Supplementary Information (SI) for Organic & Biomolecular Chemistry.

Supporting Information

Coordination Complexes of P^{III}-Doped Heterobuckybowls and Their Applications in Catalysis

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Contents

1. Materials and General methods

All chemicals and solvents were purified according to the standard procedure.[S1] The heterasumanenes (**1**-**3**) were synthesized according to our previous report.[S2]

The melting points were determined on a WRS-2 melting point apparatus. The high resolution mass spectral analysis (HRMS) was carried out on Bruker APEX II type mass spectrometer. Thermogravimetric analyses (TGA) were conducted on 1090B type thermal analyzer (Dupont Engineering Polymers).

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance III 400 MHz (101 MHz for ^{13}C NMR) or a VARIAN INOVA 600 MHz (151 MHz for ^{13}C NMR) spectrometer. Chemical shifts for ^{1}H NMR spectra are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane, and referenced internally to the residual proton in the solvent ($CDCl_3$: δ 7.26). Chemical shifts for ^{13}C NMR spectra are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane, and are referenced to the ^{13}C resonance of the NMR solvent ($CDCl_3$: δ 77.00). Data are reported as follows: Chemical shift, multiplicity (*s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *m* = multiplet), coupling constants, *J*, are reported in hertz.

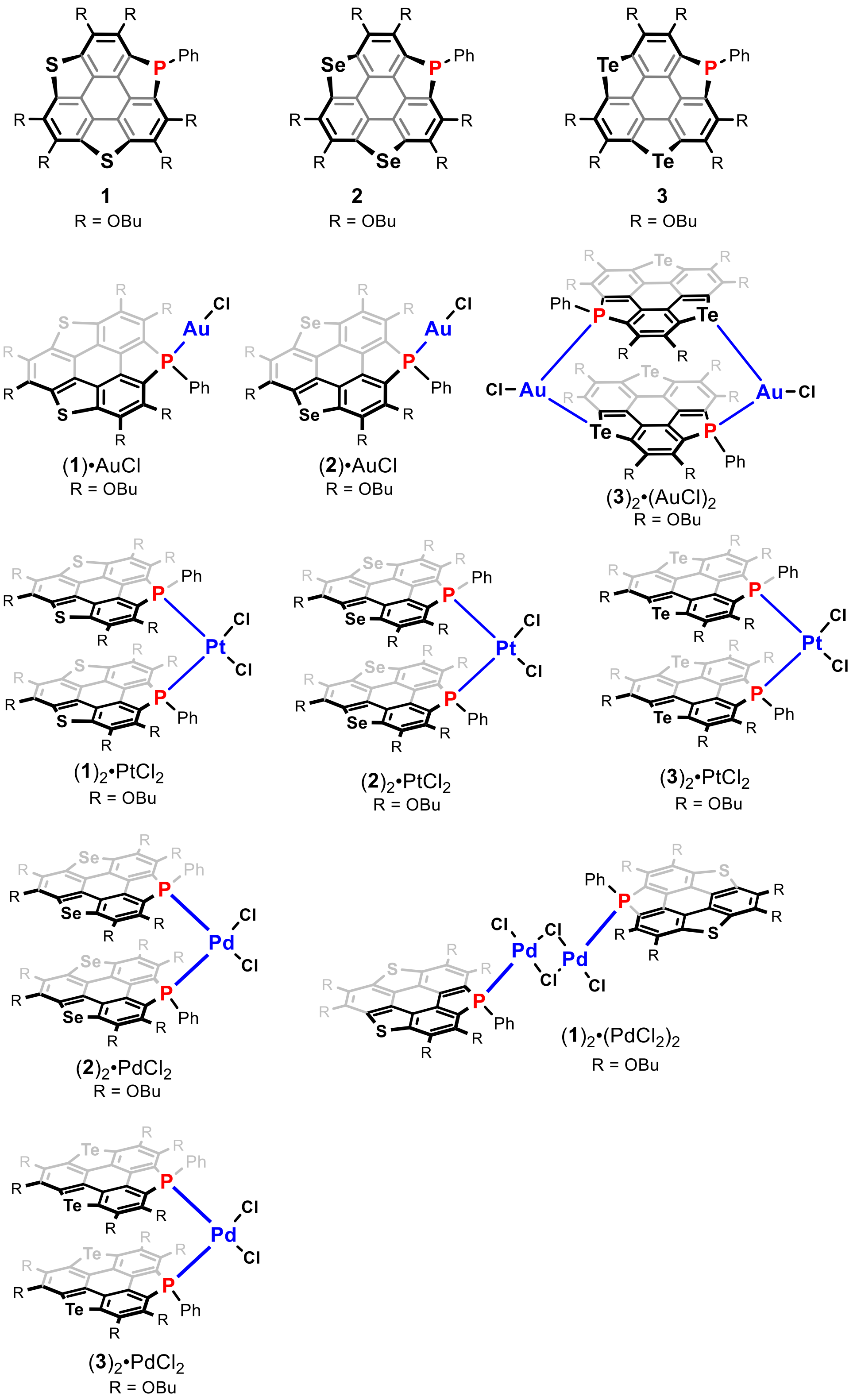
The redox potentials were obtained by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) methods on a RST 5000 electrochemical analyzer with glassy carbon discs as the working electrode, Pt wire as the counter electrode, and SCE electrode as the reference electrode. Measurement conditions: solvent, CH_2Cl_2; concentration, $c = 1 \times 10^{-4}$ mol L^{-1}; supporting electrolyte, $(n\text{-Bu})_4NPF_6$ (0.1 M); scan speed, 50 mV S^{-1}; temperature, 20 ºC.

The UV-Vis absorption spectra were measured on a UV-2006 UV-Specterophotometer. Measurement conditions: solvent, CH_2Cl_2; concentration, $c = 1.0 \times 10^{-5}$ mol L^{-1}; temperature, 20 ºC. The infrared (IR) spectra were record on the PerkinElmer Spectrum 400 spectrometer with the resolution of 2 cm^{-1}.

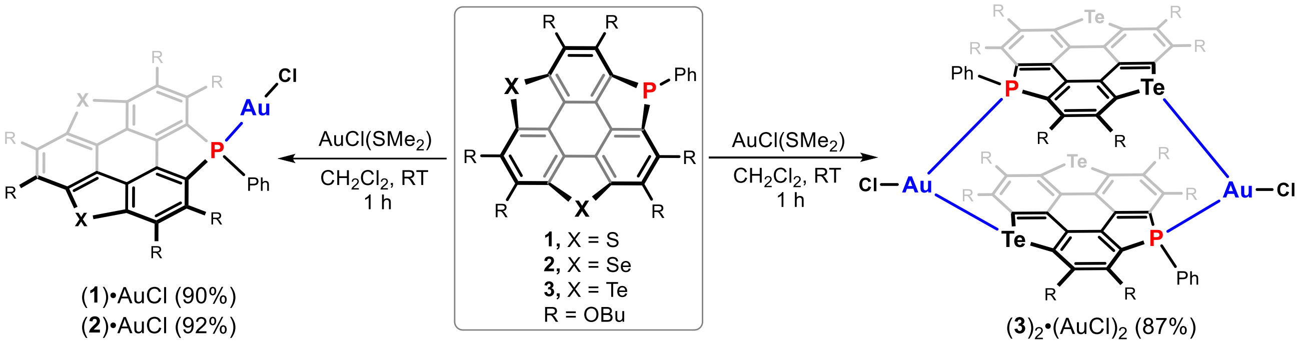
The single-crystal X-ray diffraction was carried out on a SuperNova (Agilent) diffractometer. The crystal structure was solved by a direct method *SIR*2004[S3] and refined by full-matrix least-square method on F^2 by means of *SHELX*L-97.[S4] The calculated positions of the hydrogen atoms were included in the final refinement.

2. Synthesis

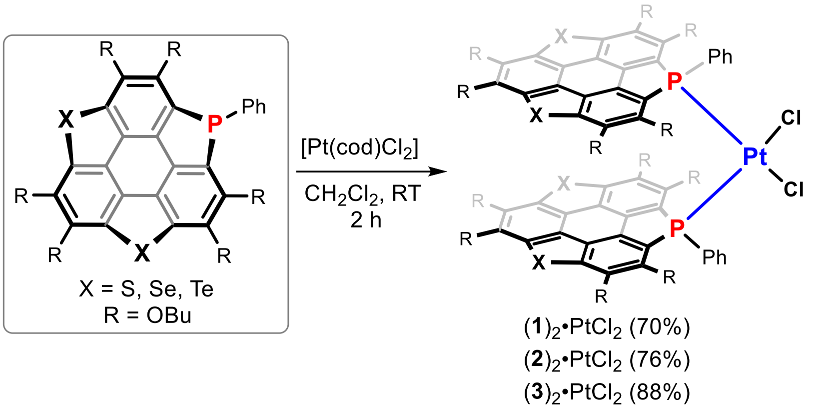
The compounds **1**-**3** were synthesized according to our previous report, and in the following, the syntheses of compounds (**1**)•AuCl, (**2**)•AuCl, (**3**)$_2$•(AuCl)$_2$, (**1**)$_2$•(PdCl$_2$)$_2$, (**2**)$_2$•PdCl$_2$, (**3**)$_2$•PdCl$_2$, (**1**)$_2$•PtCl$_2$, (**2**)$_2$•PtCl$_2$, and (**3**)$_2$•PtCl$_2$ are reported. Among them, R represents OBu.



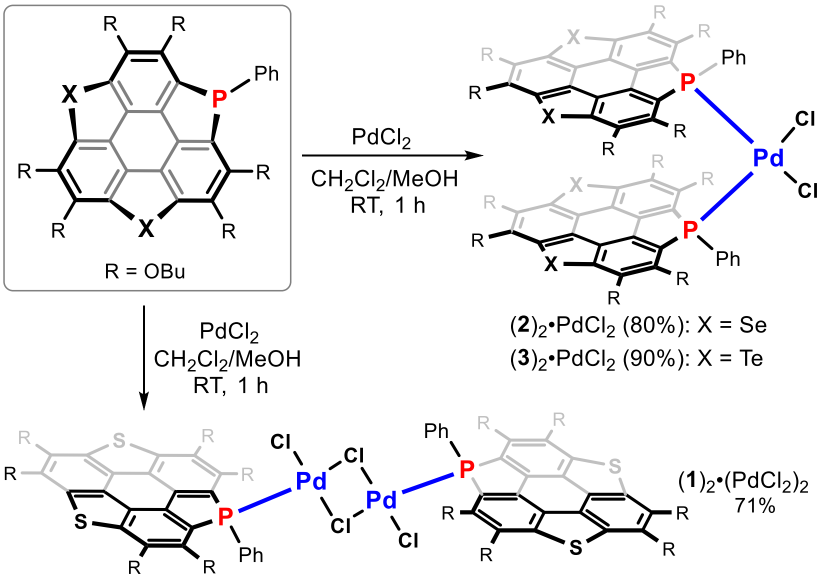
Scheme S1 The chemical structures of the compounds in this report.



Scheme S2 Synthesis of the coordination complexes of **1–3** with Au$^+$.



Scheme S3 Synthesis of the coordination complexes of **1–3** with Pt^{2+}.



Scheme S4 Synthesis of the coordination complexes of **1–3** with Pd^{2+}.

Synthesis of (1)•AuCl: To a Schlenk tube containing **1** (0.41g, 0.5 mmol) and AuCl(SMe$_2$) (0.15 g, 0.5 mmol) was added 10 mL of CH$_2$Cl$_2$. After stirring for 1.0 h at room temperature, the resulting mixture was evaporated and subjected to silica gel column chromatography (eluent, CH$_2$Cl$_2$/petro ether, 1 : 3, v:v) to give (**1**)•AuCl as a yellow solid (0.48 g, yield 90%). mp: 167.3-168.5 ºC; ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.82-7.77 (m, 2H), 7.54-7.49 (m, 1H), 7.42 (td, *J* = 7.8, 2.8 Hz, 2H), 4.46-4.33

(m, 10H), 4.20-4.15 (m, 2H), 1.94-1.82 (m, 8H), 1.72 (ddd, *J* = 7.9, 6.5, 2.8 Hz, 4H), 1.67-1.56 (m, 8H), 1.46-1.36 (m, 4H), 1.03 (dt, *J* = 15.0, 7.4 Hz, 12H), 0.90 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 152.98, 152.93, 147.36, 147.30, 147.06, 135.60, 133.76, 133.65, 132.72, 132.70, 131.84, 131.76, 129.46, 129.37, 128.62, 128.59, 128.56, 128.20, 128.09, 127.31, 120.65, 120.21, 77.25, 77.04, 76.83, 74.65, 74.64, 73.19, 72.94, 32.26, 32.24, 32.19, 19.27, 19.23, 19.09, 13.92, 13.89, 13.87; ^{31}P NMR (243 MHz, $CDCl_3$): δ 41.32. HRMS (ESI) Calcd. for $C_{48}H_{59}AuO_6PS_2$ $[M-Cl]^+$: 1023.3151, Found: 1023.3154. Elemental analysis calcd for $C_{48}H_{59}AuClO_6PS_2$: C, 54.41; H, 5.61; O, 9.06; found: C, 54.37; H, 5.58; O, 9.09.

Synthesis of (**2**)•AuCl: (**2**)•AuCl was synthesized similarly as described for synthesis of (**1**)•AuCl. For (**2**)•AuCl, yellow solid (0.53g, yield 92%). mp: 173.5-174.2 ºC; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.70 (dd, *J* = 14.8, 7.7 Hz, 2H), 7.51-7.46 (m, 1H), 7.37 (td, *J* = 7.8, 2.6 Hz, 2H), 4.65-4.27 (m, 10H), 4.27-4.15 (m, 2H), 1.93-1.83 (m, 8H), 1.75-1.69 (m, 4H), 1.68-1.56 (m, 8H), 1.51-1.36 (m, 4H), 1.10-0.99 (m, 12H), 0.92 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 152.46, 152.42, 149.93, 149.87, 148.58, 133.72, 133.62, 132.59, 131.63, 130.13, 130.05, 129.35, 129.26, 129.09, 128.70, 128.11, 128.05, 127.90, 124.80, 119.09, 118.65, 77.25, 77.04, 76.83, 74.19, 74.17, 72.51, 72.48, 32.31, 32.28, 19.37, 19.14, 13.99, 13.91; ^{31}P NMR (243 MHz, $CDCl_3$): δ 42.92. HRMS (ESI) Calcd. for $C_{48}H_{59}AuO_6PSe_2$ $[M-Cl]^+$: 1119.2040, Found: 1119.2096. Elemental analysis calcd for $C_{48}H_{59}AuClO_6PSe_2$: C, 49.99; H, 5.16; O, 8.32; found: C, 49.95; H, 5.12; O, 8,35.

Synthesis of $(\mathbf{3})_2$•$(AuCl)_2$: Compound $(\mathbf{3})_2$•$(AuCl)_2$ was synthesized similarly as described for synthesis of (**1**)•AuCl. For $(\mathbf{3})_2$•$(AuCl)_2$, yellow solid (0.54g, yield 87%). mp: 180.6-181.5 ºC; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.74-7.67 (m, 2H), 7.51-7.46 (m, 1H), 7.37 (td, *J* = 7.8, 2.8 Hz, 2H), 4.33-4.20 (m, 12H), 1.90-1.79 (m, 8H), 1.74-1.67 (m, 4H), 1.65-1.54 (m, 8H), 1.49-1.35 (m, 4H), 1.07-1.00 (m, 12H), 0.91 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.04, 153.98, 152.53, 152.48, 135.52, 133.80, 133.69, 133.24, 133.18, 132.57, 132.49, 129.36, 129.27, 128.96, 128.56, 123.19, 123.17, 120.06, 119.61, 117.79, 77.24, 77.03, 76.82, 74.09, 74.08, 73.02, 72.77, 32.59, 32.50, 32.39, 19.52, 19.46, 19.16, 14.00, 13.98, 13.92; ^{31}P NMR (243 MHz, $CDCl_3$): δ 36.72. HRMS (ESI) Calcd. for $C_{48}H_{59}AuClO_6PTe_2Na$ $[M+Na]^+$: 1275.1402, Found: 1275.1415. Elemental analysis calcd for $C_{48}H_{59}AuClO_6PTe_2$: C, 46.10; H, 4.76; O, 7.68; found: C, 46.18; H, 4.73; O, 7.54.

Synthesis of $(\mathbf{1})_2$•$PtCl_2$: To a Schlenk tube containing **1** (0.41 g, 0.5 mmol) and $PtCl_2$(Cod) (93.5 mg, 0.25 mmol) was added 10 mL of CH_2Cl_2, and the resulting mixture was stirred for 2 h at room temperature. The solution was evaporated and subjected to silica gel column chromatography (eluent, CH_2Cl_2/MeOH, 50 : 1, v:v) to give $(\mathbf{1})_2$•$PtCl_2$ as a yellow solid (0.34 g, yield 70%). mp: 205.5-206.0 ºC; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.63-7.58 (m, 4H), 7.18 (t, *J* = 7.4 Hz, 2H), 7.09 (t, *J* = 8.2, 2.2 Hz, 4H), 4.49 (d, *J* = 7.6 Hz, 4H), 4.40-4.22 (m, 20H), 1.97-1.85 (m, 24H), 1.71-1.50 (m, 24H), 1.12-1.06 (m, 24H), 1.03 (t, *J* = 7.4 Hz, 12H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 152.18, 146.93, 146.22, 132.89, 132.86, 132.82, 131.79, 130.59, 128.40, 128.37, 128.33, 128.30, 127.93, 127.91, 127.21, 127.17, 127.13, 125.42, 124.69, 124.66, 124.63, 124.04, 117.44, 116.99, 77.21, 77.00, 76.79, 73.73, 72.56, 71.69, 32.16, 32.07, 19.24, 19.22, 14.07, 13.88, 13.85; ^{31}P NMR (243 MHz, $CDCl_3$): δ 31.61. HRMS (ESI) Calcd. for $C_{96}H_{118}ClO_{12}P_2PtS_4$ $[M-Cl]^+$: 1883.6346, Found: 1883.6345. Elemental analysis calcd for $C_{96}H_{118}Cl_2O_{12}P_2PtS_4$: C, 60.05; H, 6.19; O, 10.00; found: C, 60.12; H, 6.14; O, 10.06.

Synthesis of $(\mathbf{2})_2$•$PtCl_2$: Compound $(\mathbf{2})_2$•$PtCl_2$ was synthesized similarly as described for synthesis of

(**1**)$_2$•PtCl$_2$. For (**2**)$_2$•PtCl$_2$, yellow solid (0.40g, yield 76%). mp: 214.5-215.6 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.58 (dd, *J* = 13.2, 7.7 Hz, 4H), 7.17 (t, *J* = 7.3 Hz, 2H), 7.11-7.03 (m, 4H), 5.48-2.90 (m, 24H), 1.90 (ddtd, *J* = 15.1, 12.2, 6.4, 3.2 Hz, 24H), 1.71-1.48 (m, 24H), 1.08 (td, *J* = 7.4, 3.0 Hz, 24H), 1.01 (t, *J* = 7.4 Hz, 12H); ^{31}P NMR (243 MHz, CDCl$_3$): δ 27.11. ^{13}C NMR (151 MHz, CDCl3) δ 151.97, 151.95, 151.93, 149.23, 149.20, 149.17, 148.09, 132.94, 132.90, 132.87, 130.49, 129.58, 129.23, 128.95, 128.91, 127.35, 127.30, 127.26, 126.73, 126.20, 126.17, 126.15, 124.47, 117.45, 117.10, 77.21, 77.00, 76.79, 73.68, 72.40, 71.29, 32.31, 32.23, 32.05, 19.28, 19.21, 14.07, 13.92, 13.88. HRMS (ESI) Calcd. for $C_{96}H_{118}ClO_{12}P_2PtSe_4$ [M-Cl]$^+$: 2073.4132, Found: 2073.4167. Elemental analysis calcd for $C_{96}H_{118}Cl_2O_{12}P_2PtSe_4$: C, 54.70; H, 5.64; O, 9.11; found: C, 54.66; H, 5.59; O, 9.14.

Synthesis of (**3**)$_2$•PtCl$_2$: Compound (**3**)$_2$•PtCl$_2$ was synthesized similarly as described for synthesis of (**1**)$_2$•PtCl$_2$. For (**3**)$_2$•PtCl$_2$, yellow solid (0.51g, yield 88%). mp: 219.9-221.7 °C; ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.58-7.52 (m, 4H), 7.15 (t, *J* = 7.4 Hz, 2H), 7.06-7.02 (m, 4H), 4.53-4.47 (m, 4H), 4.29-4.18 (m, 16H), 4.13-4.06 (m, 4H), 1.96-1.90 (m, 8H), 1.88-1.80 (m, 16H), 1.63-1.57 (m, 16H), 1.57-1.46 (m, 8H), 1.07 (q, *J* = 7.3 Hz, 24H), 0.99 (t, *J* = 7.4 Hz, 12H); ^{13}C NMR (151 MHz, CDCl$_3$): δ 153.08, 153.05, 153.02, 151.81, 151.78, 151.76, 134.45, 133.09, 133.06, 133.02, 131.58, 131.54, 131.51, 130.57, 128.79, 128.76, 128.33, 128.30, 127.19, 127.15, 127.11, 119.96, 118.08, 117.63, 73.54, 72.96, 71.26, 32.79, 32.57, 32.18, 19.56, 19.51, 19.28, 14.19, 14.13, 14.06; ^{31}P NMR (243 MHz, CDCl$_3$): δ 19.80. HRMS (ESI) Calcd. for $C_{96}H_{118}ClO_{12}P_2PtTe_4$ [M-Cl]$^+$: 2269.3665, Found: 2269.3660. Elemental analysis calcd for $C_{96}H_{118}Cl_2O_{12}P_2PtTe_4$: C, 50.08; H, 5.17; O, 8.34; found: C, 50.05; H, 5.13; O, 8.29.

