

Supporting Information

The SAM, Not the Electrodes, Dominates Charge Transport in

Ag^{TS}-SAM//Ga₂O₃/EGaIn Junctions

*William F. Reus,¹ Martin M. Thuo,¹ Nathan Shapiro¹, Christian A. Nijhuis,² and George
M. Whitesides^{1*}*

¹ Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford St,
Cambridge, MA 02138, USA.

² Department of Chemistry, National University of Singapore, 3 Science Drive 3,
Singapore 117543.

*corresponding author:

Tel.: 617 458 9430

Fax.: 617 458 9857

e-mail: gwhitesides@gmwgroup.harvard.edu

Table S1: Reduction Potentials for Ions of Ga, In, and Other Oxidizable Metals in

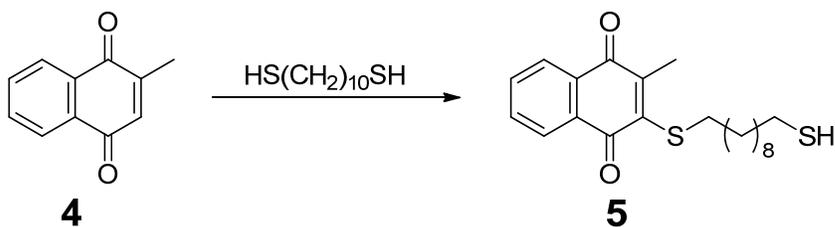
Solution

Reaction	E° (V)^a
$\text{Ga}^{3+} + 3 \text{e}^- \rightleftharpoons \text{Ga}$	-0.549
$\text{Ga}^+ + \text{e}^- \rightleftharpoons \text{Ga}$	-0.2
$\text{GaOH}^{2+} + \text{H}^+ + 3 \text{e}^- \rightleftharpoons \text{Ga} + \text{H}_2\text{O}$	-0.498
$\text{H}_2\text{GaO}_3^- + \text{H}_2\text{O} + 3 \text{e}^- \rightleftharpoons \text{Ga} + 4 \text{OH}^-$	-1.219
$\text{In}^+ + \text{e}^- \rightleftharpoons \text{In}$	-0.14
$\text{In}^{2+} + \text{e}^- \rightleftharpoons \text{In}^+$	-0.40
$\text{In}^{3+} + \text{e}^- \rightleftharpoons \text{In}^{2+}$	-0.49
$\text{In}^{3+} + 2 \text{e}^- \rightleftharpoons \text{In}^+$	-0.443
$\text{In}^{3+} + 3 \text{e}^- \rightleftharpoons \text{In}$	-0.3382
$\text{In}_2\text{O}_3 + 3 \text{H}_2\text{O} + 6 \text{e}^- \rightleftharpoons 2 \text{In} + 6 \text{OH}^-$	-1.034
$\text{Cr}^{3+} + 2 \text{e}^- \rightleftharpoons \text{Cr}$	-0.744
$\text{Fe}^{2+} + 2 \text{e}^- \rightleftharpoons \text{Fe}$	-0.447
$\text{Ni}^{2+} + 2 \text{e}^- \rightleftharpoons \text{Ni}$	-0.257
$\text{Al}^{3+} + 3 \text{e}^- \rightleftharpoons \text{Al}$	-1.662
$\text{Ti}^{2+} + 2 \text{e}^- \rightleftharpoons \text{Ti}$	-1.630
$\text{Ti}^{3+} + \text{e}^- \rightleftharpoons \text{Ti}^{2+}$	-0.9
$\text{TiO}_2 + 4 \text{H}^+ + 2 \text{e}^- \rightleftharpoons \text{Ti}^{2+} + 2 \text{H}_2\text{O}$	-0.502
$\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}$	+0.7996
$\text{Ag}_2\text{O} + \text{H}_2\text{O} + 2 \text{e}^- \rightleftharpoons 2 \text{Ag} + 2 \text{OH}^-$	+0.342
$\text{Ag}_2\text{S} + 2 \text{H}^+ + 2 \text{e}^- \rightleftharpoons 2 \text{Ag} + \text{H}_2\text{S}$	-0.0366
$\text{Pb}^{2+} + 2 \text{e}^- \rightleftharpoons \text{Pb}$	-0.1262
$\text{Sn}^{2+} + 2 \text{e}^- \rightleftharpoons \text{Sn}$	-0.1375
$\text{Sn}^{4+} + 4 \text{e}^- \rightleftharpoons \text{Sn}$	+0.151
$\text{SnO}_2 + 4 \text{H}^+ + 2 \text{e}^- \rightleftharpoons \text{Sn}^{2+} + 2 \text{H}_2\text{O}$	-0.094
$\text{SnO}_2 + 4 \text{H}^+ + 4 \text{e}^- \rightleftharpoons \text{Sn} + 2 \text{H}_2\text{O}$	-0.117
$\text{SnO}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^- \rightleftharpoons \text{Sn} + 4 \text{OH}^-$	-0.945
$\text{S} + 2 \text{e}^- \rightleftharpoons \text{S}^{2-}$	-0.4763

