Supporting Information

Efficient Electrochemical Synthesis of Robust, Densely Functionalized Water Soluble Quinones

James B. Gerken, Alexios Stamoulis, Sung-Eun Suh, Nicholas D. Fischer, Yeon J. Kim, Ilia A. Guzei,
Shannon S. Stahl*

Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue
Madison, WI, 53706, United States

stahl@chem.wisc.edu

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1. General Experimental Considerations

All commercially available compounds and solvents were purchased from Sigma-Aldrich or TCI and used as received, unless otherwise noted. 50 nm OD multi-walled carbon nanotubes (MWCNTs) were purchased from cheaptubes.com. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 MHz or Bruker Avance III 400, 500, or 600 MHz spectrometers. Unless otherwise noted, ^{13}C NMR spectra are proton-decoupled. Multiplicities are described by using the following abbreviations: d = doublet, dd = doublet of doublets, m = multiplet, q = quartet, s = singlet, t = triplet. Spectral simulation was performed using the "daisy" package in Bruker TopSpin 3.2. High-resolution mass spectra were obtained using a Thermo Q Exactive$^{\mathrm{TM}}$ Plus via (ASAP-MS) by the mass spectrometry facility at the University of Wisconsin. Cyclic voltammetry (CV) experiments were performed as described previously using an Ag/AgCl reference electrode that was referenced to NHE by measuring the potential of ferroin oxidation.[1] Elemental analyses were performed by Robertson Microlit Laboratories.

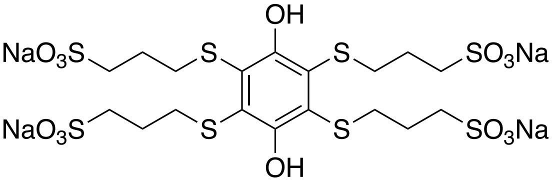
Various configurations of glassware and electrodes were used for the electrosynthetic reaction depending on the reaction scale. The reaction appeared to be robust in the face of these variations.[2] As a typical example, on a 10 g scale, the reaction was performed in a 100 ml beaker open to the air or loosely covered to limit evaporation of the solution. The RVC electrode material, which is typically available as sheets or blocks, was carved to fit in the beaker while allowing room for the counter-electrode. The typical dimensions were 8x3x0.5 cm. Various porosities of RVC were employed (incl. 10, 30 and 60 pores per inch) according to what was readily at hand, with no apparent effect on yield. A wire can be twisted into the RVC to connect it to the circuit, although a better connection is possible with the use of conductive epoxy. For the 10 g-scale reaction, the counter-electrode was made from ca. 1 m of 20 gauge nickel wire. This wire was wrapped around the plunger of a plastic 10 ml syringe barrel in a spiral to allow solution contact with as much of the wire as possible. A piece of plastic mesh was placed in the beaker to ensure that the two electrodes do not make contact. Thus prepared, the electrochemical cell was ready to use in the procedures described below. At different scales, the beaker size and electrode sizes should be changed accordingly.

Some limitations to the method have been observed. These reflect the high nucleophilicity of the thiol. Specifically, the C-H thioetherification of quinones produced from C-sulfonated or trifluoroacetylated hydroquinones and even dicyanohydroquinone is accompanied by displacement of these substituents to give low yields of **1**. However, exhaustive screening of reaction conditions has not been performed to see if this side reaction can be prevented.

SAFETY NOTE: Benzoquinone and many related quinones are allergic sensitizers and must be handled so as to minimize exposure.[3,4] Due to the lack of Michael-addition reactivity and negligible vapor pressure of the sulfonate salts of fully-substituted compounds, they can be expected to be less hazardous, but the authors have not performed any toxicity testing.

2. Synthetic Procedures and Product Characterization Data

2,3,5,6-tetrakis(propylsulfanyl-3'-sulfonate)-1,4-hydroquinone tetrasodium salt (1).



1

This electrochemical synthesis is much better than the route reported previously.[1]

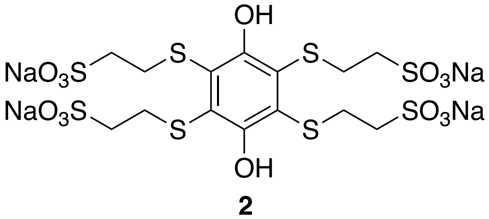
In a 1 L beaker, hydroquinone (13.844 g, 126 mmol) was wetted with 61 mL of ethanol followed by 440 mL of water. To this mixture, sodium 3-mercaptopropylsulfonate (MPSNa, 90 % technical grade, 99.62 g, 503 mmol) was added and stirred until both solids had dissolved. Aqueous sulfuric acid (1 M, 5 mL) was added, followed by a pair of reticulated vitreous carbon (RVC) anodes and a nickel wire cathode. A current of 310 mA was passed without stirring until the solution attained a persistent brown tint when the current was interrupted (94,860 C).

The electrodes were withdrawn and rinsed with 10 mL of water each into the reaction beaker and the reaction mixture was divided into two portions for isolation of the product. Each reaction mixture portion was transferred to a 3 L plastic beaker and diluted with four 300 mL portions of ethanol and two 250 mL portions of ethanol, with the first two 300 mL portions added slowly with agitation until precipitation commenced. Subsequent portions of ethanol were added with vigorous agitation of the porridge-like mass until it was thinned to a creamy suspension. This was allowed to stand for 1/2 hour and was then filtered and rinsed with two 100 mL portions of ethanol. The combined solids from both reaction mixture portions were dried overnight in a vacuum oven at 40 °C to give 97.68 g (120 mmol, 95 % yield) of **1**, as a buff-colored, granular solid with spectroscopic properties identical to those reported previously.[1]

A sample of material prepared in this fashion was recrystallized from water. These crystals were subjected to analysis by X-ray diffraction, and yielded a structure in accord with our expectations (see Section 4). The crystals were also submitted for elemental analysis. Calcd. for $C_{18}H_{26}Na_4O_{14}S_8\cdot1.25H_2O$: C, 25.82; H, 3.43; N, 0.00; S, 30.63. Found: C, 26.00; H, 3.25; N, <0.01; S, 30.25 %.

It is also possible to use benzoquinone as the starting reagent as described below for the electrosynthesis of **2**. When this was done on a scale of 1.630 g of benzoquinone and 10.706 g of MPSNA, 14.4 mmol of **1** was isolated (96 % yield). However, hydroquinone is generally easier to work with than benzoquinone.

2,3,5,6-tetrakis(ethylsulfanyl-2'-sulfonate)-1,4-hydroquinone tetrasodium salt (2).



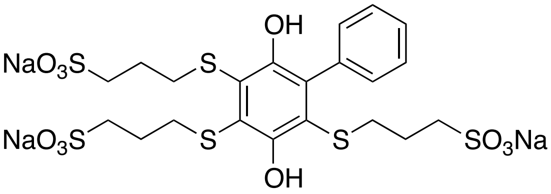
2

In this method, benzoquinone reacts with sodium 2-mercaptoethylsulfonate (MESNa) to form an adduct. This adduct is then oxidized electrochemically in the presence of further MESNa at a potential where MESNa does not oxidize readily to its disulfide. The process repeats during the electrolysis until all four thioethers are installed (Scheme 2).

A portion of benzoquinone (1.515 g, 14 mmol) was wetted with 3 mL of ethanol in a 100 mL beaker cell. To this, sodium 2-mercaptoethylsulfonate (MESNa) (9.194 g, 56 mmol) in 35 mL of water was added, being rinsed into the cell with an additional 15 mL of water. Aqueous sulfuric acid (1 M, 1 mL) was added and the mixture was stirred until the benzoquinone had dissolved. A reticulated vitreous carbon anode, a nickel wire cathode, and an Ag/AgCl reference electrode were then introduced into the cell and the mixture was electrolyzed at 0.8 V vs. NHE until the solution displayed a persistent brown color (7700 C passed). During the electrolysis, the mixture was not stirred except by the hydrogen bubbles produced at the cathode. The reaction mixture was transferred to a beaker and diluted with 300 mL of ethanol. The precipitate was allowed to flocculate overnight before being filtered. The solids were rinsed twice with ethanol and allowed to dry. In this manner, 10.482 g (13.8 mmol, 98 %) of **1a** were obtained as an off-white solid. The NMR spectral data matched with those reported in the literature.[1]

In a separate run of this method, the current was allowed to flow for a longer time. This led to oxidation of more of the product hydroquinone to the quinone. Using the same workup method as above except for allowing the precipitate to stand for two days before filtering, crystals of the pure quinone form of **2** were formed. These crystals were subjected to analysis by x-ray diffraction, and yielded a structure in accord with our expectations (see Section 5).

2-phenyl-3,5,6-tri(propylsulfanyl-3'-sulfonate)-1,4-hydroquinone trisodium salt (3).



3

In a 100 mL beaker, 2-phenylbenzoquinone (1.849 g, 10 mmol)[5] was wetted with 12 mL of acetone and suspended in 44 mL of water. To this mixture, MPSNa (90 % technical grade, 6.005 g, 30 mmol) was added, followed by aqueous sulfuric acid (1 M, 0.3 mL). The yellow quinone solids darkened and mostly dissolved as the mixture was stirred with mild heating and then left to cool overnight. At this point, a reticulated vitreous carbon (RVC) anode and a nickel wire cathode were inserted and electrolysis was commenced at a potential of 0.59 V vs. Ag/AgCl. After a total of 4358 C (3873 C theor.) was passed, the mixture was allowed to stand overnight at which time 300 mL of ethanol was added in 60 mL increments. The resulting light-colored solid was collected by filtration along with some dark material. The product was dissolved in 20 mL of water, filtered, and diluted with 250 mL of ethanol to give a granular, ecru-colored solid that was again isolated by filtration. Yield: 4.335 g, 6 mmol (61 %). This substance gave the NMR spectra shown starting on page S22.

A sample of material prepared in this fashion was recrystallized from water and submitted for elemental analysis. Calcd. for $C_{21}H_{25}Na_3O_{11}S_6 \cdot 4H_2O$: C, 32.06; H, 4.23; N, 0.00. Found: C, 32.06; H, 4.11; N, <0.10 %.

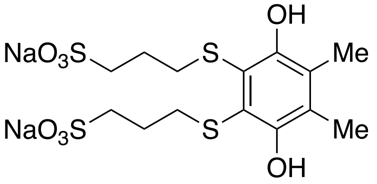
^{1}H NMR (600 MHz, D_2O, referenced to internal CH_3SO_3H at δ 2.72): δ 7.448 (dd, *J* = 7.1, 7.2 Hz, 2 H) 7.399 (t, *J* = 7.2 Hz, 1 H), 7.252 (d, *J* = 7.1 Hz, 2H), and 2.978 (m, 4H), 2.935 (m, 4H), 2.664 (m, 2H), 2.587 (m, 2H), 1.857 (m, 4H) and 1.643 (m, 2H) ppm.

^{13}C NMR (150 MHz, D_2O): δ 152.555, 148.429, 136.597, 135.661, 130.111, 128.475, 128.105, 126.440, 123.736, 121.137, 49.822, 49.770, 49.420, 34.487, 34.231, 33.215, 24.120, 24.083, 23.734 ppm.

^{1}H - ^{13}C HSQC (600 MHz, D_2O): δ 7.45:128.5, 7.40:128.1, 7.25:130.1, 2.98:49.82, 2.98:34.2, 2.94:49.77, 2.94:34.5, 2.66:33.2, 2.59:49.4, 1.86:24.1, 1.86:24.1, 1.64:23.7 ppm.

^{1}H - ^{13}C HMBC (600 MHz, D_2O): δ 7.45:128.5, 7.45:136.6, 7.40:130.1, 7.25:128.1, 7.25:130.1, 7.25:135.7, 2.98:24.1, 2.98:34.2, 2.98:49.82, 2.98:123.7, 2.94:24.1, 2.94:34.5, 2.94:49.77, 2.94:126.4, 2.66:23.7, 2.66:49.4, 2.66:121.1, 2.59:23.7, 2.59:33.2, 1.86:34.2, 1.86:34.5, 1.86:49.77, 1.86:49.82, 1.64:33.2, 1.64:49.4 ppm. The correlations between the protons at 2.98, 2.94, and 2.66 ppm and the carbons at 123.7, 126.4, and 121.1 ppm, respectively, establish that three thioether bonds have been formed.

2,3-dimethyl-5,6-di(propylsulfanyl-3'-sulfonate)-1,4-hydroquinone disodium salt (4).



4

In a 200 mL beaker, 2,3-dimethyl hydroquinone (1.383 g, 10 mmol) was wetted with 35 mL water. To this mixture, MPSNa (90 % technical grade, 3.988 g, 20 mmol) was added, followed by 70 mL of ethanol and aqueous sulfuric acid (1 M, 1 mL). The solution was stirred until everything had dissolved. After adding an RVC anode and Ni wire cathode, the solution underwent electrolysis at 15 mA for 72 hours (3901 C passed, 3863 C theor.). After electrolysis, 650 mL ethanol was added and then the solution was left to sit for 2 hours. The solution was filtered to obtain a 2.751 g crop of product, which gave the NMR spectra shown starting on page S24. The filtrate was then rotovapped down to ~25 mL, and a 200 mL portion of ethanol was added. The solution was left to sit for 25 min, and was then filtered again, resulting in a 1.419 g crop of product. Overall, this resulted in a total yield of 4.1700 g (8.5 mmol, 85 %) as a pale-pink solid.

A sample of material prepared in this fashion was recrystallized from water. During crystallization, there was a color change consistent with aerobic oxidation to the quinone. These quinone crystals were submitted for elemental analysis. Calcd. for $C_{14}H_{18}Na_2O_8S_4 \cdot 0.5H_2O$: C, 33.80; H, 3.85; N, 0.00. Found: C, 33.61; H, 3.62; N, <0.10 %.

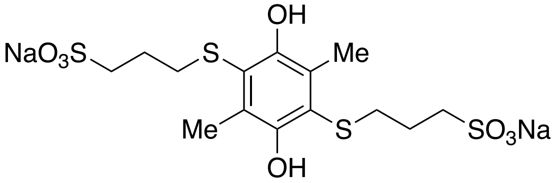
^{1}H NMR (500 MHz, D_2O, referenced to internal CH_3SO_3H at δ 2.72): δ 2.120 (s, 3 H), and 2.912 (m, 2H), 1.791 (m, 2H) and 2.823 (m, 2H) ppm in a well-resolved AA'MM'XX' coupling (J_{AM}=$J_{A'M'}$=9.7, $J_{AM'}$=$J_{A'M}$=6.0, J_{MX}=$J_{M'X'}$=6.0, $J_{MX'}$=$J_{M'X}$=8.5, $J_{AA'}$=-12.8, $J_{MM'}$=-13.0, $J_{XX'}$=-16.7 Hz).

^{13}C NMR (126 MHz, D_2O): δ 149.402, 126.982, 120.423, 49.809, 34.620, 24.019, 12.505 ppm.

^{1}H - ^{13}C HSQC (500 MHz, D_2O): δ 2.91:50, 2.82:35, 2.12:13, 1.79:24 ppm.

^{1}H - ^{13}C HMBC (500 MHz, D_2O): δ 2.91:24, 2.91:35, 2.82:24, 2.82:50, 2.82:120, 2.12:120, 2.12:127, 2.12:149, 1.79:35, 1.79:50 ppm. The correlation between the proton at 2.82 ppm and the carbon at 120 ppm establishes that the thioether has been formed.

2,5-dimethyl-3,6-di(propylsulfanyl-3'-sulfonate)-1,4-hydroquinone disodium salt (5).



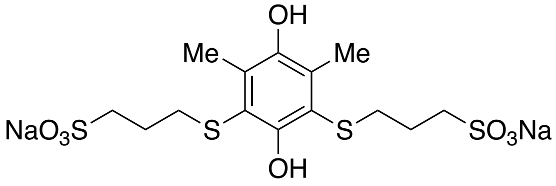
5

A portion of 2,5-dimethylbenzoquinone (1.363 g, 10 mmol) was wetted with 5 mL of ethanol followed by 35 mL of water. To this mixture, MPSNa (90 % technical grade, 3.991 g, 20 mmol) was added, followed by aqueous sulfuric acid (1 M, 0.5 mL). While stirring, 3 mL of acetone and 15 mL of ethanol were added to facilitate dissolution. A reticulated vitreous carbon (RVC) anode and a nickel wire cathode were placed in the beaker and 23 mA was passed for 23.5 hours with intermittent stirring. After electrolysis, 4 times the solution volume of ethanol was added and the suspension was allowed to sit for 30 minutes. On filtration and rinsing the solids with ethanol, further solids formed in the filtrate. Thus, the filtration and rinsing was repeated two more times until the solution volume became unwieldy. The filtrate was then rotovapped to *ca.* 50 mL volume and 200 mL of ethanol was added to produce a fourth crop of champagne-colored solid. After drying, the total yield of all four crops was 4.891 g (10 mmol, 99.7 %) and gave the NMR spectra shown starting on page S26.

A sample of material prepared in this fashion was recrystallized from water and submitted for elemental analysis. Calcd. for $C_{14}H_{20}Na_2O_{18}S_4 \cdot 0.5H_2O$: C, 33.66; H, 4.24; N, 0.00; S, 25.68. Found: C, 34.05; H, 3.92; N, <0.1; S, 25.18 %.

^{1}H NMR (600 MHz, D_2O, referenced to internal CH_3SO_3H at δ 2.72): δ 2.348 (s, 3 H), and 2.745 (m, 2H), 2.890 (m, 2H) and 1.816 (m, 2H) ppm in a well-resolved A$_2$MM'XX' coupling (J_{AX}=$J_{AX'}$=7.2, J_{MX}=$J_{M'X'}$=5.9, $J_{MX'}$=$J_{M'X}$=9.3, $J_{MM'}$=-14.0, $J_{XX'}$=-14.1 Hz).
^{13}C NMR (100 MHz, D_2O): δ 149.617, 126.282, 121.333, 49.679, 33.479, 24.293, 14.526 ppm.
^{1}H - ^{13}C HSQC (400 MHz, D_2O): δ 2.89:50, 2.75:33, 2.35:15, 1.82:24 ppm.
^{1}H - ^{13}C HMBC (400 MHz, D_2O): δ 2.89:24, 2.89:33, 2.75:24, 2.75:50, 2.75:121, 2.35:121, 2.35:126, 2.35:150, 1.82:33, 1.82:50 ppm. The correlation between the proton at 2.75 ppm and the carbon at 121 ppm establishes that the thioether has been formed.

2,6-dimethyl-3,5-bis(propylsulfanyl-3'-sulfonate)-1,4-hydroquinone disodium salt (6).



