Electronic Supplementary Information

Synthesis of heterosegment-junctioned hybrid nanotubes of polythiophene and heterometallic nanoparticles by sequential template-based electropolymerization

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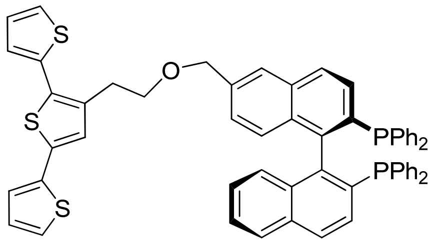
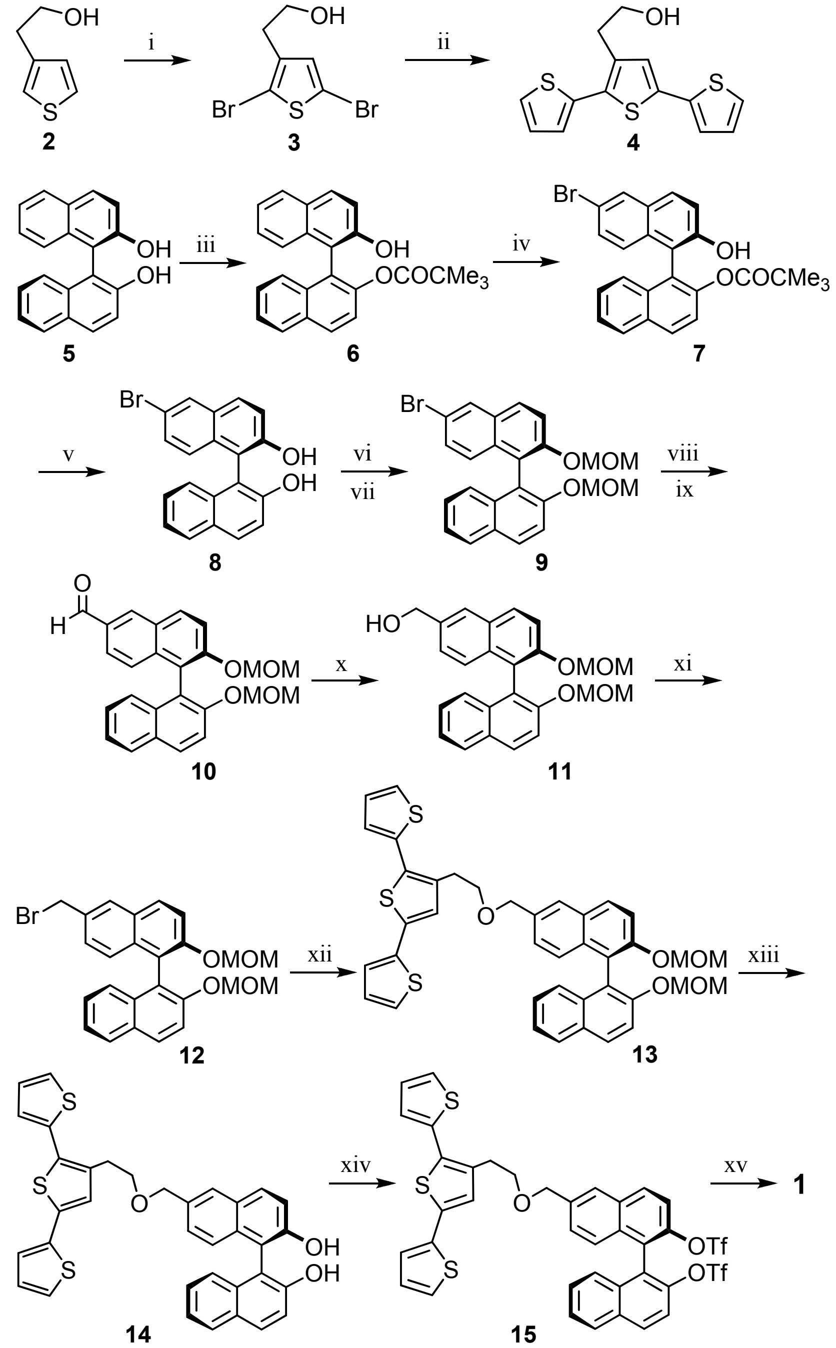
1) Protective Ligand **1**.
2) Synthesis and characterization of metal nanoparticles.
3) Fabrication of hybrid nanotubes.
4) Addendum of EDX spectral data and elemental mapping of **1**-Au/Pd-PT NTs.
5) SEM and TEM images, and EDX spectra of hybrid nanotubes.

