl sulfones via 1,2-rearrangement or 1,5-CH insertion respectively. In benzyl sulfinates, 1,5-CH insertion is not possible so addition to the aromatic ring occurs followed by ring expansion to generate novel bicyclic sulfones.

INTRODUCTION

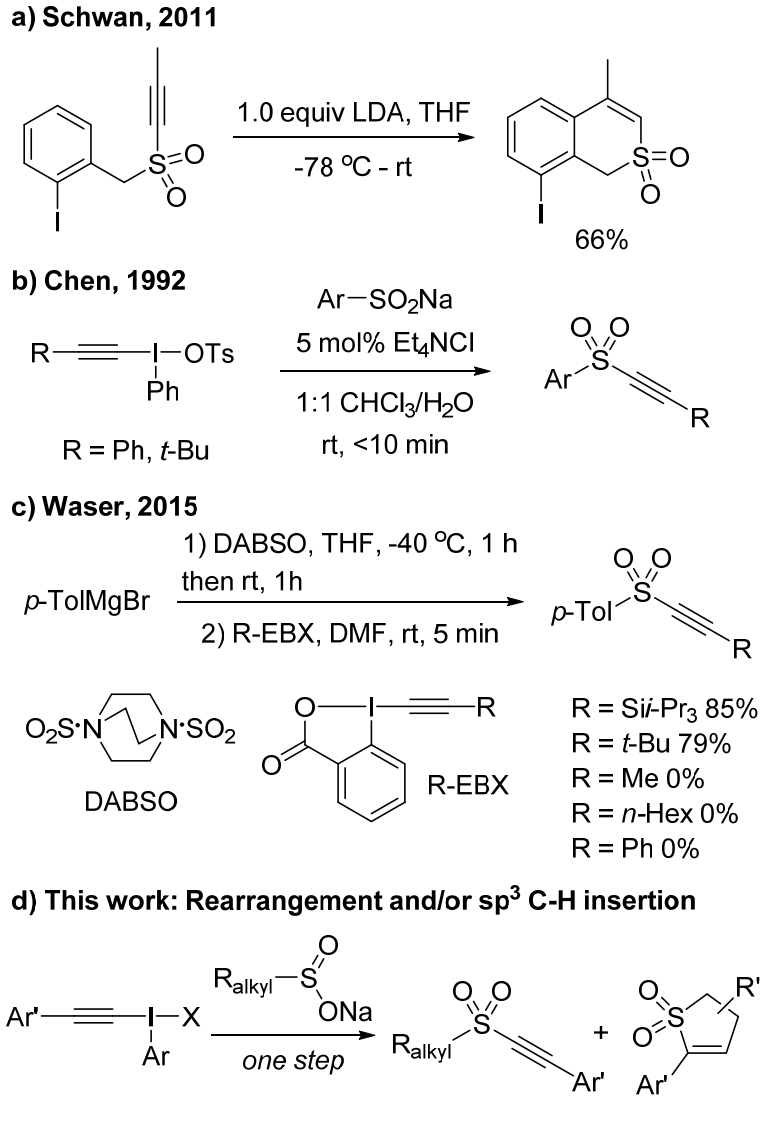
The sulfone is an important functional group found in a wide variety of useful compounds including natural products, drugs and materials. Examples of drug molecules with these characteristics include the antimigraine agent Vioxx[1] and the anti-androgen Casodex.[2]



Alkynyl sulfones and vinyl sulfones are particularly useful functional groups as these can be incorporated in to molecules and subjected to further synthetic manipulation. For example, vinyl

sulfones are useful in conjugate additions[3] and Diels-Alder cycloadditions.[4] However, there are surprisingly few syntheses of vinyl sulfones.[5] In particular, the preparation and utility of cyclic vinyl sulfones has received very little attention.[6,7] Hossain and Schwan recently reported the LDA-induced cyclisation of alkynyl sulfones, however this is not a general process. (Scheme 1a).[8] As such, a new access to cyclic sulfones should be of interest to synthetic and medicinal chemists as it will allow facile exploration of new chemical space.

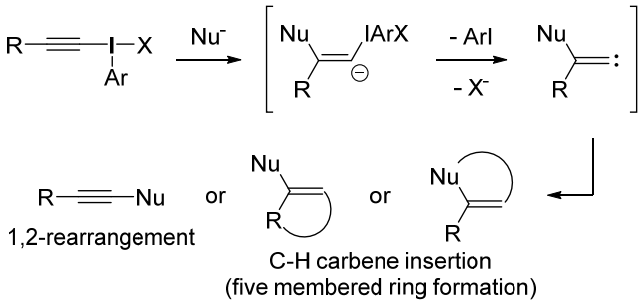
Chen and Stang independently reported that aryl alkynyl sulfones can be prepared from alkynyl(aryl)iodonium salts by addition of arylsulfinate salts (Scheme 1b).[9] Recently, Waser and co-workers reported the preparation of aryl alkynyl sulfones through addition of aryl sulfinates to ethynylbenziodoxolone derivatives (R-EBX) (Scheme 1c).[10] However, there are very few methods available to prepare alkyl alkynyl sulfones.[8] Herein, we disclose a facile one-pot procedure for the preparation of alkyl alkynyl sulfones from alkynyl(aryl)iodonium salts and alkyl sulfinate salts (Scheme 1d). In addition, depending on the substrate, the major product of this process is the cyclic sulfone.