6

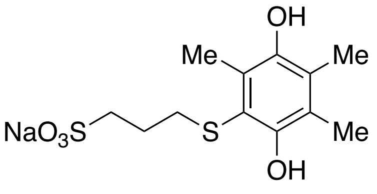
In a 100 mL beaker, 2,6-dimethyl-1,4-benzoquinone (1.362 g, 10 mmol, 1 equiv.) was mixed with 20 mL acetone, 35 mL water and aqueous sulfuric acid (1 M, 2 mL). Upon vigorous stirring, most of the starting material dissolved. To this, MPSNa (90 % technical grade, 3.960 g, 20 mmol) was added in one portion, upon which the solution turned from pale yellow to dark red/brown. A reticulated vitreous carbon (RVC) anode and a nickel wire cathode were inserted into the solution, and the current was set to 20 mA. After allowing the reaction to run for 20 h, another aliquot of MPSNa (90 % technical grade, 1.74 g 10 mmol) was added to the reaction mixture, and the reaction was allowed to run for another 8 h. By this time, NMR analysis of the crude reaction mixture showed a 97% conversion of starting material to product, with only 3% mono-adduct remaining in solution.

The electrodes were withdrawn from the solution and rinsed with 5 mL of water into the reaction beaker. This was then transferred to a 1 L Erlenmeyer flask and diluted with 250 mL of EtOH, stirred briefly and allowed to stand for 30 minutes. The product precipitated out of solution and was dried overnight in a vacuum oven at 40 °C to give 4.113 g (8.4 mmol, 84 % yield) of the desired product as a garnet-colored odorless solid that gave the NMR spectra shown starting on page S28.

A sample of material prepared in this fashion was submitted for elemental analysis. Calcd. for $C_{14}H_{20}Na_2O_8S_4 \cdot 2H_2O$: C, 31.93; H, 4.59; N, 0.00. Found: C, 32.19; H, 4.47; N, <0.1 %. On drying, the anhydrous material gave the following elemental analysis. Calcd. for $C_{14}H_{20}Na_2O_8S_4$: C, 34.28; H, 4.11; N, 0.00. Found: C, 34.54; H, 4.08; N, <0.1 %.

^{1}H NMR (300 MHz, D_2O) δ 2.95-2.98 (m, 4H), 2.80 (t, J_{HH} = 7.04 Hz, 4H), 2.39 (s, 6H), 1.81-1.88 (m, 4H).
^{13}C NMR (125 MHz, D_2O) δ 152.9, 145.2, 133.0, 116.0, 49.7, 33.3, 24.2, 14.7.

2,3,5-trimethyl-6-(propylsulfanyl-3'-sulfonate)-1,4-hydroquinone sodium salt (7).



7

Trimethylhydroquinone (1.571 g, 10 mmol) was wetted with ethanol (9 mL) and suspended in water (35 mL) at room temperature. To this mixture, MPSNa (90 % technical grade, 1.7363 g, 8.8 mmol) was added, followed by aqueous sulfuric acid (1 M, 0.5 mL). The solution underwent electrolysis at 40 mA for 14 hours. After electrolysis, the solution was treated with sodium bisulfite until it was no longer red, and then 400 mL acetone was added, and the solution was filtered. The solid (acetone bisulfite adduct) was removed and the filtrate was rotovapped and 30 mL acetone were added. The solution was then rotovapped again, and 60 mL acetone was added. The solution was then filtered, and rotovapped again, and then 90 mL acetone was added, and the solution was filtered. The filtrate was then filtered two times more. The final four filter crops resulted in a combined yield of 2.650 g (8.1 mmol, 91.7%) of a pale orange solid that gave the NMR spectra shown starting on page S30.

A sample of material prepared in this fashion was recrystallized from water. During crystallization, there was a color change consistent with aerobic oxidation to the quinone. These quinone crystals were submitted for elemental analysis. Calcd. for $C_{12}H_{15}NaO_5S_2\cdot3.5H_2O$: C, 37.01; H, 5.69; N, 0.00. Found: C, 36.84; H, 5.62; N, <0.10 %. On drying, the material gave the following elemental analysis. Calcd. for $C_{12}H_{15}NaO_5S_2\cdot H_2O$: C, 41.85; H, 4.98; N, 0.00. Found: C, 41.73; H, 5.02; N, <0.1 %.

^{1}H NMR (600 MHz, D_2O, referenced to internal CH_3SO_3H at δ 2.72): δ 2.309 (s, 3 H), 2.065 (s, 3 H), 2.047 (s, 3 H), and 2.656 (m, 2H), 2.862 (m, 2H) and 1.781 (m, 2H) ppm in a well-resolved $A_2MM'XX'$ coupling ($J_{AX}=J_{AX'}=7.2$, $J_{MX}=J_{M'X'}=5.7$, $J_{MX'}=J_{M'X}=9.5$, $J_{MM'}=-14.0$, $J_{XX'}=-13.4$ Hz).

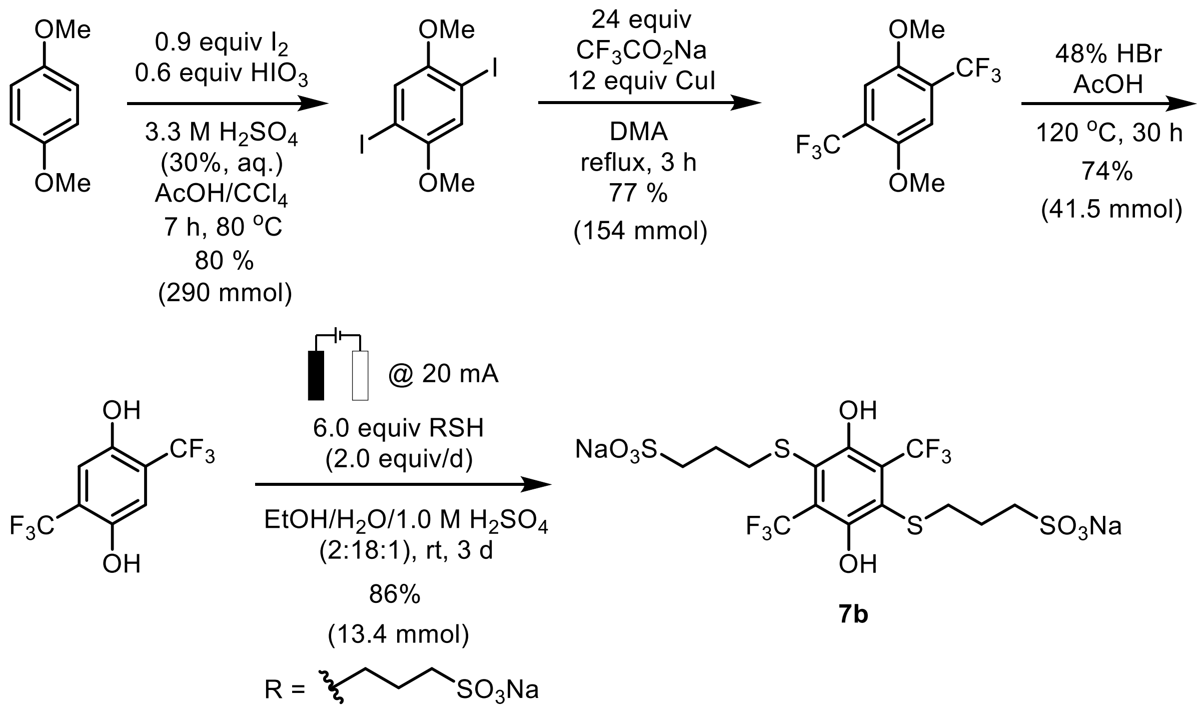
^{13}C NMR (125 MHz, D_2O): δ 148.980, 144.824, 128.334, 127.900, 120.958, 115.660, 49.732, 33.688, 24.234, 14.338, 12.171, 12.106 ppm.

^{1}H - ^{13}C HSQC (500 MHz, D_2O): δ 2.86:50, 2.66:34, 2.31:14, 2.07:12.2, 2.05:12.1, 1.78:24 ppm.

^{1}H - ^{13}C HMBC (500 MHz, D_2O): δ 2.86:24, 2.86:34, 2.66:24, 2.66:50, 2.66:116, 2.31:116, 2.31:121, 2.31:127.9, 2.31:145, 2.31:149, 2.07:116, 2.07:121, 2.07:128, 2.07:145, 2.07:149, 2.05:116, 2.05:121, 2.05:128, 2.05:145, 2.05:149, 1.78:34, 1.78:50 ppm. The correlation between the proton at 2.66 ppm and the carbon at 116 ppm establishes that the thioether has been formed.

Sodium 3,3'-((2,5-dihydroxy-3,6-bis(trifluoromethyl)-1,4-phenylene)bis(sulfanediyl))bis(propane-1-sulfonate) (8).

Scheme S1: Synthesis route to **8**.



1,4-diiodo-2,5-dimethoxybenzene: A 1 L round-bottom flask was charged with 1,4-dimethoxybenzene (40 g, 290 mmol), iodine (66 g, 261 mmol), iodic acid (31 g, 174 mmol), 30% sulfuric acid in aqueous solution (86 mL), carbon tetrachloride (120 mL), and glacial acetic acid (400 mL). The reaction mixture was stirred vigorously at 60 °C for 7 hours. After evaporation of solvent in vacuo, the crude mixture was washed with DI water (150 mL) 20 times and further washed with ethanol (100 mL) 10 times to give 90.1 g of the product. The ^1H NMR spectrum matched the literature.[6]

Note: Reactions in 1.0 and 50 mmol scale yielded the desired product in 87 and 84% respectively.

Isolated Yield: 80%

Physical Property: White solid with an odor of old newsprint.

^1H NMR (500 MHz, $CDCl_3$) δ 7.19 (s, 2H), 3.82 (s, 6H).

1,4-dimethoxy-2,5-bis(trifluoromethyl)benzene: A 1 L three-neck flask was equipped with a nitrogen gas inlet with an inner temperature probe, a gas outlet with a reflux condenser, and an overhead glass stirrer with a polytetrafluoroethylene blade. The flask was charged with 1,4-diiodo-2,5-dimethoxybenzene (60 g, 154 mmol), CuI (117 g, 615 mmol), anhydrous dimethylacetamide (500 mL), stirred vigorously, and flushed with nitrogen gas. After 30 minutes, the reaction mixture was heated to 165 °C (inner temperature) and sodium trifluoroacetate (167 g, 1.23 mol) was added in one portion. After 3 hours, the reaction mixture was cooled to room temperature and moved to two 2 L of Erlenmeyer flasks. DI water (1.0 L) was added to each flask and the reaction mixture was filtered through a celite pad. The filtrate was diluted with ethyl acetate (1.0 L), washed with ammonium chloride in aqueous solution (800 mL) four times and brine solution (500 mL) two times in a 2 L separation funnel, and dried with magnesium sulfate. Residual product was extracted with ethyl acetate from the aqueous layer repeatedly. After evaporation of solvent, filtration of the crude mixture in methylene chloride through a thick silica pad, washed with pentane (500 mL), and dried in vacuo. To achieve a full conversion, the fully dried reaction mixture was re-subjected to the same reaction condition. The work-up process stated above was repeated to give 32.5 g of the desired product as a brown solid. The ^1H NMR spectrum matched the literature.[7]

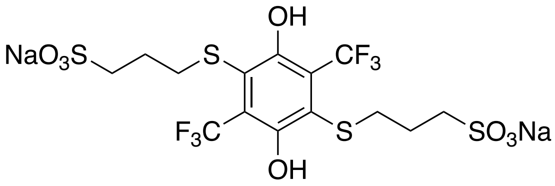
Notes: (1) After the first cycle of trifluoromethylation, 26, 51, and 154 mmol of 1,4-diiodo-2,5-dimethoxybenzene was converted into the desired product in 91, 91, and 65% respectively. (2) The reaction is temperature-dependent and inner temperature should be measured.

Isolated Yield: 77%

Physical Property: Light brown solid.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (s, 2H), 3.90 (s, 6H).

2,5-bis(trifluoromethyl)benzene-1,4-diol: A 500 mL round-bottom flask was charged with 1,4-dimethoxy-2,5-bis(trifluoromethyl)benzene (11.4g, 41.5 mmol), 48% HBr in aqueous solution (100 mL) and glacial acetic acid (100 mL). The reaction flask was equipped with a reflux condenser and the reaction mixture was stirred vigorously at 120 °C for 30 hours. During this time, the reaction was monitored by TLC using a 1:4 ethyl acetate:pentane mobile phase. The reaction mixture was neutralized with potassium bicarbonate and subsequently extracted with two 100 mL portions of diethyl ether. The combined organic layers were washed with brine, dried over magnesium sulfate and concentrated to dryness in vacuo to afford 7.6 g of product. The ^{1}H and ^{19}F NMR spectra matched with those reported in the literature.[7]
Notes: (1) Starting material sublimes at around 80 °C, so the reaction mixture should be homogeneous at the start of the reaction. (2) Heating above 120 °C will lead to significant amounts of byproduct formation, so careful temperature control is advised. (3) Glacial acetic acid is included to solubilize the starting material.
Isolated Yield: 74%
Physical Property: White solid.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (s, 2H), 5.26 (s, 2H).

Sodium 3,3'-((2,5-dihydroxy-3,6-bis(trifluoromethyl)-1,4-phenylene)bis(sulfanediyl))bis(pr-opane-1-sulfonate) (8):

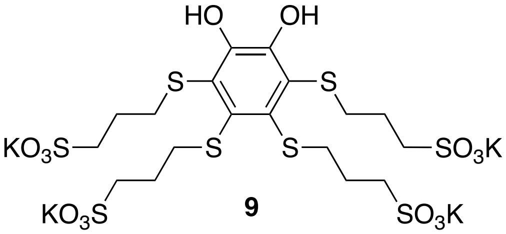


8

2,5-bis(trifluoromethyl) hydroquinone (492 mg, 2.0 mmol) was suspended in a solution of 10% ethanol in deionized water (20 mL) along with 1.0 mL of 1.0 M H_2SO_4 (aq). The first portion of MPSNa (90 % technical grade, 712 mg, 4.0 mmol) was added to the hydroquinone suspension with stirring. Once MPSNa completely dissolved, the reaction vessel was charged with a RVC working electrode and a nickel wire counter electrode. These electrodes were connected to a galvanostat and the current was set to 20 mA. Subsequent portions of MPSNa (712 mg, 4.0 mmol) were added at 24 and 48 hours after the start of the bulk electrolysis. The color of the reaction mixture turned progressively darker over the course of the electrolysis. At 72 h the NMR of the bulk electrolysis showed a >80% conversion to product by ^{19}F NMR and the electrolysis was halted. After purification on reverse-phase column with deionized H_2O, 407 mg of the product was obtained that was pure by NMR (page S33 *et seq.*).
Isolated Yield: 86%
Physical Property: Brown solid.
A sample of material prepared in this fashion was submitted for elemental analysis. Calcd. for $C_{14}H_{14}F_6Na_2O_8S_4$: C, 28.10; H, 2.36; N, 0.00. Found: C, 28.05; H, 2.13; N, <0.1 %.

^{1}H NMR (500 MHz, D_2O) δ 3.00-2.94 (m, 4H), 2.91 (t, J_{HH} = 7.3 Hz, 4H), 2.01-1.91 (m, 4H).
^{13}C NMR (125 MHz, D_2O) δ 149.58, 124.3, 123.1 (q, J_{CF} = 276.3 Hz) 122.8 (q, J_{CF} = 29.0 Hz), 49.52, 34.88, 24.19.
^{19}F NMR (338 MHz, 0.1% TFA in D_2O) δ -54.3.
HRMS (ESI) calculated for $C_{14}H_{14}F_6O_8S_4^{2-}$ $[M-2Na]^{2-}$ 275.9743, found 275.9738.

3,4,5,6-tetrakis(propylsulfanyl-3'-sulfonate)catechol (9).



9

A portion of catechol (1.104 g, 10 mmol) was placed in a 50 mL 3-neck flask with 10 mL of 0.1 M pH 7 phosphate buffer, 3 mL of 0.1 M pH 12 phosphate buffer, and 27 mL water. A portion of MPSNa (90 % technical grade, 7.634 g, 39 mmol) was added, followed by a Pt wire cathode and an RVC anode. Electrolysis was conducted at 50 mA with slow stirring for 42 h, at which time NMR of the crude reaction mixture showed consumption of the starting material. A 4 mL aliquot of the reaction mixture was diluted with 16 mL of ethanol and let stand. Crystals were formed and isolated by filtration. The remaining reaction mixture was mixed with 40 mL of ethanol and seeded with the crystals. Sequential filtration and further dilution with ethanol for three cycles gave solids that were combined and recrystallized from MeOH/H_2O to give 2.665 g of product after filtration and rinsing with 2:1 MeOH/H_2O and MeOH, which gave the NMR spectra shown starting on page S36. A second crop of crystals formed in the filtrate of the recrystallization and was isolated to give a further 0.875 g of product for a total yield of 3.540 g (4.0 mmol, 41 %) of **9** as a pigeon-gray powder.

A sample of material prepared in this fashion was recrystallized from water and submitted for elemental analysis. Calcd. for $C_{18}H_{26}K_4O_{14}S_8 \cdot 8H_2O$: C, 21.12; H, 4.14; N, 0.00; S, 25.06. Found: C, 20.93; H, 3.78; N, <0.1; S, 25.36 %. On drying, the anhydrous material gave the following elemental analysis, further confirming that the compound had been isolated with potassium from the phosphate buffer as the counterions. Calcd. for $C_{18}H_{26}K_4O_{14}S_8$: C, 24.59; H, 2.98; N, 0.00; S, 29.17. Found: C, 24.46; H, 2.82; N, <0.1; S, 29.17 %.

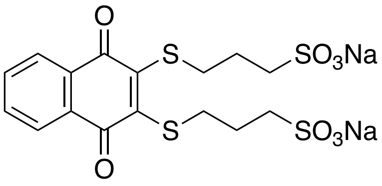
^{1}H NMR (400 MHz, D_2O, referenced to internal CH_3SO_3H at δ 2.72): δ 2.95 (m, 8H), 1.803 (m, 4H) ppm in a quagmire of accidental equivalence.

^{13}C NMR (100 MHz, D_2O): δ 147.006, 136.335, 127.166, 50.014, 49.741, 36.944, 34.587, 24.066, 23.749 ppm.

^{1}H - ^{13}C HSQC (400 MHz, D_2O): δ 2.95:50.0, 2.95:49.7, 2.95:36.9, 2.95:34.6, 1.80:24.1, 1.80:23.7 ppm.

^{1}H - ^{13}C HMBC (400 MHz, D_2O): δ 2.95:136.3, 2.95:127.2, 2.95:50.0, 2.95:49.7, 2.95:36.9, 2.95:34.6, 2.95:24.1, 2.95:23.7, 1.80:50.0, 1.80:49.7, 1.80:36.9, 1.80:34.6 ppm. The correlations between the protons at 2.95 ppm and the carbons at 136.3 and 127.2 ppm establish that two non-equivalent thioethers have been formed.

