

Supporting Information for:

**Electron Transfer through Surface-Grown,
Ferrocene-Capped Oligophenylene Molecular Wires (5–50 Å)
on *n*-Si(111) Photoelectrodes**

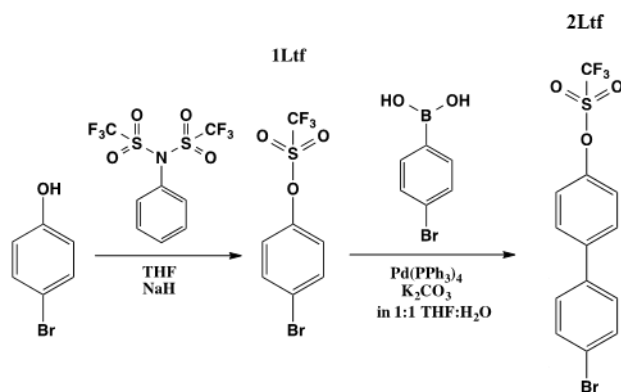
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Experimental

Chemicals and Materials. *n*-Type Si(111) oriented wafers (Cz grown, single-side polished, 350 μm thickness, 1-10 $\Omega\cdot\text{cm}$) were purchased from Virginia Semiconductor. Etching procedures were performed using buffered $\text{HF}_{(\text{aq})}$ and 11 M $\text{NH}_4\text{F}_{(\text{aq})}$ (semiconductor grade, Transene). All solvents were purchased as HPLC-grade and purified over alumina with a Pure Process Technology solvent purification system. Nanopure deionized water having a resistivity of 18 $\text{M}\Omega\cdot\text{cm}$ or higher (Barnstead Nanopure Systems) was used in all procedures involving wafer surfaces.

Synthesis of Phenylene Wires



Scheme S1. Synthetic scheme of triflate-phenylene wires.

4-Bromophenyl trifluoromethanesulfonate (1Ltf): Sodium hydride (1.40 g, 58.33 mmol), 4-bromophenol (6.055 g, 35.0 mmol), and N-phenyl-bis(trifluoromethanesulfonimide) (13.75 g, 38.5 mmol), were each dried in Schlenk flasks under vacuum for 20 minutes. All three were then separately dissolved in dry THF. The 4-bromophenol/THF solution was added via cannula to the NaH/THF Schlenk flask at 0 $^{\circ}\text{C}$. Next, the N-phenyl-bis(trifluoromethanesulfonimide)/THF solution was added via cannula to the NaH/THF solution at 0 $^{\circ}\text{C}$. The reaction was stirred at 0 $^{\circ}\text{C}$ for 10 minutes, then stirred at room temperature for 30 minutes. The reaction was refluxed

overnight. After reflux the reaction was quenched with water and extracted three times with DCM. The organic layers were collected and washed with saturated sodium bicarbonate, water, and then brine. The solution was then dried by sodium sulfate for two hours. It was then filtered and the solvent was removed, which afforded 10.67 g of clear oil, for a ~100% yield. ^1H NMR (400 MHz, CDCl_3): δ 7.60 (t, 1H), 7.57 (t, 1H), 7.18 (t, 1H), 7.16 (t, 1H). ^{13}C NMR (CDCl_3): δ 148.6, 133.6, 123.2, 122.2. ^{19}F NMR (CDCl_3): δ -72.694. HRMS (CI): m/z calculated for $\text{C}_7\text{H}_4\text{O}_3\text{SBrF}_3$ (^{79}Br) 303.9017, ($^{79}\text{Br} + \text{H}$) 304.9095, (^{81}Br) 305.8996, and ($^{81}\text{Br} + \text{H}$) 306.9074; found, 303.9017, 304.9094, 305.9005, and 306.9072 respectively.

4'-Bromo-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (2Ltf): A solution of 1:1 THF:H₂O was added to a Schlenk flask, 3 g of 4-bromophenyl trifluoromethanesulfonate (9.83 mmol) was dissolved and the solution was bubbled with nitrogen gas for 30 minutes. Then 2.37 g of 4-bromophenylboronic acid (11.8 mmol) was added slowly followed by anhydrous potassium carbonate (2.72 g, 19.67 mmol) and a solution of $\text{Pd}(\text{PPh}_3)_4$ in THF (0.113 g, 1% mmol) that was taken directly out of a dry box. The reaction was refluxed at 70 °C overnight. The solution was then cooled and immediately filtered before quenching with brine. The solution was extracted into DCM and dried in anhydrous sodium sulfate for 2 hours. The sodium sulfate was removed by filtration and then the solvent was removed to afford a yellow/white milky substance. Column chromatography in 10:1 hexanes:DCM yielded 0.774 g of a white powder, a 20.64% yield. ^1H NMR (400 MHz, CDCl_3): δ 7.60 (m, 4H), 7.43 (t, 1H), 7.41 (t, 1H), 7.36 (t, 1H), 7.34 (t, 1H). ^{13}C NMR (CDCl_3): δ 149.3, 140.6, 138.3, 133.6, 132.3, 128.9 (d), 122.7, 122.0. ^{19}F NMR (CDCl_3): δ -72.767. HRMS (CI): m/z calculated for $\text{C}_{13}\text{H}_8\text{O}_3\text{SF}_3\text{Br}$ (^{79}Br) 379.9330, ($^{79}\text{Br} + \text{H}$) 380.9408,

(^{81}Br) 381.9309, and ($^{81}\text{Br} + \text{H}$) 382.9387; found, 379.9329, 380.9405, 381.9319, and 382.9383 respectively.

Preparation and Surface Treatment of Silicon Substrates

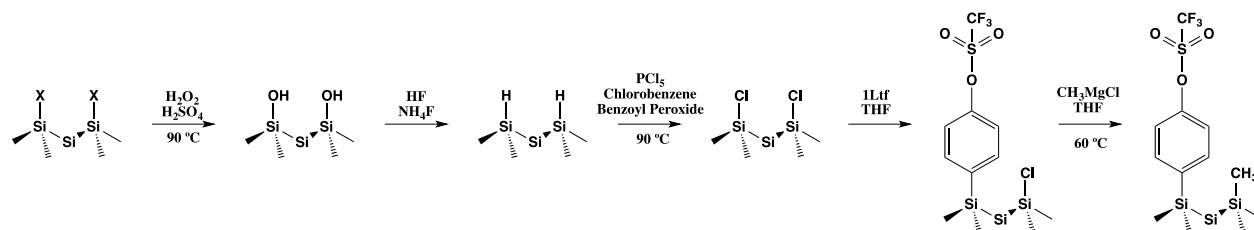
Oxidation and Removal of Organic Contaminants from Si Surfaces. Si(111) wafers were cut to the desired size and then rinsed with water, methanol, and acetone. The samples were dried under a stream of N_2 . Hot piranha acid (1:3, 30% $\text{H}_2\text{O}_{2(\text{aq})}$ /18 M H_2SO_4 , 90 °C for 10 min) was used to remove surface organic contaminants. The wafers were then rinsed with copious amounts of water and dried under N_2 . The samples were HF-etched immediately after cleaning with the Piranha solution.

Anisotropic Etching to Form Atomically Flat Si(111)-H. Si(111) samples were submerged for 10 s in buffered $\text{HF}_{(\text{aq})}$. The solution was drained, and excess HF was rinsed away with water. The substrates were submerged for 20 min in an 11 M $\text{NH}_4\text{F}_{(\text{aq})}$ solution that was previously degassed by bubbling with N_2 for 30 min. During submersion, the samples were agitated occasionally to remove bubbles from the surface of the wafer. They were then removed from the NH_4F solution, rinsed thoroughly with water, and dried under a stream of $\text{N}_{2(\text{g})}$. Within several minutes of etching, the freshly prepared Si(111) surfaces were introduced into a N_2 atmosphere glovebox.

Preparation of Chlorine-terminated Si(111) Surface. The chlorine-terminated Si(111) surface was prepared by a previously described procedure using PCl_5 . A solution of PCl_5 , in chlorobenzene solvent with a trace amount of benzoyl peroxide as a reaction initiator, was added to a hydrogen-terminated Si(111) wafer in an inert atmosphere glovebox. The entire reaction was placed in an oil bath at 90 °C for 1 hour.

The chlorine-terminated surface was removed from the solution and rinsed with dry chlorobenzene and THF.