Synthesis of (**1**)$_2$•(PdCl$_2$)$_2$: To a suspension of PdCl$_2$ (44.3 mg, 0.25 mmol) in MeOH (4.0 mL) was added a CH$_2$Cl$_2$ (8.0 mL) solution of **1** (0.41 g, 0.5 mmol). After stirring for 14 h at room temperature, the resulting mixture was evaporated and followed by recrystallization from CH$_2$Cl$_2$/MeOH gave (**1**)$_2$•(PdCl$_2$)$_2$ as brown solid (0.36 g, 71%). mp: 229.0-229.7 °C; ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.86 (dd, *J* = 14.2, 7.8 Hz, 4H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.28-6.98 (m, 4H), 5.00-4.80 (m, 8H), 4.55-4.47 (m, 4H), 4.47-4.33 (m, 12H), 2.19 (p, *J* = 6.9 Hz, 8H), 1.96-1.89 (m, 8H), 1.90-1.84 (m, 8H), 1.80-1.71 (m, 8H), 1.68-1.57 (m, 16H), 1.07 (q, *J* = 7.2 Hz, 24H), 1.02 (t, *J* = 7.4 Hz, 12H); ^{13}C NMR (151 MHz, CDCl$_3$): δ 152.19, 152.17, 148.46, 148.42, 148.39, 147.09, 134.43, 132.68, 132.63, 132.59, 131.75, 130.11, 130.04, 128.54, 128.50, 128.45, 127.89, 127.86, 127.83, 127.65, 126.63, 125.93, 125.55, 119.58, 119.14, 75.02, 73.08, 72.64, 32.70, 32.19, 19.57, 19.29, 19.24, 14.20, 13.92, 13.89; ^{31}P NMR (243 MHz, CDCl$_3$): δ 50.94. HRMS (ESI) Calcd. for $C_{96}H_{118}Cl_3O_{12}P_2Pd_2S_4$ [M-Cl]$^+$: 1972.41488, Found: 1972.41519. Elemental analysis calcd for $C_{96}H_{118}Cl_4O_{12}P_2Pd_2S_4$: C, 57.40; H, 5.92; O, 9.56; found: C, 57.47; H, 5.86; O, 9.58.

Synthesis of (**2**)$_2$•PdCl$_2$: Compound (**2**)$_2$•PdCl$_2$ was synthesized similarly as described for synthesis of (**1**)$_2$•(PdCl$_2$)$_2$. For (**2**)$_2$•PdCl$_2$, brown solid (0.40g, yield 80%). m.p. 225.4-226.0 °C; ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.56 (dd, *J* = 12.8, 8.0 Hz, 4H), 7.20-7.14 (m, 2H), 7.07 (td, *J* = 8.0, 2.6 Hz, 4H), 4.55-4.49 (m, 4H), 4.41-4.35 (m, 4H), 4.30 (t, *J* = 6.4 Hz, 8H), 4.27-4.20 (m, 8H), 2.01-1.86 (m, 24H), 1.69-1.50 (m, 24H), 1.12-1.06 (m, 24H), 1.02 (t, *J* = 7.4 Hz, 12H); ^{13}C NMR (151 MHz, CDCl$_3$): δ 153.19, 153.16, 153.13, 151.83, 151.73, 151.71, 151.68, 134.37, 133.20, 133.16, 133.12, 131.74, 131.72, 131.67, 131.64, 131.62, 131.60, 130.53, 129.92, 129.54, 127.38, 127.34, 127.30, 120.40, 118.67, 118.32, 118.14, 73.64, 72.94, 71.45, 32.80, 32.59, 32.21, 19.57, 19.52, 19.29, 14.19, 14.13, 14.07; ^{31}P NMR (243 MHz, CDCl$_3$) δ 47.29. HRMS (ESI) Calcd. for $C_{96}H_{122}Cl_2O_{12}P_2PdSe_4N$

$[M+NH_4]^+$: 2037.3551, Found: 2037.3690. Elemental analysis calcd for $C_{96}H_{118}Cl_2O_{12}P_2PdSe_4$: C, 57.11; H, 5.89; O, 9.51; found: C, 57.16; H, 5.94; O, 9.47.

Synthesis of (**3**)$_2$•$PdCl_2$: Compound (**3**)$_2$•$PdCl_2$ was synthesized similarly as described for synthesis of (**1**)$_2$•$(PdCl_2)_2$. For (**3**)$_2$•$PdCl_2$, brown solid (0.50g, yield 90%) mp: 192.4-193.2 °C; ^1H NMR (600 MHz, $CDCl_3$): δ 7.55-7.49 (m, 4H), 7.18-7.13 (m, 2H), 7.07-6.99 (m, 4H), 4.55-4.49 (m, 4H), 4.29-4.17 (m, 16H), 4.12 (dt, J = 8.7, 6.6 Hz, 4H), 1.95 (p, J = 7.3 Hz, 8H), 1.84 (tdd, J = 15.7, 7.9, 4.7 Hz, 16H), 1.64-1.45 (m, 24H), 1.07 (q, J = 7.2 Hz, 24H), 0.99 (t, J = 7.4 Hz, 12H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 153.19, 153.16, 153.13, 151.83, 151.73, 151.71, 151.68, 134.37, 133.20, 133.16, 133.12, 131.74, 131.72, 131.67, 131.64, 131.62, 131.60, 130.53, 129.92, 129.54, 127.38, 127.34, 127.30, 120.40, 118.67, 118.32, 118.14, 73.64, 72.94, 71.45, 32.80, 32.59, 32.21, 19.57, 19.52, 19.29, 14.19, 14.13, 14.07; ^{31}P NMR (243 MHz, $CDCl_3$): δ 39.47. HRMS (ESI) Calcd. for $C_{96}H_{122}ClO_{12}P_2PdTe_4N$ $[M+NH_4]^+$: 2233.3084, Found: 2233.3230. Elemental analysis calcd for $C_{96}H_{118}Cl_2O_{12}P_2PdTe_4$: C, 52.09; H, 5.37; O, 8.67; found: C, 52.03; H, 5.35; O, 8.63.

3. Scope of the Pd-Catalyzed SMC reactions employing 7 as ligand.

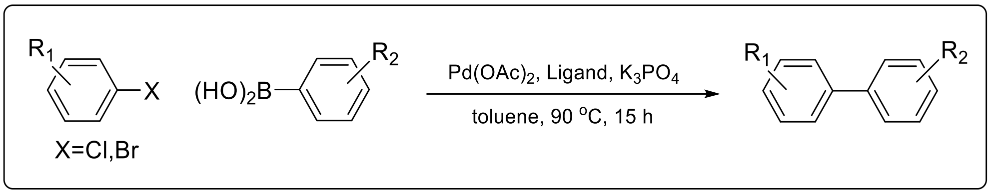


Table S1. Scope of Pd-Catalyzed Suzuki-Miyaura Cross-Coupling

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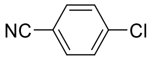
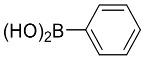
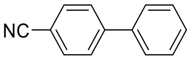
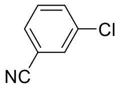
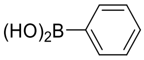
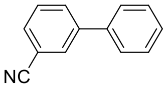
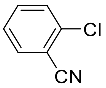
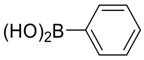
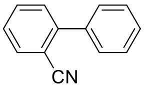
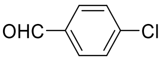
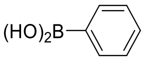
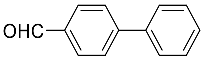
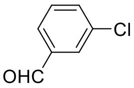
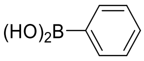
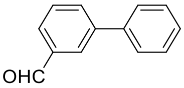
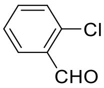
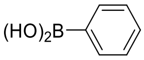
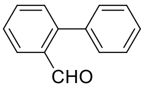
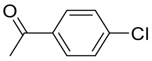
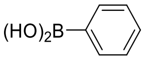
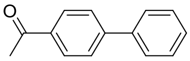
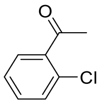
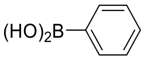
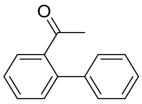
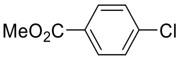
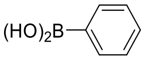
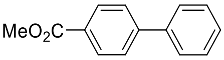
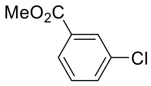
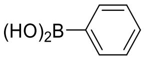
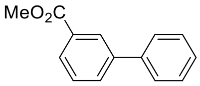
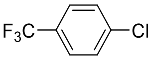
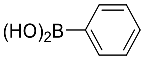
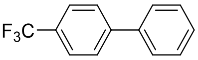
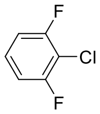
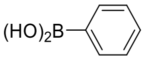
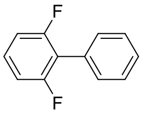
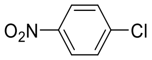
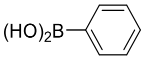
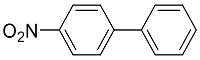
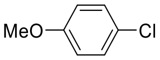
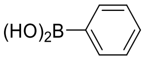
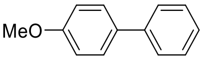
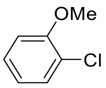
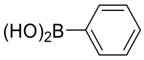
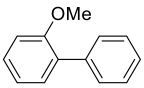
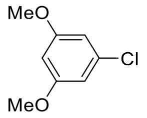
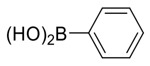
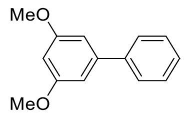
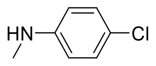
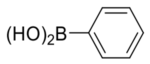
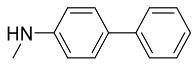
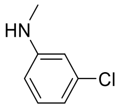
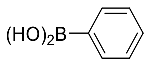
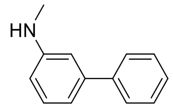
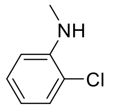
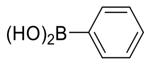
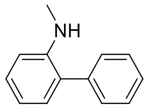
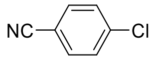
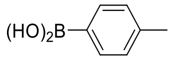
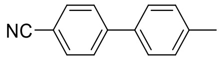
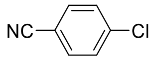
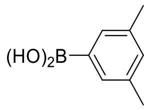
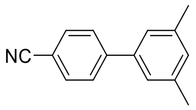
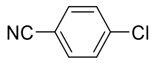
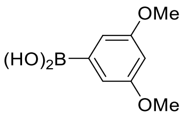
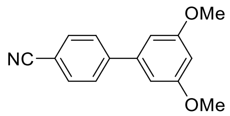
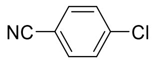
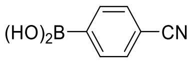
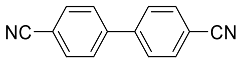
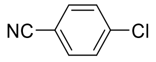
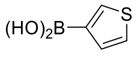
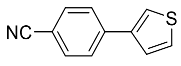
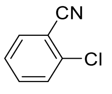
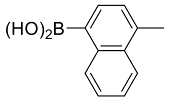
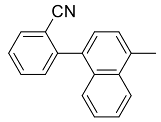
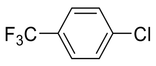
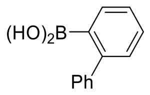
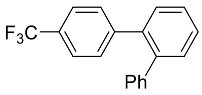
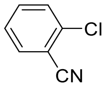
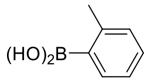
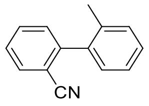
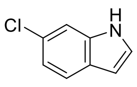
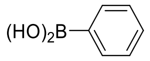
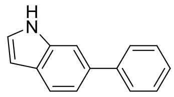
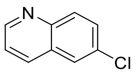
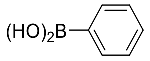
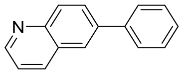
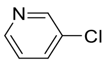
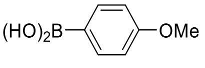
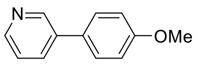
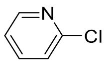
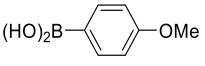
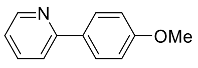
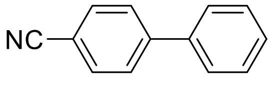
1				0.1	95
2				0.1	93
3				0.1	90
4				0.1	81
5				0.1	78
6				0.1	70
7				0.1	77
8				0.1	71
9				0.1	82
10				0.1	76
11				0.1	90
12				0.1	60
13				0.1	92
14				1	65
15				1	47

16				1	64
17				1	53
18				1	56
19				1	50
20				0.1	94
21				0.1	93
22				0.1	92
23				0.1	85
24				0.1	91
25				0.1	83
26				0.1	50
27				0.1	81
28				1	53
29				0.1	85
30				0.1	84
31				0.1	82

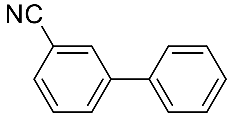
Conditions: aryl chloride (1.0 equiv), boronic acid (1.5 equiv), cat. $Pd(OAc)_2$, ligand **1**, L/Pd=2:1, K_3PO_4 (3 equiv), toluene (0.25 M), 90 °C, 15 h.

General Procedure: Pd-Catalyzed Suzuki-Miyaura Couplings of Aryl Halides with Aryl Boronic Acids.

An oven-dried Schlenk tube containing a magnetic stir bar was charged with $Pd(OAc)_2$ (2.2 mg, 1.0 mol%), **1** (16.5 mg, 2.0 mol%), aryl boronic acid (1.5 mmol, 1.5 equiv.), anhydrous K_3PO_4 (636 mg, 3.0 mmol, 3.0 equiv.).The Schlenk tube was capped with a rubber septum and then evacuated and backfilled with argon (this sequence was repeated three times). Toluene (4.0 mL) was added via syringe through the septum and the resulting mixture was stirred at room temperature for ~2 min. The aryl halide (1.0 mmol, 1.0 equiv.) was added dropwise via syringe through the septum (aryl halides which were solids at room temperature were added during the initial charge, prior to the evacuation/backfill cycles). The reaction mixture was heated at 90 °C with vigorous stirring until the aryl halide had been completely consumed as judged by thin-layer chromatography. The reaction mixture was then allowed to cool to room temperature, diluted with diethyl ether (10 mL), filtered through a thin pad of silica gel (eluting with diethyl ether) and concentrated under reduced pressure. The crude material obtained was purified by flash chromatography on silica gel.

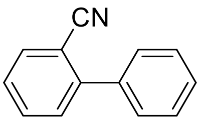


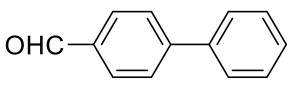
[1,1'-biphenyl]-4-carbonitrile (Table S1, entry 1). White solid; 170.3 mg, 95% yield; m.p. 85.1-86.7 ºC; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.59 (dd, *J* = 7.4, 1.8 Hz, 2H), 7.49 (dd, *J* = 8.4, 6.8 Hz, 2H), 7.46–7.40 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.62, 139.13, 132.54, 129.07, 128.62, 127.68, 127.18, 118.89, 110.87.



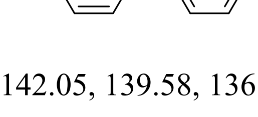
[1,1'-biphenyl]-3-carbonitrile (Table S1, entry 2). White solid; 166.7 mg, 93% yield; m.p. 44.2-44.7 ºC; ^{1}H NMR (600 MHz, C $CDCl_3$) δ 7.84 (s, 1H), 7.81 (dt, *J* = 8.0, 1.6 Hz, 1H), 7.62 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.57–7.54 (m, 3H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.44–7.41 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.27, 138.69, 131.33, 130.54, 130.52, 129.48, 129.00, 128.27, 126.93, 118.72, 112.81.

[1,1'-biphenyl]-2-carbonitrile (Table S1, entry 3). White solid; 161.3 mg, 90% yield; m.p. 35.3-36.1 ºC; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.8 Hz, 1H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.57 (d, *J* = 7.2 Hz, 2H), 7.54–7.48 (m, 3H), 7.47–7.43 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.49, 138.12, 133.73, 132.79, 130.06, 128.73, 128.70, 127.51, 118.69, 111.27.

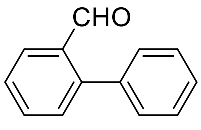




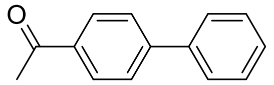
[1,1'-biphenyl]-4-carbaldehyde (Table S1, entry 4). White solid; 147.6 mg, 81% yield; m.p. 57.4-58.9 ºC; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.06 (s, 1H), 7.98–7.94 (m, 2H), 7.78–7.74 (m, 2H), 7.67–7.62 (m, 2H), 7.52–7.46 (m, 2H), 7.44–7.41 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.93, 147.20, 139.72, 135.21, 130.27, 129.02, 128.48, 127.68, 127.36.



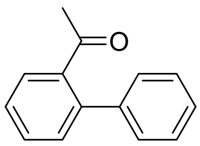
[1,1'-biphenyl]-3-carbaldehyde (Table S1, entry 5). White solid; 142.1 mg, 78% yield; m.p. 167.7-168.6 ºC; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.09 (s, 1H), 8.12–8.10 (m, 1H), 7.86 (dq, *J* = 7.8, 1.5 Hz, 2H), 7.66–7.59 (m, 3H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.44–7.38 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 192.29, 142.05, 139.58, 136.83, 132.96, 129.41, 128.93, 128.55, 128.09, 127.97, 127.05.



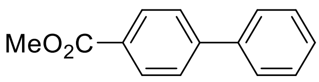
[1,1'-biphenyl]-2-carbaldehyde (Table S1, entry 6). White solid; 127.5 mg, 70% yield; m.p. 202.7-203.8 ºC; ^{1}H NMR (600 MHz, C CDCl$_3$) δ 10.00 (s, 1H), 8.05 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.62 (td, *J* = 7.5, 1.5 Hz, 1H), 7.51 – 7.40 (m, 5H), 7.39–7.35 (m, 2H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 192.11, 145.73, 137.54, 133.51, 133.35, 130.58, 129.90, 128.23, 127.92, 127.57, 127.36.



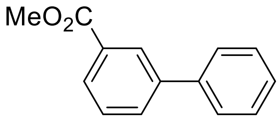
1-([1,1'-biphenyl]-4-yl)ethan-1-one (Table S1, entry 7). White solid; 151.1 mg, 77% yield; m.p. 152.7-153.7 ºC; ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.02–7.98 (m, 2H), 7.67–7.62 (m, 2H), 7.62–7.57 (m, 2H), 7.44 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.40–7.35 (m, 1H), 2.60 (s, 3H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 197.57, 145.60, 139.70, 135.73, 135.72, 128.84, 128.79, 128.12, 127.13, 127.06, 26.49.



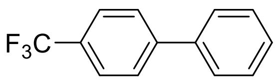
1-([1,1'-biphenyl]-2-yl)ethan-1-one (Table S1, entry 8). White solid; 139.4 mg, 71% yield; m.p. 56.1-57.7 ºC; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.55–7.52 (m, 1H), 7.46 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.41–7.34 (m, 5H), 7.33–7.31 (m, 2H), 1.98 (s, 3H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 204.51, 140.70, 140.53, 140.30, 130.52, 130.05, 128.64, 128.48, 127.69, 127.25, 30.20.



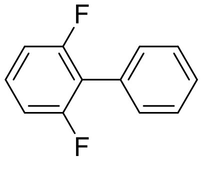
Methyl [1,1'-biphenyl]-4-carboxylate (Table S1, entry 9). White solid; 174.0 mg, 82% yield; m.p. 118.1-119.5 ºC; ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.12 (d, *J* = 7.9 Hz, 2H), 7.67 (d, *J* = 7.9 Hz, 2H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 3.95 (s, 3H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 166.96, 145.59, 139.95, 130.06, 128.88, 128.85, 128.10, 127.23, 127.00, 52.07.



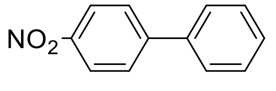
Methyl [1,1'-biphenyl]-3-carboxylate (Table S1, entry 10). White solid; 161.3 mg, 76% yield; m.p.160.5-160.9 ºC; ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.27 (t, *J* = 1.8 Hz, 1H), 7.99 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.71 (ddd, *J* = 7.7, 2.0, 1.2 Hz, 1H), 7.59–7.55 (m, 2H), 7.46–7.37 (m, 3H), 7.35–7.29 (m, 1H), 3.89 (s, 3H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 166.79, 141.24, 139.87, 131.30, 130.52, 128.71, 128.67, 128.16, 128.04, 127.56, 126.94, 51.93.



4-(trifluoromethyl)-1,1'-biphenyl (Table S1, entry 11). White solid; 200.0 mg, 90% yield; m.p. 70.7-71.5 ºC; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.70 (s, 4H), 7.62–7.59 (m, 2H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.44–7.39 (m, 1H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 144.74, 139.77, 128.98, 128.18, 127.42, 127.28, 125.74, 125.72, 125.69.

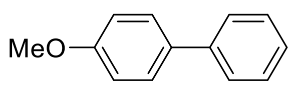


2,6-difluoro-1,1'-biphenyl (Table S1, entry 12). White solid; 114.1 mg, 60% yield; m.p. 97.2-98.7 ºC; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.47–7.41 (m, 4H), 7.39–7.34 (m, 1H), 7.25–7.17 (m, 1H), 6.98–6.90 (m, 2H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 160.95, 159.30, 130.30, 129.15, 128.81, 128.23, 118.49, 111.67.

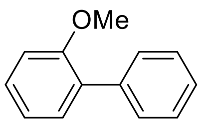


4-nitro-1,1'-biphenyl (Table S1, entry 13). White solid; 183.3 mg, 92% yield; m.p. 114.1-114.9 ºC; ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.30 (d, *J* = 8.5 Hz, 2H), 7.74 (d, *J* = 8.6 Hz, 2H), 7.63 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.45 (t, *J* = 7.3

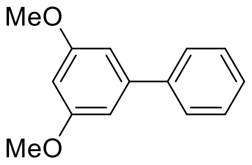
Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.64, 147.10, 138.79, 129.16, 128.91, 127.80, 127.39, 124.11.



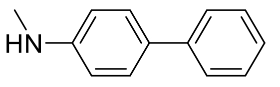
4-methoxy-1,1'-biphenyl (Table S1, entry 14). White solid; 120.0 mg, 65% yield; m.p. 86.0-87.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58–7.51 (m, 4H), 7.42 (t, J = 7.7 Hz, 2H), 7.31 (t, J = 7.4 Hz, 1H), 7.01–6.96 (m, 2H), 3.86 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.15, 140.83, 133.78, 128.80, 128.15, 126.74, 126.65, 114.19, 55.34.



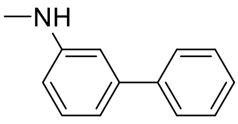
2-methoxy-1,1'-biphenyl (Table S1, entry 15). White solid; 86.6 mg, 47% yield; m.p. 50.1-51.3 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60–7.56 (m, 2H), 7.49–7.42 (m, 2H), 7.40–7.35 (m, 3H), 7.11–7.01 (m, 2H), 3.85 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.44, 138.52, 130.86, 130.69, 129.51, 128.58, 127.95, 126.88, 120.80, 111.20, 55.49.



