Electronic Supplementary Information

STM apparent height measurements of molecular wires with different physical length attached on 2-D phase separated templates for evaluation of single molecular conductance

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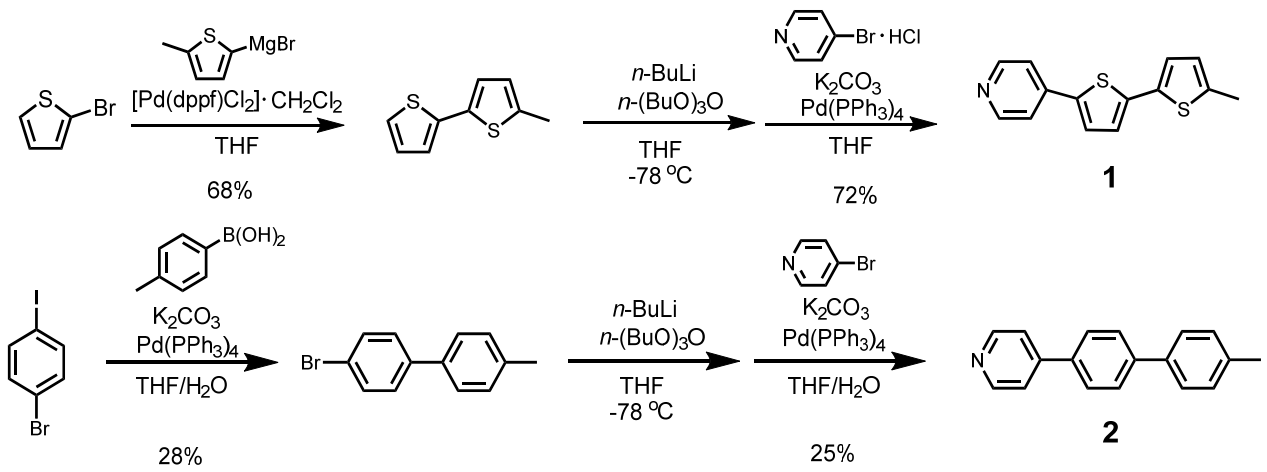
Contents:

I. Experimental Details

A. Materials and Synthesis

General. Unless specifically mentioned, reagents and solvents were obtained from commercial suppliers and used without further purification. All reactions were monitored by thin-layer chromatography carried out on 0.2 mm Merck silica gel plates (60F-254). Column chromatography was performed on silica gel (Nacalai Tesque, 70–230 mesh), on a Biotage Isolera One with a SNAP flash silica gel cartridge (KP-Sil), or on activated alumina (Nacalai Tesque, 200 mesh). Preparative gel permeation chromatography was carried out using JAIGEL1H and 2H columns (eluent: chloroform). ^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECS400, JEOL ECZ500R, or a JEOL ECA600P spectrometer. Tetramethylsilane (TMS) was used as an internal standard (δ= 0 ppm). Mass spectra were obtained on a JEOL JMS-MS700 or a Thermo Fisher Scientific EXACTIVE plus mass spectrometer. *N,N*-dimethylformamide (DMF) was dried with calcium hydride and then distilled before use.



Scheme S1. Synthetic routes of target compounds **1** and **2**.

Synthesis of 5-methyl-2,2'-bithiophene (**3**)

To a suspension of magnesium (turnings, 492.1 mg, 20.3 mmol) in dried THF (20 mL) was added dropwise 2-bromo-5-methylthiophene (1.7 mL, 15 mmol) under nitrogen atmosphere, and the resulting mixture was stirred until the mixture got room temperature. The suspension was added to a mixture of 2-bromothiophene (1.25 mL, 13.0 mmol) and $[Pd(dppf)Cl_2]\cdot CH_2Cl_2$ (39.7 mg, 48.6 μmol) in dried THF (10 mL) under nitrogen atmosphere, and the mixture was stirred at 0 °C for 2 h. The reaction mixture was poured into MeOH (3 mL), and the mixture was extracted with CH_2Cl_2. Organic layer was dried over $MgSO_4$ and concentrated. Then, purification by twice silica gel column chromatography (eluent: DCM/hexane) afforded **3** as colorless oil (1.59 g, 8.82 mmol, 68%).
3: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.16 (s, 3H), 6.65 (m, 1H), 6.94–6.99 (m, 2H), 7.08 (dd, 1H, J_1 = 3.7 Hz, J_2 = 1.3 Hz), 7.15 (dd, 1H, J_1 = 5.1 Hz, J_2 = 1.1 Hz). EI-MS (*m*/*z*): $[M]^+$ calcd for $[C_9H_8S_2]^+$, 180.01; found: 180, 181.

Synthesis of 5-methyl-5'-(4-pyridyl)-2,2'-bithiophene (**1**)

To a solution of **3** (307.1 mg, 1.70 mmol) in dried THF (7.5 mL) was added dropwise *n*-BuLi (1.6 M in hexane, 1.2 mL, 1.9 mmol, 1.1 eq) at –78 °C under nitrogen atmosphere. The mixture was stirred for 1 h, and then tri-butylborate (0.55 mL, 2.0 mmol, 1.2 eq) was added dropwisely. The mixture was stirred for 1 h and then poured onto water. Then, to the mixture, 4-bromopyridine hydrochloride (363.1 mg, 1.87 mmol, 1.1 eq), $Pd(PPh_3)_4$ (94.7 mg, 0.082 mmol), K_2CO_3 (534 mg, 3.86 mmol) and H_2O (2 mL) was added, and the resulting suspension was heated at 65 ˚C for 1 day. The reaction mixture was extracted with CH_2Cl_2, and the organic portion was washed with brine and dried over anhydrous $MgSO_4$. Obtained crude product after concentration was purified by column chromatography (silica gel, CH_2Cl_2/ethyl acetate = 9/1) to give **1** as a pale yellow solid (313.7 mg, 1.22 mmol, 72%).
1: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 2.50 (s, 3H), 6.70 (d, 1H, *J* = 3.1 Hz), 7.04 (d, 1H, *J* = 3.5 Hz), 7.10 (d, 1H, *J* = 3.8 Hz), 7.40 (d, 1H, *J* = 3.9 Hz), 7.44 (d, 2H, *J* = 4.6 Hz), 8.57 (d, 2H, *J* = 4.6 Hz); ^{13}C NMR (101 MHz, $CDCl_3$, δ): 15.42, 119.35, 123.99, 124.33, 126.08, 126.19, 134.35, 138.72, 139.75, 140.24, 141.09, 150.35; EI-MS (*m*/*z*) $[M]^+$ calcd for $[C_{14}H_{11}NS_2]^+$, 257.03; found: 257.

Synthesis of 4-bromo-4'-methyl-1-1'-biphenyl (**4**)

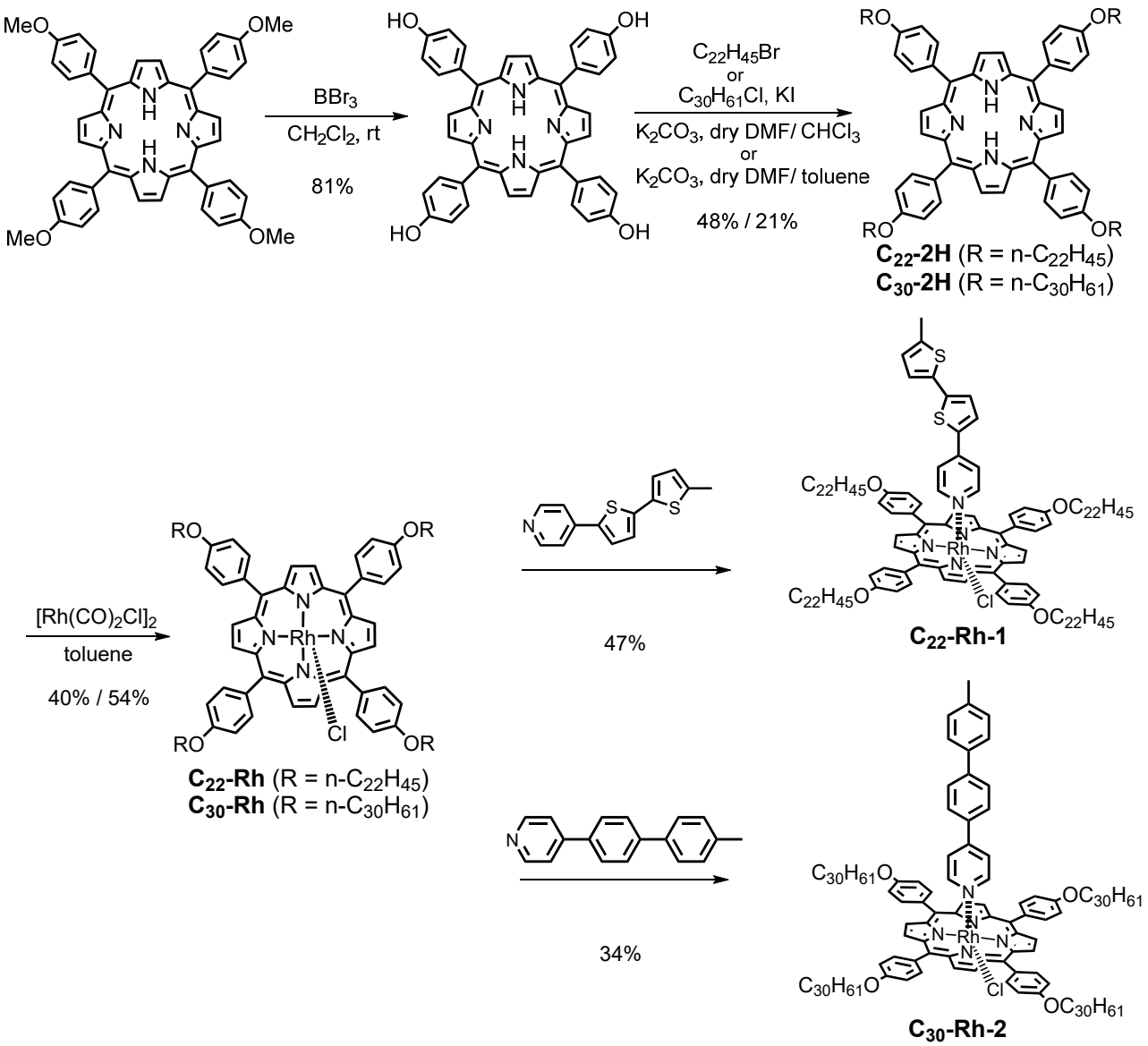
A mixture of *p*-bromoiodobenzene (2.504 g, 8.85 mmol), 4-methylphenylboronic acid (1.205 g, 8.86 mmol), $Pd(PPh_3)_4$ (0.219 g, 0.39 mmol), and K_2CO_3 (3.18 g, 23.0 mmol) in THF/water (32 mL/8 mL) was heated at 65 °C overnight under nitrogen atmosphere. The reaction mixture was extracted with CH_2Cl_2. After being dried over anhydrous $MgSO_4$, the residue obtained from combined organics, was purified by silica column chromatography (hexane) get to **4** as a white solid (0.654 g, 28%).

4: ^{1}H NMR: (400 MHz, $CDCl_3$, δ): 2.39 (s, 3H), 7.24 (2H), 7.44 (m, 4H), 7.54 (d, 2H, J = 8.6 Hz); EI-MS (*m*/*z*) $[M]^+$ calcd for $[C_{13}H_{11}Br]^+$: 246.00; found 246, 248.

Synthesis of 4-methyl-4'-(4-pyridyl)-1,1'-biphenyl (**2**)

To a solution of **4** (260 mg, 1.05 mmol) in dry THF (5 mL) was added dropwise *n*-BuLi (1.6 M in hexane, 0.75 mL, 1.2 mmol, 1.1 eq) at –78 °C under nitrogen atmosphere. The mixture was stirred for 1 h, and then tributylborate (0.35 mL, 1.31mmol, 1.2 eq) was added dropwise. The mixture was stirred for 1 h and then poured onto water. Then, to the mixture 4-bromopyridine, hydrochloride (198.4 mg, 1.02 mmol), $Pd(PPh_3)_4$ (52.2 mg, 0.045 mmol), and Na_2CO_3 (3 M in water, 3 mL, 3 mmol) was added, and resulting suspension was heated to reflux overnight. The reaction mixture was extracted with CH_2Cl_2, and the organic portion was washed with brine and dried over Na_2SO_4. Purification by silica column chromatography (CH_2Cl_2/ethyl acetate) gave **1** as a colorless solid (61.8 mg, 0.25 mmol, 25 %).

2: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 2.40 (s, 3H), 7.27 (d, 2H, J = 7.9 Hz), 7.53 (m, 4H), 7.70 (s, 4H), 8.66 (d, 2H, J = 6.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$, δ): 21.15, 121.43, 126.92, 127.34, 127.59, 129.64, 136.57, 137.29, 137,65, 141.92, 147.86, 150.31; EI-MS (*m*/*z*): $[M]^+$ calcd for $[C_{18}H_{15}N]^+$, 245.12; found: 245.



Scheme S2. Synthetic route of **1**- or **2**-coordinated TPP rhodium chlorides **C_{22}-Rh-1** and **C_{30}-Rh-2**.