Scheme 1 Previous reports on sulfone synthesis and our approach

Alkynyl(aryl)iodonium salts are useful compounds that can react with soft nucleophiles to generate alkylidene carbene intermediates under aprotic conditions (Scheme 2).[11] These carbenes can undergo 1,2-rearrangement to form a new alkyne or insert in to a C-H bond to form a five-membered ring.[12] Ochiai has also demonstrated similar reactivity with related alkynyl(aryl)bromonium salts.[13] Recently, we demonstrated that alkynyl(aryl)iodonium tosylates salts derived from 2-iodoanisole are more stable than tosylate salts derived from other aryl groups and generally lead to higher yields of products in alkynylation and C(sp^3)-H carbene insertion reactions.[14] We were interested in applying this methodology to a new synthetic route to alkyl and

cyclic sulfones due to the dearth of preparative methods and the potential value of these compounds.

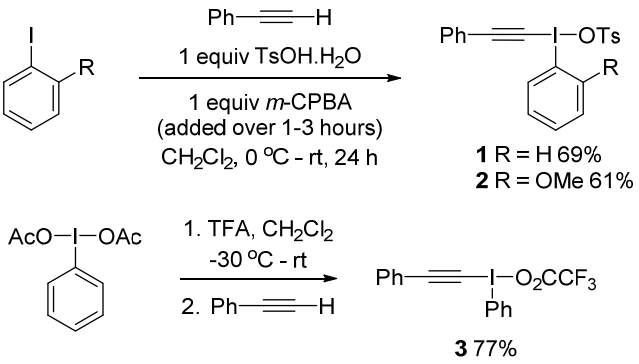


Scheme 2 Reactivity of alkynyl(aryl)iodonium salts with nucleophiles under aprotic conditions

The C(sp^3)-H carbene insertion process occurs rapidly at room temperature and is a valuable route in to cyclic compounds. Alkynyl(2-anisyl)iodonium tosylates are readily prepared in one step from terminal arylacetylenes and 2-iodoanisole under oxidative conditions,[14] using modified Olofsson's conditions,[15] and some sodium sulfinates are commercially available while others can be prepared in one step from sulfonyl chlorides.[16]

RESULTS AND DISCUSSION

We initiated our investigation with the preparation of the three alkynyliodonium salts **1**, **2** and **3** (Scheme 3). We expected to achieve greater yields with our salt **2** compared to **1**, in accordance with our previous work, and wished to compare them both with salt **3** which has been reported recently by Carroll and co-workers.[17] They found that trifluoroacetate salt **3** is readily prepared and that it is more stable than the corresponding tosylate salt **1**. Interesting, they also found that exchanging the counterion from tosylate to trifluoroacetate led to a switch in the regiochemistry in the formal cycloaddition with 2-aminopyridine.[18]



Scheme 3 Preparation of alkynyl(aryl)iodonium salts **1**-**3**

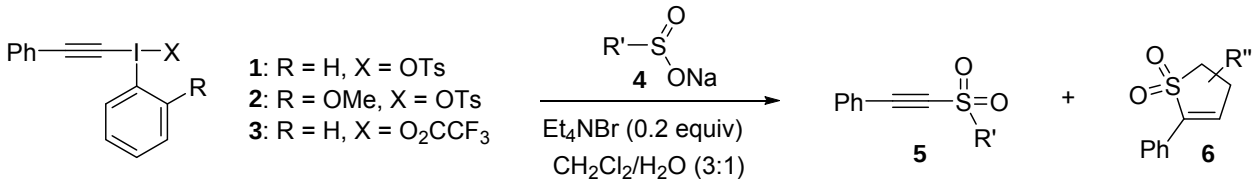
Each of these salts along with sodium sulfinate **4a** was dissolved in a 3:1 mixture of CH_2Cl_2 and water and the phase transfer catalyst tetraethylammonium bromide was added. Moderate yields of the alkyne **5a** were obtained in each case along with some of the cyclized product **6a** (table 1, entries 1-3). Attempts to improve the ratio of products in favor of the cycle **6** by varying solvents and removing the phase transfer catalyst were unsuccessful. Notably, the reaction was successful in all solvents tested including trifluoroethanol, acetonitrile, methanol, ethyl acetate and tetrahydrofuran but the yields were slightly lower. In addition, the absence of the phase transfer catalyst led to slightly diminished yields. However, with the expectation that insertion in to a secondary C-H bond would be faster than in to a primary C-H bond, sulfinates **4b** and **4c** were added to the iodonium salts and we were pleased to find that increased yields of **6** were obtained with a 2:1 preference for C-H insertion observed with **4c** (table 1, entries 4-9). When isopropyl sulfinate was used insertion in to the primary C-H bond to form **6d** was observed. Formation of cycle **6e** from sulfinate **4e** must proceed through insertion in to a tertiary C-H bond and this process was indeed favorable compared to rearrangement to **5e**, however the **5**/**6** ratio was not superior to the results with insertion in to secondary C-H bonds (table 1, entries 13-15).