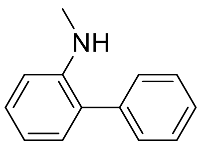
3,5-dimethoxy-1,1'-biphenyl (Table S1, entry 16). White solid; 137.1 mg, 64% yield; m.p. 64.1.7-65.3 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (dd, J = 8.0, 1.4 Hz, 2H), 7.41 (t, J = 7.7 Hz, 2H), 7.36–7.30 (m, 1H), 6.73 (d, J = 2.2 Hz, 2H), 6.46 (t, J = 2.3 Hz, 1H), 3.82 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.02, 143.44, 141.16, 128.66, 127.50, 127.14, 105.41, 99.23, 55.32.



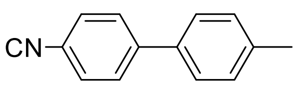
***N*-methyl-[1,1'-biphenyl]-4-amine (Table S1, entry 17).** White solid; 97.1 mg, 53% yield; m.p. 38.7-39.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55–7.52 (m, 2H), 7.47–7.44 (m, 2H), 7.38 (t, J = 7.7 Hz, 2H), 7.27–7.23 (m, 1H), 6.71–6.66 (m, 2H), 2.87 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.61, 141.28, 130.26, 128.62, 127.87, 126.29, 126.02, 112.73, 30.80.



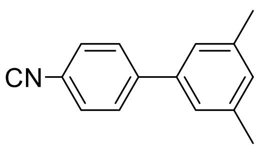
***N*-methyl-[1,1'-biphenyl]-3-amine (Table S1, entry 18).** White solid; 102.6 mg, 56% yield; m.p. 55.8-56.9 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58–7.53 (m, 2H), 7.38 (t, J = 7.7 Hz, 2H), 7.31–7.27 (m, 1H), 7.21 (d, J = 7.8 Hz, 1H), 6.92 (dt, J = 7.7, 1.3 Hz, 1H), 6.76 (t, J = 2.1 Hz, 1H), 6.54 (dd, J = 8.2, 2.5 Hz, 1H), 2.78 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.56, 142.22, 141.72, 129.47, 128.52, 127.08, 127.04, 116.28, 111.37, 111.09, 30.64.



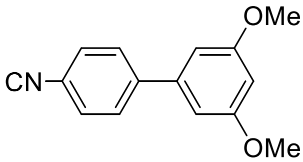
***N*-methyl-[1,1'-biphenyl]-2-amine (Table S1, entry 19).** White solid; 91.6 mg, 50% yield; m.p. 61.4-62.5 °C; ^{1}H NMR (600 MHz, C $CDCl_3$) δ 7.38 (d, J = 4.4 Hz, 4H), 7.29 (p, J = 4.3 Hz, 1H), 7.23 (ddd, J = 8.6, 7.5, 1.7 Hz, 1H), 7.06 (dd, J = 7.4, 1.7 Hz, 1H), 6.74 (td, J = 7.4, 1.2 Hz, 1H), 6.65 (d, J = 8.1 Hz, 1H), 2.72 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.06, 139.44, 129.93, 129.32, 128.76, 128.69, 127.47, 127.08, 116.71, 109.69, 30.62.



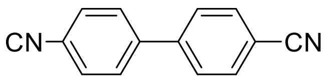
4'-methyl-[1,1'-biphenyl]-4-carbonitrile (Table S1, entry 20). White solid; 181.6 mg, 94% yield; m.p. 108.5-109.7 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70–7.64 (m, 4H), 7.50 (d, J = 7.7 Hz, 2H), 7.30 (d, J = 7.7 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.40, 138.61, 136.06, 132.39, 129.71, 127.28, 126.89, 118.89, 110.36, 21.02.



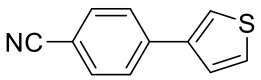
3',5'-dimethyl-[1,1'-biphenyl]-4-carbonitrile (Table S1, entry 21). White solid; 192.8 mg, 93% yield; m.p. 58.3-59.7 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73–7.64 (m, 4H), 7.20 (s, 2H), 7.07 (s, 1H), 2.39 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.96, 139.18, 138.71, 132.46, 130.26, 127.72, 125.11, 119.03, 110.65, 21.34.



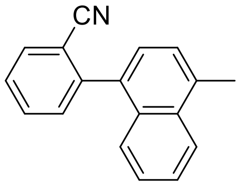
3',5'-dimethoxy-[1,1'-biphenyl]-4-carbonitrile (Table S1, entry 22). White solid; 220.1 mg, 92% yield; m.p. 65.2-66.7 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 8.3, 1.5 Hz, 2H), 7.65 (dd, *J* = 8.4 Hz, 2H), 6.70 (d, *J* = 2.2 Hz, 2H), 6.52 (t, *J* = 2.3 Hz, 1H), 3.85 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.26, 145.56, 141.25, 132.45, 127.74, 118.82, 111.08, 105.52, 100.26, 55.42.



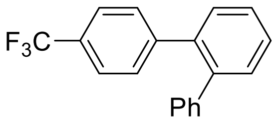
[1,1'-biphenyl]-4,4'-dicarbonitrile (Table S1, entry 23). White solid; 173.6 mg, 85% yield; m.p. 232.1-232.8 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 4H), 7.69 (d, *J* = 8.3 Hz, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.51, 132.87, 127.93, 118.38, 112.44.



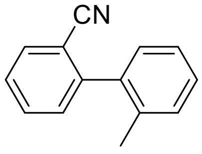
4-(thiophen-3-yl)benzonitrile (Table S1, entry 24). White solid; 168.5 mg, 91% yield; m.p. 125.7-126.7 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (s, 4H), 7.58 (s, 1H), 7.46–7.43 (m, 1H), 7.40 (d, *J* = 5.0 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.37, 140.03, 132.70, 127.15, 126.84, 125.93, 122.60, 118.93, 110.51.



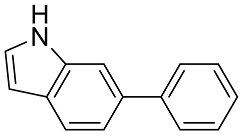
2-(4-methylnaphthalen-1-yl)benzonitrile (Table S1, entry 25). White solid; 201.9 mg, 83% yield; m.p. 125.7-126.7 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.5 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.55–7.50 (m, 2H), 7.46–7.38 (m, 3H), 7.38–7.31 (m, 2H), 2.70 (d, *J* = 2.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.53, 135.46, 134.14, 132.88, 132.67, 132.08, 131.51, 131.32, 127.62, 127.09, 126.05, 125.86, 125.82, 125.64, 124.50, 118.06, 113.48, 19.47.



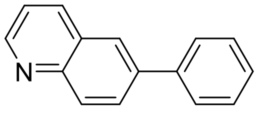
4-(trifluoromethyl)-1,1':2',1''-terphenyl (Table S1, entry 26). White solid; 149.1 mg, 50% yield; m.p. 125.7-126.7 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48–7.38 (m, 6H), 7.27–7.19 (m, 5H), 7.14–7.08 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.26, 140.90, 140.69, 139.09, 130.79, 130.46, 130.13, 129.84, 128.21, 128.09, 127.66, 126.79, 124.83, 124.81.



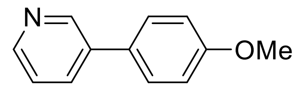
2'-methyl-[1,1'-biphenyl]-2-carbonitrile (Table S1, entry 27). White solid; 156.5 mg, 81% yield; m.p. 46.1-46.9 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.22–7.17 (m, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 2.07 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.63, 137.91, 135.49, 132.66, 132.31, 130.31, 130.25, 129.27, 128.57, 127.43, 125.70, 117.96, 112.65, 19.69.



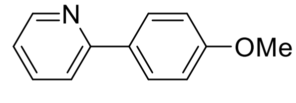
6-phenyl-1H-indole (Table S1, entry 28). White solid; 102.4 mg, 53% yield; m.p. 106.1-107.3 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.68–7.64 (m, 2H), 7.61 (dt, *J* = 1.7, 0.9 Hz, 1H), 7.45 (dd, *J* = 8.4, 7.1 Hz, 2H), 7.41 – 7.38 (m, 1H), 7.35–7.31 (m, 1H), 7.25 (t, *J* = 0.9 Hz, 1H), 6.59 (s, 1H).^{13}C NMR (151 MHz, $CDCl_3$) δ 142.31, 136.36, 135.61, 128.68, 127.38, 127.20, 126.58, 124.78, 120.89, 119.81, 109.52, 102.56.



6-phenylquinoline (Table S1, entry 29). White solid; 154.0 mg, 85% yield; m.p. 115.7-116.3 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.92 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.23–8.17 (m, 2H), 8.02–7.97 (m, 2H), 7.74–7.70 (m, 2H), 7.53–7.48 (m, 2H), 7.46–7.38 (m, 2H).



3-(4-methoxyphenyl)pyridine (Table S1, entry 30). White solid; 155.6 mg, 84% yield; m.p. 62.1-63.7 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.84–8.80 (m, 1H), 8.55 (dd, *J* = 4.7, 1.6 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.55–7.50 (m, 2H), 7.35 (dd, *J* = 7.8, 4.8 Hz, 1H), 7.04 – 6.99 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.32, 147.75, 147.61, 136.38, 134.06, 130.13, 128.22, 122.68, 115.20, 55.37.



2-(4-methoxyphenyl)pyridine (Table S1, entry 31). White solid; 151.9 mg, 82% yield; m.p. 55.2-56.4 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.67–8.65 (m, 1H), 7.98–7.94 (m, 2H), 7.72 (td, *J* = 7.7, 1.8 Hz, 1H), 7.68 (d, *J* = 7.9 Hz, 1H), 7.21–7.16 (m, 1H), 7.03–6.98 (m, 2H), 3.87 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.57, 157.00, 148.95, 136.90, 132.19, 128.22, 121.44, 119.91, 114.17, 56.25.

4. Thermogravimetric Analyses

Thermogravimetric analyses (TGA) were conducted on 1030B type thermal analyzer (Dupont Engineering Polymers).

Table S2. Thermal stability of compounds (**1**)•AuCl, (**2**)•AuCl and (**3**)$_2$•(AuCl)$_2$.

Comp	(**1**)•AuCl	(**2**)•AuCl	(**3**)$_2$•(AuCl)$_2$
T_d / °C	225	234	251

T_d : degradation temperature.

Table S3. Thermal stability of compounds (**1**)$_2$•PtCl$_2$, (**2**)$_2$•PtCl$_2$ and (**3**)$_2$•PtCl$_2$.

Comp	(**1**)$_2$•PtCl$_2$	(**2**)$_2$•PtCl$_2$	(**3**)$_2$•PtCl$_2$
T_d / °C	220	305	235

Table S4. Thermal stability of compounds (**1**)$_2$•(PdCl$_2$)$_2$, (**2**)$_2$•PdCl$_2$ and (**3**)$_2$•PdCl$_2$.

Comp	(**1**)$_2$•(PdCl$_2$)$_2$	(**2**)$_2$•PdCl$_2$	(**3**)$_2$•PdCl$_2$
T_d / °C	231	252	241

T_d : degradation temperature.

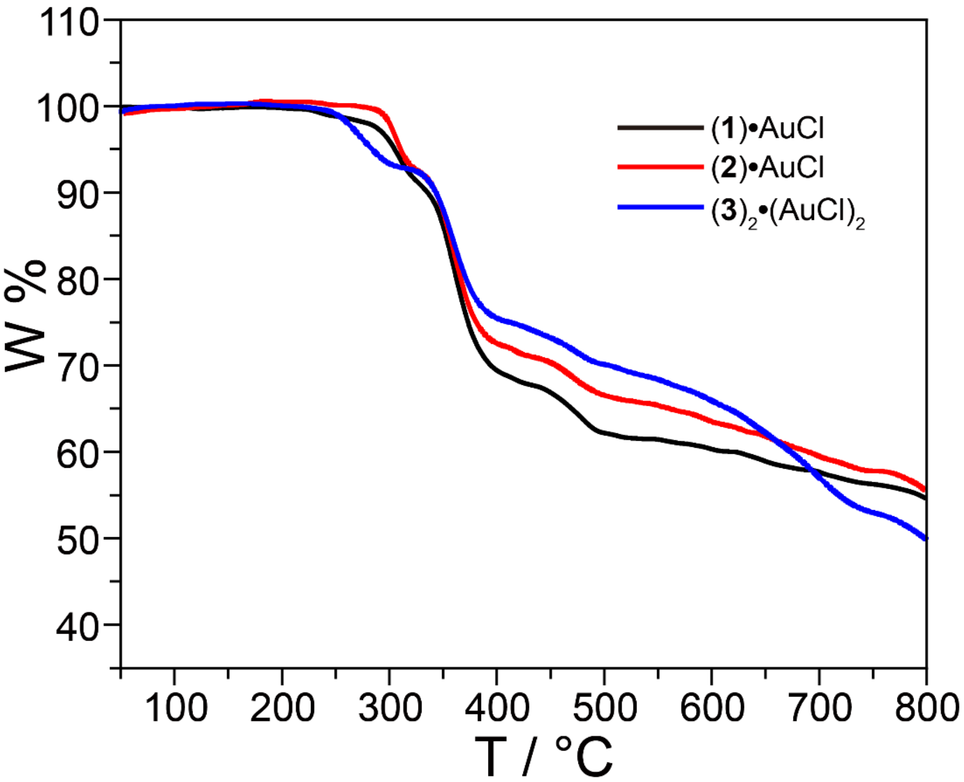


Fig. S1 Thermogravimetric analyses of compounds (**1**)•AuCl, (**2**)•AuCl and (**3**)$_2$•(AuCl)$_2$.

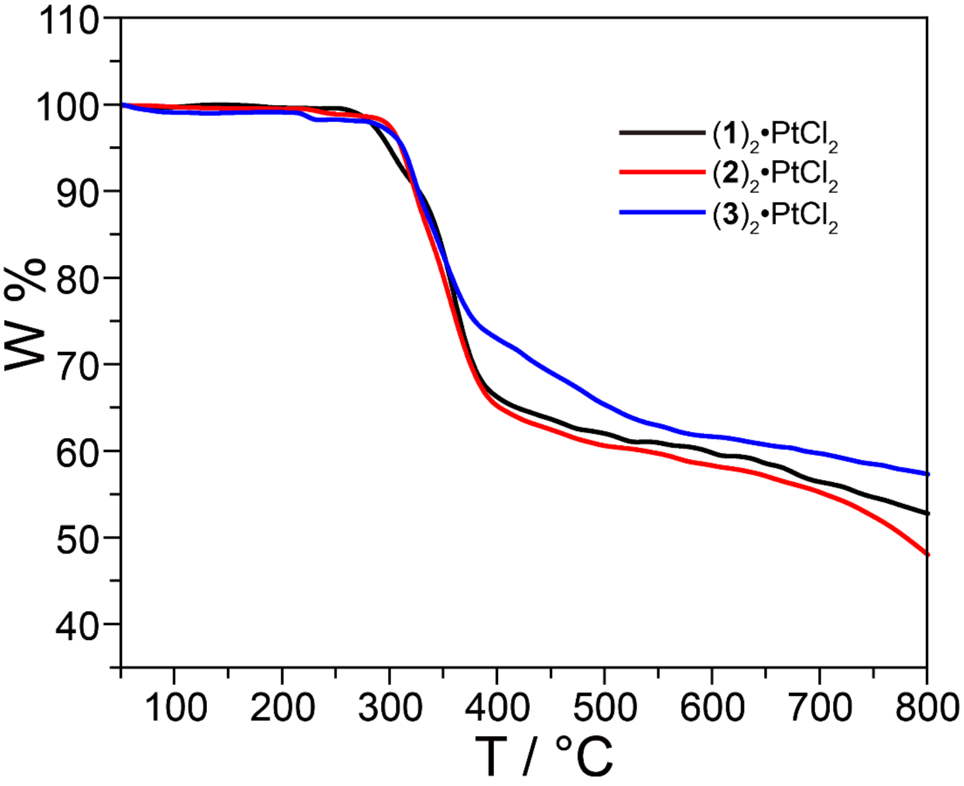


Fig. S2 Thermogravimetric analyses of compounds (**1**)$_2$•$PtCl_2$, (**2**)$_2$•$PtCl_2$ and (**3**)$_2$•$PtCl_2$.

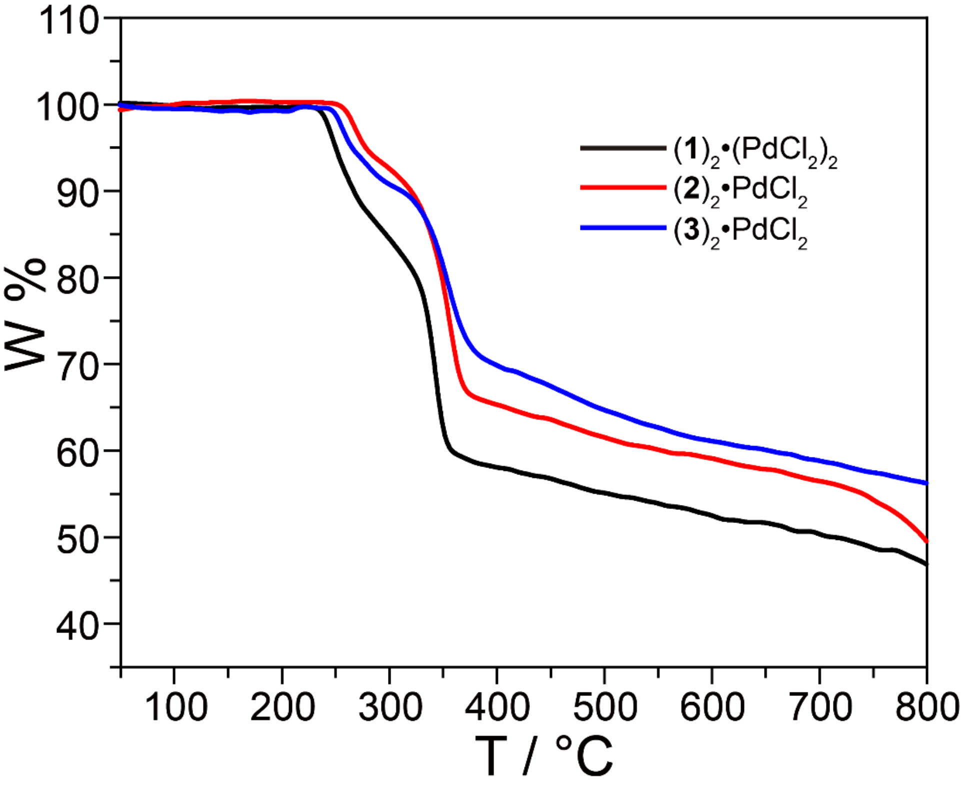


Fig. S3. Thermogravimetric analyses of compounds (**1**)$_2$•($PdCl_2$)$_2$, (**2**)$_2$•$PdCl_2$ and (**3**)$_2$•$PdCl_2$.

5. X-ray Crystal Structure Analyses

5.1 Experimental details on crystal growth

Single crystals of (**1**)•AuCl (yellow needle), (**2**)•AuCl (yellow needle) and (**3**)$_2$•(AuCl)$_2$ (yellow needle) obtained by slowly evaporating DCM-MeCN (1:2, v/v)solutions at room temperature, (**1**)$_2$•(PdCl$_2$)$_2$ (reddish brown needle) and (**2**)$_2$•PdCl$_2$ (reddish brown needle) obtained by slowly evaporating DCM-MeCN (1:1, v/v) solutions at room temperature, (**3**)$_2$•PdCl$_2$ (reddish brown needle) obtained by slowly evaporating DCM-Hexane (1:1, v/v) solutions at room temperature, (**1**)$_2$•PtCl$_2$ (yellow needle), (**2**)$_2$•PtCl$_2$ (yellow needle) and (**3**)$_2$•PtCl$_2$ (yellow needle) obtained by slowly evaporating DCM-MeCN (1:2, v/v) solutions at room temperature.

Table S5. Selected crystallographic data of (**1**)•AuCl**,** (**2**)•AuCl and (**3**)$_2$•(AuCl)$_2$.

Compounds	(**1**)•AuCl	(**2**)•AuCl	(**3**)$_2$•(AuCl)$_2$
CCDC number	2331327	2331332	2331333
Empirical formula	$C_{48}H_{59}AuClO_6PS_2$	$C_{48.5}H_{59.75}AuClN_{0.25}O_6PSe_2$	$C_{48}H_{59}AuClO_6PTe_2$
Formula weight	1059.45	1163.52	1249.02
Temperature [K]	149.99(10)	149.99(10)	149.99(11)
Crystal system	triclinic	monoclinic	monoclinic
Space group	*P*-1 (#2)	*P*2$_1$/*c* (#14)	*P*2$_1$/*c* (#14)
a [Å]	16.7310(3)	28.00533(19)	9.95628(4)
b [Å]	17.9089(4)	38.3306(3)	33.13649(19)
c [Å]	19.0611(3)	17.81397(12)	29.23546(13)
α [°]	106.6663(17)	90	90
β [°]	102.9809(16)	91.8893(6)	90.7583(4)
γ [°]	114.312(2)	90	90
V [Å^3]	4585.98(18)	19112.2(2)	9644.41(8)
Z	4	16	8
d_{calc} [g cm^{-3}]	1.534	1.617	1.72
μ [mm^{-1}]	8.124	8.73	16.274
Crystal size [mm^3]	0.17 × 0.08 × 0.04	0.13 × 0.11 × 0.05	0.05 × 0.02 × 0.01
λ [Å]	1.54184 (Cu-Kα)	1.54184 (Cu-Kα)	1.54184 (Cu-Kα)
$2\theta_{max}$ [°]	152.89	155.454	152.122
Data/restraints/parameters	18478/0/1094	38279/1632/2164	19062/1572/1230
GooF	1.063	1.04	1.057
R [$I > 2\sigma(I)$]	0.0397	0.0801	0.0434
wR_2	0.1031	0.2264	0.1102

Table S6. Selected crystallographic data of (**1**)$_2$•$PtCl_2$, (**2**)$_2$•$PtCl_2$ and (**3**)$_2$•$PtCl_2$.