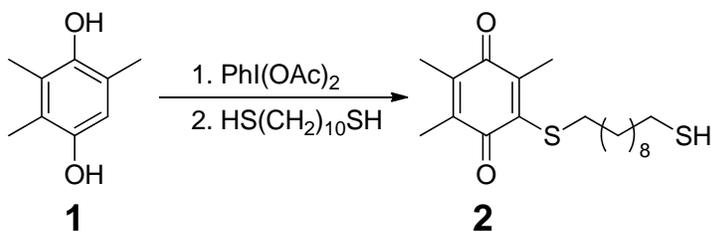
^a standard reduction potentials, with respect to the normal hydrogen electrode
($2 \text{H}^+ + 2 \text{e}^- \rightleftharpoons \text{H}_2$, $E^\circ = 0$) at 298.15 K (25°C) and 1 atm, in aqueous solution (pH 7)

Source: Vanýsek, Petr (2007). “Electrochemical Series”, in *Handbook of Chemistry and Physics*: 91st Edition (Chemical Rubber Company)

Characterization of Compounds. Figure S1 shows ^1H and ^{13}C NMR spectra for compounds **2** and **5**.



Menadione **4** (400 mg, 2.32 mmol, 1 equiv) and 1,10-decanedithiol (2.5 mL, 12 mmol, 5 equiv) were heated to 35°C in ethanol (30 mL) for 4 hours. The crude mixture was concentrated *in vacuo* and purified by flash column chromatography (CH_2Cl_2 :hexanes) to yield thiol **5** (100 mg, 11% yield). ^1H NMR (500 MHz, CDCl_3): δ 8.08-8.02 (m, 2H), 7.72-7.64 (m, 2H), 3.19 (t, 2H, $J = 7.3$ Hz), 2.50 (app q, 2H, $J = 7.3$ Hz), 2.34 (s, 3H), 1.63-1.54 (m, 4H), 1.43 – 1.20 (m, 13H). ^{13}C NMR (125 MHz, CDCl_3): δ 182.1, 181.2, 147.1, 146.4, 133.5, 133.2, 132.8, 132.0, 126.6, 126.5, 34.3, 34.0, 30.6, 29.3, 29.3, 29.0, 28.9, 28.5, 28.3, 24.6, 15.2. HRMS (EI) calc. for $[\text{C}_{21}\text{H}_{29}\text{O}_2\text{S}_2]^+$ ($\text{M}+\text{H}$) 377.1603, found 377.1595.



