**Supporting Information**

**Electrochemical decarboxylative sulfonylation of arylacetylenic acids with sodium arylsulfinates: access to arylacetylenic sulfones**

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**General information**

All reactions were carried out under air. Commercial reagent and compound were used without purification unless otherwise indicated. All products were characterized by 1H NMR and 13C NMR, using TMS as an internal reference (1H NMR: 400 MHz, 13C NMR: 100 MHz) on Bruker 400 MHz spectrometers with CDCl3 as the solvent. Flash chromatography was performed on silca gel (silca gel, 200-300 mesh).

**Synthetic methods of 3-phenylpropiolic acid 1[1]**

Aryl iodide (5.0 mmol), DBU (1.83 g, 12 mmol, 2.4 equiv), and Pd(PPh3)4 (144 mg, 2.5 mol %) were mixed in DMSO (6 mL). The solution of propiolic acid (420 mg, 6.0 mmol, 1.2 equiv) in DMSO (6 mL) was poured into the flask. The mixture was stirred at room temperature for 12 h. After the reaction was complete, EtOAc (20 mL) was poured into the reaction mixture. The reaction mixture was extracted with saturated aqueous NaHCO3 solution. The aqueous layer was separated, acidified to pH 2.0 by addition of cold HCl (1 N), and extracted with EtOAc. The combined organic layers were dried with anhydrous MgSO4 and filtered, and the solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography on silica gel.

**General procedure for the synthesis of arylacetylenic sulfones 3.**

A mixture of 3-phenylpropiolic acid **1** (0.5 mmol) and sodium benzenesulfinate **2** (1.0 mmol), *n*Bu4PF6 (1.0 mmol), and CH3CN/H2O (7/1 mL) was added to an undivided cell. The cell was equipped with a graphite rod (ϕ 6 mm) as the anode with a platinum plate (10 mm × 10 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 20 mA under room temperature for 2 h. After electrolysis, the solvent was removed with a rotary evaporator. The solution was then added to 10 mL of water and extracted with EtOAc (3 × 10 mL). The combined organic layer was dried with MgSO4 and filtered. The solvent was removed with a rotary evaporator. The resulting mixture was purified by silica gel column chromatography to afford **3**.

**Compound 3 characterization Data**



**Benzene, [(2-​phenylethynyl)​sulfonyl]​(3a).[1]** 1H NMR (400 MHz, CDCl3 ): δ 8.08 (d, *J* = 7.8 Hz, 2H), 7.69 (t, *J* = 7.2 Hz 1H), 7.60 (t, *J* = 7.78 Hz, 2H), 7.52 (d, *J* = 7.8 Hz, 2H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.8Hz, 2H).



**Benzene, 1-​methyl-​4-​[(2-​phenylethynyl)​sulfonyl] ​(3b)**​. **[1]** 1H NMR (400 MHz, CDCl3): δ 8.5 (d, *J* = 8.4Hz, 2 H), 7.6-7.56 (m, 1H), 7.56-7.44 (m, 2H), 7.39-7.28 (m, 2H), 7.18-7.02 (m, 2H), 2.27 (s, 3H).



**Benzene, 1-​methoxy-​4-​[(2-​phenylethynyl)​sulfonyl] ​(3c)**.**[2]** 1H NMR (400 MHz, CDCl3): δ 8.00 (d, *J* = 8.8 Hz, 2 H), 7.65-7.57 (m, 1H), 7.56-7.44 (m, 2H), 7.36 (t, J = 7.6 Hz 2 H), 6.82 (d, J = 8.9 Hz, 2 H), 3.74 (s, 3H).



**Benzene, 1- Fluoro -​4-​[(2-​phenylethynyl)​sulfonyl]** **​(3d)**.**[3]** 1H NMR (400 MHz, CDCl3): δ 8.08 (d, *J* = 7.2 Hz, 2H), 7.72-7.67 (m, 1H), 7.61 (t, *J* = 7.2 Hz, 2H), 7.53 (dd, *J* = 8.8, 5.6 Hz, 2 H)), 7.07 (t, *J* = 8.4 Hz, 2H).



**Benzene, 1-​chloro-​4-​[(2-​phenylethynyl)​sulfonyl]​** **​(3e)**.**[4]** 1H NMR (400 MHz, CDCl3) :δ 8.08 (d, *J* = 7.8 Hz 2H), 7.70 (t, *J* = 7.2 Hz, 1H), 7.61 (t, *J* = 7.8 Hz 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H).