Compounds	(**1**)$_2$•$PtCl_2$	(**2**)$_2$•$PtCl_2$	(**3**)$_2$•$PtCl_2$
CCDC number	2331336	2331339	2331340
Empirical formula	$C_{96.5}H_{119}Cl_2N_{0.5}O_{12.5}P_2PtS_4$	$C_{97}H_{119.5}Cl_2N_{0.5}O_{12}P_2PtSe_4$	$C_{96}H_{118}Cl_2O_{12}P_2PtTe_4$
Formula weight	1942.08	2128.19	2302.23
Temperature [K]	149.99(10)	149.96(13)	129.99(10)
Crystal system	triclinic	triclinic	triclinic
Space group	*P*-1 (#2)	*P*-1 (#2)	*P*-1 (#2)
a [Å]	17.4708(3)	17.1838(2)	16.26452(15)
b [Å]	22.2672(4)	22.6370(3)	16.53506(16)
c [Å]	24.0276(4)	24.0907(2)	19.14664(18)
α [°]	89.5107(13)	89.8577(9)	83.1891(8)
β [°]	79.0226(14)	78.6933(10)	65.4490(9)
γ [°]	86.6647(15)	86.8545(11)	88.1601(8)
V [Å^3]	9160.8(3)	9175.00(19)	4649.78(8)
Z	4	4	2
d_{calc} [g cm^{-3}]	1.408	1.541	1.644
μ [mm^{-1}]	5.072	6.024	13.85
Crystal size [mm^3]	0.15 × 0.07 × 0.05	0.05 × 0.01 × 0.01	0.14 × 0.11 × 0.09
λ [Å]	1.54184 (Cu-Kα)	1.54184 (Cu-Kα)	1.54184 (Cu-Kα)
$2\theta_{max}$ [°]	3.746 to 153.206	3.74 to 133.194	5.108 to 151.692
Data/restraints/parameters	36241/2026/2224	32357/73/2159	18064/30/1083
GooF	1.019	1.035	1.018
R [$I > 2\sigma(I)$]	0.0575	0.0636	0.0534
wR_2	0.1414	0.1810	0.1441

Table S7. Selected crystallographic data of (**1**)$_2$•$(PdCl_2)_2$, (**2**)$_2$•$PdCl_2$ and (**3**)$_2$•$PdCl_2$.

Compounds	(**1**)$_2$•$(PdCl_2)_2$	(**2**)$_2$•$PdCl_2$	(**3**)$_2$•$PdCl_2$
CCDC number	2331347	2331348	2331349
Empirical formula	$C_{98}H_{121}Cl_4NO_{12}P_2Pd_2S_4$	$C_{194}H_{239}Cl_4NO_{24}P_4Pd_2Se_8$	$C_{96}H_{118}Cl_2O_{12}P_2PdTe_4$
Formula weight	2049.73	4079.01	2213.54
Temperature [K]	149.99(10)	150.1(3)	150
Crystal system	triclinic	triclinic	triclinic
Space group	*P*-1 (#2)	*P*-1 (#2)	*P*-1 (#2)
a [Å]	16.9381(2)	17.3656(2)	15.0020(4)
b [Å]	20.3995(2)	22.3745(2)	17.4424(4)
c [Å]	29.6262(3)	24.2121(2)	17.9639(5)
α [°]	100.1680(10)	89.6800(10)	94.148(2)
β [°]	103.3670(10)	78.8790(10)	96.151(2)
γ [°]	95.8090(10)	86.7940(10)	90.060(2)
V [Å^3]	9694.55(19)	9216.30(16)	4661.1(2)
Z	4	2	2
d_{calc} [g cm^{-3}]	1.404	1.47	1.577
μ [mm^{-1}]	5.599	4.773	12.606
Crystal size [mm^3]	0.12 × 0.07 × 0.04	0.15 × 0.05 × 0.02	0.2 × 0.1 × 0.08
λ [Å]	1.54184 (Cu-Kα)	1.54184 (Cu-Kα)	1.54184 (Cu-Kα)

$2\theta_{max}$ [°]	4.45 to 155.006	3.72 to 155.258	4.96 to 152.276
Data/restraints/parameters	38957/170/2344	37106/30/2159	17836/36/1092
GooF	1.097	1.033	1.047
R [$I > 2\sigma(I)$]	0.0969	0.0703	0.0826
wR_2	0.2363	0.1922	0.2194

Table S8. Averaged C–X (X = S, Se, Te, P) and P–M (M = Au, Pd, Pt) bond lengths (Å) and bowl-depth (Å).

Compounds	**Molecular geometry parameters**				
		C–X and P–M Bond Lengths			**Bowl-depth**
(**1**)•AuCl	Mole. ***A***	C–S, 1.80	C–P, 1.86	Au–P, 2.22	0.27
	Mole. ***B***	C–S, 1.79	C–P, 1.86	Au–P, 2.22	0.56
(**2**)•AuCl	Mole. ***A***	C–Se, 1.94	C–P, 1.84	Au–P, 2.22	planar
	Mole. ***B***	C–Se, 1.94	C–P, 1.84	Au–P, 2.23	planar
	Mole. ***C***	C–Se, 1.93	C–P, 1.85	Au–P, 2.22	planar
	Mole. ***D***	C–Se, 1.94	C–P, 1.85	Au–P, 2.23	0.21
(**3**)$_2$•(AuCl)$_2$	Mole. ***A***	C–Te, 2.12	C–P, 1.83	Au–P, 2.23	0.17
	Mole. ***B***	C–Te, 2.12	C–P, 1.84	Pt–P, 2.23	planar
(**1**)$_2$•PtCl$_2$	Mole. ***A***	C–S, 1.80	C–P, 1.87	Pt–P, 2.25	0.32
	Mole. ***B***	C–S, 1.81	C–P, 1.87	Pt–P, 2.25	planar
	Mole. ***C***	C–S, 1.81	C–P, 1.87	Pt–P, 2.25	0.20
	Mole. ***D***	C–S, 1.80	C–P, 1.88	Pt–P, 2.24	planar
(**2**)$_2$•PtCl$_2$	Mole. ***A***	C–Se, 1.94	C–P, 1.87	Pt–P, 2.25	planar
	Mole. ***B***	C–Se, 1.94	C–P, 1.85	Pt–P, 2.25	0.15
	Mole. ***C***	C–Se, 1.95	C–P, 1.86	Pt–P, 2.24	planar
	Mole. ***D***	C–Se, 1.94	C–P, 1.86	Pt–P, 2.25	0.26
(**3**)$_2$•PtCl$_2$	Mole. ***A***	C–Te, 2.12	C–P, 1.85	Pt–P, 2.24	planar
	Mole. ***B***	C–Te, 2.12	C–P, 1.85	Pt–P, 2.24	0.10
(**1**)$_2$•(PdCl$_2$)$_2$	Mole. ***A***	C–S, 1.80	C–P, 1.85	Pd–P, 2.20	0.33
	Mole. ***B***	C–S, 1.80	C–P, 1.84	Pd–P, 2.20	0.39
(**1**)•(PdCl$_2$)•CH$_3$CN	Mole. ***C***	C–S, 1.80	C–P, 1.85	Pd–P, 2.22	0.50
	Mole. ***D***	C–S, 1.80	C–P, 1.84	Pd–P, 2.21	0.49
(**2**)$_2$•PdCl$_2$	Mole. ***A***	C–Se, 1.93	C–P, 1.86	Pd–P, 2.27	planar
	Mole. ***B***	C–Se, 1.94	C–P, 1.85	Pd–P, 2.28	0.18
	Mole. ***C***	C–Se, 1.94	C–P, 1.86	Pd–P, 2.27	planar
	Mole. ***D***	C–Se, 1.94	C–P, 1.87	Pd–P, 2.27	0.25
(**3**)$_2$•PdCl$_2$	Mole. ***A***	C–Te, 2.11	C–P, 1.86	Pd–P, 2.27	0.22
	Mole. ***B***	C–Te, 2.12	C–P, 1.85	Pd–P, 2.28	planar

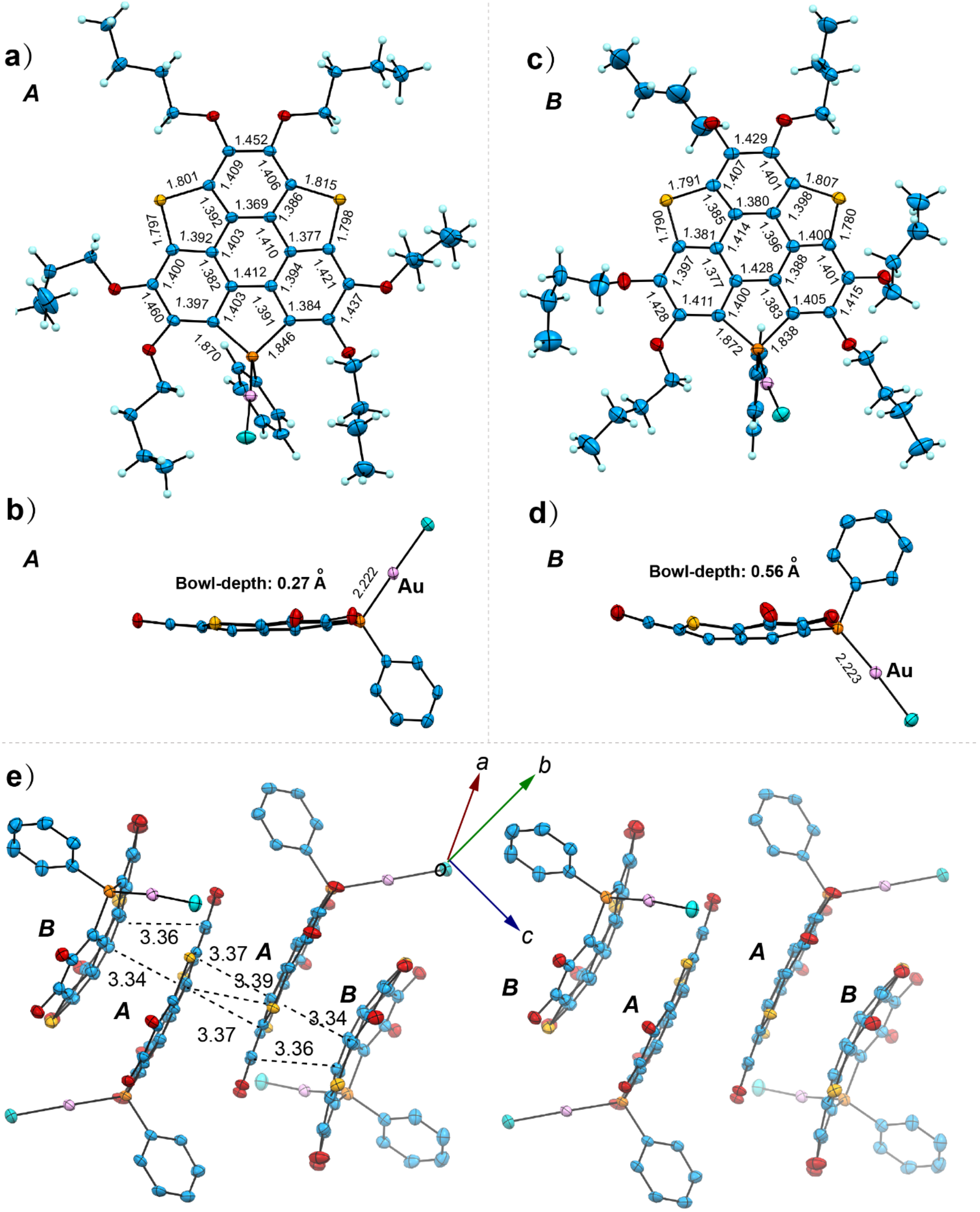


Fig. S4 Crystal structure of (**1**)•AuCl: a) top view and b) side view of coordination molecule ***A*** in (**1**)•AuCl. c) top view and d) side view of coordination molecule ***B*** in (**1**)•AuCl. e) packing motif with intermolecular contacts shown (Å). The C, H, O, S, P, Cl and Au atoms are respectively shown in blue, pale cyan, red, yellow, orange, cyan and pink. The selected bond lengths are in unit of Å. The n-Bu groups and H atoms are omitted for clarity in b), d) and e).

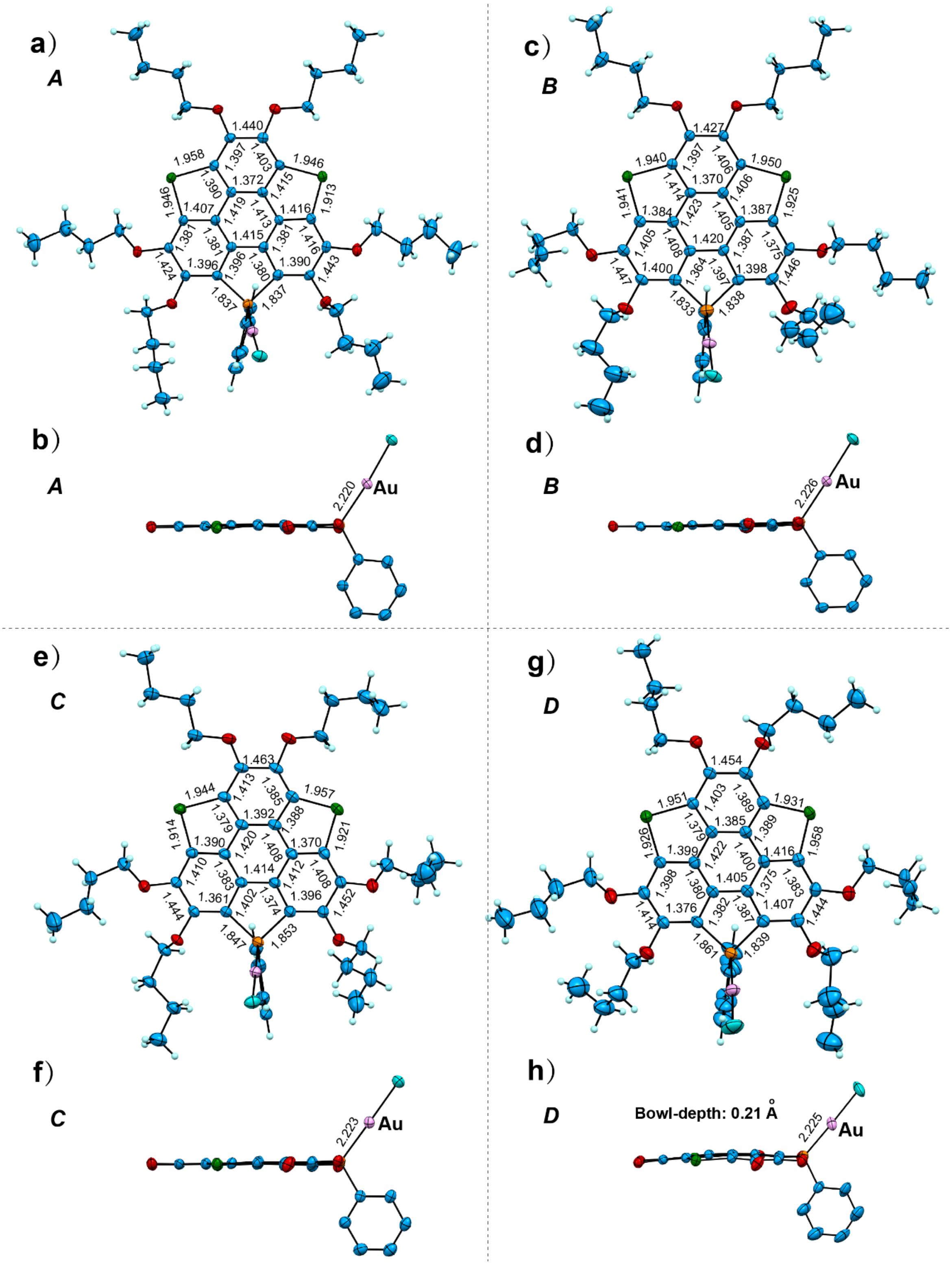


Fig. S5 Crystal structure of (**2**)•AuCl: a) top view and b) side view of coordination molecule ***A*** in (**2**)•AuCl. c) top view and d) side view of coordination molecule ***B*** in (**2**)•AuCl. e) top view and f) side view of coordination molecule ***C*** in (**2**)•AuCl. g) top view and h) side view of coordination molecule ***D*** in (**2**)•AuCl. The C, H, O, Se, P, Cl and Au atoms are respectively shown in blue, pale cyan, red, green, orange, cyan and pink. The selected bond lengths are in unit of Å. The n-Bu groups and H atoms are omitted for clarity in b), d), f) and h).

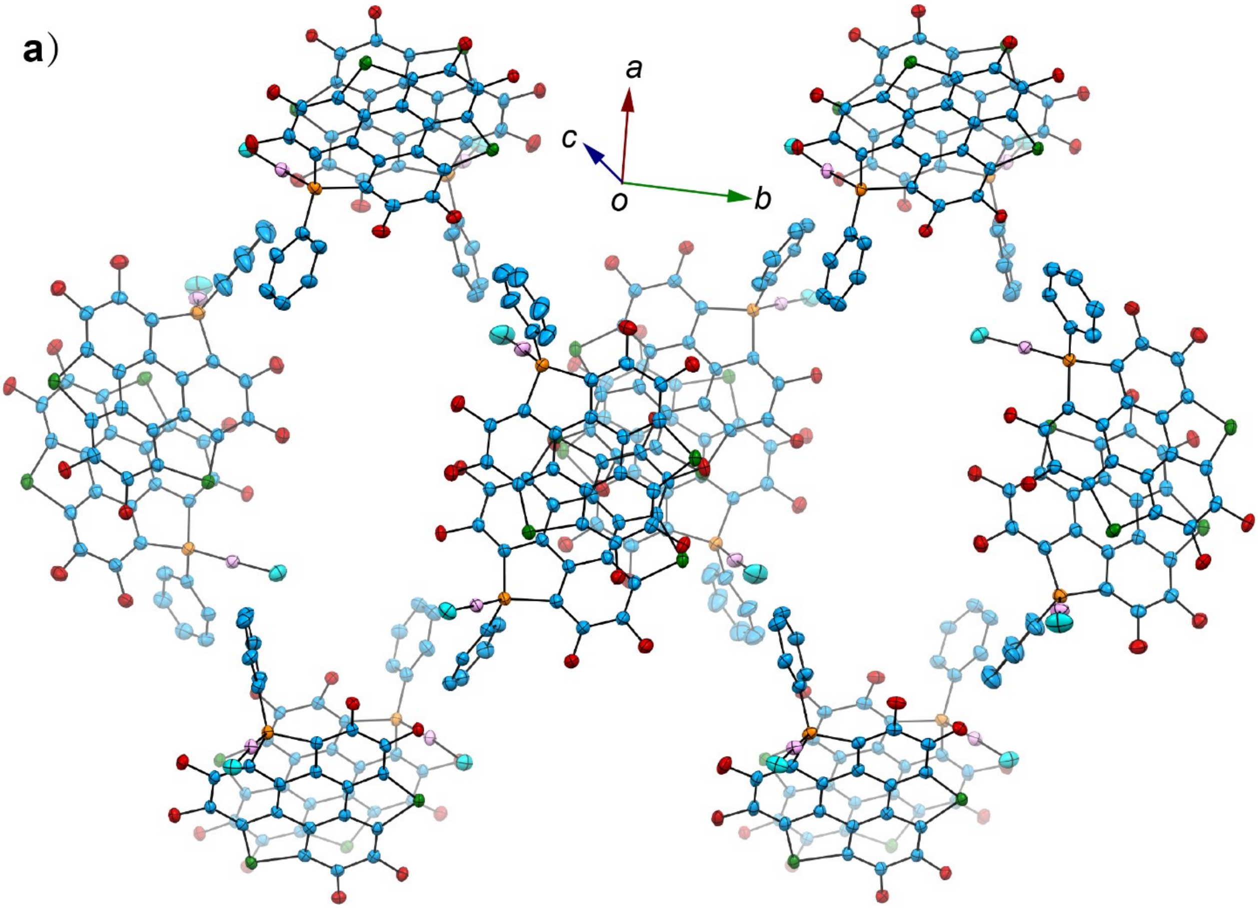


Fig. S6 a) Packing structure of (**2**)•AuCl. The C, H, O, Se, P, Cl and Au atoms are respectively shown in blue, pale cyan, red, green, orange, cyan and pink. The n-Bu groups and H atoms are omitted for clarity.

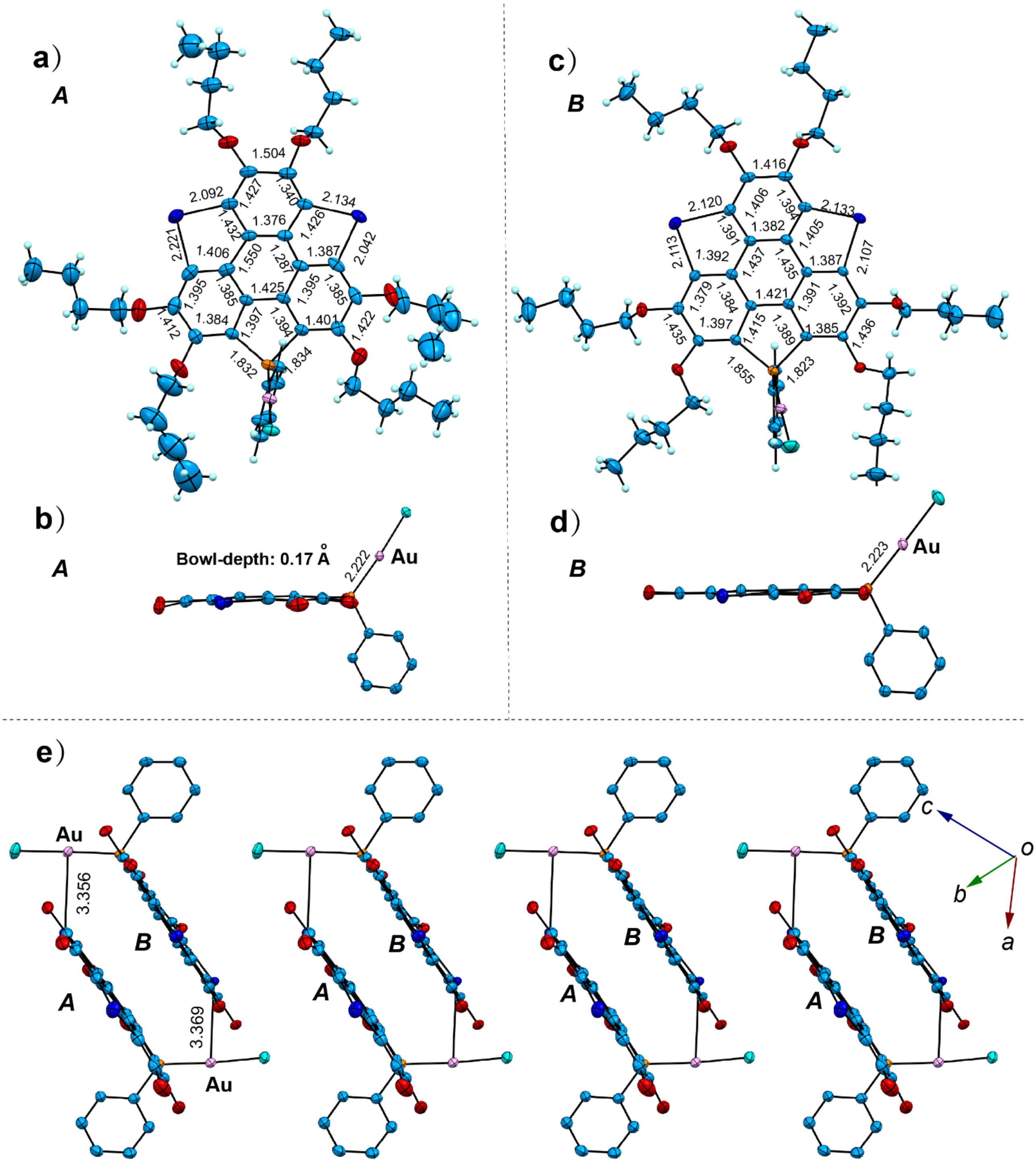


Fig. S7 Crystal structure of $(\mathbf{3})_2$•$(AuCl)_2$: a) top view and b) side view of molecule ***A*** in compound $(\mathbf{3})_2$•$(AuCl)_2$. c) top view and d) side view of molecule ***B*** in compound $(\mathbf{3})_2$•$(AuCl)_2$. e) packing motif of $(\mathbf{3})_2$•$(AuCl)_2$. The C, H, O, Te, P, Cl and Au atoms are respectively shown in blue, pale cyan, red, blue, orange, cyan and pink. The selected bond lengths are in unit of Å. The n-Bu groups and H atoms are omitted for clarity in b), d) and e).