Synthesis of 21-23-dihidro-5,10,15,20-tetrakis(4-hydroxyphenyl)porphyrin (**TPP-OH**)[S1]

Yield: 81%, violet powder. ^{1}H NMR (400 MHz, $CDCl_3$, δ): −2.89 (s, 2H), 7.20 (d, 8H, J = 8.3 Hz), 8.00 (d, 8H, J = 8.6 Hz), 8.87 (s, 8H), 9.96 (s, 4H). ESI-HRMS (*m*/*z*) $[M+H]^+$ calcd for $[C_{44}H_{31}N_4O_4]^+$: 679.2340; found: 679.2341.

Synthesis of 21-23-dihidro-5,10,15,20-tetrakis(4-docosyloxyphenyl)porphyrin (**C_{22}-2H**)[S2]

Yield: 48%, violet powder. ^{1}H NMR (400 MHz, $CDCl_3$, δ): −2.77 (s, 2H), 0.85 (t, 12H, J = 7.0 Hz), 1.20–1.50 (m, 144H), 1.60 (quint, 8H) 1.98 (quint, 8H), 4.25 (t, 8H, J = 6.6 Hz), 7.24 (s, 8H), 8.08 (d, 8H, J = 8.6 Hz), 8.84 (s, 8H). ESI-HRMS (*m*/*z*): $[M+H]^+$ calcd for $[C_{132}H_{207}N_4O_4]^+$, 1913.6145; found: 1913.6177.

Synthesis of 21,23-dihidro-5,10,15,20-tetrakis(4-triacontyloxyphenyl)porphyrin (**C_{30}-2H**)[S3]

Yield: 21%, violet powder. ^{1}H NMR (400 MHz, $CDCl_3$, δ): −2.75 (s, 2H), 0.87 (t, 12H, J = 6.8 Hz), 1.10–1.40 (m, 208H), 1.63 (quint, 8H) 1.99 (quint, 8H), 4.25 (t, 8H, J = 6.4 Hz), 7.28 (s, 8H), 8.10 (d, 8H, J = 8.5 Hz), 8.86 (s, 8H). ESI-HRMS (*m*/*z*): $[M+Na]^+$ calcd for $C_{164}H_{270}N_4O_4Na^+$, 2384.0973; found: 2384.1252.

*Synthesis of **1**-coordinated 5,10,15,20-tetrakis(4-docosyloxyphenyl)porphyrin Rhodium chloride* **C_{22}-Rh-1**

A mixture of **C_{22}-2H** (403.5 mg, 0.21 mmol) and $[Rh(CO)_2Cl]_2$ (338.5 mg, 0.87 mmol, 4.1 eq) in toluene (100 mL) was heated at 90 °C for 5 h. Obtained crude product after concentration was purified by column chromatography (silica gel, hexane/CH_2Cl_2 = 4/6) to give **C_{22}-Rh** as a red colored solid (141.2 mg, 0.069 mmol, 40%).

A mixture of **C_{22}-Rh** (43.5 mg, 21.2 μmol) and **1** in chloroform (10 mL) was heated at 70 °C for 2 h. Obtained crude product after concentration was purified by column chromatography (silica gel, hexane/CH_2Cl_2 = 3:7) and GPC to give a red colored solid **C_{22}-Rh-1** (23.0 mg, 10.0 μmol, 47%).

C_{22}-Rh-1: ^{1}H NMR (400 MHz, CD_2Cl_2, δ): 0.76–0.81 (m, 14H), 1.10–1.49 (m, 144H), 1.54 (quint, 8H, J = 8.0 Hz) 1.89 (quint, 8H, J = 6.8 Hz), 2.26 (s, 3H), 4.17 (t, 8H, J = 6.4 Hz), 5.10 (d, 2H, J = 7.2 Hz), 6.36 (d, 1H, J = 4.0 Hz). 6.44 (d, 1H, J = 3.6 Hz), 6.54 (d, 1H, J = 4.0 Hz), 6.64 (d, 1H, J = 3.6 Hz), 7.16–7.23 (m, 8H), 7.96 (dd, 4H, J_1 = 8.4 Hz, J_2 = 2.4 Hz), 8.09 (dd, 4H, J_1 = 8.4 Hz, J_2 = 2.0 Hz), 8.86 (s, 8H); ^{13}C NMR (101 MHz, CD_2Cl_2, δ): 14.25, 15.37, 23.06, 26.58, 29.73, 29.87, 30.07, 32.29, 68.73, 112.88, 113.07, 117.57, 121.49, 124.05, 125.05, 126.52, 127.57, 132.57, 134.32, 135.55, 135.92, 142.94, 145.80, 159.44; ESI-HRMS (*m*/*z*) $[M+Na]^+$ calcd for $[C_{146}H_{215}N_5O_4S_2ClRhNa]^+$: 2328.4885; found: 2329.5051.

*Synthesis of **2**-coordinated 5,10,15,20-tetrakis(4-triacontyloxyphenyl)porphyrin Rhodium chloride* **C_{30}-Rh-2**

A mixture of **C_{30}-2H** (25.9 mg, 11 μmol) and $[Rh(CO)_2Cl]_2$ (19.1 mg, 49 μmol, 4.5 eq) in toluene (10 mL) was heated at 90 °C for 4 h. Obtained crude product after concentration was purified by column chromatography (almina, chloroform) to give **C_{30}-Rh** as a red colored solid (14.8 mg, 5.9 μmol, 54%).

A mixture of **C_{30}-Rh** (14.8 mg, 5.9 μmol) and **2** (2.1 mg, 8.6 μmol) in chloroform (10 mL) was heated at 70 °C for 1.5 h. Obtained crude product after concentration was purified by column chromatography (silica gel, hexane/CH_2Cl_2 = 3:7) and GPC to give a red colored solid **C_{30}-Rh-2** (2.3 mg, 2.0 μmol, 34%).

C_{30}-Rh-2: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.85 (m, 14H), 1.15-1.40 (m, 208H), 1.60 (quint, 8H), 1.95 (quint, 8H, J = 7.5 Hz), 2.26 (s, 3H), 4.22 (t, 8H, J = 6.4 Hz), 5.26 (d, 2H, J = 6.8 Hz), 6.56 (d, 2H, J = 8.6 Hz), 7.11 (d, 2H, J = 8.0 Hz), 7.18–7.28 (m, 12H), 8.00 (dd, 4H, J_1 = 8.4 Hz, J_2 = 2.2 Hz), 8.20 (dd, 4H, J_1 = 8.2 Hz, J_2 = 2.2 Hz), 8.90 (s, 8H). ESI-HRMS (m/z): $[M+K]^+$ calcd for $[C_{182}H_{283}N_5O_4K]^+$, 2381.0504; found: 2382.0773.

B. UV-vis absorption spectra

UV–vis. absorption spectra were measured on a JASCO V-670. A quartz cuvette with 1 mm optical path was used.

C. STM measurements

All STM experiments were performed under ambient conditions. The STM images were acquired with an Agilent technologies 5500 scanning probe microscope in the constant current mode. The STM tips used in this research were mechanically cut from a Pt/Ir wire (80/20, diameter 0.25 mm). Highly oriented pyrolytic graphite (HOPG) (purchased from the Bruker Co.) was used as a substrate. Homogeneous solutions of porphyrins in octanoic acid were prepared by heating and filtering solution with membrane filter (0.20 μm hole diameter). A drop of sample solution (8−10 μL) was deposited onto a freshly cleaved HOPG surface. The tip was immersed into the solution, and then images were collected. Lattice constants were determined from two sequential images, considering the thermal drift during STM measurements. The effect of thermal drift was corrected by following procedures; one of the lattice derived from the up- and down-scan image was stretched, and the other was compressed along the vertical direction at the same scaling factor. Subsequently, the resulting set of lattices were sheared along the horizontal direction at the same shear angle with the opposite sign, so that the resulting unit cell parameters of the set of lattices are identical after the drift correction. The scaling factor and shear angle were estimated from the original unit cell parameters before the drift correction using the solver function in Microsoft Excel 2010. Apparent height analysis was performed using the STM image with compensation of the effect of the slope of HOPG substrate on the software Gwiddion.

In order to calculate conductance ratio from the difference in observed apparent height (Δh_{STM}) and estimated physical height (Δx), the the two-layer tunnel junction model proposed by Weiss *et al.*[S4] can be employed. According to the model, the total conductance (G_{total}) between an STM tip and a substrate can be described by product of the gap conductance ($G_{gap} = A\exp(-\alpha d)$) and molecular conductance ($G_{mol} = B\exp(-\beta x)$), where A and B are contact conductance, α and β are decay constant of the gap and the molecule, d is the gap distance and x is the molecular length. Under the constant current mode, G_{total} is always constant, therefore, the conductance ratio G_{mol1}/G_{mol2} is given by the following equation:

$$\frac{G_{\mathrm{mol1}}}{G_{\mathrm{mol2}}} = \frac{G_{\mathrm{gap2}}}{G_{\mathrm{gap1}}} = \frac{A_2}{A_1}\exp\{\alpha(d_1 - d_2)\} \qquad \text{(S1)}$$

When similar molecules are scanned in the same STM image, it is reasonable to approximate that contact conductance of both molecules is equal ($A_1 = A_2$). Additionally, the difference in apparent height (Δh_{STM}) is the sum of the difference in gap distance (Δd) and the one in molecular length (Δx), therefore the term $d_1 – d_2 = \Delta d$ is equal to $\Delta h_{\mathrm{STM}} – \Delta x$. Then, equation (S1) is transformed to the following form;

$$\frac{G_{\mathrm{mol1}}}{G_{\mathrm{mol2}}} = \exp\{\alpha(\Delta h_{\mathrm{STM}} - \Delta x)\} \qquad (1)$$

Thus, conductance ratio can be derived from experimentally obtained Δh_{STM} and theoretically predictable Δx.

D. Theoretical calculations

Geometrical optimization was carried out at the B3LYP/6-31G(d) (for C,H,N,O,S,Cl), LANL2DZ (for Rh) level of theory implemented on the Gaussian 16 package.[S5] Convergence at a local minimum structure was confirmed by no imaginary frequencies on frequency analysis. Stability of conformers was estimated from their values of sum of electronic and thermal Free Energies.

II. Additional Data

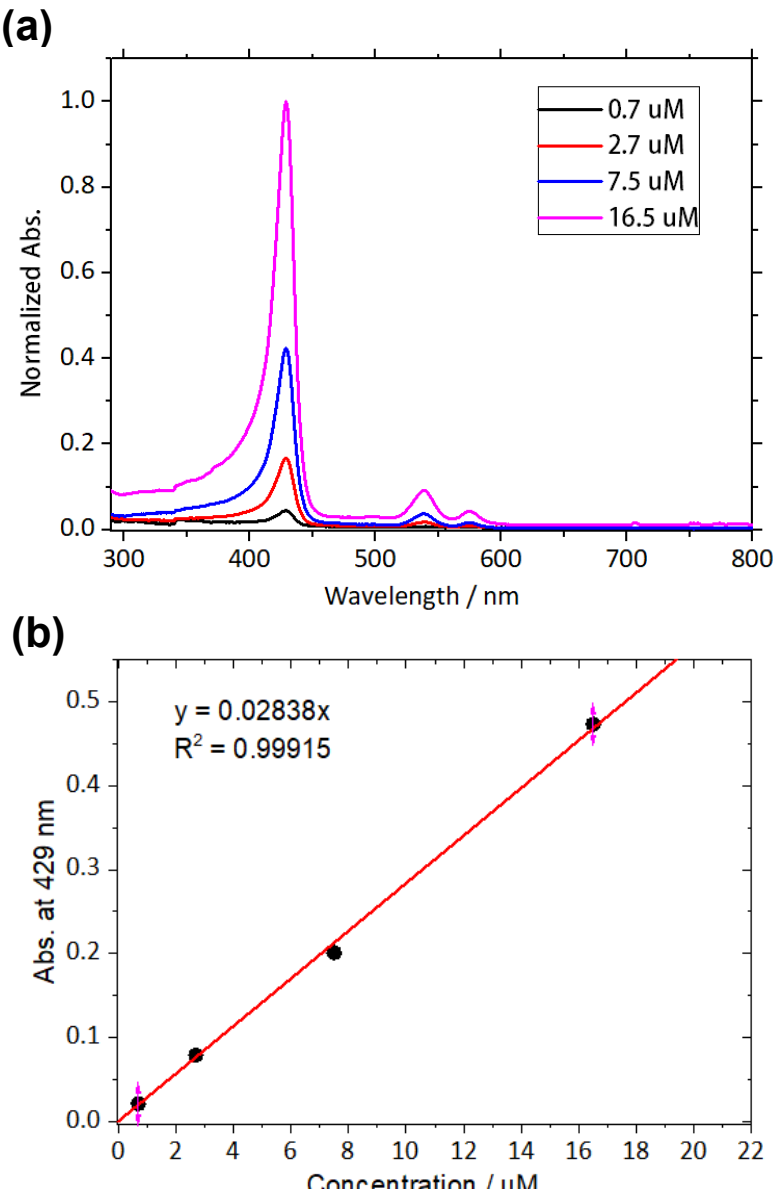


Fig. S1. (a) UV–vis absorption spectra **C_{22}-Rh-1** in 1-octanoic acid. (b) Absorbance of **C_{22}-Rh-1** in 1-octanoic acid at 429 nm. Molar extinction coefficient (ε) was calculated to be 2.84×10^5 $M^{-1}cm^{-1}$ from the slope of the plot.