1) Protective Ligand **1**: Chiral (*R*)-binaphthylbisphosphine-linked-terthiophene (**1**).



1

A new terthiophene (**1**) was synthesized according to Scheme S1. The detailed synthesis and property of **1** will be reported elsewhere. The bisphosphine **1** provides the same particle size for **1**-protected Au NPs and **1**-protected Pd NPs, respectively (*vide infra*).



Scheme S1. Reagents and Conditions: (i) *N*-Bromosuccinimide, toluene, room temp., 4 h; (ii) 2-(tributylstannyl)thiophene, $Pd(PPh_3)_4$, toluene, 95 °C, 10 h; (iii) Me_3CCOCl, Et_3N, MeCN, room temp., 3 h; (iv) Br_2, MeCN, 0 °C, 2 h; (v) KOH, THF-H_2O, room temp., 9 h; (vi) NaH, THF, 0 °C, 1 h; (vii) $MeOCH_2Cl$: $MeOCH_2$ = MOM, THF, room temp., 3 h; (viii) *n*-BuLi, THF, -78 °C, 1 h; (ix) DMF, THF, -55 °C, 2 h; (x) $LiAlH_4$, THF, 0 °C, 1 h; (xi) CBr_4, PPh_3, THF, room temp., 1 h; (xii) compound **4**, NaH, THF, room temp., 20 h; (xiii) *i*-PrOH, HCl, CH_2Cl_2, room temp., 4 h; (xiv) pyridine, $(CF_3SO_2)_2O$: CF_3SO_2 = Tf, CH_2Cl_2, 0 °C, 2 h; (xv) Ph_2PH, $NiCl_2$ dppe, DABCO, DMF, 100 °C, 72 h.

(*R*)-**1**: ^{1}H NMR (CD_2Cl_2) δ 2.95 (t, J = 6.8 Hz, 2H, CH_2), 3.61 (t, J = 6.8 Hz, 2H, CH_2), 4.48 (s, 2H, CH_2), 6.66 (d, J = 8.8 Hz, 1H, Ar-H), 6.72 (d, J = 8.4 Hz, 1H, Ar-H), 6.76 (dd, J_1 = 1.2 Hz, J_2 = 8.4 Hz, 1H, Ar-H), 6.79-6.85 (m, 1H, Ar-H), 6.85-6.89 (m, 1H, Ar-H), 6.89-7.15 (m, 25H, Ar-H), 7.18 (dd, J_1 = 0.8 Hz, J_2 = 5.2 Hz, 1H, Ar-H), 7.22-7.34 (m, 3H, Ar-H), 7.66 (s, 1H, Ar-H), 7.71-7.78 (m, 2H, Ar-H), 7.80 (d, J = 8.4 Hz, 1H, Ar-H); ^{13}C NMR (CD_2Cl_2) δ 30.2, 70.2, 72.9, 124.0, 124.9, 125.9, 126.1, 126.2, 126.3, 126.7, 127.0, 127.2, 127.7, 127.7, 127.8, 127.8, 128.0, 128.1, 128.1, 128.3, 128.4, 128.4, 128.5, 128.5, 128.5, 128.8, 128.8, 130.9, 130.9, 131.0, 131.2, 131.2, 133.2, 133.2, 133.2, 133.3, 133.3, 133.3, 133.4, 133.6, 133.7, 133.7, 133.8, 133.8, 134.2, 134.2, 134.3, 134.3, 134.4, 134.4, 134.5, 134.5, 135.5, 135.5, 135.6, 135.8, 135.8, 137.0, 137.3, 137.4, 137.5, 137.5, 137.6, 137.6, 137.7, 137.8, 138.2, 138.3, 138.3, 145.3, 145.4, 145.5, 145.6, 145.7, 145.8; ^{31}P NMR ($CDCl_3$) δ -15.7; MS (FAB) m/z 927 (MH^+). $[\alpha]_D^{20}$ = +88.2°(c = 1.0, $CHCl_3$).

The ^{1}H and ^{13}C NMR spectra of **1** are described in pages S7-S9.

2) Synthesis and characterization of metal nanoparticles.