Hydroquinone **1** (0.76 g, 5.0 mmol, 1 equiv) was dissolved in methanol (30 mL) and treated with (diacetoxyiodo)benzene (1.61 g, 5.0 mmol, 1 equiv). After 5 minutes TLC analysis revealed complete conversion to the quinone. 1,10-decanedithiol (6.0 mL, 28

mmol, 5.5 equiv) was added and the mixture was stirred overnight at 35 °C. The crude mixture was concentrated *in vacuo* and purified by flash column chromatography (CH₂Cl₂:hexanes) to yield thiol **2** (550 mg, 31% yield). ¹H NMR (300 MHz, CDCl₃): δ 3.03 (t, 2H, *J* = 7.3 Hz), 2.51 (app q, 2H, *J* = 7.3 Hz), 2.20 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.65-1.48 (m, 5H), 1.42 – 1.20 (m, 12H). ¹³C NMR: δ 184.7, 183.4, 144.6, 143.6, 141.6, 140.8, 34.2, 34.0, 30.5, 29.3, 29.0, 29.0, 28.5, 28.3, 24.6, 14.7, 12.8, 12.5. HRMS (EI) calc. for [C₁₉H₃₁O₂S₂]⁺ (M+H) 355.1760, found 355.1750.

Multiple Comparison Test. We used statistical tests to determine the significance of the eleven values of *R* reported in this paper. Using t-tests in a pairwise fashion is problematic because i) it only allows the comparison of one value against another, not of one value against many other values, and ii) applying *n* successive t-tests at a confidence level of 95% yields a probability $1 - (0.95)^n$ of at least one type I error (rejecting a true null hypothesis). For *n* = 11, this probability is 43%. Using successive t-tests is, therefore, likely to find statistically significant differences where they do not exist. To correct this tendency, we used a multiple comparison test, which is similar to a t-test but adjusted to reduce the global probability of a type I error to the desired confidence level (5%, in our case). This multiple comparison test was implemented in MATLAB 7.10.0.499 (R2010a) using the “multcompare” function with Tukey’s honestly significant difference criterion.^{ref} This function is an extension of one-way analysis of variance (ANOVA). Figure S2 shows the results of this multiple comparison test: values of $\langle \log|r| \rangle$ (vertical lines) surrounded by 95% confidence intervals (horizontal lines). Any two values are statistically distinguishable from one another, at the 95% level, if and only

if their horizontal lines do not overlap. We defined a “molecular diode” as any compound with a value of $\langle \log|r| \rangle$ that was statistically distinguishable, at the 95% level, from *both* alkanethiols: $S(CH_2)_{10}CH_3$ and $S(CH_2)_{14}CH_3$ (indicated by arrows in the figure). The dotted lines in figure S2 show the range encompassed by the confidence intervals of both alkanethiols; a compound qualifies as a molecular diode if and only if the entire confidence interval on its value of $\langle \log|r| \rangle$ lies outside this range. The compounds that qualify as molecular diodes, by this criterion, are the three Fc-terminated compounds, as well as **5** (the naphthoquinone-terminated compound). The values of $\langle \log|r| \rangle$ for the other six compounds are not statistically distinguishable from each other, according to the multiple comparison tests.

Histograms of $\log|r|$ for all compounds appear in the main text of the paper. Figure S3 presents box-and-whisker plots – an alternative method for visualizing distributions of $\log|r|$ that affords an information-rich, side-by-side comparison of the distributions for all 11 compounds reported in this paper. The features of the box-and-whisker representation are described in the caption. A median not vertically centered between the quartiles (top and bottom of the box) implies skewness (departure from a normal distribution) in the distributions. Some of the distributions are slightly skewed, usually towards zero (no rectification). The notches in the boxes around the median represent the 95% confidence interval of the median; for any two boxes with non-overlapping notches, a t-test would show that they have statistically distinguishable medians, at the 95% level. Comparing the notches on the boxes suggests the tendency of pairwise t-tests to yield type I errors: almost every possible t-test would reject the null hypothesis, whereas the multiple comparison test in figure S2 is clearly more stringent.