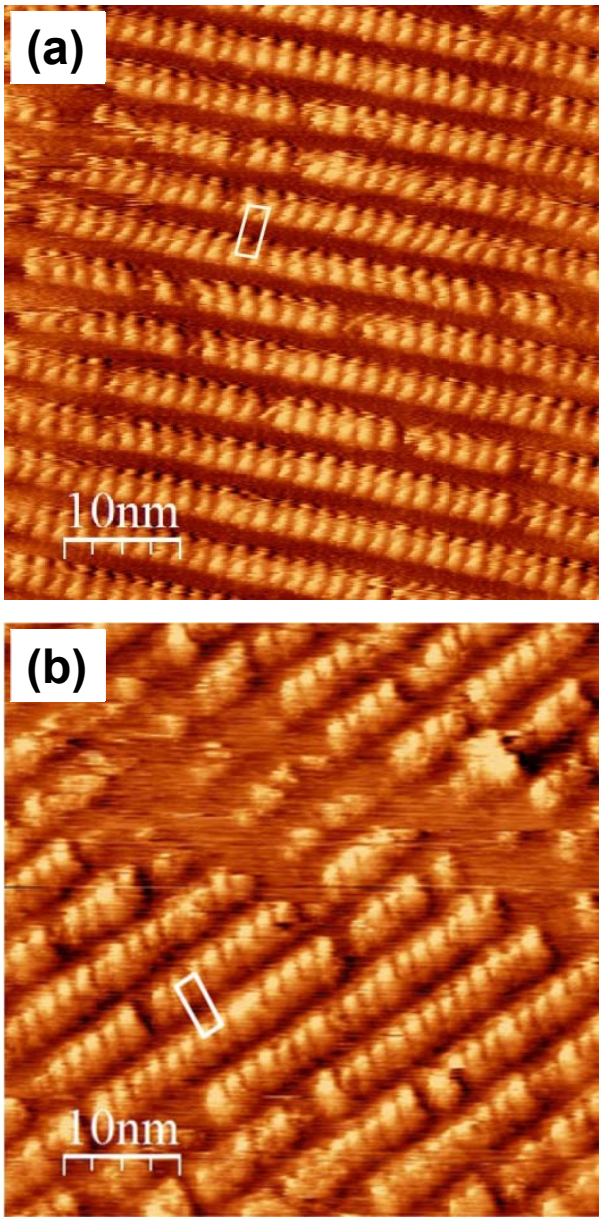


Fig. S2. STM images of a solution of (a) **C_{22}-Rh-1** (4×10^{-6} M) and (b) **C_{30}-Rh-2** (4×10^{-7} M) at the 1-octanoic acid–HOPG interface in the constant current mode (50×50 nm^2, $I_{set} = 30$ pA, $V_{bias} = -1.0$ V). White parallelograms show the unit cells.

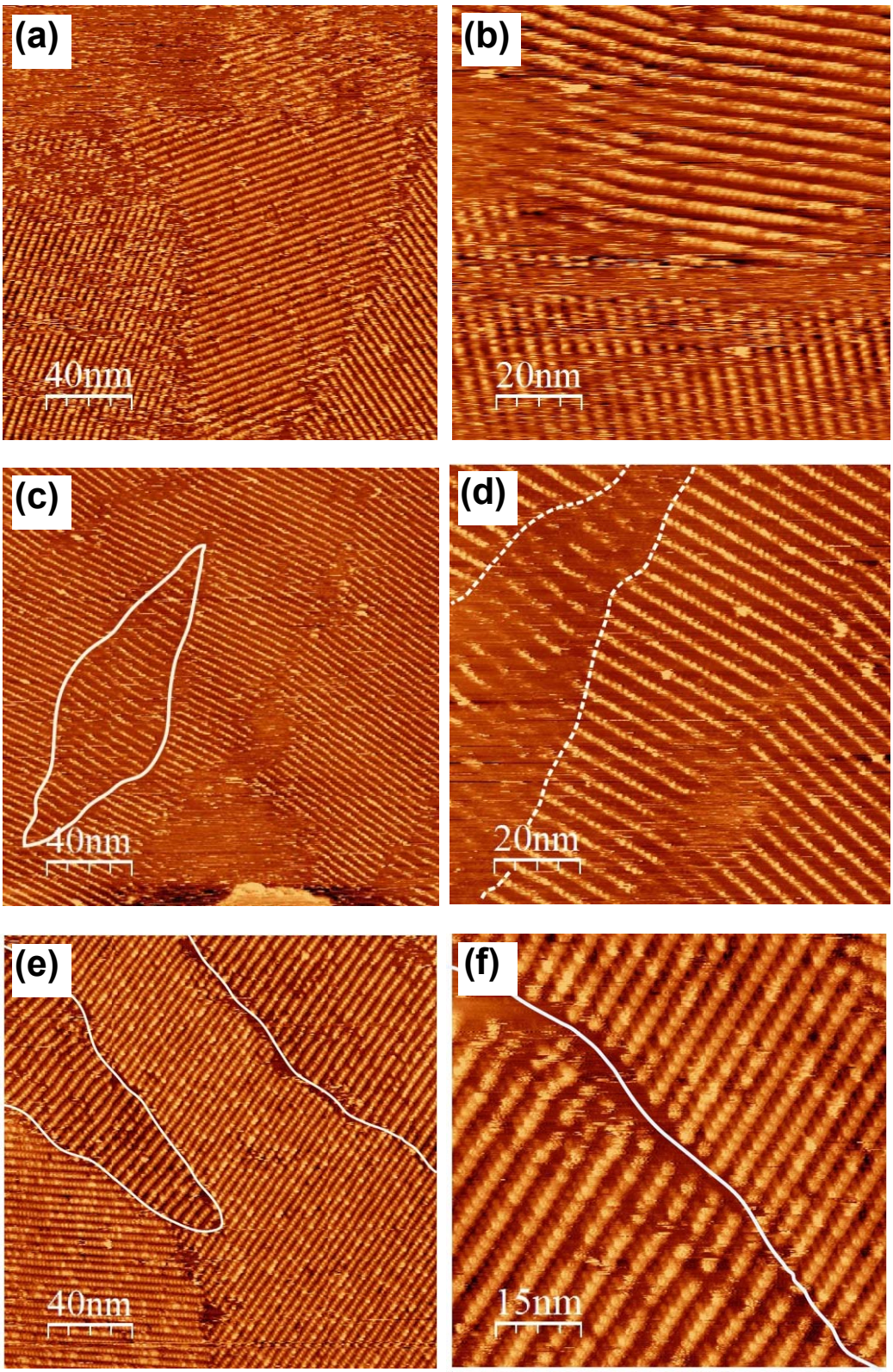


Fig. S3. STM images of a mixed solution of **C_{22}-Rh-1** and **C_{30}-Rh-2** at the 1-octanoic acid–HOPG interface in the constant current mode White solid or broken lines show the boundaries between neighboring domains of **C_{22}-Rh-1** and **C_{30}-Rh-2**. Measurement conditions in each image are shown in Table S1.

Table S1. Measurement conditions; concentrations of **C_{22}-Rh-1** and **C_{30}-Rh-2**, setpoint currents, bias voltages and scan sizes of the STM images in Figure S3.

Figure	[**C_{22}-Rh-1**] / M	[**C_{30}-Rh-2**] / M	I_{set} / pA	V_{bias} / V	Scan area / nm^2
a	1.7×10^{-5}	6.4×10^{-7}	30	−1.0	200
b	1.7×10^{-5}	6.4×10^{-7}	30	−1.0	100
c	6.4×10^{-6}	6.4×10^{-7}	30	−1.0	200
d	6.4×10^{-6}	6.4×10^{-7}	30	−1.0	100
e	3.1×10^{-7}	1.4×10^{-7}	20	−1.2	200
f	3.1×10^{-7}	1.4×10^{-7}	20	−1.2	75

Table S2. Obtained lattice parameters of unit cells.

compound		a / nm	b / nm	α
C_{22}-Rh-1 (Fig. S2a)		3.88±0.01	1.72±0.01	82°
C_{30}-Rh-2 (Fig. S2b)		5.04±0.04	1.77±0.01	83°
C_{22}-Rh-1 + **C_{30}-Rh-2** (Fig. 3a)	Domain A	3.90±0.04	1.83±0.02	83°
	Domain B	4.87±0.01	1.82±0.01	86°

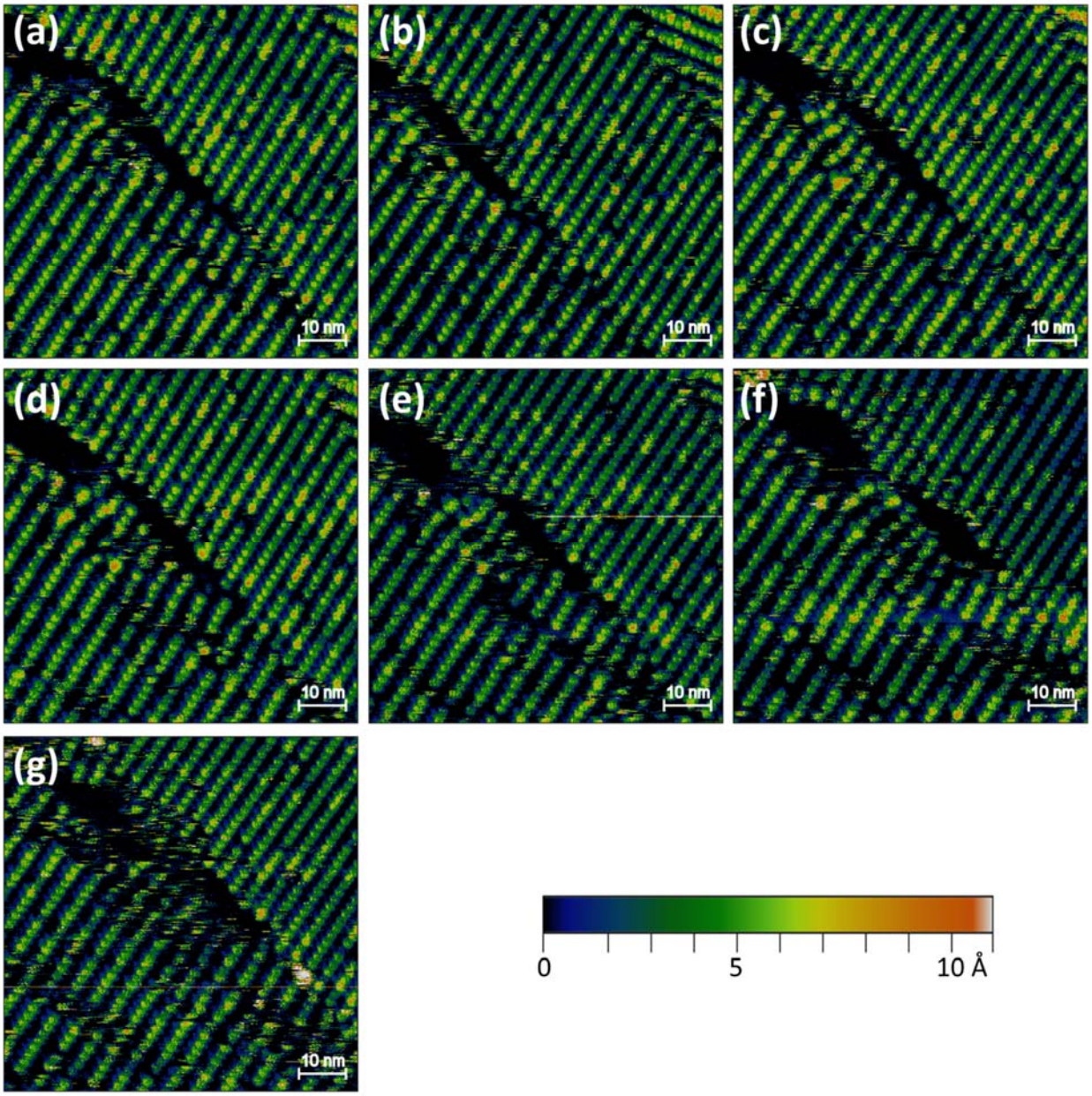


Fig. S4. Sequential STM images of a mixed solution of **C_{22}-Rh-1** and **C_{30}-Rh-2** at the 1-octanoic acid–HOPG interface in the constant current mode in the same condition and scan area with Figure S3f.