Typical procedure for the preparation of **1**-Au NPs is as follows. To a vigorously stirred solution of $HAuCl_4.4H_2O$ (82 mg, 0.20 mmol) in 10 mL of H_2O was added phosphine **1** (185 mg, 0.20 mmol) in 30 mL of THF. $NaBH_4$ (76 mg, 2.0 mmol) in 8 mL of H_2O was then added. The mixture was stirred for 1 h at room temperature. After the reaction, the filtrate was evaporated in *vacuo* to yield **1**-Au NPs, which were washed several times with *n*-hexane. The nanoparticles were dissolved in CH_2Cl_2 to purify and precipitated with *n*-hexane, and then the particles were isolated by filtration. These processes were repeated until no free phosphine remained, as detected by TLC, ^{1}H and ^{13}C NMR spectroscopy. Analogously, **1**-Pd NPs were prepared by the similar procedures as **1**-Au NPs using K_2PdCl_4 instead of $HAuCl_4$. **1**-Au and **1**-Pd NPs are remarkably stable both in solution, as well as in the solid state.

The particle size and size distribution of **1**-Au NPs and **1**-Pd NPs were analyzed with transmission electron microscopy (TEM). The core size of the metal NPs is 1.2 ± 0.1 nm for **1**-Au NPs and 1.2 ± 0.1 nm for **1**-Pd NPs (Figure S1). The X-ray photoelectron spectroscopy (XPS) spectrum of **1**-Au NPs shows the Au 4f binding energies at 84.0 and 87.6 eV, corresponding to the Au^0 state (Fig. S1-A). The XPS spectrum of **1**-Pd NPs display that the binding energies for the Pd 3d doublet are 335.3 and 340.5 eV (Fig. S1-B).

The UV-vis spectra of **1**-Au NPs and **1**-Pd NPs in $CHCl_3$ exhibit the absorption peak due to the terthiophene at 340 nm (Fig. S2). **1**-Au NPs shows no significant plasmon peak which is consistent with the smaller particle size.

The TEM findings indicate that the ligand **1** provides small particle size with extremely narrow size distribution.

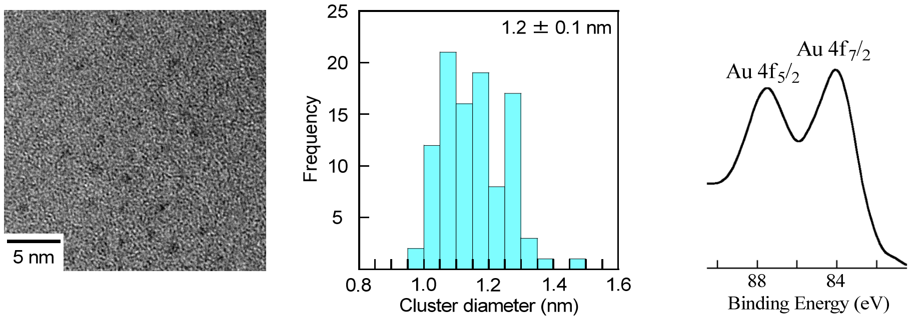


Fig. S1-A TEM image (left) and size distribution (center) of **1**-Au NPs, and XPS spectrum (right) in the Au region of **1**-Au NPs.

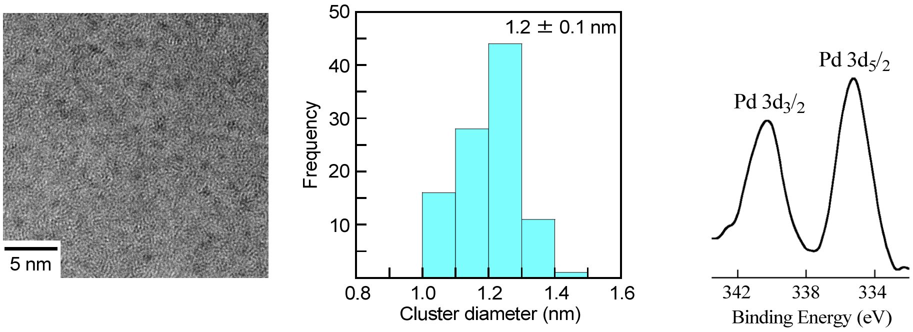


Fig. S1-B TEM image (left) and size distribution (center) of **1**-Pd NPs, and XPS spectrum (right) in the Pd region of **1**-Pd NPs.

