



Supplementary Information

Electrochemical Synthesis of Sulfonamides in Graphite Powder Macro Electrode

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1. General procedures

All reagents and solvents used were previously purified and dried in agreement with the literature.¹ Amines (**1a-m**) and sodium aryl sulfinates (**2a-b**) were purchased from Aldrich Chemicals Co. The GC/FID analysis was performed on a Varian CP-3380 gas chromatograph system coupled with a flame ionization detector. The chromatographic column was a Chrompack CP-SPL5CB capillary column (30 m × 0.25 mm, 0.25 μm) using the initial temperature 60 °C then increased to 220 °C at 10 °C min⁻¹. ¹H and ¹³C NMR data were recorded in CDCl₃. The chemical shifts are reported as delta (δ) units in parts per million (ppm) relative to the solvent residual peak as the internal reference [δ 7.26 (¹H NMR) and δ 77.16 (¹³C NMR)]. Coupling constants (*J*) for all spectra are reported in Hertz (Hz). Linear scan voltammeters were performed using an Autolab Metrohm PGSTAT 30 potentiostat/galvanostat, using the NOVA 2.1 program for data acquisition. Electrolysis was performed on an Instrutherm FA-3005 DC power source or on the Autolab Metrohm PGSTAT 30 potentiostat/galvanostat.

2. Experimental Procedures

2.1 Thermal treatment of graphite powder used as the macroelectrode (anode): Graphite powder was purchased from Sigma-Aldrich (particle size < 20 μm). The procedure was divided in two stages: 1) addition of concentrated HCl (37%) (20 mL) to the graphite powder (2 g) followed by stirring for 30 minutes at 25 °C. After decanting the graphite powder, it was washed with distilled water (5 X 50 mL). 2) The solid was then heated at 280 °C, during 4 hours. This treatment is necessary to eliminate possible oxygenated functions on the surface of the graphite powder that could negatively interfere in the expected results of the electrochemical method.²

2.2 Representative Procedure for the Synthesis of N-benzyl-4-methylbenzenesulfonamide (3a): A graphite stick with a length of 4.5 cm and a diameter of 1.0 cm, wrapped with Teflon[®] tape on its top was fitted to the Teflon[®] base (Figure S1a). A small space was left (~ 5 mm) at which a cavity was formed in order to add the graphite powder and reagents (Figures S1b and S1c). The rod is also used as the electrical contact. After this stage, the set was placed on a universal support for pressing.

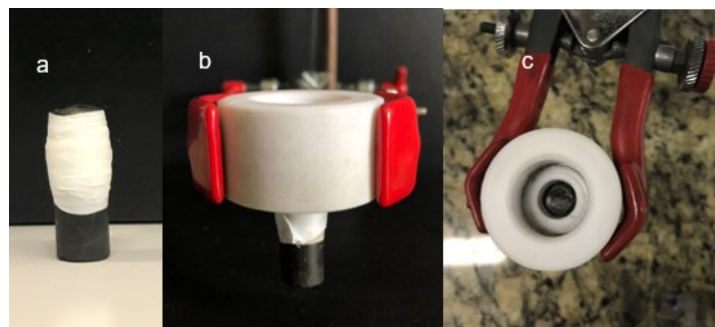


Figure S1. (a) Graphite stick wrapped with Teflon[®] tape; (b) cavity formed between the graphite stick and the Teflon[®] base compartment; and (c) Teflon[®] compartment coupled to the graphite stick.

The working electrode (graphite powder, 300 mg) was weighed, mixed with sodium *p*-toluenesulfinate, **2a** (178 mg, 1.0 mmol) and added to the cavity formed between the graphite stick and Teflon[®] base (Figure S2a). An aluminum rod of the same cavity diameter was placed over the mixture, and a weight of 2.5 kg placed over aluminum rod during 10 minutes, Fig. S2b. Benzylamine, **1a** (54 mg, 55 μ L, 0.5 mmol) was dropwise added to the compressed graphite powder + **2a** mixture, with the aid of an automatic pipette (Labmate soft 10-100 μ L). In order to avoid diffusion of the pressed material into the electrolytic solution, a filter paper containing small holes was added above the compressed material. This technique assists in the diffusion of oxygen gas that may be formed during the electrolysis (Figure S2c).