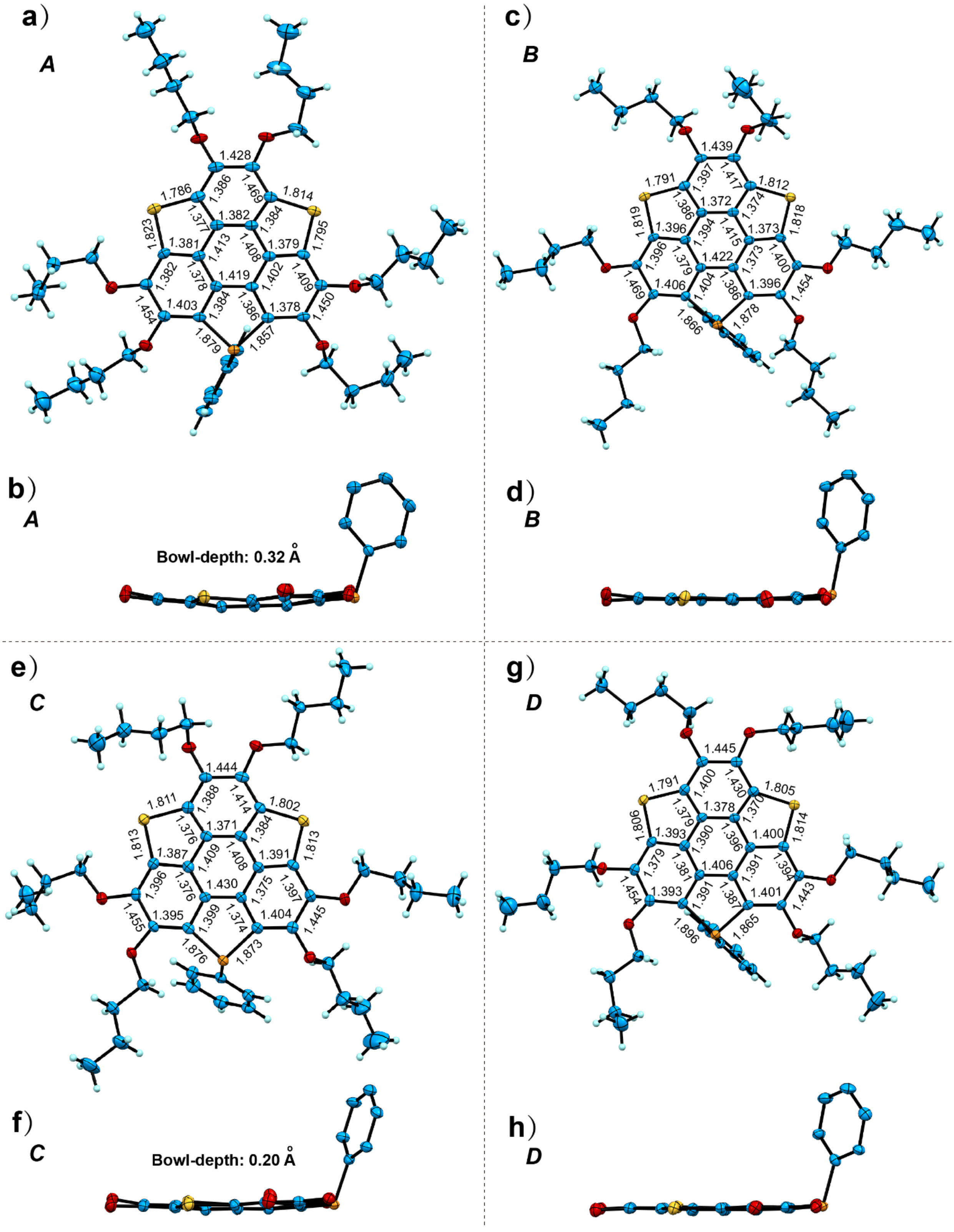


Fig. S8 Crystal structure of (**1**)$_2$•PtCl$_2$: a) top view and b) side view of molecule ***A*** in (**1**)$_2$•PtCl$_2$. c) top view and d) side view of molecule ***B*** in (**1**)$_2$•PtCl$_2$. e) top view and f) side view of molecule ***C*** in (**1**)$_2$•PtCl$_2$. g) top view and h) side view of molecule ***D*** in (**1**)$_2$•PtCl$_2$. The C, H, O, S and P atoms are respectively shown in blue, pale cyan, red, yellow and orange. The selected bond lengths are in unit of Å. The n-Bu groups and H atoms are omitted for clarity in b), d), f) and h).

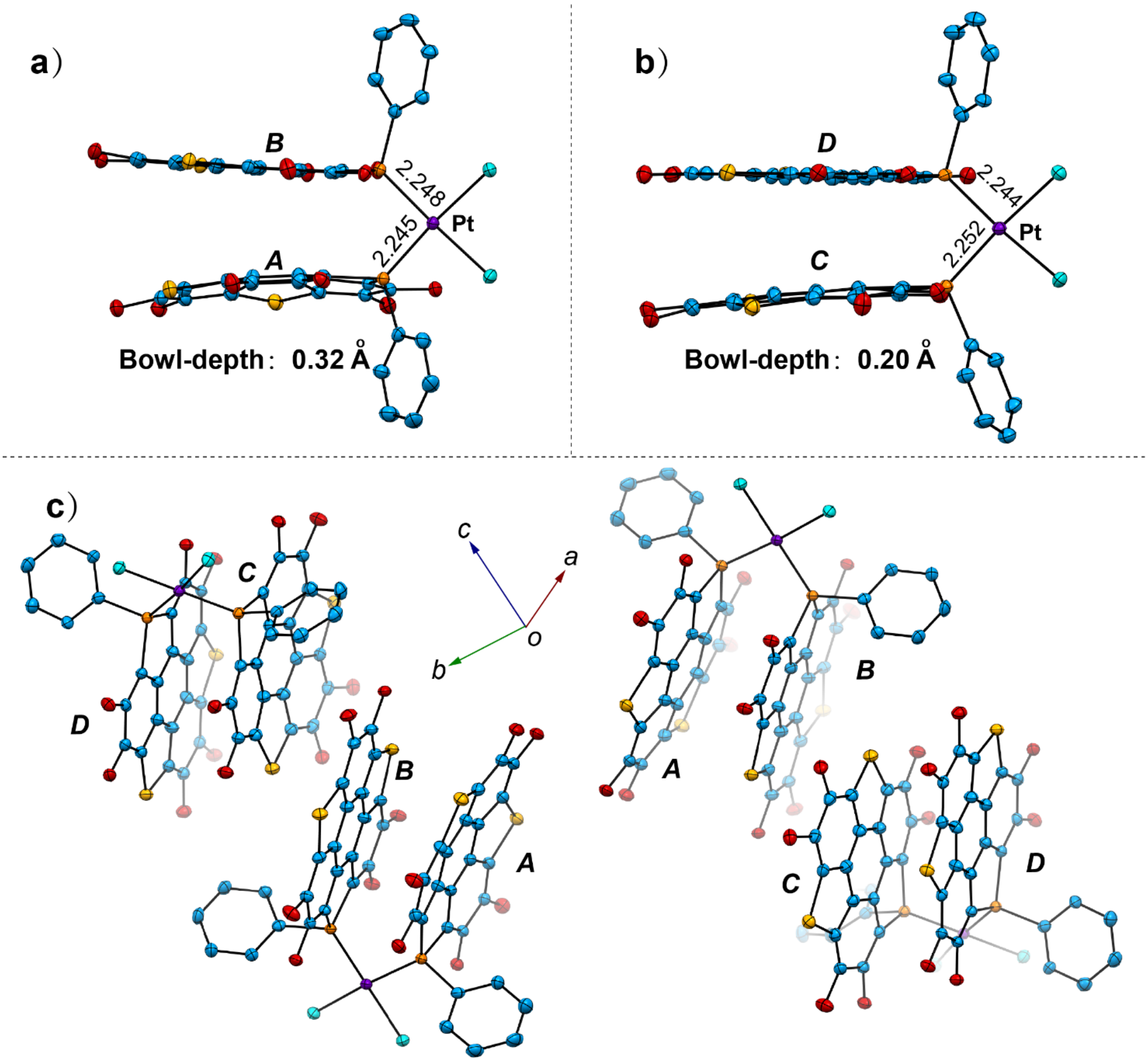


Fig. S9 Crystal structure of $(\mathbf{1})_2$•$PtCl_2$ with n-Bu groups and H atoms omitted for clarity: a) and b) structures of two kinds of $(\mathbf{1})_2$•$PtCl_2$ with Pt-P bond length and bowl-depth shown (Å); c) packing structure of compound $(\mathbf{1})_2$•$PtCl_2$**.** The C, H, O, S, P, Cl and Pt atoms are respectively shown in blue, pale cyan, red, yellow, orange, cyan and violet.

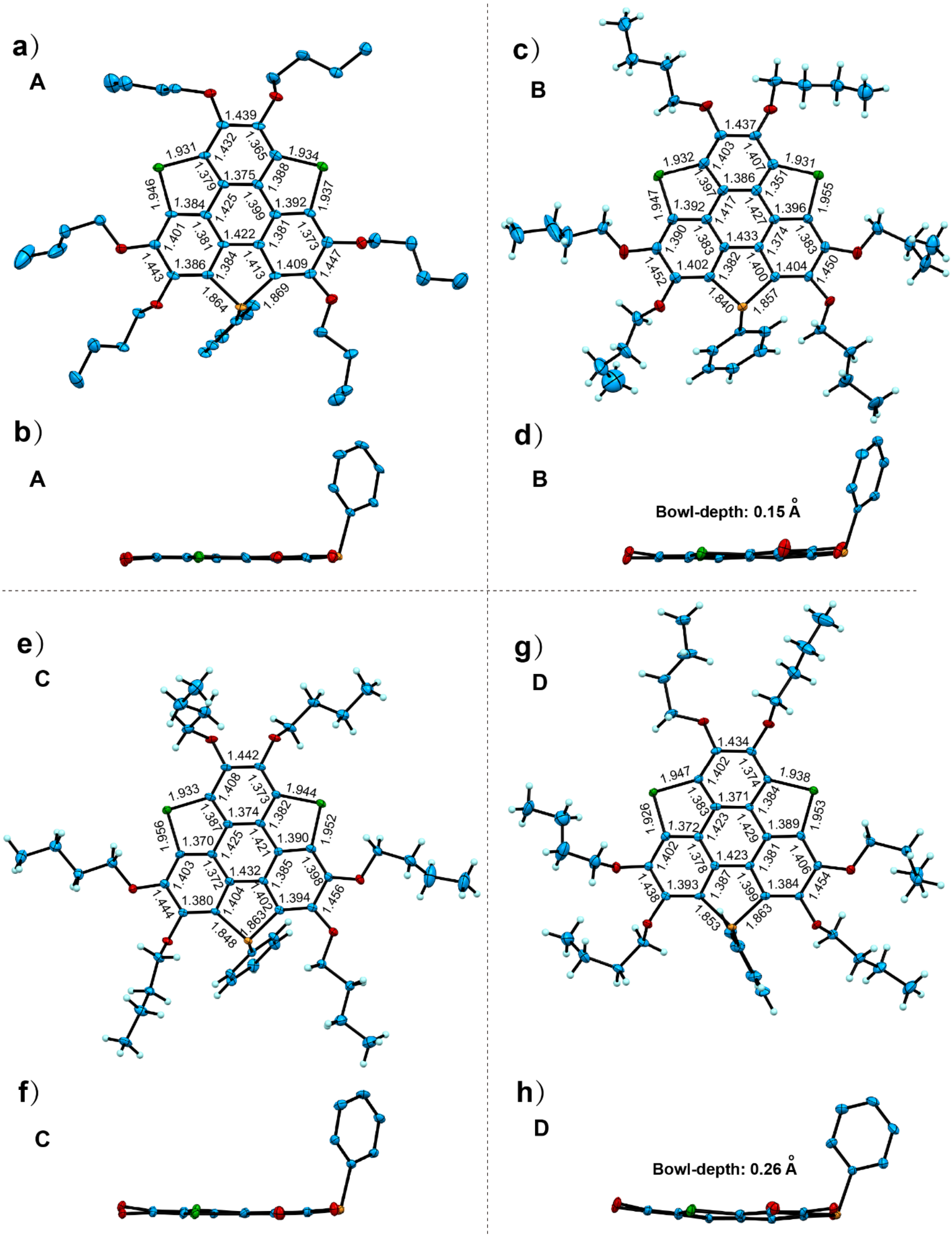


Fig. S10 Crystal structure of (**2**)$_2$•PtCl$_2$: a) top view and b) side view of molecule ***A*** in (**2**)$_2$•PtCl$_2$. c) top view and d) side view of molecule ***B*** in (**2**)$_2$•PtCl$_2$. e) top view and f) side view of molecule ***C*** in (**2**)$_2$•PtCl$_2$. g) top view and h) side view of molecule ***D*** in (**2**)$_2$•PtCl$_2$. The C, H, O, Se and P atoms are respectively shown in blue, pale cyan, red, green and orange. The selected bond lengths are in unit of Å. The n-Bu groups and H atoms are omitted for clarity in b), d), f) and h).

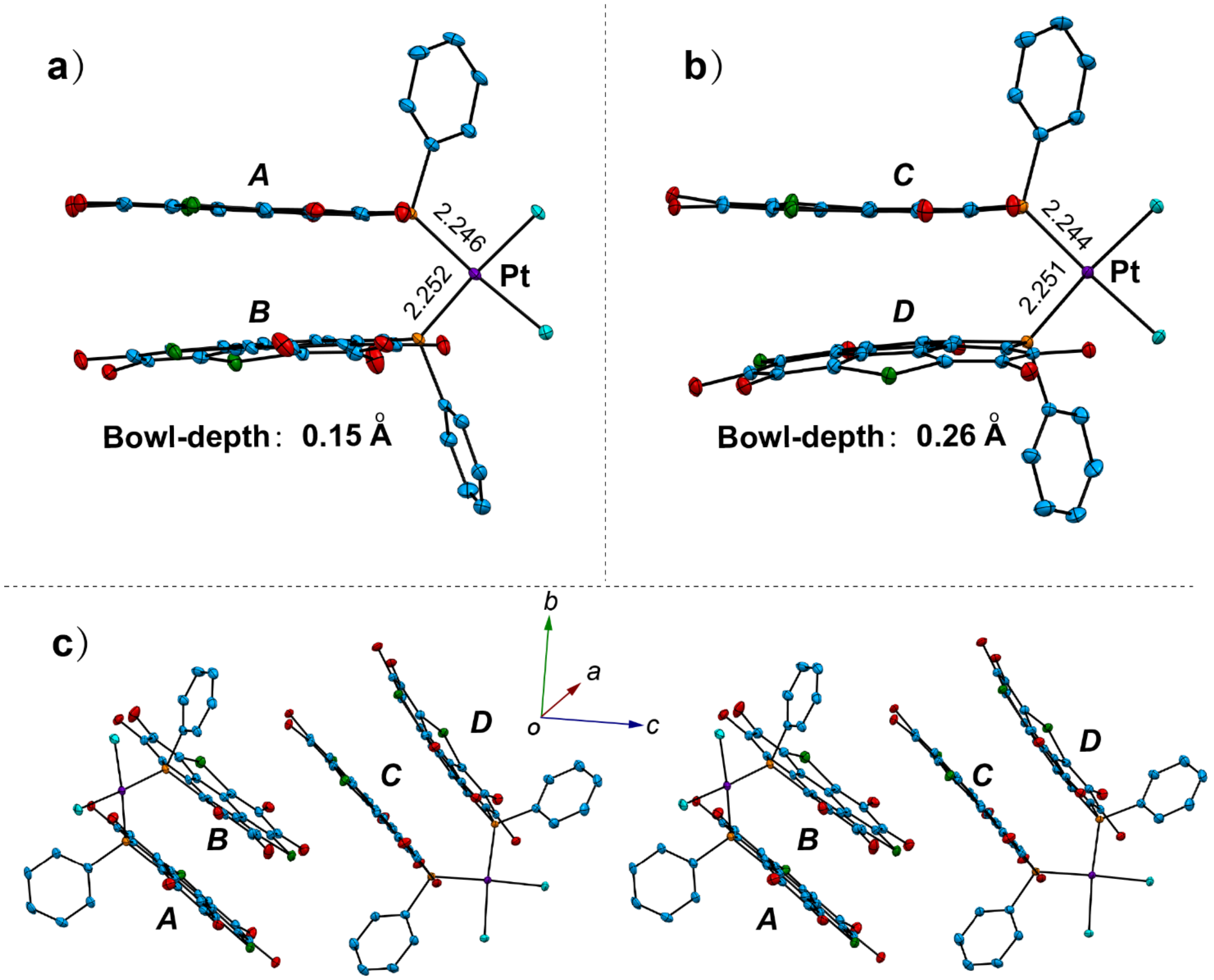


Fig. S11 Crystal structure of (**2**)$_2$•$PtCl_2$ with n-Bu groups and H atoms omitted for clarity: a) and b) structures of two kinds of (**2**)$_2$•$PtCl_2$ with Pt-P bond length and bowl-depth shown (Å); c) packing structure of compound (**2**)$_2$•$PtCl_2$**.** The C, H, O, Se, P, Cl and Pt atoms are respectively shown in blue, pale cyan, red, green, orange, cyan and violet.

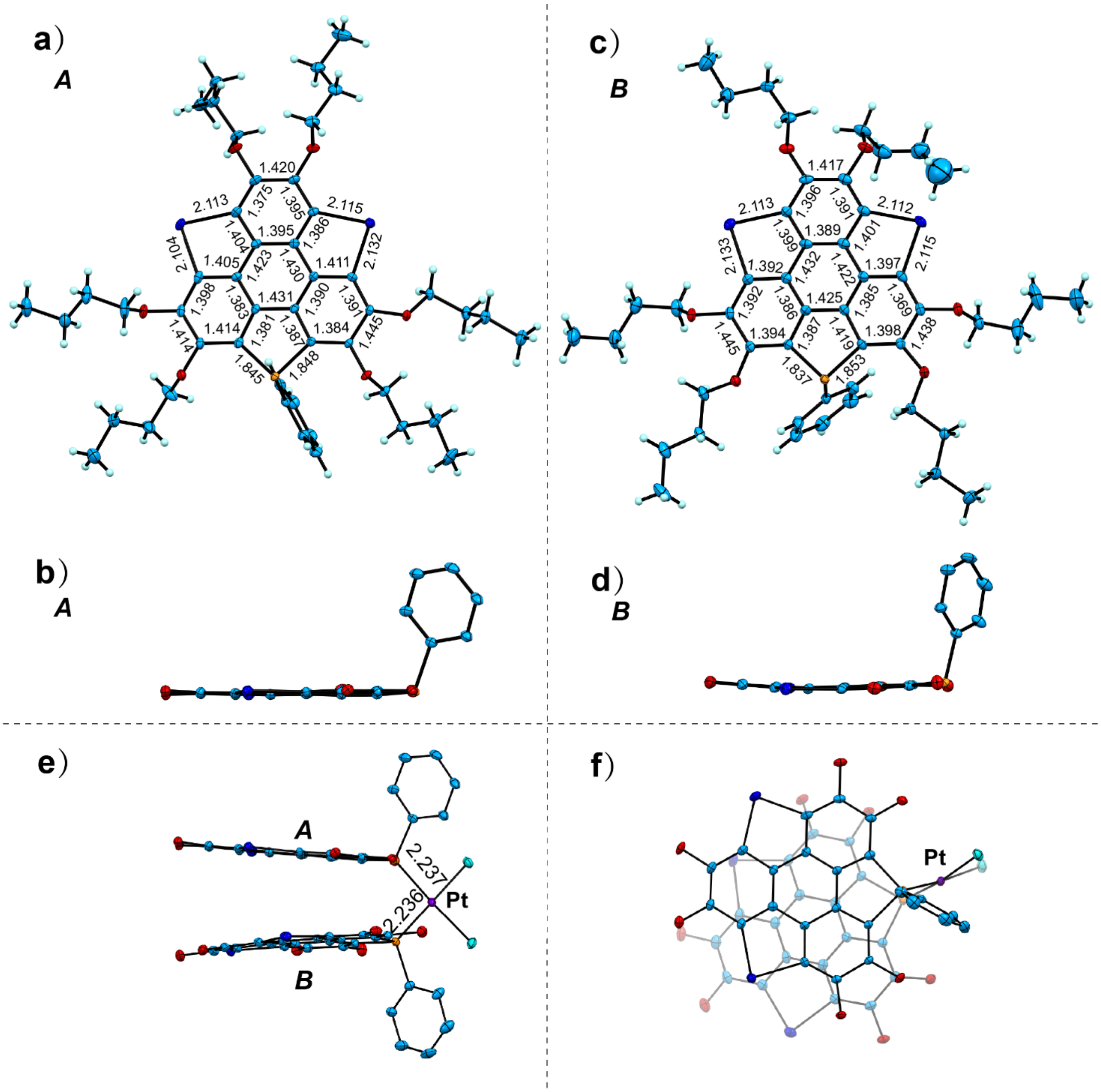


Fig. S12 Crystal structure of (**3**)$_2$•PtCl$_2$: a) top view and b) side view of molecule **A** in (**3**)$_2$•PtCl$_2$. c) top view and d) side view of molecule ***B*** in (**3**)$_2$•PtCl$_2$. e) Side view and f) top view of molecule (**3**)$_2$•PtCl$_2$. The C, H, O, Te, P, Cl and Pt atoms are respectively shown in blue, pale cyan, red, blue, orange, cyan and violet. The selected bond lengths are in unit of Å. The n-Bu groups and H atoms are omitted for clarity in b), d), e) and f).