**Benzene, 1-​bromo-​4-​[(2-​phenylethynyl)​sulfonyl]** **​(3f)**.**[5]** 1H NMR (400 MHz, CDCl3) :δ 8.07 (d, *J* = 7.5 Hz, 2H), 7.70 (t, *J* = 7.2 Hz 1H), 7.61 (t, *J* = 7.8 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H).



**Benzene, 1-​methyl-3-​[(2-​phenylethynyl)​sulfonyl]** **​(3g)**.**[3]** 1H NMR (400 MHz, CDCl3): δ 8.11 (d, *J* = 7.8 Hz, 2H), 7.72 (t, *J* = 7.4 Hz, 1H), 7.63 (t, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 7.2 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 2H), 2.35 (s, 3H).



**Benzene, 1-methoxy-3-[(2-phenylethynyl)sulfonyl]** **​(3h)**. **[6]**  1H NMR (400 MHz, CDCl3): δ 8.08 (d, *J* = 7.8 Hz, 2H), 7.68 (d, *J* = 7.2 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 9.2 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 6.4 Hz, 2H), 3.79 (s, 3H).



**1,3-Dimethyl-5-[2-(phenylsulfonyl)ethynyl]benzene​ (3i)**. **[6]** 1H NMR (400 MHz, CDCl3) :δ 7.99 (d, *J* = 7.6 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.06 (s, 2H), 7.01 (s, 1H), 2.19 (s, 6H).



**Benzene, 1-​methyl-2-​[(2-​phenylethynyl)​sulfonyl]** **​(3j)**.**[6]** 1H NMR (400 MHz, Chloroform-d) δ 8.14 (d, *J* = 7.6 Hz 2H), 7.74 (t, *J* = 7.4 Hz 1H), 7.65 (t, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.29-7.20 (m, 2H), 2.43 (s, 3H).



**Benzene, 1-methoxy-2-[(2-phenylethynyl)sulfonyl]** **​(3k)**.**[6]** 1H NMR (400 MHz, CDCl3) :δ 8.09 (d, *J* = 7.2 Hz, 2H), 7.65 (d, *J* = 7.2 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 2H), 7.50-7.37 (m, 2H), 6.93-6.86 (m, 2H), 3.83 (s, 3H).



**Benzene, 1-chloro-2-[(2-phenylethynyl)sulfonyl]** **​(3l)**.**[6]** 1H NMR (400 MHz, CDCl3) :δ 8.21 (d, *J* = 7.6 Hz, 1H), 7.59 (s, 2H), 7.57 (s, 1H), 7.50 (t, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 7.5 Hz 2H).



**Naphthalene, [(2-​phenylethynyl)​sulfonyl]** **​(3m)**. **[6]** 1H NMR (400 MHz, CDCl3) :δ 8.16 (d, *J* = 7.8 Hz, 2H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 7.2 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 2H), 7.60-7.53 (m, 2H), 7.45 (t, *J* = 7.8 Hz, 1H).



**Benzene, 1-​methyl-​4-​[(2-​phenylethynyl)​sulfonyl]**​ **​(3n)**. **[1]** 1H NMR (400 MHz, CDCl3) :δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.37 (q, *J* = 7.6 Hz, 4H), 2.47 (s, 3H).



**Benzene, 1-​[(2-​phenylethynyl)​sulfonyl]​-​4-​(trifluoromethyl)** **​(3o)**. **[1]** 1H NMR (400 MHz, CDCl3): δ 8.28-8.21 (m, 2H), 7.99-7.79 (m, 3H), 7.56-7.50 (m, 2H), 7.39 (t, *J* = 7.6 Hz, 2H).



**Benzene, 1-​chloro-​2-​[(2-​phenylethynyl)​sulfonyl] ​(3p)​**. **[7]** 1H NMR (400 MHz, CDCl3):δ 8.21 (d, *J* = 8.8 Hz, 1H), 7.60 (d, *J* = 1.6 Hz, 1H), 7.59 (s, 2H), 7.57 (d, *J* = 1.6 Hz, 1H), 7.52-7.47 (m, 2H), 7.39 (t, *J* = 7.6 Hz, 2H).

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**Copy of NMR spectra** .





























 