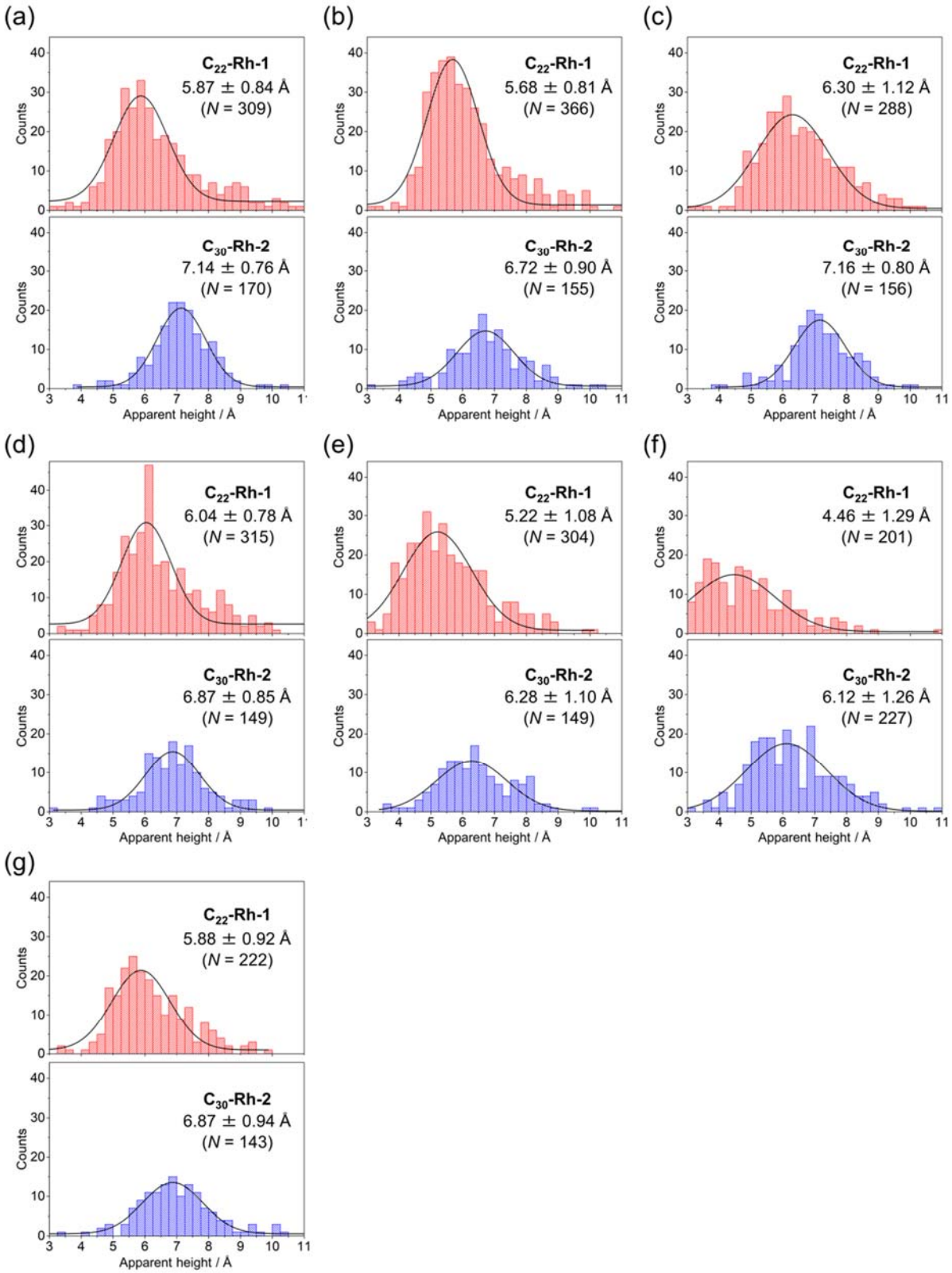


Fig. S5. Histograms of apparent height in the domain of (top) **C_{22}-Rh-1** and (bottom) **C_{30}-Rh-2** for the STM images in Figure S4.

Table S3. Apparent heights of **C_{22}-Rh-1** and **C_{30}-Rh-2**, their difference Δh_{STM} from each STM images in Fig. S4 and averaged Δh_{STM}.

Scan	**C_{22}-Rh-1** / Å	**C_{30}-Rh-2** / Å	Δh_{STM} / Å
a	5.87±0.85	7.14±0.76	−1.27±1.14
b	5.69±0.81	6.72±0.90	−1.03±1.21
c	6.30±1.12	7.16±0.80	−0.86±1.37
d	6.04±0.78	6.87±0.85	−0.83±1.15
e	5.22±1.08	6.28±1.10	−1.07±1.54
f	4.46±1.29	6.12±1.26	−1.65±2.10
g	5.88±0.92	6.87±0.94	−1.00±1.36
Average	−	−	−1.10±0.55

Table S4. Physical heights, energies, and abundance ratio at 298 K of **C_1-Rh-1-*trans***, **C_1-Rh-1-*cis***, and **C_1-Rh-2** calculated at the B3LYP/6-31G(d)(for C,H,N,O,S,Cl),LANL2DZ(for Rh) level.

	C_1-Rh-1-*trans*	**C_1-Rh-1-*cis***	**C_1-Rh-2**
Physical height[1] / Å	16.498	15.347	17.563
Energy[2] /a.u	–4330.722981	–4330.721758	−
Abundance ratio	1	0.27	−

[1]Physical height of the complexes were calculated as sum of the Rh–Cl bond length and wire height. Wire height of each complex was measured as the distance between the top methyl carbon atom of the wire unit and the mean plane of porphyrin defined by porphyrynic 24 atoms. We consider that *trans*-effect of these wires was essentially the same because optimized Rh–Cl lengths of these complexes were all the same as 2.385 Å.

[2]Energies after correction of zero-point vibration.

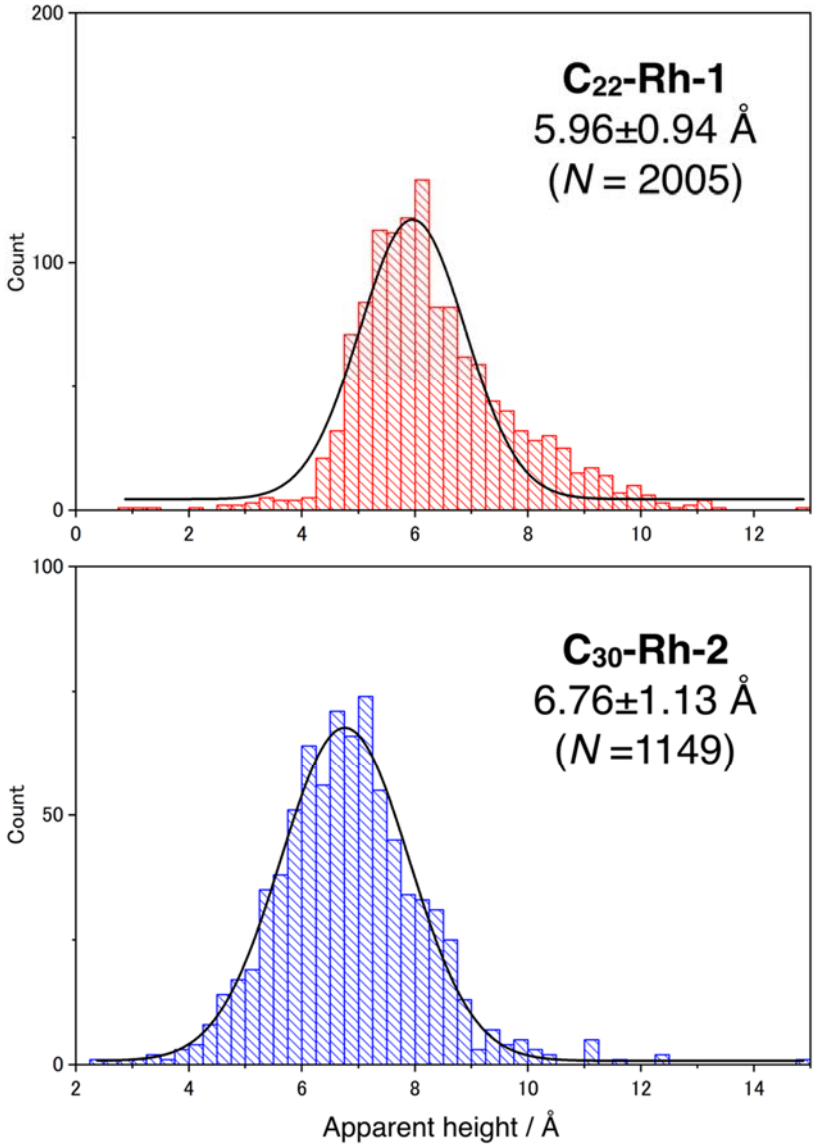


Fig. S6. Merged histograms of apparent height in the domain of **C_{22}-Rh-1** and **C_{30}-Rh-2** for all the seven STM images in Figure S4.

Cartesian coordinate [Å] of optimized structure and the sum of electronic and thermal Free Energies

1-*trans*

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-1.062374	1.685034	1.652033
2	7	0	0.368712	0.045289	-0.379965
3	6	0	-0.849595	5.712547	-0.310495
4	1	0	0.135512	5.253708	-0.311400
5	7	0	-2.061885	-1.657363	-0.544663
6	7	0	-2.311753	1.212007	-0.948147
7	6	0	-1.302816	2.985004	1.285728
8	7	0	-0.817546	-1.185748	2.052681
9	6	0	-2.218580	7.696687	-0.497681
10	6	0	1.485291	0.249747	0.341802
11	1	0	1.347623	0.399997	1.404677
12	6	0	-1.979001	4.905616	-0.132368
13	6	0	-0.593558	1.694234	2.942869
14	6	0	-5.409668	-1.267700	-6.097003
15	6	0	-0.534225	3.061732	3.409864
16	1	0	-0.222512	3.365933	4.398071
17	6	0	-0.309940	-0.761373	3.254912
18	6	0	-2.956325	3.042767	-2.169291
19	1	0	-3.087258	4.078076	-2.447168
20	6	0	0.288265	0.801781	5.090324
21	6	0	-3.239579	5.531285	-0.137139
22	1	0	-4.130954	4.928569	0.011770
23	6	0	-1.848284	3.426937	0.067694
24	6	0	-0.961099	3.853834	2.390478
25	1	0	-1.067001	4.928564	2.387067
26	6	0	0.503182	-0.143511	-1.706472
27	1	0	-0.411102	-0.312186	-2.260425
28	6	0	-0.440810	0.367342	6.204406
29	1	0	-1.391694	-0.134833	6.050621
30	6	0	0.017612	0.575107	7.508205
31	6	0	2.751156	0.276688	-0.224609
32	1	0	3.605276	0.464642	0.418006
33	6	0	-2.758821	-1.672867	-1.727172
34	6	0	0.164633	-1.911035	3.993694
35	1	0	0.638332	-1.870998	4.963432
36	6	0	1.509202	1.460587	5.324348
37	1	0	2.097793	1.806028	4.478711
38	6	0	-3.361646	6.903246	-0.316884
39	6	0	1.235604	1.232240	7.718139
40	6	0	-3.387586	-0.533635	-4.988110
41	6	0	-2.323620	2.583823	-0.951662
42	6	0	-0.725036	-2.554218	2.017781
43	6	0	1.979747	1.674088	6.613905
44	6	0	-3.358882	1.939789	-2.855080
45	1	0	-3.887123	1.901766	-3.796298
46	6	0	-0.223152	0.570103	3.703012
47	6	0	-1.830109	-2.958766	-0.178063
48	6	0	-0.955129	7.094822	-0.493219
49	6	0	-3.182254	-0.550473	-2.461313
50	6	0	-2.949658	0.784956	-2.086318
51	6	0	-2.957591	-3.046251	-2.135264
52	1	0	-3.467223	-3.356626	-3.035453
53	6	0	-3.947737	-0.797274	-3.725363
54	6	0	1.732992	-0.136901	-2.345301
55	1	0	1.767290	-0.320728	-3.413315
56	6	0	-0.084189	-3.009932	3.231955
57	1	0	0.145473	-4.039922	3.461401
58	6	0	-1.183962	-3.397368	0.990763
59	6	0	-4.102179	-0.762816	-6.157526
60	6	0	2.913052	0.081645	-1.608495
61	6	0	-5.985955	-1.537301	-4.850224
62	6	0	-5.253557	-1.300312	-3.683453
63	6	0	-2.392563	-3.834903	-1.182387
64	1	0	-2.361564	-4.913950	-1.149205
65	1	0	2.924602	2.177896	6.793173
66	1	0	-0.582985	0.229215	8.341808