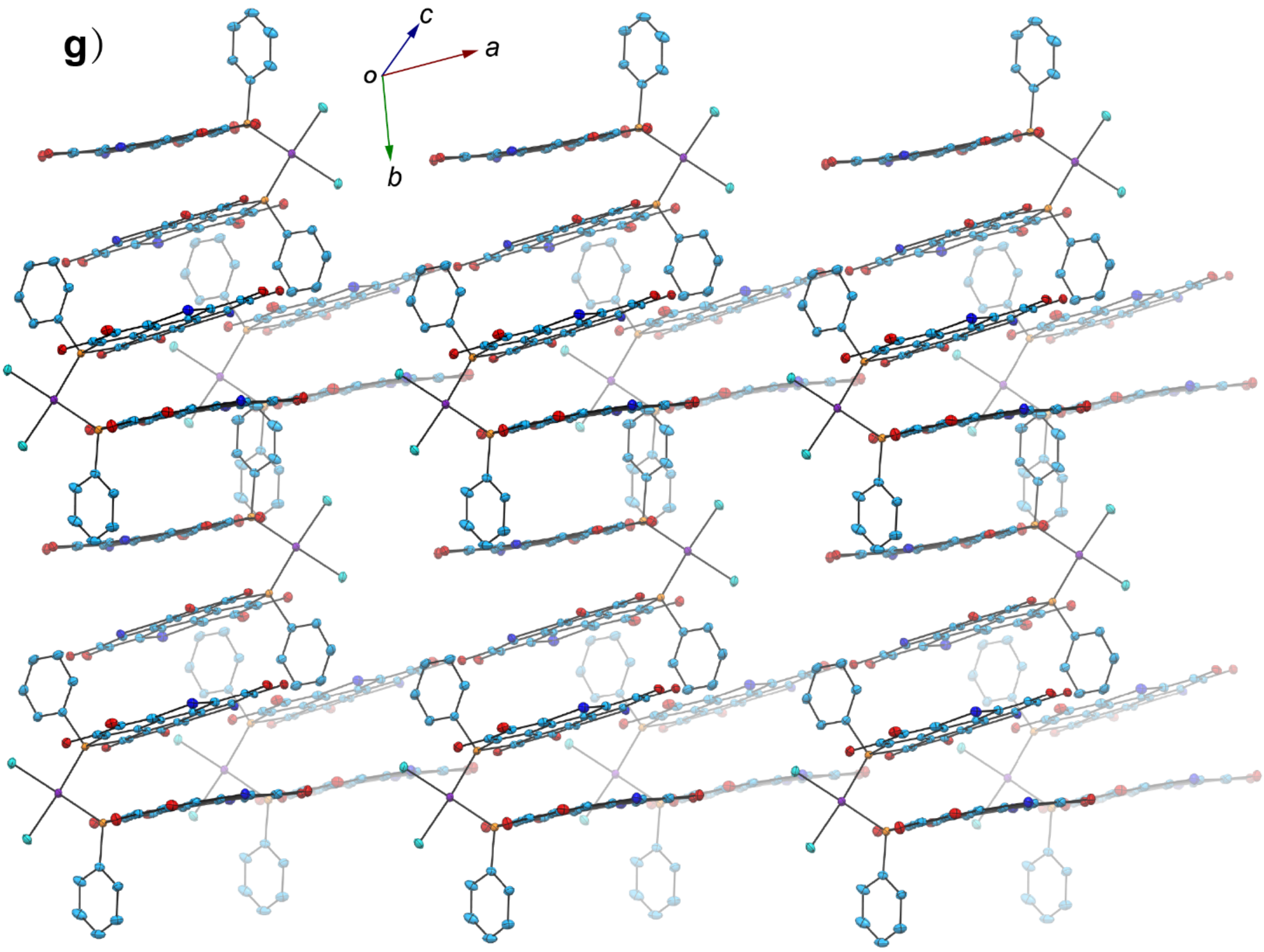


Fig. S13 g) packing motif of crystal structure of (**3**)$_2$•PtCl$_2$.The C, H, O, Te, P, Cl and Pt atoms are respectively shown in blue, pale cyan, red, blue, orange, cyan and violet. The n-Bu groups and H atoms are omitted for clarity.

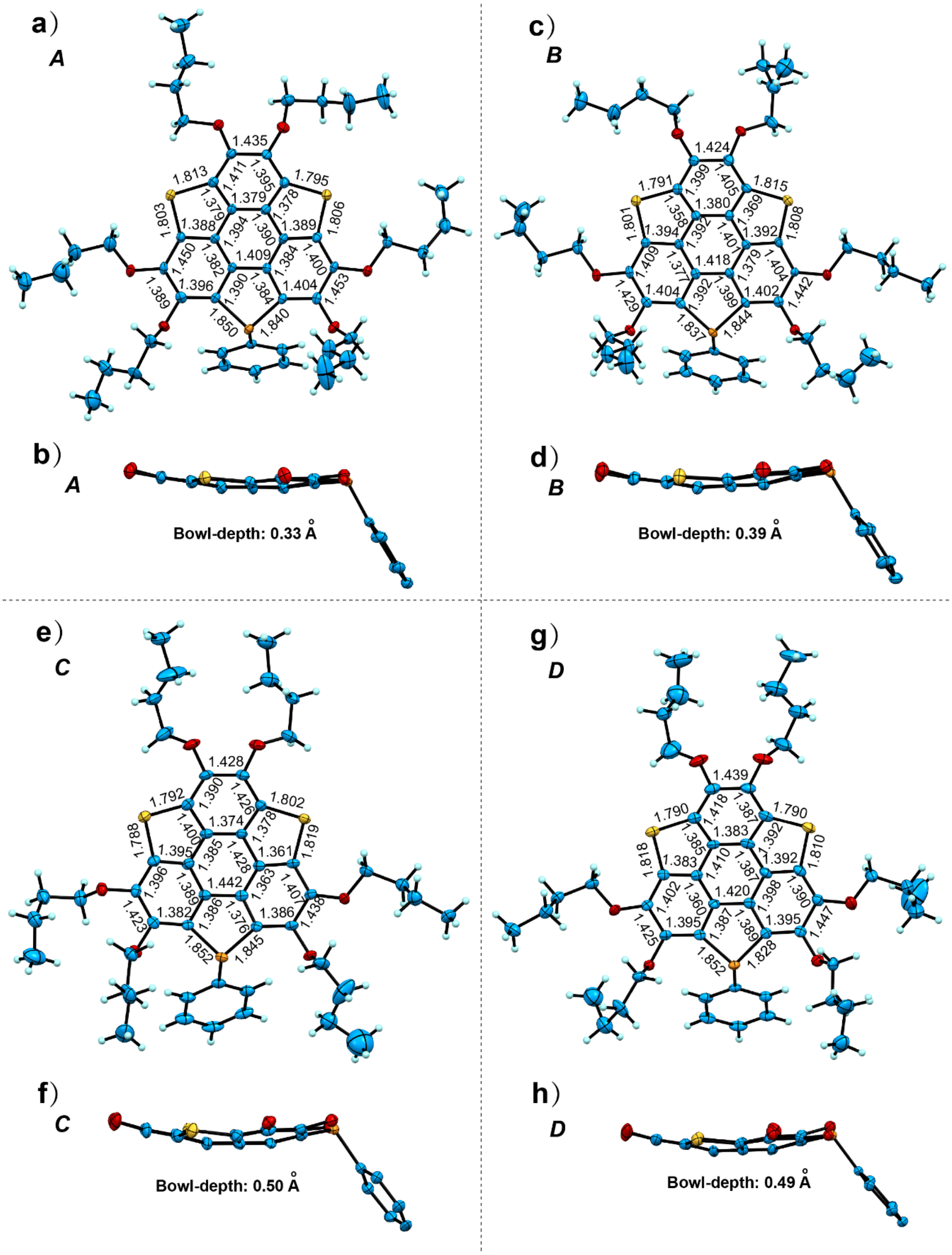


Fig. S14 Crystal structure of $(\mathbf{1})_2\bullet(PdCl_2)_2$: a) top view and b) side view of molecule ***A*** in $(\mathbf{1})_2\bullet(PdCl_2)_2$; c) top view and d) side view of molecule ***B*** in $(\mathbf{1})_2\bullet(PdCl_2)_2$. e) top view and f) side view of molecule ***C*** in $(\mathbf{1})\bullet PdCl_2\bullet MeCN$; g) top view and h) side view of molecule ***D*** in $(\mathbf{1})\bullet PdCl_2\bullet\mathbf{MeCN}$. C, H, O, S and P atoms are respectively shown in blue, pale cyan, red, yellow and orange. The selected bond lengths are in unit of Å. *n*-Bu groups and H atoms are omitted for clarity in b), d), f) and h).

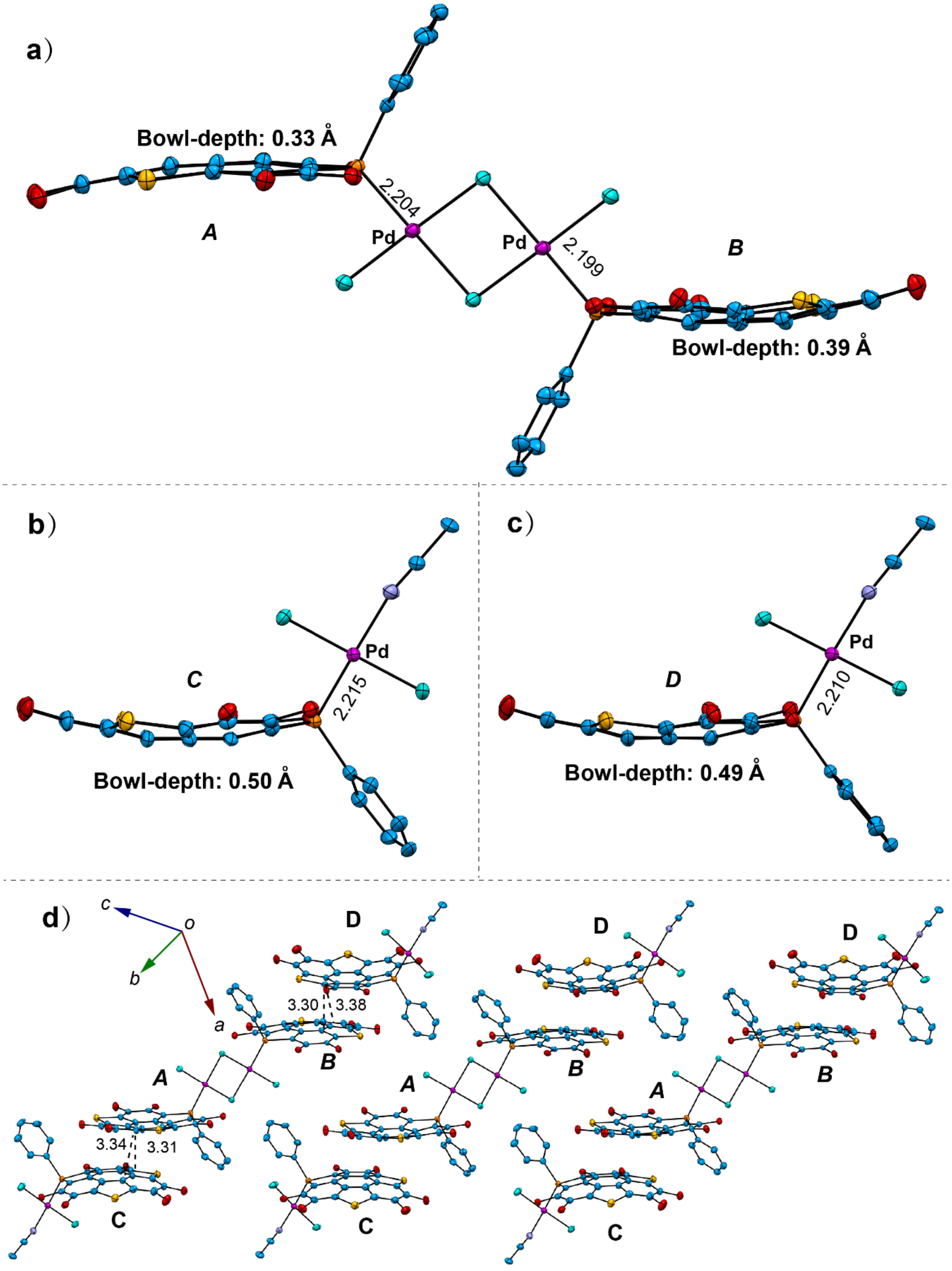


Fig. S15 Packing structure of $(\mathbf{1})_2\bullet(\mathrm{PdCl}_2)_2$: a) side view of $(\mathbf{1})_2\bullet(\mathrm{PdCl}_2)_2$ with Pd-P bond length and bowl-depth shown (Å); b) and c) side view of two kinds of $(\mathbf{1})\bullet\mathrm{PdCl}_2\bullet\mathbf{MeCN}$ with Pd-P bond length and bowl-depth shown (Å); d) packing motif with intermolecular contacts shown (Å). The C, H, O, N, S, P, Cl and Pd atoms are respectively shown in blue, pale cyan, red, cyan, yellow, orange, cyan and pink. The n-Bu groups and H atoms are omitted for clarity.

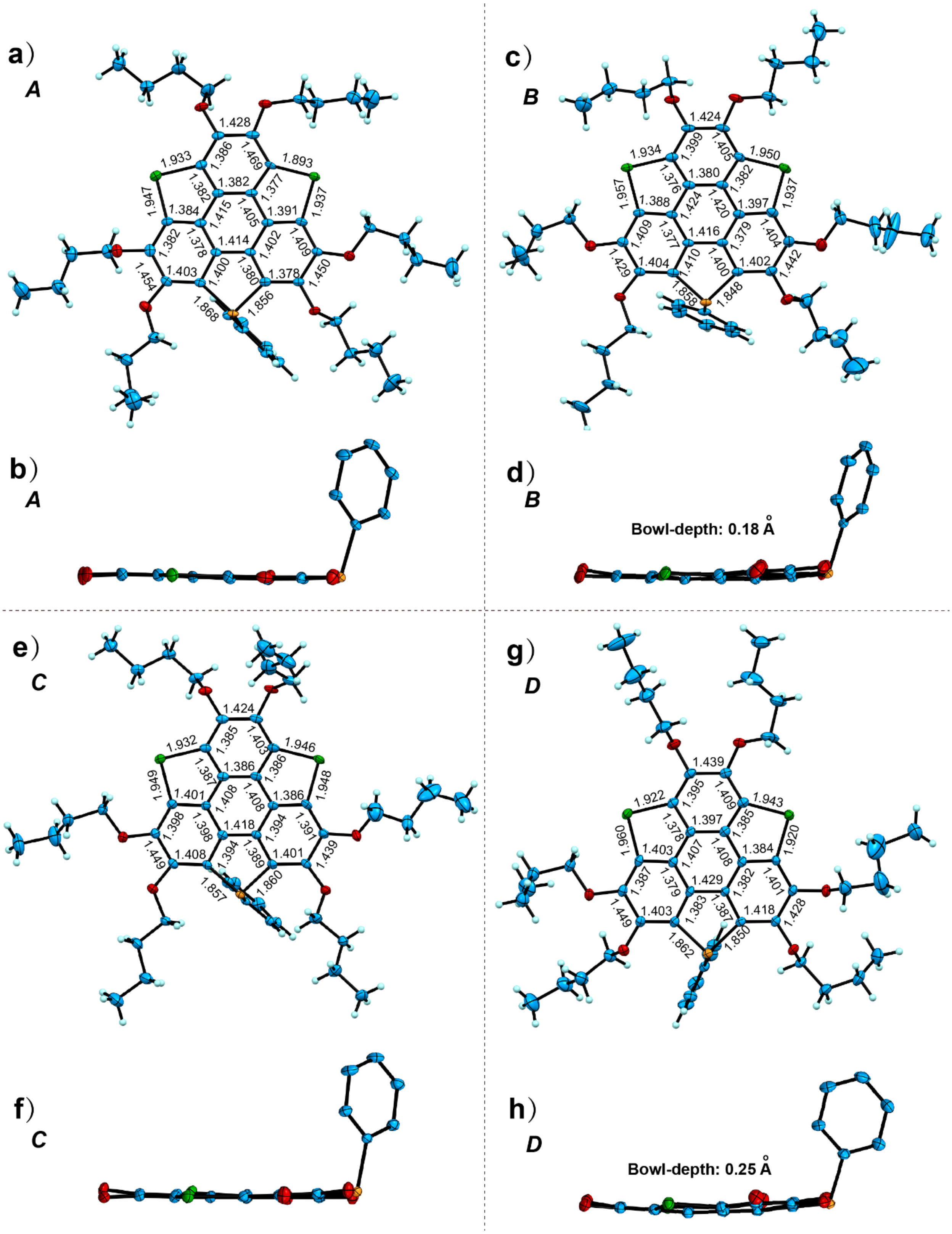


Fig. S16 Crystal structure of (**2**)$_2$•PdCl$_2$: a) top view and b) side view of molecule ***A*** in (**2**)$_2$•PdCl$_2$. c) top view and d) side view of molecule ***B*** in (**2**)$_2$•PdCl$_2$. e) top view and f) side view of molecule ***C*** in (**2**)$_2$•PdCl$_2$. g) top view and h) side view of molecule ***D*** in (**2**)$_2$•PdCl$_2$. The selected bond lengths are in unit of Å. The n-Bu groups and H atoms are omitted for clarity in b), d), f) and h). The C, H, O, Se and P atoms are respectively shown in blue, pale cyan, red, green and orange.

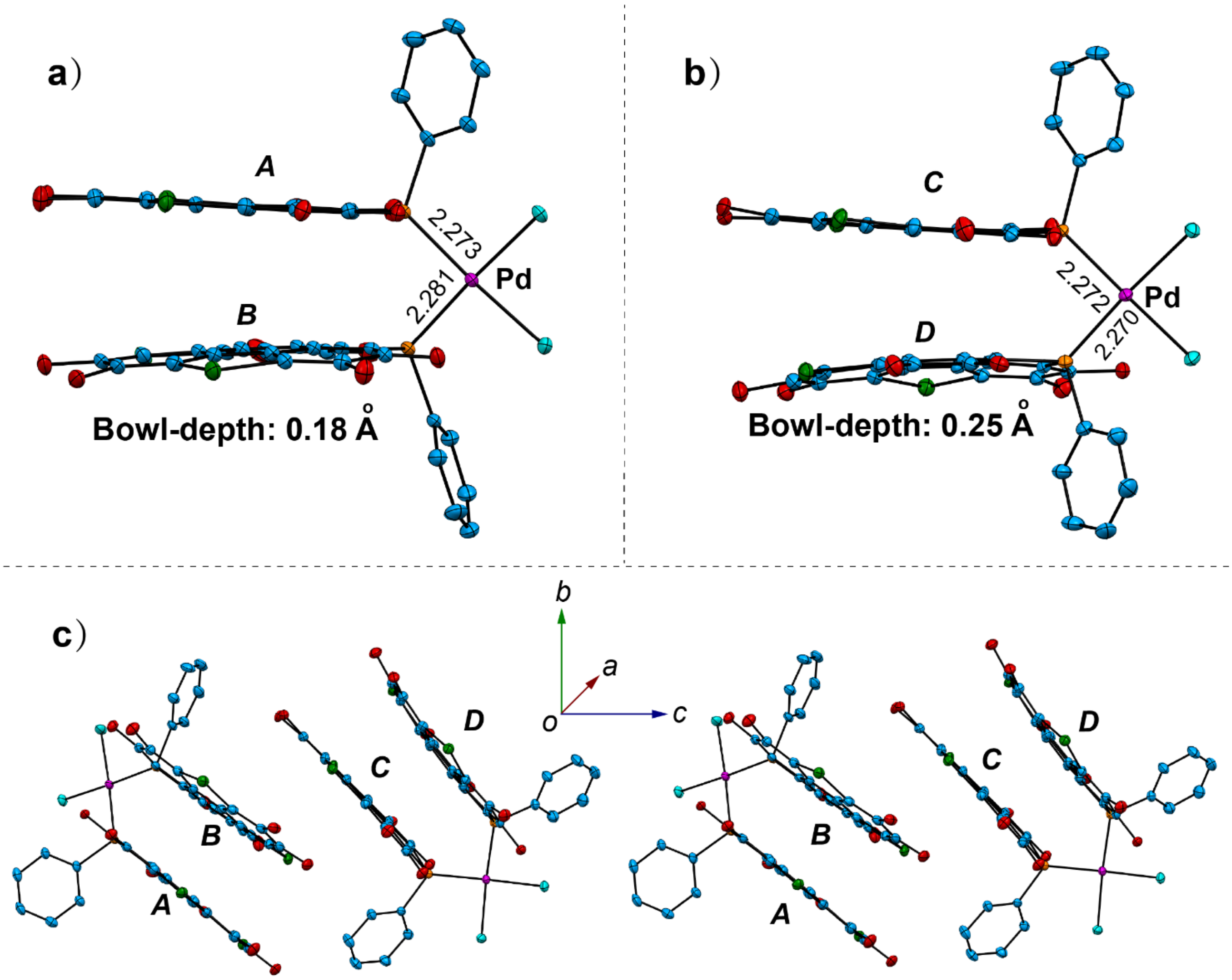


Fig. S17 Crystal structure of (**2**)$_2$•PdCl$_2$ with n-Bu groups and H atoms omitted for clarity: a) and b) structures of two kinds of (**2**)$_2$•PdCl$_2$ with Pd-P bond length and bowl-depth shown (Å); c) packing structure of compound (**2**)$_2$•PdCl$_2$. The C, H, O, Se, P, Cl and Pd atoms are respectively shown in blue, pale cyan, red, green, orange, cyan and pink.

