

Supporting Information:

Odd-Even Effects in Charge Transport Across Self-Assembled Monolayers.

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Experimental

Materials: All reagents were purchased from Aldrich and were used as supplied unless otherwise specified. All organic solvents were purchased from Aldrich (EtOAc, DCM, hexanes) or Fisher (diethyl ether, 200 proof ethanol) while water used in the synthesis was purified using a Millipore Q-POD water purification system. For the contact electrode, high purity eutectic gallium-indium (EGaIn) was obtained from Aldrich and used as supplied. All compounds (synthesized or commercially available) were purified by silica gel column chromatography (100% hexane by gravity elution). All

purified thiols were maintained under N₂ atmosphere and <4 °C, and purity was checked right before use (These precautions were necessary as primary thiols readily react in an O₂ atmosphere to give disulfides, sulfonates and sulfonic acids). To ensure purity, all stored compounds were checked by ¹H NMR before use and sample spectra of the compounds are attached (Figure S3-S6). All SAMs were prepared at ambient conditions as previously described.¹⁻³

Characterization: ¹H and ¹³C NMR spectra were recorded on a Bruker DPX 400 or a varian INOVA 500 instrument using CDCl₃ as solvent and TMS as an internal standard. All ¹H NMR spectral data was compared to literature and are attached (Figure S3-S6).

General procedure for the preparation of alkanethiols; 1-tridecanethiol: To a flask containing 50 mL EtOH was added 1-bromotridecane (1.03 g, 3.9 mmol) followed by thiourea (0.36 g, 4.7 mmol) dissolved in 50 mL EtOH. The reaction mixture was then heated to reflux for 12 h after which the solvent was removed *in vacuo* to give a residual oil. To this was added NaOH (0.47 g, 11.73 mmol) in 50 mL water and heated to reflux for 1 h. The reaction was then cooled to room temperature and extracted with 3 x 30 mL Et₂O. The ethereal extracts were dried over anhydrous MgSO₄, solvent was removed *in vacuo*, and the product was purified by passing through a silica gel column eluting with n-hexanes. The title compound was obtained from the second band eluting from the column after removing the solvent *in vacuo*. After purification, the product was stored under nitrogen at <4 °C and periodically checked for purity before use. The ¹H and ¹³C NMR data matched literature values.⁴ ¹H NMR (CDCl₃): δ 0.799 (t, 3H, *J* = 7.2 Hz), 1.176 – 1.266 (m, 20H), 1.524 (m, 2H), 2.44 (q, 2H, *J* = 7.2 Hz). ¹³C NMR

(CDCl₃): δ 14.11, 22.68, 24.66, 28.38, 29.08, 29.34, 29.51, 29.59, 29.64, 29.66, 31.91, 34.06.

1-Heptadecanethiol: Reaction of 1-bromoheptadecane according to the previous procedure gave the title compound. ¹H NMR (CDCl₃): δ 0.889 (t, 3H, $J = 7.2$ Hz), 1.263 (m, 28H), 1.566 (s, 1H), 1.577 – 1.66 (m, 2H), 2.53 (q, 2H, $J = 7.2$ Hz).

1-Nonadecanethiol: Reaction of 1-bromononadecane according to the procedure above gave the title compound. The ¹H NMR data matched literature values.⁴ ¹H NMR (CDCl₃): δ 0.888 (t, 3H, $J = 7.2$ Hz), 1.262 (m, 32H), 1.569 (s, 1H), 1.605 (m, 2H), 2.529 (q, 2H, $J = 7.2$ Hz).

1-Nonanethiol: Reaction of 1-bromononane according to the procedure above gave the title compound. The ¹H NMR data matched literature values.⁴ ¹H NMR (CDCl₃): δ 0.81 (t, 3H, $J = 7.2$ Hz), 1.2 – 1.32 (m, 12H), 1.472 (s, 1H), 1.535 (m, 2H), 2.451 (q, 2H, $J = 7.2$ Hz).

