Supporting Information

Imine Linkers Enable the Formation of Robust Single-Molecule Junctions

Yidong Xiao,[1†] Chaochao Xie,[2†] Ya-Qi Kong,[3] Guang-Ping Zhang,[3*] Xuefeng Tan,[2*] Haixing Li,[1*]

[1]Department of Physics, City University of Hong Kong, Kowloon 999077, Hong Kong SAR, China

[2]Department of Chemistry, City University of Hong Kong, Kowloon 999077, Hong Kong SAR, China

[3]School of Physics and Electronics, Shandong Normal University, Jinan 250358, China

[†]These authors contributed equally to this work.

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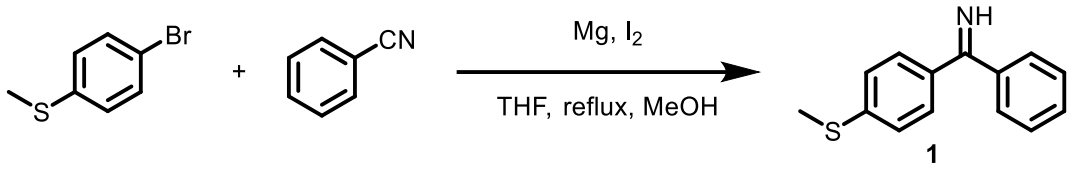
I. Synthetic procedures and characterization of compounds

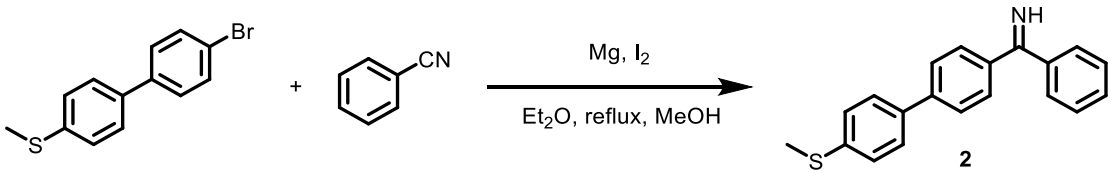
If not stated otherwise, all reagents and starting materials were obtained from commercial suppliers and used without further purification. Anhydrous *n*-hexane, Et_2O, and THF were distilled from sodium-benzophenone and stored over activated 4Å molecular sieves. Reactions involving air- and moisture-sensitive compounds were performed under an atmosphere of pre-dried nitrogen using standard Schlenk-technique or within an argon-filled glovebox. The ^1H NMR spectra were recorded in solution of $CDCl_3$ on Bruker 300 MHz *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.



(4-(methylthio)phenyl)(phenyl)methanimine (1)

To an oven-dried 100 mL round bottom flask was added magnesium turnings (0.36 g, 15.0 mmol, 1.5 equiv.), iodine crystals (50.0 mg, 0.2 mmol, 0.02 equiv.) and THF (30.0 mL). A solution of (4-bromophenyl)(methyl)sulfane (2.0 g, 10.0 mmol, 1.0 equiv.) in THF (15.0 mL) was added dropwise. After stirred at 70 °C for 2 h, a solution of benzonitrile (1.0 g, 10.0 mmol, 1.0 equiv.) in THF (10.0 mL) was added dropwise at ambient temperature. The reaction mixture was stirred under reflux for further 8 h. Upon completion, the resulting mixture was cooled to 0 °C and dry MeOH (4.0 mL, 90.0 mmol, 9.0 equiv.) was added to give an orange solution. The mixture was filtered through celite and the precipitate was rinsed with THF. The resulting filtrate was concentrated under reduced pressure and purified by flash column chromatography (*n*-hexane/EtOAc/TEA = 6:1:0.1→3:1:0.1) to give desired imine product **1** as a yellow oil (1.5 g, 65% yield). The collected ^1H NMR data was consistent with the literature report.[1]

^1H NMR (300 MHz, $CDCl_3$) δ 9.63 (s, 1H), 7.80 – 7.36 (m, 7H), 7.27 (d, *J* = 8.18 Hz, 2H), 2.54 (s, 3H) ppm.



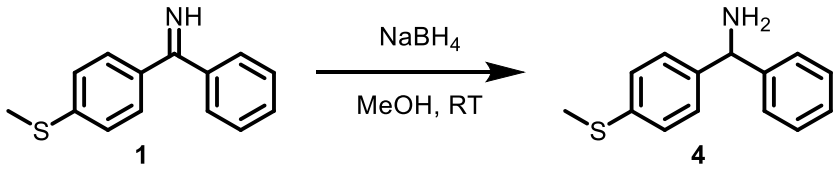
(4'-(methylthio)-[1,1'-biphenyl]-4-yl)(phenyl)methanimine (2)

To an oven-dried 100 mL round bottom flask was added magnesium turnings (0.36 g, 15.0 mmol, 1.5 equiv.), iodine crystals (50.0 mg, 0.2 mmol, 0.02 equiv.) and THF (30.0 mL). A solution of (4'-bromo-[1,1'-biphenyl]-4-yl)(methyl)sulfane (2.8 g, 10.0 mmol, 1.0 equiv.) in THF (15.0 mL) was added dropwise. After stirred at 70 °C for 2 h, a solution of benzonitrile (1.0 g, 10.0 mmol, 1.0 equiv.) in THF (10.0 mL) was added dropwise at ambient temperature. The reaction mixture was stirred under reflux for further 8 h. Upon completion, the resulting mixture was cooled to 0 °C and dry MeOH (4.0 mL, 90.0 mmol, 9.0 equiv.) was added to give an orange solution. The mixture was filtered through celite and the precipitate was rinsed with THF. The resulting filtrate was concentrated under reduced pressure and purified by flash column chromatography (*n*-hexane/EtOAc/TEA = 4:1:0.1→3:1:0.1) to give desired imine product **2** as a white solid (1.7 g, 56% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 – 7.56 (m, 7H), 7.55 – 7.43 (m, 4H), 7.40 – 7.34 (m, 2H), 2.56 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0, 142.5, 138.5, 136.9, 130.3, 129.1 (2C), 128.4 (2C), 128.3, 127.5, 126.9, 126.7, 15.8 ppm.

HR-MS (ESI) *m/z* Calcd. for $C_{20}H_{18}NS^+$ $[M+H]^+$: 304.1154, found: 304.1159.

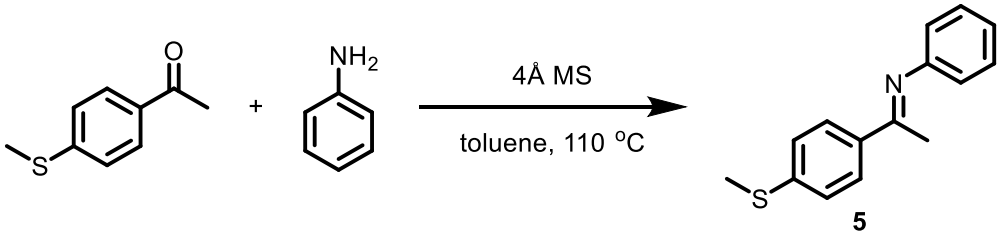


1 **4**

(4-(methylthio)phenyl)(phenyl)methanamine (4)

To a stirred solution of compound **1** (50.0 mg, 0.25 mmol, 1.0 equiv.) in dry MeOH (2.0 mL) at room temperature, $NaBH_4$ (14.0 mg, 0.38 mmol, 1.5 equiv.) was added. After stirring for 30 minutes, the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel (eluent: *n*-hexane/EtOAc = 3:1→1:1) to yield the target product as a white solid (46.5 mg, 93% yield). The collected ^{1}H NMR data was consistent with the literature report.[2]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.31 (m, 6H), 7.30 – 7.22 (m, 3H), 5.20 (s, 1H), 2.49 (s, 3H), 1.91 (s, 2H) ppm.

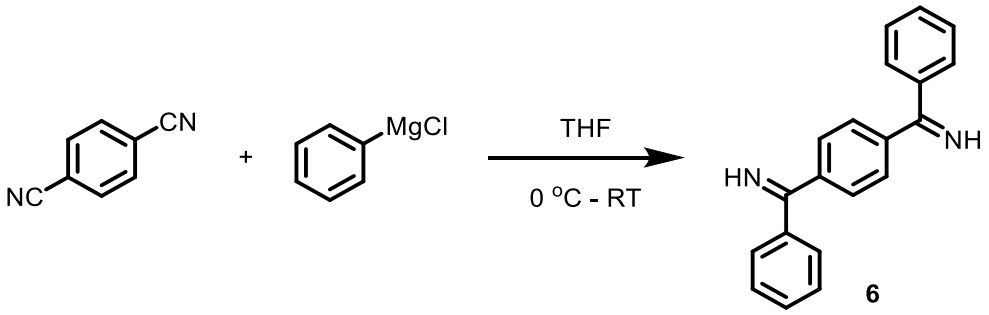


5

(*E*)-1-(4-(methylthio)phenyl)-N-phenylethan-1-imine (5)

To a flask was added 1-(4-(methylthio)phenyl)ethan-1-one (2.5 g, 15.0 mmol, 1.0 equiv.), aniline (1.7 g, 18.0 mmol, 1.2 equiv.), 4 Å molecular sieves and toluene (30 mL). Then, the mixture was refluxed for 24 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (eluent: *n*-hexane/EtOAc/TEA = 5:1:0.1→3:1:0.1) to yield the product as a yellow solid (2.9 g, 80% yield). The collected ^{1}H NMR data was consistent with the literature report.[3]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 – 7.89 (m, 2H), 7.43 – 7.25 (m, 4H), 7.17 – 7.07 (m, 1H), 6.82 (dd, *J* = 8.36, 1.11 Hz, 2H), 2.55 (s, 3H), 2.23 (s, 3H) ppm.