Attachment of Wires to the Si(111) Substrate

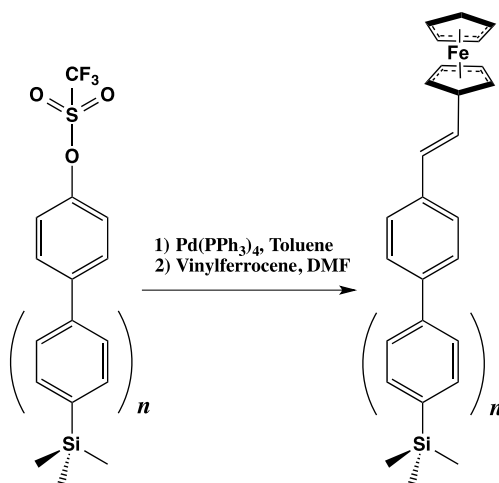


Scheme S2. Attachment of lithiated linkers to Si(111) and subsequent passivation by methylations.

First, n-type silicon(111) wafers were cut and sonicated in water, methanol, and acetone for 10 minutes each. The wafers were submerged in piranha acid (1:3 30% H_2O_2 :18 M H_2SO_4) at 90 °C for 10 minutes, then immediately rinsed with water and etched in hydrofluoric acid for 20 seconds. The wafers were submerged in 11 M dry NH_4F (dried by N_2 bubbling for 30 minutes) for 30 minutes and bubbled under N_2 gas to obtain a hydrogen-terminated surface. After that, they were quickly rinsed with water and dried in a stream of N_2 gas, then placed inside a pressure vessel that was purged with N_2 and taken into a flushbox. The wafers were submerged in a solution of PCl_5 in chlorobenzene, with a trace amount of reaction initiator, benzoyl peroxide, for 50 minutes at 90 °C to obtain a chlorine-terminated surface. Separately, 32 mg (0.084 mmol) of **2Ltf** in dry THF was cooled to -80 °C in a dry ice/acetone bath, and 50 μL of 1.6 M n-BuLi (0.08 mmol) was added; the reaction was allowed to lithiate for 30 minutes. The wafers in the box were rinsed with chlorobenzene and then THF; next they were transferred

out of the flush box, into the solution with the lithiated wires, and the attachment reaction was slowly warmed to room temperature over 2.5 hours. To passivate remaining chlorine-terminated sites with methyl groups, the wafers were transferred back into the flushbox and rinsed with THF. The wafers were submerged in 1:1 THF:1.0 M CH_3MgCl in a sealed pressure vessel at 60 °C for 3 hours. The wafers were then exposed to air and sonicated in THF, methanol, and water for 10 minutes each, then dried with a stream of N_2 gas.

Coupling of Vinylferrocene to the Surface-Attached Wire

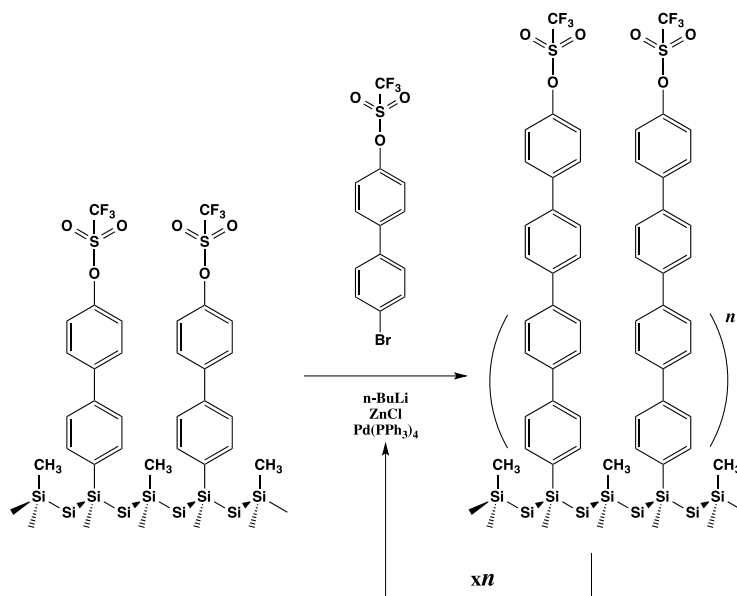


Scheme S3. Heck-coupling scheme.

To convert the triflate-functionalized wires to ferrocene-functionalized wires, a Heck-coupling reaction was performed in a dry box. First the wafers were submerged in a solution of 5 mg/mL $[\text{Pd}(\text{PPh}_3)_4]$ in toluene for 3 hours that was kept in the dark. The wafers were rinsed with toluene and then DMF. They were then submerged in a solution of 10 mM vinylferrocene in DMF in a sealed pressure vessel and heated to 100 °C and allowed to react overnight to obtain

ferrocene-functionalized wires (**2LFc**). Lastly, the wafers were exposed to air and sonicated in water, methanol, and acetone for 10 minutes each.

Growth of Phenylene Wires on the Surface



Scheme S4. Synthetic scheme for growing wires on the surface.

The wires were grown on the surface using a Negishi coupling: 1 equivalent of the **2Ltf** wire was dissolved in dry THF and cooled to -80 °C in an acetone/dry ice bath, to which 1 equivalent of 1.6 M $n\text{-BuLi}$ and 1.5 equivalents of ZnCl_2 were added, this was stirred for 30 min. The reaction was then allowed to warm to room temperature, and the solution allowed to react for 1 hour. At the same time, the silicon surface with n number of phenylenes attached (i.e. **2LFc**, **4LFc**, etc.) was immersed in a solution of $\text{Pd(PPh}_3)_4$ in THF in a glove box. This reaction was protected from light and was allowed to react for 3 hours. The surface was then transferred into the solution with the **2Ltf** wire and was reacted overnight at room temperature. The wafers were then exposed to air

and sonicated in THF, methanol, and water for 10 minutes each, then dried with a stream of N₂ gas.

Physical Measurements

Surface Characterization Methods. X-ray photoelectron spectroscopy data was acquired using a Kratos Axis Ultra XPS fitted with an Al-K α X-ray source. The pressure in the acquisition chamber was on the order of 10⁻⁹ torr and electrons were collected perpendicular to the surface. Region scans were taken in one spot for carbon, silicon, and iron on each surface. Electrochemical measurements were carried out using a functionalized Si(111) substrate as working electrode (electrode area: 0.44 cm², defined by the O-ring between working electrode and electrolyte), a Pt wire counter electrode, and a Ag wire reference electrode; degassed (N₂) 1 M LiClO₄/CH₃CN electrolyte solution was used in a one-compartment cell. Substrates were illuminated with an Oriel 150 W light source fitted with an AM 1.5 filter, with an intensity at the sample of 100 mW/cm² (1 sun). Dark measurements were performed as control for each substrate (< 1 μ A dark current). Cyclic voltammetry data was obtained using a Pine Wavenow potentiostat driven by AfterMath software v1.2.5033.

Synthetic Data (ensuing pages):