General procedure for the preparation of the SAM; undecanethiol: To a scintillation vial was added undecanethiol (3.5 μ L, 0.015 mmoles) in 5 mL EtOH (200 proof). The solution was sonicated for 5 mins, sealed and further degassed by bubbling nitrogen through the solution for *ca.* 3 mins. To the solution of alkanethiols was placed glass supported template stripped silver film (Ag^{TS}) with the exposed metal face up. The solution was then degassed by bubbling N₂ for 2 minutes and allowed to stand under an inert atmosphere for a further 3 h. The Ag^{TS} film with the SAM on it was removed from solution and rinsed by repeatedly dipping the chip into clean EtOH. The solvent on the SAM was then gently evaporated by gently blowing a stream of nitrogen over chip. Measurements on the chip were then taken in less than 2.5 h after the SAM formation.

All other SAMs were prepared in a similar manner.

Electrical measurements; i). *Tip formation:* To generate a fine conical tip from EGaIn for use as a top contact, a 10 μL gas-tight syringe was filled with EGaIn (\geq 99.99%, Aldrich). A drop of EGaIn was then pushed to the tip of the syringe needle and the hanging drop was brought into contact with a surface on which the EGaIn would stick (e.g. an oxidized Ag surface) and the needle gently pulled away from the drop using a micromanipulator. This generates an hour-glass shape as previously described.¹ Upon breaking from the bulk EGaIn on the surface, a fine conical shaped tip is obtained.

Electrical measurements; ii). *Junction formation and measurements:* To form a molecular tunnel junction, the SAM is gently brought into contact first with the gold metal electrode. Then using a micromanipulator, the EGaIn tip is gently brought into contact with its own reflection on the Ag surface, at which point a conformal contact has been established between the SAM and the EGaIn tip. The contact area is derived from measuring the diameter of the contact area at high magnification. Assuming a circular contact, the area is derived from the measured diameter from which the current densities are calculated. The contact and presence of a SAM is confirmed by running a single scan after which 20 more scans are run if there is indication of contact and tunneling. At least 10 junctions were formed per molecule studied and each SAM was randomly sampled. The total number of working junctions versus those that shorted was used to calculate the yield.

Table S1. Results of Student t-tests Comparing the Population Means of Adjacent Odd and Even Alkanethiols (Supplemental)

Comparison	<i>p</i> value	Inference
SC₉ vs. SC₁₀	<<0.001	$\mu_{SC9} > \mu_{SC10}$
SC₁₀ vs. SC₁₁	<<0.001	$\mu_{SC10} > \mu_{SC11}$
SC₁₁ vs. SC₁₂	<<0.001	$\mu_{SC11} < \mu_{SC12}$
SC₁₂ vs. SC₁₃	<<0.001	$\mu_{SC12} > \mu_{SC13}$
SC₁₃ vs. SC₁₄	<<0.001	$\mu_{SC13} > \mu_{SC14}$
SC₁₄ vs. SC₁₅	<<0.001	$\mu_{SC14} > \mu_{SC15}$
SC₁₅ vs. SC₁₆	0.75	$\mu_{SC15} \approx \mu_{SC16}$
SC₁₆ vs. SC₁₇	<<0.001	$\mu_{SC16} > \mu_{SC17}$
SC₁₇ vs. SC₁₈	<<0.001	$\mu_{SC17} < \mu_{SC18}$

Table S2: Comparison of $\log(|J|)$ at $V = -0.5$ V for SC₁₈ Across Multiple Users

User	$\mu_{\log} \pm \sigma_{\log}$ (calculated) ^a	$\mu_{\log} \pm \sigma_{\log}$ (Gaussian) ^b	Comparison	<i>p</i> -value
1	-4.28 ± 1.1	-4.65 ± 0.61	1 vs. 2	0.157
2	-5.45 ± 0.58	-5.44 ± 0.41	2 vs. 3	$\ll 0.001$
3	-5.23 ± 1.0	-5.24 ± 0.97	1 vs. 3	0.157

^a Calculated by taking the arithmetic average and standard deviation of $\log(|J|)$ after excluding shorts.

^b The parameters of the Gaussian function that was the least-squares fit to the histogram of $\log(|J|)$. No data were excluded.

Figure S1: Proton and ^{13}C NMR spectra for tridecanethiol.