6

1,4-phenylenebis(phenylmethanimine) (6)

To an oven-dried 100 mL flask, terephthalonitrile (1.3 g, 10.0 mmol, 1.0 equiv.) and anhydrous THF (20.0 mL) were added. At 0 °C, phenylmagnesium chloride (11.0 mL, 22.0 mmol, 2.2 equiv., 2.0 M in THF) was added dropwise and the mixture was stirred at room temperature overnight. The resulting mixture was cooled to 0 °C and dry MeOH (4.0 mL, 90.0 mmol, 9.0 equiv.) was added to give an orange solution. The mixture was filtered through celite and the precipitate was washed with THF. The resulting filtrate was then concentrated under reduced pressure and purified by flash column chromatography (eluecnt: *n*-hexane/EtOAc/TEA = 4:1:0.1→3:1:0.1) to give desired imine product **6** as a white solid (1.5 g, 53% yield). The collected ^{1}H NMR data was consistent with the literature report.[4]

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (s, 4H), 7.60 (d, *J* = 7.13 Hz, 4H), 7.53 – 7.42 (m, 6H) ppm.

II. Scanning tunneling microscope break junction experiment details

Single-molecule conductance measurements were carried out using a custom-built scanning tunneling microscope break-junction (STM-BJ) setup operated at room temperature under ambient conditions,[5-7] and the details are provided in the supplementary information of a previous work.[8] Gold substrates were prepared by thermally evaporating approximately 100 nm of 99.999% gold onto mechanically-polished steel discs (diameter ~15 mm). Prior to each experiment, the gold-coated substrates were cleaned using an UV-ozone cleaner for 20 minutes to remove surface contaminants. Gold STM tips were prepared by mechanically cutting a 0.25 mm diameter gold wire with a wire cutter to form a sharp apex. For measurements conducted in propylene carbonate (PC), the tip was coated with Apiezon wax to insulate the shaft, leaving only the apex exposed, in order to minimize leakage current in the polar solvent.

Molecular solutions were prepared at a concentration of 1 mM in either 1,2,4-trichlorobenzene (TCB) or PC. The solution was dropped onto the cleaned gold substrate in each measurement. During STM-BJ experiments, the gold tip was repeatedly brought into and out of contact with the substrate at a constant speed of 18 nm/s while a fixed bias voltage of 90 mV, 450 mV, or 0.9 V was applied between the tip and the substrate. The resulting current versus distance traces were recorded automatically during each breaking cycle.

Approximately 10,000 individual conductance traces were collected in each measurement. These traces were used to construct both one-dimensional (1D) and two-dimensional (2D) conductance histograms without any data selection. 1D histograms display the statistical distribution of conductance values, showing the most probable single-molecule conductance, while 2D histograms correlate conductance with tip displacement, offering information about the plateau length and junction evolution.

III. Density functional theory calculation details

In our calculations, the geometric optimization of the bare molecules **1**, **3**, and **4** was performed using density functional theory (DFT) within the QuantumATK package.[9, 10] Subsequently, the optimized molecules were sandwiched between two pyramid Au electrodes on 6x6 Au (111) surfaces and the geometric configurations of single-molecule junctions were further optimized. During these optimizations, the force criteria were set to 0.02 eV/Å. The transmission spectra of single-molecule junctions of **1**, **3**, and **4** were investigated by using the nonequilibrium Green's function (NEGF) method[11] in combination with DFT in the QuantumATK package. In the geometric optimizations and subsequent electronic transport calculations, the effects of atomic nuclei and core electrons were described using Troullier-Martins-type norm-conserving pseudopotentials.[12] For the valence electrons, the Perdew-Burke-Ernzerhof (PBE) functional[13] was used for the exchange-correlation effect and a single-ζ plus single polarization (SZP) basis set was employed for Au atoms while a double-ζ plus single polarization (DZP) basis set was used for the other atoms (i.e., H, C, N, and S). The mesh cutoff used to determine the real-space density grid sampling was chosen to be 200 Rydberg and the *k*-point sampling was set to 6×6×150. The convergence criterion of Hamiltonian was set to be 1.0×10^{-4} Hartree for the electronic self-consistent loop.

Optimized single-molecule junction structure of **1**

atom	x	y	z
Au	1.441857	1.24868	8.548191
Au	1.444242	1.24788	15.81595
Au	-2.2E-05	3.746088	8.548191
Au	0.003825	3.735772	15.82226
Au	-1.4419	6.243496	8.548191
Au	-1.45334	6.213507	15.8097
Au	-2.88378	8.740904	8.548191
Au	-2.93675	8.709693	15.88458
Au	-4.32566	11.23831	8.548191
Au	-4.35895	11.23989	15.80535
Au	-5.76754	13.73572	8.548191
Au	-5.77332	13.74258	15.82343
Au	4.325615	1.24868	8.548191
Au	4.32245	1.257193	15.82468
Au	2.883736	3.746088	8.548191
Au	2.889364	3.735469	15.82458
Au	1.441857	6.243496	8.548191

Au	1.460907	6.212939	15.80645
Au	-2.2E-05	8.740904	8.548191
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Au	-2.90025	13.76334	15.8062
Au	7.209373	1.24868	8.548191
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Au	5.767494	3.746088	8.548191
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Au	4.325615	11.23831	8.548191
Au	4.36445	11.24327	15.808
Au	2.883736	13.73572	8.548191
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Au	12.97689	1.24868	8.548191
Au	12.98991	1.258663	15.8252
Au	11.53501	3.746088	8.548191
Au	11.53946	3.749001	15.83268
Au	10.09313	6.243496	8.548191
Au	10.08995	6.240773	15.82567
Au	8.651252	8.740904	8.548191

Au	8.655936	8.741237	15.83251
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Au	0.25697	12.2219	32.10858
Au	-1.21922	14.68922	39.25315
Au	8.873933	2.202181	39.25315
Au	7.432054	4.699588	39.25315
Au	5.990175	7.196996	39.25315
Au	4.548296	9.694404	39.25315

Au	3.106416	12.19181	39.25315
Au	1.664537	14.68922	39.25315
Au	11.75769	2.202181	39.25315
Au	10.31581	4.699588	39.25315
Au	8.873933	7.196996	39.25315
Au	7.432054	9.694404	39.25315
Au	5.990175	12.19181	39.25315
Au	4.548296	14.68922	39.25315
Au	14.64145	2.202181	39.25315
Au	13.19957	4.699588	39.25315
Au	11.75769	7.196996	39.25315
Au	10.31581	9.694404	39.25315
Au	8.873933	12.19181	39.25315
Au	7.432054	14.68922	39.25315
Au	0.222658	0.537242	36.89857
Au	-1.21922	3.03465	36.89857
Au	-2.6611	5.532058	36.89857
Au	-4.10298	8.029466	36.89857
Au	-5.54486	10.52687	36.89857
Au	-6.98674	13.02428	36.89857
Au	3.106416	0.537242	36.89857
Au	1.664537	3.03465	36.89857
Au	0.222658	5.532058	36.89857
Au	-1.21922	8.029466	36.89857
Au	-2.6611	10.52687	36.89857
Au	-4.10298	13.02428	36.89857
Au	5.990175	0.537242	36.89857
Au	4.548296	3.03465	36.89857
Au	3.106416	5.532058	36.89857
Au	1.664537	8.029466	36.89857
Au	0.222658	10.52687	36.89857
Au	0.108879	10.59093	29.95192
Au	-1.21922	13.02428	36.89857
Au	8.873933	0.537242	36.89857
Au	7.432054	3.03465	36.89857
Au	5.990175	5.532058	36.89857
Au	4.548296	8.029466	36.89857
Au	3.106416	10.52687	36.89857