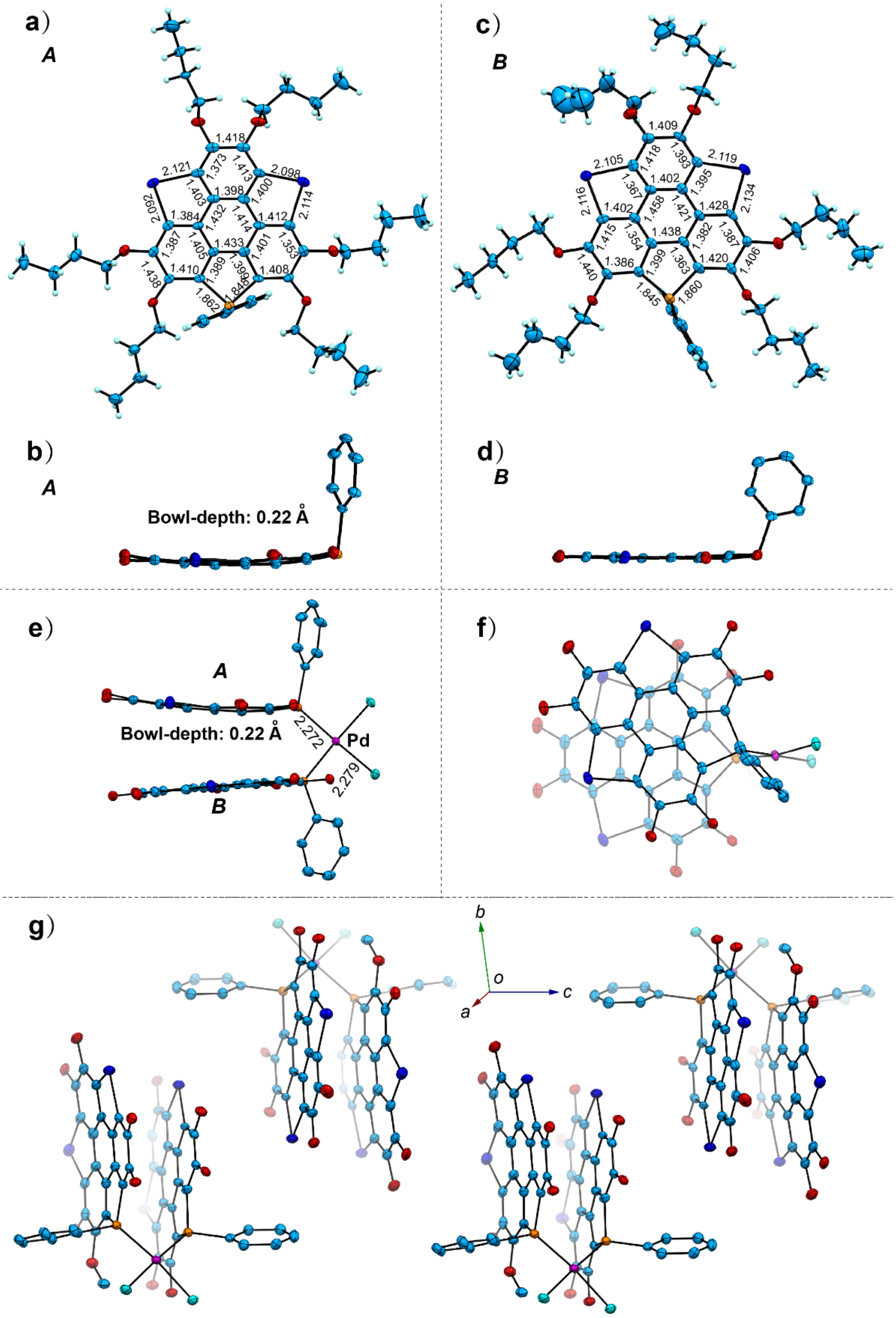


Fig. S18 Crystal structure of ($\mathbf{3}$)$_2$•PdCl$_2$: a) top view and b) side view of molecule ***A*** in ($\mathbf{3}$)$_2$•PdCl$_2$; c) top view and d) side view of molecule ***B*** in ($\mathbf{3}$)$_2$•PdCl$_2$; e) side view and f) top view of molecule ($\mathbf{3}$)$_2$•PdCl$_2$; g) packing structure of compound ($\mathbf{3}$)$_2$•PdCl$_2$. The C, H, O, Te, P, Cl and Pd atoms are respectively shown in blue, pale cyan, red, blue, orange, cyan and pink. The selected bond lengths are in unit of Å. The n-Bu groups and H atoms are omitted for clarity in b), d), e), f)

6. Electrochemical spectra

Table S9. Electrochemical data, estimated HOMO levels.

comp.	E_{ox}^{1}(V)	E_{ox}^{2}(V)	E_{ox}^{3}(V)	E_{HOMO} (eV)
1	0.76	1.21	–	-5.16
2	0.78	1.21	1.39	-5.18
3	0.78	1.11	1.39	-5.18
(**1**)•AuCl	0.97	1.27	1.47	-5.37
(**2**)•AuCl	0.98	1.28	1.48	-5.38
$(\mathbf{3})_2$•$(AuCl)_2$	0.96	1.22	1.61	-5.36
$(\mathbf{1})_2$•$(PdCl_2)_2$	0.97	1.30	1.48	-5.37
$(\mathbf{2})_2$•$PdCl_2$	0.86	1.06	1.43	-5.26
$(\mathbf{3})_2$•$PdCl_2$	0.81	1.13	1.38	-5.21
$(\mathbf{1})_2$•$PtCl_2$	0.83	1.07	1.43	-5.23
$(\mathbf{2})_2$•$PtCl_2$	0.83	1.05	1.42	-5.23
$(\mathbf{3})_2$•$PtCl_2$	0.80	0.92	1.28	-5.20

The HOMO energy levels are estimated from electrochemical data, $E_{HOMO} = -e\ (E_{ox}^{1} + 4.40)$ (eV).

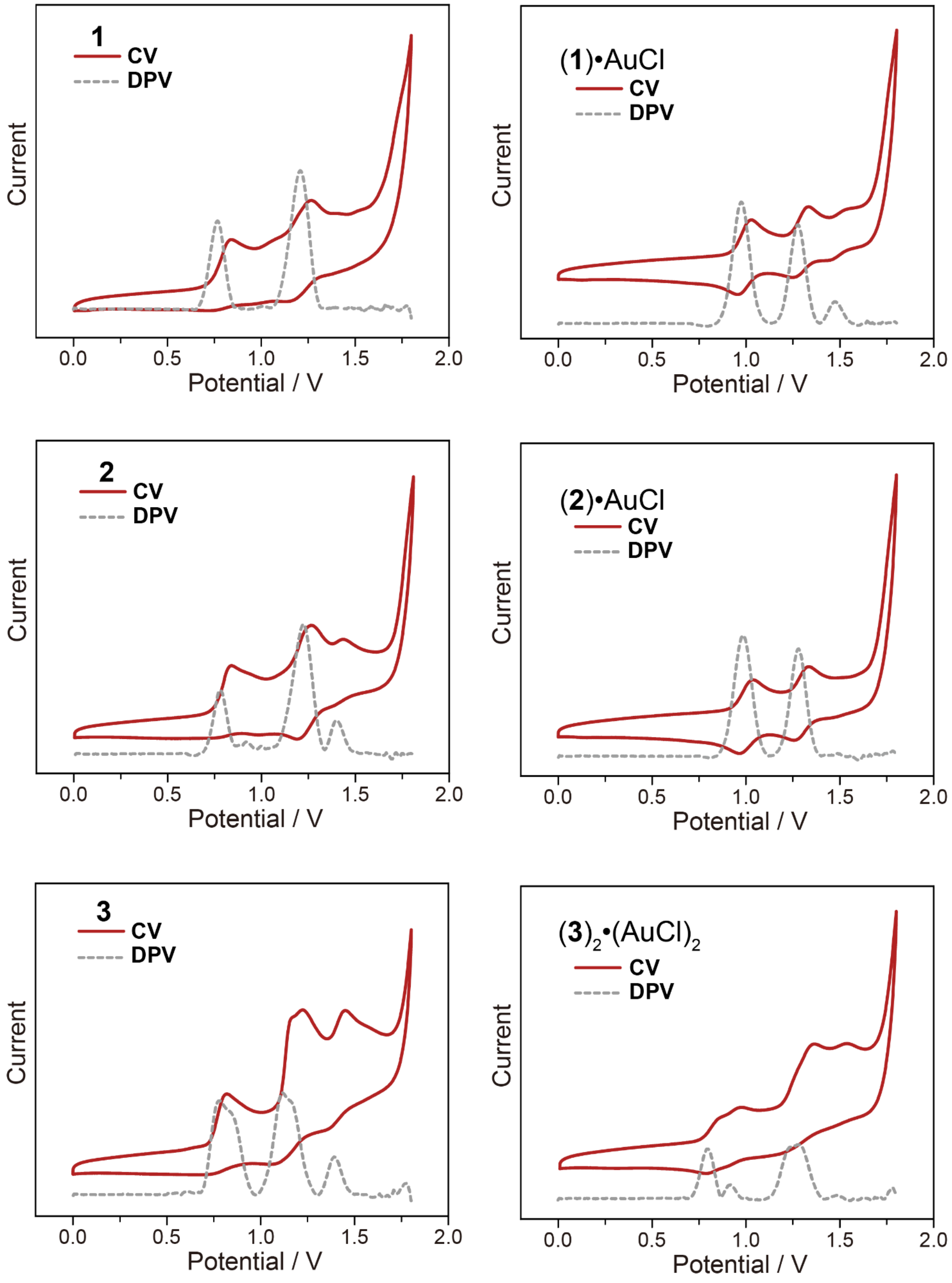


Fig. S19 CV and DPV of **1**, **2**, **3**, (**1**)•AuCl, (**2**)•AuCl and (**3**)$_2$•(AuCl)$_2$ in CH_2Cl_2 (c = 10^{-4} mol·L^{-1}) at RT. Reference electrode: SCE.

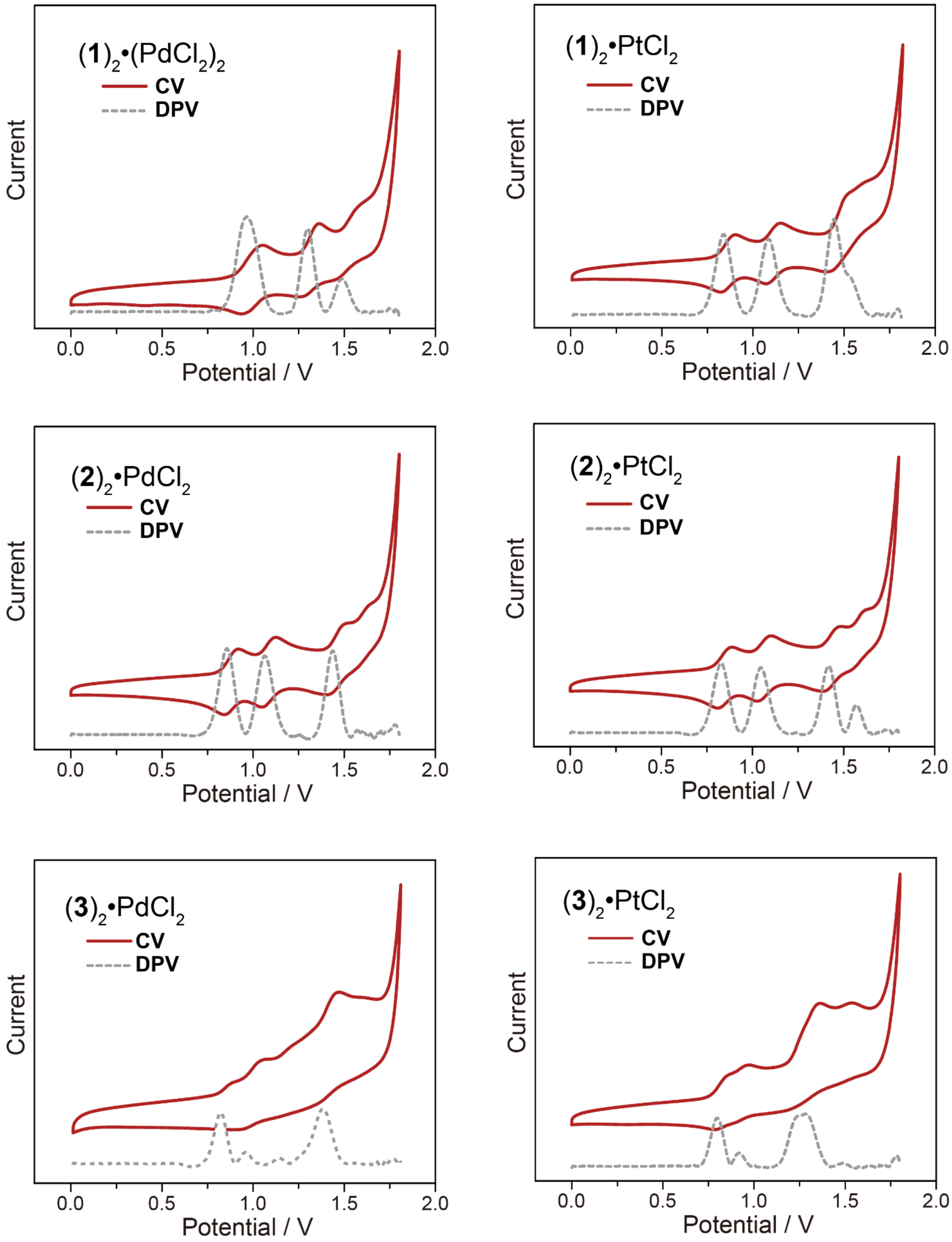


Fig. S20 CV and DPV of (**1**)$_2$•PtCl$_2$, (**2**)$_2$•PtCl$_2$, (**3**)$_2$•PtCl$_2$, (**1**)$_2$•(PdCl$_2$)$_2$, (**2**)$_2$•PdCl$_2$ and (**3**)$_2$•PdCl$_2$ in CH$_2$Cl$_2$ (c = 10^{-4} mol·L^{-1}) at RT. Reference electrode: SCE.

7. Photophysical Study

The UV-Vis spectra of the compounds so far obtained were measured in their dichloromethane (CH_2Cl_2) solution (c=1.0 ×10^{-5} mol·L^{-1}) at 20℃ on a UV-2600 UV-Vis spectrometer (Shimadzu).

Table S10. UV-Vis spectra of compounds **1-3,** (**1**)•AuCl, (**2**)•AuCl, (**3**)$_2$•$(AuCl)_2$, (**1**)$_2$•$(PdCl_2)_2$, (**2**)$_2$•$PdCl_2$**,** (**3**)$_2$•$PdCl_2$, (**1**)$_2$•$PtCl_2$, (**2**)$_2$•$PtCl_2$, and (**3**)$_2$•$PtCl_2$ in CH_2Cl_2 solution.

Comp.	**λ_{max}/nm**	**log ε**	**λ_{max}/nm**	**log ε**	**λ_{max}/nm**	**log ε**
1	306	4.96	403	3.60	–	–
2	305	4.72	397	3.60	–	–
3	307	4.86	398	3.60	–	–
(**1**)•AuCl	305	4.83	407	3.85	–	–
(**2**)•AuCl	301	4.91	401	3.90	–	–
(**3**)$_2$•$(AuCl)_2$	303	4.89	378	3.90	401	3.78
(**1**)$_2$•$(PdCl_2)_2$	305	5.32	390	4.40	466	4.08
(**2**)$_2$•$PdCl_2$	298	5.23	391	4.30	–	–
(**3**)$_2$•$PdCl_2$	291	5.02	393	4.26	–	–
(**1**)$_2$•$PtCl_2$	299	5.14	412	4.11	–	–
(**2**)$_2$•$PtCl_2$	295	5.15	405	4.04	–	–
(**3**)$_2$•$PtCl_2$	303	5.00	405	3.90	–	–

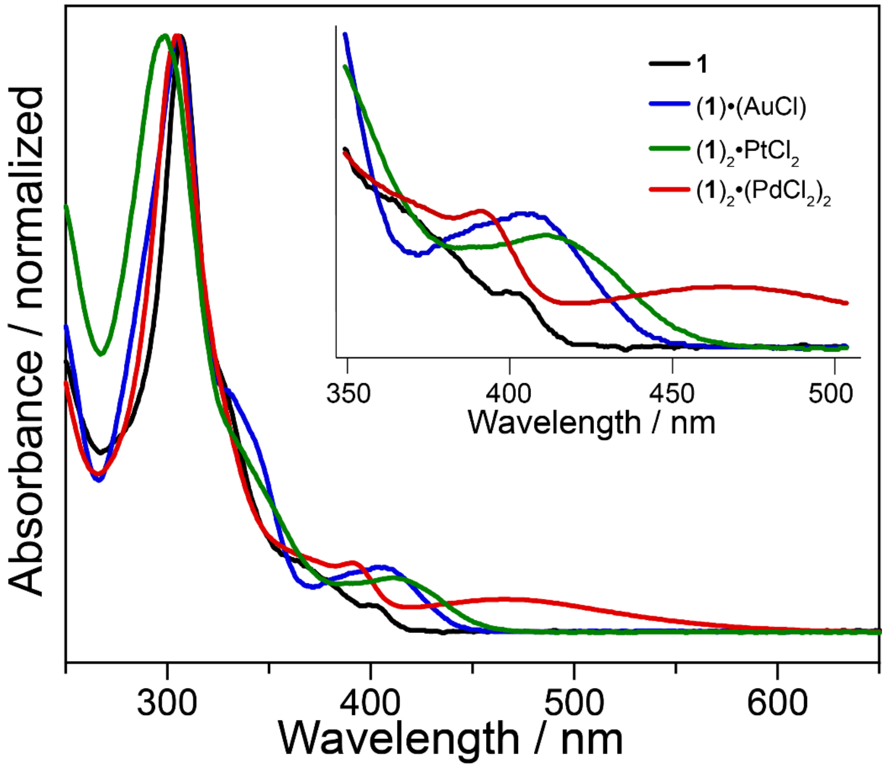


Fig. S21 UV-Vis absorption spectra of **1**, (**1**)•AuCl, (**1**)$_2$•$PtCl_2$ and (**1**)$_2$•$(PdCl_2)_2$ in CH_2Cl_2 solution (c = 10^{-5} mol·L^{-1}) at 20 ºC.

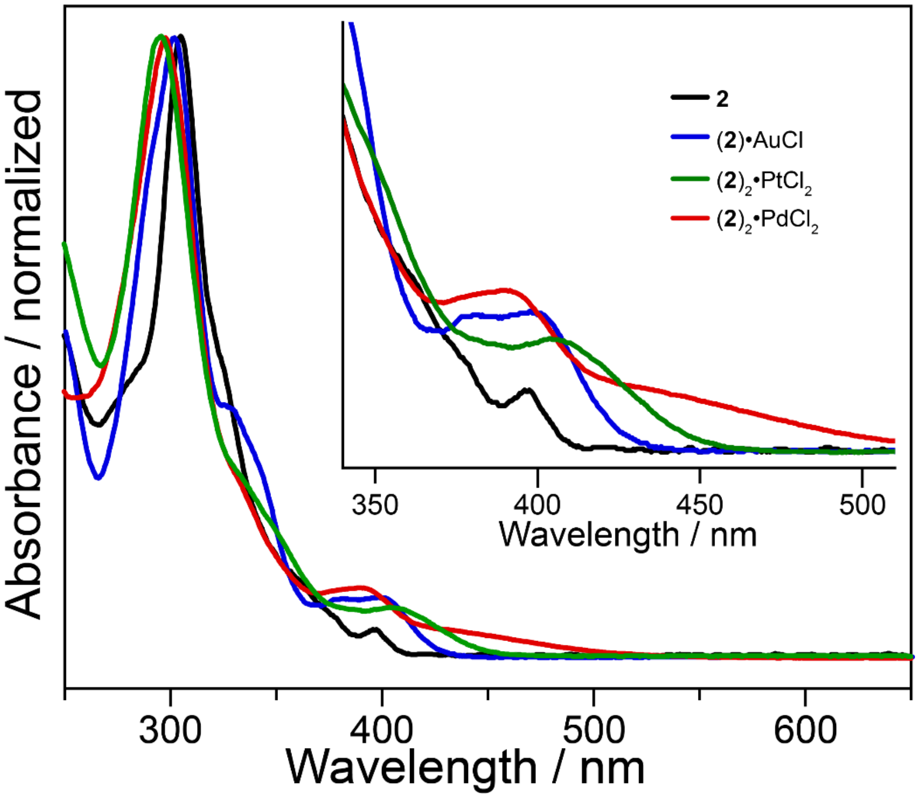


Fig. S22 UV-Vis absorption spectra of **2**, (**2**)•AuCl, (**2**)$_2$•PtCl$_2$ and (**2**)$_2$•PdCl$_2$ in CH$_2$Cl$_2$ solution (c = 10^{-5} mol·L^{-1}) at 20 ºC.

