

Formation of New Alkynyl(phenyl)iodonium Salts and Their Use in the Synthesis of Phenylsulfonyl Indenes and Acetylenes

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Abstract: The preparation of phenylsulfonyl indene derivatives and phenylsulfonyl-acetylenes from readily available alkynyl(phenyl)iodonium tetrafluoroborates and triflates was investigated using phenylsulfinate as nucleophile.

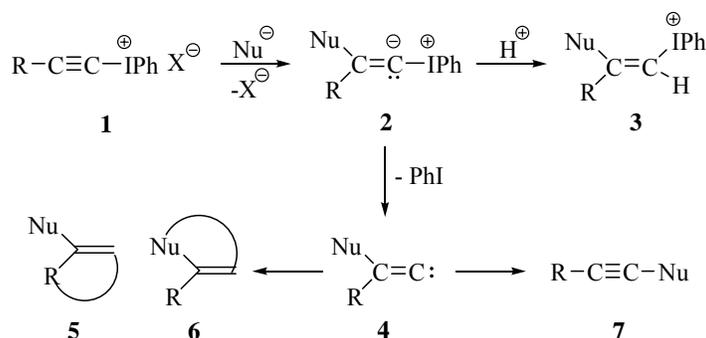
Keywords: Indene, alkynyl(phenyl)iodonium salt, sulfinate, carbene, rearrangement.

Introduction

Among the various known hypervalent iodine species alkynyliodonium salts represent an interesting class of compounds regarding their applications in organic synthesis [1-9]. Their major subgroup comprises a multitude of stable alkynyl(aryl)iodonium salts (**1**, Scheme 1) [9]. Since the first preparation of a labile alkynyl(aryl)iodonium salt [10] and the isolation of the first stable one [11] their reactivity patterns have been thoroughly studied. It is nowadays well established that **1** are, among other things, excellent partners for Michael-type conjugate additions as well as dienophiles in Diels-Alder reactions and dipolarophiles in 1,3-dipolar cycloadditions [9]. The great tendency of **1** to react with nucleophiles via conjugate addition is a result of the highly electrophilic nature of the β -acetylenic carbon. The subsequent fate of the initially formed iodonium ylide **2** depends on the reaction conditions (Scheme 1). Thus, reaction with a proton donor will yield an alkenyliodonium ion **3**, whereas carbene **4** is formed via iodobenzene elimination. This carbene then either inserts intramolecularly into any suitable bond available (mainly a C-H bond from either R or Nu) to produce five-membered ring systems **5** and **6** or rearranges to give a new alkyne **7**. By employing C-, O-, N-

and S-nucleophiles [6-9,12] several substituted cyclopentenes [13], cyclopentenones [14] or heterocyclic derivatives such as pyrroles [15], indoles [16], thiazoles [17] and benzofurans [12,18] have been obtained. Sulfinate anions in particular were used as nucleophiles in the construction of cyclopentenes [13,19-20] and cyclopentenones [14]. Herein we wish to report our latest results concerning the additions of benzenesulfinate to alkynyl(phenyl)iodonium salts in order to obtain indene and (or) alkyne derivatives.

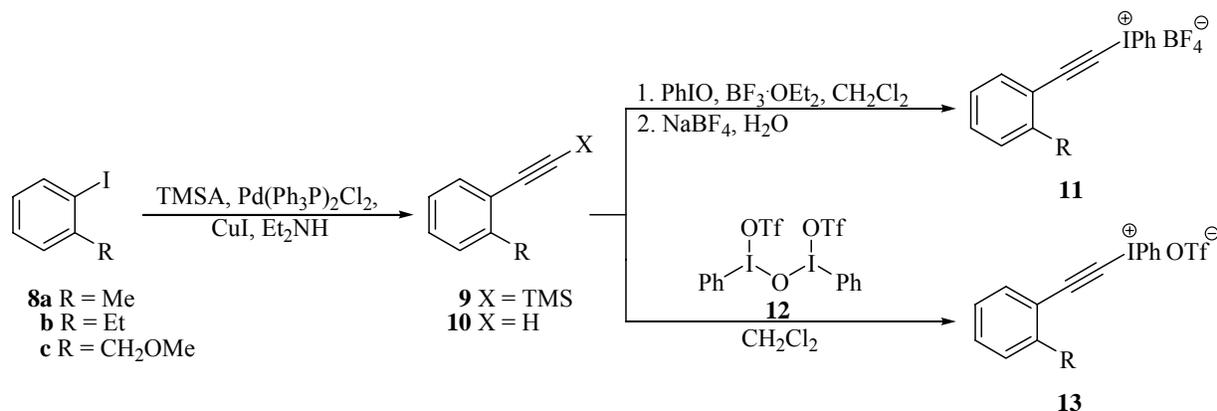
Scheme 1.