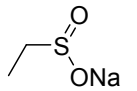
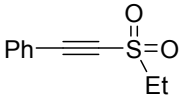
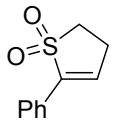
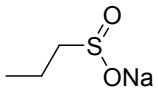
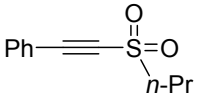
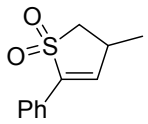
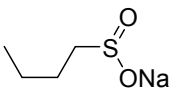
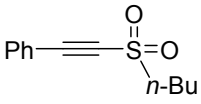
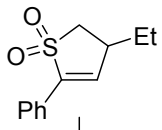
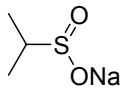
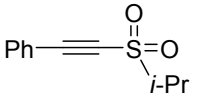
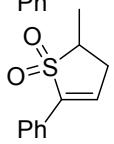
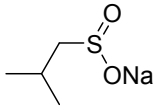
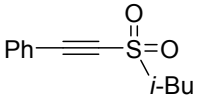
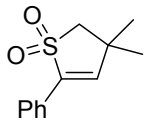
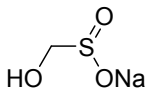
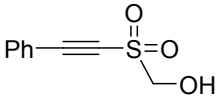
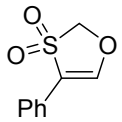
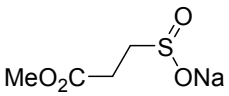
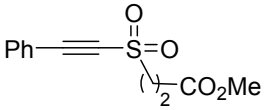
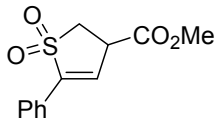
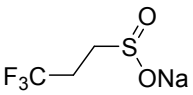
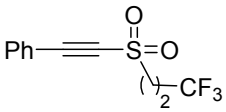
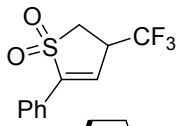
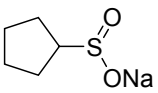
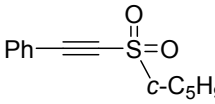
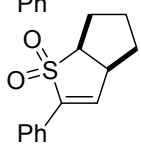
When the sulfinate contains a pendant alcohol, ester or trifluoromethane group, 1,2-rearrangement is the exclusive reaction pathway (table 1, entries 16-24). This suggests that insertion into the O-H bond to form **6f** is not facile and the electron-withdrawing effects of the ester and trifluoromethane groups make insertion into the adjacent C-H bond more difficult. However, when cyclopentane

sulfinate **4i** was used the C-H insertion was favored in a 2:1 ratio as expected, but iodonium salt **1** proved completely ineffective (table 1, entries 25-27).

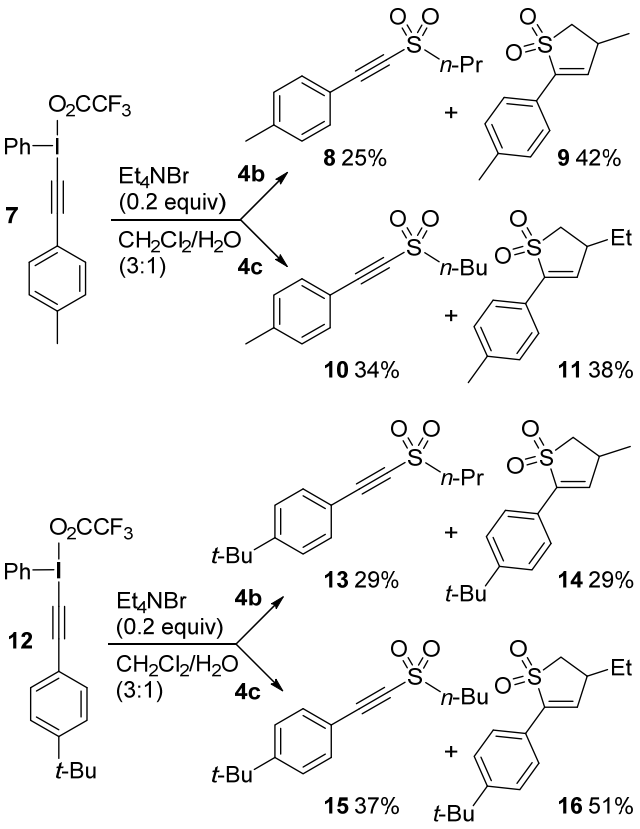
From the full set of results, it can be seen that the 2-iodoanisole derived iodonium salt **2** does lead to better yields than iodobenzene derivative **1**, in many but not all cases, and trifluoroacetate salt **3** is competitive with **2** and is superior in some cases. However, the ease of preparation of **3**, alongside these results, means that its use is preferable to **1** or **2**.

Table 1. Reactivity of three different alkynyl(aryl)iodonium salts with a variety of alkyl sulfinates