2,3-bis(propylsulfanyl-3'-sulfonate)-1,4-naphthoquinone disodium salt (10).



10

In a 100 mL beaker was added 1.582 g of naphthoquinone (10 mmol), which was subsequently complemented with 30 mL acetone, 35 mL water and 2 mL of 1 M H_2SO_4. To this was added MPSNa (90 % technical grade, 3.960 g, 20 mmol). A reticulated vitreous carbon (RVC) anode and a nickel wire cathode were inserted into the solution, along with an Ag/AgCl reference electrode and the potential was set to 450 mV. The bulk electrolysis was allowed to run for 24 h, by which point NMR analysis of the crude reaction mixture revealed a quantitative conversion to product with no remaining MPSNa.

Due to the emulsifying properties of the compound, the best purification procedure involved subjection to a reverse-phase column, which used a gradient H_2O:MeOH elution. The desired fractions were collected and the solvent removed under reduced pressure. The crude product was dried overnight in a vacuum oven at 40 °C to give 4.5 g (95 % yield) of **10** as an odorless red/purple solid that gave the NMR spectra shown starting on page S38.

A sample of material prepared in this fashion was submitted for elemental analysis. Calcd. for $C_{16}H_{16}Na_2O_8S_4$: C, 37.64; H, 3.16; N, 0.00. Found: C, 37.37; H, 2.76; N, <0.1 %.

^{1}H NMR (300 MHz, D_2O) δ 7.80 (dd, J_{HH} = 5.74, 3.35 Hz, 2H), 7.69 (dd, J_{HH} = 5.86, 3.29 Hz, 2H), 3.27 (t, J_{HH} = 7.2 Hz, 4H), 3.04 (m, 4H), 2.03 (m, 4H).

^{13}C NMR (125 MHz, D_2O) δ 179.9, 148.2, 134.3, 132.1, 126.9, 49.6, 33.3, 25.1.

3. Cyclic Voltammetry Procedures and Data and Product Solubility Data

Cyclic voltammetry experiments were performed in N_2-purged 1 M aqueous sulfuric acid. A freshly-polished glassy carbon was used, either without or with a coating of multi-wall carbon nanotubes as described previously.[1] Voltammograms of each compound (ca. 5 mM) were obtained at 10, 25, 50, 100, 200, and 400 mV/s; data at 10 mV/s are representative.

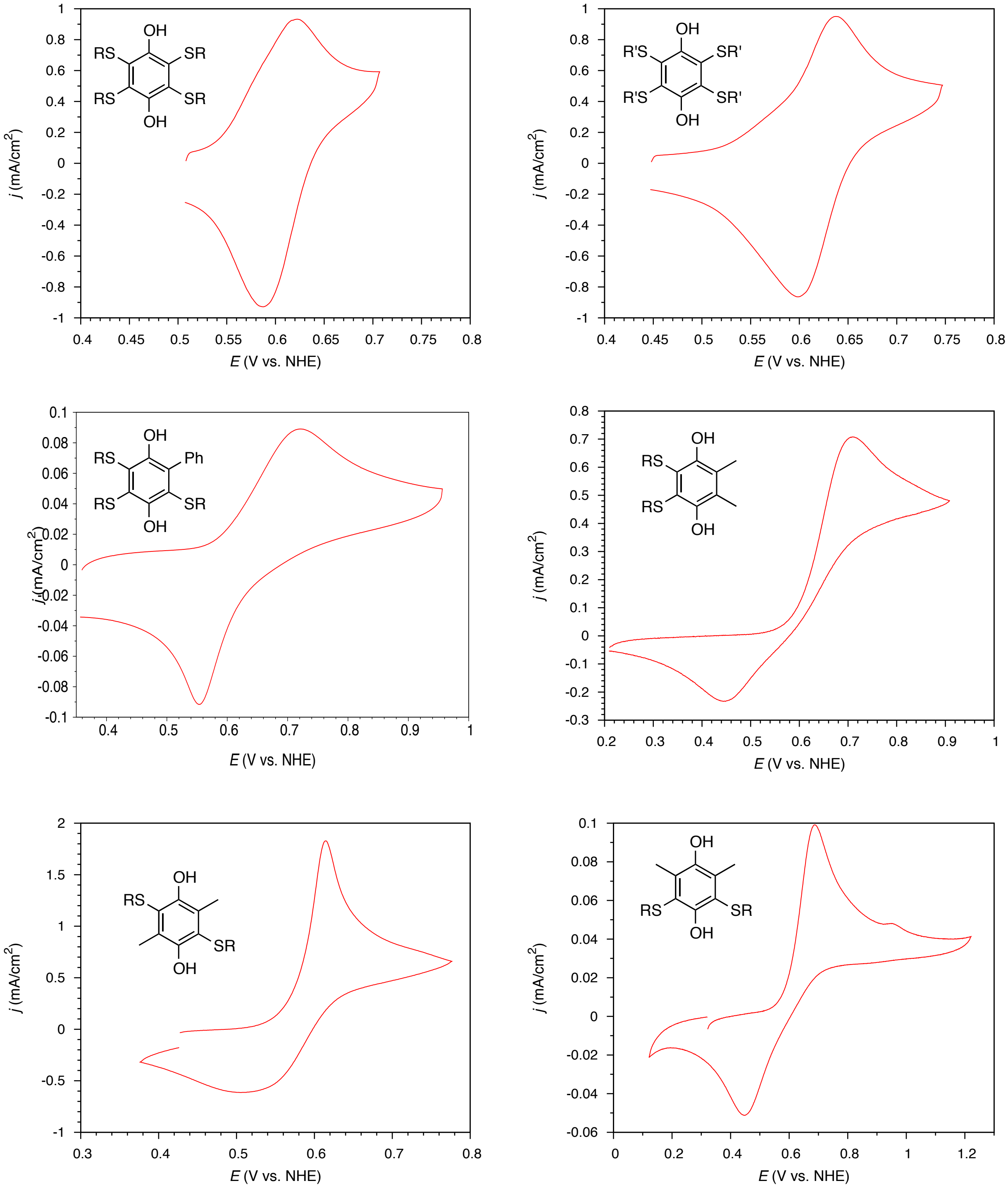


Figure S1. CV data for compounds **1** - **6**. Data were acquired at 10 mV/s.

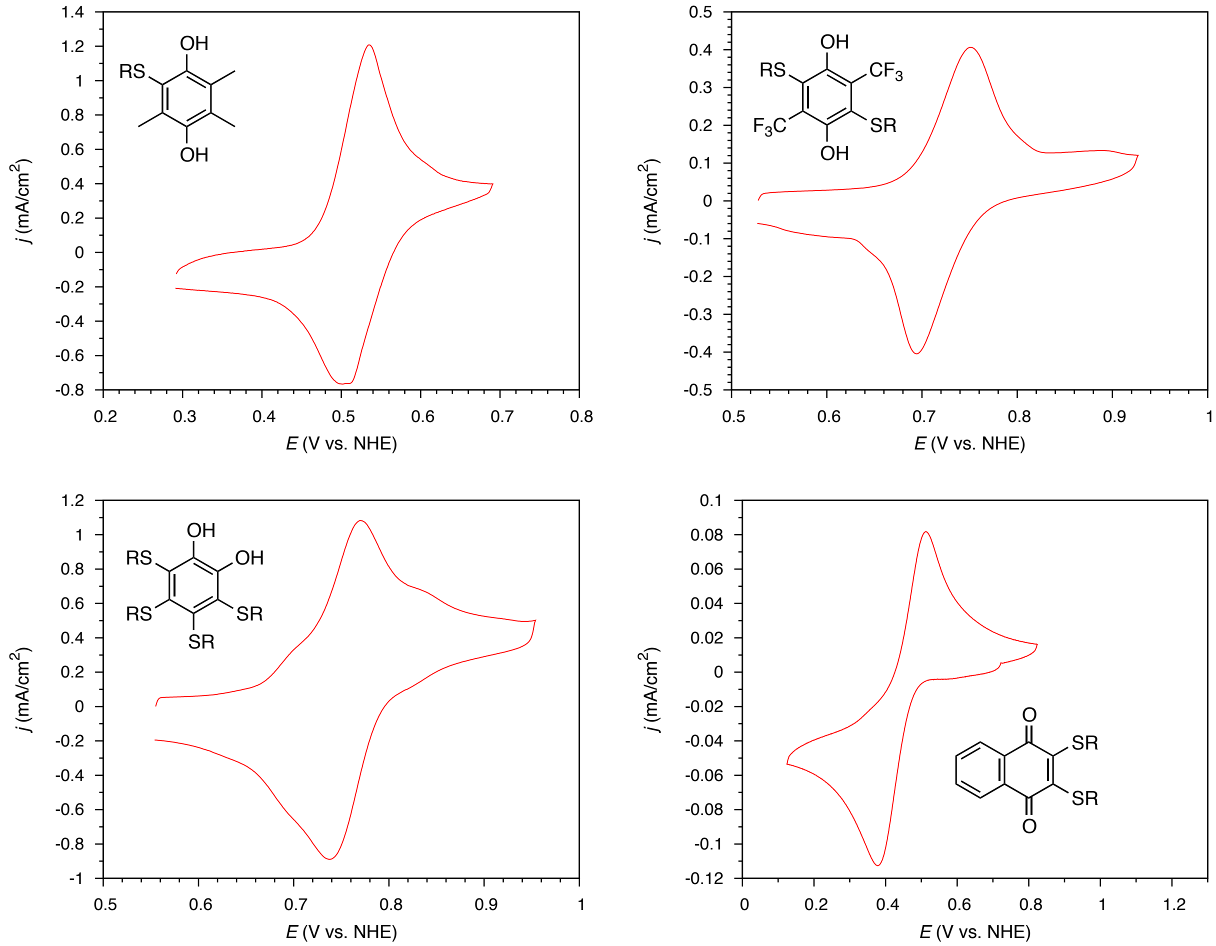


Figure S2. CV data for compounds **7 - 10**. Data were acquired at 10 mV/s.

Solubility test procedure: The compound was added to 0.6 ml of deionized water at room temperature and allowed to dissolve until undissolved solids persisted. The saturated solution was filtered through a plug of cotton and 0.3 ml of the solution was transferred to a weighed flask where ca. 3 ml of dry acetonitrile was added. This mixture was rotovapped twice, with the addition of ca. 2 ml of dry acetonitrile in between and was then subjected to drying under 50 mTorr vacuum. The flask and solids were then weighed.

Table S1: Thioether hydroquinone solubilities and reduction potentials of thioether quinones and their C-H precursors

Compound	r.t. aqueous solubility (M)	*E*° (mV vs. NHE)	Reference	Precursor *E*°	Reference
1	0.32	605	[1]	699	[8]
2	0.58	618	this work	699	[8]
3	0.97	643	this work	634	[9]
4	0.55	559	this work	553	[9]
5	0.19	634	this work	590	[8]
6	2.01	578	this work	546	[9]
7	0.94	518	this work	487	[9]
8	0.19	703	this work	804	this work
9	0.65	754	this work	831	[10]
10	0.27	439	this work	483	[11]

4. X-ray Structure of 2,3,5,6-tetrakis(propylsulfanyl-3'-sulfonate)-1,4-hydroquinone tetrasodium salt (1)

Data Collection

A colorless crystal with approximate dimensions 0.11 x 0.08 x 0.01 mm^3 was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera. The crystal evaluation and data collection were performed on a Bruker Quazar SMART APEXII diffractometer with Mo Kα (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 4.96 cm.[12]

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5º in a 6º range about ω with the exposure time of 10 seconds per frame. The reflections were successfully indexed by an automated indexing routine built in the APEX3 program suite. The final cell constants were calculated from a set of 9980 strong reflections from the actual data collection.

The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.75 Å. A total of 30138 data were harvested by collecting 4 sets of frames with 0.6º scans in ω and φ with exposure times of 45 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.[13]

Structure Solution and Refinement

The systematic absences in the diffraction data were consistent for the space groups *Cc* and *C*2/*c*. The *E*-statistics strongly suggested the centrosymmetric space group *C*2/*c* that yielded chemically reasonable and computationally stable results of refinement. [,15,16,17,18,19,20]

A successful solution by the direct methods provided all non-hydrogen atoms from the *E*-map. The aqua-ligand and hydroxyl H-atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms (except the aqua-ligand and hydroxyl H-atoms) were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

The tetraanion resides on a crystallographic inversion center, thus only one half of it is symmetry-independent. The charge of this half-molecule is balanced by two Na cations, each bearing two aqua ligands. The full coordination environment of the two Na atoms is different.

The final least-squares refinement of 271 parameters against 4670 data resulted in residuals *R* (based on F^2 for $I \geq 2\sigma$) and *wR* (based on F^2 for all data) of 0.0237 and 0.0619, respectively. The final difference Fourier map was featureless.

Summary

Crystal Data for $C_{18}H_{42}Na_4O_{22}S_8$ (M =958.95 g/mol): monoclinic, space group *C*2/*c* (no. 15), a = 35.431(11) Å, b = 5.4941(16) Å, c = 20.150(8) Å, β = 108.517(8)°, V = 3719(2) Å^3, Z = 4, T = 100.0 K, μ(MoKα) = 0.610 mm^{-1}, *Dcalc* = 1.713 g/cm^3, 30138 reflections measured ($2.424° \leq 2\Theta \leq 56.842°$), 4670 unique ($R_{int}$ = 0.0351, R_{sigma} = 0.0223) which were used in all calculations. The final R_1 was 0.0237 (I > 2σ(I)) and wR_2 was 0.0619 (all data).

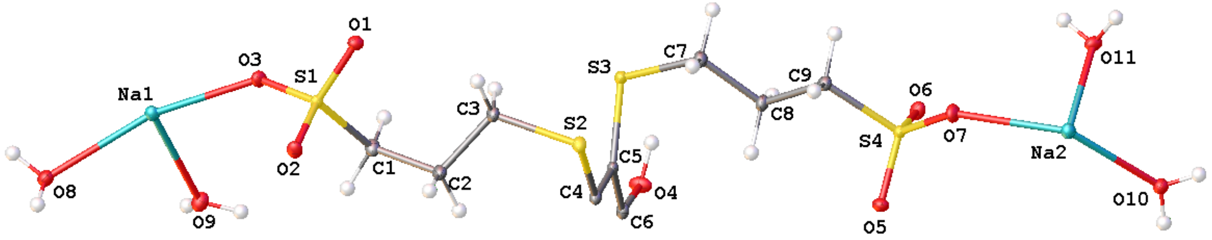


Figure S3. A molecular drawing of the symmetry-independent part (half molecule) of **1** shown with 50% probability ellipsoids.

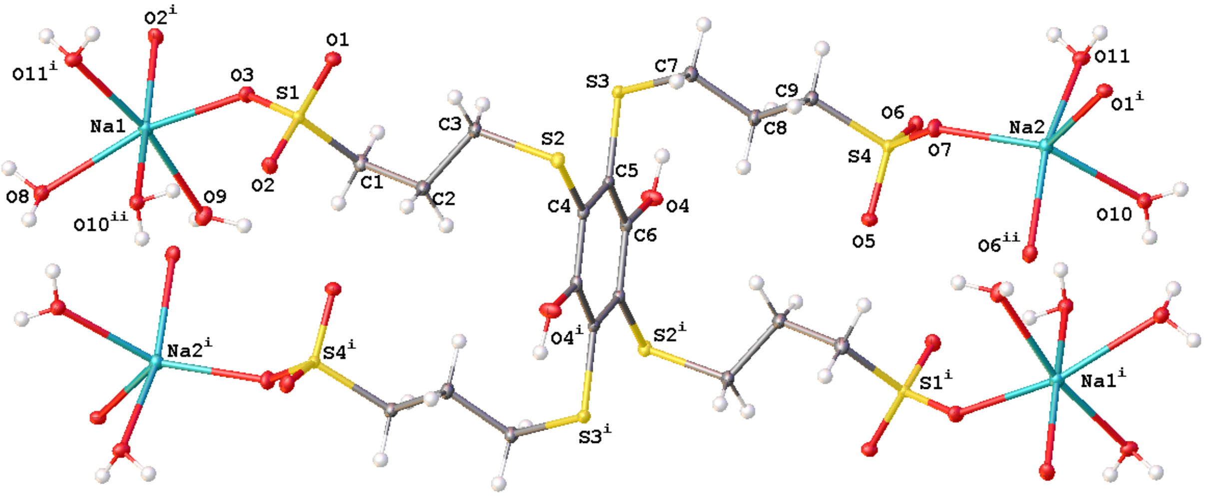


Figure S4. A molecular drawing of Stahl253 shown with 50% probability ellipsoids. Symmetry codes: i O2 +X,-1+Y,+Z, ii O10 -1/2+X,-3/2+Y,+Z.

Table S2. Crystal data and structure refinement for hydroquinone **1**.

Empirical formula	$Na_4(C_{18}H_{26}O_{14}S_8)\cdot 8H_2O$
Formula weight	958.95
Temperature/K	100.0
Crystal system	monoclinic
Space group	C2/c
a/Å	35.431(11)
b/Å	5.4941(16)
c/Å	20.150(8)
α/°	90
β/°	108.517(8)
γ/°	90
Volume/Å^3	3719(2)
Z	4
ρ_{calc}g/cm^3	1.713
μ/mm^{-1}	0.610
F(000)	1992.0
Crystal size/mm^3	0.11 × 0.08 × 0.01
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.424 to 56.842
Index ranges	$-46 \leq h \leq 46$, $-6 \leq k \leq 7$, $-26 \leq l \leq 26$
Reflections collected	30138
Independent reflections	4670 [R_{int} = 0.0351, R_{sigma} = 0.0223]
Data/restraints/parameters	4670/0/271
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0237, wR_2 = 0.0599
Final R indexes [all data]	R_1 = 0.0275, wR_2 = 0.0619
Largest diff. peak/hole / e Å^{-3}	0.45/-0.38

5. X-ray Structure of 2,3,5,6-tetrakis(ethylsulfanyl-2'-sulfonate)-1,4-benzoquinone tetrasodium salt (2)

Data Collection

A red crystal with approximate dimensions 0.118 x 0.043 x 0.036 mm^3 was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera. The crystal evaluation and data collection were performed on a Bruker Quazar SMART APEXII diffractometer with Mo K_α (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 4.96 cm.[12]

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5° in a 6° range about ω with the exposure time of 20 seconds per frame. The reflections were successfully indexed by an automated indexing routine built in the APEX3 program suite. The final cell constants were calculated from a set of 9956 strong reflections from the actual data collection.