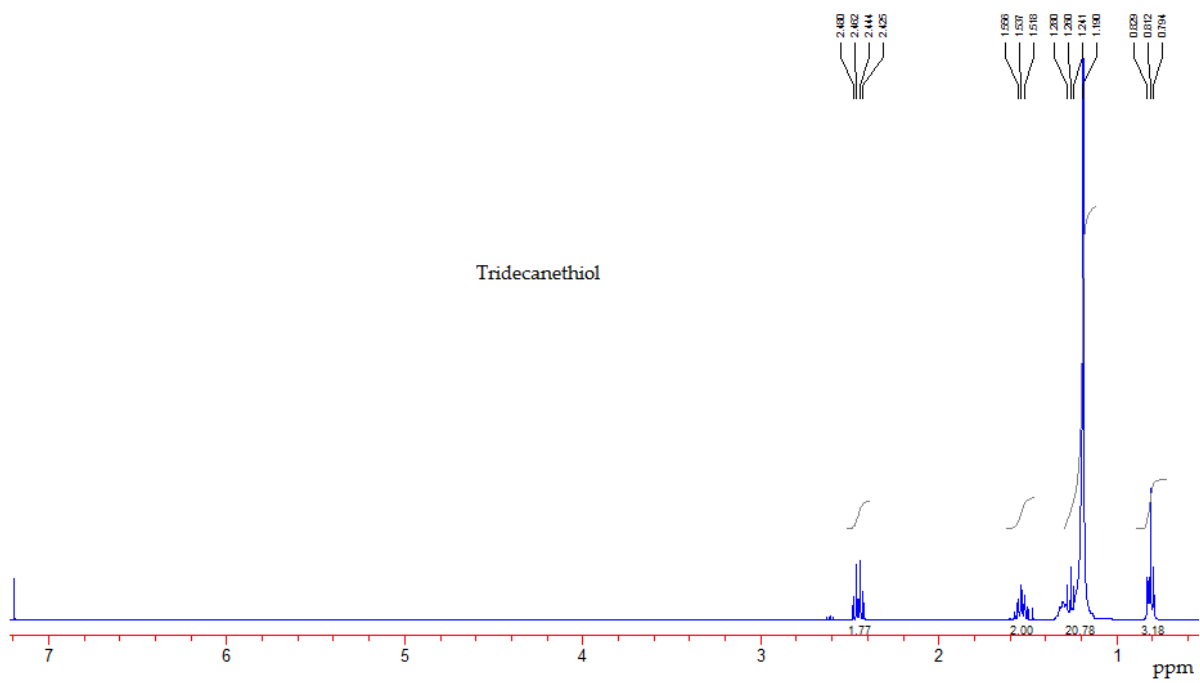


Figure S2: Proton NMR spectra for nonanethiol.