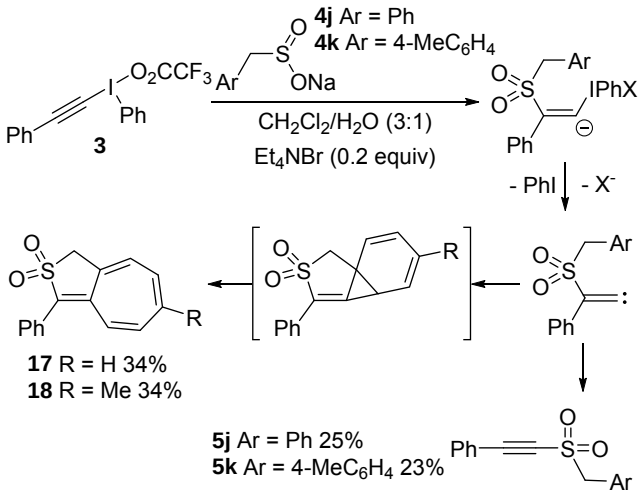
Entry	Salt	Sulfinate **4**		**5**, Yield (%)		**6**, Yield (%)	
1	**1**		**4a**		**5a** 49		**6a** 12
2	**2**		**4a**		**5a** 59		**6a** 15
3	**3**		**4a**		**5a** 55		**6a** 16
4	**1**		**4b**		**5b** 43		**6b** 39
5	**2**		**4b**		**5b** 38		**6b** 19
6	**3**		**4b**		**5b** 27		**6b** 42
7	**1**		**4c**		**5c** 32		**6c** 57
8	**2**		**4c**		**5c** 24		**6c** 48
9	**3**		**4c**		**5c** 32		**6c** 67
10	**1**		**4d**		**5d** 27		**6d** 0
11	**2**		**4d**		**5d** 36		**6d** 12
12	**3**		**4d**		**5d** 52		**6d** 40
13	**1**		**4e**		**5e** 9		**6e** 12
14	**2**		**4e**		**5e** 18		**6e** 43
15	**3**		**4e**		**5e** 42		**6e** 52
16	**1**		**4f**		**5f** 7		**6f** 0
17	**2**		**4f**		**5f** 76		**6f** <5
18	**3**		**4f**		**5f** 12		**6f** <5
19	**1**		**4g**		**5g** 52		**6g** 0
20	**2**		**4g**		**5g** 71		**6g** 0
21	**3**		**4g**		**5g** 54		**6g** 0
22	**1**		**4h**		**5h** 52		**6h** 0
23	**2**		**4h**		**5h** 71		**6h** 0
24	**3**		**4h**		**5h** 89		**6h** 0
25	**1**		**4i**		**5i** <5		**6i** <5
26	**2**		**4i**		**5i** 19		**6i** 43
27	**3**		**4i**		**5i** 17		**6i** 29

Substituted alkynyliodonium trifluoroacetate salts **7** and **12** were prepared and treated with sulfinates **4b** and **4c** under our standard conditions (Scheme 4). 1,5-C-H insertion was the dominant process in these cases but rearrangement also occurred.



Scheme 4 Reactivity of alkynyl(aryl)iodonium salt derivatives

Next, we turned our attention to the use of benzyl sulfinates **4j** and **4k** to see if the absence of a β-C-H bond would lead to the exclusive formation of the rearrangement products **5j** and **5k** or if different reactivity would be revealed. In the event, rearrangement products **5j** and **5k** were formed, however the major compounds formed were **17** and **18** via cyclopropanation of the benzene ring followed by Buchner-type ring expansion (Scheme 5).[19] These compounds can be isolated from the reaction mixture by flash chromatography but, unfortunately, they decompose overnight on standing at room temperature. Feldman reported the formation of unstable, non-isolable aza-analogues of these compounds through a related pathway.[20]



Scheme 5 Addition of benzyl sulfinates leads to Buchner-type ring expansion

In conclusion, we report the facile preparation of alkyl alkynyl sulfones and cyclic vinyl sulfones from alkynyl(aryl)iodonium salts and alkyl sulfinates in one step. When benzyl sulfinates are used the major products formed are via cyclopropanation of the benzene ring followed by Buchner-type ring expansion. These sulfone compounds are otherwise difficult to access so this method should allow their exploitation.

EXPERIMENTAL SECTION

General. ^{1}H NMR and ^{13}C NMR spectra were recorded in ppm from tetramethylsilane with the solvent resonance as the internal standard. Mass spectrometry (m/z) was performed in ESI mode (qTOF), with only molecular ions being reported. Infrared (IR) spectra ν_{max} are reported in cm^{-1}. All purchased reagents were used as received without further purification. Petroleum ether refers to the fraction boiling between 40 – 60 ^{o}C. Sodium sulfinate salts were synthesized from the corresponding sulfonyl chlorides using a published method and used straightaway.[16] Phenyl iodonium tosylates were prepared according to Olofsson's method.[15] 2-Anisyl iodonium tosylates were prepared according to our previously published procedure.[14] Iodonium trifluoroacetates were prepared according to Carroll's method.[16]

General Procedure. To a solution of the iodonium salt (0.54 mmol) in dichloromethane/water (4 mL, 3:1 mixture) at room temperature was added the sodium sulfinate salt (0.81 mmol) and

tetraethylammonium bromide (0.11 mmol). After two hours, distilled water was added (2 mL). After a further five minutes stirring at room temperature, the aqueous layer was separated and extracted with dichloromethane, dried with magnesium sulfate, filtered and concentrated under vacuum to yield a viscous oil. Purification by column chromatography (petroleum ether/ethyl acetate 3:1) afforded the two products in pure form.

((Ethylsulfonyl)ethynyl)benzene 5a. Product synthesized following the general procedure. A yellow oil was obtained (23 mg, 59%).^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.62 (m, 2H), 7.48-7.54 (m, 1H), 7.34-7.45 (m, 2H), 3.29 (q, 2H, *J* = 7.5 Hz), 1.53 (t, 3H, *J* = 7.5 Hz). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 133.2, 132.1, 129.2, 117.9, 92.9, 83.0, 53.1, 8.1. IR (film): cm^{-1}: 1137 (s), 1282 (m), 1321 (s), 1444 (w), 2180 (m), 2927 (w). HRMS: cald. for $[C_{10}H_{10}O_2S+NH_4]^+$ 212.0740; found 212.0744.

