

ChemElectroChem

Supporting Information

Behaviour of 3,4-Dihydroxy-9,10-Anthraquinone-2-Sulfonic Acid in Alkaline Medium: Towards a Long-Cycling Aqueous Organic Redox Flow Battery

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EXPERIMENTAL PART

General

All reagents were used without further purification. ARS sodium salt **ARSNa** (81% mainly due to the presence of inorganic salts, 50-80 €/kg for 1 ton of ARS 80%) was purchased from Fluorochem (UK). Sodium chloride (99%+) was purchased from Sigma-Aldrich (USA). Potassium chloride (99%) and alizarin (94%) were purchased from Alfa Aesar. Oleum 20% was purchased from Fisher Chemicals. Potassium hydroxide (85%), sodium hydroxide (98%), potassium ferrocyanide hexahydrate (96%) were purchased from VWR (US). NMR deuterated solvents were purchased from Euriso-top (France). All solutions were prepared with ultrapure water (18.2 M Ω , Millipore Simplicity).

^1H NMR spectra were recorded on BRUKER AC 300 P (300 MHz) spectrometer and ^{13}C NMR spectra on BRUKER AC 300 P (75 MHz) spectrometer. Chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. Data are given in the following order: δ value, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad), number of protons, coupling constants J is given in Hertz. The mass spectra were realized on a Waters Q-Tof 2 at the Centre Régional de Mesures Physiques de l'Ouest (CRMPO, Rennes). UV-Vis measurements were performed on an Agilent Technologies Cary 60. The rheology measurements were performed on an Anton Paar MCR301 rheometer between 5 and 100 s^{-1} shear rates at 20°C and 40°C with a plate-plate setup (diameter: 75 mm and gap: 1 mm). Shear rate γ was calculated using the relationship $\gamma=v/h$, where v is the velocity of the moving plate (m s^{-1}) and h is the distance between the two parallel plates (m). Viscosity values are in mPa s. Cations titrations were performed on an Ionic chromatography Metrohm Compact IC Pro 881 with a Metrosep C 4 - 250/4.0 column. 3 mmol L^{-1} nitric acid in a mixture of water and acetonitrile 3 : 1 was used as eluant. The analysis was performed at 35°C with a flow rate

of 0.9 mL min⁻¹. The detection was made by conductimetry. Electrolytes were diluted by 1000 or 10000 and filtered on 0.22 μm filters before injection.

Electrochemical experiments

Cyclic voltammetry analysis was performed with a SP50 (Biologic) potentiostat/galvanostat with a glassy carbon electrode (diameter 3 mm), a platinum wire auxiliary electrode, and a Ag/AgCl reference electrode in a bridge tube in a standard three-electrode configuration. Linear Sweep Voltammetry (LSV) at a 0.071 cm² glassy carbon rotating disc electrode (Metrohm) was performed at 20 mV s⁻¹ scan rate with a rotation rate of 1000 rpm, under a dinitrogen atmosphere. The state of charge (SOC) of negolyte and posolyte was calculated as follows:

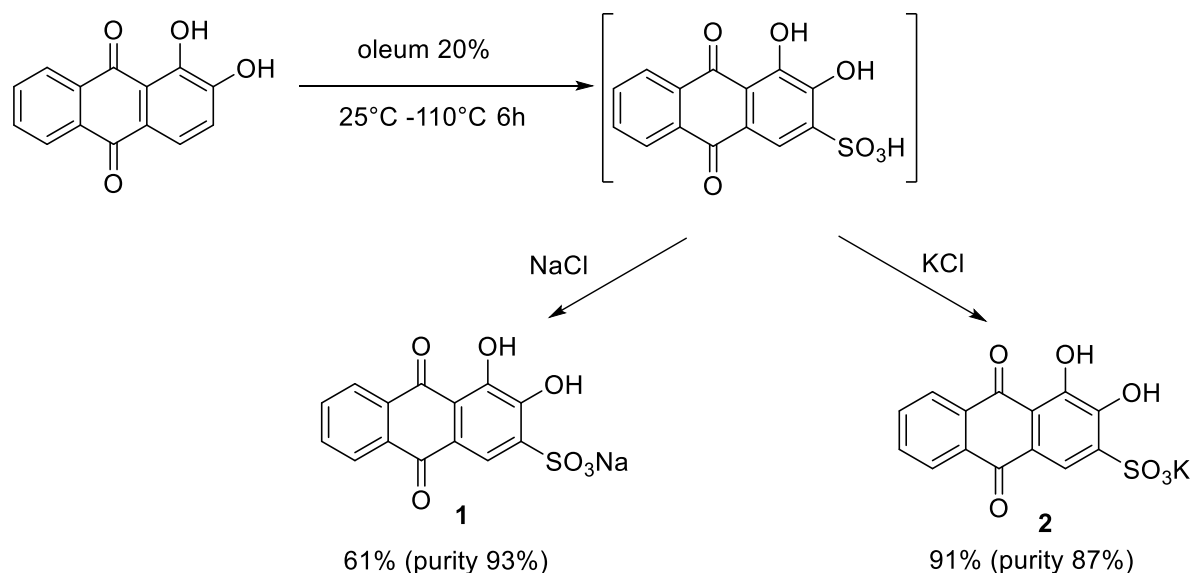
$$SOC(negolyte) = \frac{I^-}{I^- + I^+} \times 100$$

$$SOC(posolyte) = \frac{I^+}{I^- + I^+} \times 100$$

with I⁻ and I⁺ the negative and positive current, respectively, measured by LSV.

RFB experiments were carried out in a home-made cell with graphite felt electrodes (SGL carbon SE; square cuboid 50 × 50 × 4.6 mm with a geometrical surface area of 25 cm²; 35% compression of the thickness leading to 95.5% porosity), composite graphite current collectors and cationic ion-exchange membrane (80 μm Nafion membrane). The positive and negative electrolytes were pumped at a flow rate of 150 mL min⁻¹ through KNF Pump (Liquipor® 1.100 version KT). The battery was operated through a BT-Lab V1-57 software controlling a BioLogic Science Instruments BCS 815. The cycling current was set at 40 mA cm² both in charge and discharge and voltage cut-offs were set at 0.6 and 1.4-1.7 V, respectively. All the other parameters of the battery have been calculated as usual.^[1]

Organic synthesis.