Figure S1: ^1H NMR (A and C) and ^{13}C NMR (B and D) spectra for compounds **5** (A and B) and **2** (C and D).

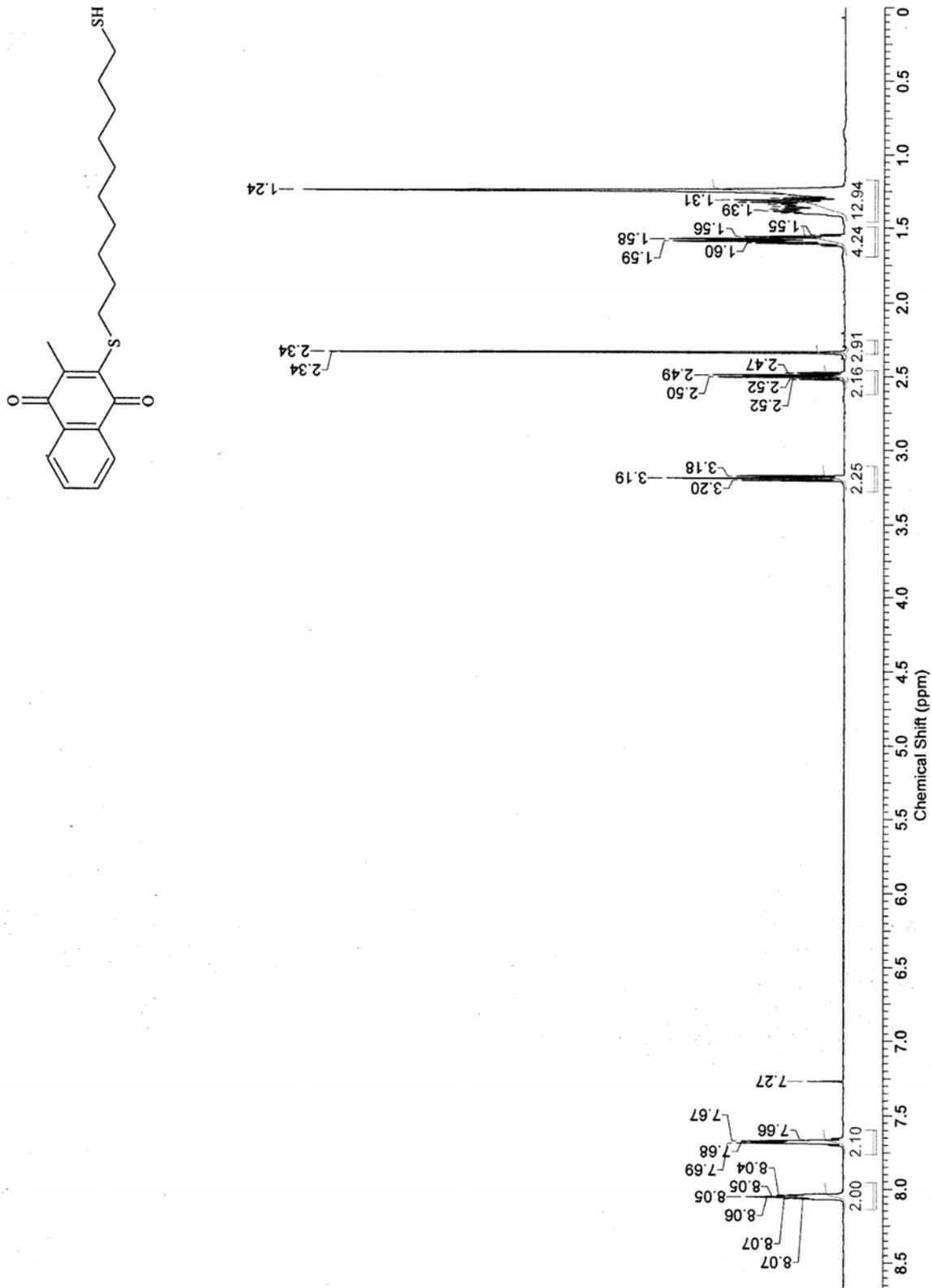


Figure S1A

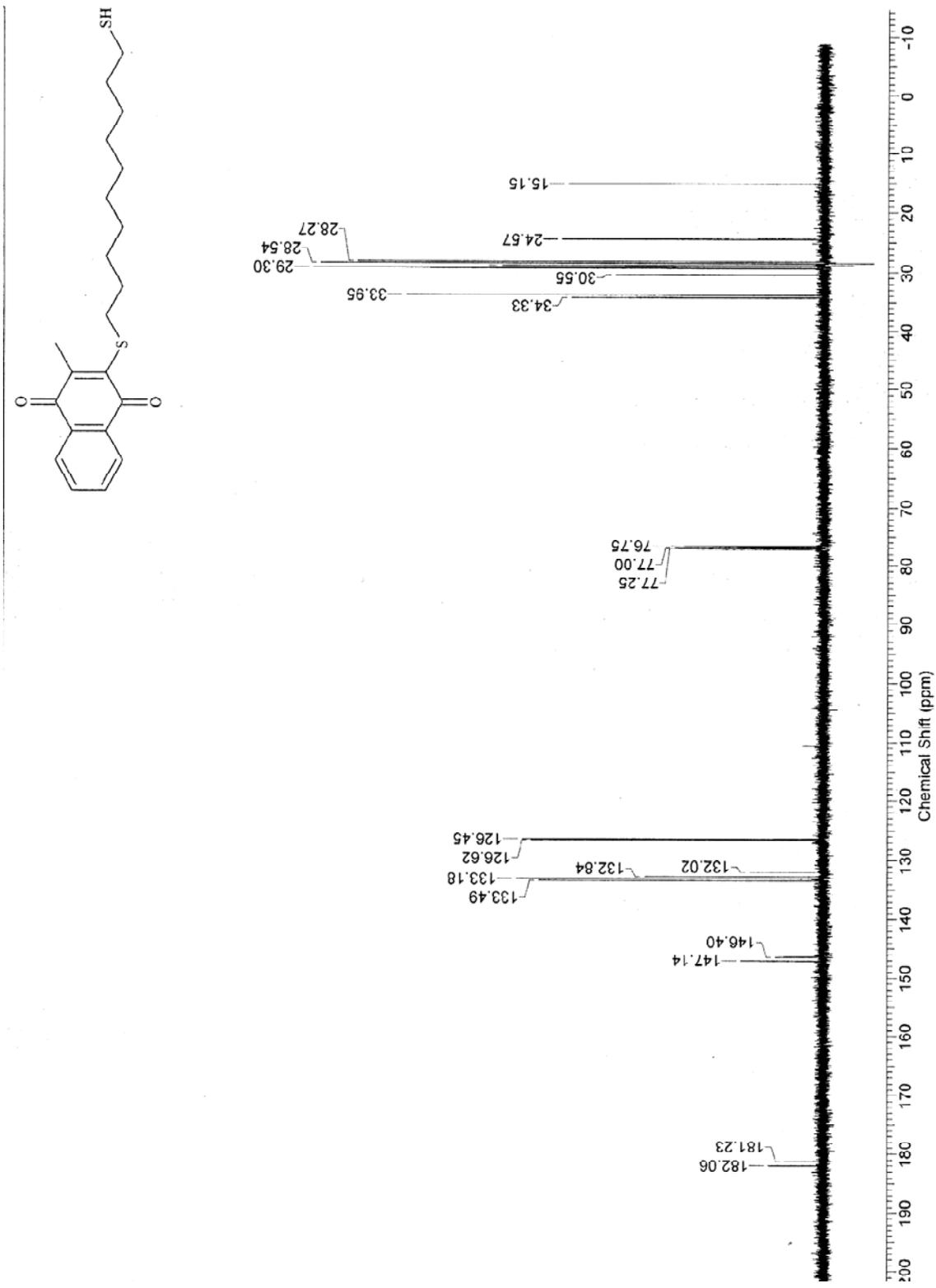


Figure S1B

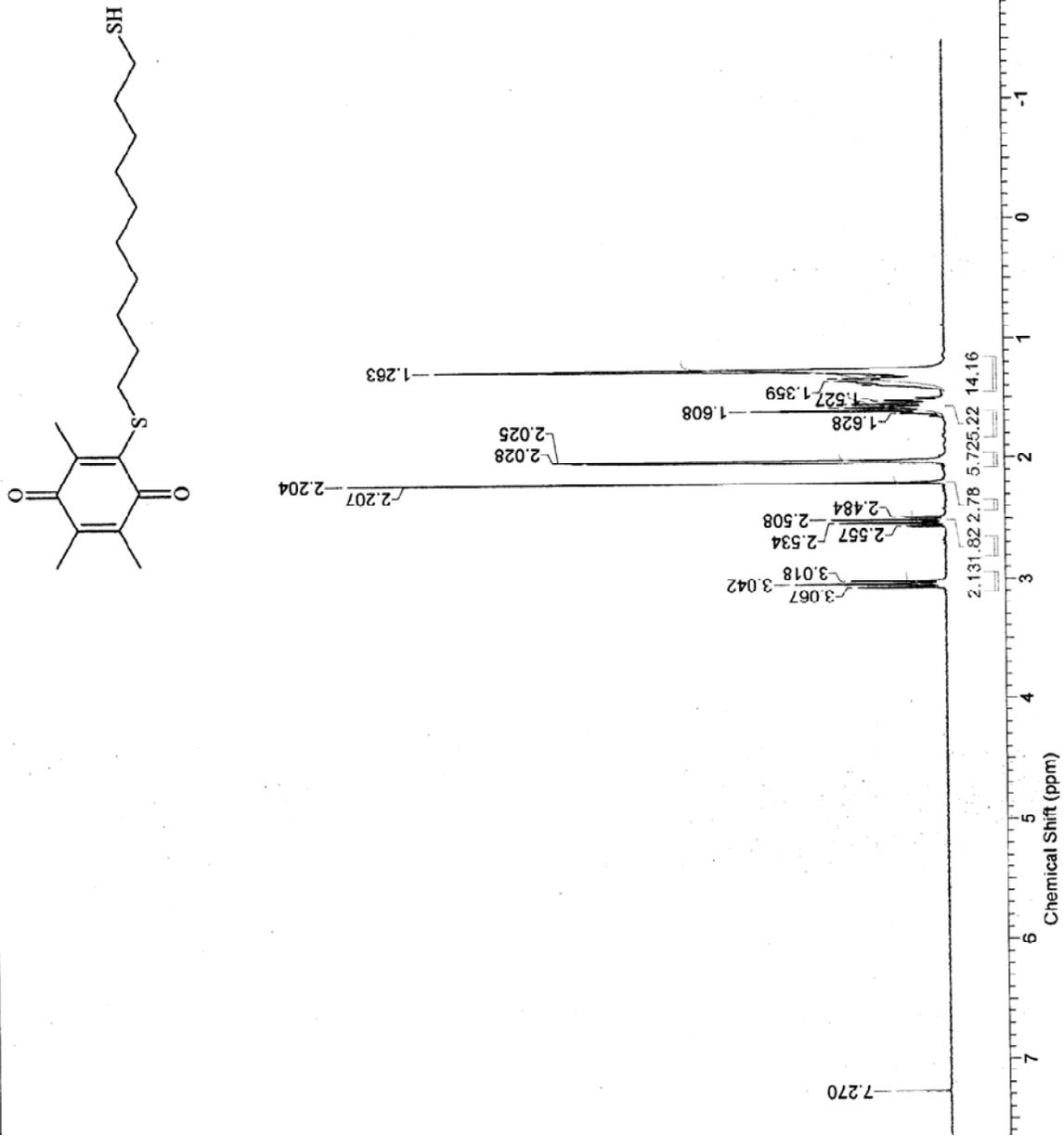


Figure S1C