Results and Discussion

The required alkynyl(phenyl)iodonium salts, **11** and **13**, were prepared from the corresponding *o*-substituted phenyliodides **8a-c** [21-22] (Scheme 2). These were first converted to arylalkynes **9** in very good yields through a Sonogashira reaction [23-24]. Some of the corresponding desilylated products **10** were also obtained in these reactions. Arylalkynes **9** were then treated first with iodobenzene in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ [25] and subsequently with aqueous NaBF_4 [26-27] to produce tetrafluoroborates **11**. The Zefirov reagent **12** [28] was also used to prepare the triflate analogues **13** directly from the same intermediates **9** [29-30].

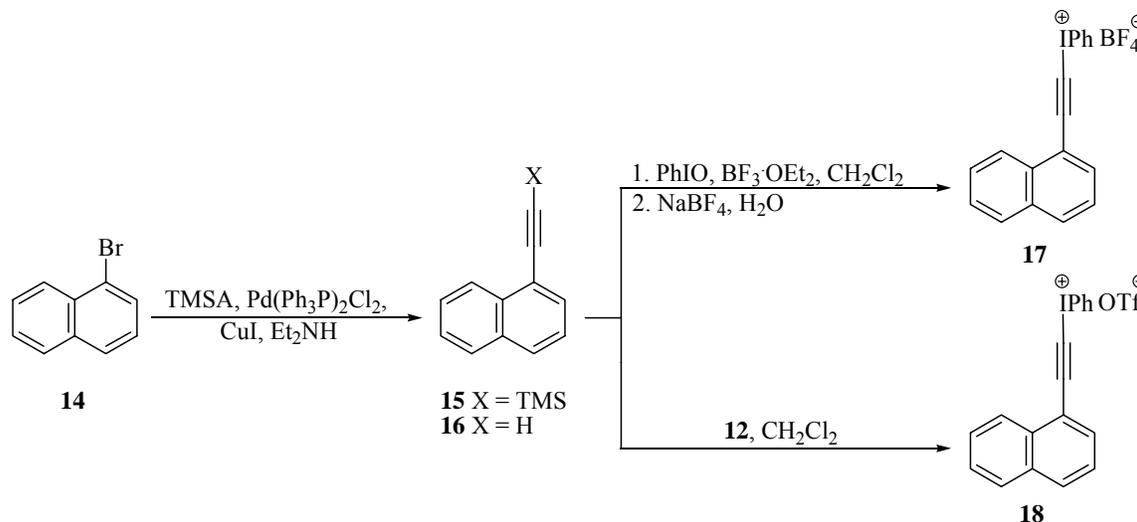
Scheme 2.



1-Bromonaphthalene (**14**) was similarly used to prepare the corresponding iodonium salts (Scheme 3). First the major Sonogashira reaction product **15** was obtained from **14**, along with some of the desilylated product **16**. Compound **15** then furnished 1-alkynyl(naphthyl)iodonium tetrafluoroborate (**17**) and the triflate analogue **18** upon reaction with iodobenzene/ NaBF_4 or the Zefirov reagent,

respectively. We did not try to isolate and characterize all these iodonium salts (assumed to be reasonably stable) since they could be successfully employed in their reactions with benzenesulfinate without any further purification.

Scheme 3.