67	1	0	-2.374647	-0.144774	-5.050463
68	1	0	-3.668036	-0.562594	-7.132282
69	1	0	-6.996386	-1.922185	-4.771798
70	1	0	-5.710938	-1.504491	-2.719446
71	1	0	-4.333620	7.386843	-0.314178
72	1	0	-0.054482	7.681960	-0.633009
73	6	0	-1.010875	-4.873922	1.172250
74	6	0	-0.119034	-5.605266	0.366877
75	6	0	-1.735839	-5.573654	2.144234
76	6	0	0.042164	-6.975648	0.529267
77	1	0	0.457876	-5.085861	-0.393455
78	6	0	-1.586043	-6.952373	2.320036
79	1	0	-2.438749	-5.032914	2.771742
80	6	0	-0.691733	-7.660827	1.509165
81	1	0	0.734503	-7.538979	-0.088824
82	1	0	-2.172109	-7.455991	3.080443
83	17	0	-3.709914	-0.023880	1.589678
84	45	0	-1.562501	0.013245	0.552444
85	8	0	-2.443834	9.032963	-0.666669
86	8	0	-0.463779	-9.004795	1.590491
87	8	0	-6.028364	-1.459241	-7.299004
88	6	0	-1.324865	9.883995	-0.846232
89	1	0	-1.728913	10.892174	-0.956519
90	1	0	-0.651946	9.856766	0.021470
91	1	0	-0.756720	9.621300	-1.748870
92	6	0	-7.353656	-1.963469	-7.297613
93	1	0	-7.648130	-2.035973	-8.346335
94	1	0	-7.407416	-2.958941	-6.836813
95	1	0	-8.043041	-1.287913	-6.773787
96	6	0	-1.181286	-9.748623	2.560961
97	1	0	-0.849546	-10.782981	2.451888
98	1	0	-0.960848	-9.403371	3.580038
99	1	0	-2.265090	-9.696281	2.391226
100	8	0	1.781021	1.489364	8.943012
101	6	0	1.068460	1.070734	10.095272
102	1	0	1.675746	1.374169	10.950207
103	1	0	0.084507	1.554049	10.160244
104	1	0	0.934892	-0.019215	10.114700
105	6	0	4.218785	0.101842	-2.256922
106	6	0	4.507301	0.219366	-3.601906
107	16	0	5.706524	-0.027864	-1.334247
108	6	0	5.890841	0.223089	-3.894143
109	1	0	3.743432	0.332306	-4.363112
110	6	0	6.693442	0.104682	-2.774599
111	1	0	6.291071	0.331650	-4.896298
112	6	0	8.136759	0.071158	-2.689529
113	6	0	8.946339	0.219527	-1.584154
114	16	0	9.119863	-0.192052	-4.122911
115	6	0	10.334368	0.129352	-1.880806
116	1	0	8.557165	0.404792	-0.588364
117	6	0	10.605164	-0.085529	-3.207962
118	1	0	11.115001	0.227287	-1.133301
119	6	0	11.939421	-0.225194	-3.877289
120	1	0	12.048449	-1.196237	-4.375787
121	1	0	12.101519	0.552056	-4.634245
122	1	0	12.736364	-0.139316	-3.132135

Zero-point correction= 0.945227 (Hartree/Particle)
Thermal correction to Energy= 1.010665
Thermal correction to Enthalpy= 1.011609
Thermal correction to Gibbs Free Energy= 0.834279
Sum of electronic and zero-point Energies= -4330.722981
Sum of electronic and thermal Energies= -4330.657542
Sum of electronic and thermal Enthalpies= -4330.656598
Sum of electronic and thermal Free Energies= -4330.833928

C_1-Rh-1-*cis*

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-0.654100	1.544070	1.884386
2	7	0	0.279971	0.052652	-0.517214
3	6	0	-0.557445	5.729490	0.277592
4	1	0	0.380679	5.229485	0.052022
5	7	0	-2.237009	-1.521628	-0.372037
6	7	0	-2.383271	1.381445	-0.466426
7	6	0	-0.878535	2.882754	1.685710
8	7	0	-0.510724	-1.359430	1.975853
9	6	0	-1.812224	7.781390	0.524506
10	6	0	1.520106	0.142104	-0.003762
11	1	0	1.589224	0.194765	1.074963
12	6	0	-1.683053	4.960152	0.593048
13	6	0	0.042525	1.406996	3.060043
14	6	0	-6.514649	-0.447297	-5.140149
15	6	0	0.268189	2.718365	3.626529
16	1	0	0.773097	2.910711	4.561543
17	6	0	0.233327	-1.076798	3.093722
18	6	0	-3.127743	3.348721	-1.379800
19	1	0	-3.244119	4.410884	-1.536255
20	6	0	1.249317	0.271658	4.915307
21	6	0	-2.882197	5.638791	0.879442
22	1	0	-3.766931	5.064711	1.139553
23	6	0	-1.609031	3.464695	0.634907
24	6	0	-0.289171	3.623924	2.779103
25	1	0	-0.328717	4.697418	2.890204
26	6	0	0.156956	-0.012956	-1.856455
27	1	0	-0.851766	-0.091002	-2.240622
28	6	0	0.712434	-0.238855	6.103802
29	1	0	-0.279054	-0.682358	6.088133
30	6	0	1.414435	-0.180507	7.310894
31	6	0	2.659585	0.173175	-0.794107
32	1	0	3.626831	0.264413	-0.310360
33	6	0	-3.139373	-1.391545	-1.398292
34	6	0	0.766971	-2.312171	3.624438
35	1	0	1.412649	-2.387285	4.486890
36	6	0	2.530076	0.851237	4.972232
37	1	0	2.973151	1.252588	4.064788
38	6	0	-2.949937	7.025835	0.846394
39	6	0	2.687890	0.399620	7.344669
40	6	0	-4.282537	0.083949	-4.370304
41	6	0	-2.312335	2.746279	-0.347476
42	6	0	-0.507567	-2.720646	1.802860
43	6	0	3.241749	0.915991	6.163579
44	6	0	-3.715007	2.336340	-2.071996
45	1	0	-4.407503	2.413124	-2.897197
46	6	0	0.478973	0.199283	3.634213
47	6	0	-2.020993	-2.861395	-0.171394
48	6	0	-0.608877	7.126246	0.239395
49	6	0	-3.621282	-0.185633	-1.937986
50	6	0	-3.243228	1.095508	-1.497745
51	6	0	-3.492934	-2.708704	-1.880165
52	1	0	-4.177622	-2.907501	-2.691403
53	6	0	-4.618490	-0.274639	-3.052624
54	6	0	1.246611	0.006087	-2.712657
55	1	0	1.073502	-0.075637	-3.779896
56	6	0	0.317779	-3.319587	2.828816
57	1	0	0.524658	-4.375722	2.918275
58	6	0	-1.197830	-3.439168	0.810993
59	6	0	-5.211176	0.001256	-5.400576
60	6	0	2.552370	0.106075	-2.195246
61	6	0	-6.869726	-0.809496	-3.835577
62	6	0	-5.923575	-0.719628	-2.810535
63	6	0	-2.811140	-3.610224	-1.124058
64	1	0	-2.840405	-4.687695	-1.192017
65	1	0	4.232329	1.358387	6.205290
66	1	0	0.957465	-0.580805	8.208783
67	1	0	-3.275690	0.430800	-4.587350
68	1	0	-4.950393	0.274761	-6.418377

69	1	0	-7.870970	-1.153900	-3.602855
70	1	0	-6.209421	-0.994840	-1.799230
71	1	0	-3.873292	7.549692	1.073558
72	1	0	0.285679	7.683438	-0.014951
73	6	0	-1.083638	-4.932413	0.825694
74	6	0	-0.405336	-5.619366	-0.197517
75	6	0	-1.654455	-5.691985	1.853928
76	6	0	-0.300421	-7.004731	-0.190147
77	1	0	0.049047	-5.053477	-1.006236
78	6	0	-1.558630	-7.086453	1.875896
79	1	0	-2.192895	-5.185431	2.649984
80	6	0	-0.877496	-7.750134	0.848886
81	1	0	0.227879	-7.534252	-0.977068
82	1	0	-2.021122	-7.636263	2.687761
83	17	0	-3.366125	-0.037695	2.170003
84	45	0	-1.446440	0.010030	0.755528
85	8	0	-1.981375	9.136489	0.518077
86	8	0	-0.720710	-9.104215	0.766554
87	8	0	-7.352761	-0.493616	-6.217030
88	6	0	-0.863449	9.950159	0.207101
89	1	0	-1.217681	10.981307	0.262747
90	1	0	-0.046651	9.808807	0.927665
91	1	0	-0.486690	9.751293	-0.805344
92	6	0	-8.684532	-0.934652	-6.011114
93	1	0	-9.169049	-0.892295	-6.988495
94	1	0	-8.715818	-1.966384	-5.635979
95	1	0	-9.223249	-0.281925	-5.311294
96	6	0	-1.286306	-9.907568	1.788618
97	1	0	-1.043944	-10.939630	1.527865
98	1	0	-0.857660	-9.672487	2.772187
99	1	0	-2.377568	-9.793012	1.836403
100	8	0	3.463730	0.510701	8.462548
101	6	0	2.951499	0.009782	9.686177
102	1	0	3.723134	0.199812	10.434666
103	1	0	2.027592	0.525823	9.979494
104	1	0	2.757753	-1.069864	9.631923
105	6	0	3.715565	0.137357	-3.074245
106	6	0	3.758142	0.381326	-4.433072
107	16	0	5.336207	-0.147103	-2.466601
108	6	0	5.062427	0.365017	-4.978735
109	1	0	2.875081	0.606046	-5.020979
110	6	0	6.047464	0.095218	-4.046454
111	1	0	5.282686	0.576116	-6.018971
112	6	0	7.473774	-0.017836	-4.273295
113	6	0	8.116194	-0.325308	-5.453315
114	16	0	8.652538	0.261729	-3.001677
115	6	0	9.533737	-0.338623	-5.338959
116	1	0	7.583061	-0.561052	-6.367849
117	6	0	9.992245	-0.051182	-4.078337
118	1	0	10.200162	-0.566392	-6.164792
119	6	0	11.409390	0.012172	-3.592769
120	1	0	11.663997	1.003259	-3.197571
121	1	0	11.602458	-0.717704	-2.796984
122	1	0	12.092497	-0.204606	-4.419915

Zero-point correction= 0.945230 (Hartree/Particle)
Thermal correction to Energy= 1.010640
Thermal correction to Enthalpy= 1.011584
Thermal correction to Gibbs Free Energy= 0.834665
Sum of electronic and zero-point Energies= -4330.721758
Sum of electronic and thermal Energies= -4330.656348
Sum of electronic and thermal Enthalpies= -4330.655404
Sum of electronic and thermal Free Energies= -4330.832323