The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.70 Å. A total of 42054 data were harvested by collecting 8 sets of frames with 0.5° scans in ω and φ with exposure times of 80sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.[13]

Structure Solution and Refinement

The systematic absences in the diffraction data were consistent for the space groups *Cc* and *C2/c*. The *E*-statistics strongly suggested the centrosymmetric space group *C2/c* that yielded chemically reasonable and computationally stable results of refinement.[13–19]

A successful solution by the direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms, except for H atoms on the water molecules, were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The H atoms bonded to the water molecule were found in the Fourier difference map. The bond distances O2–H2A and O2–H2B were restrained to be similar.

The crystal structure is polymeric. Only half of the monomer resides in the asymmetric unit. The whole monomer is generated by an inversion center located at the center of the tetrasulfanylcyclohexane. Atom O1 resides on a two-fold rotation axis, which generates the second H atom.

The final least-squares refinement of 200 parameters against 4344 data resulted in residuals *R* (based on F^2 for $I \geq 2\sigma$) and *wR* (based on F^2 for all data) of 0.0336 and 0.0820, respectively. The final difference Fourier map was featureless.

Summary Crystal Data for $C_{14}H_{22}Na_4O_{17}S_8$ (M =810.75 g/mol): monoclinic, space group *C2/c* (no. 15), a = 19.151(5) Å, b = 5.1130(16) Å, c = 29.210(7) Å, β = 96.888(13)°, V = 2839.6(13) Å^3, Z = 4, T = 100.01 K, μ(MoKα) = 0.767 mm^{-1}, $Dcalc$ = 1.896 g/cm^3, 42054 reflections measured (2.808° ≤ 2Θ ≤ 61.12°), 4344 unique (R_{int} = 0.0442, R_{sigma} = 0.0242) which were used in all calculations. The final R_1 was 0.0334 (I > 2σ(I)) and wR_2 was 0.0818 (all data).

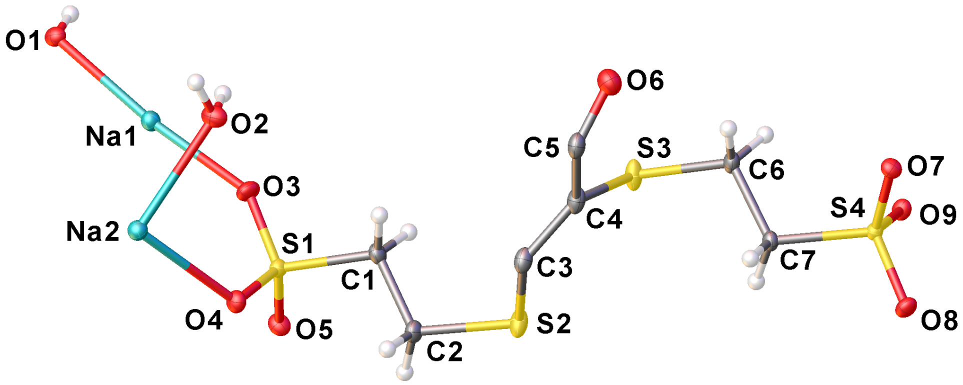


Figure S5. A molecular drawing of quinone **2** asymmetric unit shown with 50% probability ellipsoids.

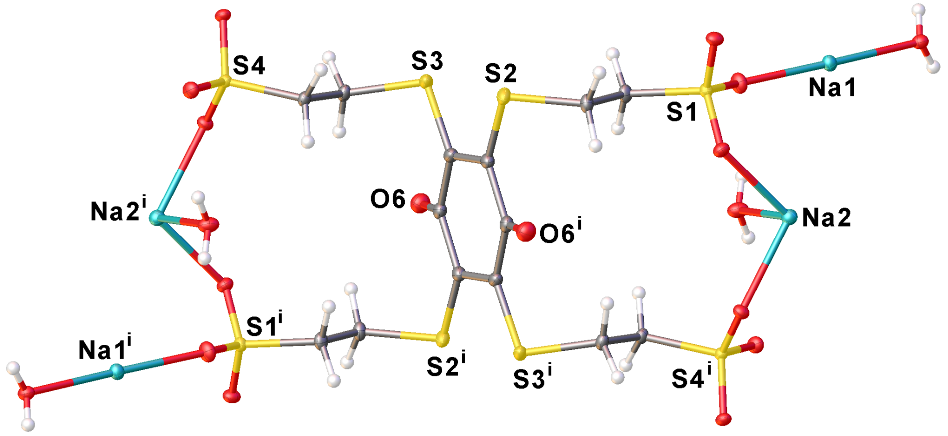


Figure S6. A molecular drawing of the partially grown quinone **2** structure shown with 50% probability ellipsoids. Symmetry code: i (3/2-X, 1/2-Y, 1-Z).

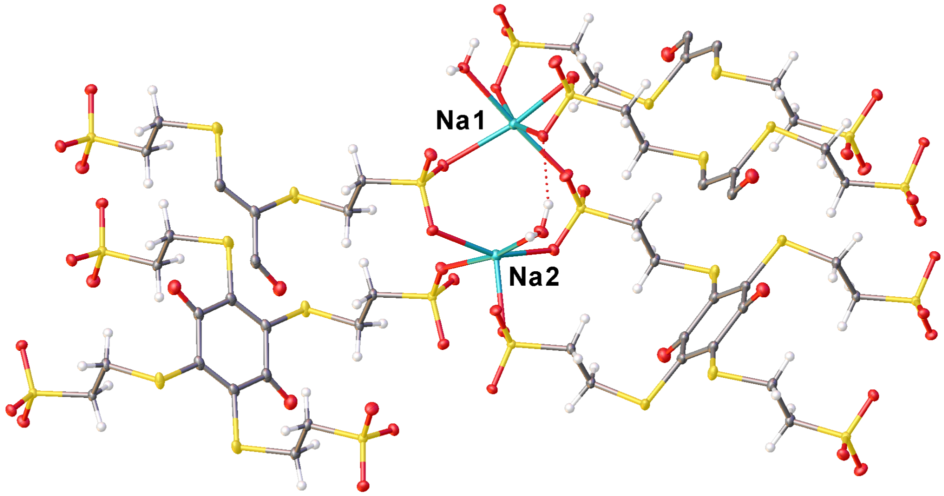


Figure S7. A molecular drawing of quinone **2** showing the local environments around the two Na atoms with 50% probability ellipsoids. For clarity additional Na atoms were omitted, so the presented fragment is not charge balanced.

Table S3. Crystal data and structure refinement for quinone **2**.

Empirical formula	$C_{14}H_{22}Na_4O_{17}S_8$
Formula weight	810.75
Temperature/K	100.01
Crystal system	monoclinic
Space group	C2/c
a/Å	19.151(5)
b/Å	5.1130(16)
c/Å	29.210(7)
α/°	90
β/°	96.888(13)
γ/°	90
Volume/Å^3	2839.6(13)
Z	4
ρ_{calc}g/cm^3	1.896
μ/mm^{-1}	0.767
F(000)	1656.0
Crystal size/mm^3	0.118 × 0.043 × 0.036
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.808 to 61.12
Index ranges	$-27 \leq h \leq 27$, $-7 \leq k \leq 7$, $-41 \leq l \leq 41$
Reflections collected	42054
Independent reflections	4344 [R_{int} = 0.0442, R_{sigma} = 0.0242]
Data/restraints/parameters	4344/1/205
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0334, wR_2 = 0.0778
Final R indexes [all data]	R_1 = 0.0425, wR_2 = 0.0818
Largest diff. peak/hole / e Å^{-3}	0.64/-0.29

6. References

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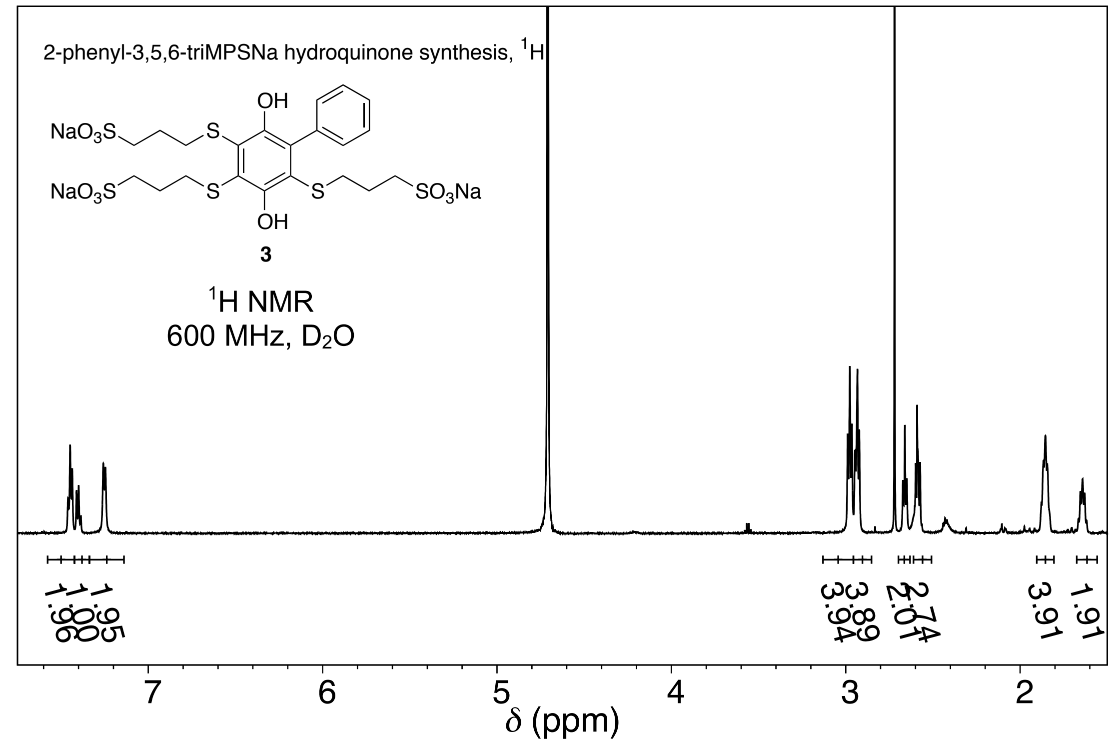
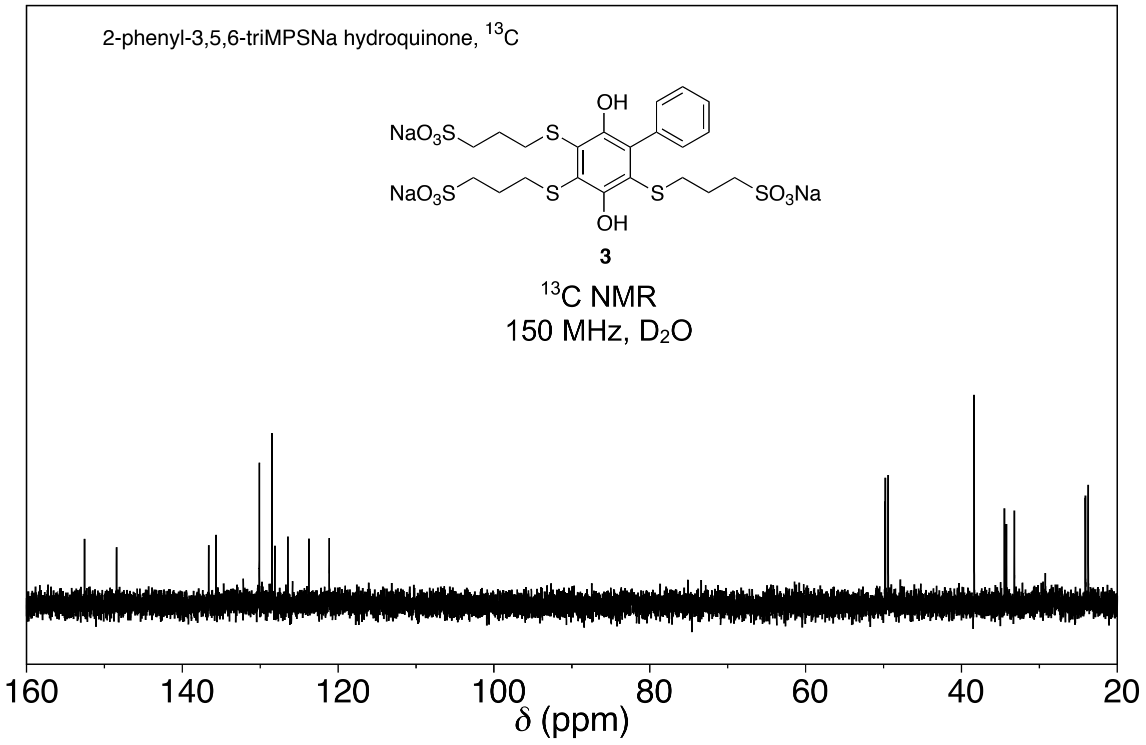
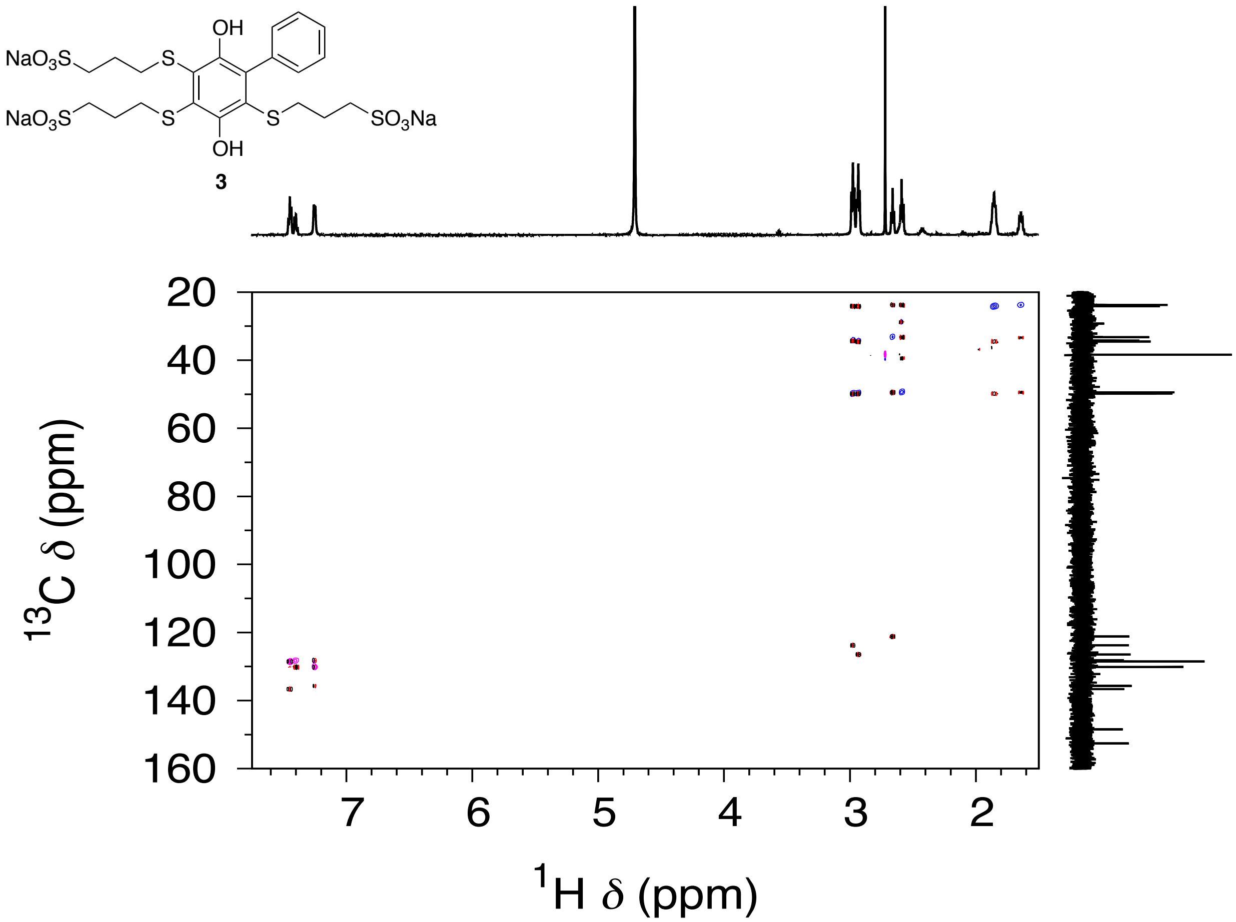
7. NMR Spectra

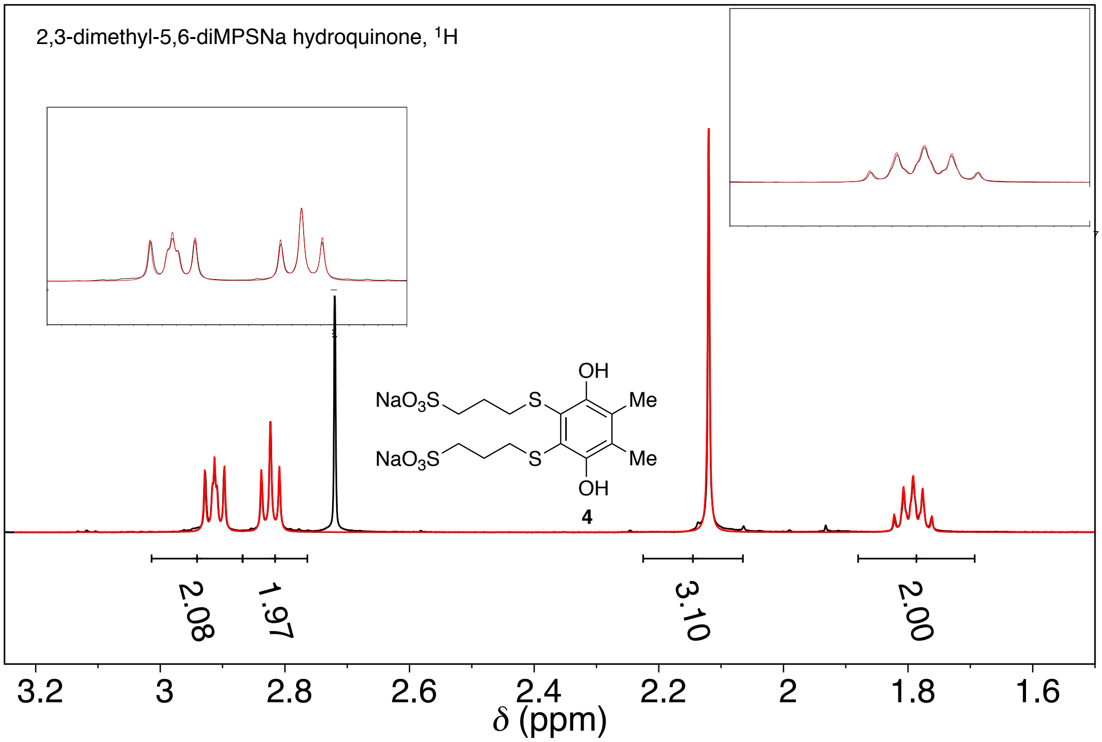




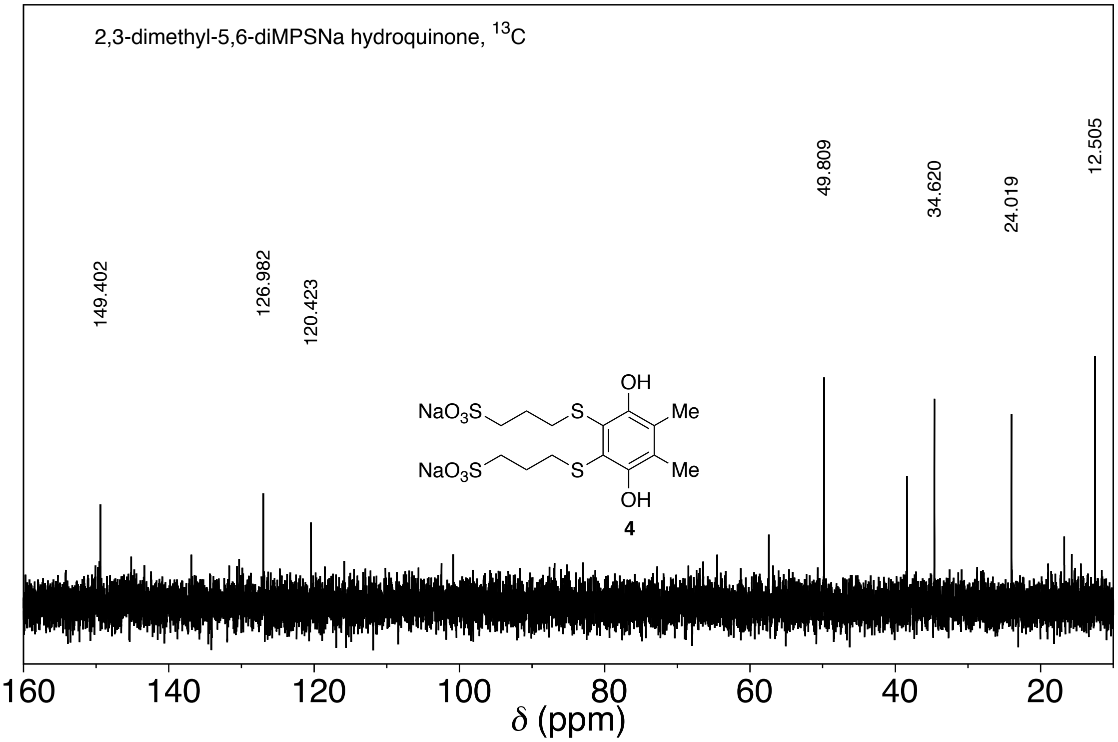
Combined ^{1}H-^{13}C HSQC (blue/magenta) and HMBC (red/black) spectra of compound **3**.