Au	1.664537	13.02428	36.89857
Au	11.75769	0.537242	36.89857
Au	10.31581	3.03465	36.89857
Au	8.873933	5.532058	36.89857
Au	7.432054	8.029466	36.89857
Au	5.990175	10.52687	36.89857
Au	4.548296	13.02428	36.89857
Au	14.64145	0.537242	36.89857
Au	13.19957	3.03465	36.89857
Au	11.75769	5.532058	36.89857
Au	10.31581	8.029466	36.89857
Au	8.873933	10.52687	36.89857
Au	7.432054	13.02428	36.89857
C	0.779095	10.70379	23.84226
C	1.626534	9.598135	24.08937
C	1.52303	8.8864	25.28447
C	0.56959	9.247159	26.26935
C	-0.23677	10.38574	26.02966
C	-0.14269	11.10494	24.83574
H	2.367257	9.299233	23.33201
H	2.196698	8.037021	25.46512
H	-0.96799	10.67984	26.79715
H	-0.79668	11.97292	24.67839
C	0.356636	8.439475	27.48602
N	-0.31541	8.939842	28.50101
C	0.830872	7.032272	27.56173
C	1.376175	6.569705	28.78354
C	0.681755	6.124806	26.48893
C	1.76352	5.232331	28.92687
H	1.516778	7.280965	29.61547
C	1.064307	4.785923	26.63994
H	0.228847	6.467686	25.54715
C	1.606608	4.337516	27.85534
H	2.189528	4.887324	29.88099
H	0.927952	4.083794	25.80436
H	1.906906	3.285403	27.96752
H	-0.50933	8.190405	29.18318
S	1.007451	11.5071	22.28471

C	-0.13908	12.90897	22.32643
H	-1.17849	12.57785	22.50196
H	0.176386	13.64927	23.08528
H	-0.07567	13.34897	21.31256

Optimized single-molecule junction structure of **3**

atom	x	y	z
Au	1.441857	1.24868	8.548191
Au	1.437502	1.243181	15.81534
Au	-2.23456E-05	3.746088	8.548191
Au	-0.001867072	3.731208	15.82545
Au	-1.441901	6.243496	8.548191
Au	-1.461613	6.204942	15.80879
Au	-2.883781	8.740904	8.548191
Au	-2.976593	8.686049	15.75844
Au	-4.32566	11.23831	8.548191
Au	-4.361093	11.23698	15.80865
Au	-5.767539	13.73572	8.548191
Au	-5.779106	13.73701	15.8243
Au	4.325615	1.24868	8.548191
Au	4.314062	1.254343	15.82432
Au	2.883736	3.746088	8.548191
Au	2.883731	3.731531	15.82468
Au	1.441857	6.243496	8.548191
Au	1.455644	6.204581	15.80908
Au	-2.23456E-05	8.740904	8.548191
Au	0.004174416	8.668086	15.664
Au	-1.441901	11.23831	8.548191
Au	-1.490985	11.29934	15.67732
Au	-2.883781	13.73572	8.548191
Au	-2.908365	13.7688	15.81041
Au	7.209373	1.24868	8.548191
Au	7.198081	1.273607	15.79939
Au	5.767494	3.746088	8.548191
Au	5.766011	3.741796	15.83322
Au	4.325615	6.243496	8.548191
Au	4.344684	6.215333	15.80108
Au	2.883736	8.740904	8.548191

Au	2.943851	8.701333	15.83489
Au	1.441857	11.23831	8.548191
Au	1.492478	11.28111	15.68919
Au	-2.23456E-05	13.73572	8.548191
Au	3.72924E-05	13.80238	15.88765
Au	10.09313	1.24868	8.548191
Au	10.09968	1.272037	15.79936
Au	8.651252	3.746088	8.548191
Au	8.647545	3.749749	15.82414
Au	7.209373	6.243496	8.548191
Au	7.211589	6.235022	15.8274
Au	5.767494	8.740904	8.548191
Au	5.794161	8.732157	15.8021
Au	4.325615	11.23831	8.548191
Au	4.356833	11.23891	15.8061
Au	2.883736	13.73572	8.548191
Au	2.9028	13.76378	15.80915
Au	12.97689	1.24868	8.548191
Au	12.98455	1.252046	15.822
Au	11.53501	3.746088	8.548191
Au	11.52992	3.737767	15.83325
Au	10.09313	6.243496	8.548191
Au	10.07776	6.232733	15.82853
Au	8.651252	8.740904	8.548191
Au	8.643677	8.736428	15.83436
Au	7.209373	11.23831	8.548191
Au	7.216874	11.23919	15.82339
Au	5.767494	13.73572	8.548191
Au	5.775968	13.73842	15.82334
Au	15.86065	1.24868	8.548191
Au	15.86288	1.243227	15.81476
Au	14.41877	3.746088	8.548191
Au	14.41534	3.729032	15.8258
Au	12.97689	6.243496	8.548191
Au	12.94381	6.20233	15.80635
Au	11.53501	8.740904	8.548191
Au	11.4854	8.728978	15.80385
Au	10.09313	11.23831	8.548191

Au	10.07964	11.23959	15.82475
Au	8.651252	13.73572	8.548191
Au	8.649496	13.7362	15.81559
Au	-2.23456E-05	2.08115	10.90277
Au	-1.441901	4.578557	10.90277
Au	-2.883781	7.075965	10.90277
Au	-4.32566	9.573373	10.90277
Au	-5.767539	12.07078	10.90277
Au	-7.209418	14.56819	10.90277
Au	2.883736	2.08115	10.90277
Au	1.441857	4.578557	10.90277
Au	-2.23456E-05	7.075965	10.90277
Au	-1.441901	9.573373	10.90277
Au	-1.536747	9.542251	17.88606
Au	-2.883781	12.07078	10.90277
Au	-4.32566	14.56819	10.90277
Au	5.767494	2.08115	10.90277
Au	4.325615	4.578557	10.90277
Au	2.883736	7.075965	10.90277
Au	1.441857	9.573373	10.90277
Au	1.429454	9.561154	17.98033
Au	-2.23456E-05	12.07078	10.90277
Au	0.02147844	12.05459	18.06499
Au	-1.441901	14.56819	10.90277
Au	8.651252	2.08115	10.90277
Au	7.209373	4.578557	10.90277
Au	5.767494	7.075965	10.90277
Au	4.325615	9.573373	10.90277
Au	2.883736	12.07078	10.90277
Au	1.441857	14.56819	10.90277
Au	11.53501	2.08115	10.90277
Au	10.09313	4.578557	10.90277
Au	8.651252	7.075965	10.90277
Au	7.209373	9.573373	10.90277
Au	5.767494	12.07078	10.90277
Au	4.325615	14.56819	10.90277
Au	14.41877	2.08115	10.90277
Au	12.97689	4.578557	10.90277

Au	11.53501	7.075965	10.90277
Au	10.09313	9.573373	10.90277
Au	8.651252	12.07078	10.90277
Au	7.209373	14.56819	10.90277
Au	-2.23456E-05	0.416211	13.25735
Au	-1.441901	2.913619	13.25735
Au	-2.883781	5.411027	13.25735
Au	-4.32566	7.908435	13.25735
Au	-5.767539	10.40584	13.25735
Au	-7.209418	12.90325	13.25735
Au	2.883736	0.416211	13.25735
Au	1.441857	2.913619	13.25735
Au	-2.23456E-05	5.411027	13.25735
Au	-1.441901	7.908435	13.25735
Au	-2.883781	10.40584	13.25735
Au	-4.32566	12.90325	13.25735
Au	5.767494	0.416211	13.25735
Au	4.325615	2.913619	13.25735
Au	2.883736	5.411027	13.25735
Au	1.441857	7.908435	13.25735
Au	-2.23456E-05	10.40584	13.25735
Au	-0.1959361	10.31366	20.15482
Au	-1.441901	12.90325	13.25735
Au	8.651252	0.416211	13.25735
Au	7.209373	2.913619	13.25735
Au	5.767494	5.411027	13.25735
Au	4.325615	7.908435	13.25735
Au	2.883736	10.40584	13.25735
Au	1.441857	12.90325	13.25735
Au	11.53501	0.416211	13.25735
Au	10.09313	2.913619	13.25735
Au	8.651252	5.411027	13.25735
Au	7.209373	7.908435	13.25735
Au	5.767494	10.40584	13.25735
Au	4.325615	12.90325	13.25735
Au	14.41877	0.416211	13.25735
Au	12.97689	2.913619	13.25735
Au	11.53501	5.411027	13.25735