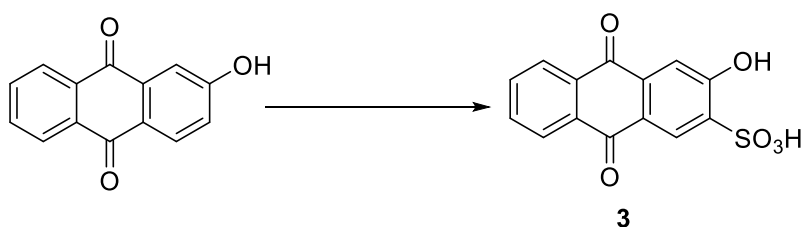


Synthesis of 3,4-dihydroxy-9,10-dioxo-9,10-dihydroanthracene-2-sulfonate sodium salt (ARSNa*). ARS was synthesized according to literature.^[2] Alizarin (15 g, 124.9 mmol) was dissolved in oleum 20% (40 mL) and the mixture was stirred at 25°C for 30 min. Then, the temperature was raised to 40°C for 30 min and 110°C for 6h. After cooling to room temperature, the crude product was added by portions to 150 mL of water at 0°C. After filtration, 40 g of sodium chloride were added and the formed precipitate was collected by filtration on fritted glass. The solid was washed with 150 mL of a 10% aqueous solution of sodium chloride and three times with 50 mL of deionized water. The product was dried under vacuum at 40°C for 8h. An orange powder was obtained as the desired product (12.95 g with a 93% purity, 61% yield).

¹H NMR (300 MHz, DMSO-*d*₆) δ 8.29 – 8.16 (m, 2H), 7.99 – 7.91 (m, 3H).

Synthesis of 3,4-dihydroxy-9,10-dioxo-9,10-dihydroanthracene-2-sulfonate potassium salt (ARSK). The same procedure as for the synthesis of 3,4-dihydroxy-9,10-dioxo-9,10-dihydroanthracene-2-sulfonate sodium salt was used except that the precipitation of the potassium salt of ARS was performed adding 30 g of potassium chloride. After precipitation, the solid was washed twice with 150 mL of a 10% aqueous solution of potassium chloride and with 50 mL of deionized water. The product was dried under vacuum at 40°C for 8h. An orange powder was obtained as the desired product (20.29 g with a 87% purity, 91% yield).

^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ 8.37 – 8.09 (m, 2H), 8.09 – 7.80 (m, 3H).



Synthesis of 3-hydroxy-9,10-dioxo-9,10-dihydroanthracene-2-sulfonic acid (HAQS).^[3] 2-hydroxyanthraquinone (5 g, 22.3 mmol) was dissolved in oleum 20% (6.7 mL) and the mixture was stirred at 25°C for 30 min. The temperature was raised to 40°C for 30 min and then to 110°C for 6h. After cooling to room temperature, the crude product was added by portions to 75 mL of water at 0°C and the formed precipitate was collected by filtration on fritted glass. The solid was washed with 150 mL of a 10% aqueous solution of sodium chloride and three times with 50 mL of deionized water. The compound was dried under vacuum at 40°C for 8h. An orange powder was obtained as the desired product (5.82 g with a 86% purity, 74% yield).

^1H NMR (300 MHz, $\text{DMSO-}d_6$) δ 8.33 (s, 1H), 8.25 – 8.14 (m, 2H), 7.99 – 7.85 (m, 2H), 7.48 (s, 1H).

^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) δ 182.45, 181.41, 158.97, 136.42, 136.07, 135.07, 134.64, 133.70, 133.63, 127.72, 127.18, 127.16, 125.36, 114.64.

[M-H]⁻ (C₁₄ H₇ O₆ S) Theoretical mass : 302.99633 z = 1 ; theoretical m/z : 302.99688 ; found : 302.9969.

Solubility measurements

The solubility of the compounds was determined by the shake-flask method in 2 mol L⁻¹ aqueous potassium hydroxide in triplicate. First 100 mg of the tested compound was mixed with the evaluated solvent by 100 µL portions until saturation. Then UV-Vis titration at 20°C was performed on the diluted (1/10000^e) solution isolated after filtration (0.22 µm filter) of the supernatant liquid obtained from saturated samples. The experiment was performed in triplicate after 24h, 48h and 72h of stirring of the saturated solution.

To measure the solubility of the reduced form of ARS, a charge was performed in a glovebox with a RFB to reach 100% of state of charge. The negolyte was a 0.18 mol L⁻¹ solution of commercial ARS sodium salt in a 1.2 mol L⁻¹ KOH aqueous solution and the posolyte was a 0.5 mol L⁻¹ solution of potassium ferrocyanide in a 0.2 mol L⁻¹ NaOH aqueous solution. 1 mL of the charged negolyte was collected and water was removed under vacuum. Oxygen-free distilled water was added and after filtration on a 0.22 µm filter, the solubility was estimated by UV-Visible (0.47 mol L⁻¹).

pKa determination

ARSNa was titrated in order to determine the different forms of this molecule depending on the pH. This molecule has three acidic hydrogen atoms. In order to determine their pKa a direct titration was carried out. A 25 mL solution containing 0.01 mol L⁻¹ of alizarin red S and 0.02 mol L⁻¹ of hydrochloric acid was titrated with a 0.05 mol L⁻¹ solution of potassium hydroxide. Hydrochloric acid was used to assure that the molecule was totally protonated at the beginning of the experiment.

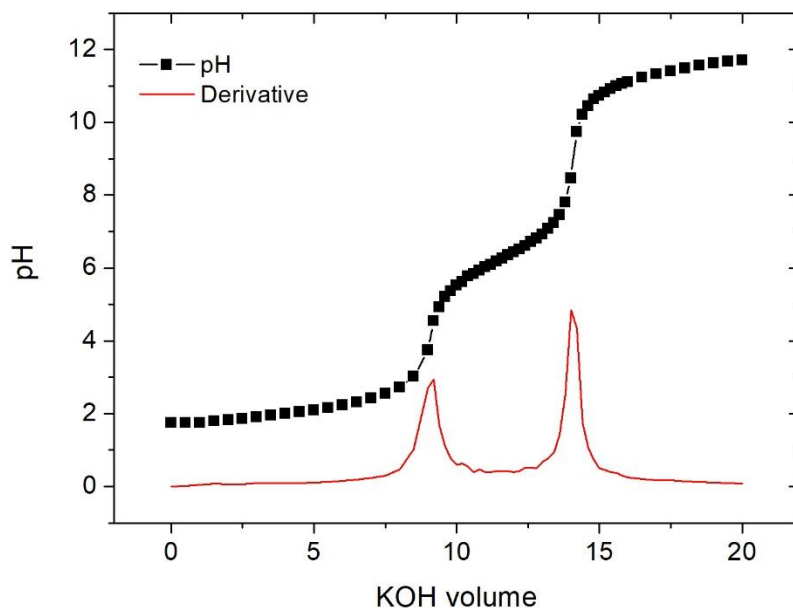


Figure S1. pHmetric titration of acidified 0.01 mol L⁻¹ ARS solution with a 0.05 mol L⁻¹ KOH solution.