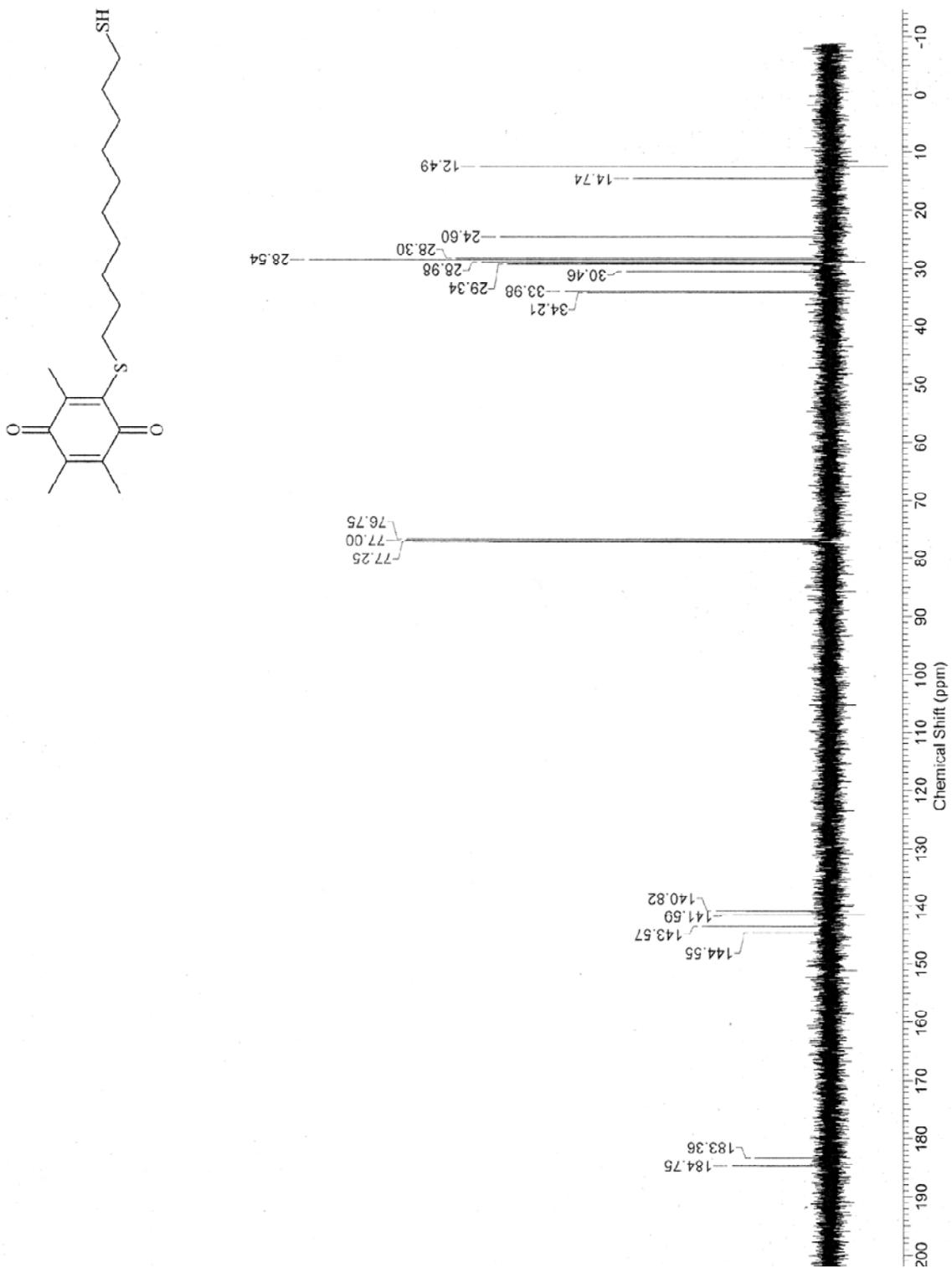


Figure S1D

Figure S2: A multiple comparison test on the distributions of $\log|r|$ for all ten SAMs reported in this paper. Vertical marks represent values of $\langle \log|r| \rangle$, and the horizontal lines on either side represent the 95% confidence interval