Au	10.09313	7.908435	13.25735
Au	8.651252	10.40584	13.25735
Au	7.209373	12.90325	13.25735
Au	1.647861	1.198705	41.61544
Au	1.645407	1.19612	34.34549
Au	0.205982	3.696113	41.61544
Au	0.2077788	3.684093	34.33747
Au	-1.235897	6.19352	41.61544
Au	-1.251044	6.158505	34.3515
Au	-2.677776	8.690928	41.61544
Au	-2.746641	8.64789	34.33123
Au	-4.119655	11.18834	41.61544
Au	-4.154866	11.18984	34.35022
Au	-5.561535	13.68574	41.61544
Au	-5.569389	13.68969	34.3381
Au	4.531619	1.198705	41.61544
Au	4.522455	1.205617	34.33637
Au	3.08974	3.696113	41.61544
Au	3.091782	3.684269	34.33699
Au	1.647861	6.19352	41.61544
Au	1.66488	6.160917	34.35076
Au	0.205982	8.690928	41.61544
Au	0.2056692	8.618169	34.48198
Au	-1.235897	11.18834	41.61544
Au	-1.296234	11.22695	34.49344
Au	-2.677776	13.68574	41.61544
Au	-2.695928	13.71757	34.34921
Au	7.415378	1.198705	41.61544
Au	7.402814	1.233328	34.35869
Au	5.973498	3.696113	41.61544
Au	5.972174	3.694969	34.32864
Au	4.531619	6.19352	41.61544
Au	4.552744	6.168964	34.36114
Au	3.08974	8.690928	41.61544
Au	3.153331	8.654692	34.32379
Au	1.647861	11.18834	41.61544
Au	1.710379	11.22826	34.49757
Au	0.205982	13.68574	41.61544

Au	0.2075659	13.77146	34.33898
Au	10.29914	1.198705	41.61544
Au	10.31128	1.233191	34.3586
Au	8.857257	3.696113	41.61544
Au	8.857259	3.705848	34.33476
Au	7.415378	6.19352	41.61544
Au	7.422829	6.186647	34.33487
Au	5.973498	8.690928	41.61544
Au	6.0047	8.683864	34.36136
Au	4.531619	11.18834	41.61544
Au	4.567977	11.19115	34.34976
Au	3.08974	13.68574	41.61544
Au	3.111903	13.71749	34.34955
Au	13.18289	1.198705	41.61544
Au	13.19325	1.206861	34.33886
Au	11.74101	3.696113	41.61544
Au	11.74105	3.69703	34.32792
Au	10.29914	6.19352	41.61544
Au	10.29172	6.18888	34.33501
Au	8.857257	8.690928	41.61544
Au	8.855969	8.68976	34.3292
Au	7.415378	11.18834	41.61544
Au	7.426503	11.19124	34.33661
Au	5.973498	13.68574	41.61544
Au	5.985366	13.69074	34.33773
Au	16.06665	1.198705	41.61544
Au	16.06992	1.197042	34.34654
Au	14.62477	3.696113	41.61544
Au	14.62328	3.683498	34.33615
Au	13.18289	6.19352	41.61544
Au	13.16033	6.165748	34.35872
Au	11.74101	8.690928	41.61544
Au	11.70649	8.683001	34.35894
Au	10.29914	11.18834	41.61544
Au	10.28814	11.19031	34.33616
Au	8.857257	13.68574	41.61544
Au	8.857672	13.68671	34.34441
Au	0.205982	2.031174	39.26086

Au	-1.235897	4.528582	39.26086
Au	-2.677776	7.02599	39.26086
Au	-4.119655	9.523398	39.26086
Au	-5.561535	12.02081	39.26086
Au	-7.003414	14.51821	39.26086
Au	3.08974	2.031174	39.26086
Au	1.647861	4.528582	39.26086
Au	0.205982	7.02599	39.26086
Au	-1.235897	9.523398	39.26086
Au	-1.258456	9.534929	32.19005
Au	-2.677776	12.02081	39.26086
Au	-4.119655	14.51821	39.26086
Au	5.973498	2.031174	39.26086
Au	4.531619	4.528582	39.26086
Au	3.08974	7.02599	39.26086
Au	1.647861	9.523398	39.26086
Au	1.654716	9.548168	32.18549
Au	0.205982	12.02081	39.26086
Au	0.2120737	12.05342	32.19509
Au	-1.235897	14.51821	39.26086
Au	8.857257	2.031174	39.26086
Au	7.415378	4.528582	39.26086
Au	5.973498	7.02599	39.26086
Au	4.531619	9.523398	39.26086
Au	3.08974	12.02081	39.26086
Au	1.647861	14.51821	39.26086
Au	11.74101	2.031174	39.26086
Au	10.29914	4.528582	39.26086
Au	8.857257	7.02599	39.26086
Au	7.415378	9.523398	39.26086
Au	5.973498	12.02081	39.26086
Au	4.531619	14.51821	39.26086
Au	14.62477	2.031174	39.26086
Au	13.18289	4.528582	39.26086
Au	11.74101	7.02599	39.26086
Au	10.29914	9.523398	39.26086
Au	8.857257	12.02081	39.26086
Au	7.415378	14.51821	39.26086

Au	0.205982	0.3662353	36.90628
Au	-1.235897	2.863643	36.90628
Au	-2.677776	5.361051	36.90628
Au	-4.119655	7.858459	36.90628
Au	-5.561535	10.35587	36.90628
Au	-7.003414	12.85327	36.90628
Au	3.08974	0.3662353	36.90628
Au	1.647861	2.863643	36.90628
Au	0.205982	5.361051	36.90628
Au	-1.235897	7.858459	36.90628
Au	-2.677776	10.35587	36.90628
Au	-4.119655	12.85327	36.90628
Au	5.973498	0.3662353	36.90628
Au	4.531619	2.863643	36.90628
Au	3.08974	5.361051	36.90628
Au	1.647861	7.858459	36.90628
Au	0.205982	10.35587	36.90628
Au	0.2168287	10.42355	30.00162
Au	-1.235897	12.85327	36.90628
Au	8.857257	0.3662353	36.90628
Au	7.415378	2.863643	36.90628
Au	5.973498	5.361051	36.90628
Au	4.531619	7.858459	36.90628
Au	3.08974	10.35587	36.90628
Au	1.647861	12.85327	36.90628
Au	11.74101	0.3662353	36.90628
Au	10.29914	2.863643	36.90628
Au	8.857257	5.361051	36.90628
Au	7.415378	7.858459	36.90628
Au	5.973498	10.35587	36.90628
Au	4.531619	12.85327	36.90628
Au	14.62477	0.3662353	36.90628
Au	13.18289	2.863643	36.90628
Au	11.74101	5.361051	36.90628
Au	10.29914	7.858459	36.90628
Au	8.857257	10.35587	36.90628
Au	7.415378	12.85327	36.90628
C	-1.425959	8.750124	23.16455

C	-1.927195	9.982052	23.63149
C	-1.989091	10.22496	25.00715
C	-1.536509	9.261021	25.93208
C	-1.040838	8.032187	25.45305
C	-0.9885074	7.772116	24.07927
H	-2.247421	10.75191	22.91318
H	-2.383458	11.18696	25.37132
H	-0.702317	7.261728	26.16418
H	-0.6164162	6.808689	23.70104
C	-1.444896	9.586287	27.40121
N	-0.1028315	10.1363	27.73816
H	0.6200283	9.490436	27.39265
S	-1.254927	8.385912	21.4384
C	-2.970917	8.588159	20.85647
H	-3.630188	7.908386	21.4281
H	-3.310004	9.63567	20.9421
H	-2.96394	8.30613	19.78132
H	-2.198742	10.33713	27.70573
H	-1.599437	8.689987	28.03288
H	0.04455218	11.01487	27.2238

Optimized single-molecule junction structure of **4**

atom	x	y	z
Au	1.441857	1.24868	8.548191
Au	1.438636	1.247849	15.81598
Au	-2.23456E-05	3.746088	8.548191
Au	-0.001521043	3.735256	15.82222
Au	-1.441901	6.243496	8.548191
Au	-1.45848	6.212605	15.8095
Au	-2.883781	8.740904	8.548191
Au	-2.945107	8.704663	15.8606
Au	-4.32566	11.23831	8.548191
Au	-4.364179	11.23944	15.81061
Au	-5.767539	13.73572	8.548191
Au	-5.779369	13.7413	15.82406
Au	4.325615	1.24868	8.548191
Au	4.316778	1.254706	15.82546
Au	2.883736	3.746088	8.548191

Au	2.88453	3.734651	15.82294
Au	1.441857	6.243496	8.548191
Au	1.455886	6.211308	15.8074
Au	-2.23456E-05	8.740904	8.548191
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Au	-2.883781	13.73572	8.548191
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Au	7.196747	1.279536	15.79975
Au	5.767494	3.746088	8.548191
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Au	4.325615	6.243496	8.548191
Au	4.344322	6.221611	15.79969
Au	2.883736	8.740904	8.548191
Au	2.944397	8.70711	15.8627
Au	1.441857	11.23831	8.548191
Au	1.501804	11.26765	15.68868
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Au	7.214833	6.240418	15.82582
Au	5.767494	8.740904	8.548191
Au	5.797145	8.736608	15.80058
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Au	2.883736	13.73572	8.548191
Au	2.902274	13.76474	15.80821
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Au	10.09313	6.243496	8.548191