C_1-Rh-2

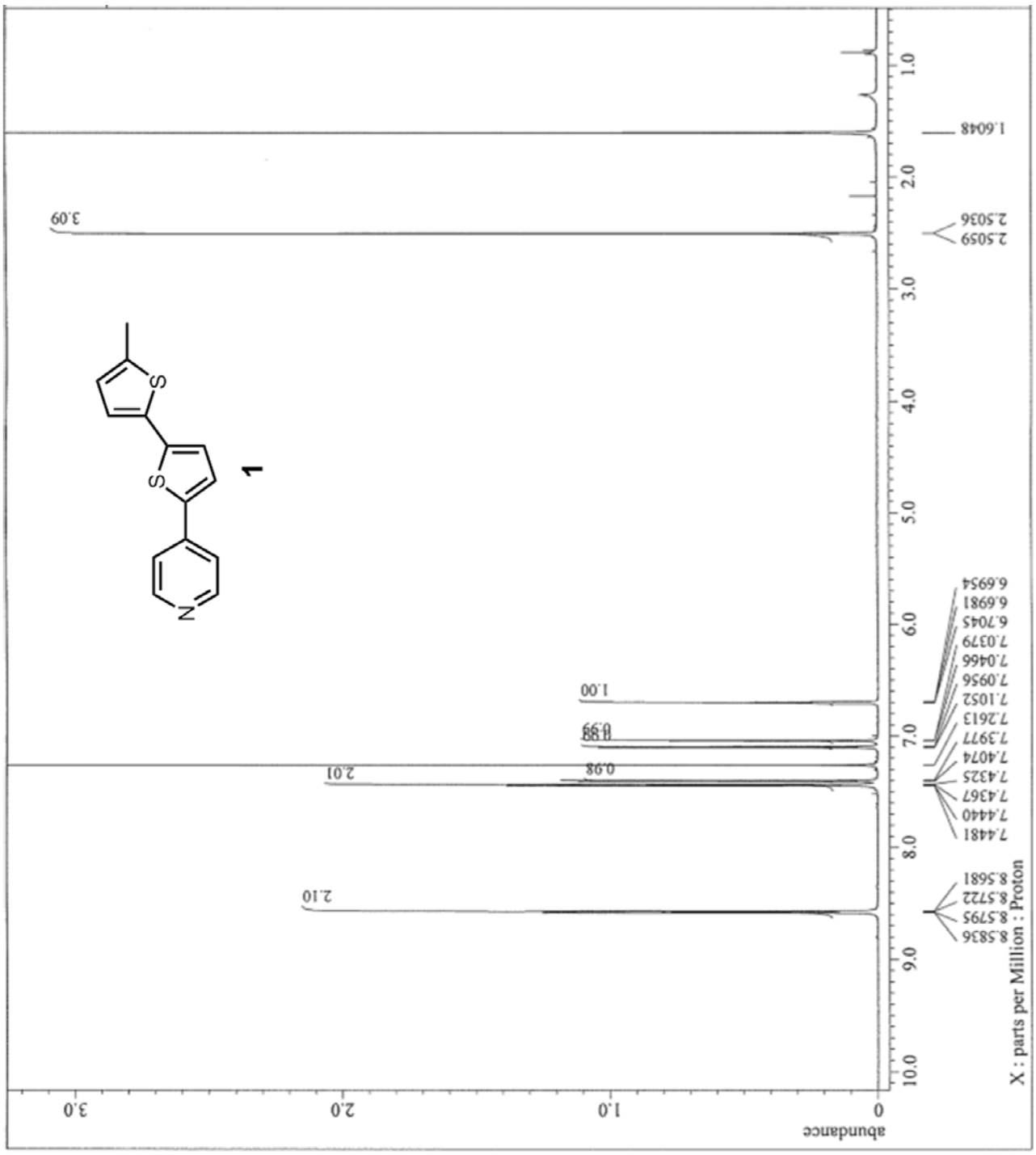
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	-1.596129	0.477630	2.077812
2	7	0	0.464294	0.002811	-0.020825
3	6	0	-0.270037	4.489804	3.574066
4	1	0	0.579854	3.813702	3.534535
5	7	0	-1.761934	-0.295887	-1.968271
6	7	0	-1.612961	2.112360	-0.345018
7	6	0	-1.563042	1.721737	2.654398
8	7	0	-1.745844	-1.929634	0.449350
9	6	0	-1.274647	6.518274	4.423774
10	6	0	1.161758	-0.658156	0.920564
11	1	0	0.581711	-1.127114	1.704710
12	6	0	-1.414874	4.192534	2.826064
13	6	0	-1.740668	-0.445946	3.083892
14	6	0	-2.322825	4.446842	-6.370199
15	6	0	-1.799878	0.247843	4.351511
16	1	0	-1.933199	-0.227084	5.312201
17	6	0	-1.786614	-2.511953	1.691359
18	6	0	-1.528797	4.390223	-0.093678
19	1	0	-1.451813	5.352084	0.391242
20	6	0	-1.946007	-2.676340	4.164824
21	6	0	-2.497283	5.088983	2.899401
22	1	0	-3.402326	4.874130	2.338399
23	6	0	-1.487941	2.955560	1.984708
24	6	0	-1.682148	1.576725	4.088615
25	1	0	-1.702959	2.395105	4.792957
26	6	0	1.150107	0.606630	-1.008080
27	1	0	0.559954	1.122981	-1.754022
28	6	0	-3.113613	-3.407473	4.416818
29	1	0	-3.933359	-3.355753	3.705953
30	6	0	-3.255630	-4.190806	5.565580
31	6	0	2.547784	-0.736646	0.908060
32	1	0	3.050784	-1.263102	1.712200
33	6	0	-1.874642	0.637449	-2.968687
34	6	0	-1.759936	-3.949743	1.533946
35	1	0	-1.755205	-4.661312	2.346388
36	6	0	-0.908555	-2.754455	5.112123
37	1	0	0.010346	-2.200033	4.941446
38	6	0	-2.432090	6.233788	3.683338
39	6	0	-2.210460	-4.254713	6.494548
40	6	0	-0.938260	3.617574	-4.566673
41	6	0	-1.526134	3.114154	0.588489
42	6	0	-1.740298	-2.933868	-0.485289
43	6	0	-1.033075	-3.529226	6.258399
44	6	0	-1.667676	4.137024	-1.422384
45	1	0	-1.732341	4.851868	-2.229369
46	6	0	-1.815662	-1.842165	2.929103
47	6	0	-1.803793	-1.538503	-2.548212
48	6	0	-0.188051	5.638021	4.367790
49	6	0	-1.856884	2.034909	-2.812279
50	6	0	-1.717912	2.700265	-1.581101
51	6	0	-1.971347	-0.047459	-4.238931
52	1	0	-2.059326	0.439328	-5.198986
53	6	0	-2.010853	2.872478	-4.044993
54	6	0	2.535949	0.570587	-1.087150
55	1	0	3.026552	1.054724	-1.924848
56	6	0	-1.724924	-4.208231	0.199085
57	1	0	-1.688272	-5.171663	-0.287440
58	6	0	-1.762473	-2.775747	-1.882095
59	6	0	-1.086293	4.393689	-5.709644
60	6	0	3.282110	-0.113657	-0.113883
61	6	0	-3.403367	3.712601	-5.867584
62	6	0	-3.237646	2.937446	-4.716197
63	6	0	-1.933122	-1.381938	-3.980498
64	1	0	-1.994976	-2.195183	-4.688488
65	1	0	-0.229834	-3.592834	6.986051
66	1	0	-4.180205	-4.734025	5.724741
67	1	0	0.026362	3.583717	-4.067140
68	1	0	-0.256990	4.965673	-6.114367
69	1	0	-4.372343	3.738674	-6.353028

70	1	0	-4.083261	2.376763	-4.327888
71	1	0	-3.269413	6.922059	3.744882
72	1	0	0.719963	5.832687	4.927310
73	6	0	-1.786146	-4.014838	-2.722926
74	6	0	-0.686885	-4.368576	-3.526333
75	6	0	-2.904800	-4.856512	-2.741013
76	6	0	-0.705186	-5.515487	-4.310228
77	1	0	0.194844	-3.733537	-3.529168
78	6	0	-2.939666	-6.013680	-3.524539
79	1	0	-3.770711	-4.599153	-2.137545
80	6	0	-1.834102	-6.348478	-4.315005
81	1	0	0.145338	-5.791022	-4.926193
82	1	0	-3.828841	-6.633824	-3.513854
83	17	0	-4.060679	0.187016	0.132407
84	45	0	-1.679147	0.090337	0.051989
85	8	0	-1.308959	7.666871	5.161539
86	8	0	-1.755537	-7.450705	-5.117259
87	8	0	-2.367695	5.236042	-7.483504
88	6	0	-0.169282	8.001375	5.934720
89	1	0	-0.411586	8.940329	6.436201
90	1	0	0.047541	7.233432	6.689507
91	1	0	0.719130	8.146301	5.305201
92	6	0	-3.593946	5.330320	-8.189285
93	1	0	-3.405719	6.001645	-9.029332
94	1	0	-3.916586	4.352848	-8.572204
95	1	0	-4.390959	5.750584	-7.561466
96	6	0	-2.869885	-8.325938	-5.164522
97	1	0	-2.594707	-9.125171	-5.855414
98	1	0	-3.087002	-8.758482	-4.178592
99	1	0	-3.768507	-7.817396	-5.538769
100	8	0	-2.236698	-4.984594	7.647951
101	6	0	-3.403906	-5.734856	7.940345
102	1	0	-3.209956	-6.232439	8.892475
103	1	0	-4.285472	-5.088090	8.042701
104	1	0	-3.601817	-6.492032	7.169809
105	6	0	4.759865	-0.175001	-0.161654
106	6	0	5.452807	-1.315914	0.277545
107	6	0	5.515750	0.905528	-0.647243
108	6	0	6.841671	-1.373372	0.231244
109	1	0	4.898108	-2.176364	0.640887
110	6	0	6.904764	0.847490	-0.689156
111	1	0	5.012303	1.809740	-0.977464
112	6	0	7.600977	-0.293208	-0.251977
113	1	0	7.348253	-2.263306	0.593119
114	1	0	7.459642	1.693135	-1.084892
115	6	0	9.081989	-0.354390	-0.299163
116	6	0	9.865346	0.779876	-0.027044
117	6	0	9.751035	-1.549406	-0.613259
118	6	0	11.256336	0.718983	-0.068374
119	1	0	9.381114	1.711802	0.251600
120	6	0	11.142197	-1.604253	-0.654464
121	1	0	9.175682	-2.439808	-0.851427
122	6	0	11.923005	-0.471912	-0.386226
123	1	0	11.835410	1.610920	0.160529
124	1	0	11.630801	-2.542862	-0.906616
125	6	0	13.430678	-0.527197	-0.461854
126	1	0	13.809566	-1.521542	-0.202260
127	1	0	13.786428	-0.298738	-1.475710
128	1	0	13.893080	0.199246	0.214932

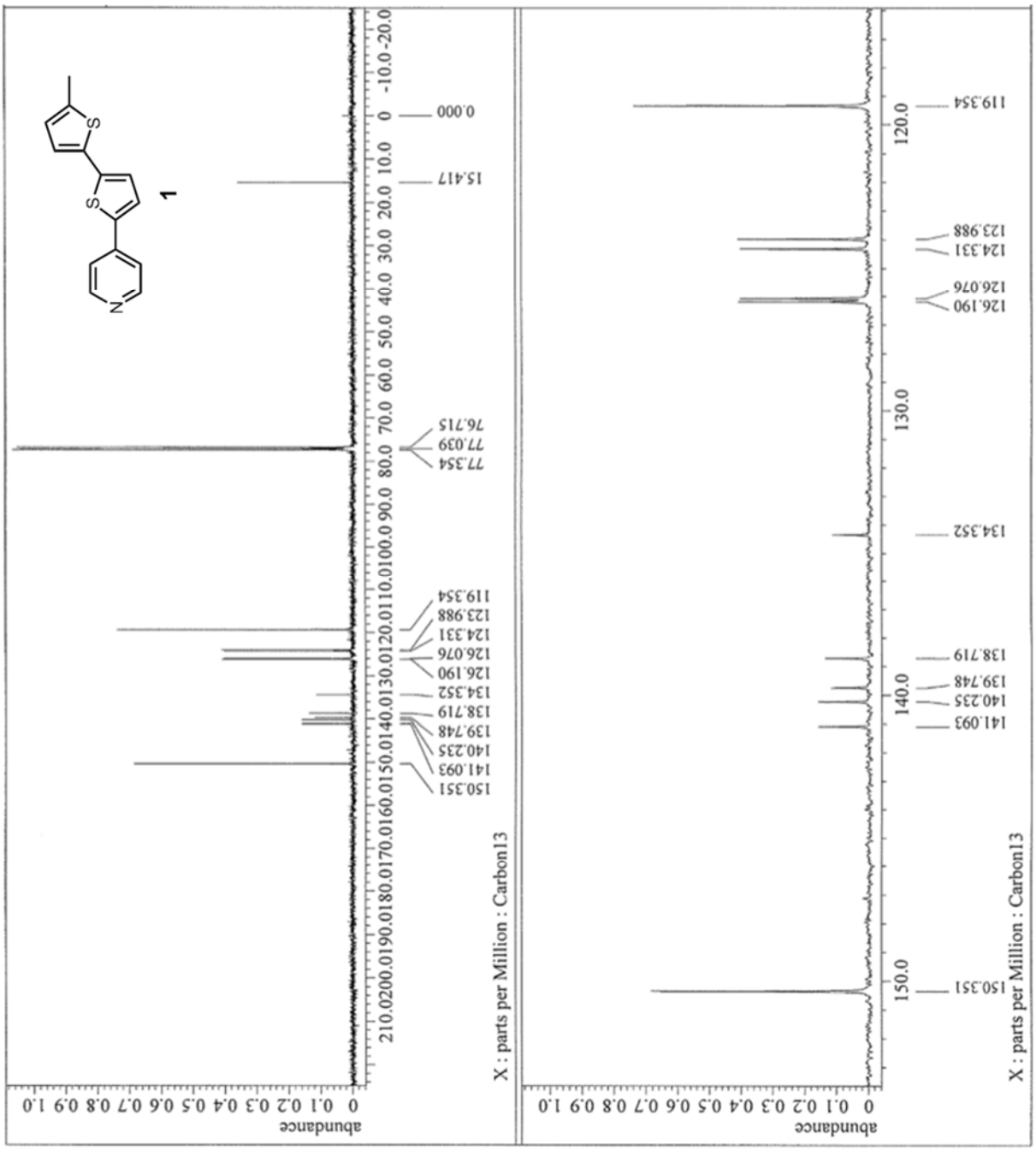
Zero-point correction=	1.012584 (Hartree/Particle)
Thermal correction to Energy=	1.078450
Thermal correction to Enthalpy=	1.079394
Thermal correction to Gibbs Free Energy=	0.901912
Sum of electronic and zero-point Energies=	-3689.143809
Sum of electronic and thermal Energies=	-3689.077944
Sum of electronic and thermal Enthalpies=	-3689.077000
Sum of electronic and thermal Free Energies=	-3689.254481