3) Fabrication of hybrid nanotubes.

3.1) 1-Au-PT NTs

The electrochemical synthesis was performed by attaching the alumina membrane (Whatman Anodisc; pore diameter of about 200-250 nm, thickness of 60 μm) to a Pt electrode, another Pt electrode was used as the counter electrode, and Ag/0.1 M $AgNO_3$ was used as the reference electrode. The electrolysis solution contains **1**-Au NPs (15 mg: 1.2 nm) in 0.1 M Bu_4NPF_6-CH_2Cl_2 (1 mL). A voltage of 1.0 V was applied for 30 min. After the electrochemical synthesis, removal of the alumina membranes with 1 M NaOH led to the release of **1**-Au-PT NTs.

3.2) 1-Pd-PT NTs

The electrochemical synthesis was performed by attaching the alumina membrane (Whatman Anodisc; pore diameter of about 200-250 nm, thickness of 60 μm) to a Pt electrode, another Pt electrode was used as the counter electrode, and Ag/0.1 M $AgNO_3$ was used as the reference electrode. The electrolysis solution contains **1**-Pd NPs (15 mg: 1.2 nm) in 0.1 M Bu_4NPF_6-CH_2Cl_2 (1 mL). A voltage of 1.0 V was applied for 30 min. After the electrochemical synthesis, removal of the alumina membranes with 1 M NaOH led to the release of **1**-Pd-PT NTs.

3.3) 1-Au/Pd-PT NTs : Heterojunction

The electrochemical synthesis was performed by attaching the alumina membrane (Whatman Anodisc; pore diameter of about 200-250 nm, thickness of 60 μm) to a Pt electrode, another Pt electrode was used as the counter electrode and Ag/0.1 M $AgNO_3$ was used as the reference electrode. The electrolysis solution contains **1**-Au NPs (15 mg) in 0.1 M Bu_4NPF_6-CH_2Cl_2 (1 mL). A voltage of 1.0 V (vs. Ag/0.1 M $AgNO_3$) was applied for 20 min. After the electropolymerization of **1**-Au NPs, the resulting **1**-Au-PT NT-modified membrane was rinsed in acetone and then CH_2Cl_2. Subsequently, the electropolymerization (1.0 V) of **1**-Pd NPs (15 mg) in 0.1 M Bu_4NPF_6-CH_2Cl_2 (1 mL) was performed for 30 min by using **1**-Au-PT NT-modified alumina membrane. After the electrochemical synthesis, removal of the alumina membranes with 1 M NaOH led to the release of **1**-Au/Pd-PT NTs.

3.4) **1-Au/Pd/Au-PT NTs** : Heterojunction

The electrochemical synthesis was performed by attaching the alumina membrane (Whatman Anodisc; pore diameter of about 200-250 nm, thickness of 60 μm) to a Pt electrode, another Pt electrode was used as the counter electrode and Ag/0.1 M $AgNO_3$ was used as the reference electrode. The electrolysis solution contains **1**-Au NPs (15 mg) in 0.1 M Bu_4NPF_6-CH_2Cl_2 (1 mL). A voltage of 1.0 V was applied for 10 min. The resulting **1**-Au-PT NT-modified membrane was rinsed in acetone and then CH_2Cl_2. Second, the electropolymerization (1.0 V) of **1**-Pd NPs (15 mg) in 0.1 M Bu_4NPF_6-CH_2Cl_2 (1 mL) was performed for 45 min by using **1**-Au-PT NT-modified alumina membrane. The resulting **1**-Au/Pd-PT NT-modified membrane was rinsed in acetone and then CH_2Cl_2. Subsequently, the electropolymerization (1.0 V) of **1**-Au NPs (15 mg) in 0.1 M Bu_4NPF_6-CH_2Cl_2 (1 mL) was performed for 10 min by using **1**-Au/Pd-PT NT-modified alumina membrane. After the electrochemical synthesis, removal of the alumina membranes with 1 M NaOH led to the release of **1**-Au/Pd/Au-PT NTs. These NTs were characterized by SEM, TEM, and EDX spectroscopy.

3.5) UV-vis spectra of nanotubes.

The UV-vis spectra of the hybrid nanotubes in $CHCl_3$ exhibit the absorption peak due to the polythiophene at 430 nm for **1**-Au-PT NTs and **1**-Pd-PT NTs, and at 470 nm for **1**-Au/Pd-PT NTs (Fig. S2). **1**-Au/Pd/Au-PT NTs show the similar spectrum as **1**-Au/Pd-PT NTs.