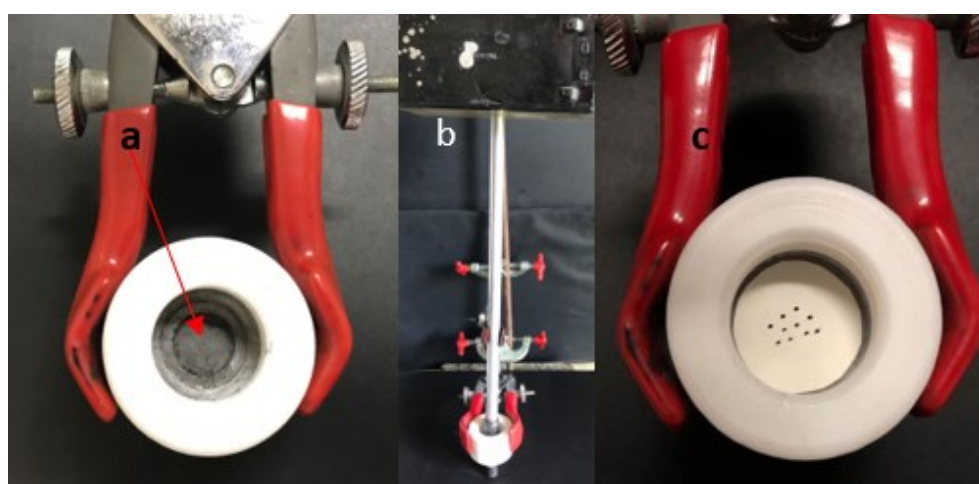


Figure S2. (a) Anodic material (graphite powder + **2a**) added to the cavity; (b) compression of the anodic material under 2.5 kg; and (c) perforated filter paper placed over the cavity surface (graphite powder macroelectrode).



With the reagents properly added, a glass compartment (Figure S3a) was screwed to the Teflon[®] base (Figure S3a) to which 0.1 mol.L⁻¹ LiClO₄ aqueous solution (10 mL) was added. A graphite rod of 0.8 cm in diameter and 6 cm in length (cathode) was then immersed in the electrolytic solution. To the ends of the graphite rods, two metal clamps were attached, which served as electrical contacts, which would later be connected to the metal claws from a DC source to initiate electrolysis (Figure S3b).



Figure S3. (a) glass compartment; and (b) assembled electrochemical cell.

The reagents were subjected to constant current electrolysis for 1 hour. Then, the electrolytic solution (LiClO₄) was transferred to a becker, and the glass compartment was unscrewed from the Teflon[®] base. The filter paper was carefully removed and washed with EtOAc. (3 mL). Another glass compartment with a plastic cap (called extractor) was screwed to the Teflon[®] base (Figures S4a and S4b). EtOAc (3 mL) used to wash filter paper was then added to the extractor and the mixture was stirred vigorously to remove all material from inside the Teflon[®] cavity. The extraction procedure was repeated three times.

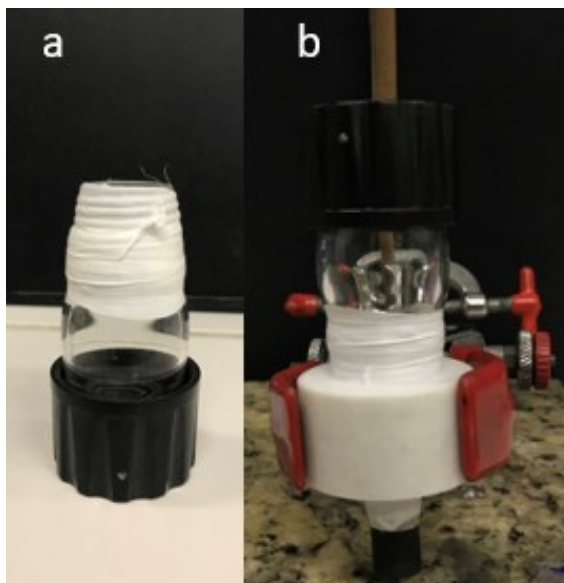
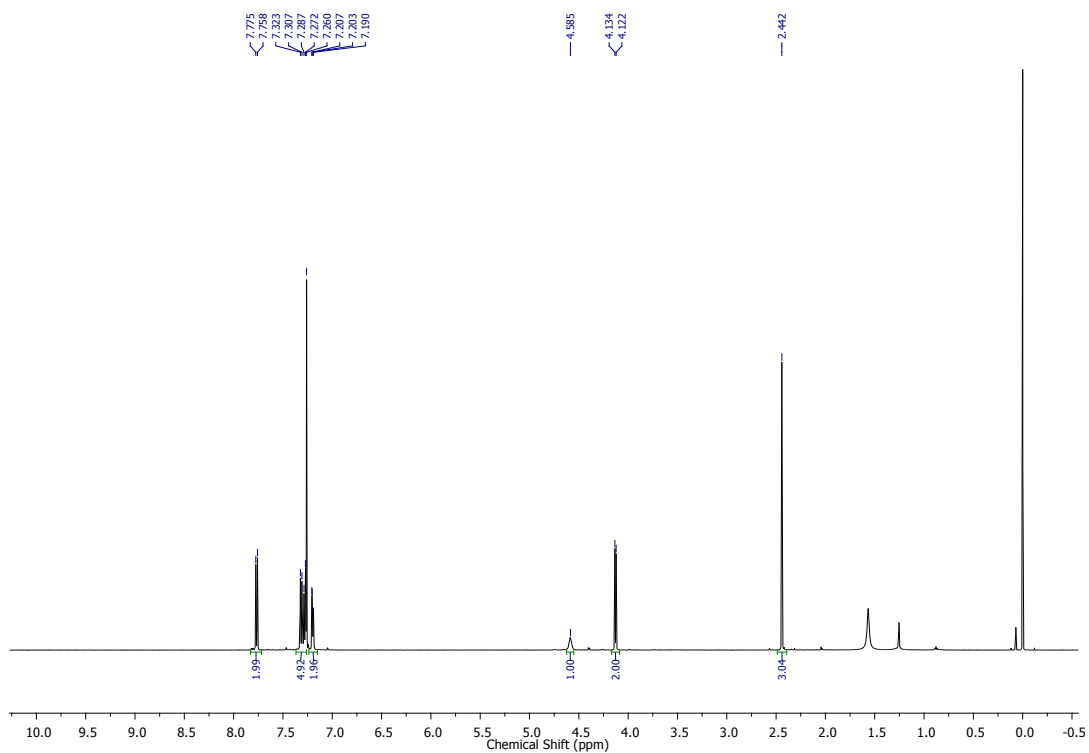


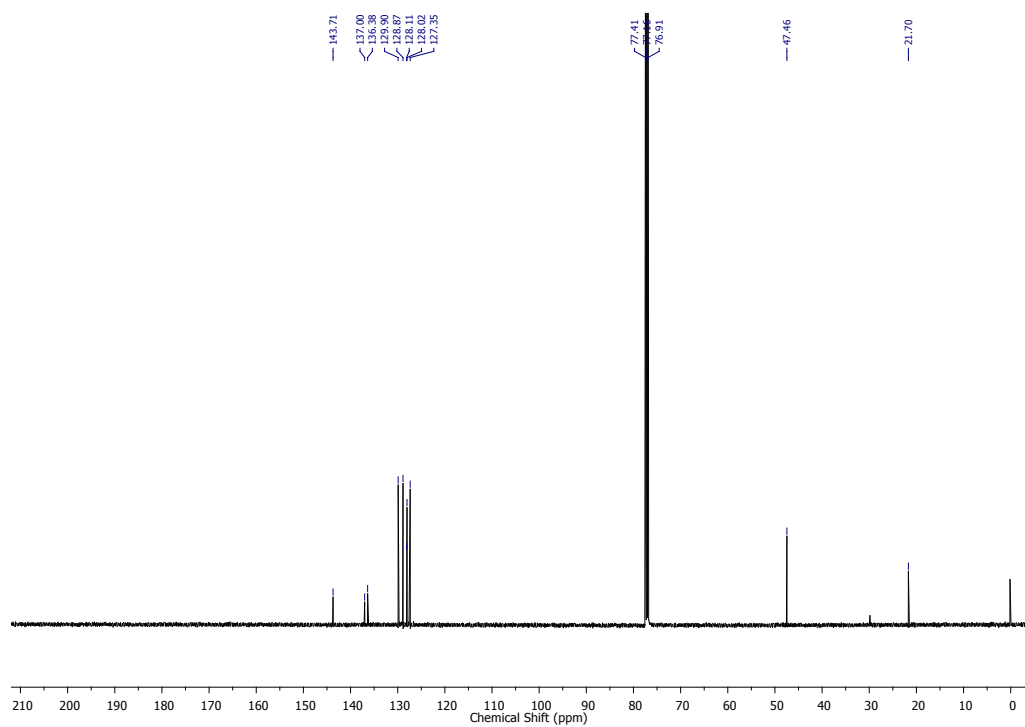
Figure S4. (a) Extractor glass and (b) extractor glass screwed to the Teflon® compartment.

The mixture (graphite powder + EtOAc solution) was additionally sonicated for 10 minutes and filtered under reduced pressure. The filtered organic phase was washed with water (3 x 10 mL) and dried over anhydrous Na_2SO_4 . The mixture was filtered and the solvent removed *in vacuo*. 5% NaOH solution (10 mL) was added to the residue and then sonicated for another 10 minutes. After that time, the aqueous solution was extracted with EtOAc (3 x 3 mL). The EtOAc phase was discarded, and the aqueous phase was then mixed to a 5% NaHCO_3 solution (10 mL) and again extracted with EtOAc (3 x 3 mL). The organic phase was dried over anhydrous Na_2SO_4 , filtered and the solvent removed to give 86 mg of the title compound without the need of further purification. ^1H NMR (500 MHz, CDCl_3) δ 7.77 (d, J = 8.3 Hz, 1H), 7.32 – 7.19 (m, 7H), 4.59 (br s, 1H), 4.13 (d, J = 6.2 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 143.7, 137.0, 136.3, 129.9, 128.8, 128.1, 128.0, 127.3, 47.4, 21.7. The data match to the previously described compound.³

3. Spectra



¹H NMR spectrum (500 MHz, CDCl₃) of compound **3a**



¹³C NMR spectrum (125 MHz, CDCl₃) of compound **3a**



4. Voltammetry Studies

4.1 General Procedure for Linear Sweep Voltammetry in Conventional Electrochemical Cell: The linear sweep voltammograms were carried out in an electrochemical cell of three electrodes (Figure S6a), using a glassy carbon as working electrode (disk $\phi = 3$ mm, Fig. 5b), Ag/AgCl, KCl (sat.) as reference electrode (Figure S6a), and a stainless steel grid as counter electrode (Figure S6c). Benzylamine, **1a** (1.0 mmol) and sodium *p*-toluenesulfonate, **2a** (1.0 mmol) voltammograms were carried out in 20 mL electrolytic solution [0.1 mol.L⁻¹ LiClO₄ in MeCN/H₂O (7:3)]. The potential window was 0.0 V to 1.8 V and scan rate = 100 mV.s⁻¹. It was used NOVA 2.1 software for data acquisition.

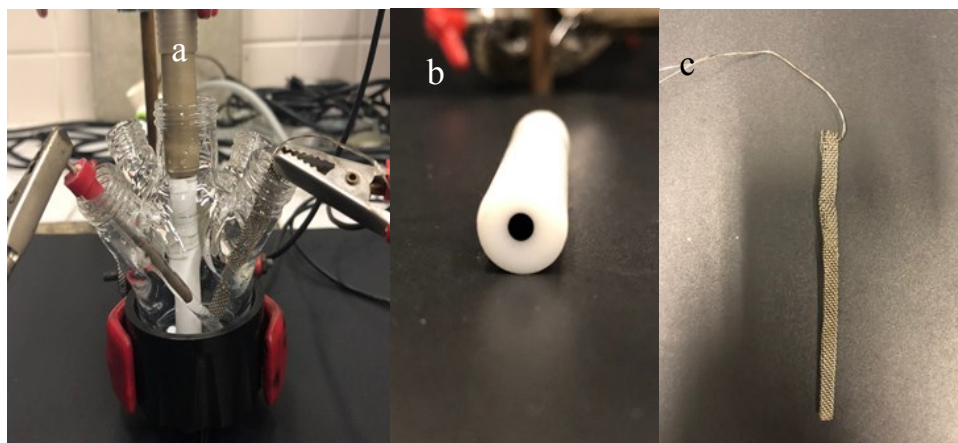
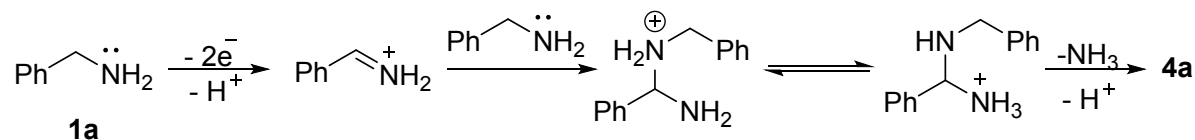


Figure S5. (a) Conventional electrochemical cell of three electrodes and reference electrode (red cap), (b) glassy carbon electrode (working electrode) and (c) stainless steel grid (auxiliary electrode).



5. Mechanistic Proposal for 4a⁴⁻⁶



6. References

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