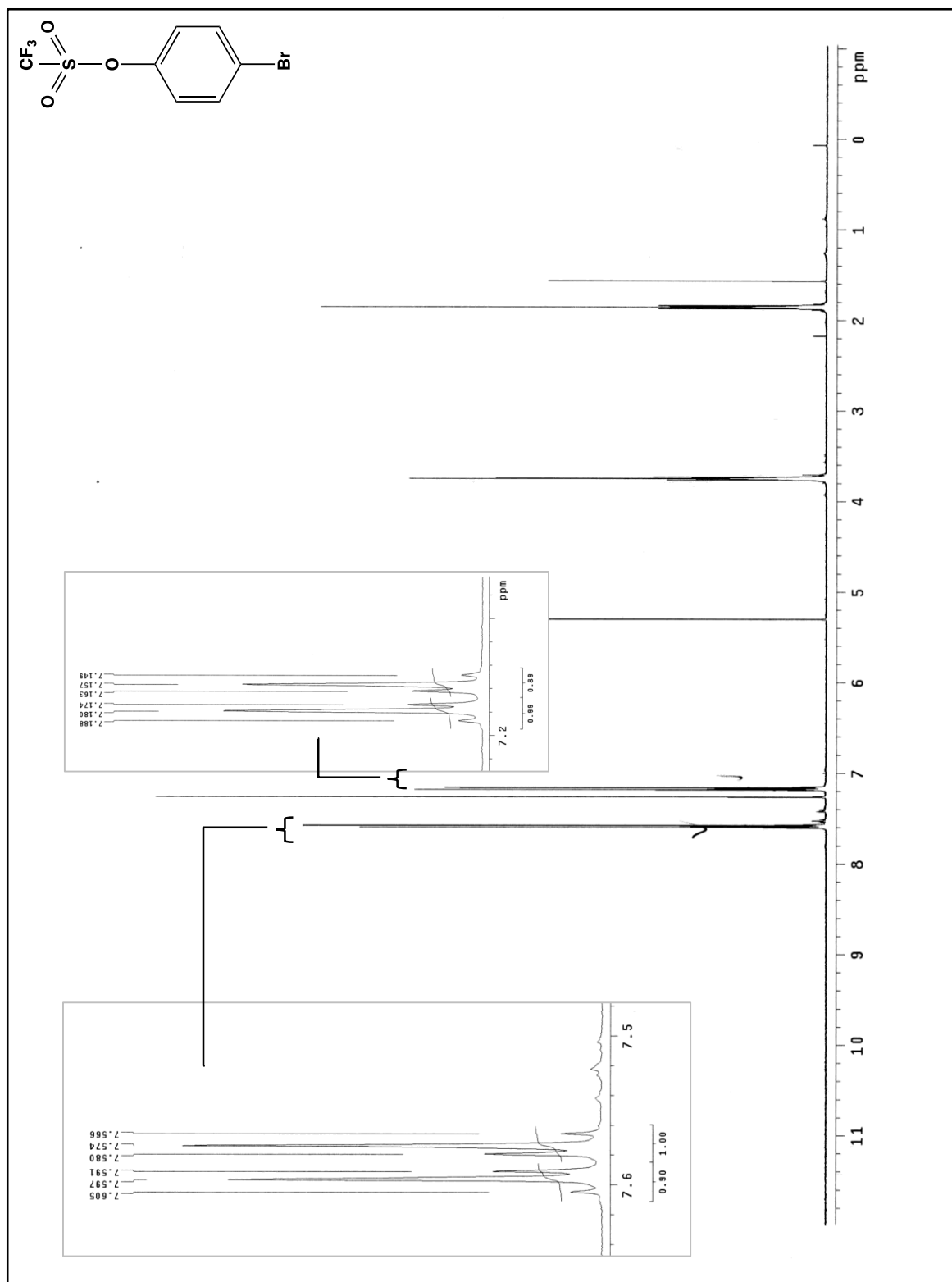


Figure S1. ¹H NMR for **1Ltf** (CDCl₃, 400 MHz).

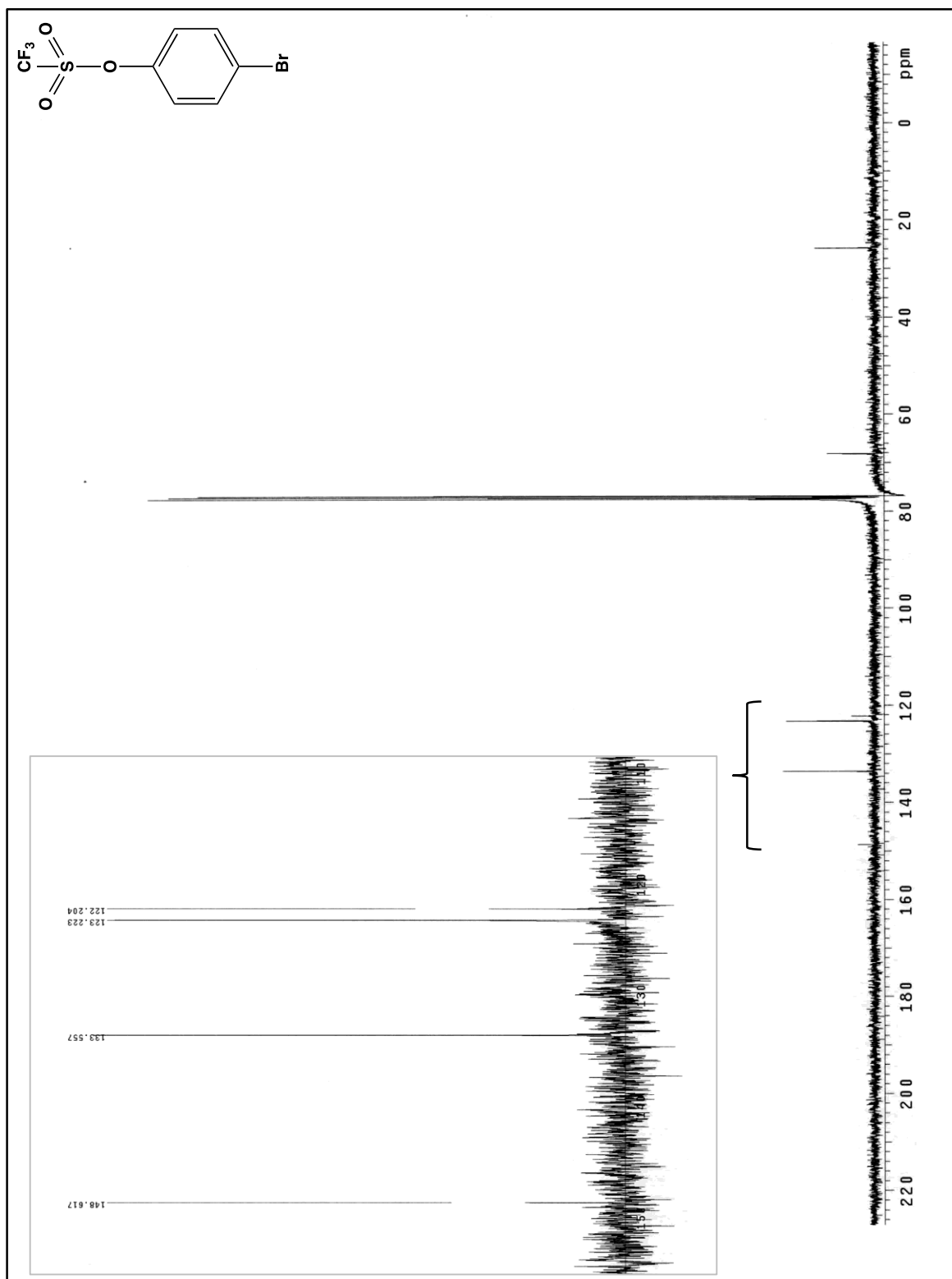


Figure S2. ^{13}C NMR for **1Ltf** (CDCl₃).