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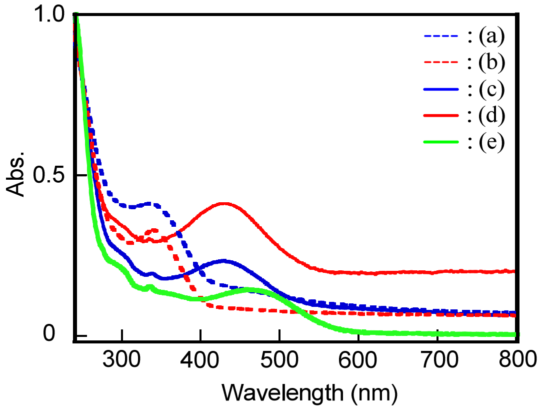


Fig. S2 UV-vis spectra of (a) **1**-Au NPs, (b) **1**-Pd NPs, (c) **1**-Au-PT NTs, (d) **1**-Pd-PT NTs, and (e) **1**-Au/Pd-PT NTs in $CHCl_3$.

4) Addendum of EDX spectral data and elemental mapping of 1-Au/Pd-PT NTs.

The chemical composition of **1**-Au/Pd-PT NTs was determined by EDX as shown in Fig. 3. The quantitative analysis results in each point (A1, A2, and A3) of EDX spectra (Fig. 3) indicate atomic composition of 2.3 % Pd and 17.9 % Au for A1, 8.6 % Pd and 8.2 % Au for A2, and 13.2 % Pd and 5.5 % Au for A3, respectively.

The elemental mapping of **1**-Au/Pd-PT NTs is displayed in Fig. S3.

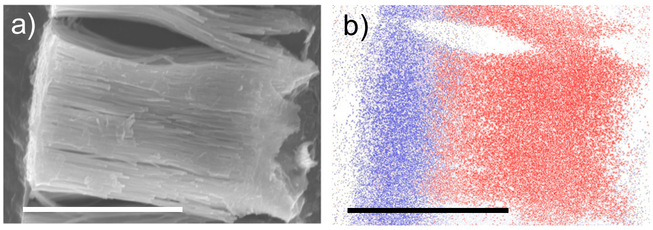


Fig. S3 **1**-Au/Pd-PT NTs: (a) SEM image [scale bar =20 μm]. (b) Elemental mapping of the Au (shown blue) and Pd (shown red).

5) SEM and TEM images, and EDX spectra of hybrid nanotubes.

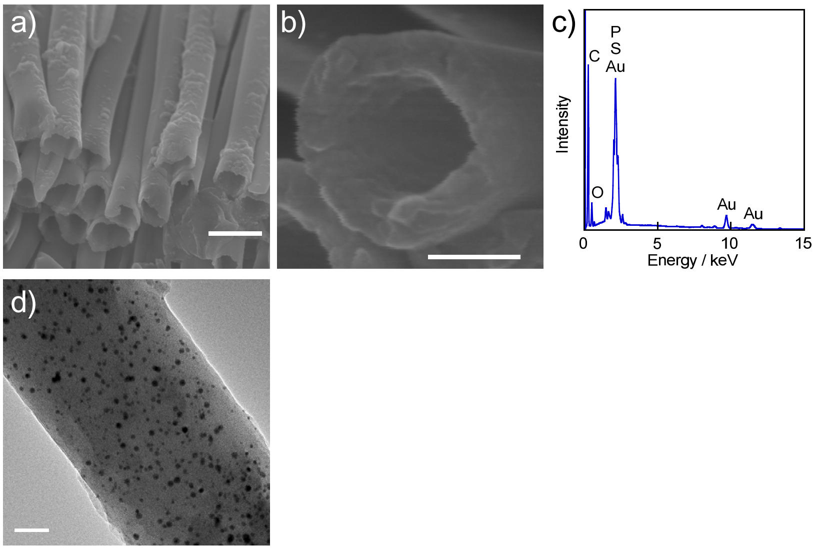


Fig. S4 **1**-Au-PT NTs: (a, b) SEM image [scale bar: (a) 500 nm; (b) 100 nm]. (c) EDX spectrum. (d) TEM image [scale bar = 50 nm].