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Au	-7.209418	12.90325	13.25735
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Au	-2.883781	10.40584	13.25735
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Au	10.09313	7.908435	13.25735
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Au	0.03090365	3.433944	41.60932
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Au	4.349397	0.9438031	34.33199
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Au	2.916511	3.422934	34.32794
Au	1.472783	5.931352	41.60932
Au	1.489943	5.89821	34.33673
Au	0.03090365	8.42876	41.60932

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Au	7.240299	0.9365363	41.60932
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Au	2.914662	8.42876	41.60932
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Au	10.12406	0.9365363	41.60932
Au	10.13531	0.963393	34.35401
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Au	8.681214	3.442133	34.33028
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Au	8.682178	8.42876	41.60932
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Au	7.240299	10.92617	41.60932

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Au	10.12406	2.601475	36.90016
Au	8.682178	5.098883	36.90016
Au	7.240299	7.596291	36.90016
Au	5.79842	10.0937	36.90016
Au	4.356541	12.59111	36.90016
Au	14.44969	0.104067	36.90016
Au	13.00782	2.601475	36.90016
Au	11.56594	5.098883	36.90016
Au	10.12406	7.596291	36.90016
Au	8.682178	10.0937	36.90016
Au	7.240299	12.59111	36.90016
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C	1.359349	1.359349	8.565384
C	0.854843	0.854843	9.096066
C	0.327178	0.3271784	10.40379
C	0.293146	0.2931459	11.15596
H	1.655259	1.655259	8.855922
H	1.766751	1.766751	7.542256
H	-0.06880104	10.8367	27.13528
H	-0.119198	12.1761	25.01932
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C	1.977853	1.977853	8.471982
C	2.700959	2.700959	9.681482
C	2.179204	2.179204	7.515304
C	3.578613	3.578613	9.950171
H	2.570841	2.570841	10.41937
C	3.023917	3.023917	7.795125
H	1.651036	1.651036	6.548706
C	3.72304	3.72304	9.02892
H	4.140429	4.140429	10.8948
H	3.193627	3.193627	7.044405
H	4.410372	4.410372	9.229864

H	-0.5974219	7.746751	28.8924
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C	2.347078	2.347078	11.8069
H	2.870574	2.870574	12.495
H	2.869524	2.869524	10.83595
H	2.287298	2.287298	12.24002
H	-1.229223	8.550885	27.58986
H	0.863593	0.8635927	7.177076

IV. Additional figures and tables

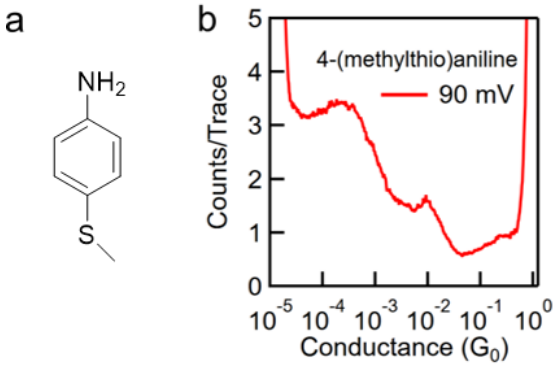


Figure S1. (a) Chemical structure of 4-(methylthio)aniline. (b) 1D conductance histogram of 4-(methylthio)aniline measured in TCB under 90 mV tip bias.

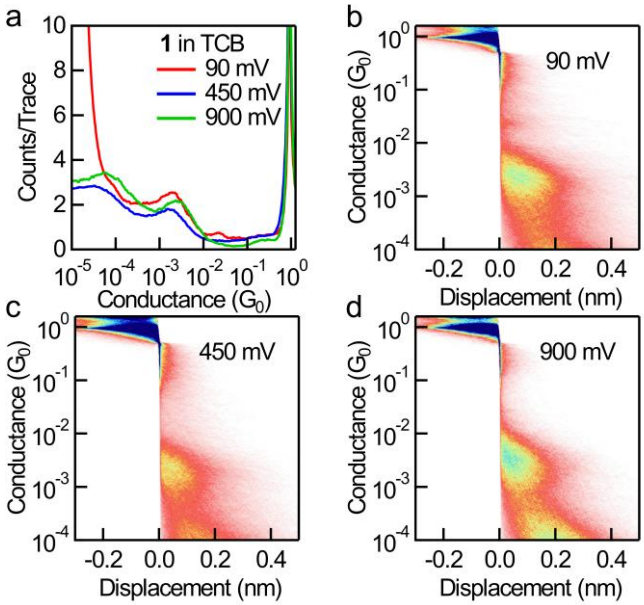


Figure S2. (a) 1D conductance histograms of **1** measured in TCB under 90 mV, 450 mV, and 900 mV tip biases. (b-d) 2D conductance histograms of **1** measured in TCB under (b) 90 mV, (c) 450 mV, and (d) 900 mV.

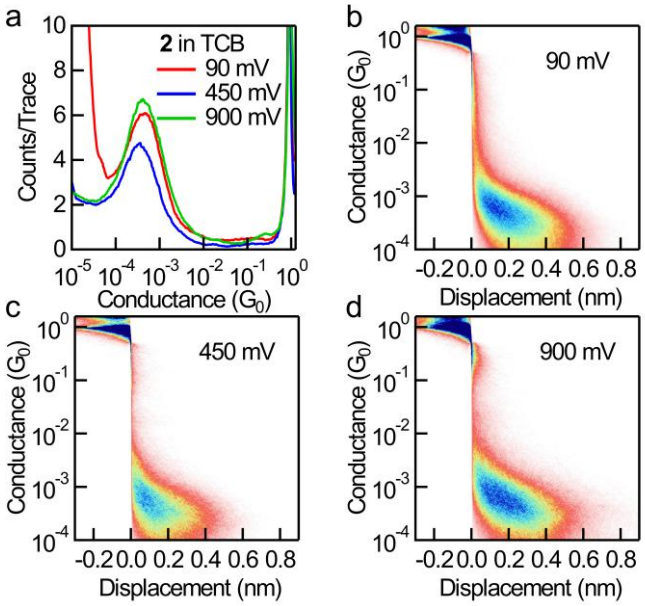


Figure S3. (a) 1D conductance histograms of **2** measured in TCB under 90 mV, 450 mV, and 900 mV tip biases. (b-d) 2D conductance histograms of **2** measured in TCB under (b) 90 mV, (c) 450 mV, and (d) 900 mV.

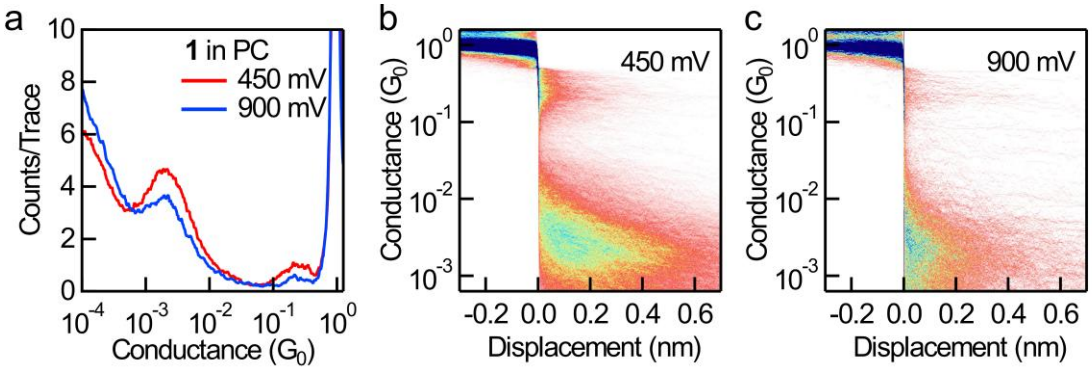


Figure S4. (a) 1D conductance histograms of **1** measured in PC under 450 mV and 900 mV. (b,c) 2D conductance histograms of **1** measured in PC under (b) 450 mV and (d) 900 mV.

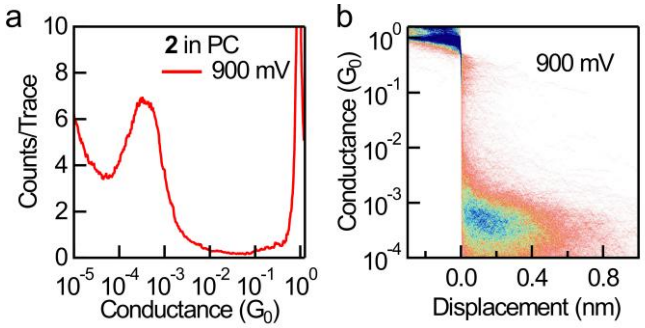


Figure S5. (a) 1D and (b) 2D conductance histogram of **2** measured in PC under 900 mV tip bias.