III. NMR and MASS spectra

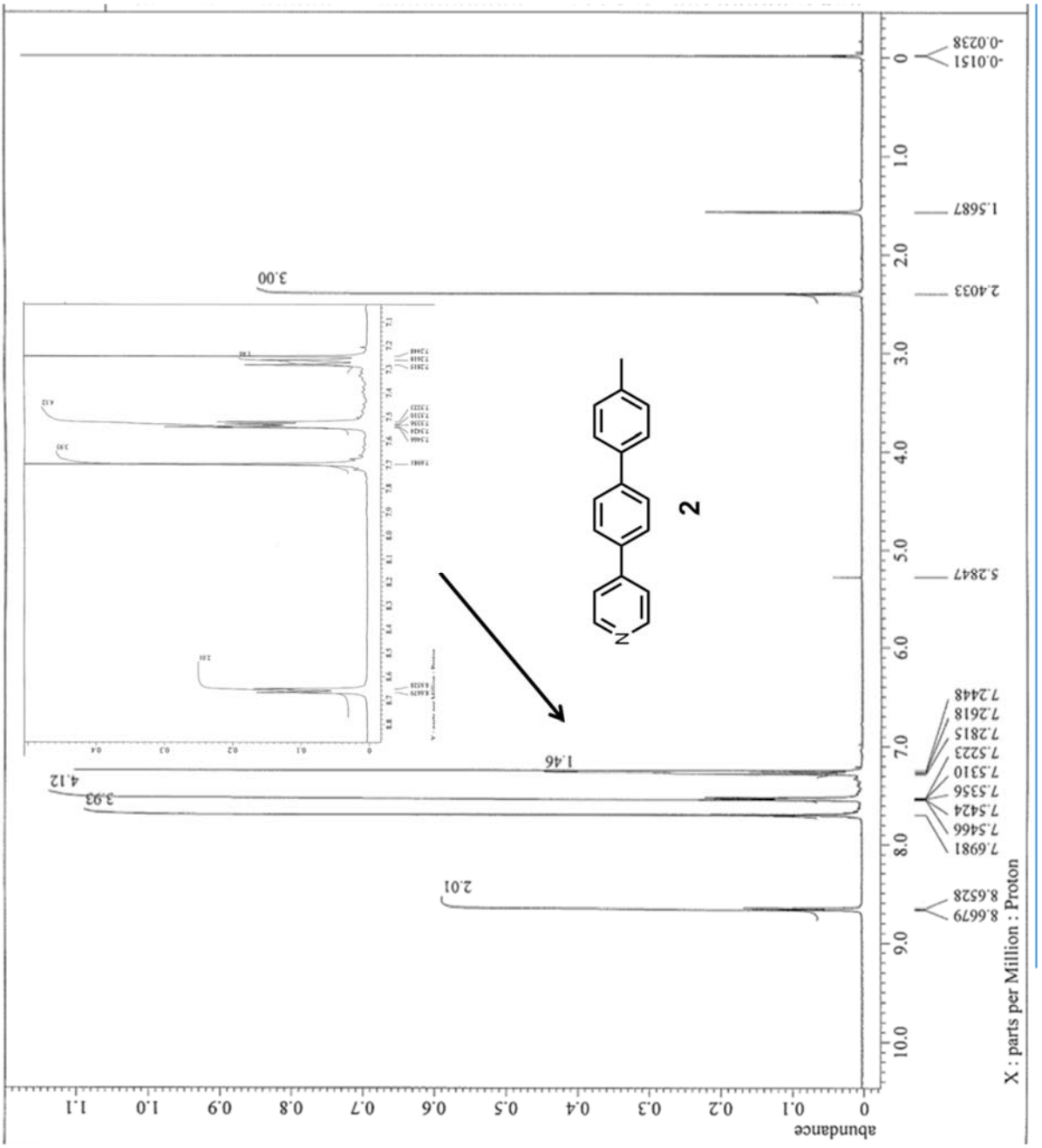
^{1}H NMR spectrum of **1** (400 MHz, $CDCl_3$)



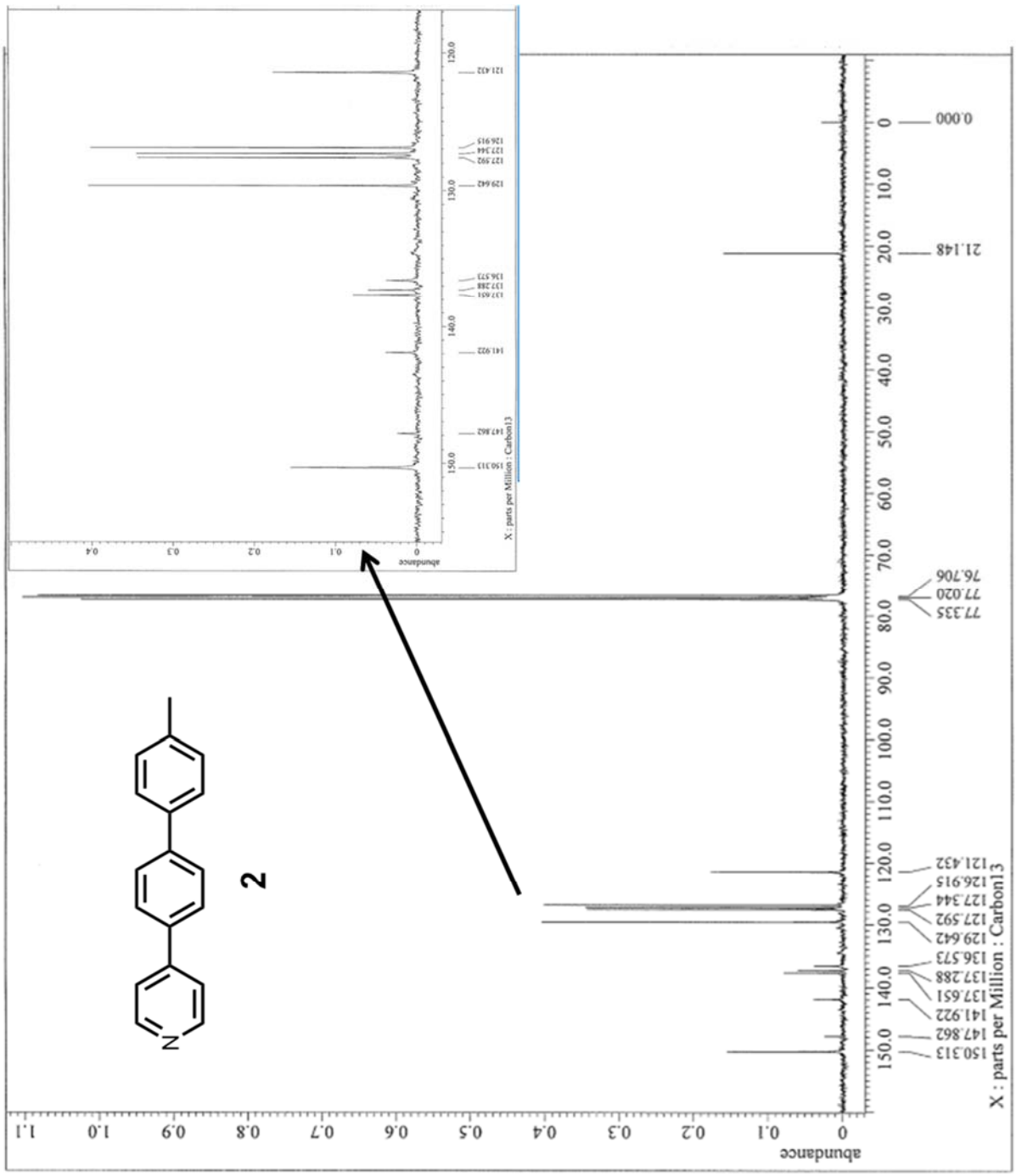
^{13}C NMR spectrum of **1** (101 MHz, $CDCl_3$)



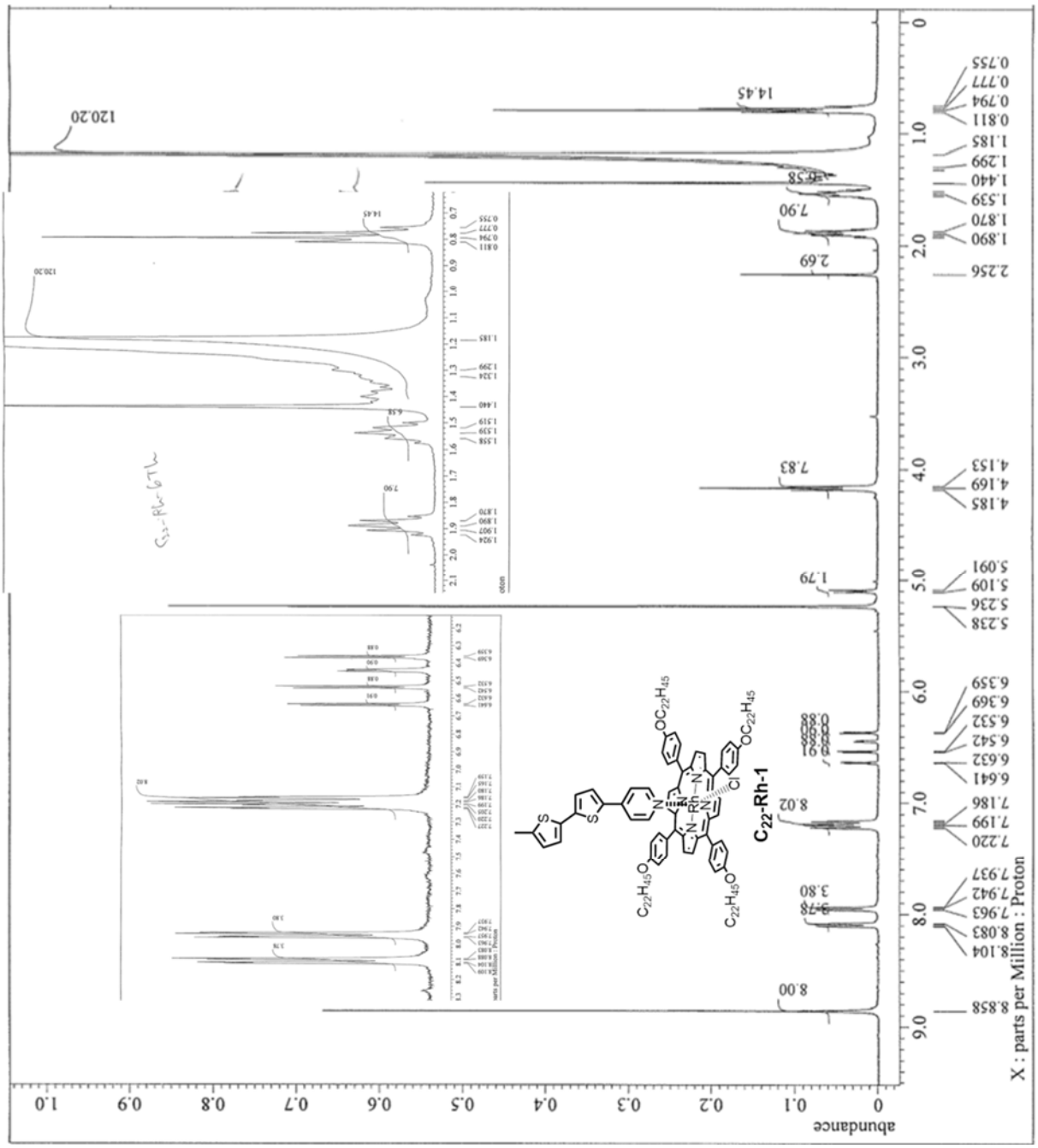
^{1}H NMR spectrum of **2** (400 MHz, $CDCl_3$)



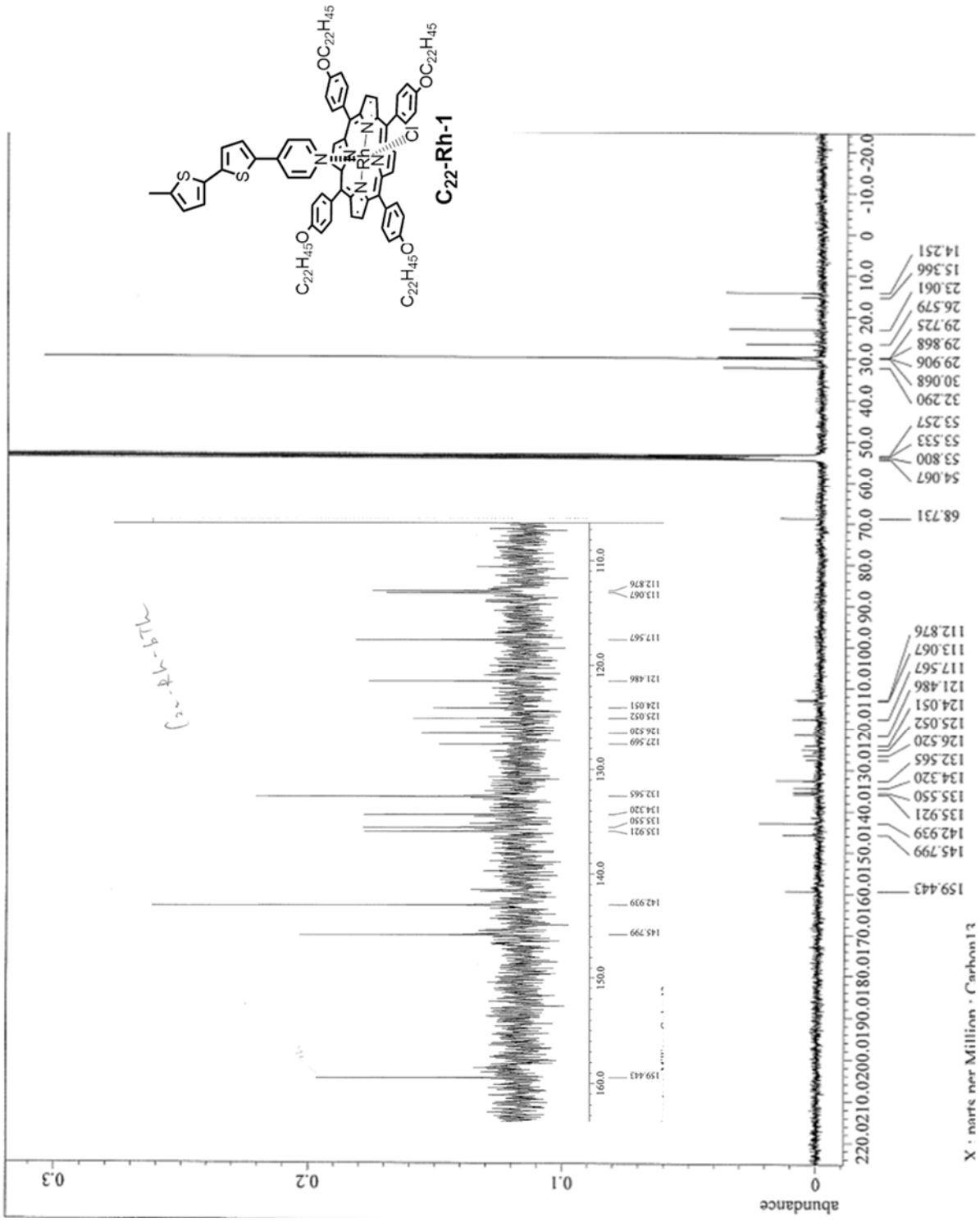
^{13}C NMR spectrum of **2** (101 MHz, $CDCl_3$)