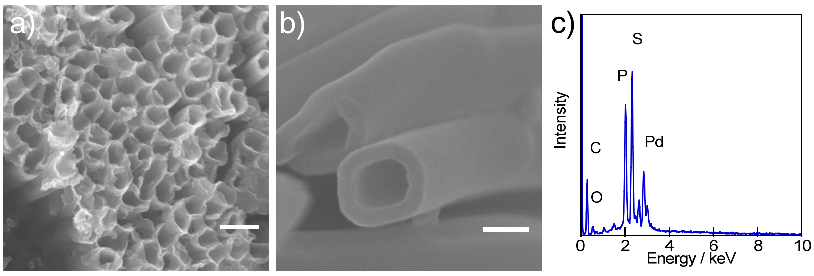
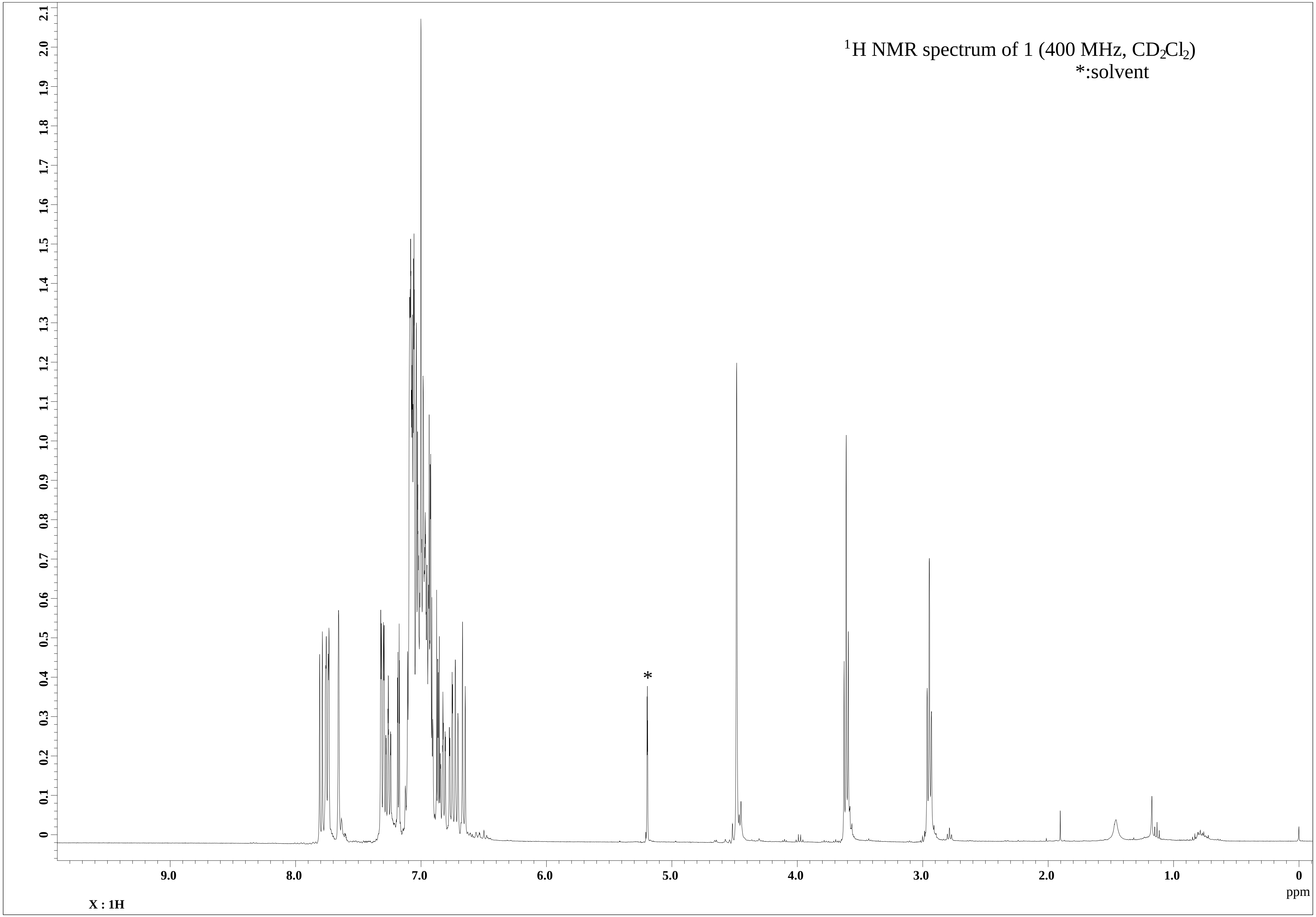
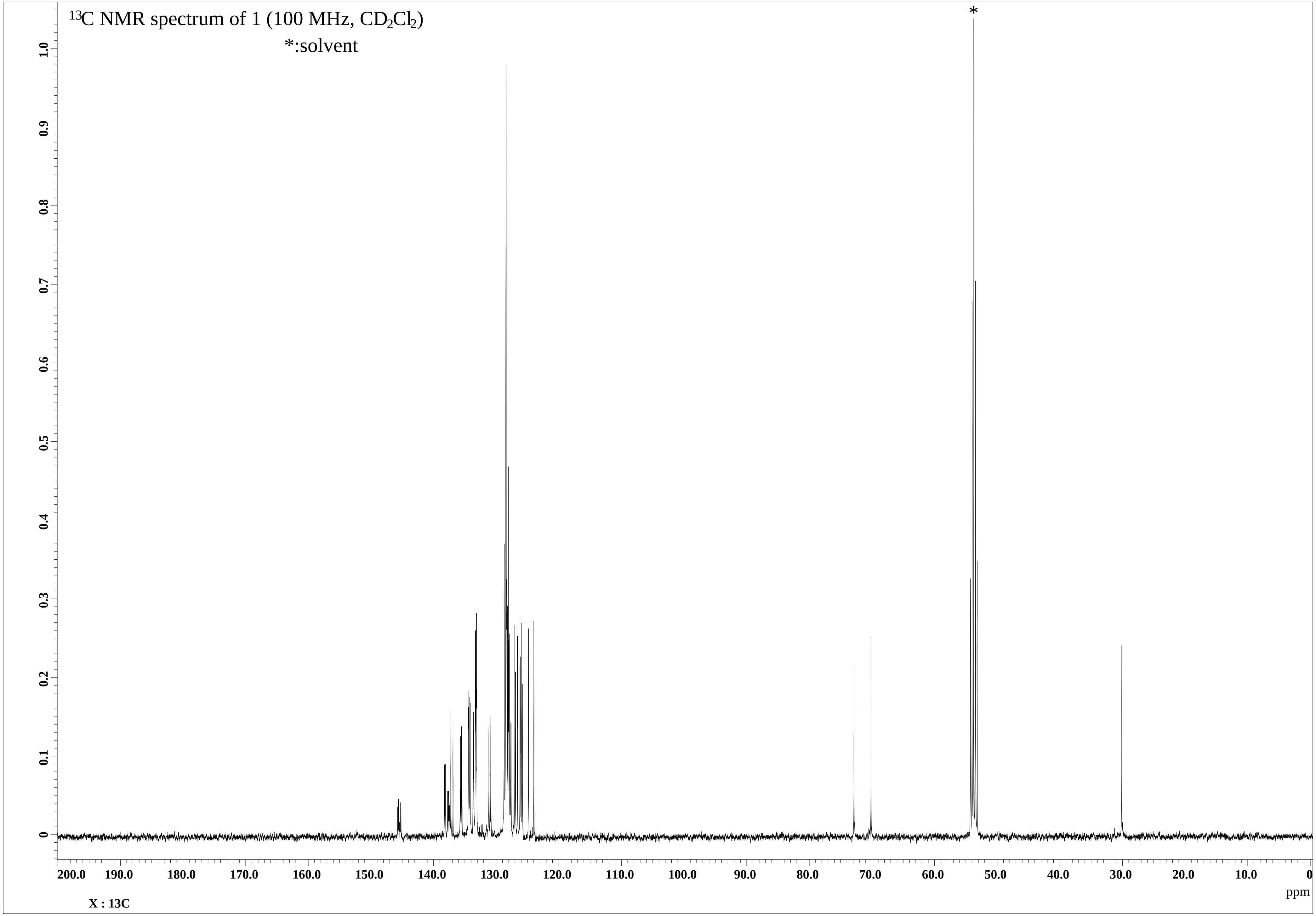
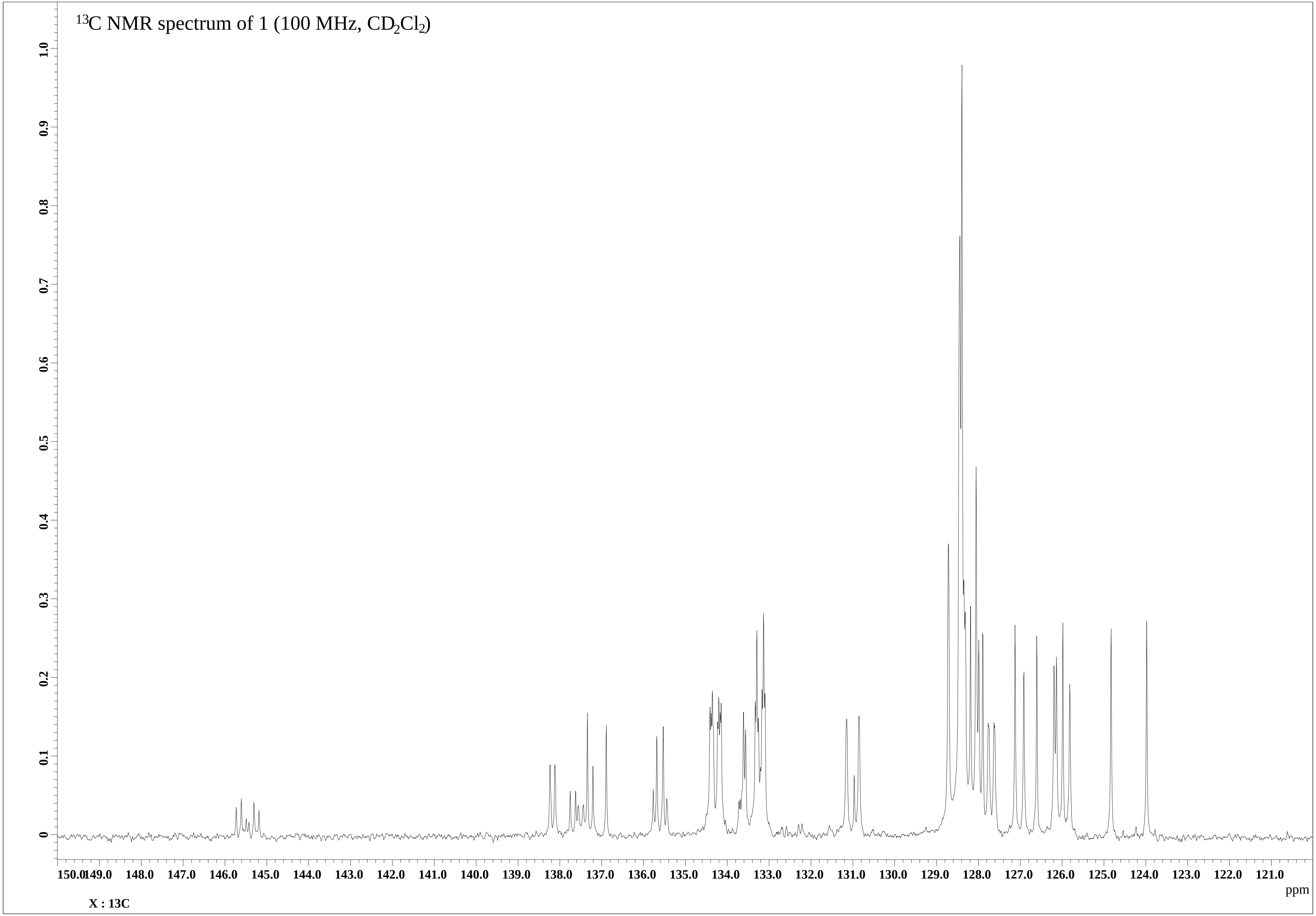


Fig. S5 **1**-Pd-PT NTs: (a, b) SEM image [scale bar: (a) 500 nm; (b) 200 nm]. (c) EDX spectrum.



^{1}H NMR spectrum of 1 (400 MHz, CD_2Cl_2)
*:solvent


^{13}C NMR spectrum of 1 (100 MHz, CD_2Cl_2)
*:solvent
*
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
ppm
X : 13C


^{13}C NMR spectrum of 1 (100 MHz, CD_2Cl_2)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
150.0
149.0
148.0
147.0
146.0
145.0
144.0
143.0
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X : 13C