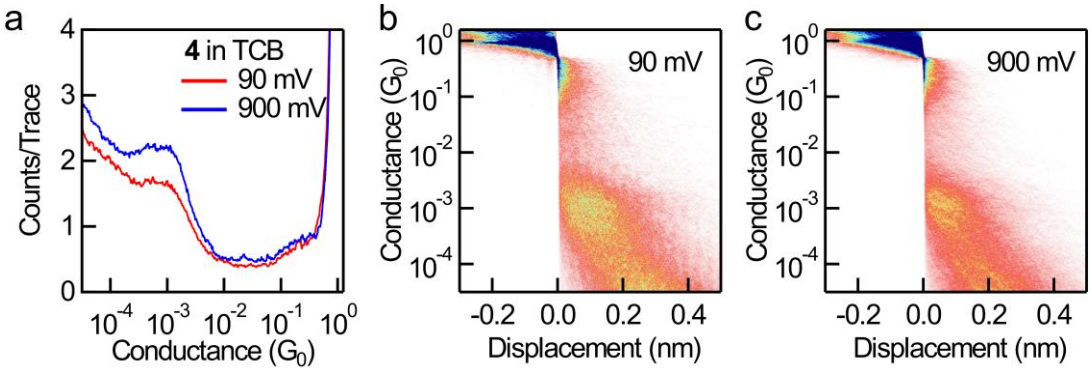


Figure S6. (a) 1D conductance histograms of **4** measured in TCB under 90 mV and 900 mV. (b,c) 2D conductance histograms of **4** measured in TCB under (b) 90 mV and (d) 900 mV.

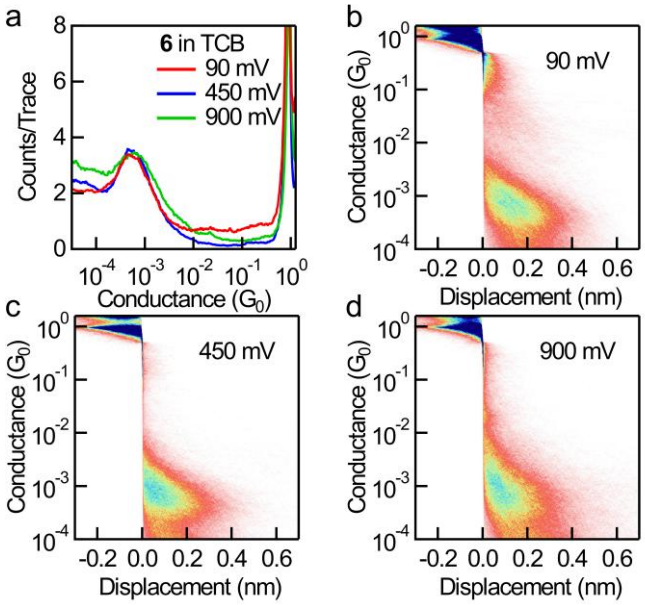


Figure S7. (a) 1D conductance histograms of **6** measured in TCB under 90 mV, 450 mV, and 900 mV tip biases. (b-d) 2D conductance histograms of **6** measured in TCB under (b) 90 mV, (c) 450 mV, and (d) 900 mV tip biases.

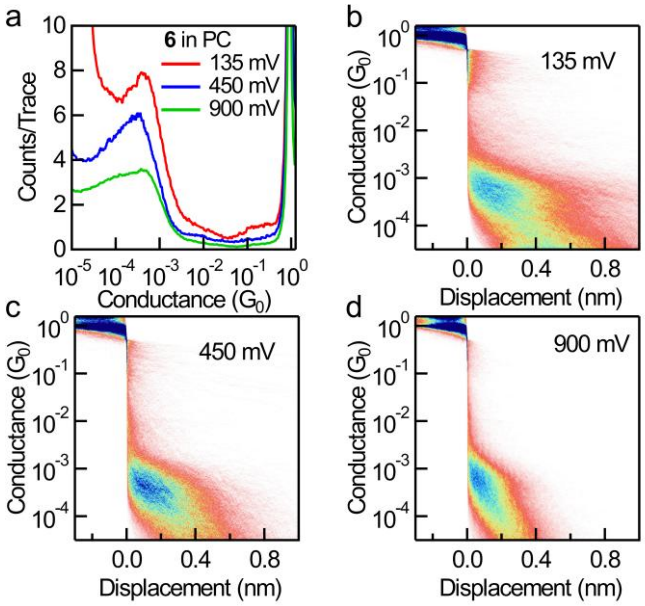


Figure S8. (a) 1D conductance histograms of **6** measured in PC under 135 mV, 450 mV, and 900 mV tip biases. (b-d) 2D conductance histograms of **6** measured in PC under (b) 135 mV, (c) 450 mV, and (d) 900 mV.

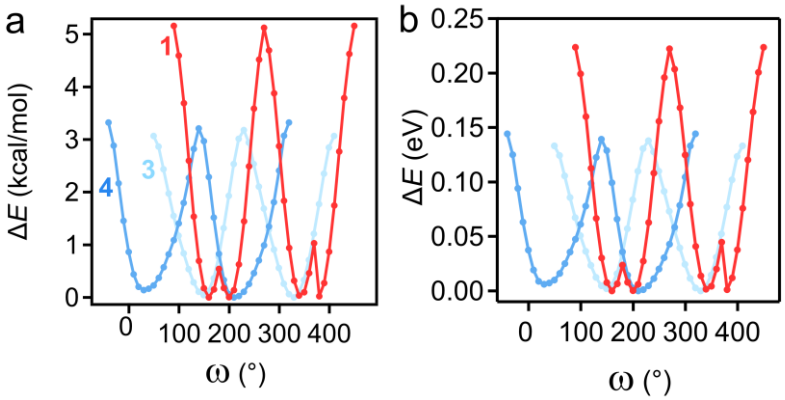


Figure S9. The calculated relative energy *ΔE* (a) in kcal/mol and (b) in eV for isolated **1**, **3**, and **4** with respect to their individual ground states as a function of the dihedral angle ω.

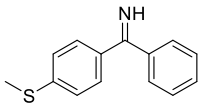
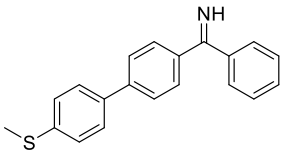
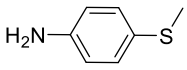
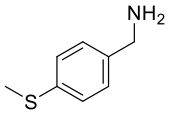
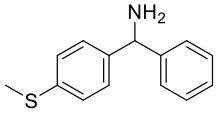
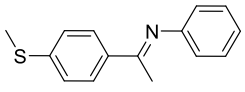
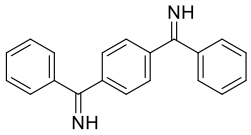
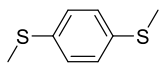
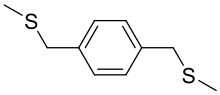
Notes about Figure S9.

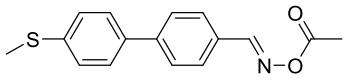
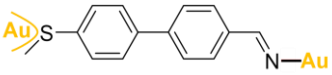
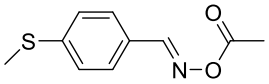
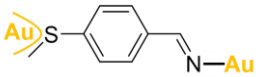
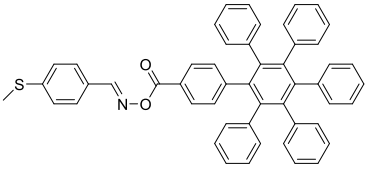
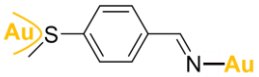
We compare the conformational differences between imines and amines by focusing on the key N-C1-C2-C3 dihedral angle (ω) in compounds **1**, **3**, and **4**, as illustrated in Figure 4a in the manuscript. For each value of ω, the molecular geometry was fully relaxed except for the dihedral angle. The calculated relative energies ΔE with respect to their individual ground states as a function of ω are presented in Figure S9. Here, the results of one rotation period of 360° around the C-C axis (indicated by the arrows in Figure 4a in the manuscript) are presented.

We find that compound **1** exhibits four local energy minima. A low energy barrier

of 0.024 eV (0.544 kcal/mol) is seen between the 160° and 200° conformations and a second low energy barrier of 0.045 eV (1.029 kcal/mol) is observed between 340° and 380° conformations. In contrast, **3** and **4** exhibit only two local energy minima. We now focus on the largest energy barrier for **1**, **3**, and **4** presented in Figure S9. Both **3** and **4** have an energy barrier of ~0.14 eV (~3.2 kcal/mol) for the rotation while **1** exhibits a ×1.6 larger value for its largest energy barrier. We emphasize that the energy barriers for **3** and **4** and this largest energy barrier for **1** are sufficiently high at room temperature (300 K, ~0.025 eV), so that transitions across these energy barriers for these compounds are likely not occurring in these room temperature experiments.