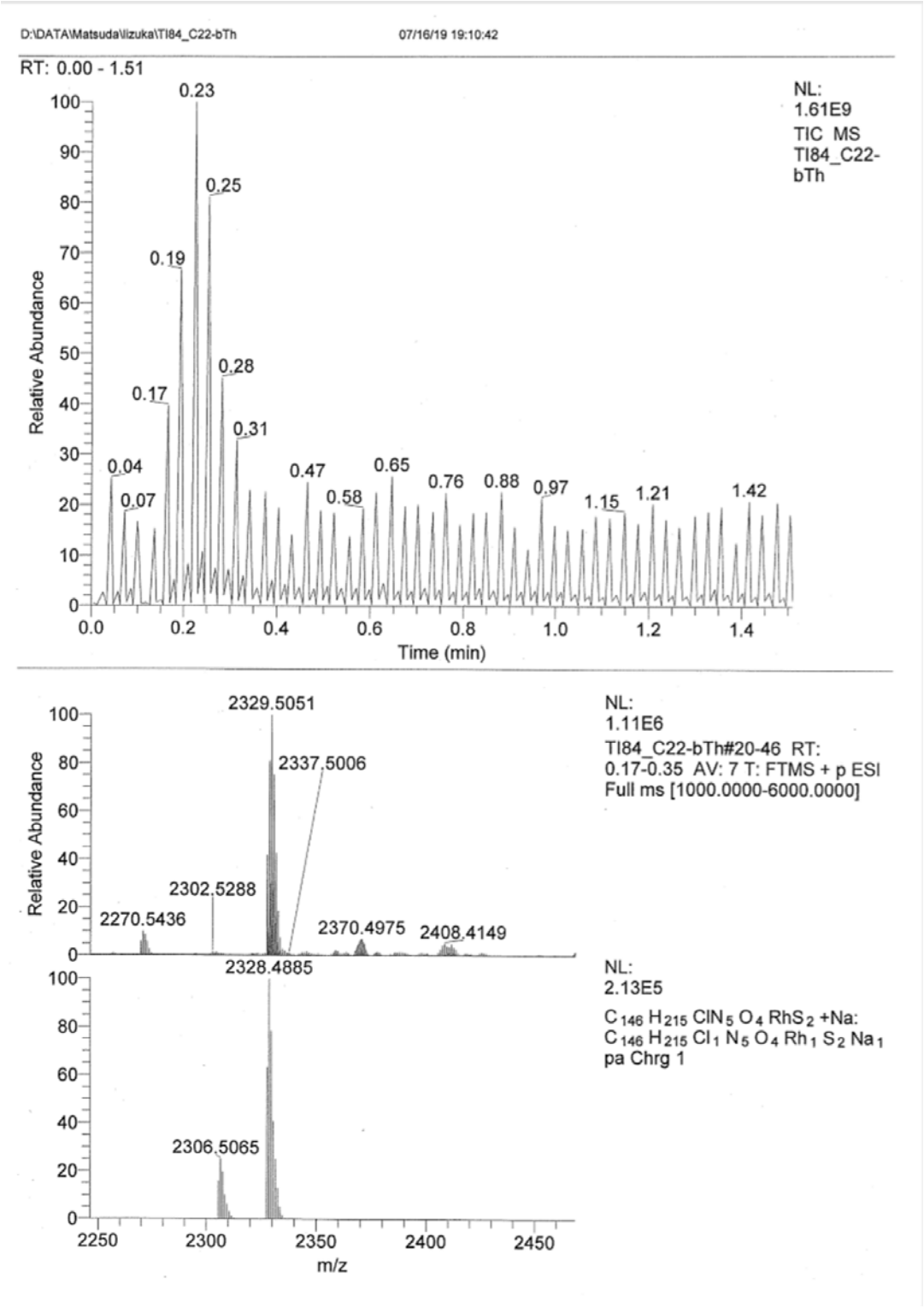
^{1}H NMR spectrum of **C_{22}-Rh-1** (400 MHz, CD_2Cl_2)



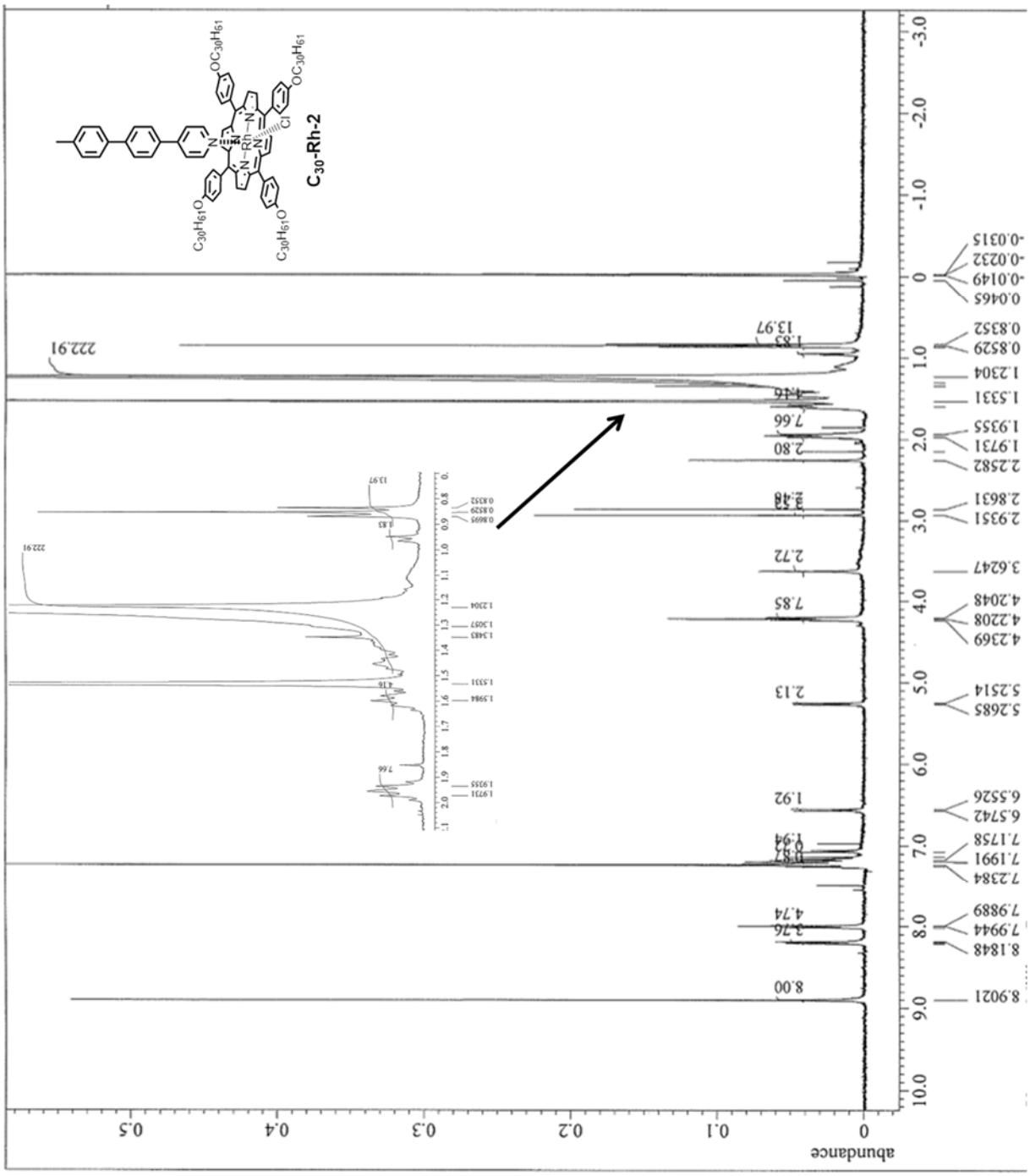
^{13}C NMR spectrum of **C_{22}-Rh-1** (101 MHz, CD_2Cl_2)



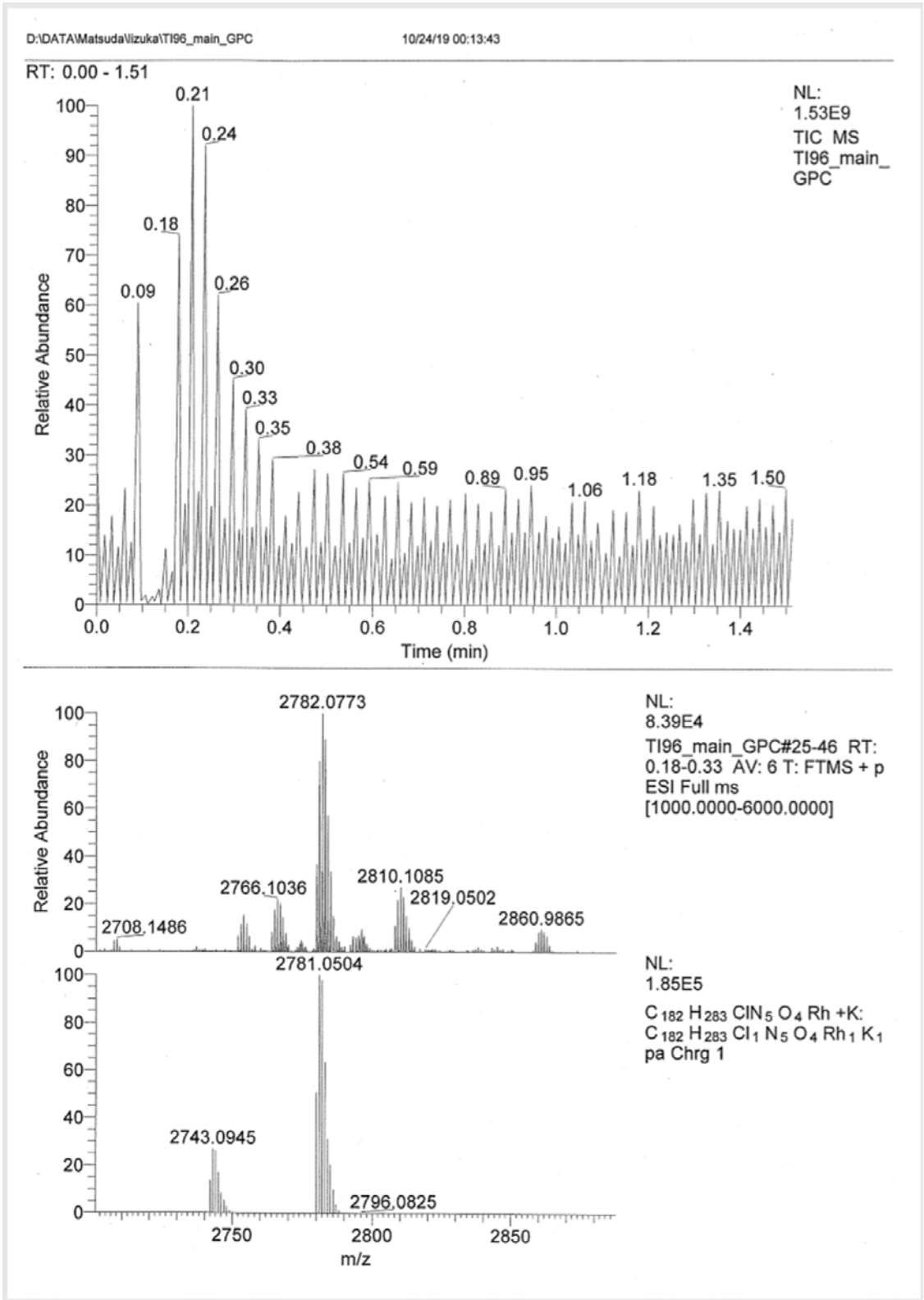
MASS spectrum of **C_{22}-Rh-1** (ESI)



^{1}H NMR spectrum of **C_{30}-Rh-2** (400 MHz, $CDCl_3$)



MASS spectrum of **C_{30}-Rh-2** (ESI)



References

S1. S.-T. Liu, K. V. Reddy and R.-Y. Lai, *Tetrahedron*, 2007, **63**, 1821–1825.

S2. J. Otsuki, S. Kawaguchi, T. Yamakawa, M. Asakawa and K. Miyake, *Langmuir*, 2006, **22**, 5708–5715.

S3. T. Ikeda, M. Asakawa, M. Goto, K. Miyake, T. Ishida and T. Shimizu, *Langmuir*, 2004, **22**, 5454–5459.

S4. L. A. Bumm, J. J. Arnold, T. D. Dunbar, D. L. Allara and P. S. Weiss, *J. Phys. Chem B*, 1999, **103**, 8122–8127.

S5. Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.