Tetrafluoroborate **11a** reacted first with PhSO₂Na according to the general scheme shown in Table 1 (see also Figure 1). This reaction (entry 1) furnished in moderate yield the indene derivatives **19a** and **20a** as an inseparable mixture, along with the rearrangement product, phenylsulfonylacetylene **21a**. The observations that **19a** and **20a** could not be separated (although they have slightly different R_f values) and that they were always obtained in the same ratio (*ca.* 5:1) from several runs points to the existence of an equilibrium between them. Thus, indene **20a**, initially formed from **23a** through carbene insertion to the C-H of methyl group, partially isomerized to the more stable **19a** (Scheme 4). Indeed, addition of Et₃N to a solution of **19a** and **20a** in CH₂Cl₂ did not alter this equilibrium and only slow decomposition was observed after prolonged stirring (two weeks) at room temperature [31].

Next we explored the reactivity of **11b** which, in contrast with **11a**, yielded a single phenylsulfonyl indene derivative, **19b**, accompanied again by the acetylene sulfone **21b** (entry 3). It is assumed that in this case the carbene insertion product **20b** was irreversibly isomerized to **19b** (Scheme 4). Generally, the sulfone group lacks the ability to participate in conjugation, therefore indenenes **19**, in which conjugation with the aromatic ring is possible, are favored. One would expect that, concerning **20b**, the introduction of an extra methyl group, would lead to a less favorable 1,3-H shift system (in comparison with the **19a-20a** pair). However, from the experimental results it becomes apparent that this is not the case. Due probably to steric factors, this shift is not reversible and once **20b** is isomerized to **19b** the indene system is locked. Another plausible explanation could be that alkene **19b** is thermodynamically more stable since the conjugated double bond is trisubstituted.

The same reactions were also investigated employing the corresponding triflates **13a** and **13b** (entries 2 and 4, Table 1). Product distributions were similar to those obtained from tetrafluoroborates, but reaction mixtures were easier to resolve and the phenylsulfonylindenenes were isolated in higher yields. Additionally, although not completely rationalized, annulation was slightly favored over rearrangement.

Figure 1.

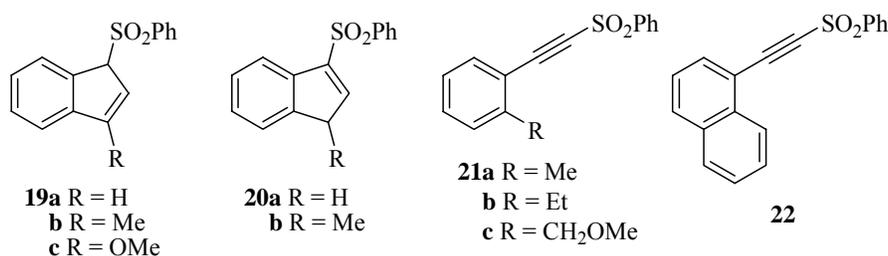
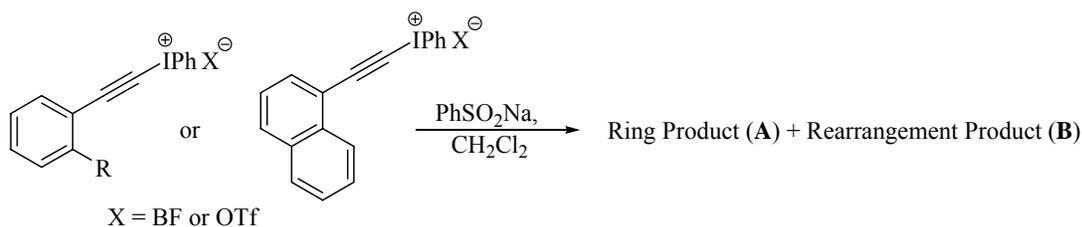


Table 1.