5-Phenyl-2,3-dihydrothiophene 1,1-dioxide 6a. Product synthesized following the general procedure. A white solid was obtained (6 mg, 15%). Melting point: 107-109 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.71 (m, 2H), 7.36-7.48 (m, 3H), 6.71-6.79 (m, 1H), 3.44 (t, 2H, *J* = 7.0 Hz), 2.92-3.00 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 144.4, 132.0, 130.2, 129.4, 127.9, 127.2, 49.3, 24.0. IR (film): cm^{-1}: 1125 (s), 1196 (m), 1268 (s), 1432 (m), 2915 (w). HRMS: cald. for $[C_{10}H_{10}O_2S+NH_4]^+$ 212.0740; found 212.0743.

((Propylsulfonyl)ethynyl)benzene 5b. Product synthesized following the general procedure. A yellow oil was obtained (30 mg, 27%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.62 (m, 2H), 7.49-7.55 (m, 1H), 7.39-7.46 (m, 2H), 3.23-3.30 (m, 2H), 1.97-2.08 (m, 2H), 1.14 (t, 3H, *J* = 7.5 Hz). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 133.3, 132.1, 129.2, 118.0, 92.6, 83.7, 60.3, 17.2, 13.2. IR (film): cm^{-1}: 1058 (s), 1135 (s), 1320 (m), 2182 (m), 2925 (w). HRMS: cald. for $[C_{11}H_{12}O_2S+NH_4]^+$ 226.0896; found 226.0900.

3-Methyl-5-phenyl-2,3-dihydrothiophene 1,1-dioxide 6b. Product synthesized following the general procedure. A yellow oil was obtained (47 mg, 42%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64-7.71 (m, 2H), 6.34-7.45 (m, 3H), 6.33-6.37 (m, 1H), 3.06 (dd, 1H, *J* = 8.0, 14 Hz), 3.20-3.30 (m, 1H), 3.05 (dd, 1H, *J* = 5.0, 14 Hz), 1.38 (d, 3H, *J* = 7.0 Hz). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 143.6, 137.6, 130.2, 129.4, 127.7, 127.2, 57.0, 31.4, 20.6. IR (film): cm^{-1}: 1125 (s), 1288 (s), 1447 (w), 1493 (w), 2969 (w). HRMS: cald. for $[C_{11}H_{12}O_2S+NH_4]^+$ 226.0896; found 226.0903.

((Butylsulfonyl)ethynyl)benzene 5c. Product synthesized following the general procedure. A yellow oil was obtained (39 mg, 32%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.62 (m, 2H), 7.48-7.55 (m, 1H), 7.38-7.45 (m, 2H), 3.24-3.32 (2H, m), 1.91-2.01 (m, 2H), 1.53 (sext, 2H, *J* = 7.5 Hz), 0.99 (t, 3H, *J* = 7.5 Hz). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 133.2, 132.0, 129.2, 118.0, 92.6, 83.6, 58.4, 25.2, 21.7, 13.9. IR (film): 1136 (s), 1324 (s), 1444 (w), 1489 (w), 2182 (s), 2961 (w) cm^{-1}. HRMS: cald. for $[C_{12}H_{14}O_2S+NH_4]^+$ 240.1053; found 240.1054.

3-Ethyl-5-phenyl-2,3-dihydrothiophene 1,1-dioxide 6c. Product synthesized following the general procedure. A white solid was obtained (81 mg, 67%). Melting point: 71-72 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.71 (m, 2H), 7.31-7.47 (m, 3H), 6.66-6.71 (m, 1H), 3.50-3.60 (m, 1H), 3.02-3.12 (m, 2H), 1.56-1.85 (m, 2H), 1.03 (t, 3H, *J* = 7.5 Hz). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 143.6, 136.2, 129.9, 129.1, 127.6, 127.0, 55.0, 37.9, 27.8, 11.5. IR (film): 1128 (s), 1285 (s), 1446 (w), 1492 (w), 2965 (w) cm^{-1}. HRMS: cald. for $[C_{12}H_{14}O_2S+NH_4]^+$ 240.1053; found 240.1058.

((Isopropylsulfonyl)ethynyl)benzene 5d. Product synthesized following the general procedure. A yellow oil was obtained (61 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.61 (m, 2H), 7.48-7.55 (m, 1H), 7.38-7.45 (m, 2H), 3.31 (heptet, 1H, *J* = 7.0 Hz), 1.51 (d, 6H, *J* = 7.0 Hz), ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 133.2, 132.0, 129.2, 118.1, 93.7, 81.6, 58.0, 16.0. IR (film): 1055 (m), 1128 (s), 1314 (s), 1444 (w), 2719 (s), 2981 (w) cm^{-1}. HRMS: cald. for $[C_{11}H_{12}O_2S+NH_4]^+$ 226.0896; found 226.0901.

2-Methyl-5-phenyl-2,3-dihydrothiophene 1,1-dioxide 6d. Product synthesized following the general procedure. A white solid was obtained (47 mg, 40%). Melting point: 88-90 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64-7.72 (m, 2H), 7.37-7.48 (m, 3H), 6.69-6.75 (m, 1H), 3.45 (sextet, 1H, *J* = 7.0 Hz), 3.04-3.16 (m, 1H), 2.43-2.55 (m, 1H), 1.50 (d, 3H, *J* = 7.0 Hz). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 143.8, 131.4, 130.1, 129.3, 128.3, 127.1, 54.8, 32.9, 13.7. IR (film): 1123 (s), 1232 (m), 1285 (s), 1446 (w), 2940 (w) cm^{-1}. HRMS: cald. for $[C_{11}H_{12}O_2S+H]^+$ 209.0631; found 209.0631.