The titration showed two equivalence points (Figure S1). The pKa can then be deduced as:

$$pH = pKa + \log \frac{[A^-]}{[HA]} \quad (1)$$

with [A⁻] the molar concentration of the basic form and [HA] the concentration of the corresponding acid form.

Thus, $pH = pKa$ when $[A^-] = [HA]$, which occurs halfway from the equivalence point. Therefore, the pKa can be read for a volume equal to half of the equivalent volume. In the case of ARS, two pKa were determined. The first one at 2.2 was associated to the sulfonic acid group as such group is known to be more acidic than hydroxide groups. The second one at 6.3 was associated with one of the hydroxide group. The hydroxide group located in α -position of the sulfonic acid group is more likely to be deprotonated due to the electro-withdrawing effect of the sulfonic acid group.

To determine the last pKa, spectrophotometric titration was carried out.^[4-6] Eq. 1 can be written as:

$$pK_a = pH_i - \log \frac{A_i - A_{HA}^\circ}{A_{A^-}^\circ - A_i} \quad (2)$$

with A_{HA}° the absorbance due to HA, $A_{A^-}^\circ$ the absorbance due to A and A_i the total absorbance of the solution.

Four solutions were prepared at pH 6.6, 9.3, 10.8 and 14.0 (Figure S2). Considering that the molecule has already lost two of its protons at pH = 6.6, this medium was used as an acidic reference (A_{HA}°) for the last acid/base couple and the solution at pH = 14.0, as an alkaline reference ($A_{A^-}^\circ$).

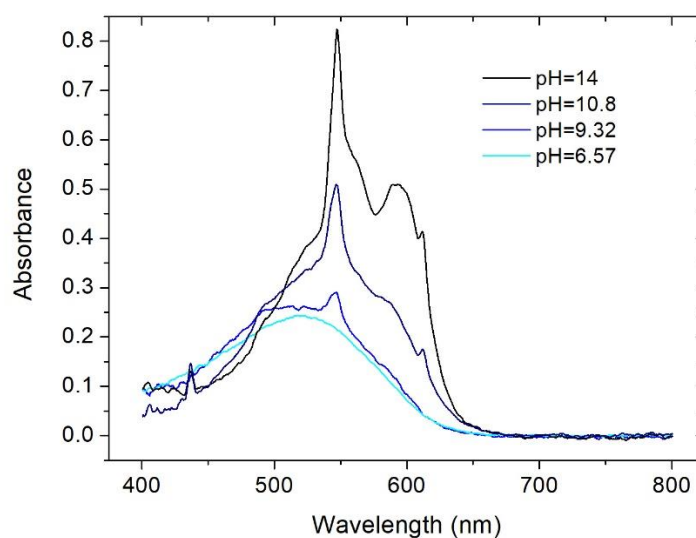


Figure S2. Absorbance spectra of alizarin red S at different pH

The acidic form was characterized by a broad absorption band at $\lambda = 520$ nm giving the solution its red color. As the pH increased, a bathochromic displacement can be seen and the band shifted to $\lambda = 548$ nm, whereas a second band appeared at $\lambda = 594$ nm. The color of the solution was

then violet. Using equation 2, experimental pKa values were calculated for each wavelength of the absorbance spectra for the solutions at pH = 9.3 and pH = 10.8 (Figure S3), and the pKa was determined as the average of these values: $pK_a = 10.4 \pm 0.9$.

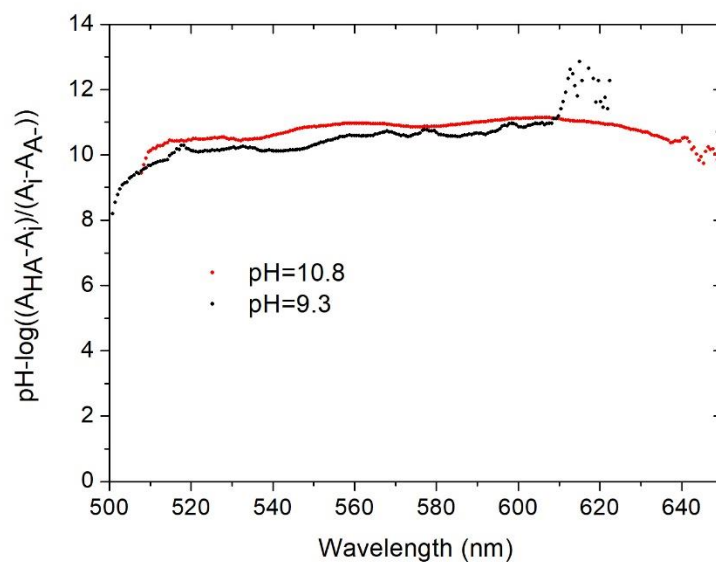
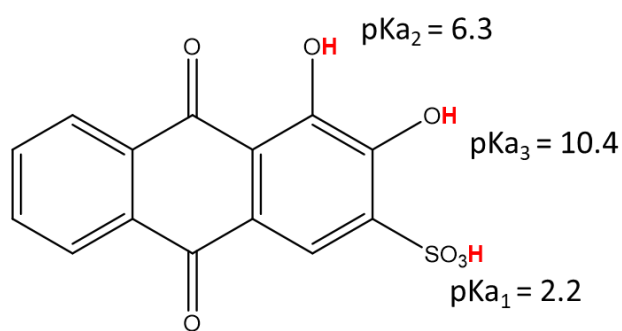


Figure S3. pKa vs wavelength calculated from the UV spectra of the solutions at pH = 9.3 and pH = 10.8.



Protonation of the reduced form of ARS

Using Nernst equation, the evolution of the redox potential vs the pH of the solution can be predicted. The equation was simplified using concentrations instead of chemical activities. In acidic medium, two protons also intervene in the reduction of the molecule so that the potential can be written for $T = 298 \text{ K}$:

$$E = E^{0'} + 0.03 \log \frac{[Ox]}{[Red]} - 0.06 \text{ pH} \quad (3)$$

In the case of a two electrons/one proton reaction, the Nernst equation becomes:

$$E = E^{0'} + 0.03 \log \frac{[Ox]}{[Red]} - 0.03 \text{ pH} \quad (4)$$

And when no protons intervened, the potential becomes constant regardless of the pH:

$$E = E^{0'} + 0.03 \log \frac{[Ox]}{[Red]} \quad (5)$$

A various amount of potassium hydroxide was added to modulate the pH between 12 and 14 and 0.1 mol L^{-1} of potassium chloride was added to ensure a good conductivity.

Figure S4 a) shows the voltammograms obtained at different pH and in Figure S4 b), the values of $E^{0'}$ vs pH are reported. The potential decreased by approximately 36 mV per pH units, which corresponds to a two-electrons/one-proton process.

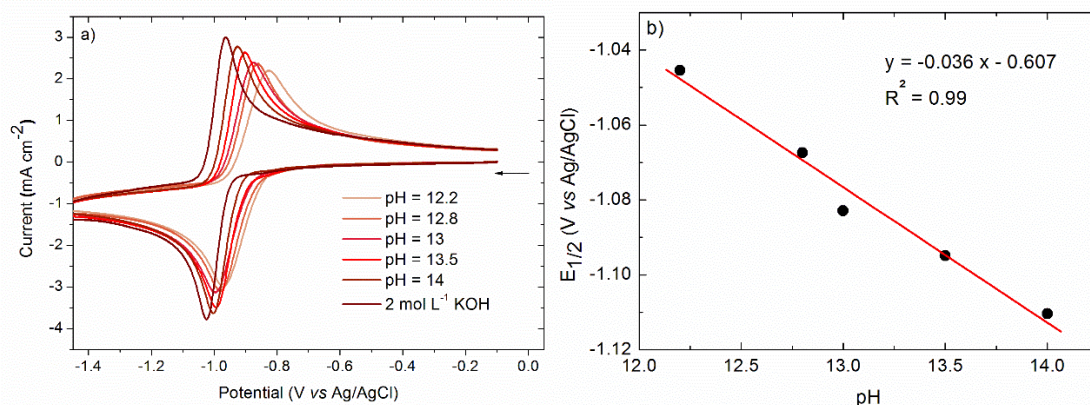
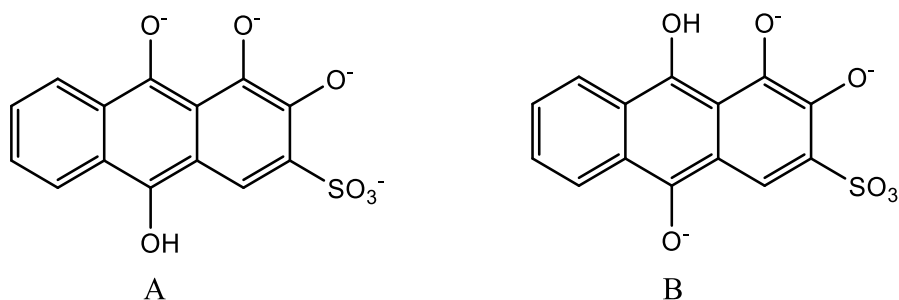


Figure S4. a) Cyclic voltammogram of 10^{-2} mol L⁻¹ **ARSNa** at different pH on a 0.071 cm² glassy carbon electrode, 100 mV s⁻¹. b) Redox potential of **ARSNa** vs pH.

The electron donating effect of the multiple deprotonated hydroxide groups -O⁻ may destabilize the negative charge of the oxygen in position 9 (Scheme S1: molecule A). Thus, molecule B is more likely to be the reduced form of ARS.



Scheme S1. Possible reduced forms of ARS

Besides, the proton may be more stable due to the oxygen in γ -position. This hypothesis seems to be confirmed by energy calculation in HF/ 6-31++G** level. The energy of molecule A was calculated at -1457.042 Ha and the energy of molecule B was calculated at -1457.051 Ha, showing that molecule B is more stable.

Determination of the diffusion coefficient and the electron transfer rate constant k_s

The Levich equation was used to calculate the diffusion coefficient D at a rotating disk electrode considering that the current is proportional to the square root of rotation speed (Figure S6a).

$$i = 0.62 n F A D^{2/3} \omega^{1/2} \nu^{-1/6} C$$

with i the current (A), n the number of electrons transferred ($n=2$), F the Faraday constant (96485 C mol⁻¹), A the electrode area (0.07 cm²), D the diffusion coefficient (cm² s⁻¹), ω the

rotation speed (radian s^{-1}), ν the kinematic viscosity of the solution ($8.85 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$) and C the concentration of the electroactive species ($5 \times 10^{-6} \text{ mol cm}^{-3}$).

The Koutecky-Levich plot for several overpotentials is drawn in Figure S6b. The kinetic current i_k was obtained from the inverse of the intercepts of the fitted lines. The Tafel plot of the kinetic current vs. potential is given in Figure S6c, giving rise to the calculation of the electron transfer rate constant k_s .

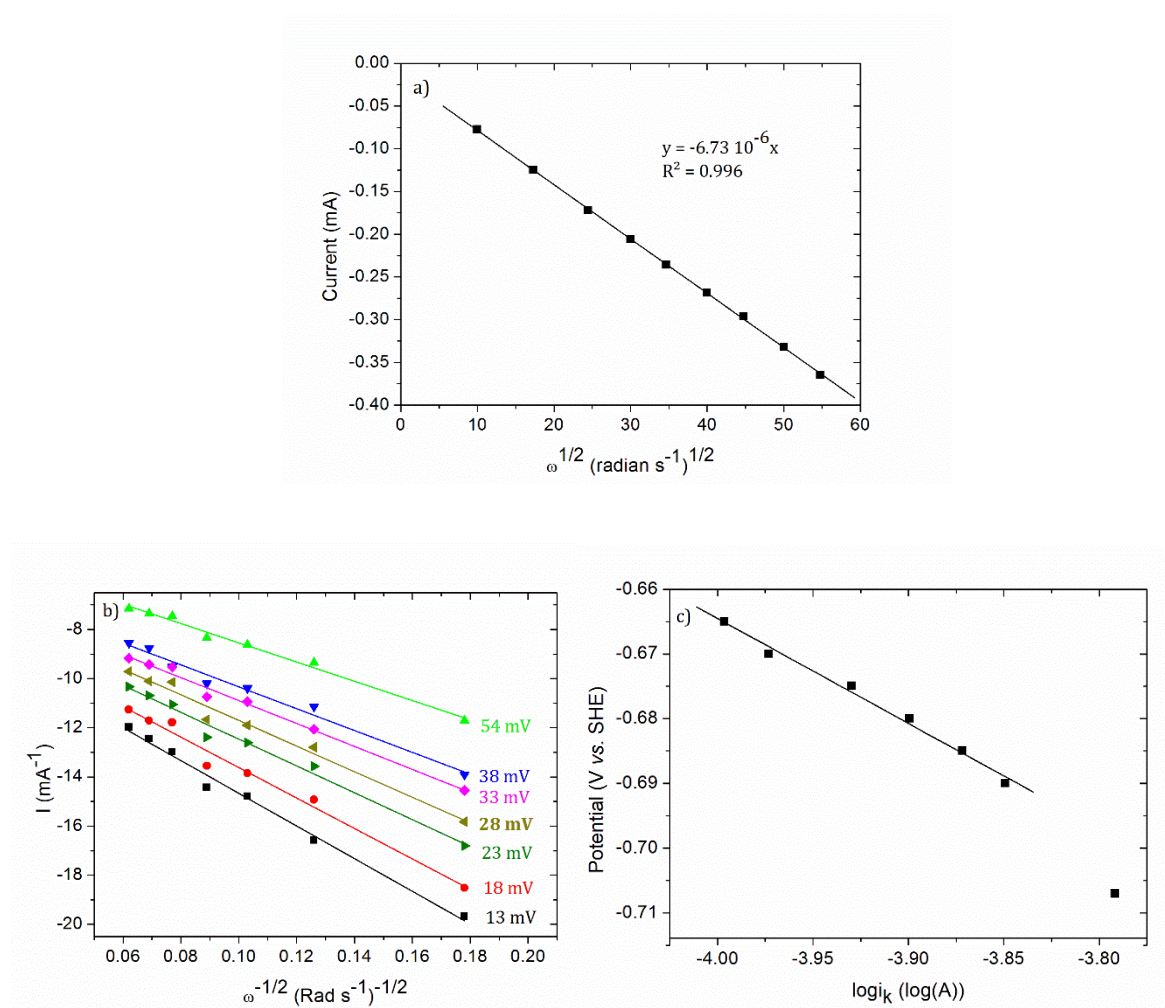


Figure S5. a) Levich b) Koutecky-Levich and c) Tafel plots from I-E analysis of **ARSNa** ($5 \times 10^{-3} \text{ mol L}^{-1}$) in $0.1 \text{ mol L}^{-1} \text{ KOH}$ on a gold rotating disk electrode (0.07 cm^2) at a scan rate of 20 mV s^{-1} .

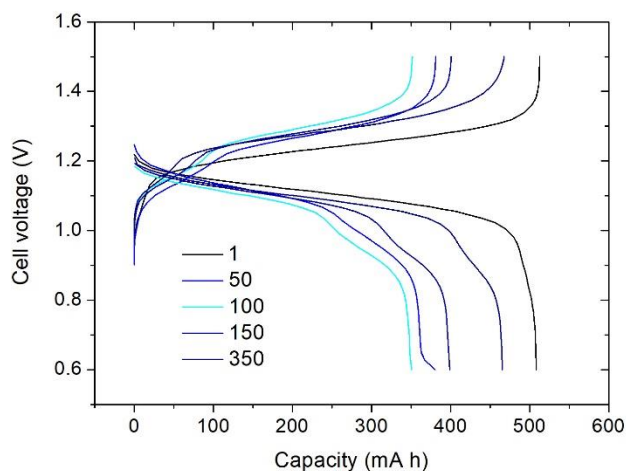


Figure S6. Charge-discharge curves according to the cycle numbers for 0.5 mol L^{-1} $\text{K}_4[\text{Fe}(\text{CN})_6]$ in 0.2 mol L^{-1} NaOH posolyte (100 mL) and 0.2 mol L^{-1} commercial **ARSNa** in 1.2 mol L^{-1} KOH negolyte (100 mL) (40 mA cm^{-2} ; cut-off voltage 1.5 V)

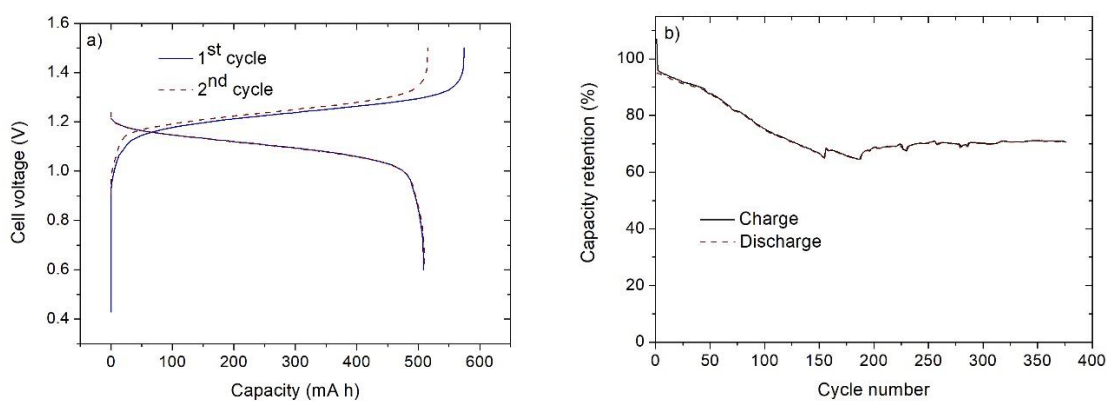


Figure S7. a) Charge-discharge curves of the two first cycles and b) evolution of the capacity with time for 0.5 mol L^{-1} $\text{K}_4[\text{Fe}(\text{CN})_6]$ in 0.2 mol L^{-1} NaOH posolyte (50 mL) and 0.2 mol L^{-1} synthesized **ARSNa*** in 1.2 mol L^{-1} KOH negolyte (50 mL) (40 mA cm^{-2} ; cut-off voltage 1.5 V)

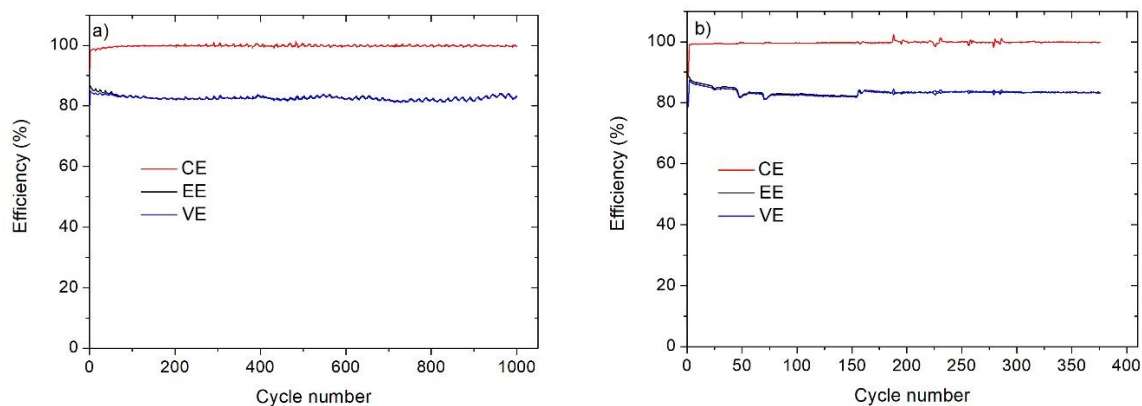


Figure S8. a) Coulombic efficiency (CE), voltage efficiency (VE) and round-trip energy efficiency (EE) vs number of cycles for RFB with a) $0.5 \text{ mol L}^{-1} \text{ K}_4[\text{Fe}(\text{CN})_6]$ in $0.2 \text{ mol L}^{-1} \text{ NaOH}$ posolyte and 0.2 mol L^{-1} a) commercial **ARSNa** and b) synthesized **ARSNa*** in $1.2 \text{ mol L}^{-1} \text{ KOH}$ negolyte.

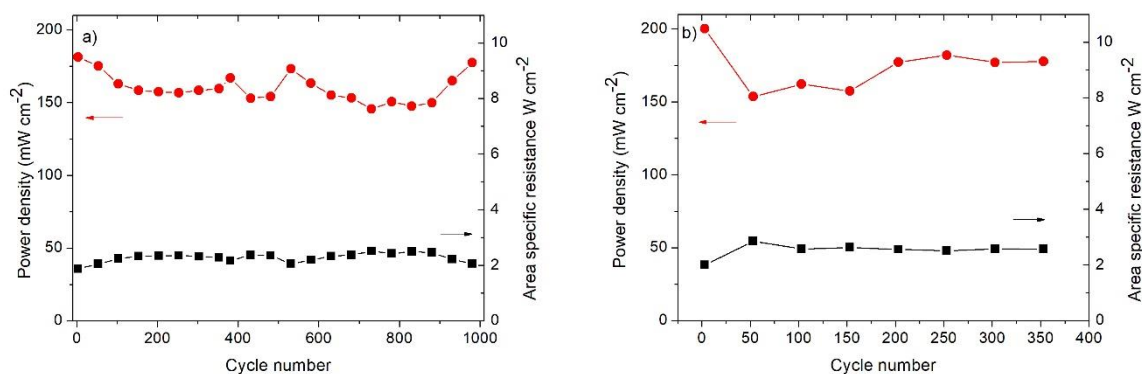


Figure S9. a) Maximum power density obtained by polarization curves performed at a 50% state of charge (SOC) and cell resistance vs number of cycles for RFB with a) $0.5 \text{ mol L}^{-1} \text{ K}_4[\text{Fe}(\text{CN})_6]$ in $0.2 \text{ mol L}^{-1} \text{ NaOH}$ posolyte and 0.2 mol L^{-1} a) commercial **ARSNa** and b) synthesized **ARSNa*** in $1.2 \text{ mol L}^{-1} \text{ KOH}$ negolyte.

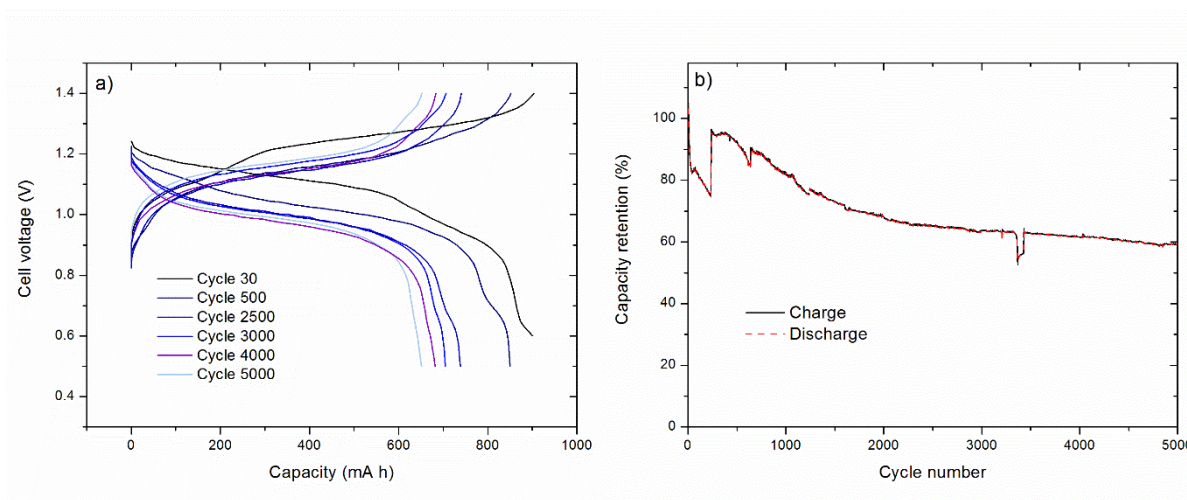


Figure S10. a) Charge-discharge curves and b) Evolution of the capacity with time according to the cycle numbers for $0.5 \text{ mol L}^{-1} \text{ K}_4[\text{Fe}(\text{CN})_6]$ in $0.2 \text{ mol L}^{-1} \text{ NaOH}$ posolyte and 0.2 mol L^{-1} commercial **ARSNa** in $1.2 \text{ mol L}^{-1} \text{ KOH}$ negolyte (40 mA cm^{-2} ; cut-off voltage 1.4 V)

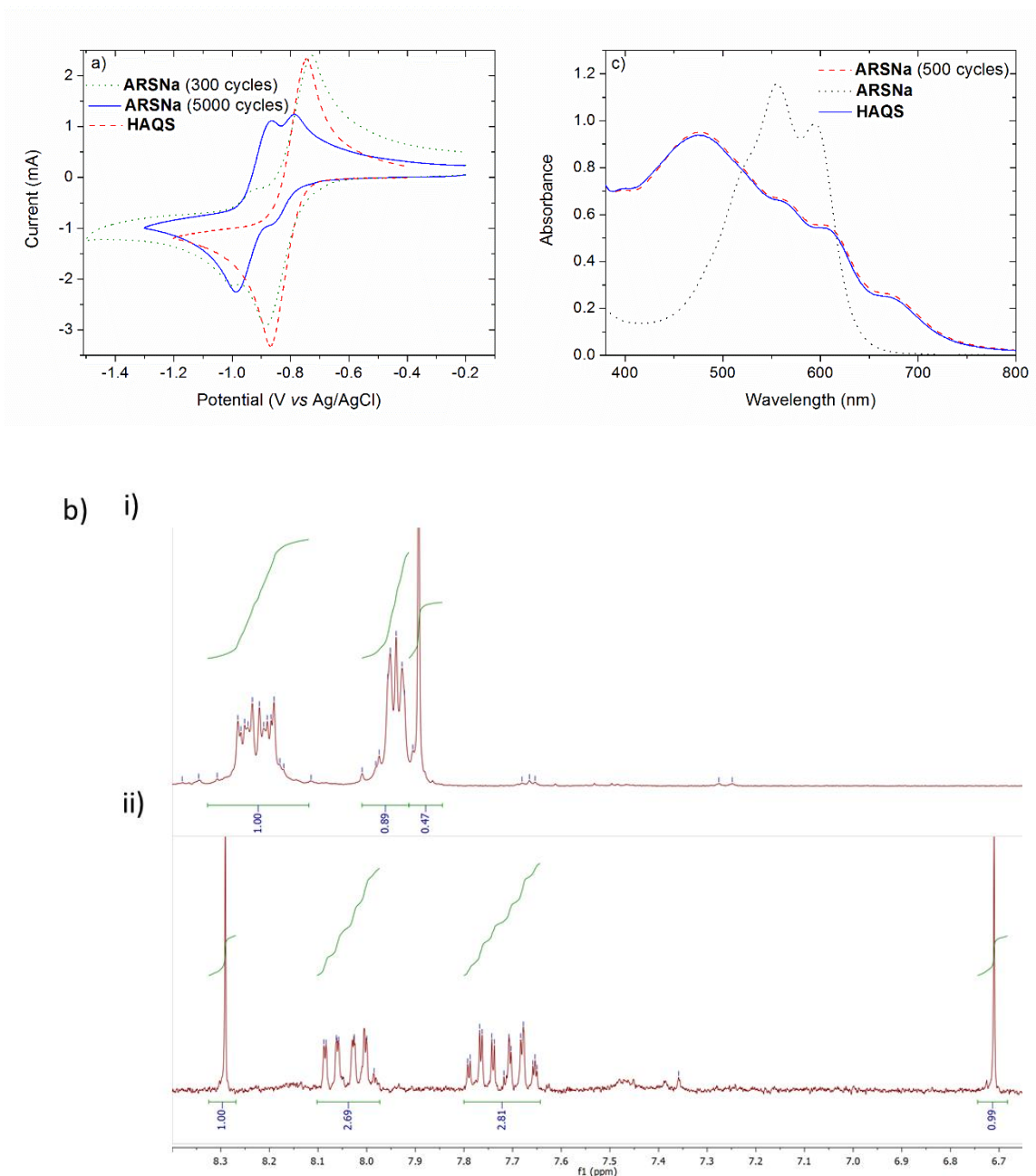
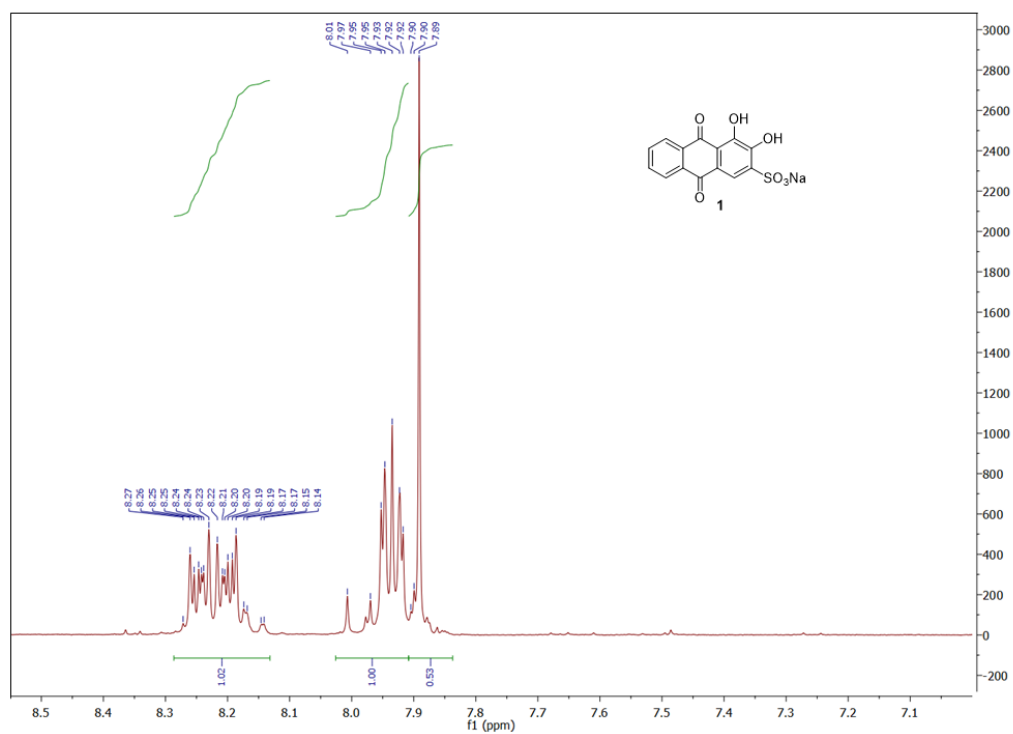
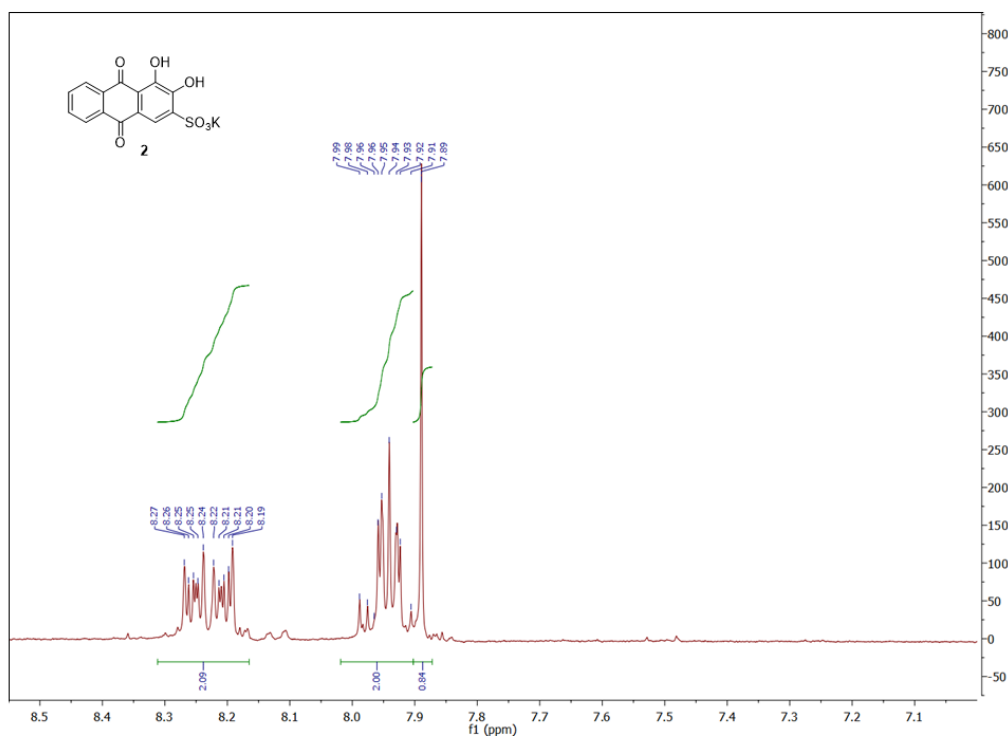


Figure S11. a) Cyclic voltammogram of **HAQS** (0.2 mol L^{-1}) and **ARSNa** after RFB operation ($0.5 \text{ mol L}^{-1} \text{ K}_4[\text{Fe}(\text{CN})_6]$ in $0.2 \text{ mol L}^{-1} \text{ NaOH}$ posolyte and $0.2 \text{ mol L}^{-1} \text{ ARSNa}$ in $1.2 \text{ mol L}^{-1} \text{ KOH}$ negolyte). Scan rate 100 mV s^{-1} b) $^1\text{H-NMR}$ in $\text{DMSO-}d_6$ data of ARS i) before and ii) after RFB cycling c) Comparison of UV-vis spectra between **ARSNa** before and after 500 cycles in RFB and **HAQS**.

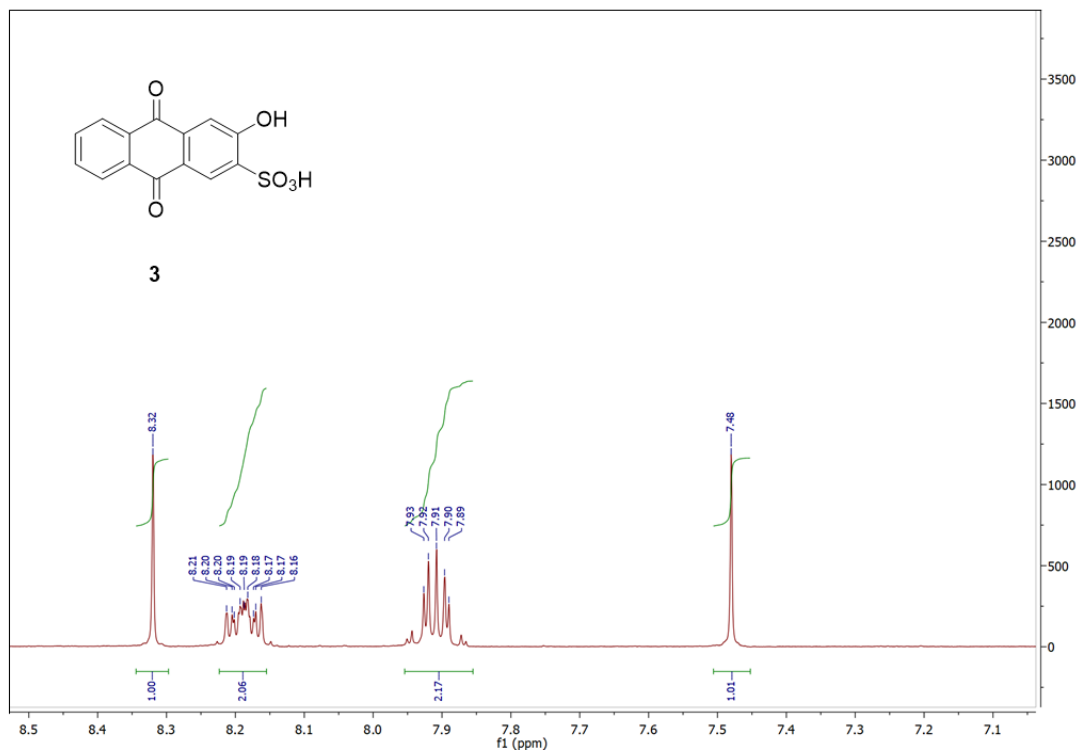
^1H NMR of synthesized **ARsNa** in $\text{DMSO-}d_6$



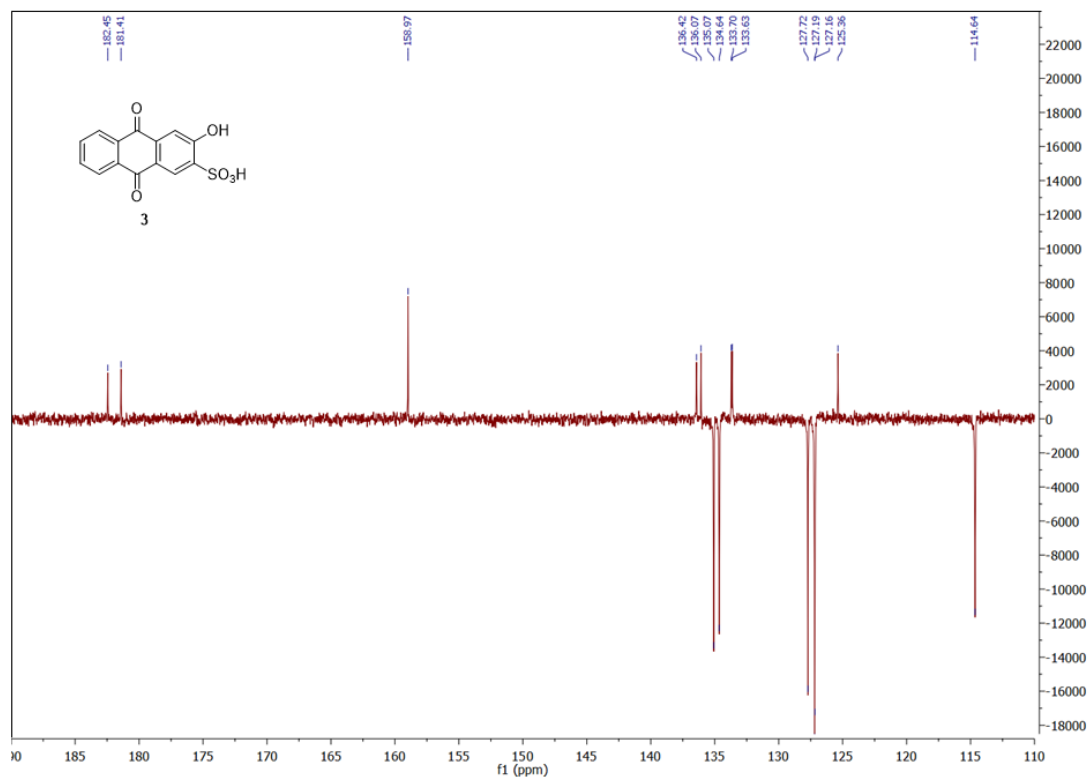
^1H NMR of synthesized **ARsK** in $\text{DMSO-}d_6$



^1H NMR of **HAQS** in $\text{DMSO-}d_6$



^{13}C NMR of **HAQS** in $\text{DMSO-}d_6$



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