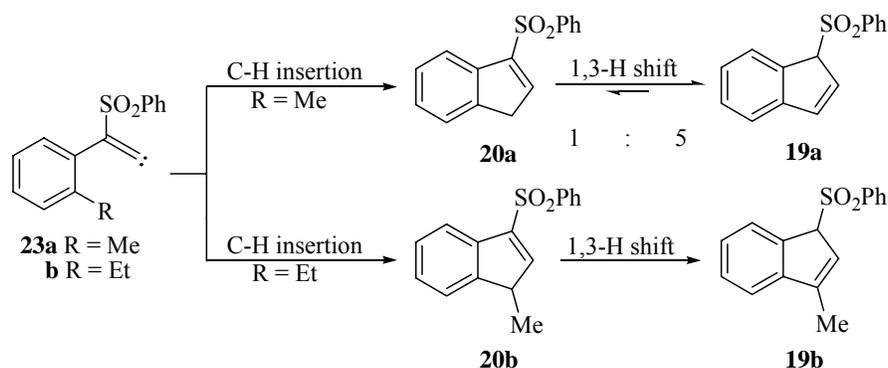


Entry	Substrate	Ring type products (A)	Rearrangement type products (B)
1	11a	19a + 20a (32%, 5:1) ^a	21a (26%)
2	13a	19a + 20a (44%, 5:1)	21a (26%)
3	11b	19b (40%)	21b (26%)
4	13b	19b (51%)	21b (20%)
5	11c	-	-
6	13c	-	-
7	17	-	22 (15%)
8	18	-	22 (16%)

^aAll yields refer to isolated products (overall from the corresponding halides), unless otherwise mentioned. For details see the Experimental section.

We sought next to explore the reactivity of methoxy iodonium salts **11c** and **13c** (entries 5 and 6), but these substrates yielded very complex reaction mixtures with PhSO₂Na, which after chromatographic separations did not furnish any of the expected methoxy analogues **19c** and **21c** [32]. The situation was not improved when the reaction with the nucleophile was performed at lower temperatures. The different reactivity behavior of **11c** and **13c** might be due to an interaction of the ether oxygen with the initially formed carbene [33] and it is possible that in our case this kind of insertion does not lead to stable products.

Scheme 4.



Carbene insertion to an aromatic C-H bond is another feasible reaction pathway [34-37], but none of the reactions with **11** and **13** we investigated produced such derivatives. In order to check this reactivity pattern phenylsulfonate addition to the naphthyl iodonium salts **17** and **18** was examined, since these substrates lack the possibility of insertion to an sp^3C-H , but these derivatives gave only the rearrangement product **22** in low yield upon nucleophile addition (entries 7 and 8).

Conclusions

In this article we have presented an investigation of the reactivity patterns of some new alkynyl(phenyl)iodonium tetrafluoroborates and triflates upon addition of phenylsulfonate. The preparation of indene and phenylsulfonyl acetylene derivatives was accomplished in moderate to good yields depending on the exact reaction conditions and substrates involved. Further exploration of this kind of iodonium salts could lead to a general scheme for the synthesis of such systems.

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Experimental

General

All reagents are commercially available and were used without further purification unless otherwise mentioned. Solvents were dried by standard methods. The progress of the reactions was checked by thin layer chromatography (TLC) on Merck silica gel 60F254 glass plates (0.25 mm). Column chromatography was performed with Merck silica gel 60 (0.063–0.200 mm). The 1H - and ^{13}C -NMR spectra were recorded at 300 and 75 MHz, respectively, on a Bruker 300 AM spectrometer, with tetramethylsilane (TMS) as internal standard. High-resolution mass spectra (HRMS) were obtained on a VG ZAB-ZSE mass spectrometer under fast-atom bombardment (FAB) conditions with nitrobenzyl alcohol (NBA) as the matrix or on an IONSPEC FTMS spectrometer (matrix-assisted laser-desorption ionization, MALDI) with 2,5-dihydroxybenzoic acid (DHB) as matrix.