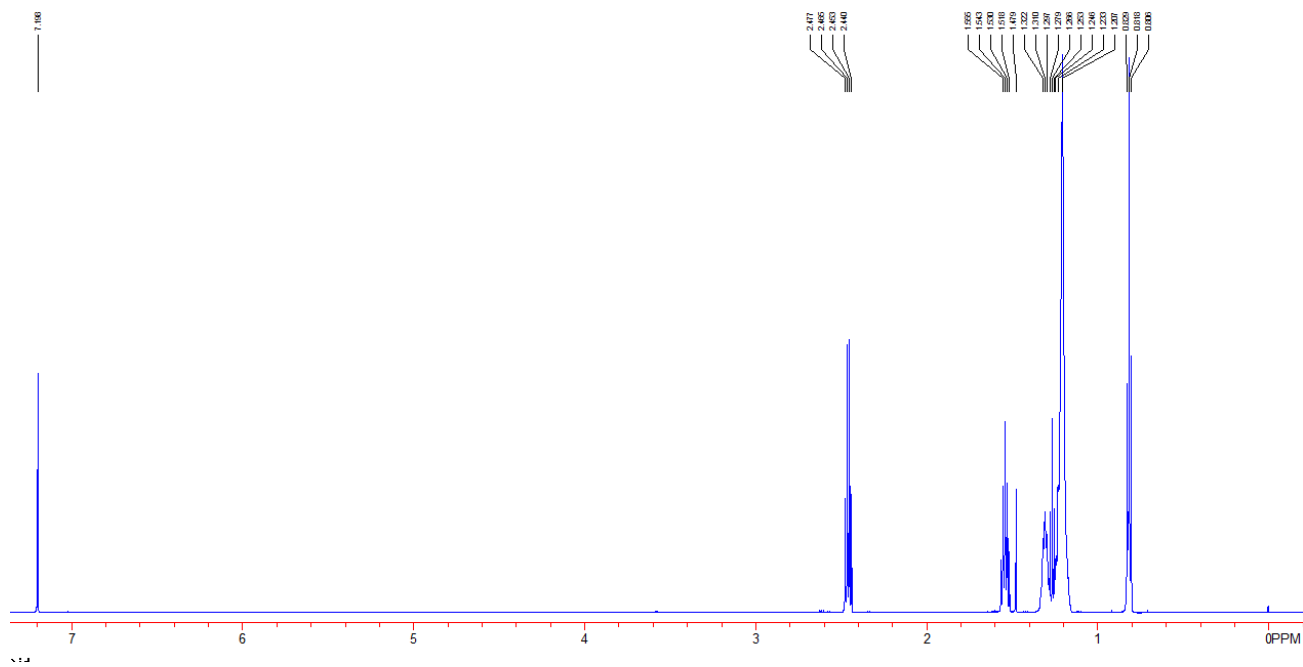


Figure S3: Proton NMR spectra for heptadecanethiol.

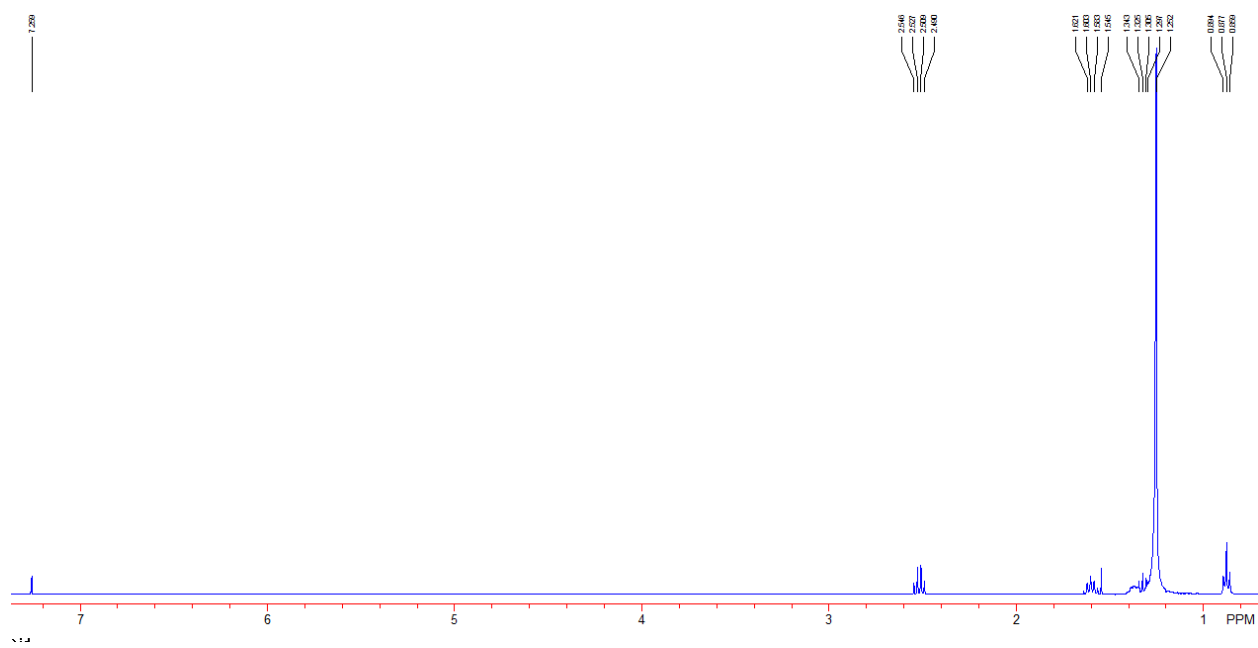


Figure S4: Proton NMR spectra for nonadecanethiol.