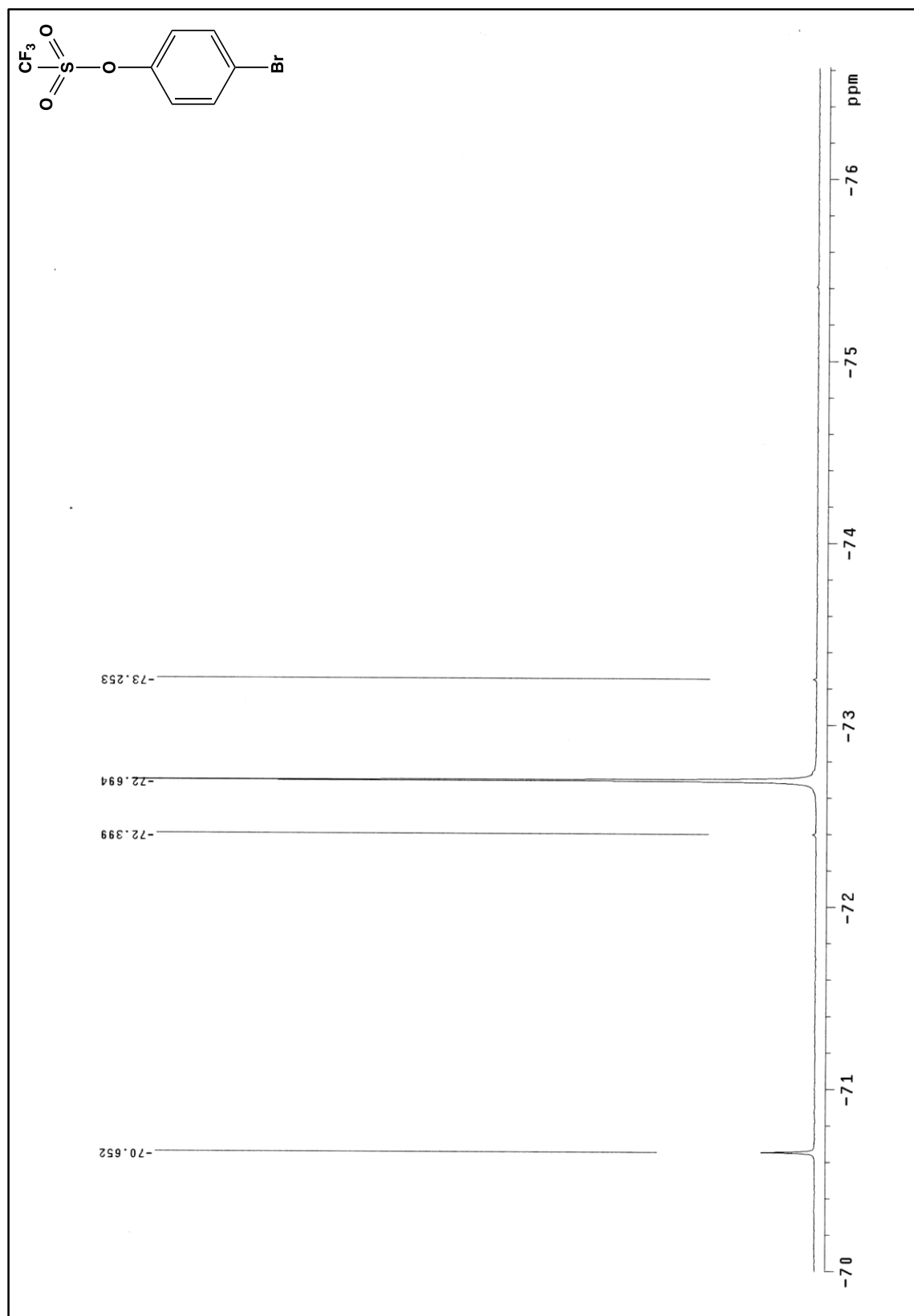


Figure S3. ^{19}F NMR for **1Ltf** (CDCl_3).

Multiple Mass Analysis: 5 mass(es) processed - displaying only valid results

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

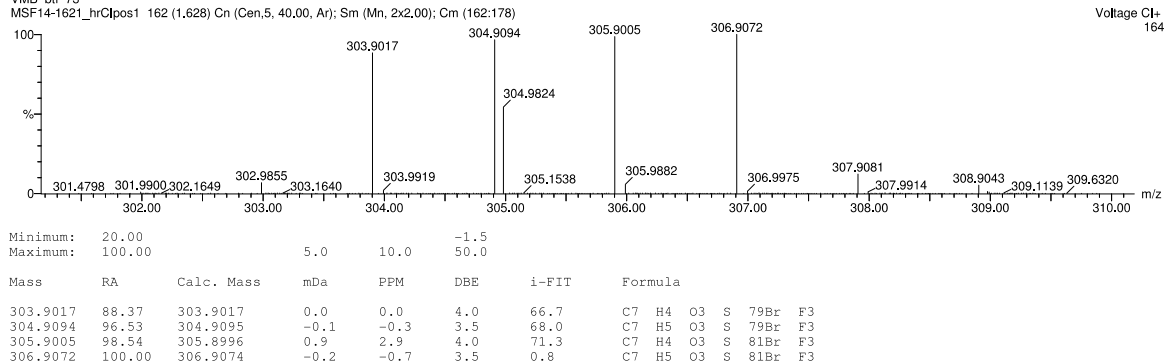
40 formula(e) evaluated with 4 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 O: 3-3 S: 1-1 79Br: 0-10 81Br: 0-10 F: 3-3

VMB btf 73

MSF14-1621_hrClpos1 162 (1,628) Cn (Cen,5, 40,00, Ar); Sm (Mn, 2x2,00); Cm (162:178)

**Figure S4. CI-HRMS for 1Ltf.**

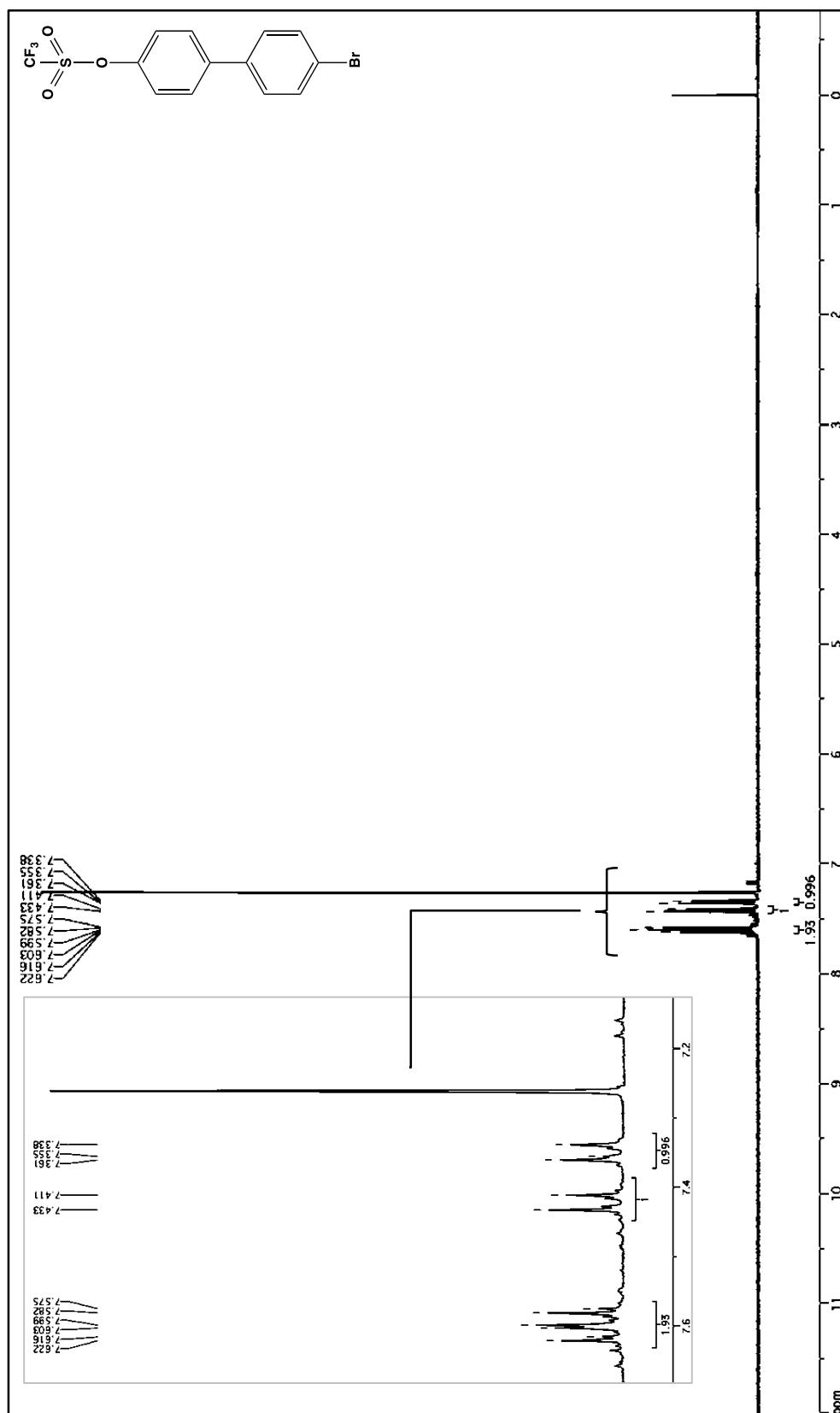


Figure S5. ¹H NMR for **2Ltf** (CDCl₃, 400 MHz).