General procedure for the preparation of 2-aryl-trimethylsilylacetylenes 9 and 15 [23-24]

Aryl halides **8** or **14** (20 mmol) were dissolved in Et₂NH (80 mL) under an inert atmosphere. Trimethylsilylacetylene (TMSA, 2.36 g, 24 mmol), Pd(Ph₃)₂Cl₂ (0.28 g, 0.4 mmol) and CuI (40 mg, 0.2 mmol) were then added successively and the mixture was left under vigorous stirring for 5 h at room temperature. The solvent was evaporated and hexane (50 mL) was added to the residue. After stirring for 1 h the supernatant solution was collected and concentrated to a volume of ca. 10 mL. This was chromatographed on a silica gel column (hexane eluent) to afford 2-aryltrimethylsilylacetylenes **9** and **15** and the corresponding desilylated by-products **10** and **16** in this order.

Trimethyl(2-o-tolyethynyl)silane (9a). Obtained from **8a** (3.42 g, 91%). This compound had identical physical and spectra data with those reported in the literature [38].

1-Ethynyl-2-methylbenzene (10a). Obtained from **8a** (120 mg, 5%); ¹H-NMR (CDCl₃) δ: 7.51 (d, *J* = 7.9 Hz, 1H), 7.26-7.19 (m, 2H), 7.16 (t, *J* = 7.9 Hz, 1H), 2.53 (s, 1H), 2.50 (s, 3H); ¹³C-NMR (CDCl₃) δ: 140.1, 132.7, 131.4, 129.8, 125.0, 121.7, 81.8, 81.4, 18.2; HRMS *m/e* Calc. for C₉H₉ [(M+H)⁺]: 117.0704. Found: 117.0707.

[2-(2-ethylphenyl)ethynyl]trimethylsilane (9b). Obtained from **8b** (3.65 g, 90%); ¹H-NMR (CDCl₃) δ: 7.43 (d, *J* = 7.3 Hz, 1H), 7.25 (d, *J* = 4.3 Hz, 1H), 7.20 (t, *J* = 6.1 Hz), 1H), 7.12 (t, *J* = 7.3 Hz, 1H), 2.81 (q, *J* = 7.3 Hz, 2H), 1.24 (t, *J* = 7.3 Hz, 3H), 0.26 (s, 9H); ¹³C NMR (CDCl₃) δ: 146.7, 132.4, 128.7, 127.9, 125.5, 122.2, 103.9, 97.7, 27.7, 14.6, -0.1; HRMS *m/e* Calc. for C₁₃H₁₉Si [(M+H)⁺]: 203.1256. Found: 203.1257.

1-Ethyl-2-ethynylbenzene (10b). Obtained from **8b** (105 mg, 4%); ¹H-NMR (CDCl₃) δ: 7.50 (d, *J* = 7.5 Hz, 1H), 7.26-7.20 (m, 2H), 7.12 (t, *J* = 7.3 Hz, 1H), 2.89 (s, 1H), 2.79 (q, *J* = 7.3 Hz, 2H), 1.24 (t, *J* = 7.3 Hz, 3H); ¹³C-NMR (CDCl₃) δ: 142.3, 132.8, 128.8, 127.8, 125.5, 121.5, 82.0, 81.3, 27.2, 15.7; HRMS *m/e* Calc. for C₁₀H₁₁ [(M+H)⁺]: 131.0861. Found: 131.0879.

[2-[2-(Methoxymethyl)phenyl]ethynyl]trimethylsilane (9c). Obtained from **8c** (4.17 g, 96%). This compound had been previously prepared following the same procedure [39].

1-Ethynyl-2-(methoxymethyl)benzene (10c). Obtained from **8c** (60 mg, 2%). This compound had identical physical and spectra data identical with those reported in the literature [39].

Trimethyl[2-(naphthalen-5-yl)ethynyl]silane (15). Obtained from **14** (3.90 g, 87%). This compound had been previously prepared using the corresponding iodide as starting material according to the same procedure [40]. ¹H-NMR (CDCl₃) δ: 8.41 (d, *J* = 8.3 Hz, 1H), 7.87 (d, *J* = 7.0 Hz, 1H), 7.85 (d, *J* = 7.2 Hz, 1H), 7.76 (d, *J* = 7.3 Hz, 1H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 0.40 (s, 9H); ¹³C-NMR (CDCl₃) δ: 133.4, 133.1, 130.8, 129.0, 128.2, 126.8, 126.3, 126.2, 125.1, 120.8, 103.1, 99.4, 0.01.