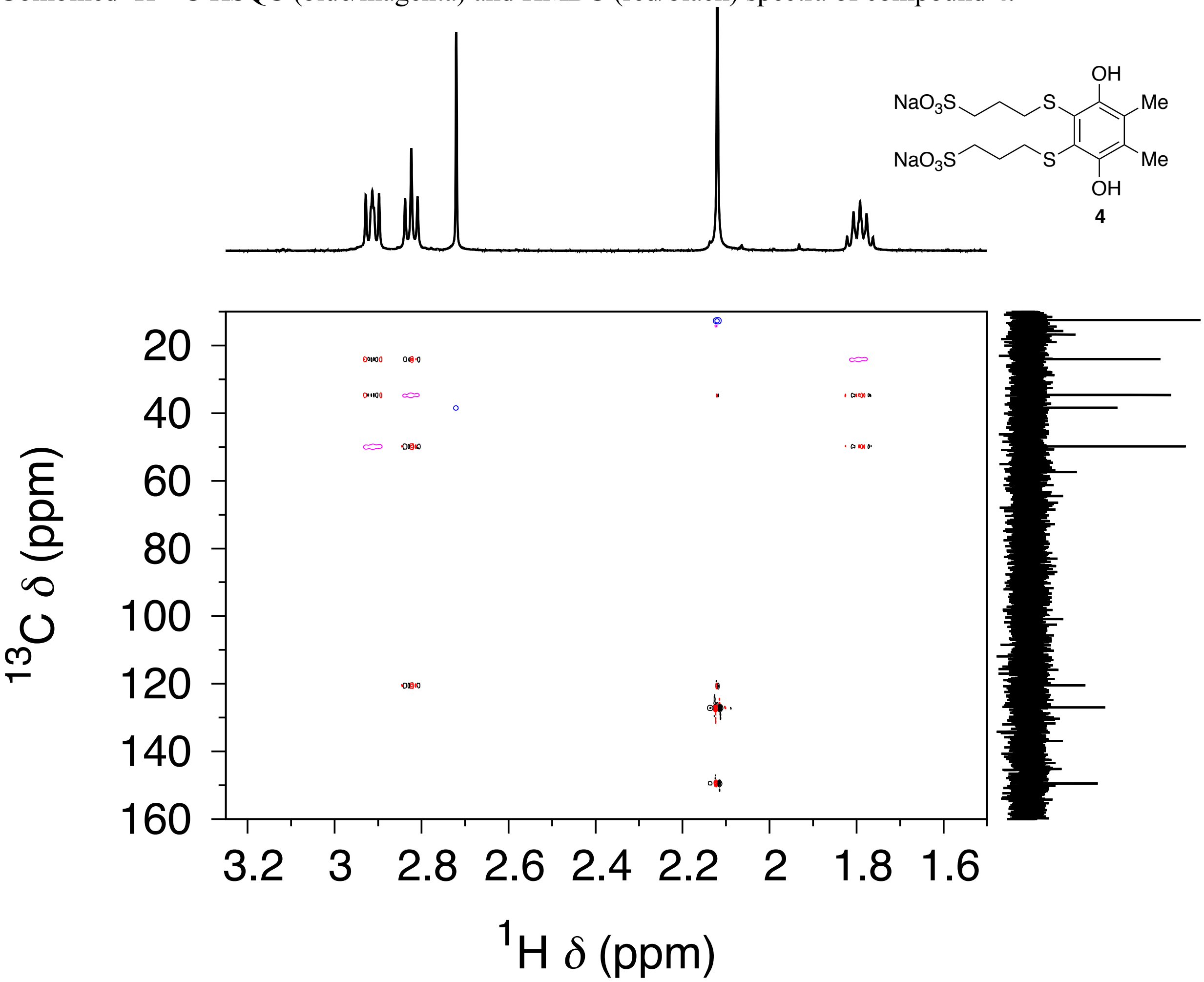
3

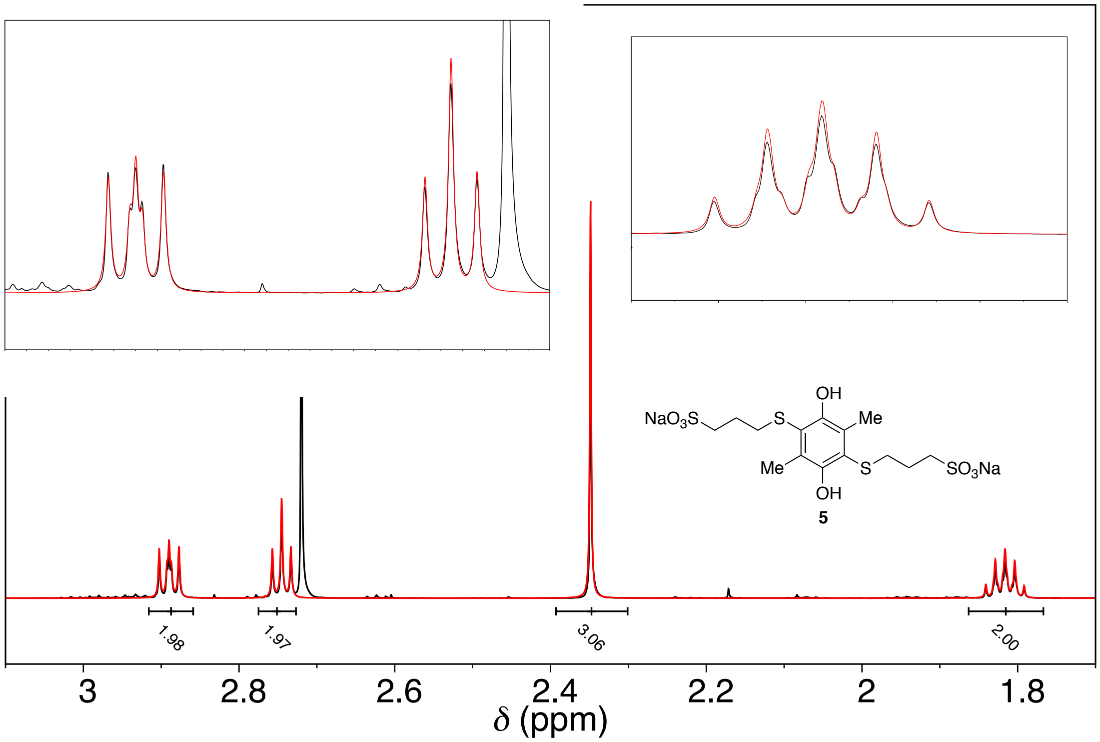


The black trace is experimental data, red trace is spectral simulation.

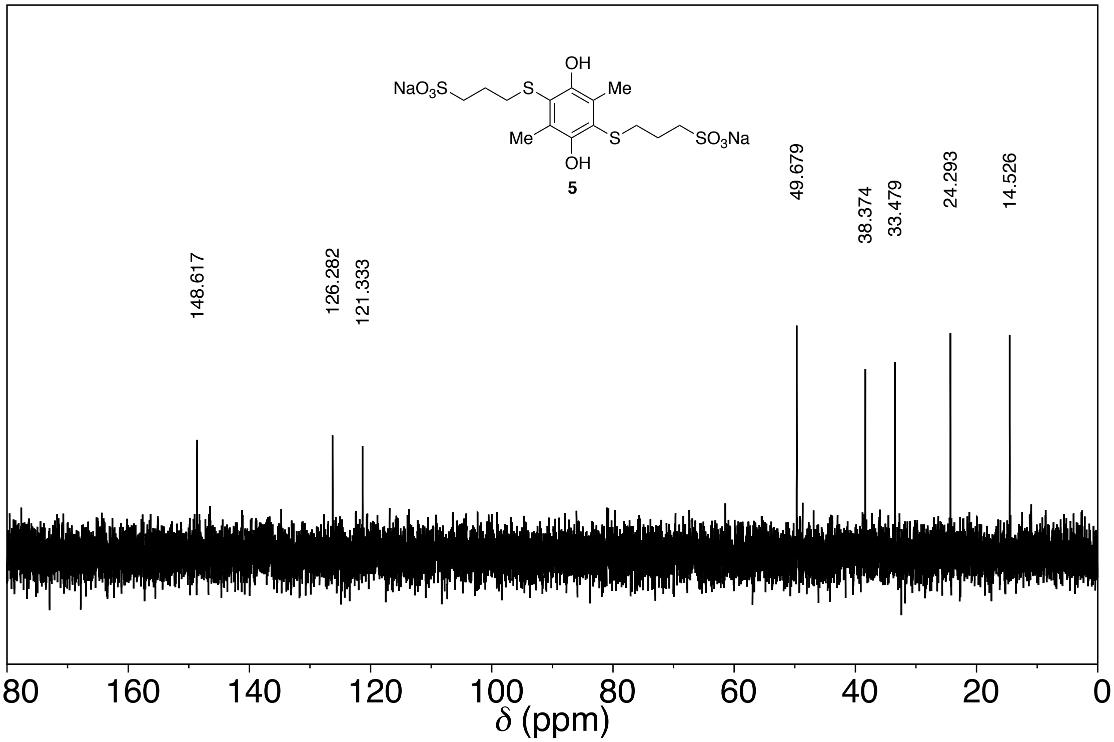


Combined ^{1}H-^{13}C HSQC (blue/magenta) and HMBC (red/black) spectra of compound **4**.