Table S1. Measured single-molecule conductance for the compounds discussed in the manuscript

Molecule	Structure	Conductance	Reference
1		2.1×10^{-3} G_0	This work
2		4.2×10^{-4} G_0	This work
4-(methylthio)aniline		1×10^{-2} G_0	This work
3		1.7×10^{-3} G_0	This work
4		No clear junction formation	This work
5		No clear junction formation	This work
6		5.5×10^{-4} G_0	This work
7		1×10^{-2} G_0	Ref. 14
8		3.3×10^{-4} G_0	Ref. 15

AI-2			
(AI-2 junction**)**		1.6×10^{-3} G_0	Ref. 14
AI-1			
(AI-1 junction**)**		6.3×10^{-3} G_0	Ref. 14
ZL-05			
(ZL-05 junction**)**		1.48×10^{-3} G_0	Ref. 16

V. NMR spectra

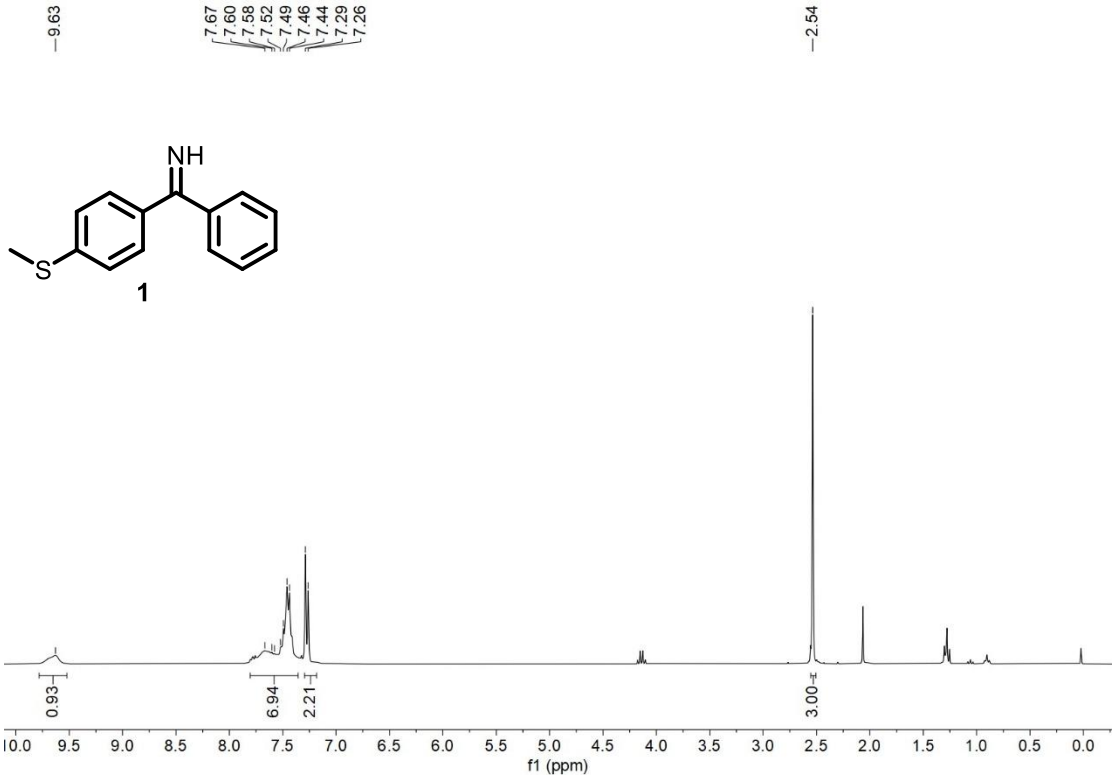


Figure S10. ^{1}H NMR spectrum of compound **1** in $CDCl_3$.

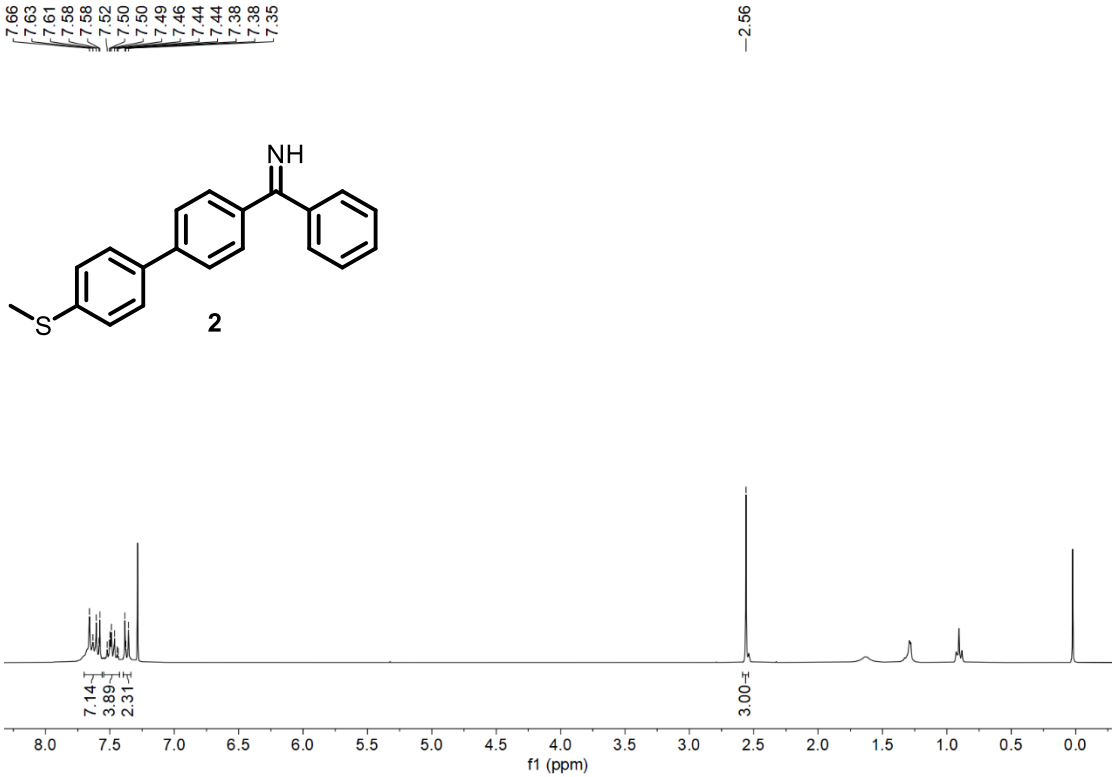


Figure S11. ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

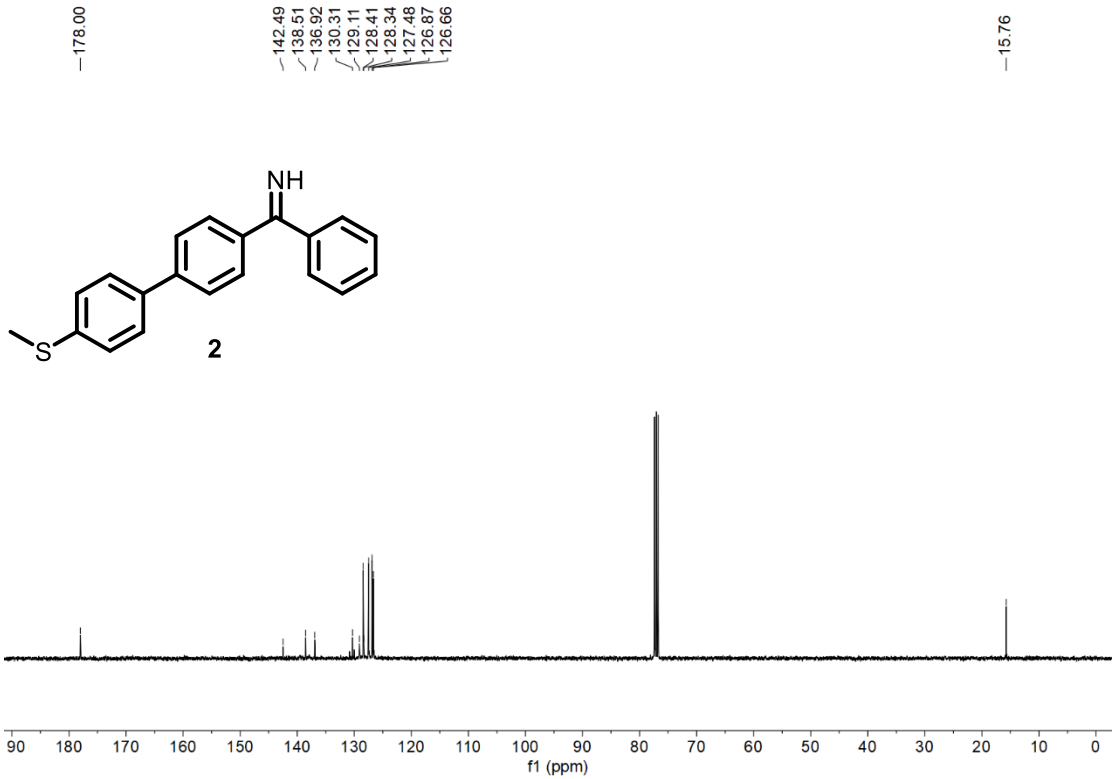


Figure S12. ^{13}C NMR spectrum of product **2** in $CDCl_3$.