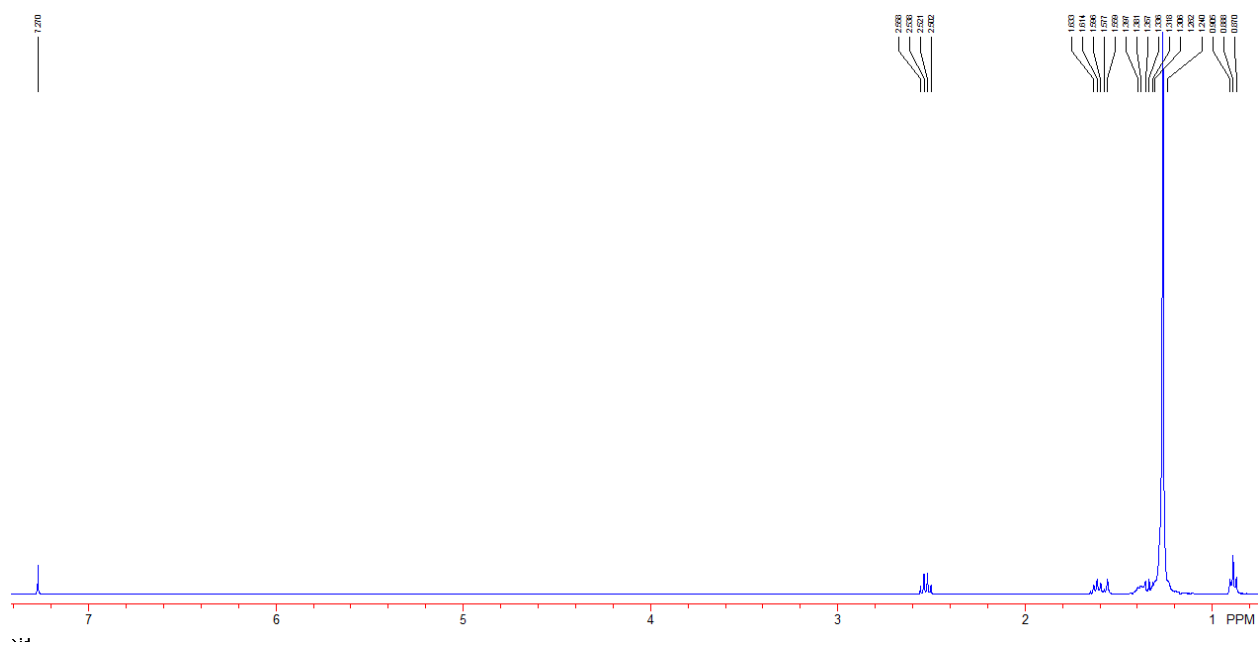
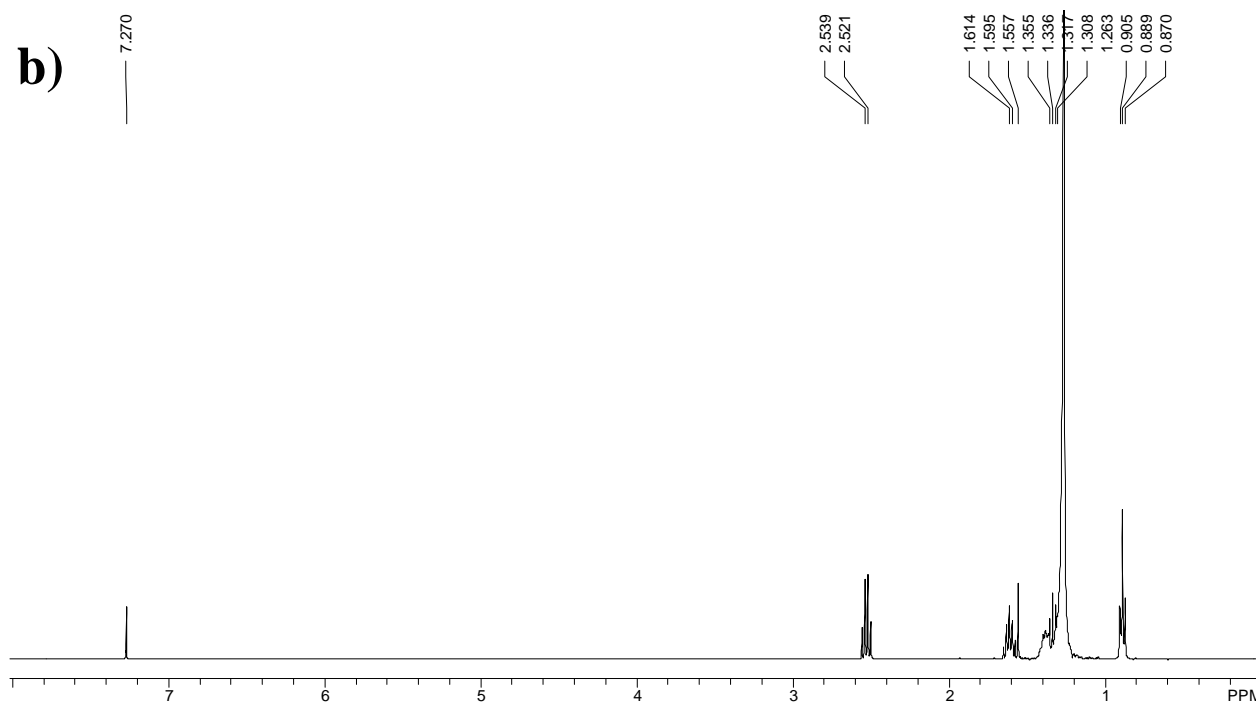
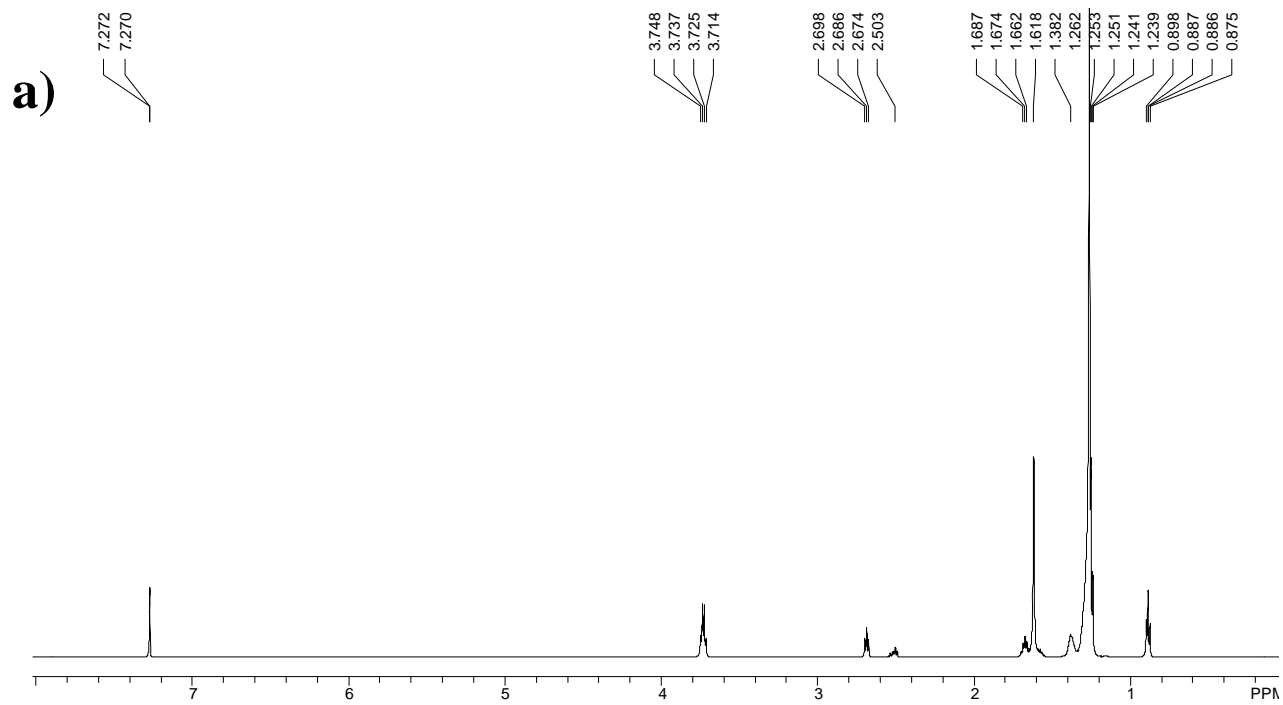


Figure S5: Proton NMR spectra for the commercially available hexadecanethiol before and after purification to illustrate the effect of storage at ambient conditions. a). Proton Nmr spectra from a sample of the hexadecane thiol after standing sealed for over a month at room temperature. Peak at 2.7 ppm and 3.7 ppm are characteristic of the disulfide and sulfur oxides respectively. b). upon purification by column chromatography, the thiol is obtained as characterized by the peak at 2.5 ppm and absence of the downfield peaks. Spectra were obtained in CDCl₃ with TMS as an internal standard.



Refs

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