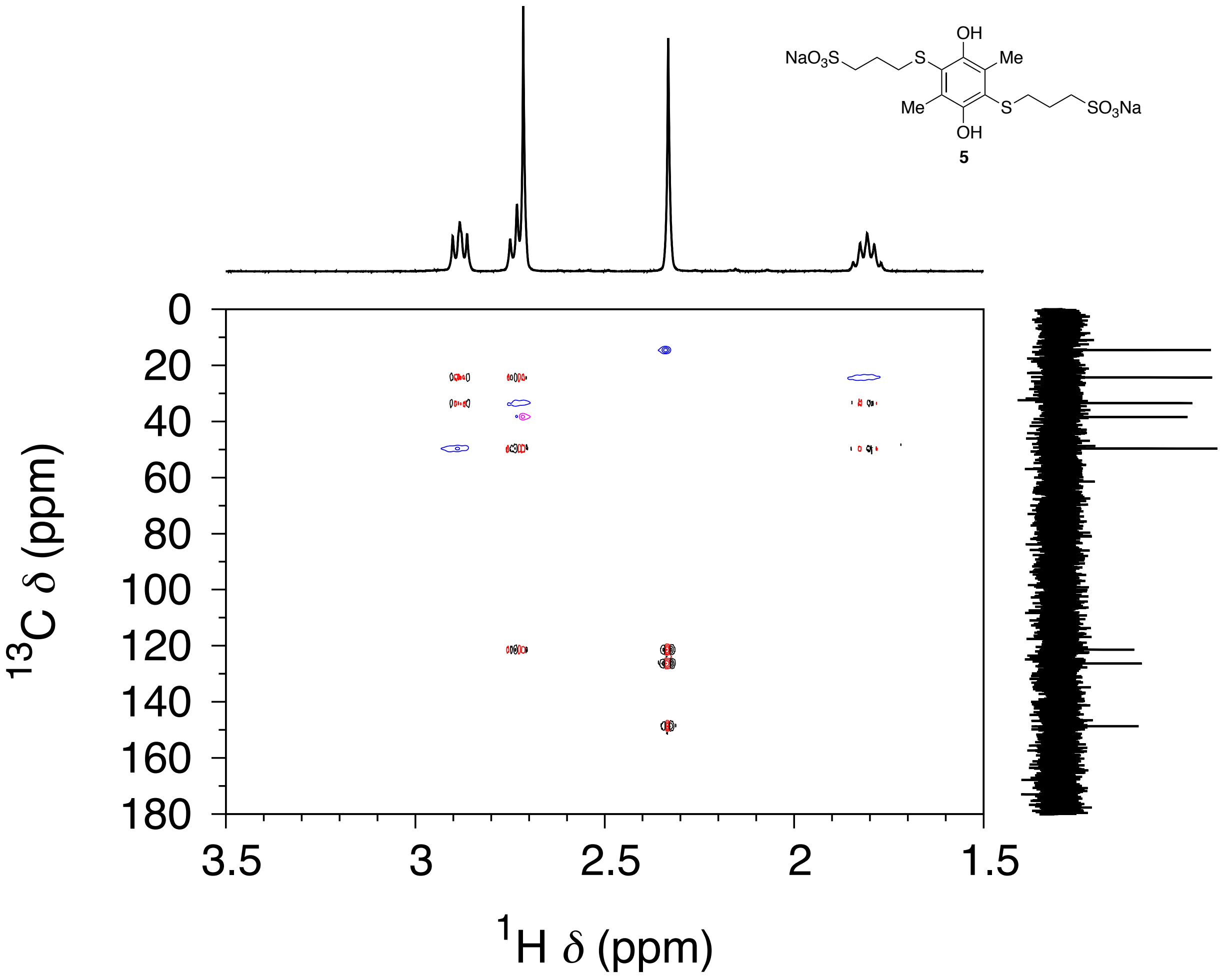


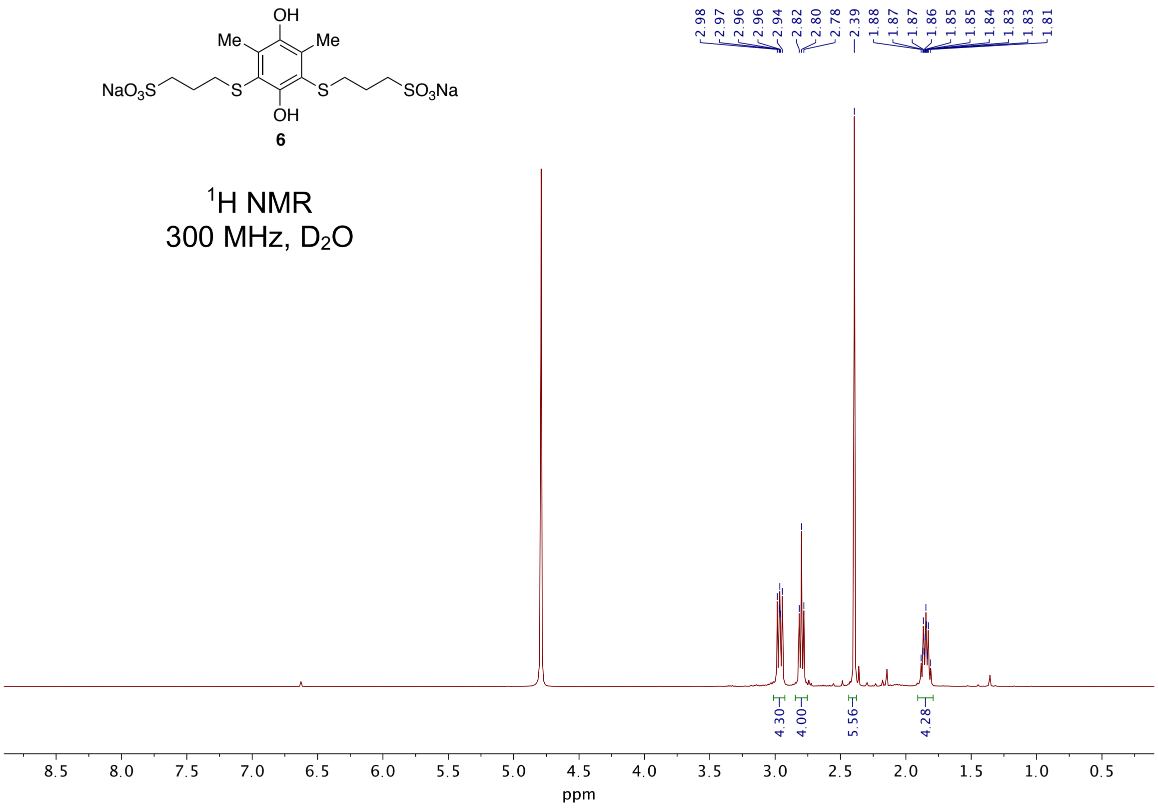


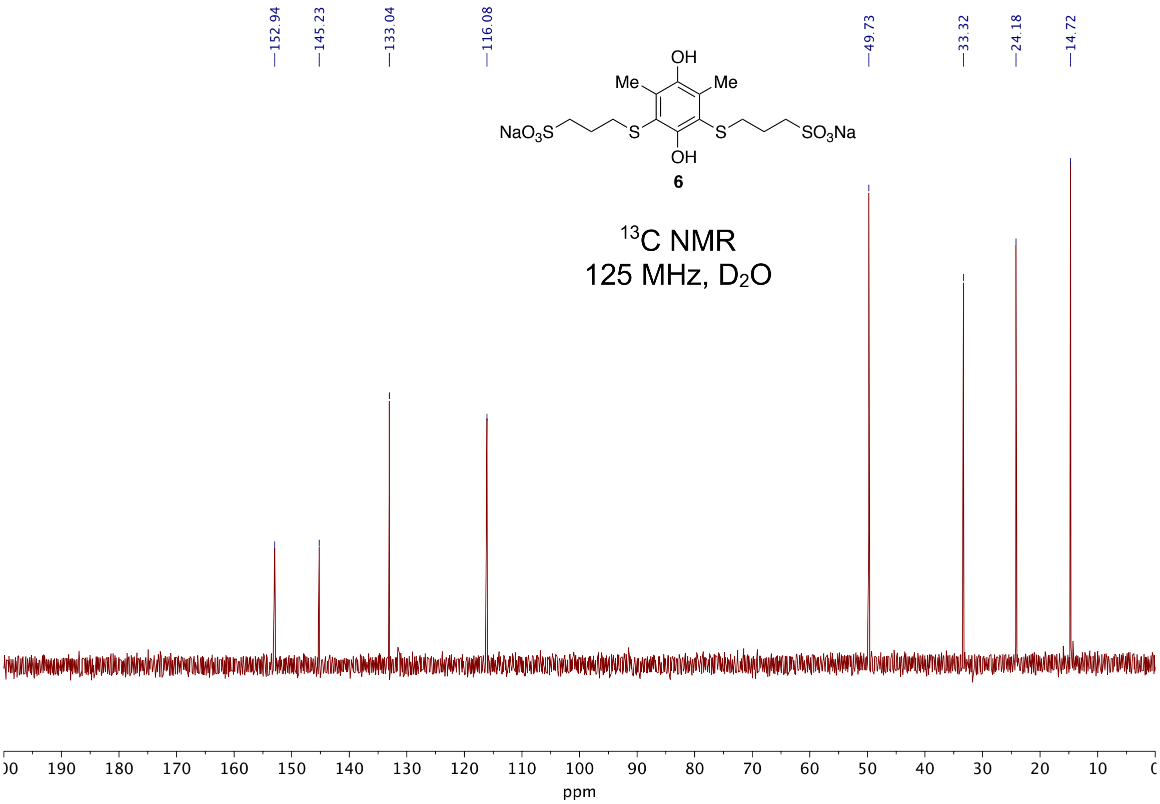
The black trace is experimental data, red trace is spectral simulation.



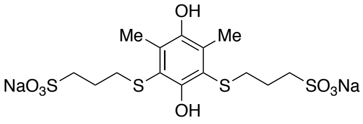
Combined ^{1}H-^{13}C HSQC (blue/magenta) and HMBC (red/black) spectra of compound **5**.



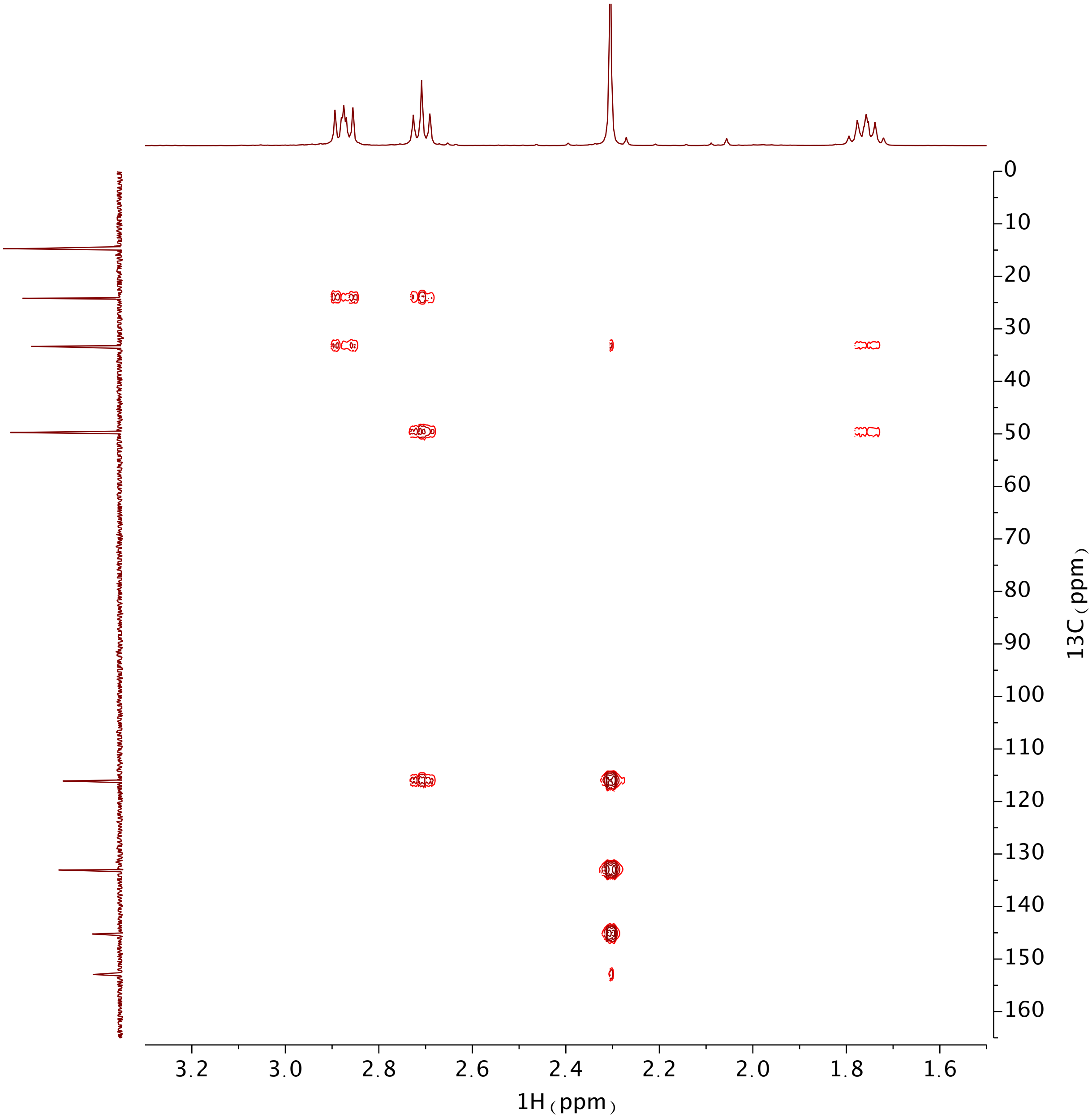

6
^{1}H NMR
300 MHz, D_2O
2.98
2.97
2.96
2.96
2.94
2.82
2.80
2.78
2.39
1.88
1.87
1.87
1.86
1.85
1.85
1.84
1.83
1.83
1.81
4.30
4.00
5.56
4.28
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

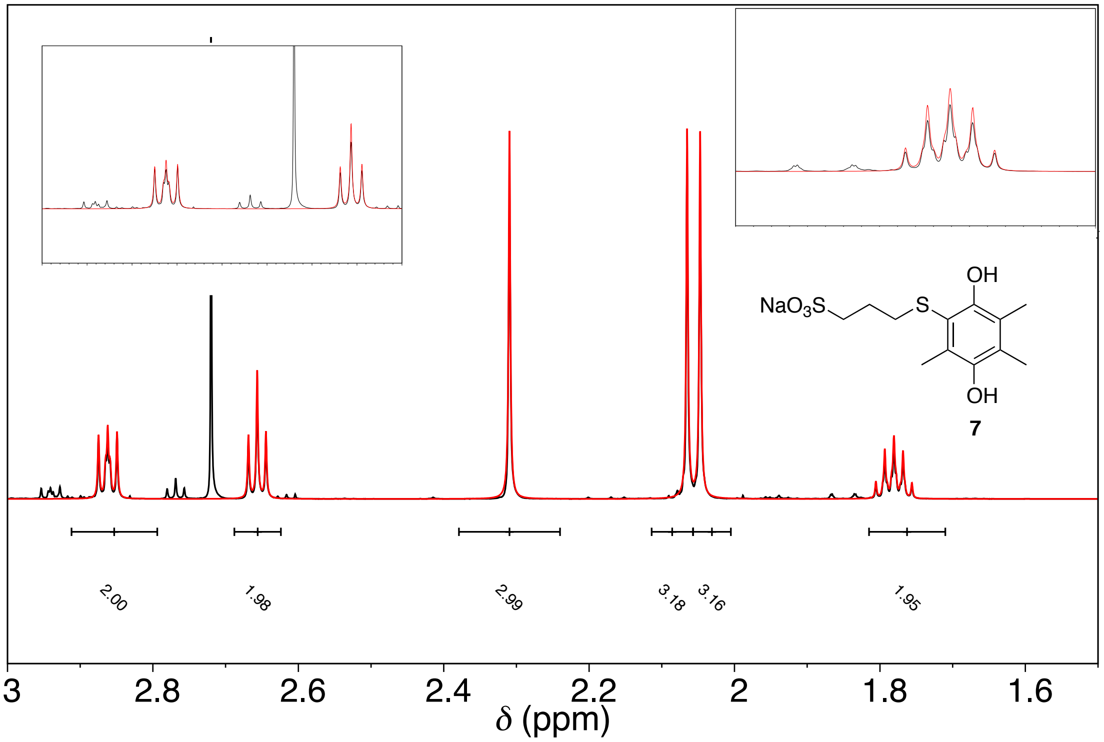

152.94
145.23
133.04
116.08
49.73
33.32
24.18
14.72
6
^{13}C NMR
125 MHz, D_2O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

^{1}H-^{13}C HMBC to confirm connectivity between the α-thioether protons and the aromatic *ipso* thioether carbon.