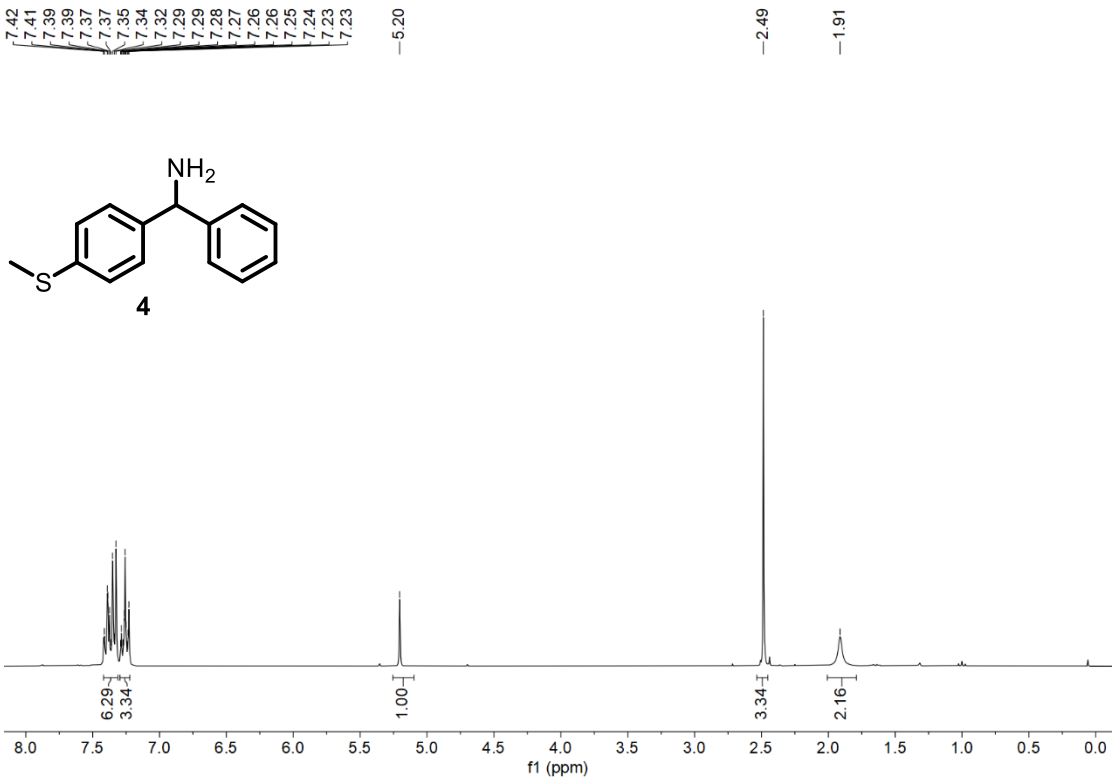


Figure S13. ^{1}H NMR spectrum of compound **4** in $CDCl_3$.

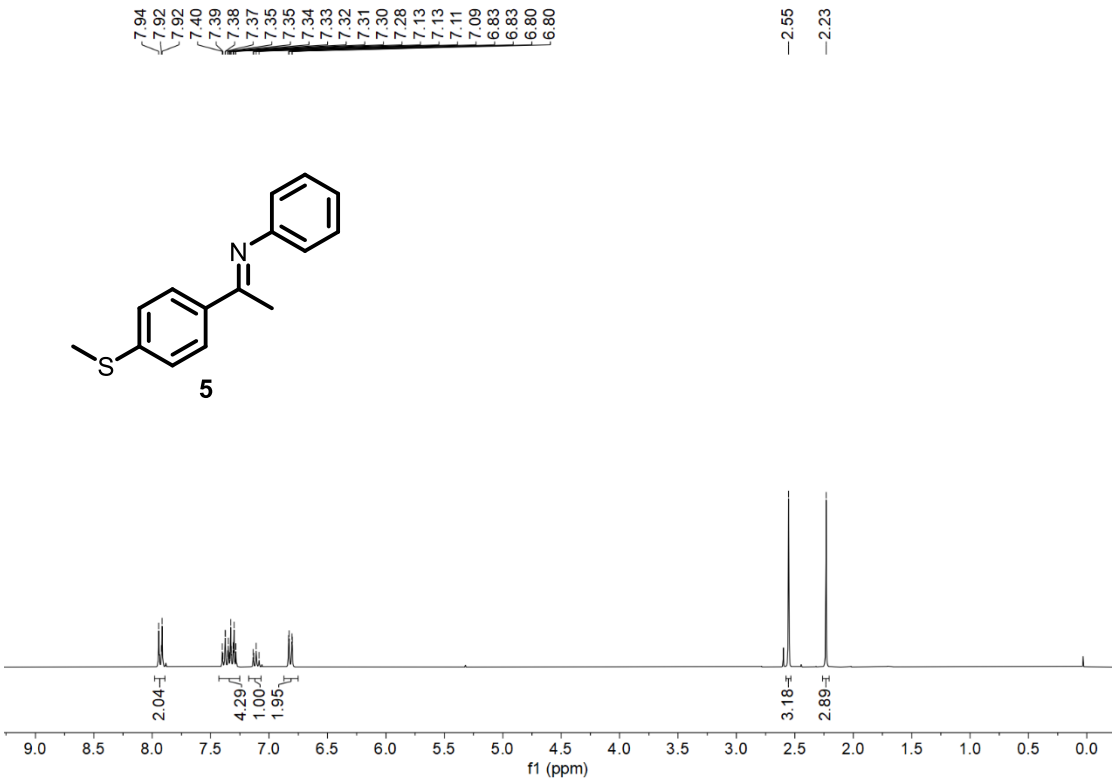


Figure S14. ^{1}H NMR spectrum of compound **5** in $CDCl_3$.

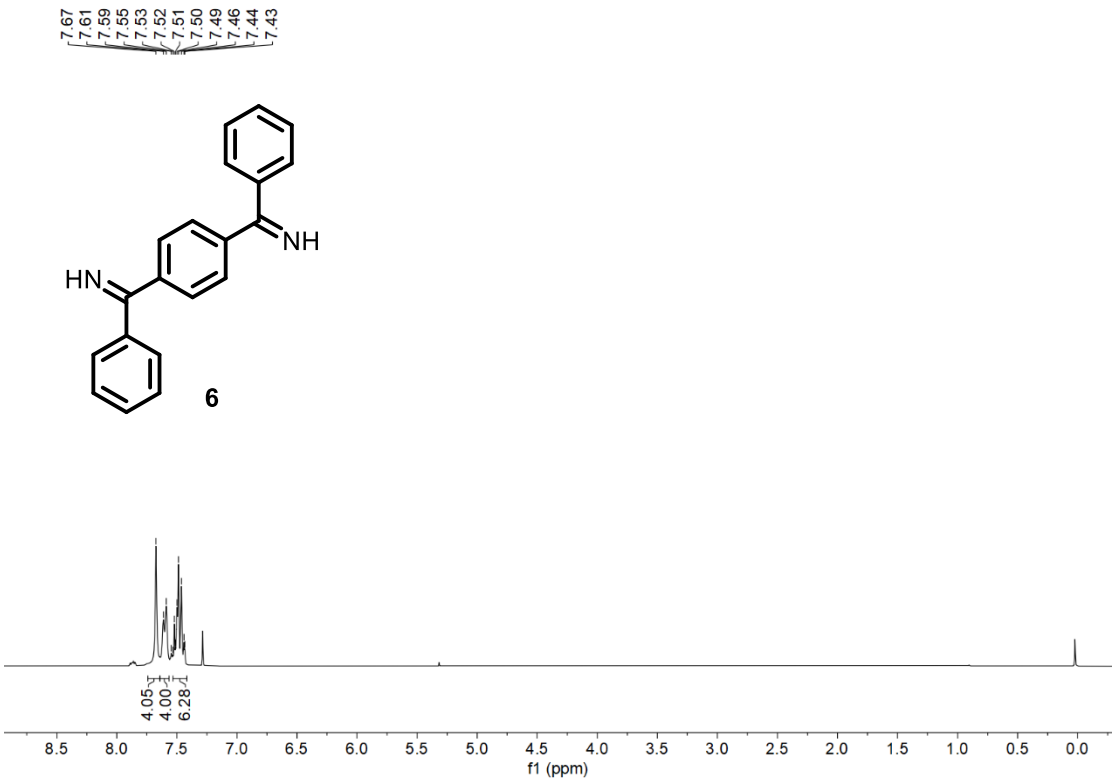


Figure S15. ^{1}H NMR spectrum of compound **6** in $CDCl_3$.

VI. References

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