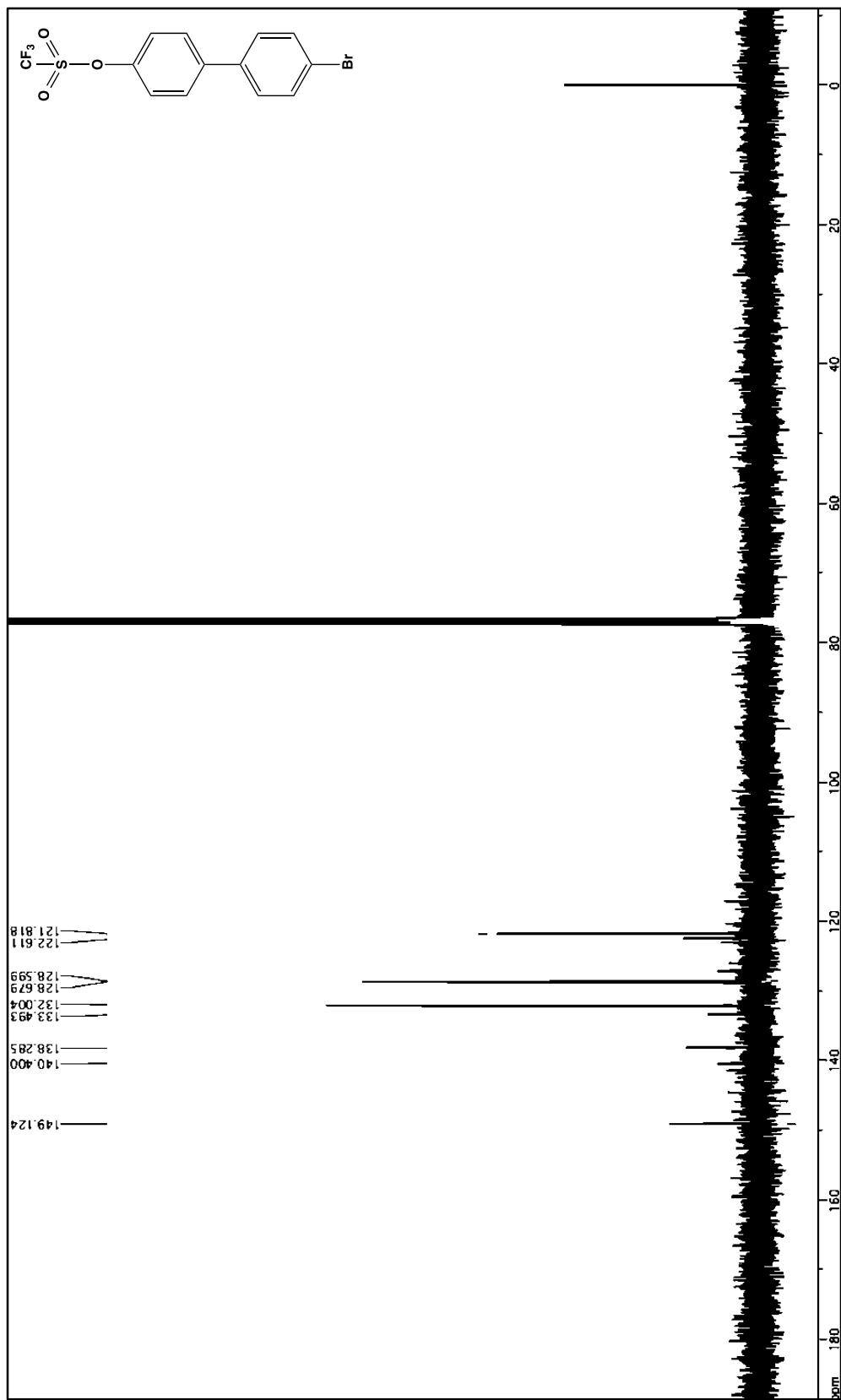


Figure S6. ¹³C NMR for **2Ltf** (CDCl₃).

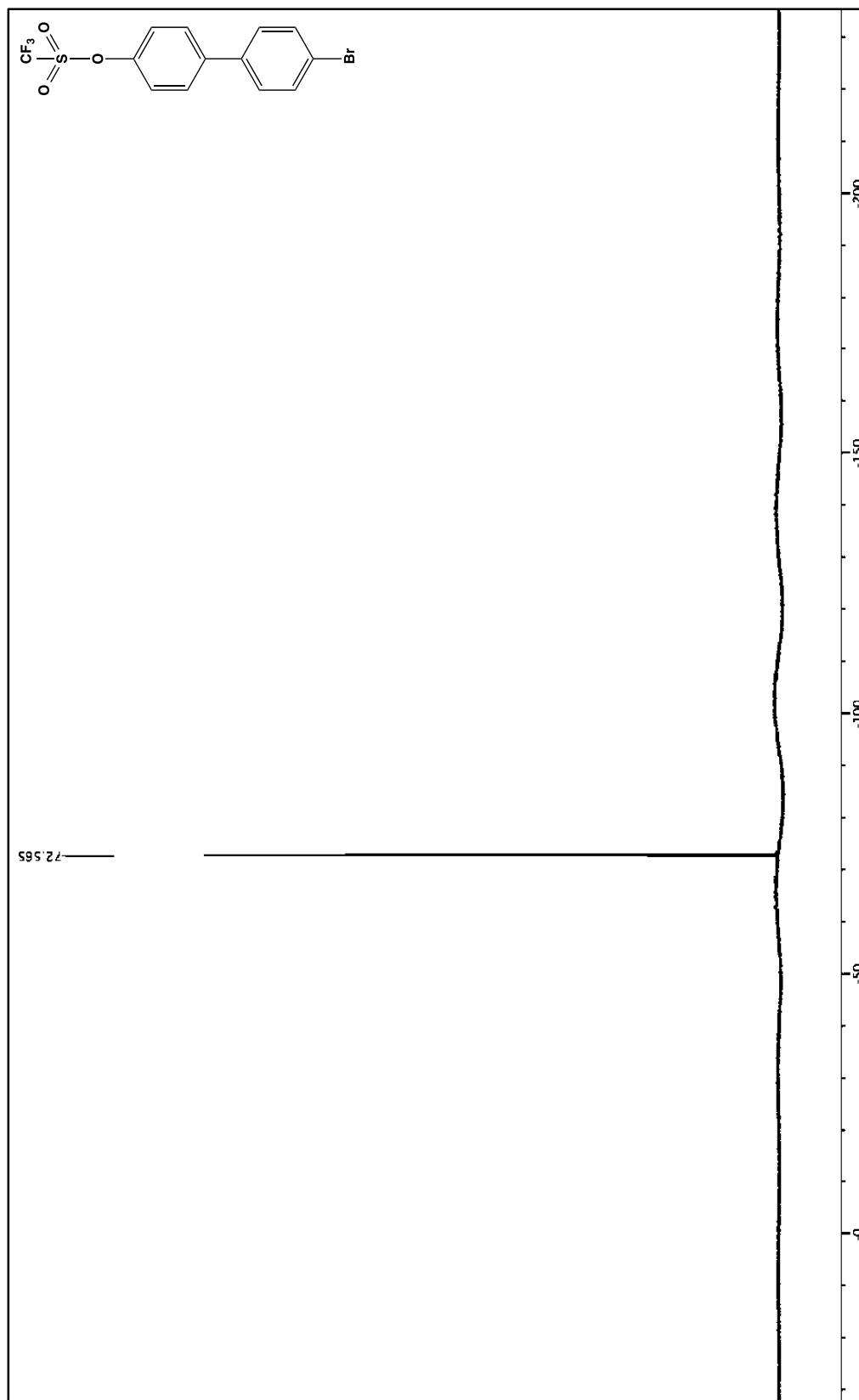


Figure S7. ^{19}F NMR for **1Ltf** (CDCl₃).

Multiple Mass Analysis: 8 mass(es) processed - displaying only valid results

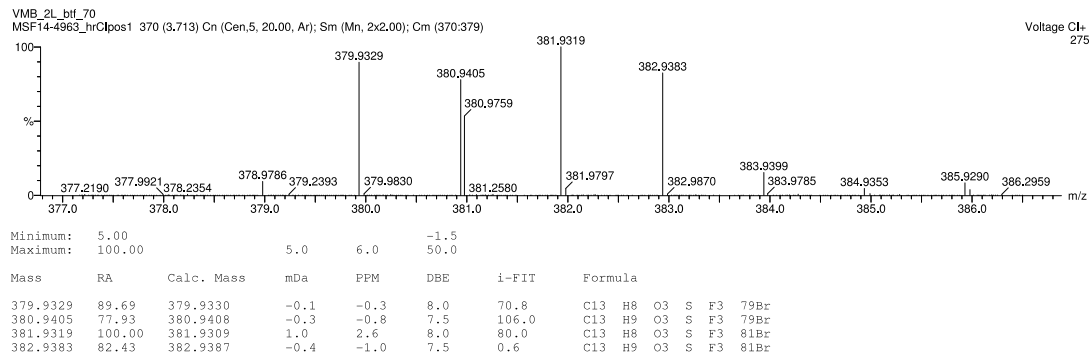
Tolerance = 6.0 PPM / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

133 formula(e) evaluated with 4 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 O: 3-3 S: 1-1 F: 3-3 ⁷⁹Br: 0-10 ⁸¹Br: 0-10**Figure S8. CI-HRMS for 2Ltf.****Electrochemical Data (ensuing pages):**

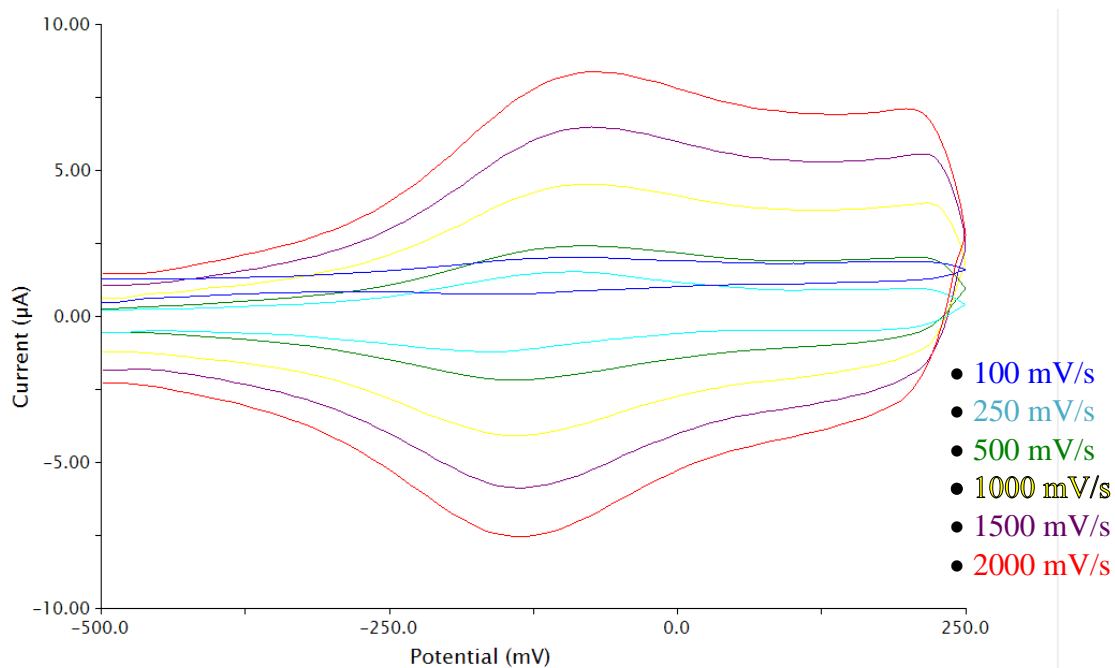


Figure S9. CV traces and scan rate dependence for (Si)–1-Ph-Fc.

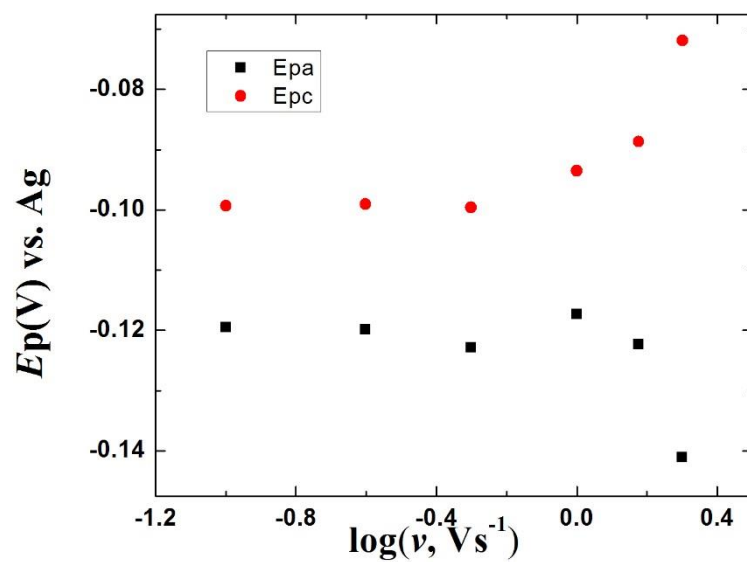


Figure S10. Laviron analysis for (Si)–1-Ph-Fc.

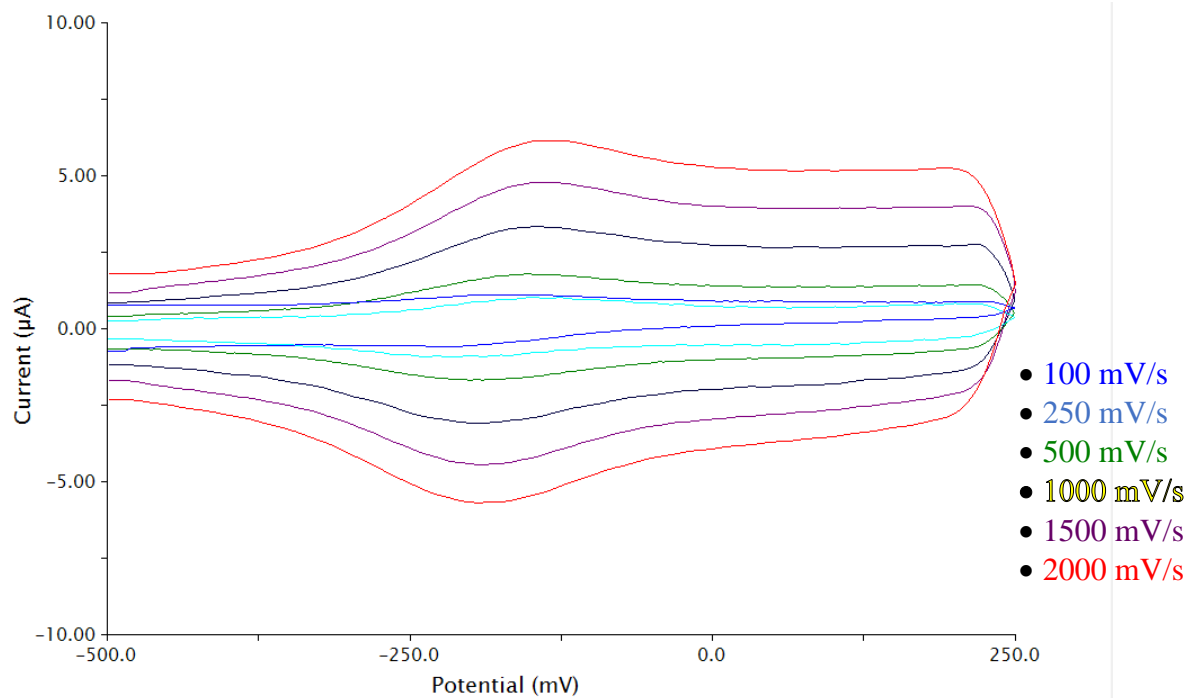


Figure S11. CV traces and scan rate dependence for (Si)-2-Ph-Fc.

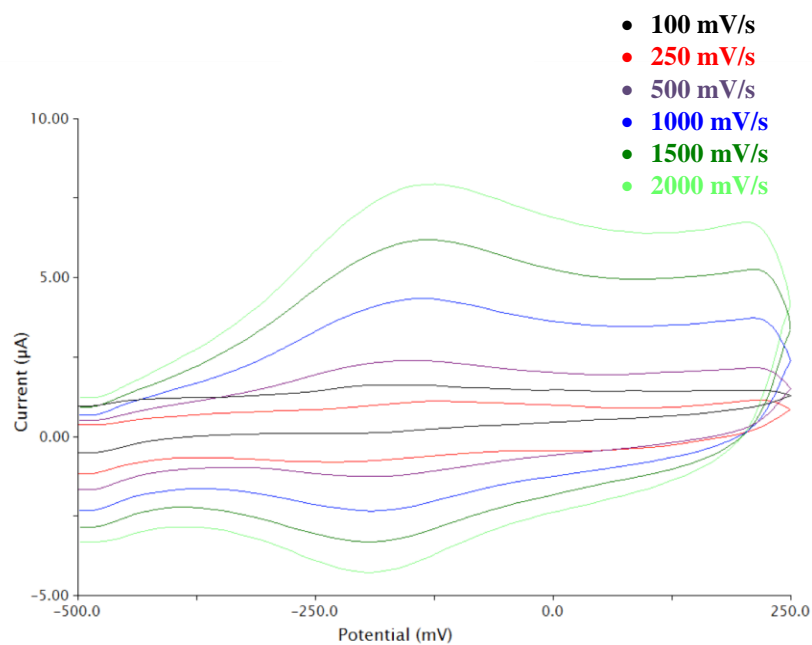


Figure S12. CV traces and scan rate dependence for (Si)-4-Ph-Fc.

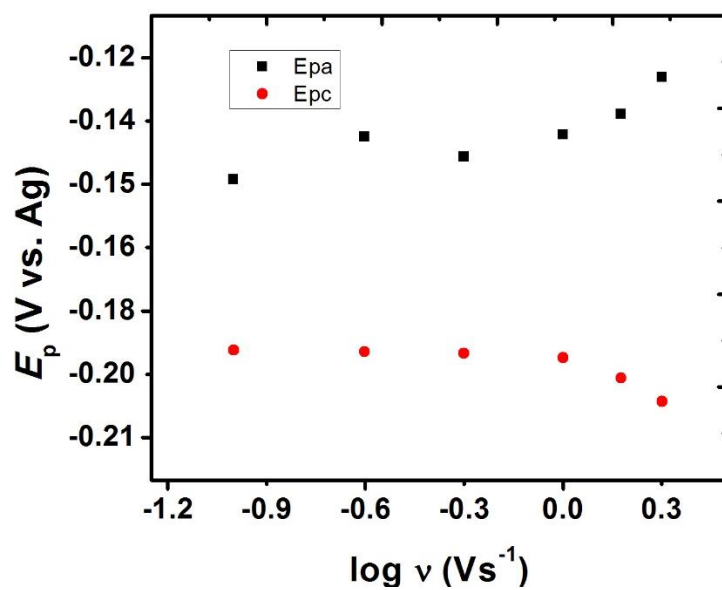


Figure S13. Laviron analysis for (Si)-4-Ph-Fc.

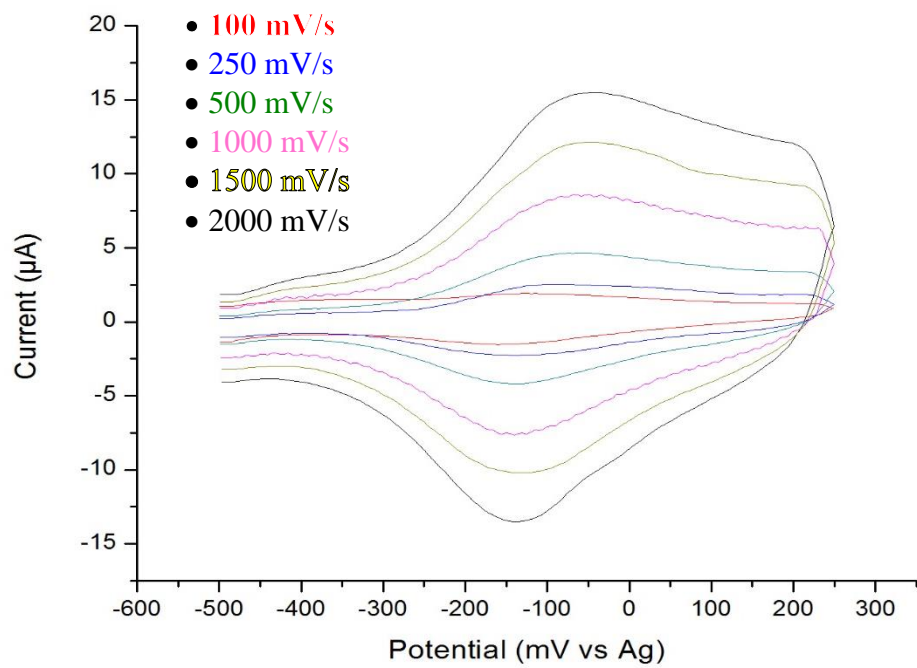


Figure S14. CV traces and scan rate dependence for (Si)–6-Ph-Fc.

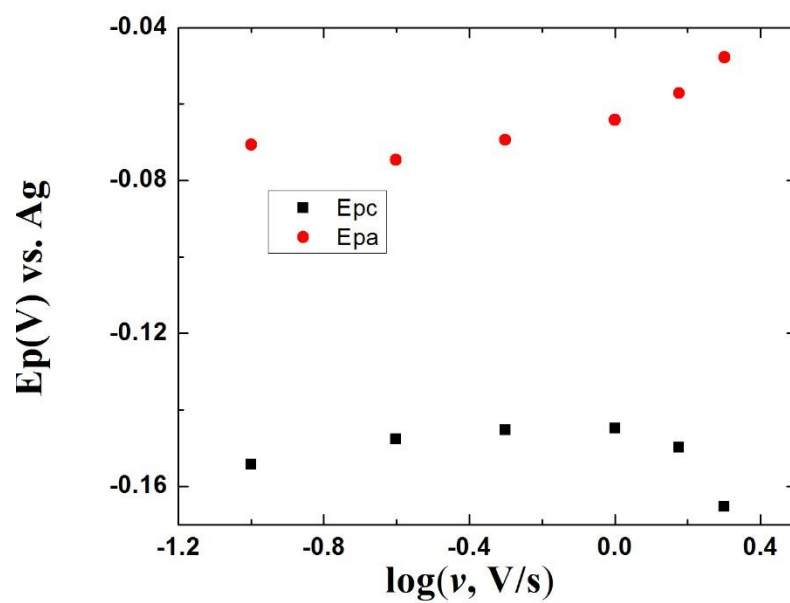


Figure S15. Laviron analysis for (Si)–6-Ph-Fc.

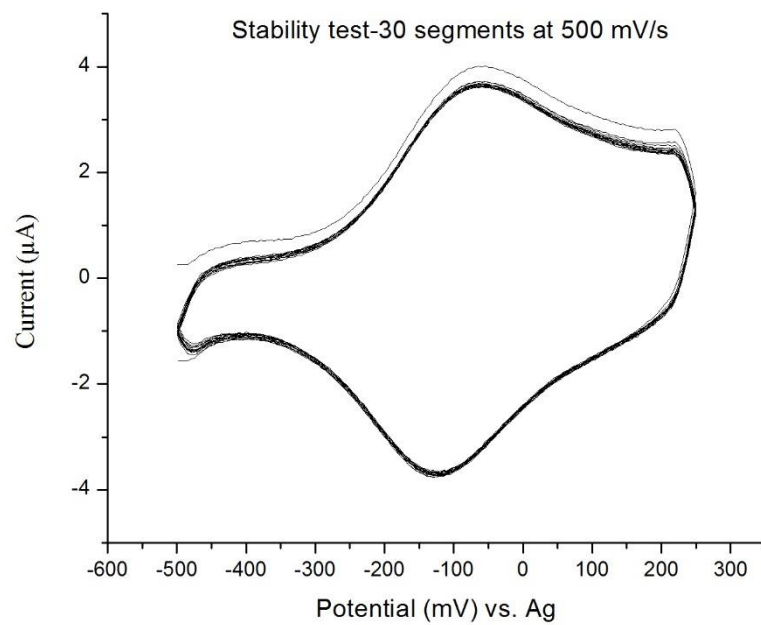


Figure S16. CV traces for the stability test for **(Si)-6-Ph-Fc**.

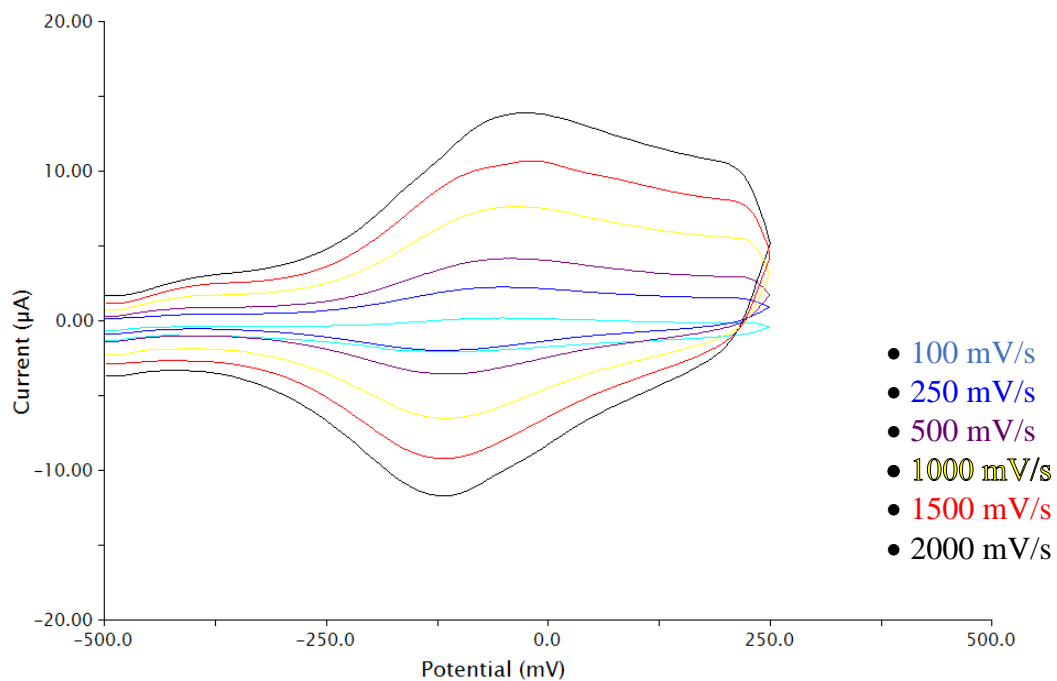


Figure S17. CV traces and scan rate dependence for (Si)-8-Ph-Fc.

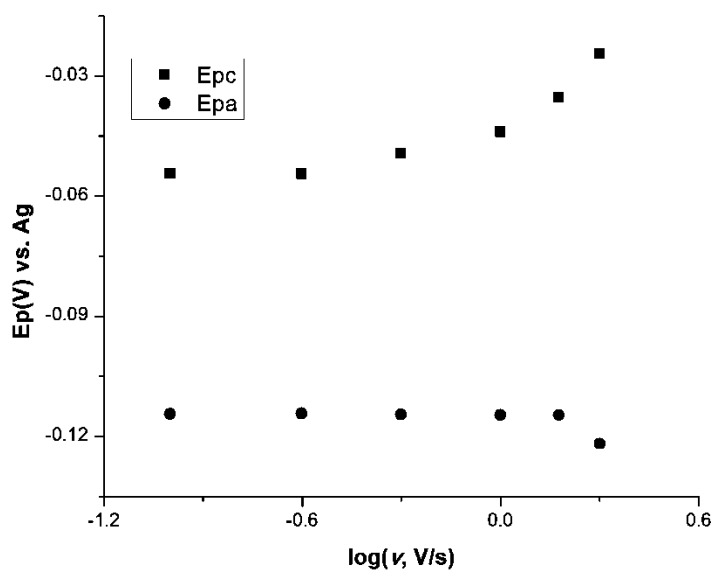


Figure S18. Laviron analysis for (Si)-8-Ph-Fc.

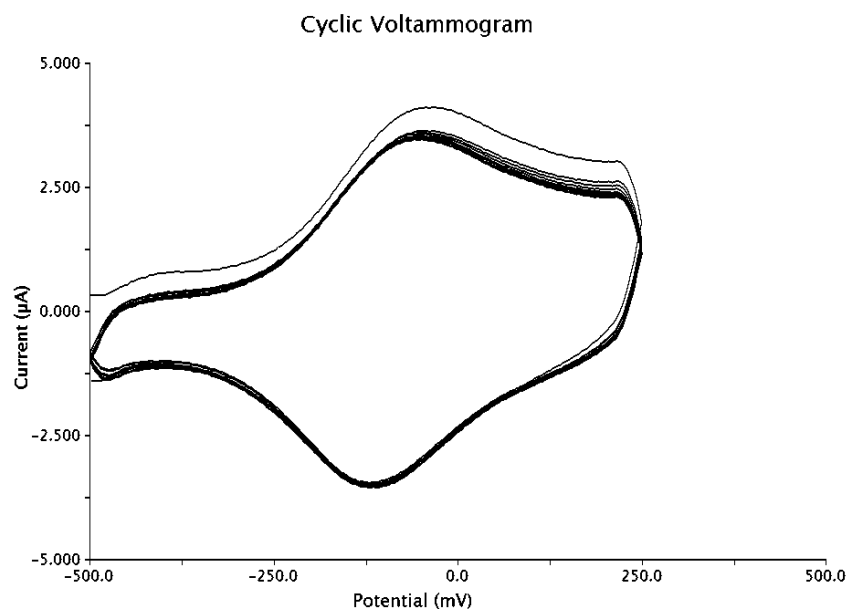


Figure S19. CV traces for the stability test of **(Si)-8-Ph-Fc**.

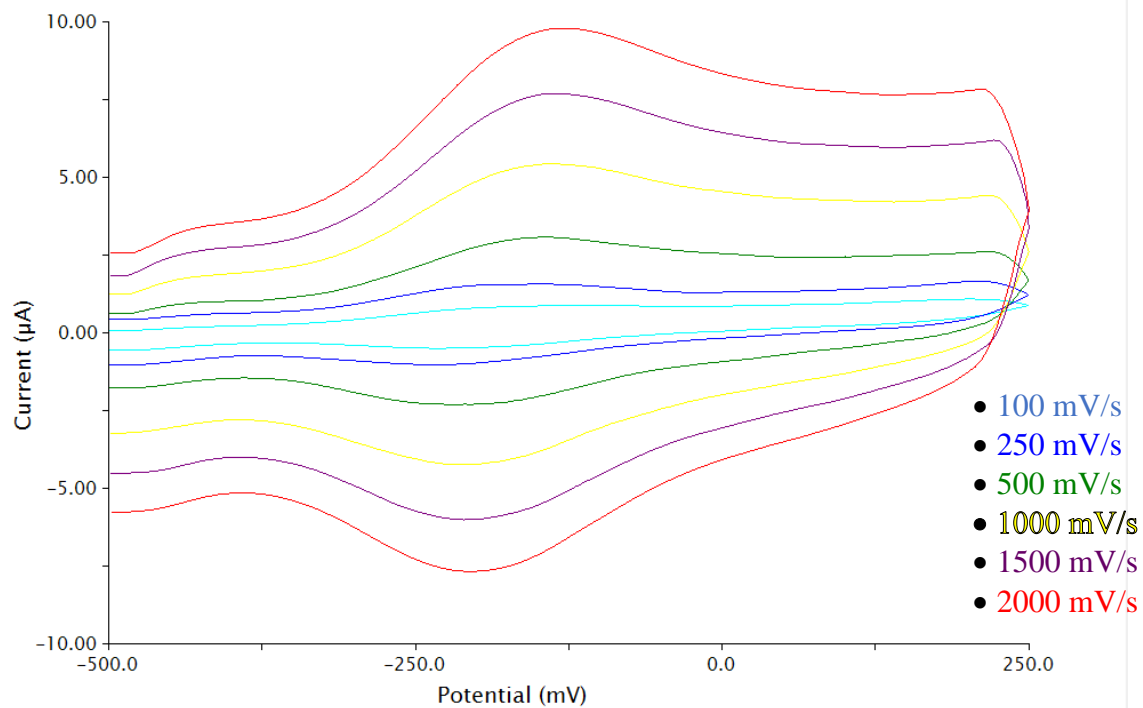


Figure S20. CV traces and scan rate dependence for (Si)-12-Ph-Fc.

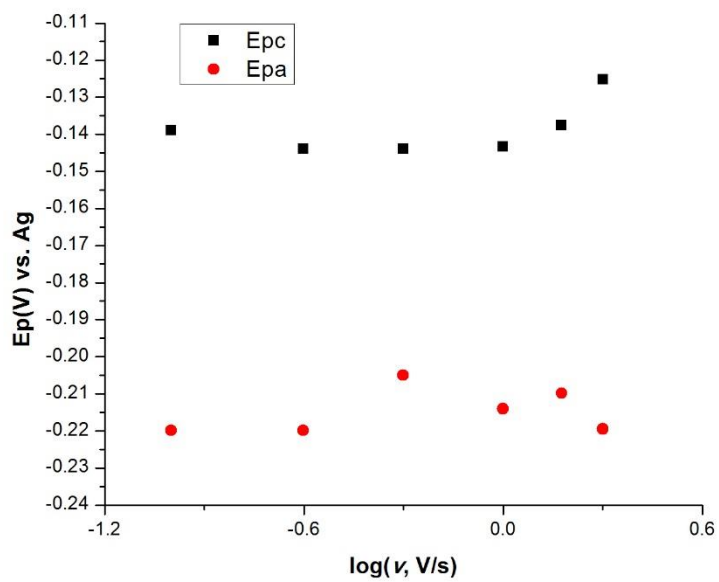


Figure S21. Laviron analysis for (Si)-12-Ph-Fc.