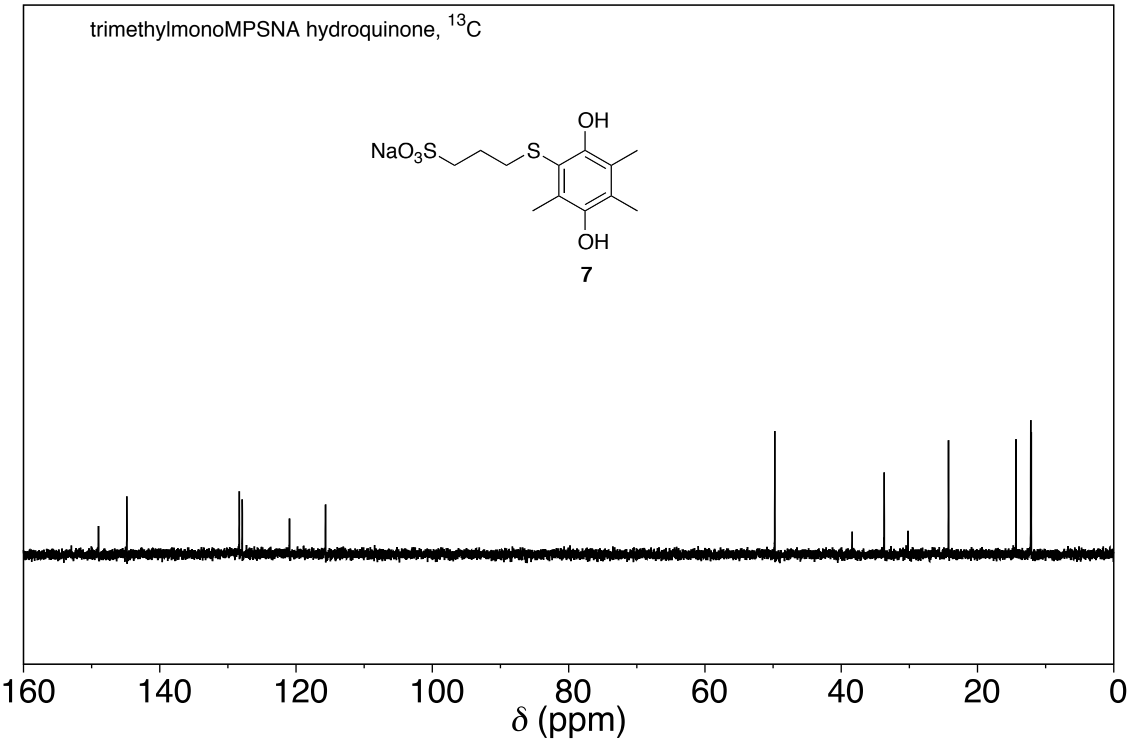


6

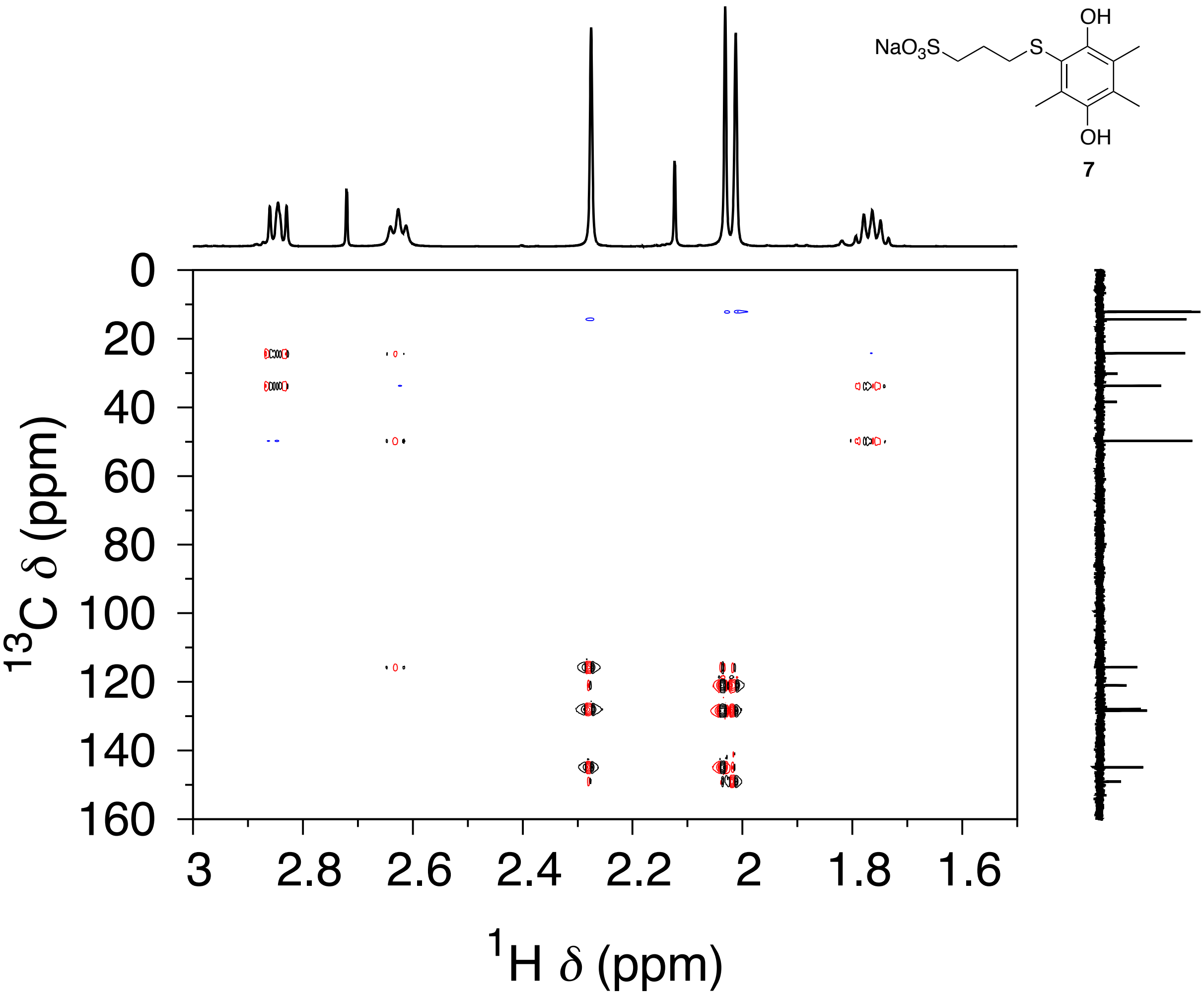


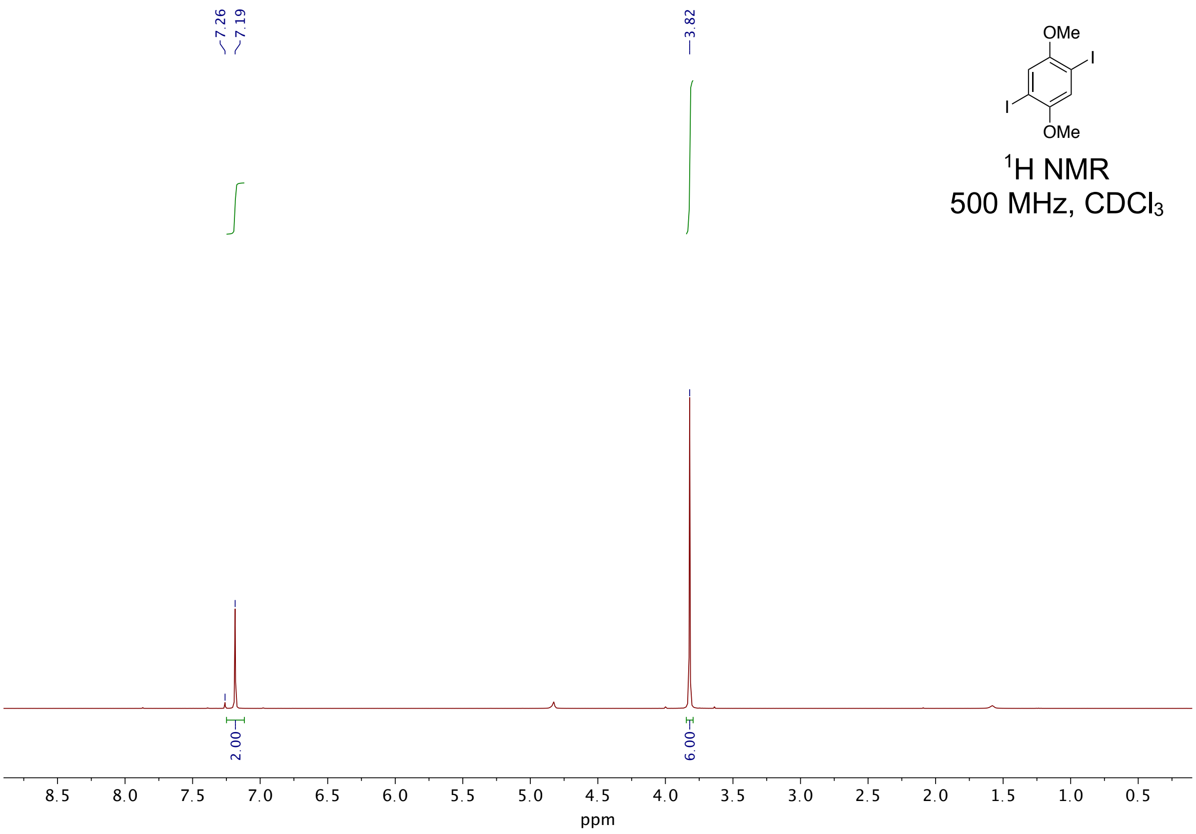


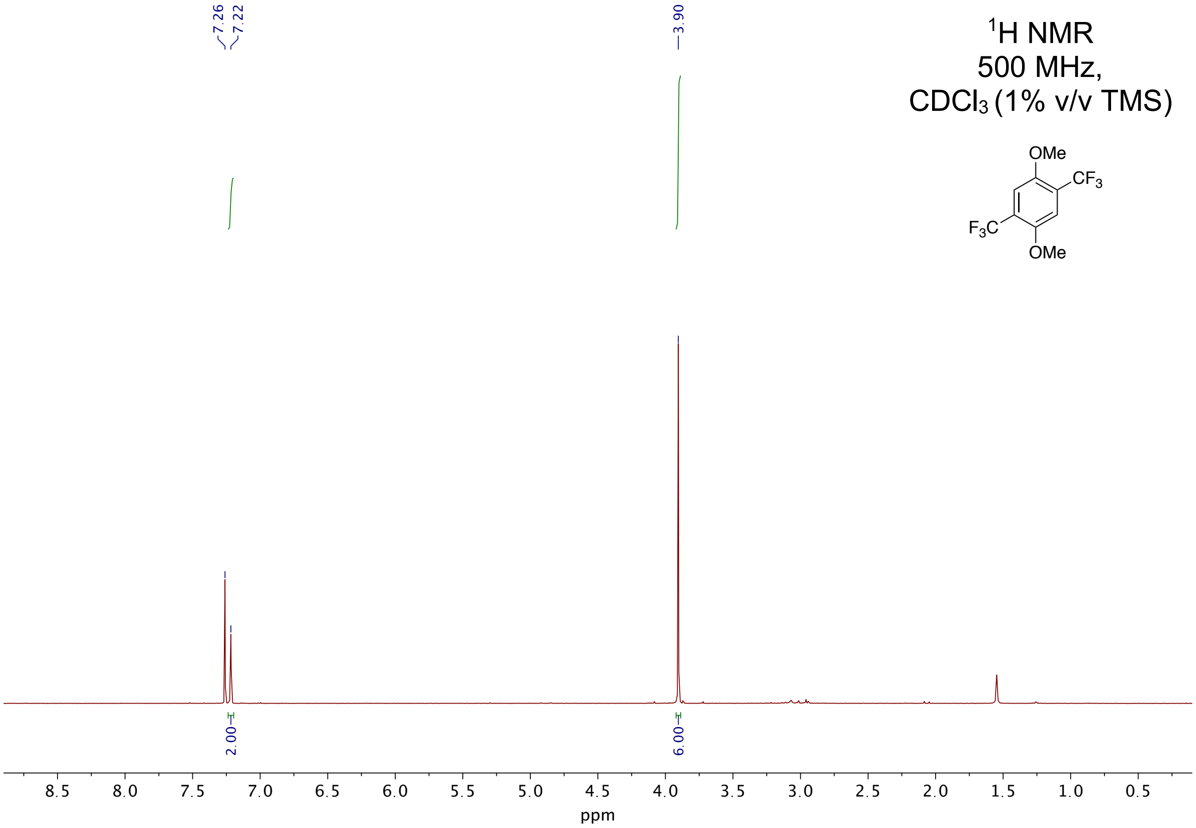
The black trace is experimental data, red trace is spectral simulation.

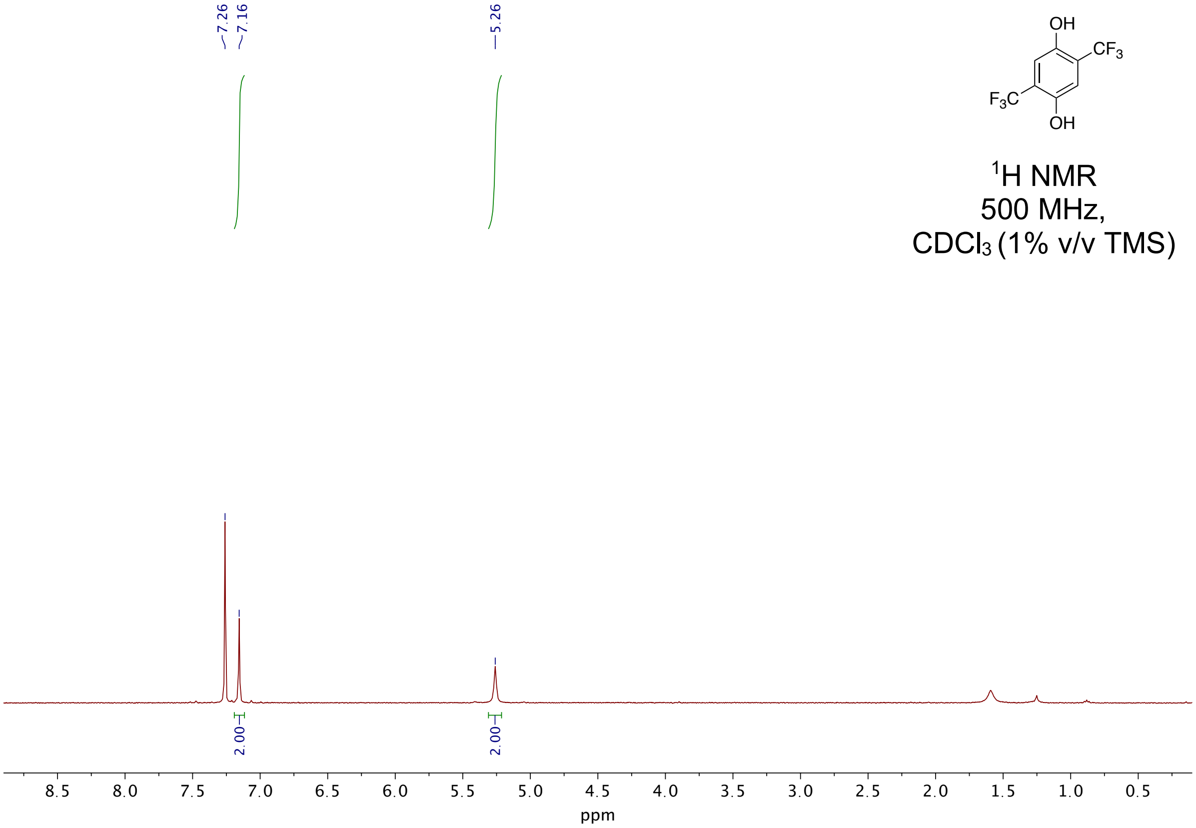


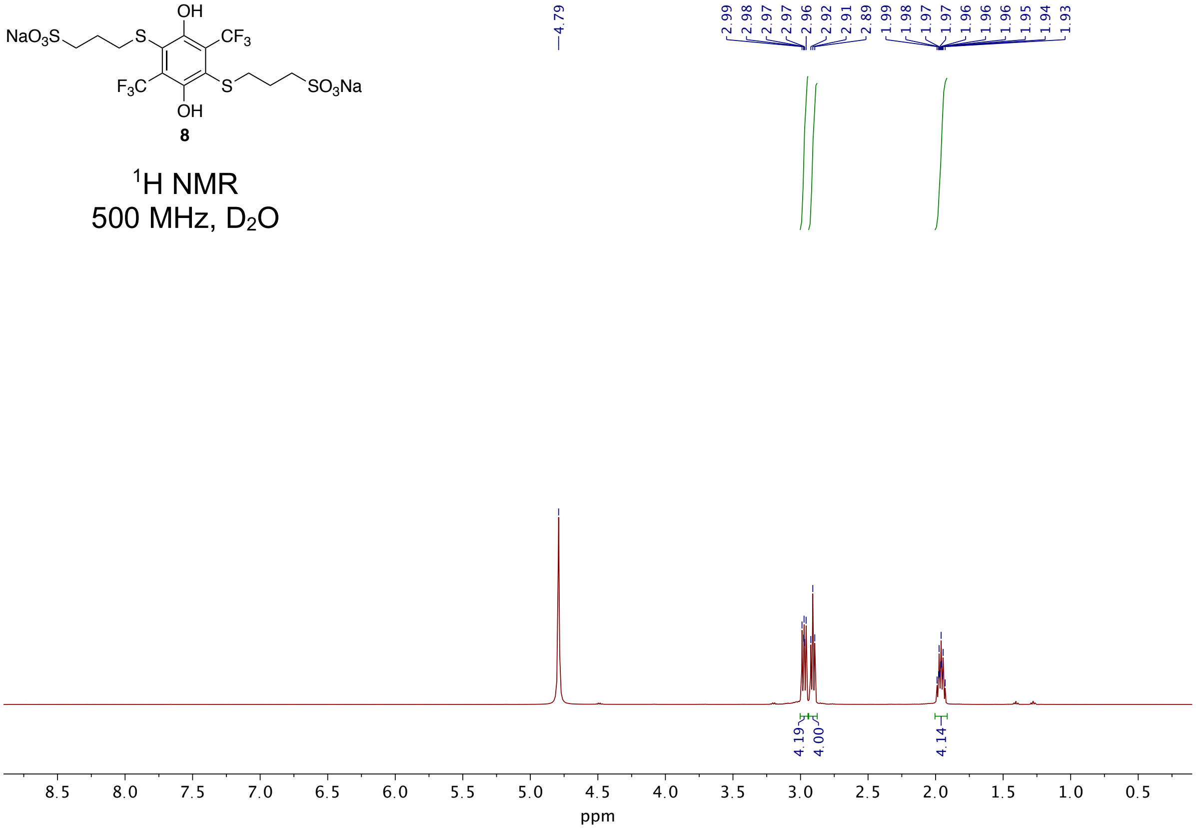
Combined ^1H-^{13}C HSQC (blue/magenta) and HMBC (red/black) spectra of compound **7**.

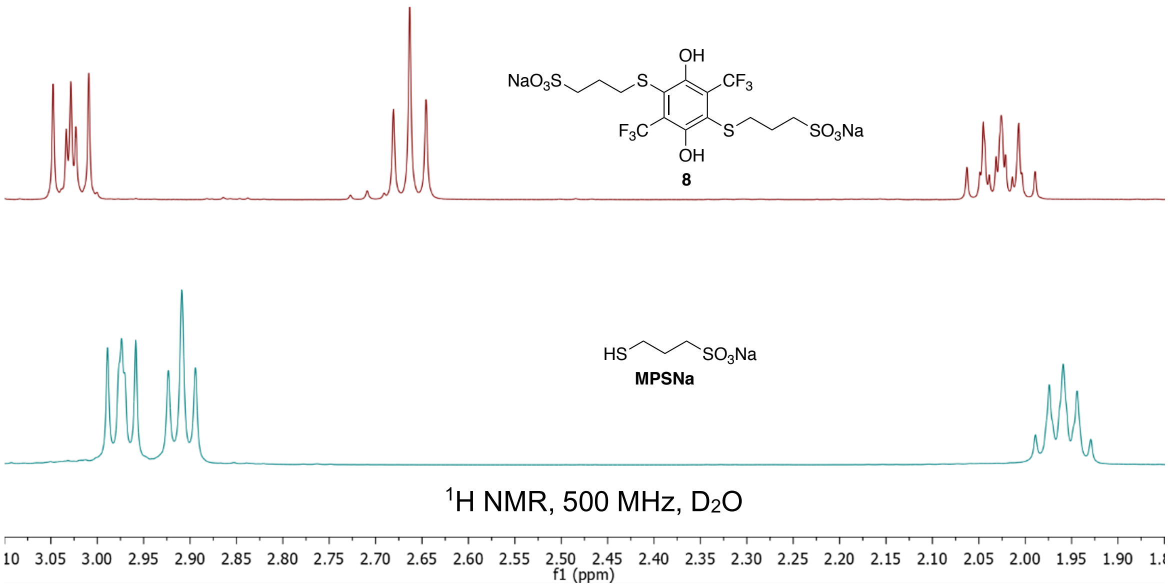



7.26
7.19
3.82
OMe
I
I
OMe
¹H NMR
500 MHz, CDCl₃
2.00
6.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

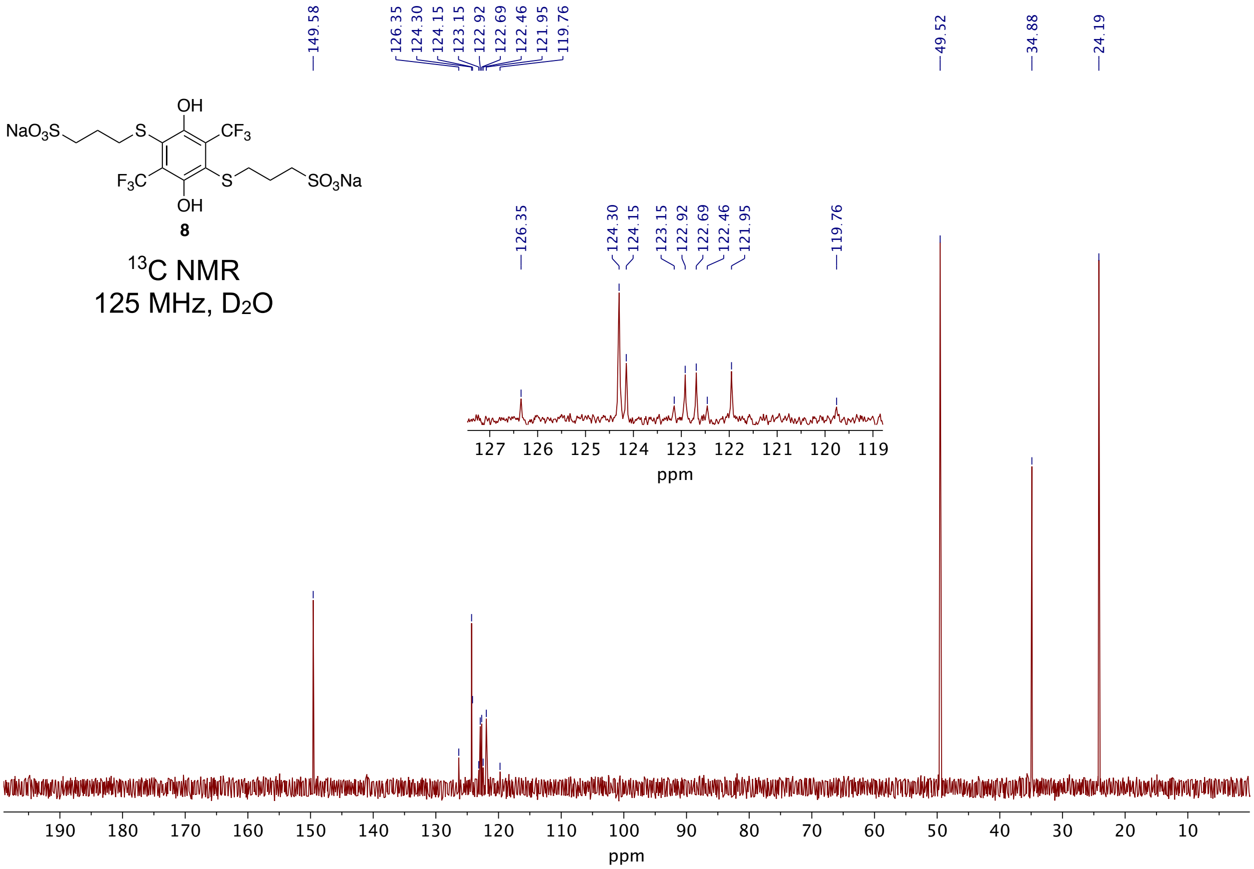

7.26
7.22
3.90
¹H NMR
500 MHz,
CDCl₃ (1% v/v TMS)
OMe
CF₃
F₃C
OMe
2.00
6.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


7.26
7.16
5.26
1H NMR
500 MHz,
CDCl3 (1% v/v TMS)
OH
CF3
F3C
OH
2.00
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

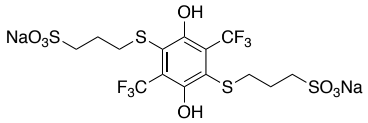

NaO3S
S
OH
CF3
F3C
OH
S
SO3Na
8
1H NMR
500 MHz, D2O
4.79
2.99
2.98
2.97
2.97
2.96
2.92
2.91
2.89
1.99
1.98
1.97
1.97
1.96
1.96
1.96
1.95
1.94
1.93
4.19
4.00
4.14
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm



OH
NaO$_3$S
S
CF$_3$
F$_3$C
S
SO$_3$Na
OH
8
HS
SO$_3$Na
MPSNa
^{1}H NMR, 500 MHz, D$_2$O
10
3.05
3.00
2.95
2.90
2.85
2.80
2.75
2.70
2.65
2.60
2.55
2.50
2.45
2.40
2.35
2.30
2.25
2.20
2.15
2.10
2.05
2.00
1.95
1.90
1.8
f1 (ppm)