((Isobutylsulfonyl)ethynyl)benzene 5e. Product synthesized following the general procedure. A yellow oil was obtained (50 mg, 42%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.61 (m, 2H), 7.48-7.55 (m, 1H), 7.39-7.45 (m, 2H), 3.22 (d, 2H, *J* = 7.0 Hz), 2.41-2.57 (m, 1H), 1.19 (d, 6H, *J* = 7.0 Hz). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 133.2, 132.0, 129.2, 118.1, 92.3, 84.5, 66.4, 24.5, 22.9. IR

(film): cm^{-1}: 1135 (s), 1314 (s), 1489 (w), 2181 (s), 2964 (w). HRMS: cald. for $[C_{12}H_{14}O_2S+NH_4]^+$ 240.1053; found 240.1055.

3,3-Dimethyl-5-phenyl-2,3-dihydrothiophene 1,1-dioxide 6e. Product synthesized following the general procedure. A white solid was obtained (63 mg, 52%). Melting point: 89-90 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 7.63-7.71 (m, 2H), 7.36-7.45 (m, 3H), 6.53 (s, 1H), 3.28 (s, 2H), 1.40 (s, 6H). ^{13}C $\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 141.9, 141.8, 130.1, 129.3, 127.6, 127.2, 63.1, 37.8, 28.9. IR (film): cm^{-1}: 1119 (s), 1289 (s), 1446 (m), 2966 (w). HRMS: cald. for $[C_{12}H_{14}O_2S+NH_4]^+$ 240.1053; found 240.1055.

((Phenylethynyl)sulfonyl)methanol 5f. Product synthesized following the general procedure. A white solid was obtained (30 mg, 76%). Melting point: 109-112 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 7.48.7.53 (m, 2H), 7.35-7.44 (m, 4H), 4.99 (s, 2H). ^{13}C $\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 150.5, 129.7, 129.6, 126.7, 124.2, 121.1, 81.8. IR (film): cm^{-1}: 1074 (s), 1125 (s), 1286 (m), 1615 (m), 3077 (w). HRMS: cald. for $[C_9H_8O_3S+NH_4]^+$ 214.0532; found 214.0539.

Methyl 3-((phenylethynyl)sulfonyl)propanoate 5g. Product synthesized following the general procedure. A white solid was obtained (97 mg, 71%). Melting point: 65-66 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 7.58-7.63 (m, 2H), 7.52-7.56 (m, 1H), 7.41-7.45 (m, 2H), 3.73 (s, 3H), 3.64 (t, 2H, J = 8.0 Hz), 2.99 (t, 2H, J = 8.0 Hz). ^{13}C $\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 170.5, 133.4, 132.4, 129.2, 117.6, 93.6, 83.0, 53.9, 52.9, 28.3. IR (film): cm^{-1}: 1130 (s), 1321 (s), 1725 (s), 2184 (s), 2924 (w). HRMS: cald. for $[C_{12}H_{12}O_4S+Na]^+$ 275.0359; found 275.0354.

(((3,3,3-Trifluoropropyl)sulfonyl)ethynyl)benzene 5h. Product synthesized following the general procedure. A white solid was obtained (126 mg, 89%). Melting point: 63-64 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 7.51-7.65 (m, 3H), 7.41-7.49 (m, 2H), 3.47-3.58 (m, 2H), 2.71-2.88 (m, 2H). ^{13}C $\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 133.4, 132.6, 129.3, 125.6 (q, J = 277 Hz), 117.3, 94.3, 82.5, 51.8 (q, J = 3.0 Hz), 28.9 (q, J = 32 Hz). IR (film): 1086 (s), 1134 (s), 1249 (m), 1279 (s), 2184 (m) cm^{-1}. HRMS: cald. for $[C_{11}H_9F_3O_2S+NH_4]^+$ 280.0614; found 280.0626.

((Cyclopentylsulfonyl)ethynyl)benzene 5i. Product synthesized following the general procedure. A yellow oil was obtained (9 mg, 19%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.55-7.61 (m, 2H), 7.46-7.54 (m, 1H), 7.38-7.46 (m, 2H), 3.62-3.72 (m, 1H), 2.19-2.30 (m, 2H), 2.07-2.19 (m, 2H), 1.80-1.93 (m, 2H), 1.64-1.75 (m, 2H). ^{13}C $\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 133.2, 132.0, 129.2, 118.2, 93.0, 83.0,

67.0, 28.0, 26.5. IR (film): cm^{-1}: 1124 (s), 1310 (s), 1444 (m), 2180 (s), 2959 (w). HRMS: cald. for $[C_{13}H_{14}O_2S+NH_4]^+$ 252.1053; found 252.1056.

(3aS,6aS)-2-Phenyl-3a,5,6,6a-tetrahydro-4*H*-cyclopenta[b]thiophene 1,1-dioxide 6i. Product synthesized following the general procedure. A white solid was obtained (20 mg, 43%). Melting point: 114-116 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 7.72-7.75 (m, 2H), 7.35-7.46 (m, 3H), 6.58-6.62 (m, 1H), 3.61-3.72 (m, 2H), 2.47-2.60 (m, 1H), 1.85-2.03 (m, 2H), 1.68-1.84 (m, 2H), 1.50-1.65 (m, 1H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 144.4, 135.2, 130.1, 129.3, 128.0, 127.2, 63.2, 44.1, 32.7, 29.2, 25.1. IR (film): cm^{-1}: 1119 (s), 1282 (s), 1449 (m), 1630 (w), 2967 (m). HRMS: cald. for $[C_{13}H_{14}O_2S+NH_4]^+$ 252.1053; found 252.1056.

1-Methyl-4-((propylsulfonyl)ethynyl)benzene 8. Product synthesized following the general procedure. A white solid was obtained (30 mg, 25%). Melting point: 71-72 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, 2H, *J* = 8.0 *Hz*), 7.22 (d, 2H, *J* = 8.0 *Hz*), 3.21-3.29 (m, 2H), 2.40 (s, 3H), 2.02 (sextet, 2H, *J* = 7.5 Hz), 1.13 (t, 3H, *J* = 7.5 Hz). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ142.9, 133.2, 129.9, 114.9, 93.3, 83.2, 60.3, 22.2, 17.2, 13.2. IR (film): 1132 (s), 1284 (s), 1314 (s), 2182 (s), 2969 (w) cm^{-1}. HRMS: cald. for $[C_{12}H_{14}O_2S+NH_4]^+$ 240.1053; found 240.1058.

3-Methyl-5-(*p*-tolyl)-2,3-dihydrothiophene 1,1-dioxide 9. Product synthesized following the general procedure. A white solid was obtained (50 mg, 42%). Melting point: 86-88 ^oC.^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, 2H, *J* = 8.0 Hz), 7.20 (d, 2H, *J* = 8.0 Hz), 6.54-6.65 (m, 1H), 3.59 (dd, 1H, *J* = 8.0, 13.5 Hz), 3.15-3.28 (m, 1H), 3.00 (dd, 1H, *J* = 5.0, 13.5 Hz), 2.36 (s, 3H), 1.35 (d, 3H, *J* = 7.0 Hz). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 143.4, 140.3, 136.7, 130.0, 127.0, 124.8, 56.9, 31.3, 21.7, 20.6. IR (film): 1113 (s), 1161 (m), 1280 (s), 1512 (w), 2966 (w) cm^{-1}. HRMS: cald. for $[C_{12}H_{14}O_2S+NH_4]^+$ 240.1053; found 240.1057.

1-((Butylsulfonyl)ethynyl)-4-methylbenzene 10. Product synthesized following the general procedure. A yellow oil was obtained (44 mg, 34%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, 2H, *J* = 8.0 Hz), 7.21 (d, 2H, *J* = 8.0 Hz), 3.21-3.33 (m, 2H), 2.40 (s, 3H), 1.89-2.02 (m, 2H), 1.53 (sextet, 2H, *J* = 7.5 Hz), 0.98 (t, 3H, *J* = 7.5 Hz). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 142.9, 133.2, 129.9, 114.8, 93.3, 83.2, 58.4, 25.2, 22.2, 21.7, 13.9. IR (film): 1136 (s), 1324 (s), 1508 (m), 2177 (s), 2961 (w) cm^{-1}. HRMS: cald. for $[C_{13}H_{16}O_2S+NH_4]^+$ 254.1209; found 254.1214.

3-Ethyl-5-(p-tolyl)-2,3-dihydrothiophene 1,1-dioxide 11. Product synthesized following the general procedure. A white solid was obtained (49 mg, 38%). Melting point: 111-112 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, 2H, *J* = 8.0 Hz), 7.21 (d, 2H, *J* = 8.0 Hz), 6.60-6.68 (m, 1H), 3.51-3.61 (m, 1H), 3.02-3.14 (m, 2H), 2.36 (s, 3H), 1.57-1.84 (m, 2H), 1.04 (t, 3H, *J* = 7.5 Hz). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 143.9, 140.3, 135.3, 130.0, 127.0, 124.9, 55.2, 38.0, 28.1, 21.7, 11.7. IR (film): 1123 (s), 1209 (m), 1284 (s), 1455 (m), 2959 (w) cm^{-1}. HRMS: cald. for $[C_{13}H_{16}O_2S+NH_4]^+$ 254.1209; found 254.1219.

1-(*tert*-Butyl)-4-((propylsulfonyl)ethynyl)benzene 13. Product synthesized following the general procedure. A yellow oil was obtained (41 mg, 29%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.57 (m, 2H), 7.40-7.47 (m, 2H), 3.22-3.29 (m, 2H), 2.02 (sext, 2H, *J* = 8.0 Hz), 1.32 (s, 9H), 1.13 (t, 3H, *J* = 7.5 Hz). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.0, 133.1, 126.3, 114.9, 93.3, 83.2, 60.4, 35.6, 31.4, 17.2, 13.2. IR (film): 1129 (s), 1309 (s), 1494 (w), 1682 (w), 2180 (s), 2926 (w) cm^{-1}. HRMS: cald. for $[C_{15}H_{20}O_2S+H]^+$ 265.1257; found 265.1247.

5-(4-(*tert*-Butyl)phenyl)-3-methyl-2,3-dihydrothiophene 1,1-dioxide 14. Product synthesized following the general procedure. A white solid was obtained (42 mg, 29%). Melting point: 113-114 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.64 (m, 2H), 7.40-7.46 (m, 2H), 6.59-6.62 (m, 1H), 3.60 (dd, 1H, *J* = 8.0, 13.5 Hz), 3.17-3.28 (m, 1H), 3.01 (dd, 1H, *J* = 5.0, 13.5 Hz), 1.36 (d, 3H, *J* = 7.5 Hz), 1.31 (s, 9H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.4, 143.4, 136.7, 126.9, 126.3, 124.7, 56.9, 35.1, 31.5, 31.4, 20.6. IR (film): 1129 (s), 1309 (s), 1494 (w), 1682 (w), 2926 (w) cm^{-1}. HRMS: cald. for $[C_{15}H_{20}O_2S+NH_4]^+$ 282.1522; found 282.1515.

1-(*tert*-Butyl)-4-((butylsulfonyl)ethynyl)benzene 15. Product synthesized following the general procedure. A yellow oil was obtained (55 mg, 37%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, 2H, *J* = 8.4 Hz), 7.43 (d, 2H, *J* = 8.4 Hz), 3.24-3.31 (m, 2H), 1.90-2.02 (m, 2H), 1.53 (sext, 2H, *J* = 7.5 Hz), 1.32 (s, 9H), 0.98 (t, 3H, *J* = 7.5 Hz). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.9, 133.1, 126.3, 114.9, 93.3, 83.2, 58.5, 35.6, 31.4, 25.3, 21.7, 13.9. IR (film): 1138 (s), 1325 (s), 1504 (w), 2178 (s), 2961 (m) cm^{-1}. HRMS: cald. for $[C_{16}H_{22}O_2S+NH_4]^+$ 296.1679; found 296.1677.

5-(4-(*tert*-Butyl)phenyl)-3-ethyl-2,3-dihydrothiophene 1,1-dioxide 16. Product synthesized following the general procedure. A white solid was obtained (77 mg, 51%). Melting point: 77-79 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.65 (m, 2H), 7.38-7.46 (m, 2H), 6.61-6.67 (m, 1H), 3.49-

3.66 (m, 1H), 2.98-3.17 (m, 2H), 1.56-1.88 (m, 2H), 1.32 (s, 9H), 1.05 (t, 3H, *J* = 7.5 Hz). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.5, 143.9, 135.3, 126.9, 126.4, 124.9, 55.2, 38.1, 35.2, 31.5, 28.2, 11.7. IR (film): 1114 (s), 1130 (s), 1276 (s), 1462 (m), 2964 (m) cm^{-1}. HRMS: cald. for $[C_{16}H_{22}O_2S+NH_4]^+$ 296.1679; found 296.1681.

((Benzylsulfonyl)ethynyl)benzene 5j. Product synthesized following the general procedure. A brown wax was obtained (34 mg, 25%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.55 (m, 10H), 4.50 (s, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 133.2, 132.1, 131.6, 129.8, 129.3, 129.1, 127.6, 117.9, 94.5, 82.9, 65.0. IR (film): 1148 (s), 1160 (s), 1318 (s), 1488 (s), 2182 (s), 2917 (w) cm^{-1}. HRMS: cald. for $[C_{15}H_{12}O_2S+NH_4]^+$ 274.0896; found 274.0902.

3-Phenyl-1H-cyclohepta[c]thiophene 2,2-dioxide 17. Product synthesized following the general procedure. A white solid was obtained (47 mg, 34%). Melting point: 130-134 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.57 (m, 2H), 7.35-7.48 (m, 3H), 6.34-6.43 (m, 1H), 6.06-6.22 (m, 4H), 3.96 (s, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 144.0, 137.6, 134.5, 132.4, 131.8, 130.8, 129.9, 129.5, 129.4, 128.7, 127.9, 127.7, 55.4. IR (film): 1122 (s), 1288 (m), 1563 (w), 2359 (w) cm^{-1}. HRMS: cald. for $[C_{15}H_{12}O_2S+H]^+$ 274.0896; found 274.0896.

1-Methyl-4-(((phenylethynyl)sulfonyl)methyl)benzene 5k. Product synthesized following the general procedure. A brown wax was obtained (34 mg, 23%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.54 (m, 3H), 7.34-7.44 (m, 4H), 7.23 (d, 2H, *J* = 7.8 Hz), 4.47 (s, 2H), 2.38 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 139.8, 133.1, 132.0, 131.4, 130.0, 129.1, 124.4, 117.9, 94.3, 83.0, 64.7, 21.6. IR (film): 1125 (s), 1146 (s), 1325 (s), 1488 (w), 2180 (s), 2921 (w) cm^{-1}. HRMS: cald. for $[C_{16}H_{14}O_2S+NH_4]^+$ 288.1053; found 288.1053.

6-Methyl-3-phenyl-1H-cyclohepta[c]thiophene 2,2-dioxide 18. Product synthesized following the general procedure. A white solid was obtained (49 mg, 34%). Melting point: 93-94 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.58 (m, 2H), 7.34-7.49 (m, 3H), 6.38 (d, 1H, *J* = 12 Hz), 6.08 (d, 2H, *J* = 10.3 Hz), 6.00 (d, 1H, *J* = 8.5 Hz), 3.96 (s, 2H), 1.96 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 143.5, 142.4, 138.3, 134.6, 130.2, 129.8, 129.5, 129.4, 128.9, 128.1, 127.5, 127.4, 55.4, 26.2. IR (film): 1129 (s), 1309 (s), 1494 (w), 1682 (w), 2926 (w) cm^{-1}. HRMS: cald. for $[C_{16}H_{14}O_2S+NH_4]^+$ 288.1053; found 288.1053.

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SUPPORTING INFORMATION

Experimental procedures and full characterization data for novel compounds including copies of ^{1}H and ^{13}C NMR spectra.

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