1-Ethynyl-naphthalene (16). Obtained from **14** (150 mg, 5%). This compound had physical and spectra data identical with those reported in the literature [41-42].

General procedure for the preparation of tetrafluoroborates 11 and 17 [26-27]

PhIO (3.52 g, 16 mmol) [25] and $\text{BF}_3 \cdot \text{OEt}_2$ (2 mL, 16 mmol) were added to a solution of 2-aryl-trimethylsilylacetylenes **9** or **15** (10 mmol) in dry CH_2Cl_2 (40 mL) and the mixture was stirred under an inert atmosphere at room temperature for 4 h. Then a solution of NaBF_4 (5.5 g, 50 mmol) in H_2O (20 mL) was added and the resulting two phase system was vigorously stirred for 15 min at room temperature. The organic layer was collected, the aqueous one was extracted with CH_2Cl_2 (25 mL) and the combined organic phases were dried over MgSO_4 . Filtration of the drying agent afforded a solution of crude tetrafluoroborates **11** and **17**, which were used in the next step without further purification.

General procedure for the preparation of triflates 13 and 18 [29-30]

A solution of 2-aryltrimethylsilylacetylenes **9** or **15** (10 mmol) in dry CH_2Cl_2 (10 mL) was added dropwise to a previously prepared solution of the Zefirov reagent (**12**, *ca.* 7 mmol) in dry CH_2Cl_2 [28] at 0 °C. The reaction mixture was allowed to stir for 1 h at the same temperature to provide a solution of crude triflates **13** and **18**, which was used in the next step without further purification.

General procedure for the nucleophilic addition of sodium benzenesulfinate to iodonium salts

Sodium benzenesulfinate (1.8 g, 11 mmol) was added to a solution of the above mentioned solutions of tetrafluoroborates or triflates (*ca.* 10 mmol) and the mixture was stirred under an inert atmosphere for 1 h. Then CH_2Cl_2 (30 mL) and H_2O (20 mL) were added and after extraction the organic phase was dried over MgSO_4 . Evaporation of the solvent yielded a residue which was purified by column chromatography (silica gel) using as eluent a 1/10 mixture of ethyl acetate and hexane.

1-(Phenylsulfonyl)-1H-indene (19a) and *3-(phenylsulfonyl)-1H-indene (20)*. Prepared from either **11a** (820 mg, 32% overall from **9a**) or **13a** (1.13 g, 44% overall from **9a**), these compounds were obtained as an inseparable mixture (ratio *ca.* 5:1). **19a**: $^1\text{H-NMR}$ (CDCl_3) δ : 7.91 (bd, $J = 7.5$ Hz, 1H), 7.50-7.43 (m, 3H), 7.31-7.23 (m, 4H), 7.12 (bd, $J = 7.9$ Hz, 1H), 6.77 (d, $J = 5.5$ Hz, 1H), 6.47 (d, $J = 5.5$ Hz, 1H), 5.07 (s, 1H); $^{13}\text{C-NMR}$ (CDCl_3) δ : 144.3, 143.4, 137.4, 135.5, 133.5, 129.1, 129.0, 127.9, 127.8, 126.3, 125.7, 121.6, 73.5; HRMS (for the mixture) m/e Calc. for $\text{C}_{15}\text{H}_{13}\text{O}_2\text{S}$ [(M+H) $^+$]: 257.0636. Found: 257.0640. **20**: $^1\text{H-NMR}$ (CDCl_3) δ : 8.06 (d, $J = 7.9$ Hz, 2H), 7.73 (d, $J = 7.3$ Hz, 1H), 7.63-7.43 (m, 3H, partially obscured), 7.30-7.25 (m, 3H, obscured), 7.00 (bs, 1H), 3.61 (bs, 2H).

1-(2-o-Tolyethynylsulfonyl)benzene (21a). Prepared from either **11a** (670 mg, 26% overall from **9a**) or **13a** (510 mg, 20% overall from **9a**). $^1\text{H-NMR}$ (CDCl_3) δ : 8.09 (d, $J = 7.3$ Hz, 2H), 7.70 (t, $J = 7.3$ Hz, 1H), 7.63 (t, $J = 8.0$ Hz, 2H), 7.47 (d, $J = 7.3$ Hz, 1H), 7.36 (t, $J = 7.3$ Hz, 1H), 7.22 (d, $J = 8.0$ Hz, 1H), 7.18 (t, $J = 7.3$ Hz, 1H); $^{13}\text{C-NMR}$ (CDCl_3) δ : 142.2, 142.0, 133.8, 132.8, 131.3, 129.8, 129.2, 127.9, 127.1, 115.7, 93.1, 88.9, 20.2; HRMS m/e Calc. for $\text{C}_{15}\text{H}_{13}\text{O}_2\text{S}$ [(M+H) $^+$]: 257.0636. Found: 257.0633.

3-Methyl-1-(phenylsulfonyl)-1H-indene (19b). Prepared from either **11b** (1.08 g, 40% overall from **15**) or **13b** (1.375 g, 51% overall from **15**). ¹H-NMR (CDCl₃) δ: 7.83 (bd, *J* = 7.9 Hz, 1H), 7.46 (d, *J* = 7.9 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.33-7.28 (m, 2H), 7.23 (t, *J* = 7.9 Hz, 2H), 7.04 (bd, *J* = 7.9 Hz, 1H), 6.11 (bs, 1H), 4.97 (bs, 1H), 1.94 (s, 3H); ¹³C-NMR (CDCl₃) δ: 146.4, 145.5, 135.9, 135.0, 133.3, 129.0, 128.8, 127.6, 126.1, 125.4, 122.4, 119.4, 72.3, 12.7; HRMS m/e Calc. for C₁₆H₁₅O₂S [(M+H)⁺]: 271.0793. Found: 271.0797.

1-[2-(2-Ethylphenyl)ethynylsulfonyl]benzene (21b). Prepared from either **11b** (760 mg, 26% overall from **9b**) or **13b** (700 mg, 20% overall from **9b**); ¹H-NMR (CDCl₃) δ: 8.09 (d, *J* = 8.1 Hz, 2H), 7.69 (t, *J* = 7.1 Hz, 1H), 7.60 (t, *J* = 6.8 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.26 (bs, 1H), 7.19 (t, *J* = 7.4 Hz, 1H), 2.69 (q, *J* = 7.8 Hz, 2H), 1.38 (t, *J* = 7.8 Hz, 3H); ¹³C-NMR (CDCl₃) δ: 148.6, 134.0, 133.4, 133.3, 131.8, 129.3, 128.4, 127.3, 126.0, 122.5, 94.3, 72.4, 27.6, 14.8; HRMS m/e Calc. for C₁₆H₁₅O₂S [(M+H)⁺]: 271.0793. Found: 270.0792.

1-(2-(Phenylsulfonyl)ethynyl)naphthalene (22). Prepared from either **17** (440 mg, 15% overall from **15**) or **18** (465 mg, 16% overall from **15**); ¹H-NMR (CDCl₃) δ: 8.77 (d, *J* = 8.2 Hz, 1H), 8.12 (d, *J* = 7.0 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 2H), 8.00 (d, *J* = 7.1 Hz, 1H), 8.06 (d, *J* = 7.3 Hz, 1H), 7.81 (t, *J* = 7.7 Hz, 1H), 7.86 (t, *J* = 7.3 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 7.3 Hz, 1H); ¹³C-NMR (CDCl₃) δ: 134.5, 134.2, 134.0, 132.0, 131.9, 130.2, 128.6, 128.5, 127.1, 126.3, 124.7, 124.5, 124.1, 120.5, 98.3, 72.6; HRMS m/e Calc. for C₁₈H₁₃O₂S [(M+H)⁺]: 293.0636. Found: 293.0633.

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