for the value, according to this test. Vertical, dotted lines denote the range encompassing both of the confidence intervals of the alkanethiolate controls (themselves indicated by arrows).

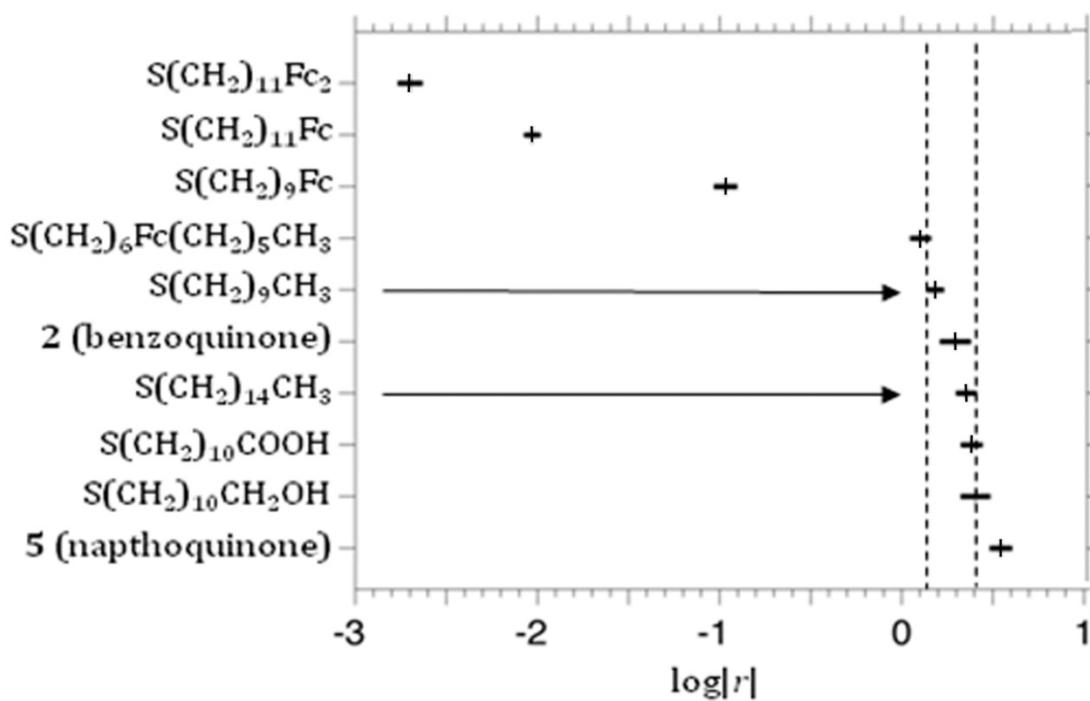


Figure S3: Box and whisker plots of $\log|r|$ for all 11 compounds reported in this paper. For each box and whisker plot, the features are: i) the red line in the middle of the box is the median of the data, ii) the top and bottom of the blue box are the quartiles (the 25th and 75th percentiles of the data), ii) the black whiskers terminate at the most extreme value less than 1.5 times the interquartile range (the height of the box) away from the box, iii) the red crosses are outliers (defined as lying beyond the cutoff for the whiskers), and iv) the width of the notches surrounding the median are the 95% confidence interval for the median.