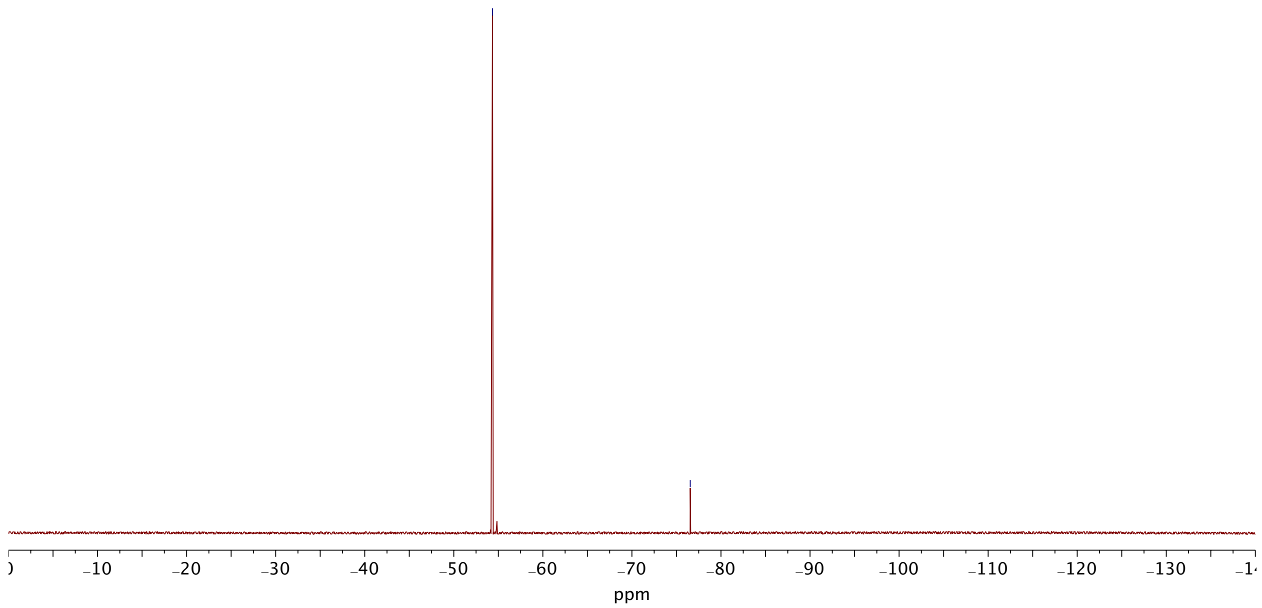


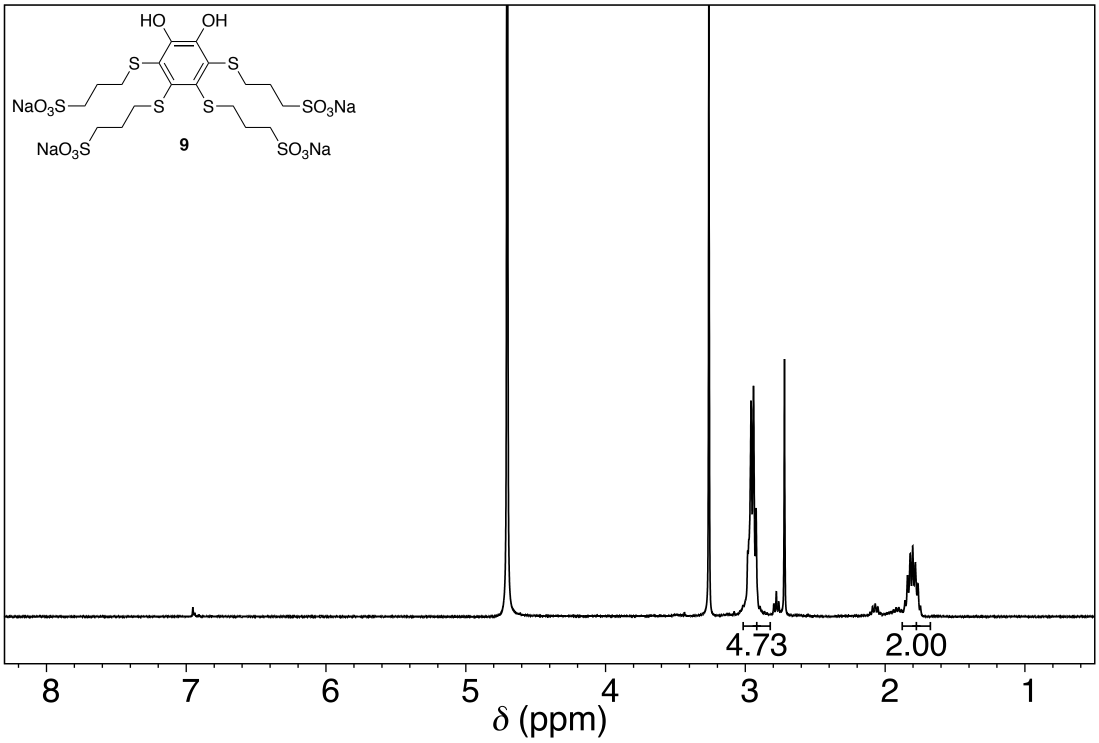
149.58
126.35
124.30
124.15
123.15
122.92
122.69
122.46
121.95
119.76
49.52
34.88
24.19
OH
NaO$_3$S
S
CF$_3$
F$_3$C
S
SO$_3$Na
OH
8
^{13}C NMR
125 MHz, D$_2$O
126.35
124.30
124.15
123.15
122.92
122.69
122.46
121.95
119.76
127
126
125
124
123
122
121
120
119
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

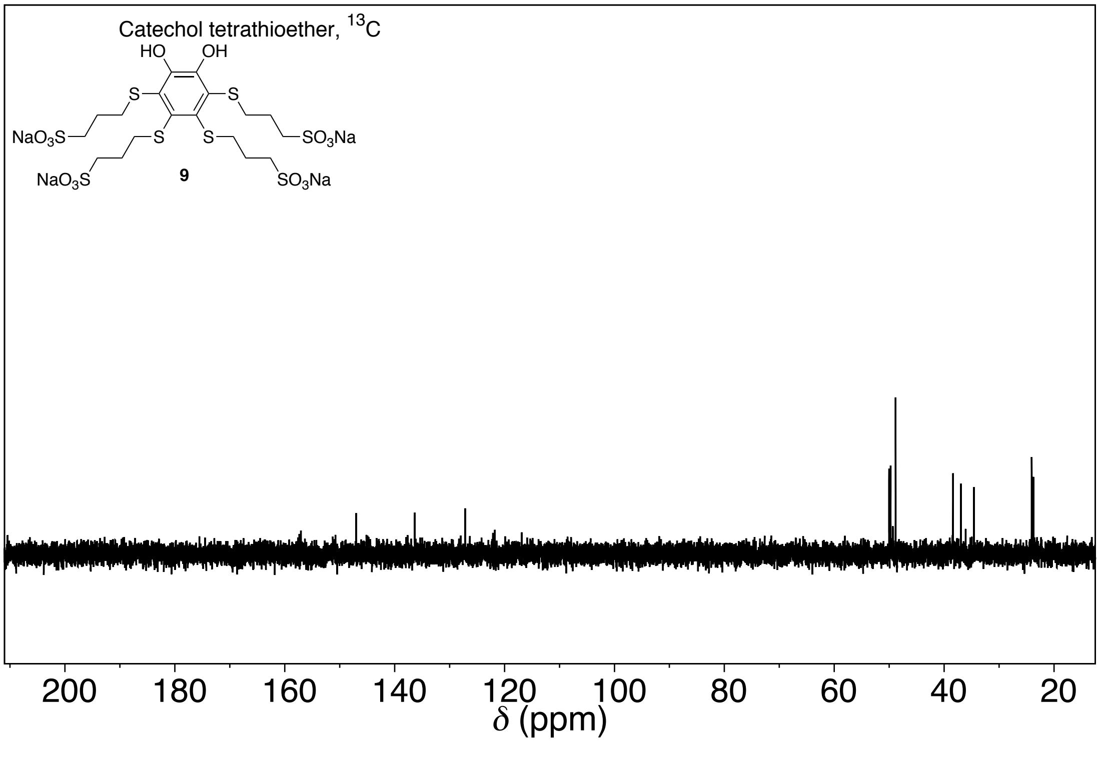


8

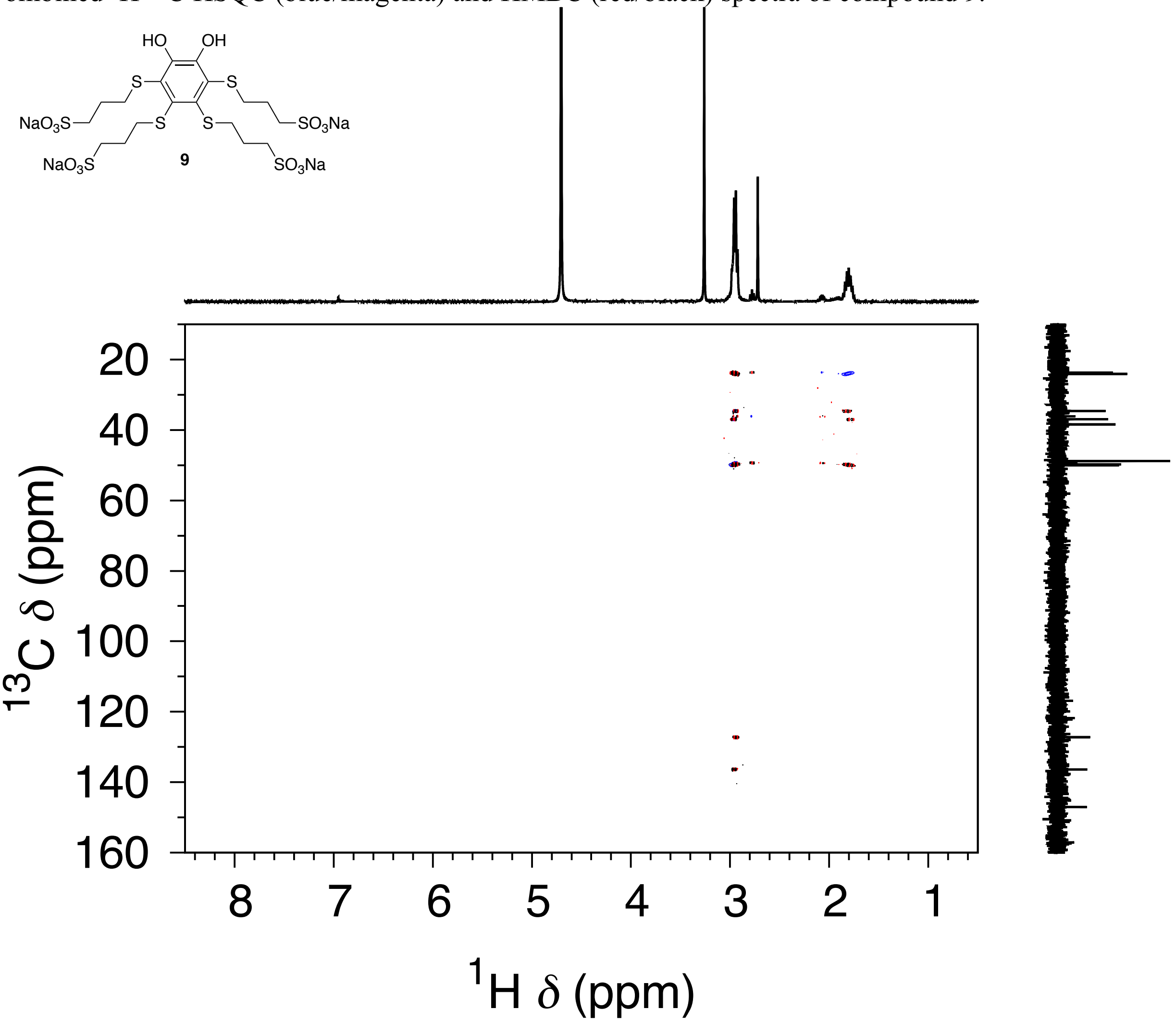
^{19}F NMR
338 MHz
0.1% TFA inD$_2$O

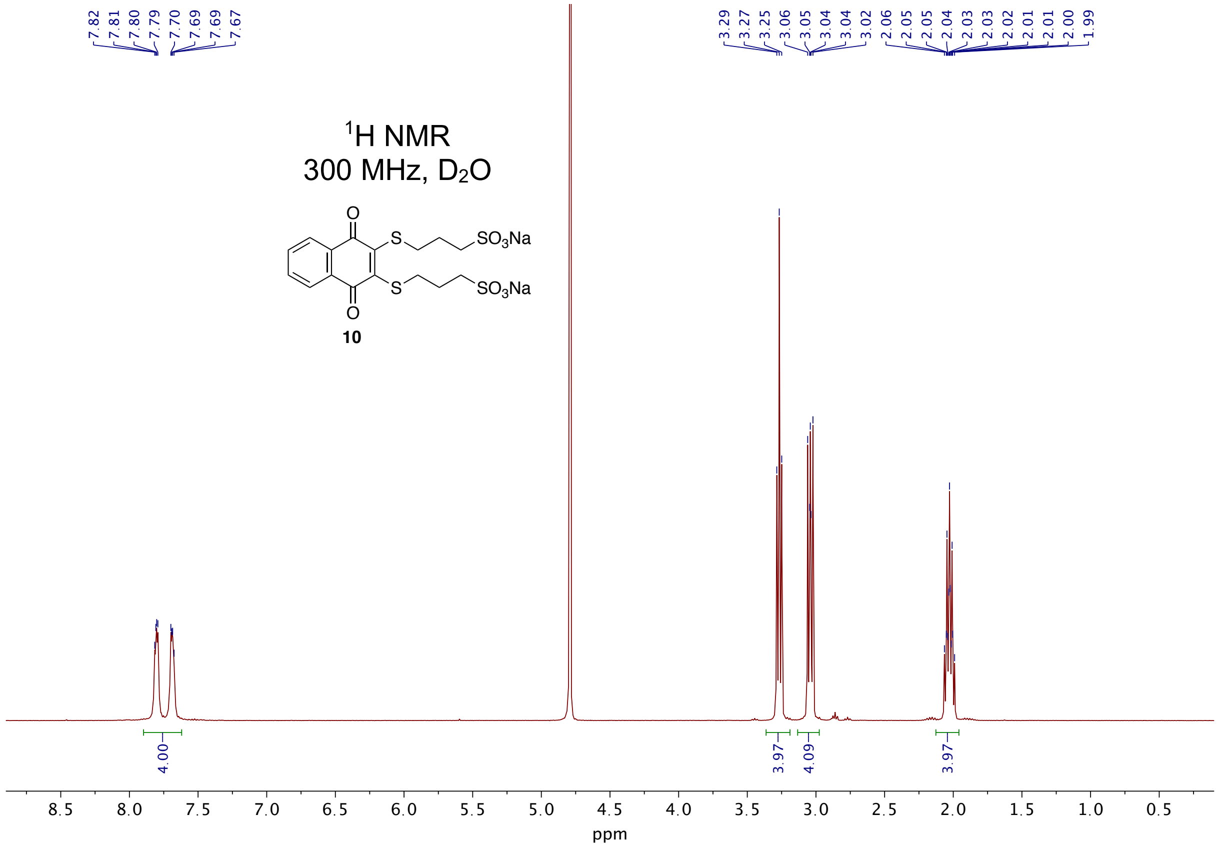


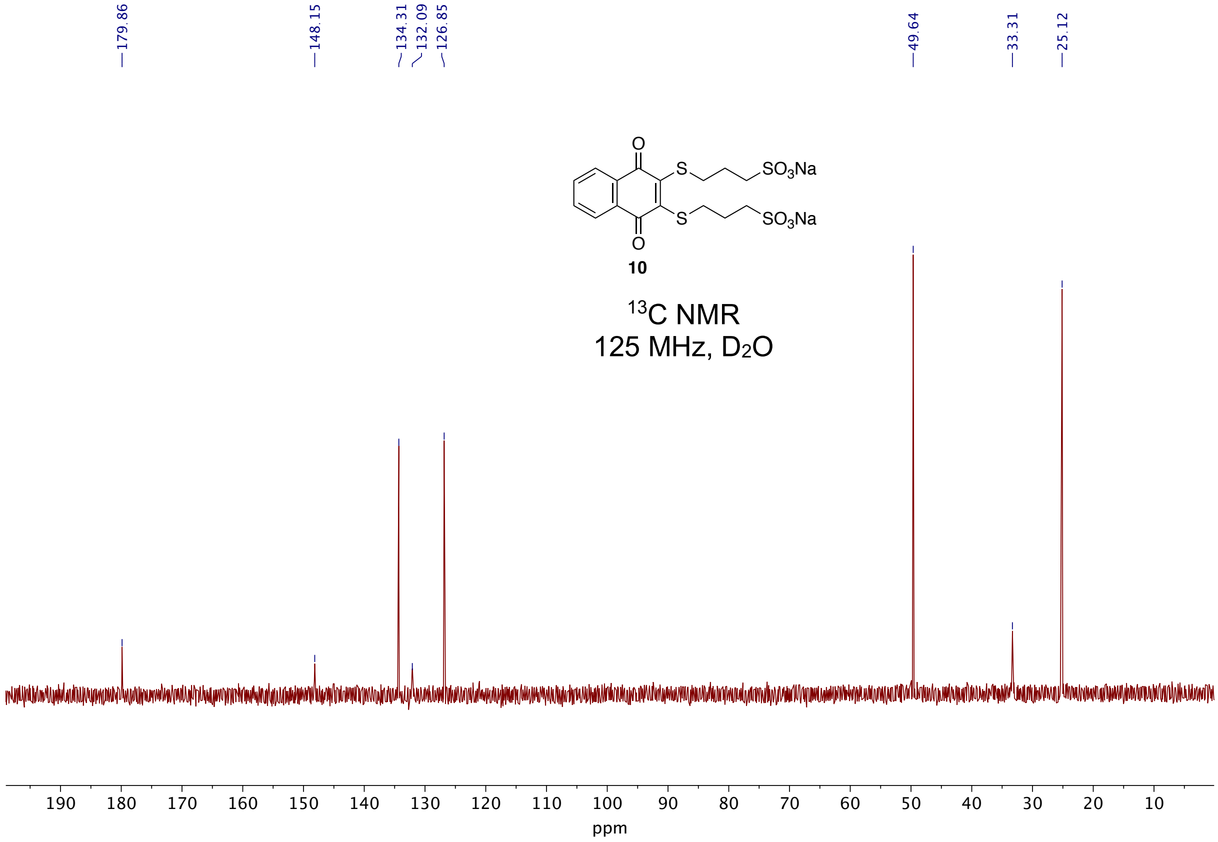

HO
OH
S
S
S
S
NaO3S
SO3Na
NaO3S
SO3Na
9
4.73
2.00
8
7
6
5
4
3
2
1
δ (ppm)


Catechol tetrathioether, 13C
HO
OH
S
S
S
S
NaO3S
SO3Na
NaO3S
SO3Na
9
200
180
160
140
120
100
80
60
40
20
δ (ppm)

Combined ^{1}H-^{13}C HSQC (blue/magenta) and HMBC (red/black) spectra of compound **9**.




7.82
7.81
7.80
7.79
7.70
7.69
7.69
7.67
3.29
3.27
3.25
3.06
3.05
3.04
3.04
3.02
2.06
2.05
2.05
2.04
2.03
2.03
2.02
2.01
2.01
2.00
1.99
^{1}H NMR
300 MHz, D_2O
O
S
SO_3Na
S
SO_3Na
O
10
4.00
3.97
4.09
3.97
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


179.86
148.15
134.31
132.09
126.85
49.64
33.31
25.12
O
S
SO_3Na
S
SO_3Na
O
10
^{13}C NMR
125 MHz, D_2O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm