Supporting Information

Covalent Au−C Contact Formation and C−C Homocoupling Reaction from Organotin Compounds in Single-Molecule Junctions

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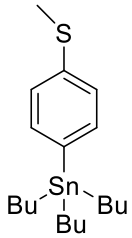
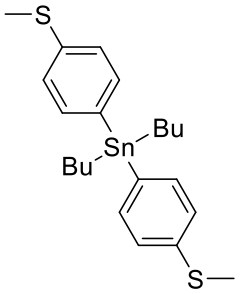
I. Synthetic procedures and characterization of compounds

If not stated otherwise, all reagents and starting materials were obtained from commercial suppliers and used without further purification. Anhydrous *n*-hexane, Et_2O, and THF were distilled from sodium-benzophenone and stored over activated 4Å molecular sieves. Reactions involving air- and moisture-sensitive compounds were performed under an atmosphere of pre-dried nitrogen using standard Schlenk-technique or within an argon-filled glovebox. The ^1H NMR and ^{13}C NMR spectra were recorded in solution of $CDCl_3$ on Bruker 400MHz *AVANCE III* NMR spectrometer. All chemical shifts are quoted in ppm, relative to tetramethylsilane, using the residual solvent peak as a reference standard ($^1H/^{13}C\{^1H\}$: δ = 7.26/77.16). High-resolution mass spectra were recorded via a Sciex X500R Q-TOF mass spectrometer.



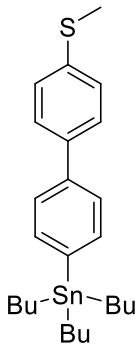
Tributyl(4-(methylthio)phenyl)stannane (1)

To 4-bromothioanisole (0.83 g, 4.1 mmol) in THF (8.0 mL) at –78 ºC was added *n*-BuLi (1.6 M in hexane, 2.6 mL, 4.1 mmol). The reaction mixture was stirred at this temperature for 1 h before the addition of *n*-Bu_3SnCl (1.40 g, 4.3 mmol) in THF (8 mL). After stirring for another 1 hour at –78 ºC, the reaction mixture was allowed to warm to ambient temperature slowly and stir for overnight. The solvent was evaporated to dryness and the residue was purified by column chromatography on silica gel using hexane as eluent. After fractional distillation, the target product was isolated as a light-yellow oil (1.12 g, 2.7 mmol, 66 %). ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.30 (m, 2H), 7.25 – 7.22 (m, 2H), 2.48 (s, 3H), 1.62 – 1.44 (m, 6H), 1.37 – 1.26 (m, 6H), 1.15 – 0.98 (m, 6H), 0.88 (t, J = 7.3 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.33, 138.04, 136.93, 126.22, 29.21, 27.52, 15.72, 13.83, 9.71. The data is consistent with the previous report.[1]



Dibutylbis(4-(methylthio)phenyl)stannane (2)

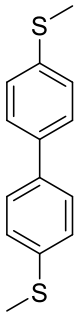
To a 50 mL Schlenk tube, 4-bromophenyl methyl sulfide (0.41 g, 2.0 mmol) and fresh hexane (10 mL) were added. The reaction was then cooled to –78 °C before the slow addition of *n*-BuLi (1.6 M in hexane, 1.3 mL). The resulting mixture was allowed to warm to room temperature slowly and stirred for overnight. The reaction mixture was cooled back to –78℃, and then Bu_3SnCl (0.30 g, 1.0 mmol) was added via syringe. The reaction mixture was kept stirring at r.t. overnight. All volatile was removed by fine vacuum and the resulting oil was extracted by hexane. Finally, the combined organic phase was concentrated and was purified by column chromatography on silica gel (eluent: 1-5 % ethyl acetate in hexane) to afford the desired product as a colorless oil (0.46 g, 0.96 mmol, 94 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.38 (m, 4H), 7.33 – 7.26 (m, 4H), 2.51 (s, 6H), 1.75 – 1.56 (m, 4H), 1.49 – 1.27 (m, 8H), 0.93 (t, J = 7.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.04, 137.10, 136.17, 126.23, 28.98, 27.40, 15.48, 13.74, 10.41; HRMS (EI) m/z: Calcd for M 490.1716; Found 490.3580.



Tributyl(4'-(methylthio)-[1,1'-biphenyl]-4-yl)stannane (3)

The precursor (4'-bromo-[1,1'-biphenyl]-4-yl)(methyl)sulfane can be prepared following a similar procedure to prepare **1** using 1-bromo-4-iodobenzene instead of 4-bromothioanisole. The data is in agreement with published data.[2]

To the solution of (4'-bromo-[1,1'-biphenyl]-4-yl)(methyl)sulfane (0.32 g, 1.17 mmol) in THF (3 mL) was added *n*-BuLi (1.6 M in hexane, 0.74 mL, 1.17 mmol) at –78 °C. The reaction mixture was stirred at this temperature for 1 h. After dropwise addition of *n*-Bu_3SnCl (0.38 g, 1.17 mmol) in THF (2 mL), the mixture was warmed to room temperature and stirred for overnight. All volatile was removed by fine vacuum and the resulting oil was extracted by hexane. Finally, the combined organic phase was concentrated and was purified by PTLC (hexane) to afford the desired product as a transparent oil (0.32 g, 0.65 mmol, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.59 (m, 6H), 7.42 (d, J = 8.4 Hz, 2H), 2.59 (s, 3H), 1.85 – 1.62 (m, 6H), 1.56 – 1.40 (m, 6H), 1.34 – 1.13 (m, 6H), 1.05 (t, J = 7.3 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.82, 140.12, 138.11, 137.62, 137.02, 127.45, 126.96, 126.35, 29.24, 27.52, 15.85, 13.82, 9.72. HRMS (EI) m/z: Calcd for M^+-Bu 423.0267; Found 423.0258.



4,4'-bis(methylthio)-1,1'-biphenyl (P2)

4-Bromothioanisole (1.10 g, 5.4 mmol), 4-(Methylthio) phenylboronic acid (1.82 g, 10.8 mmol), K_2CO_3 (1.50 g, 10.8 mmol), and $Pd(PPh_3)_4$ (0.31 g, 0.26 mmol) were placed into a 250 mL Schlenk tube. A mixture of toluene (36.0 mL), ethanol (12.0 mL), and H_2O (12.0 mL) was degassed by triplicate freeze-pump-thaw cycles before added into the tube under argon. The reaction mixture was allowed to reflux for 24 h and cooled to room temperature. After diluted with water, the mixture was extracted with dichloromethane three times. The combined organic layers were dried over $MgSO_4$. After filtration, the solvent was evaporated to dryness, The target product was purified by column chromatography (30 % DCM in hexanes) and a colorless crystalline solid was collected after drying under vacuum (4.1 mmol, 1.01 g, 76 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 8.2 Hz, 4H), 7.32 (d, J = 8.3 Hz, 4H), 2.52 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.65, 137.46, 127.28, 127.12, 16.05. Spectral data was in agreement with published data.[3]

II. Scanning tunneling microscope break junction experiment details

Single molecule conductance measurements were performed using a custom-built scanning tunneling microscope break junction (STM-BJ) technique that has been described in detail previously.[4] We prepare the Au substrates by using the Sputter deposition method of ejecting Au vapor from an Au target onto a polished steel disk with the diameter of 15 mm. A prepared gold substrate was treated with UV-Ozone (UV Ozone cleaner L2002A2-UK, Ossila Limited, Sheffield, UK) for 20 min immediately before use in each conductance measurement. A freshly cut Au wire (Ø = 0.25 mm, 99.999%, Hebei Hongju Metal Materials Co. Ltd) was used as the STM tip.

Solutions of 0.1 - 1 mM target molecules were dropped onto the substrate for molecular conductance measurements. 1,2,4-trichlorobenzene (TCB) was purchased from Alfa Aesar (≥ 99%) or Aladdin (anhydrous, ≥ 99%). Other solvents including tetradecane (TD; ≥ 99%), 1,3,5-trimethylbenzene (TMB; ≥ 98%), and 2-methoxyethyl ether (2-ME; ≥ 99.5%) were purchased from Aladdin and used without further purification. The tip was displaced at a speed of 18 nm/s and the current and voltage data were acquired at 40 kHz acquisition rate for all measurements.

Below we describe the experimental procedure for HPLC analysis of the STM-BJ solution of **1**. We first drop ~ 50 μL solution of 1mM **1** onto the substrate for single molecule conductance experiment. After performing STM-BJ measurement for 3 hours, we wash the substrate which contains the product **P2**, tin-cleaved species, remaining **1** and solvent TCB with 0.5 mL isopropanol and store this 0.5 mL solution for HPLC characterization. In the HPLC experiment, 10 μL solution is injected to the column for characterization.

III. Additional figures

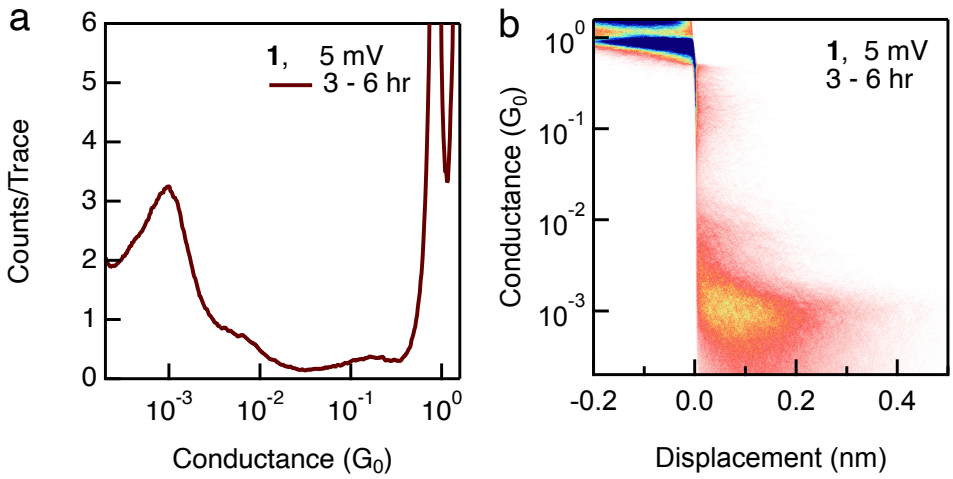


Figure S1. (a) 1D and (b) 2D conductance histograms of **1** measured in TCB under 5 mV in 3–6 hours measurement.

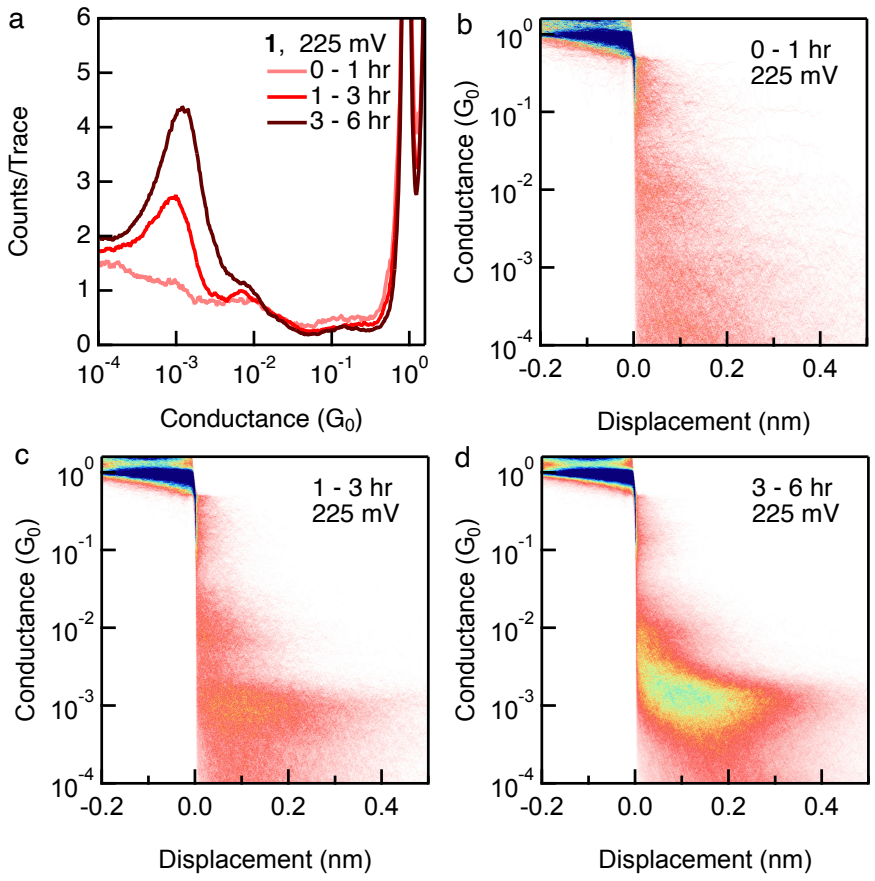


Figure S2. (a) 1D conductance histograms of **1** measured in TCB under 225 mV showing an increase in both high and low conductance peak intensities over a 6-hour time period. (b-d) 2D conductance histograms of **1** measured in TCB under 225 mV in the (b) 0–1 hour, (c) 1–3 hours, and (d) 3–6 hours measurement.

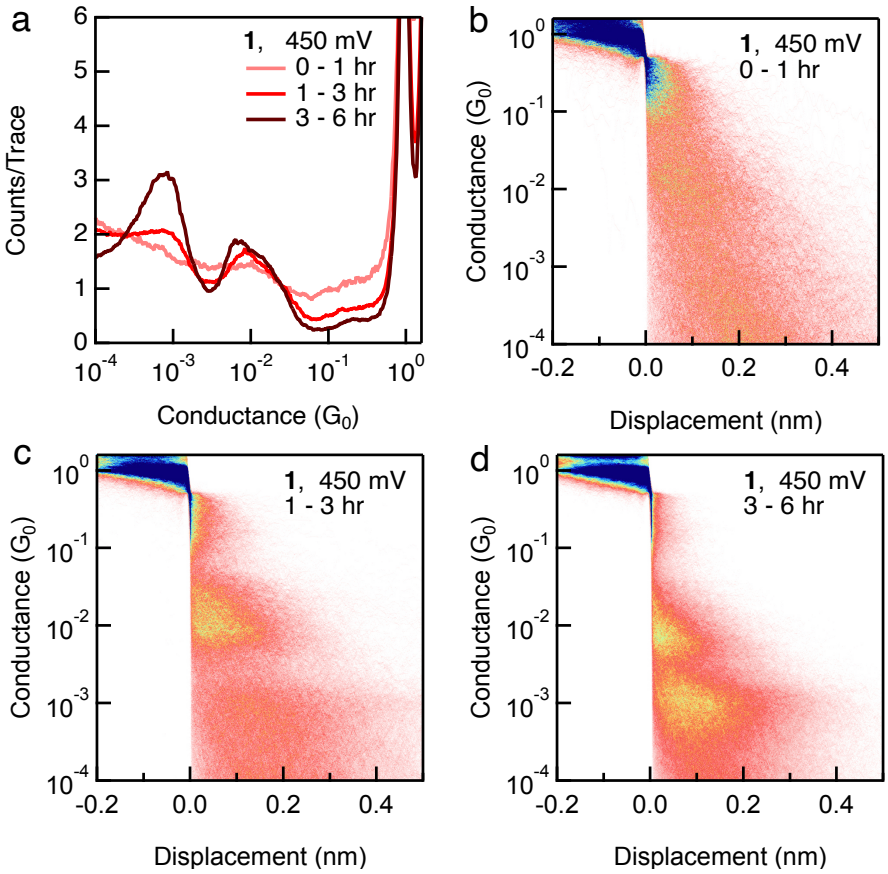


Figure S3. (a) 1D conductance histograms of **1** measured in TCB under 450 mV showing a change in both high and low conductance peak intensities over a 6-hour time period. (b-d) 2D conductance histograms of **1** measured in TCB under 450 mV in the (b) 0–1 hour, (c) 1–3 hours, and (d) 3–6 hours measurement.

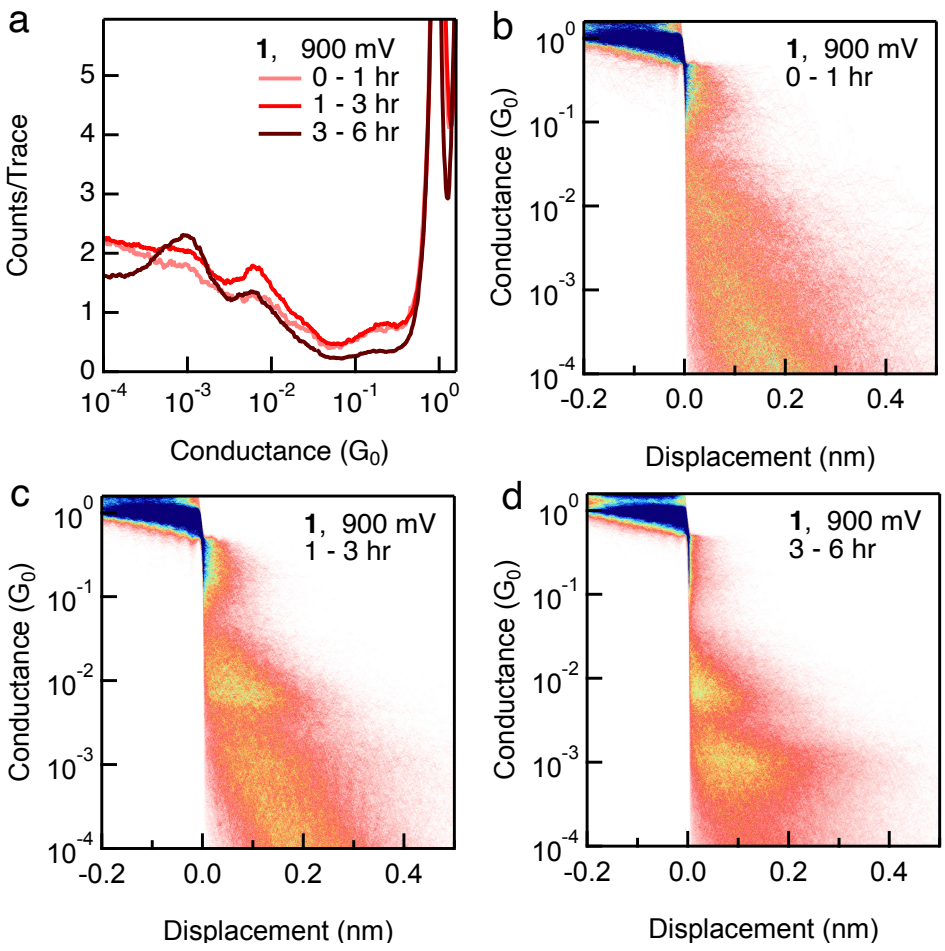


Figure S4. (a) 1D conductance histograms of **1** measured in TCB under 900 mV showing a change in both high and low conductance peak intensities over a 6-hour time period. (b-d) 2D conductance histograms of **1** measured in TCB under 900 mV in the (b) 0–1 hour, (c) 1–3 hours, and (d) 3–6 hours measurement.

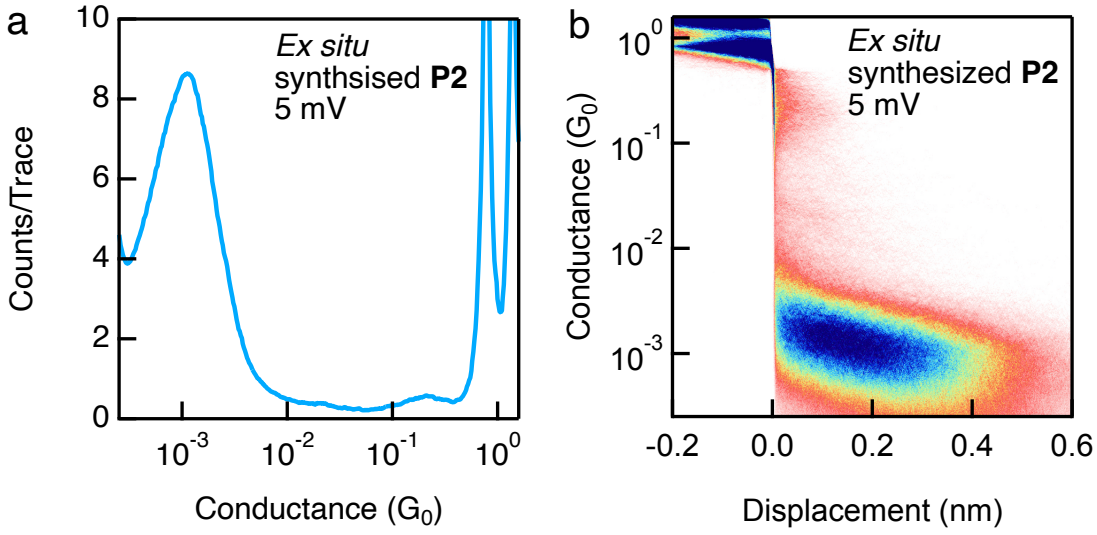


Figure S5. (a) 1D and (b) 2D conductance histograms of **P2** measured in TCB under 5 mV.

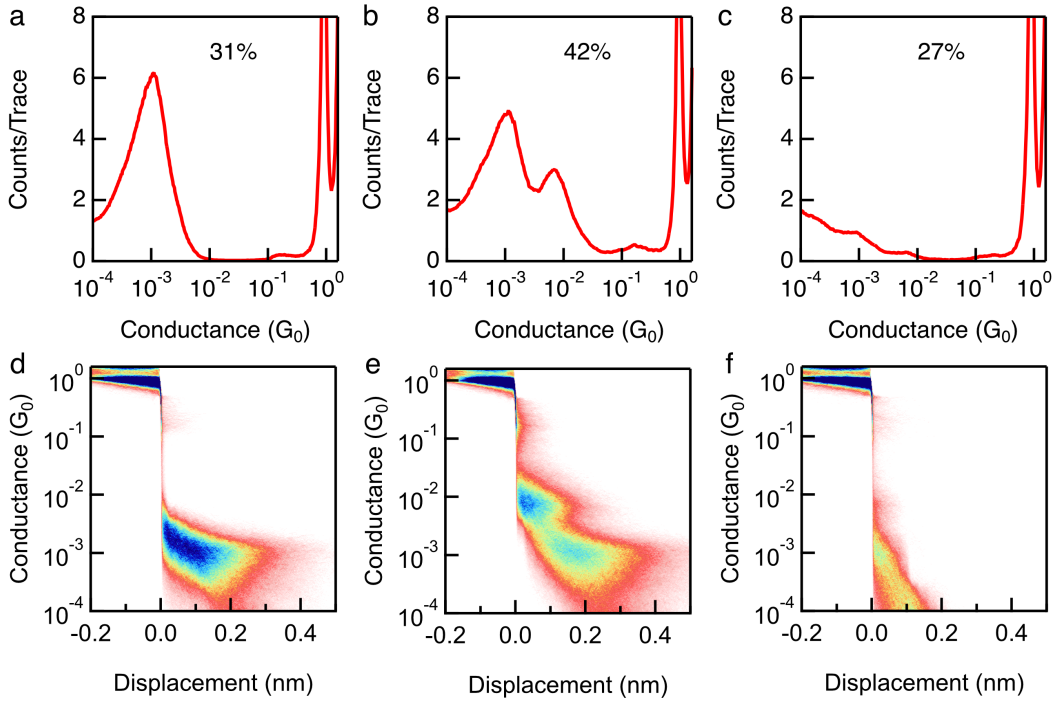


Figure S6. Categorization of 39,000 traces collected during 3–12 hours measurement for **1** in TCB under 225 mV tip bias. (a-c) 1D conductance histograms of (a) 31% of the traces that show molecular plateau at low conductance state of ~ 1.0×10^{-3} G_0, (b) 42% of the traces that show a high to low molecular conductance transition, and (c) 27% of the traces that show no clear molecular conductance feature. The corresponding 2D histograms are displayed in (d-f).

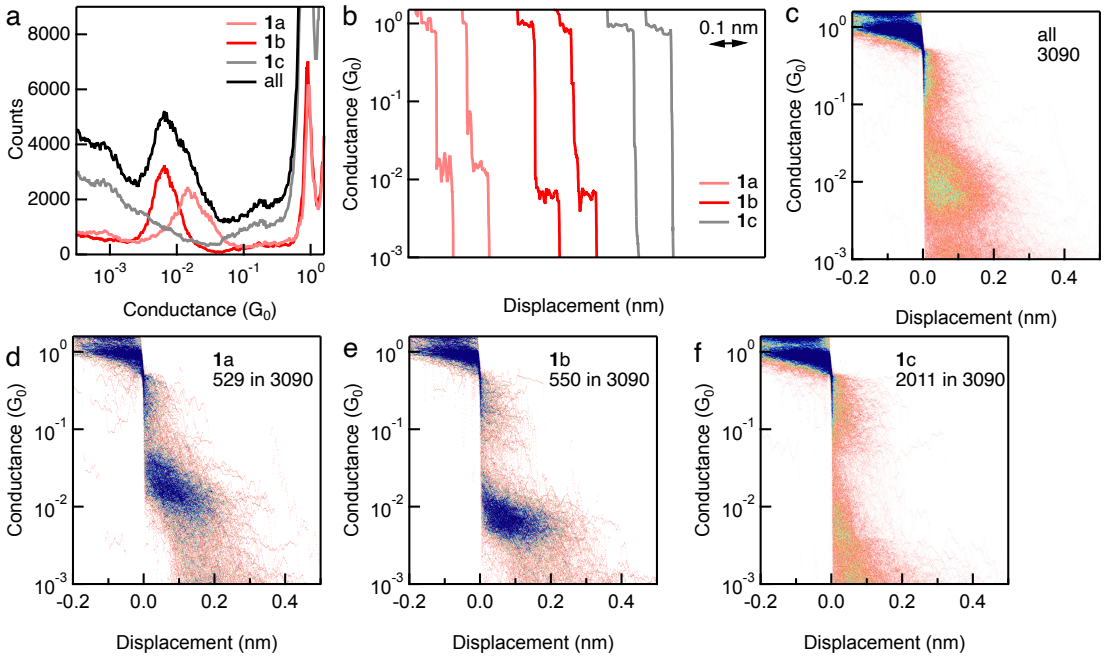


Figure S7. Conductance analysis of **1** measured under 5 mV during 0–1 hour. (a) 1D conductance histogram generated from all 3090 traces measured (black)

for **1**; the traces were categorized into three groups and traces in each group were compiled into a separate histogram: **1**a (high molecular conductance peak compiled from 529 traces (pink)), **1**b (low molecular conductance peak compiled from 550 traces (red)), and **1**c (no molecular conductance peak compiled from 2011 traces (grey)). Counts are not normalized by the number of traces for comparing the total counts in each group of traces. (b) Example **1**a, **1**b, and **1**c individual conductance traces. (c-f) 2D conductance histograms generated from (c) all 3090 traces and from each selected group (d) **1**a (529 traces), (e) **1**b (550 traces), and (f) **1**c (2011 traces).

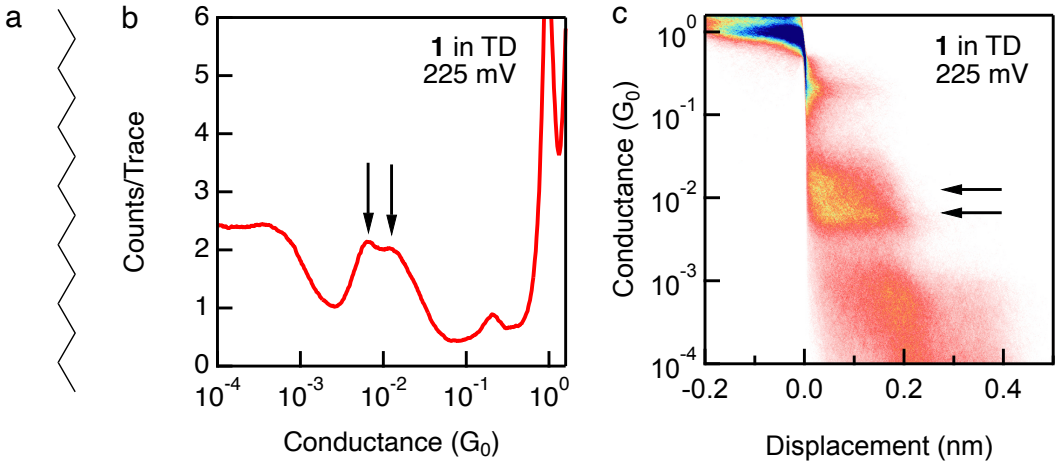


Figure S8. (a) Chemical structure of the solvent tetradecane (TD). (b)1D and (c) 2D conductance histograms of **1** measured in TD under 225 mV. The arrows in b and c indicate the double-peak conductance feature of 6.6×10^{-3} G_0 and 1.3×10^{-2} G_0 respectively. The conductance peak at 1.3×10^{-2} G_0 is about two times of the conductance peak at 6.6×10^{-3} G_0 and possibly arises from the formation of two **A1** attached in parallel between the two Au electrodes.

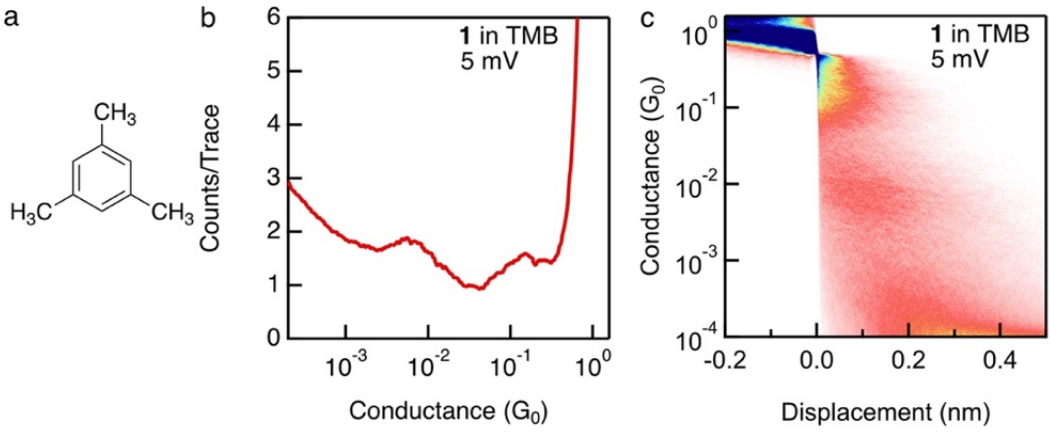


Figure S9. (a) Chemical structure of the solvent 1,3,5-trimethylbenzene (TMB). (b) 1D and (c) 2D conductance histograms of **1** measured in TMB under 5 mV.

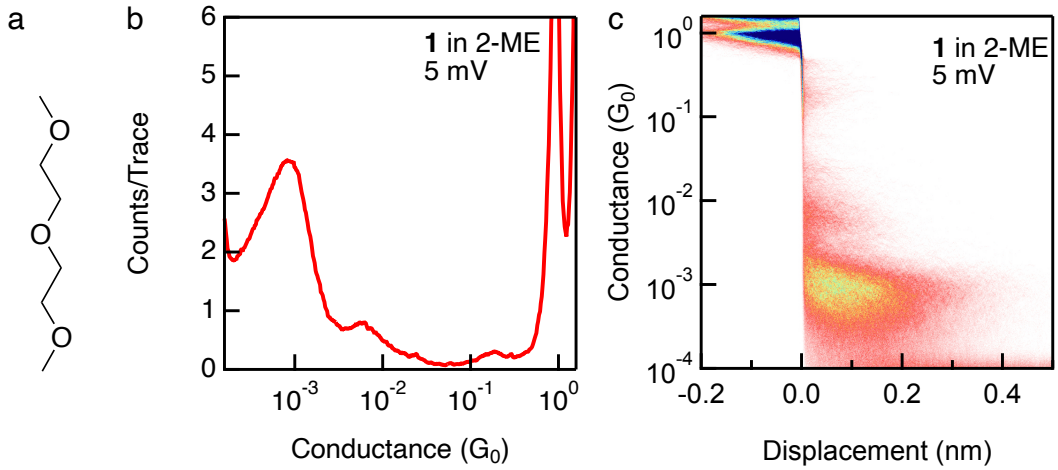


Figure S10. (a) Chemical structure of the solvent 2-methoxyethyl ether (2-ME). (b) 1D and (c) 2D conductance histograms of **1** measured in 2-ME under 5 mV.

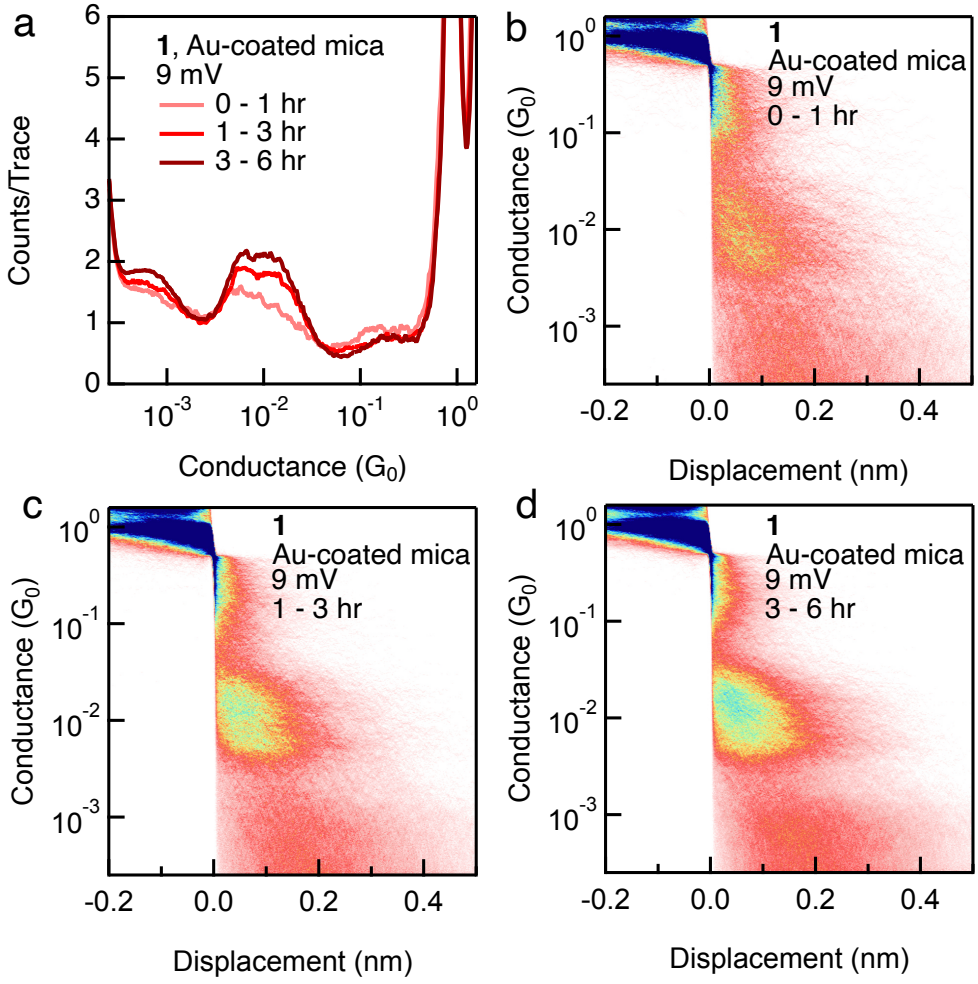


Figure 11. (a) 1D conductance histograms of **1** measured in TCB on an Au-coated mica substrate under 9 mV over a 6-hour time period. (b-d) 2D conductance histograms of **1** measured in TCB on an Au-coated mica substrate under 9 mV in the (b) 0–1 hour, (c) 1–3 hours, and (d) 3–6 hours measurement.

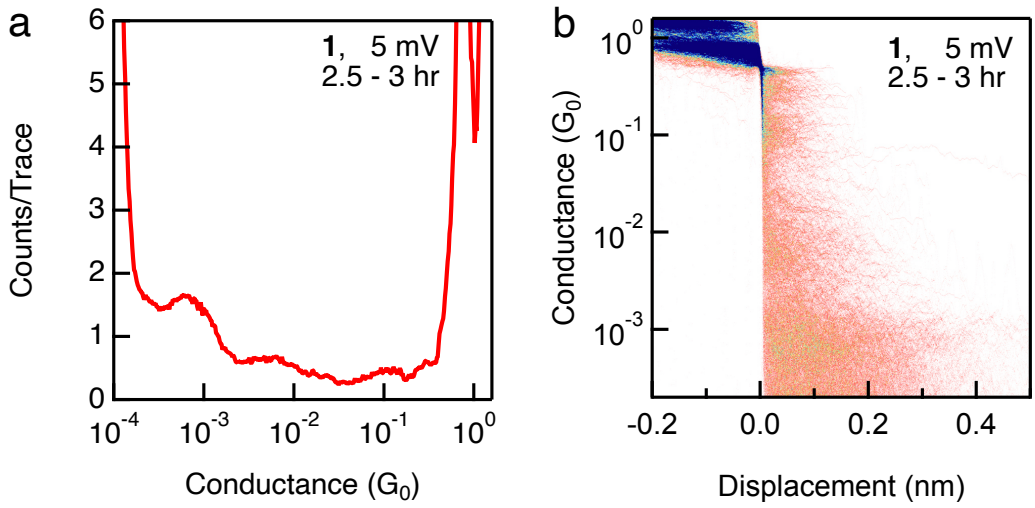


Figure S12. (a) 1D and (b) 2D conductance histograms of **1** measured in TCB under 5 mV for 3 hours. The solution from this measurement was collected and used for HPLC analysis as shown in Figure 2 in the main text.

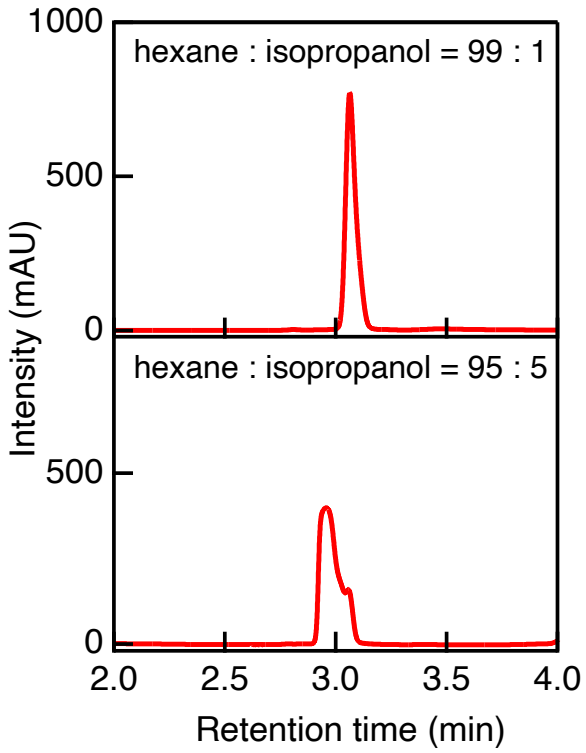


Figure S13. Comparison of HPLC spectra of **1** obtained in a hexane : isopropanol = 99 : 1 (top) and 95 : 5 (bottom) (volume ratio) mobile phase. This suggests that use of isopropanol as a solvent is not preferred for the HPLC analysis of **1**.

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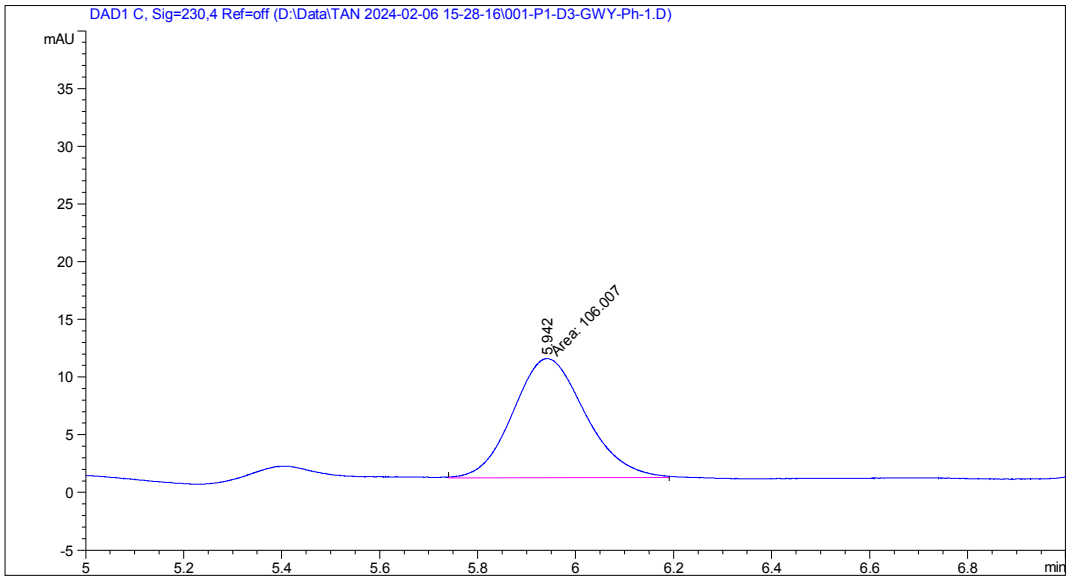


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Do not use Multiplier & Dilution Factor with ISTDs


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Figure S14. HPLC spectrum of *in situ* formed **P2** in a hexane : isopropanol = 95 : 5 (volume ratio) mobile phase.

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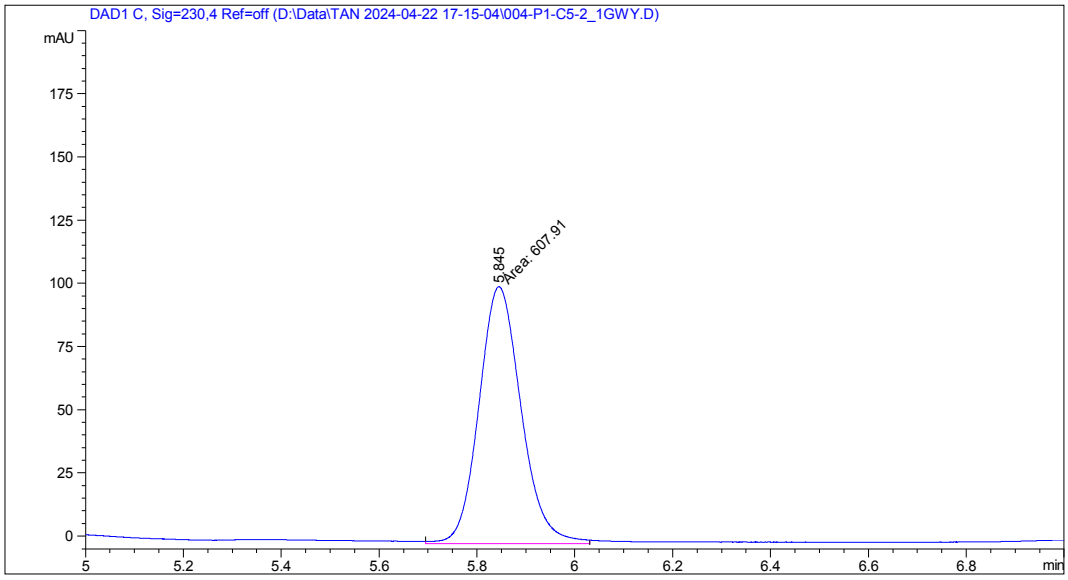


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Figure S15. HPLC spectrum of 0.3 mM *ex situ* synthesized **P2** in a hexane : isopropanol = 95 : 5 (volume ratio) mobile phase.

Note about **Figure S14** and **S15**:
We integrate the area under the peaks corresponding to **P2** in the HPLC spectra for both the reaction solution and a pure 0.3 mM **P2** solution. The area ratio S_{sol}

/ S_{P2} = 106 / 608 = 0.17. Considering the 10 µL injection volume of the reaction solution and 5 µL injection volume of the pure **P2** solution, the concentration of **P2** in the STM-BJ solution is about 0.3 mM × 0.17 / 2 = 0.026 mM. Thus, the approximated amount of the **P2** that is formed *in situ* is 0.5 mL × 0.026 mM = 13 nmol. We approximate the amount of the starting molecule **1** is 50 µL × 1 mM = 50 nmol.

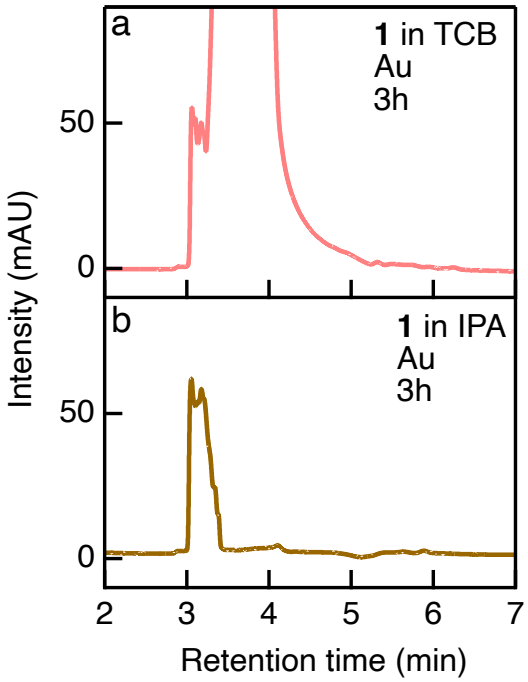

Figure S16. High performance liquid chromatography results of (a) 1 mM **1** in TCB and (b) 1 mM **1** in isopropanol (IPA) that was deposited on an Au substrate for 3 hours.

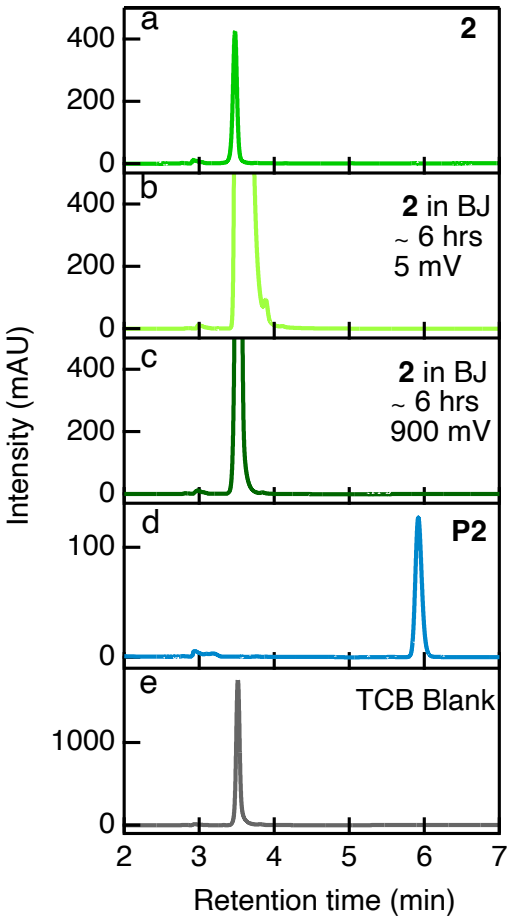

Figure S17. High performance liquid chromatography results of (a) **2**, (b) **2** in TCB subject to STM-BJ measurements for 6 hours under 5 mV, (c) **2** in TCB subject to STM-BJ measurements for 6 hours under 900 mV, (d) *ex situ* synthesized **P2**, and (d) TCB blank.

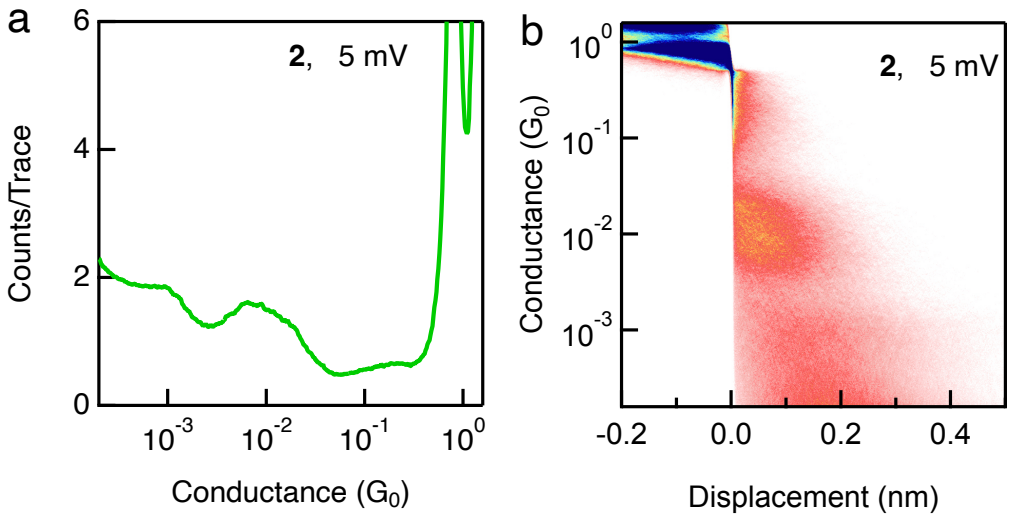

Figure S18. (a) 1D and (b) 2D conductance histograms of **2** measured in TCB under 5 mV.

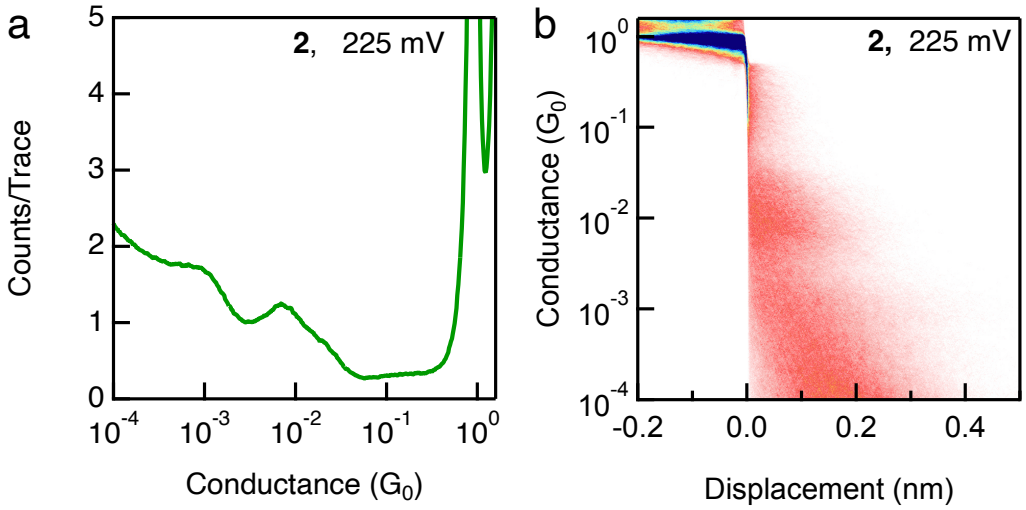

Figure S19. (a) 1D and (b) 2D conductance histograms of **2** measured in TCB under 225 mV.

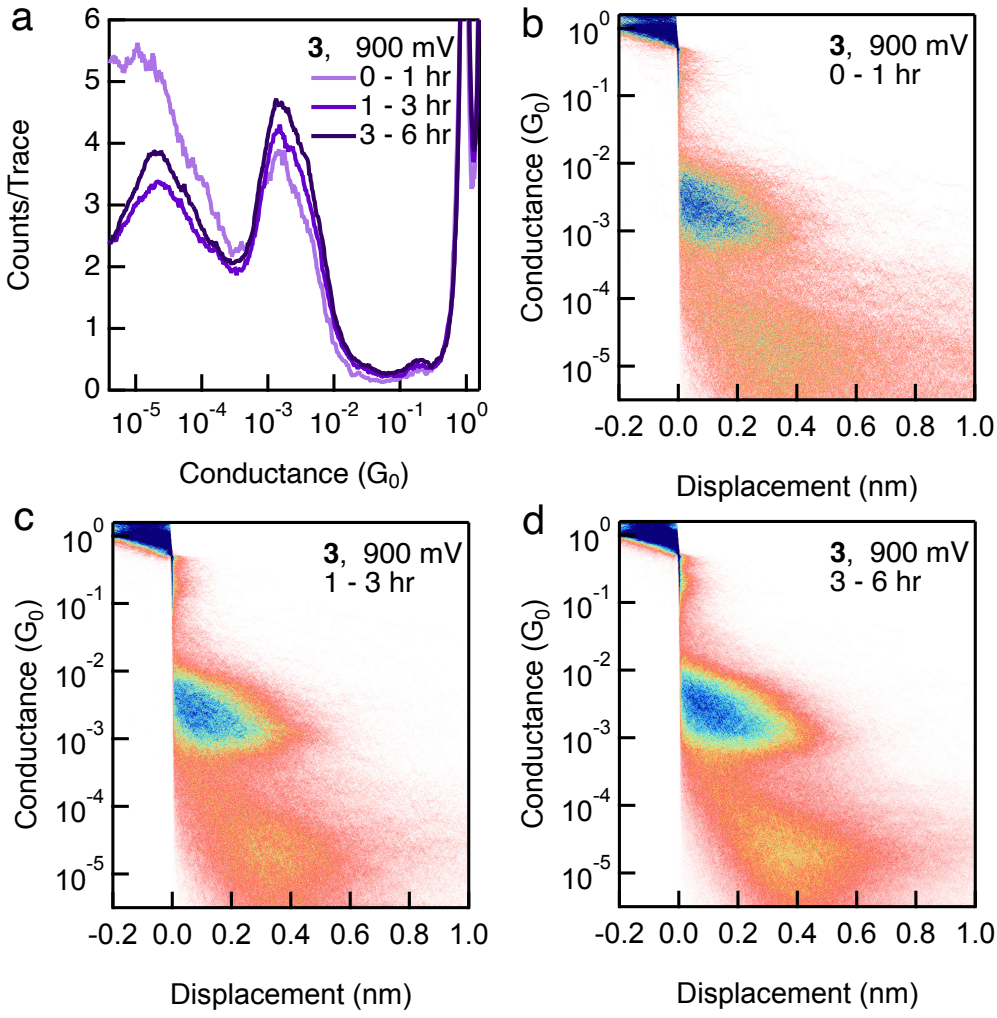

Figure S20. (a) 1D conductance histograms of **3** measured in TCB under 900 mV over a 6-hour time period. (b-d) 2D conductance histograms of **1** measured in TCB under 900 mV in the (b) 0–1 hour, (c) 1–3 hours, and (d) 3–6 hours measurement.

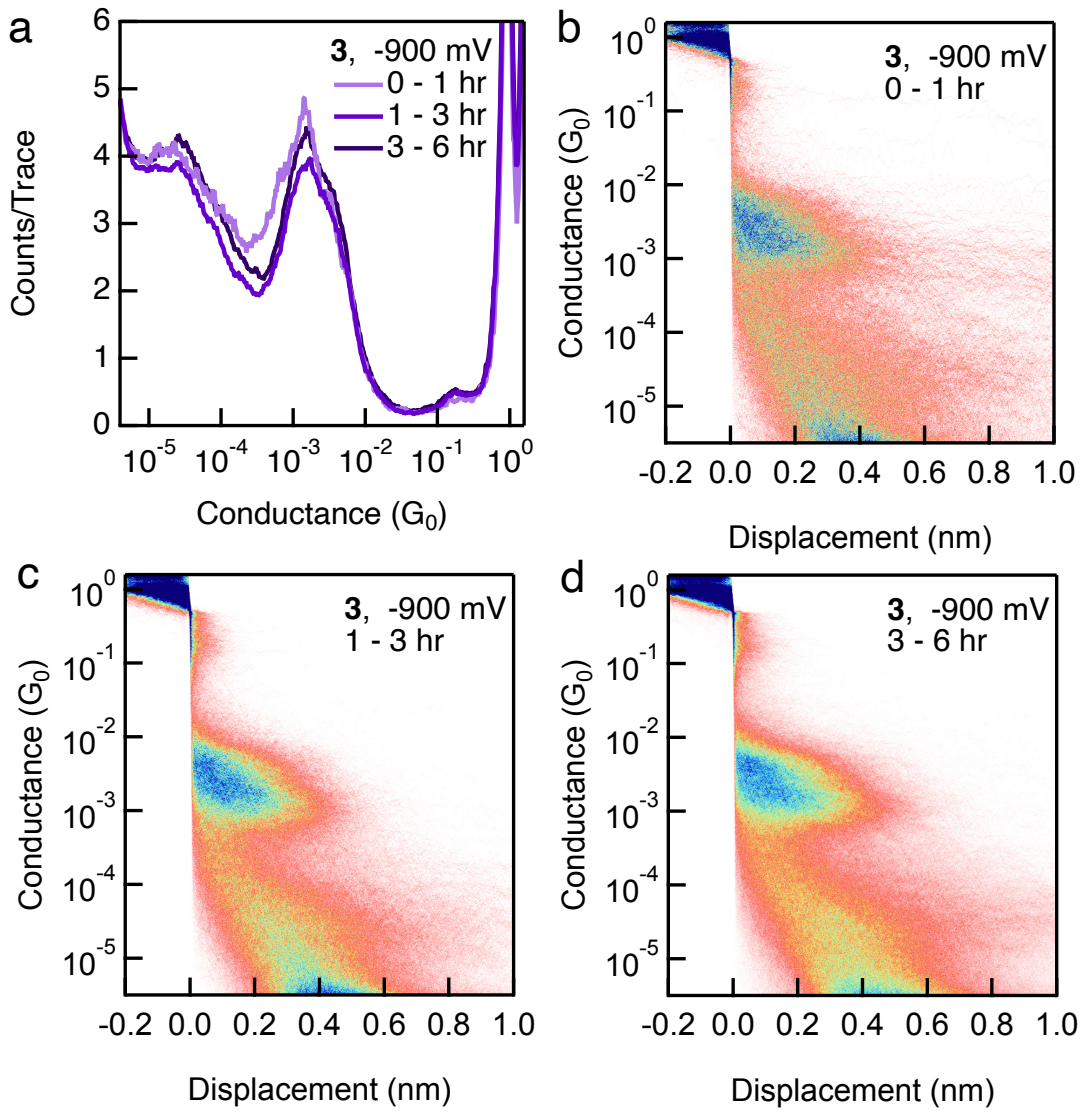

Figure S21. (a) 1D conductance histograms of **3** measured in TCB under -900 mV over a 6-hour time period. (b-d) 2D conductance histograms of **1** measured in TCB under -900 mV in the (b) 0–1 hour, (c) 1–3 hours, and (d) 3–6 hours measurement.

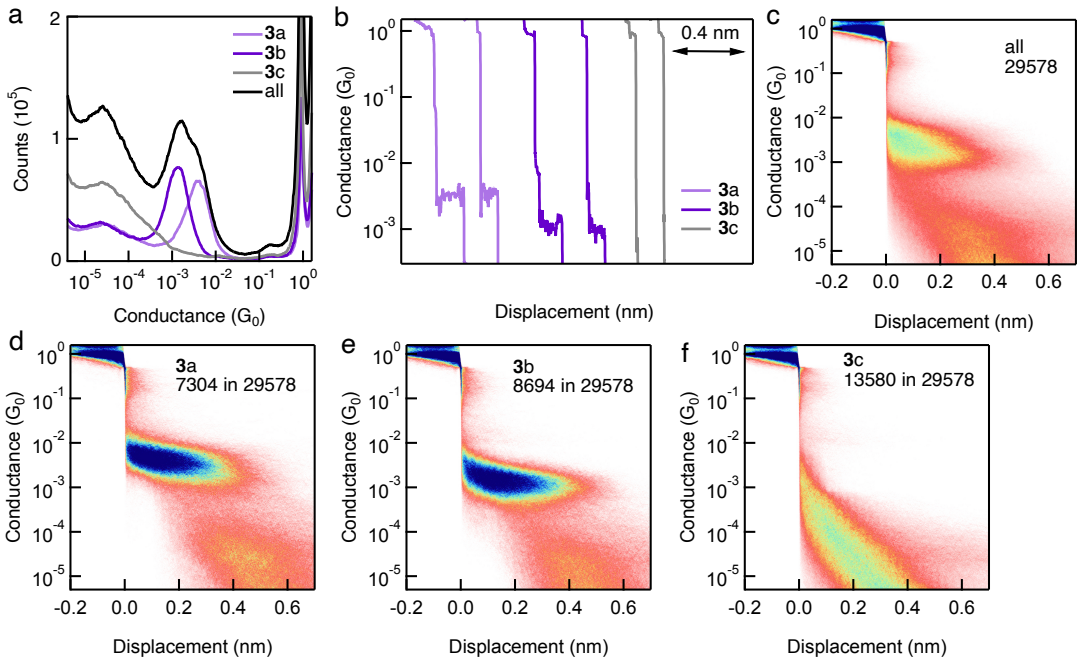

Figure S22. Conductance analysis of **3** measured under -900 mV. (a) 1D conductance histogram generated from all 29578 traces measured (black) for **3**; the traces were categorized into three groups and traces in each group were compiled into a separate histogram: **3**a (high molecular conductance peak compiled from 7304 traces (light purple)), **3**b (low molecular conductance peak compiled from 8694 traces (dark purple)), and **3**c (no molecular conductance peak compiled from 13580 traces (grey)). Counts are not normalized by the number of traces for comparing the total counts in each group of traces. (b) Example **3**a, **3**b, and **3**c individual conductance traces. (c-f) 2D conductance histograms generated from (c) all 29578 traces and from each selected group (d) **3**a (7304 traces), (e) **3**b (8694 traces), and (f) **3**c (13580 traces).

IV. NMR spectra

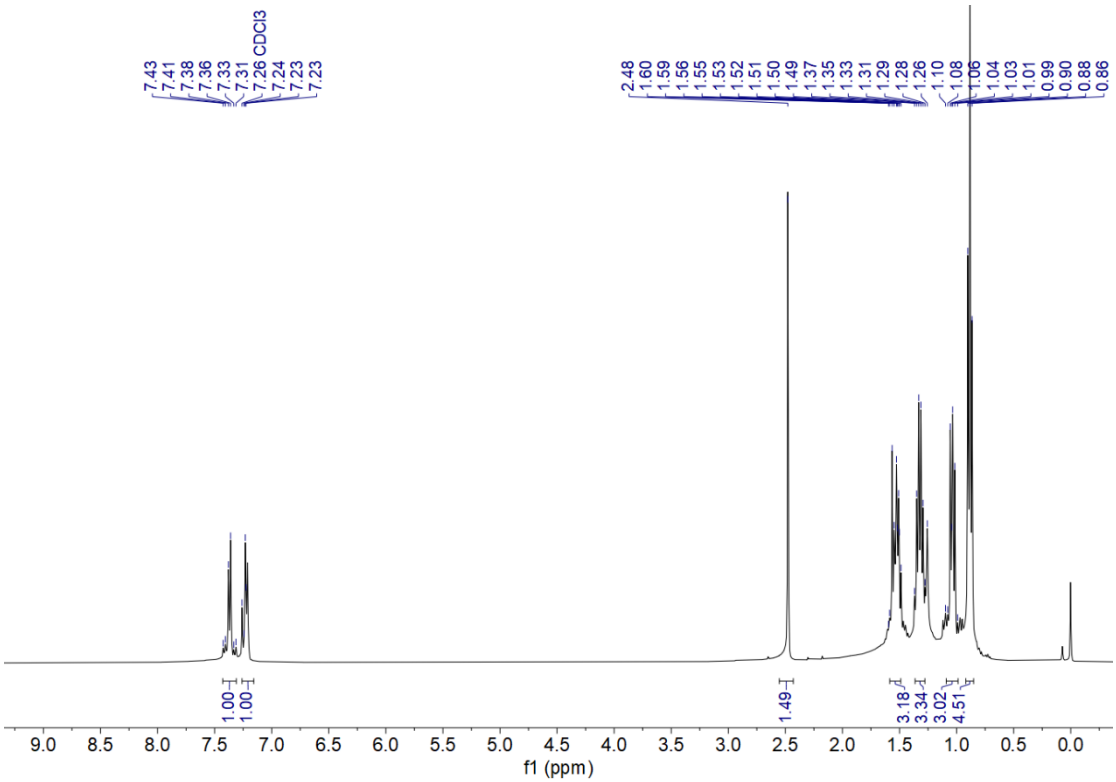

Figure S23. ^{1}H NMR spectrum of compound **1** in $CDCl_3$.

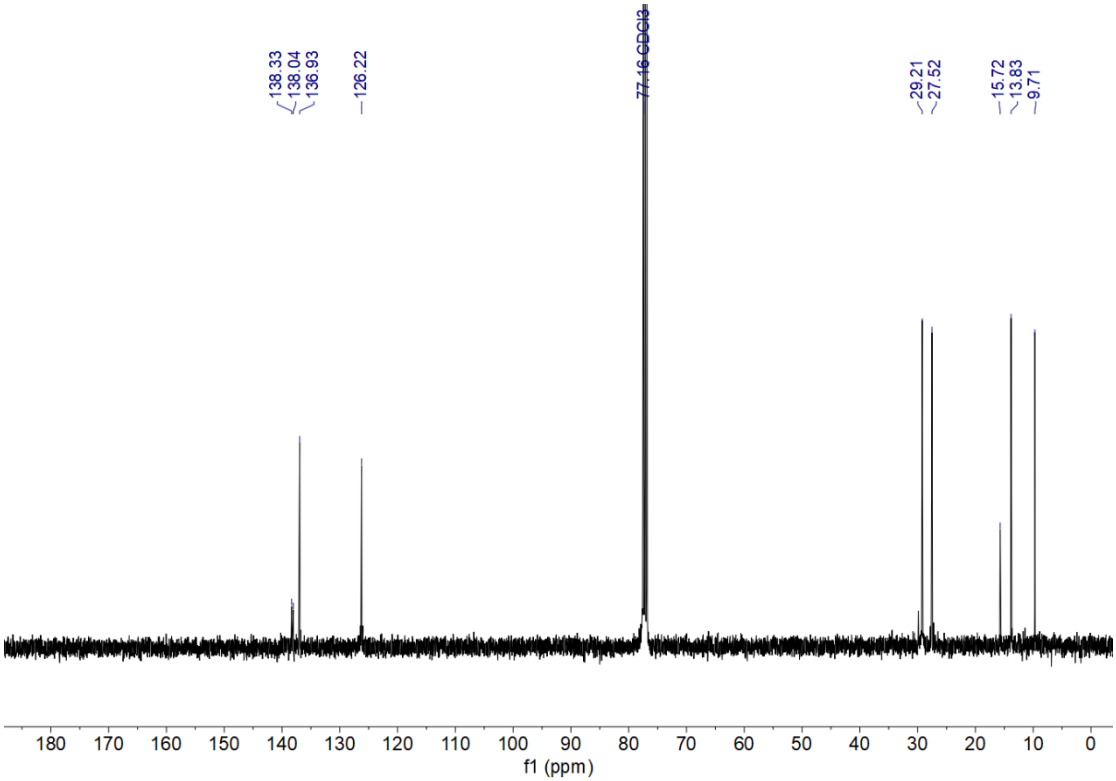

Figure S24. ^{13}C NMR spectrum of compound **1** in $CDCl_3$.

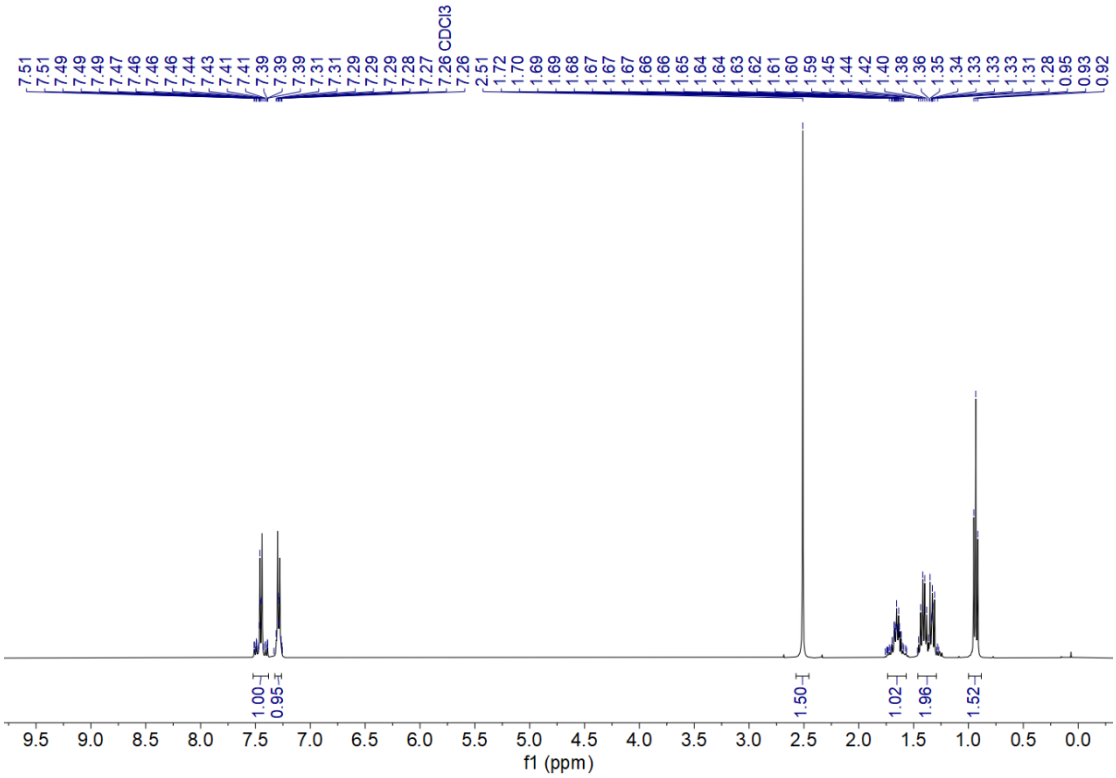

Figure S25. ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

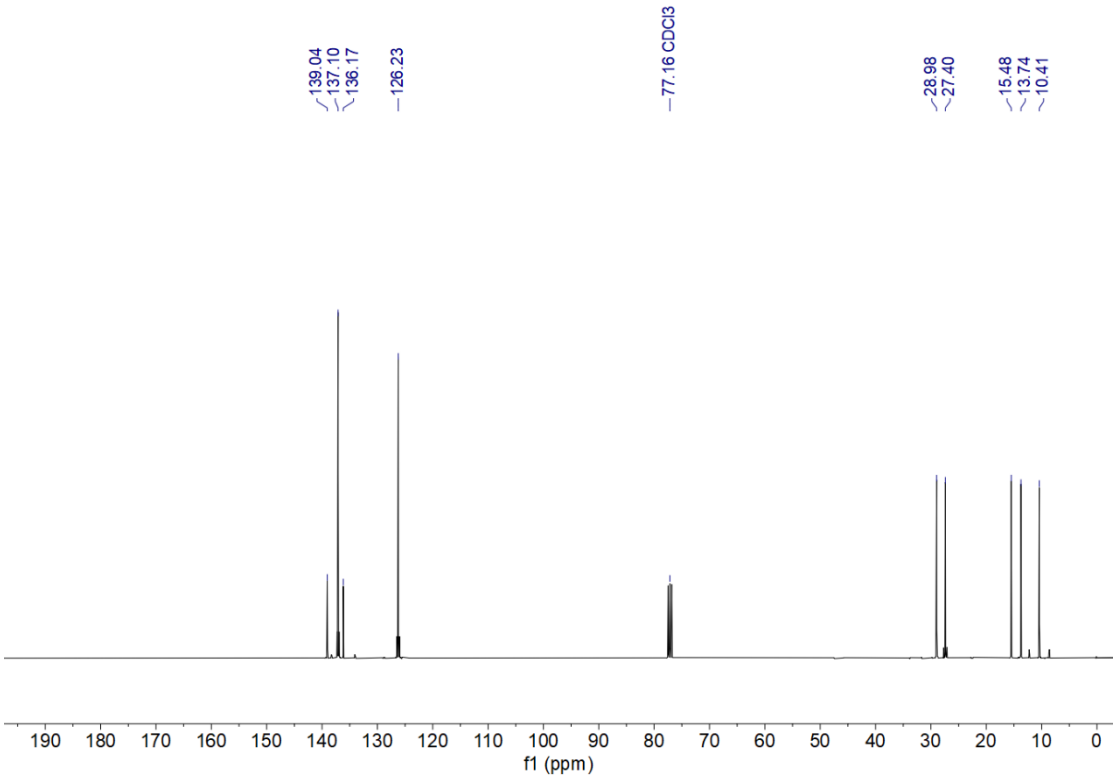

Figure S26. ^{13}C NMR spectrum of compound **2** in $CDCl_3$.

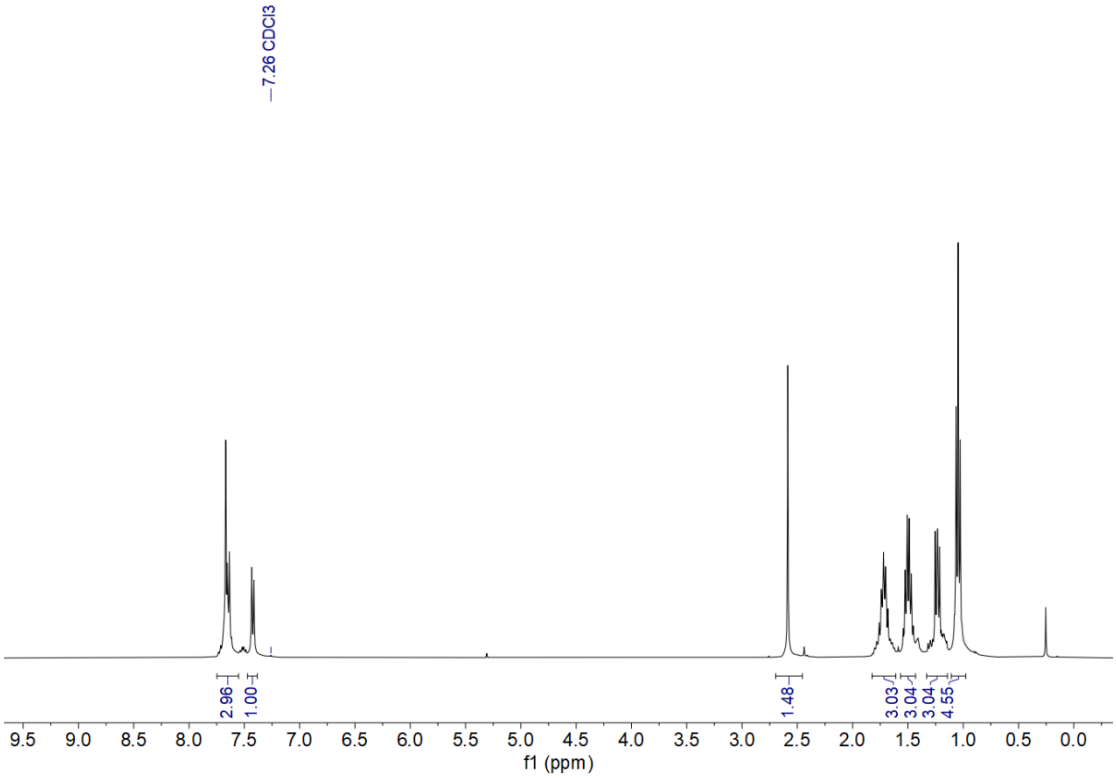

Figure S27. ^{1}H NMR spectrum of compound **3** in $CDCl_3$.

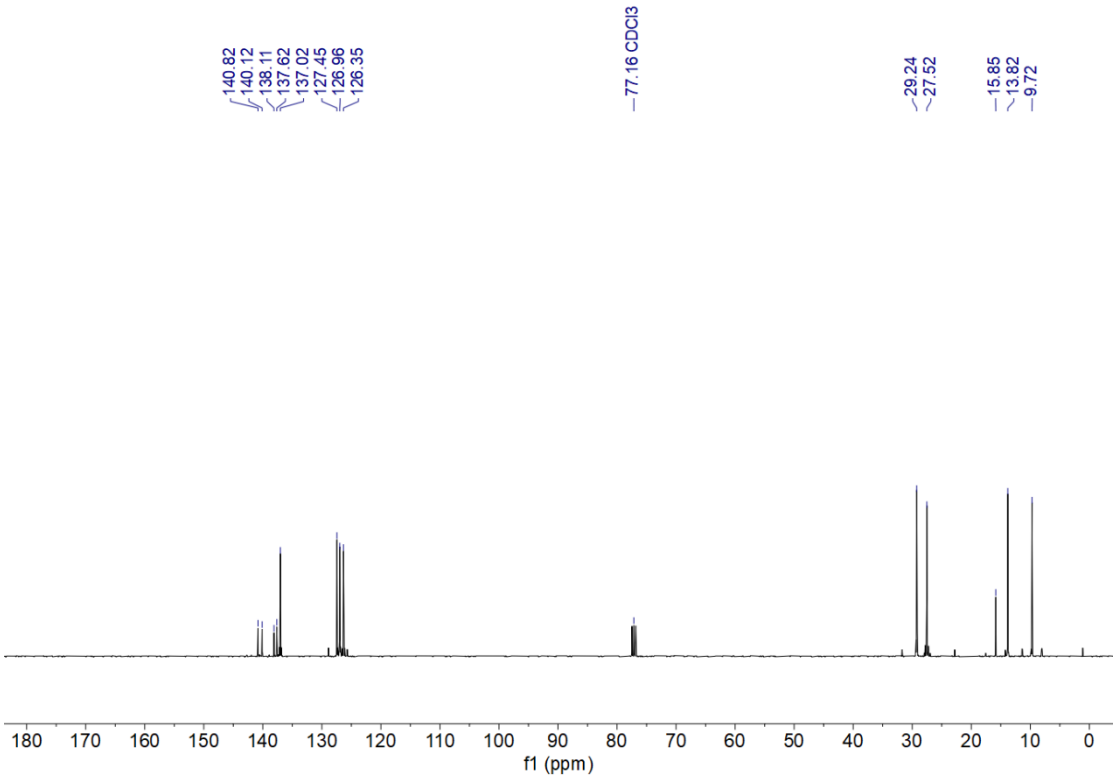

Figure S28. ^{13}C NMR spectrum of compound **3** in $CDCl_3$.

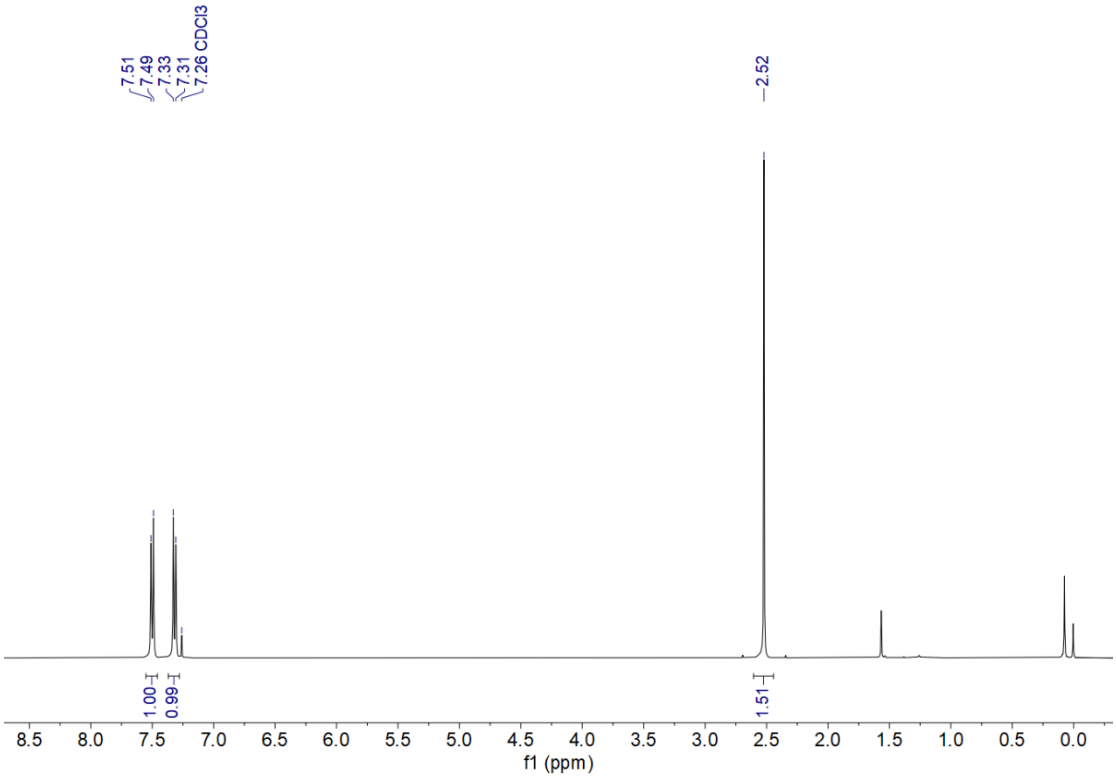

Figure S29. ^{1}H NMR spectrum of product **P2** in $CDCl_3$.

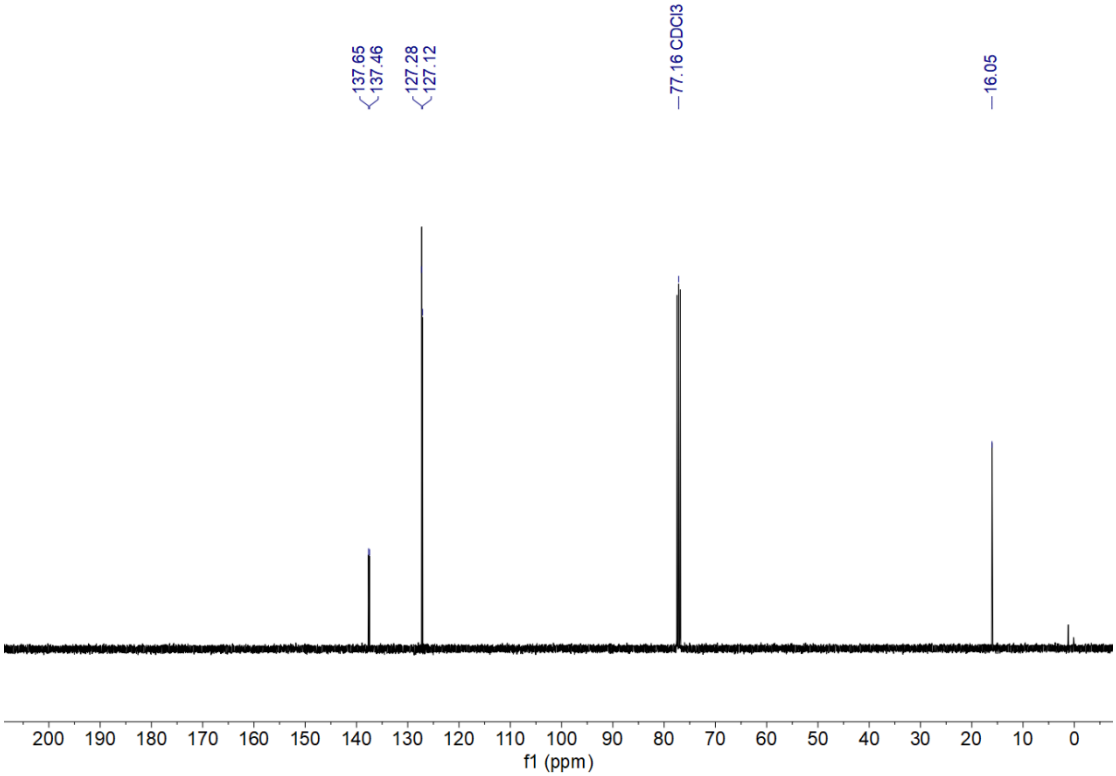

Figure S30. ^{13}C NMR spectrum of product **P2** in $CDCl_3$.

V. References

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