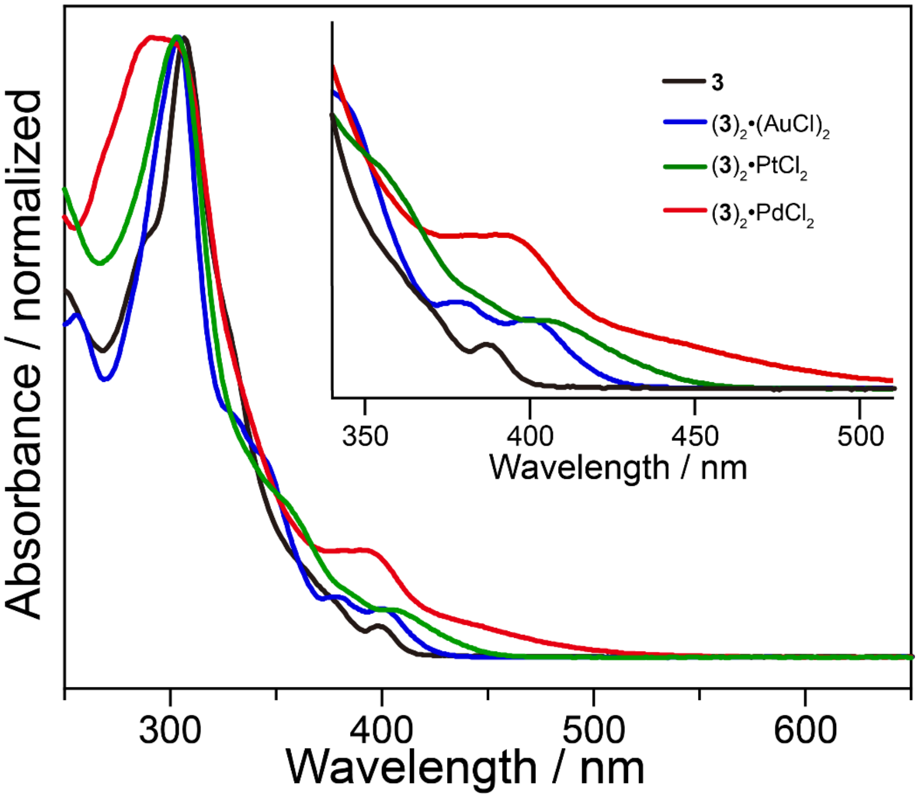
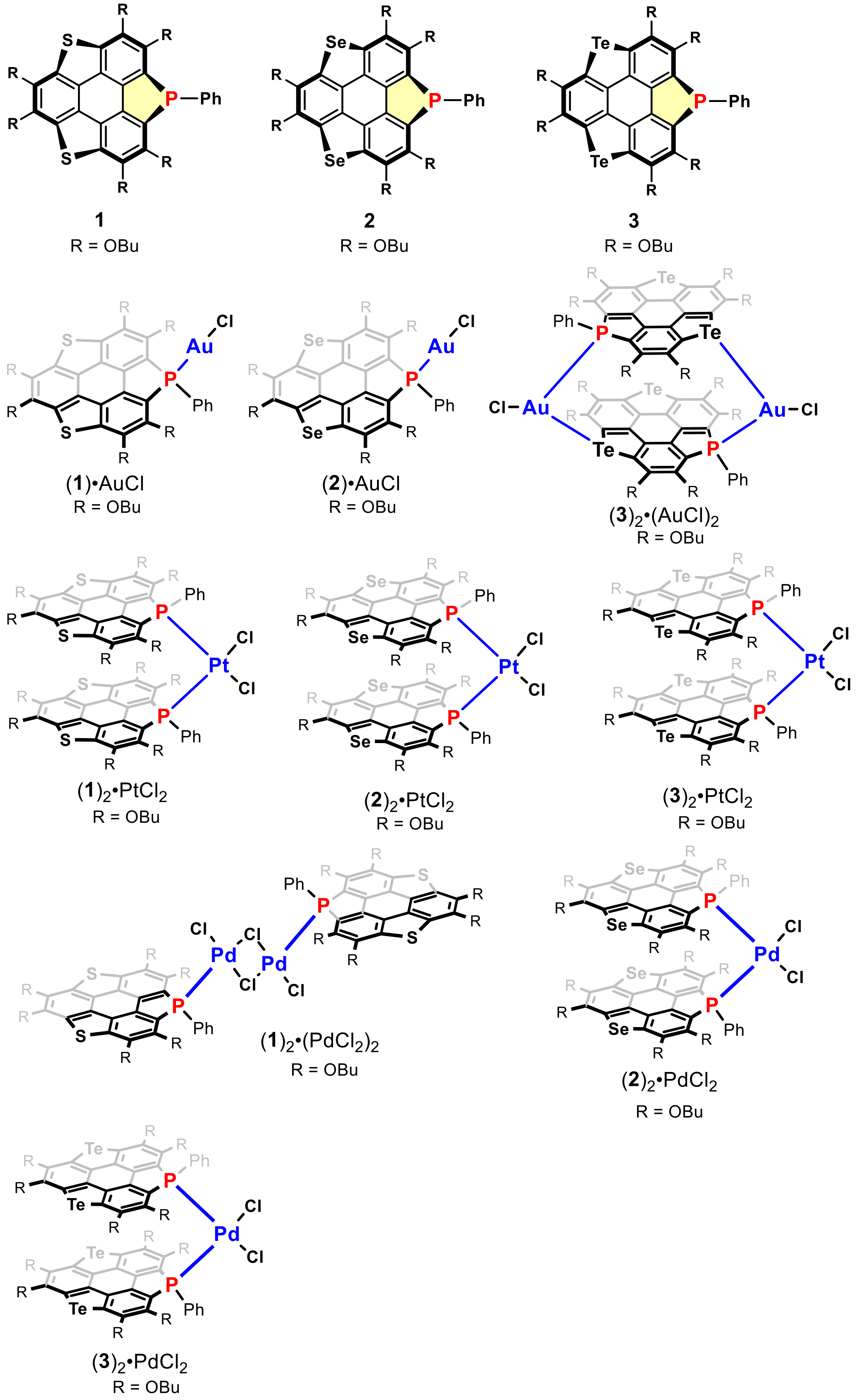


Fig. S23 UV-Vis absorption spectra of **3**, (**3**)$_2$•(AuCl)$_2$, (**3**)$_2$•PtCl$_2$ and (**3**)$_2$•PdCl$_2$ in CH$_2$Cl$_2$ solution (c = 10^{-5} mol·L^{-1}) at 20 ºC.

8. Calculations

During the structure optimizations and frontier orbital calculations, the butyl groups on calculated molecules were replaced by methyl groups to give the corresponding molecules (**Scheme S7**), because alkyl groups have almost no contribution to the HOMO and LUMO orbitals and the geometry of the conjugated framework.

All the calculations were performed with Gaussian 16 software package[S5]. Geometry optimizations were carried out using B3LYP[S6]/Def2-SVP[S7]/ method. Molecular orbital energies were calculated at B3LYP/Def2-TZVP level of theory using optimized structures. Aromaticity of each ring was measured by nucleus independent chemical shift (NICS)[S8][S9], which was computed using the gauge invariant atomic orbital (GIAO)[S10-13]approach at the GIAO-B3LYP/Def2-SVP level with optimized structures.



Scheme S5 The chemical structures of calculated molecules.

8.1 Optimized Structures, Molecular Orbitals and Corresponding Energies

Table S11 The calculated energy levels for the frontier orbitals for **1'**, **2'**, **3'**, (**1'**)•AuCl, (**2'**)•AuCl, (**3'**)$_2$•(AuCl)$_2$, (**1'**)$_2$•(PdCl$_2$)$_2$, (**2'**)$_2$•PdCl$_2$, (**3'**)$_2$•PdCl$_2$, (**1'**)$_2$•PtCl$_2$, (**2'**)$_2$•PtCl$_2$ and (**3'**)$_2$•PtCl$_2$.

Comp.	**Energy levels /eV**				
	HOMO-1	**HOMO**	**LUMO**	**LUMO+1**	**Eg**[a]
1'	-5.66	-5.47	-1.45	-1.36	4.02
2'	-5.65	-5.42	-1.39	-1.32	4.03
3'	-5.56	-5.27	-1.31	-1.27	3.95
(**1'**)•AuCl	-5.99	-5.62	-1.96	-1.68	3.66
(**2'**)•AuCl	-5.98	-5.57	-1.82	-1.54	3.75
(**3'**)$_2$•(AuCl)$_2$	-5.44	-5.18	-1.85	-1.88	3.33
(**1'**)$_2$•PtCl$_2$	-5.67	-5.52	-2.20	-2.13	3.32
(**2'**)$_2$•PtCl$_2$	-5.61	-5.46	-2.17	-2.11	3.29
(**3'**)$_2$•PtCl$_2$	-5.58	-5.32	-2.04	-1.96	3.28
(**1'**)$_2$•(PdCl$_2$)$_2$	-5.64	-5.61	-3.04	-2.99	2.57
(**2'**)$_2$•PdCl$_2$	-5.70	-5.48	-2.62	-2.11	2.86
(**3'**)$_2$•PdCl$_2$	-5.58	-5.34	-2.33	-2.07	3.01

[a] $E_g = E_{LUMO} - E_{HOMO}$

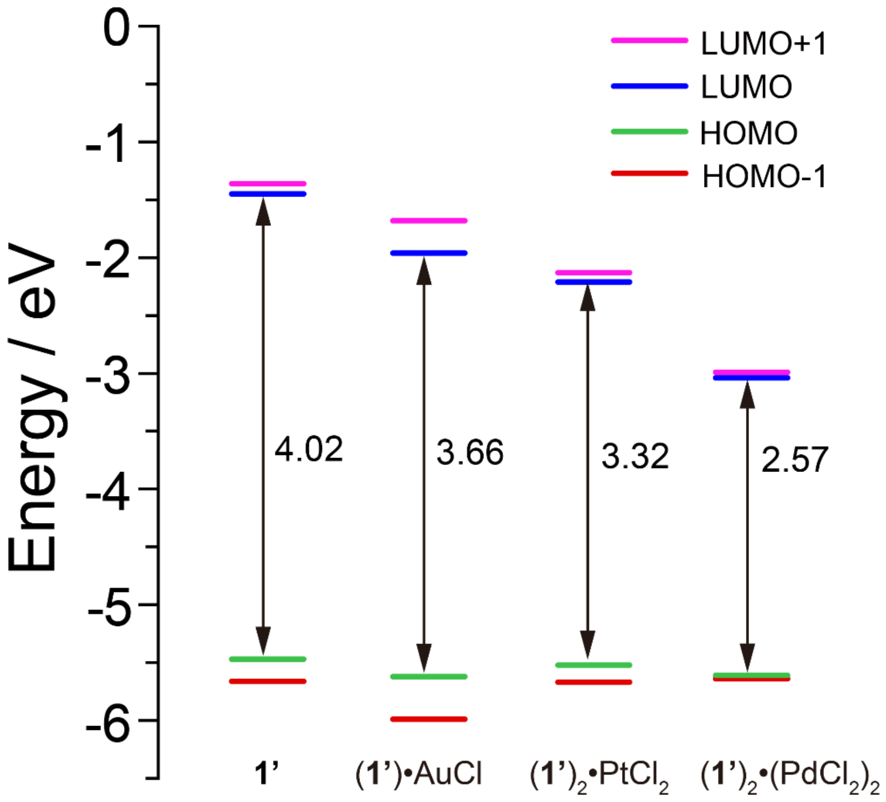


Fig. S24 HOMO-LUMO level gaps of **1'**, (**1'**)•AuCl, (**1'**)$_2$•(PdCl$_2$)$_2$ and (**1'**)$_2$•PtCl$_2$.

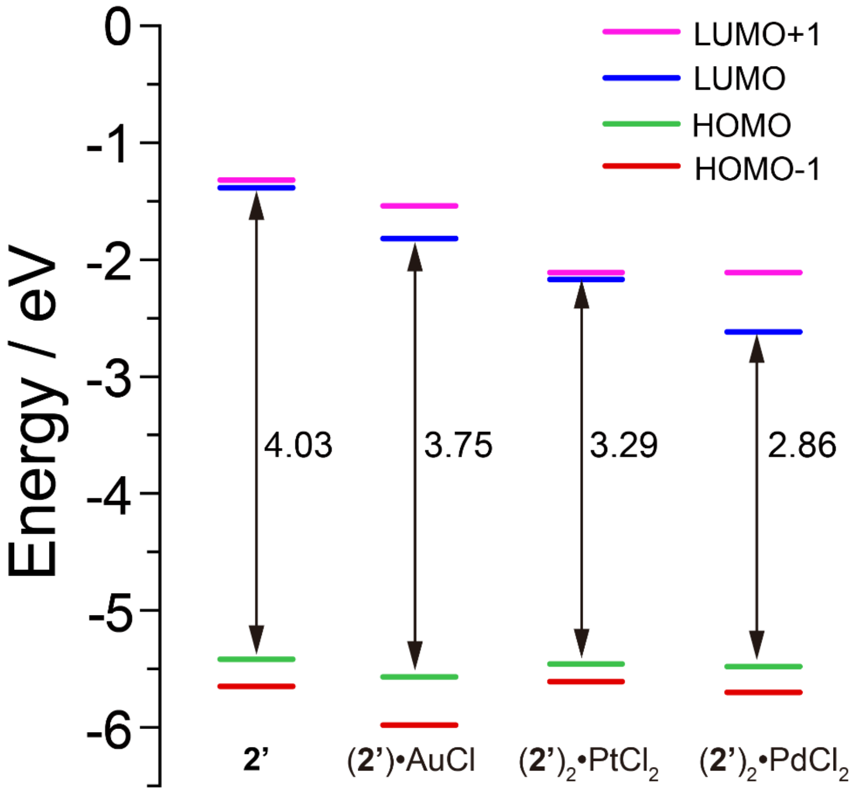


Fig. S25 HOMO-LUMO level gaps of **2'**, (**2'**)•AuCl, (**2'**)$_2$•PdCl$_2$ and. (**2'**)$_2$•PtCl$_2$.

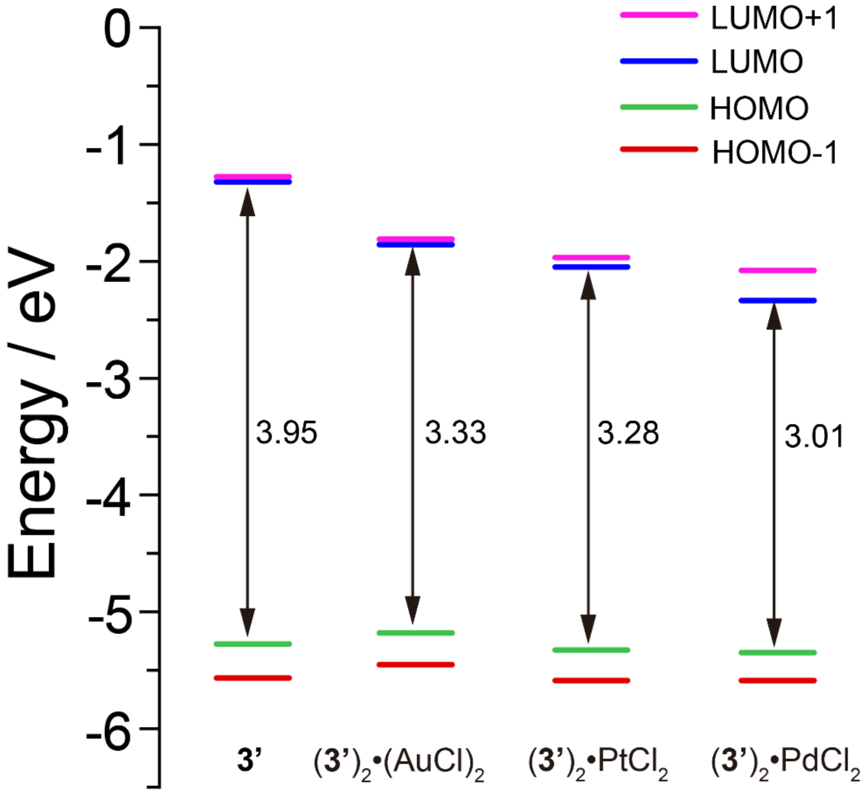


Fig. S26 HOMO-LUMO level gaps of **3'**, (**3'**)$_2$•(AuCl)$_2$, (**3'**)$_2$•PdCl$_2$ and (**3'**)$_2$•PtCl$_2$.

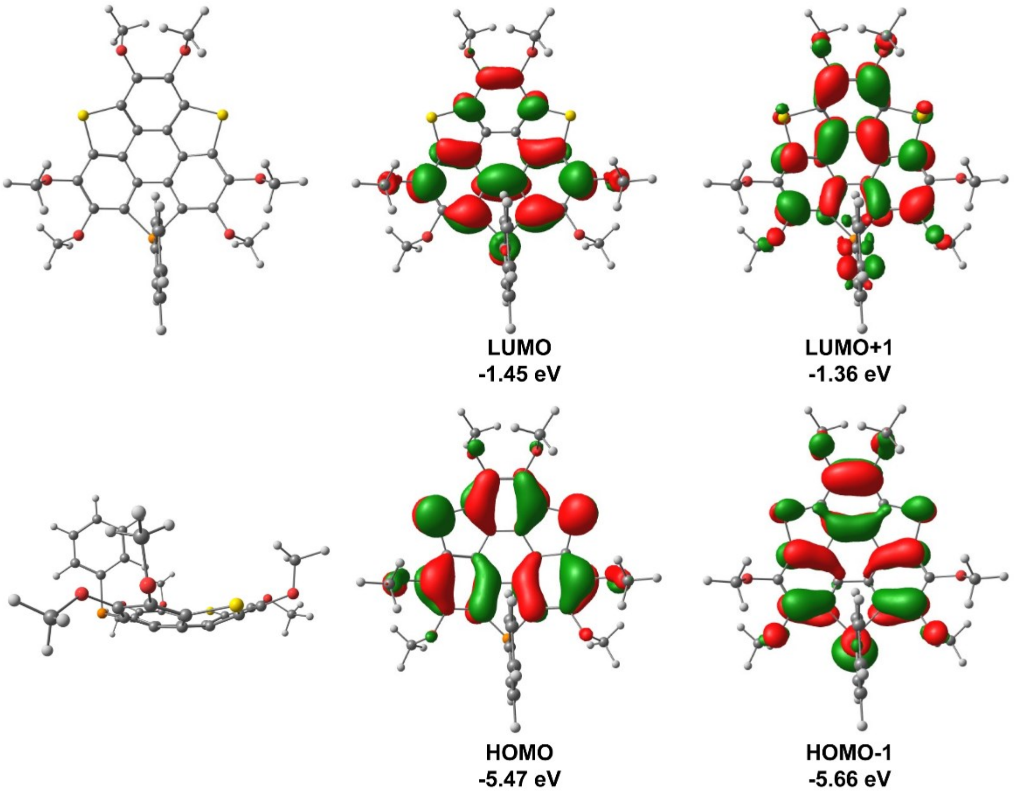


Fig. S27 Calculated molecular orbitals of compound **1’**.

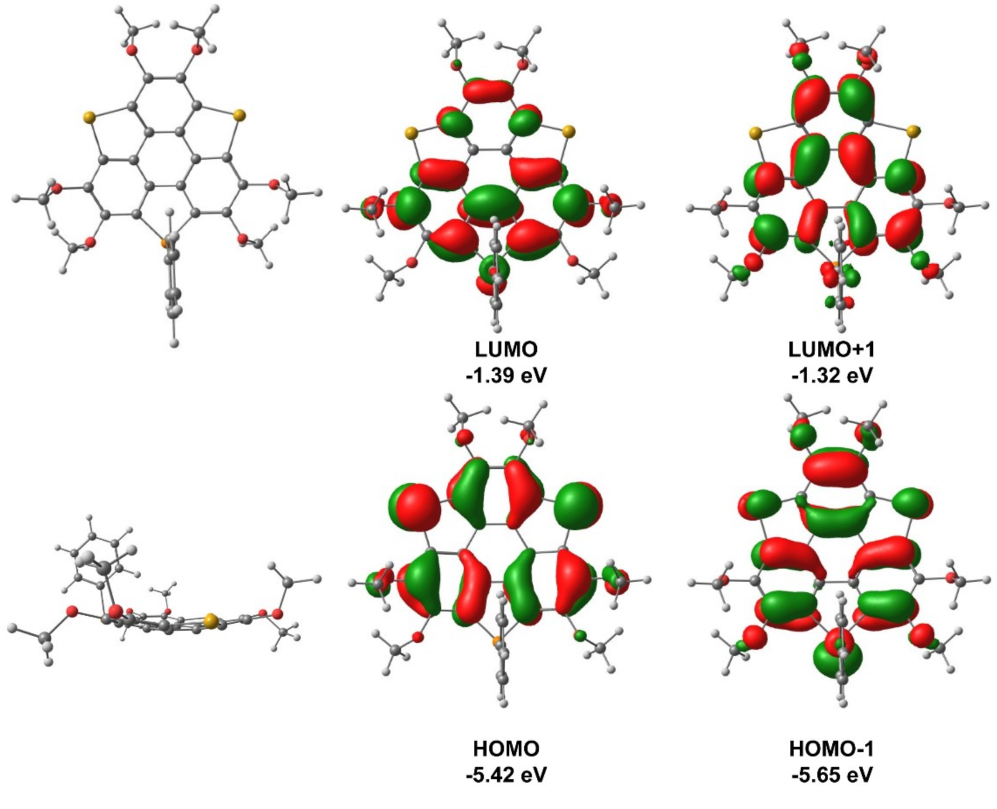


Fig. S28 Calculated molecular orbitals of compound **2’**.

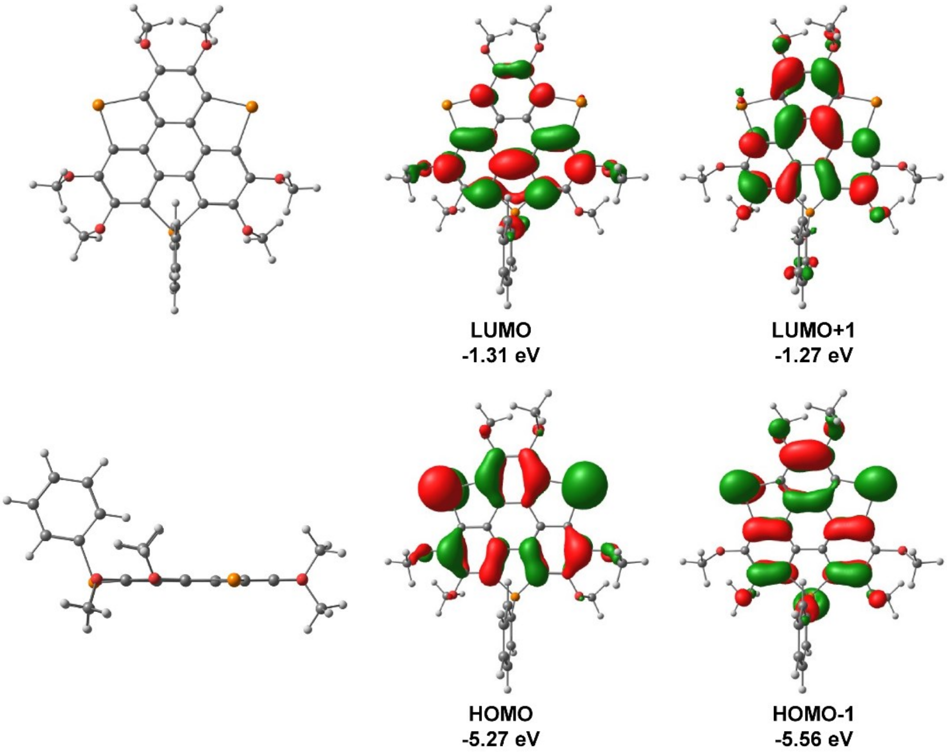


Fig. S29 Calculated molecular orbitals of compound **3’**.

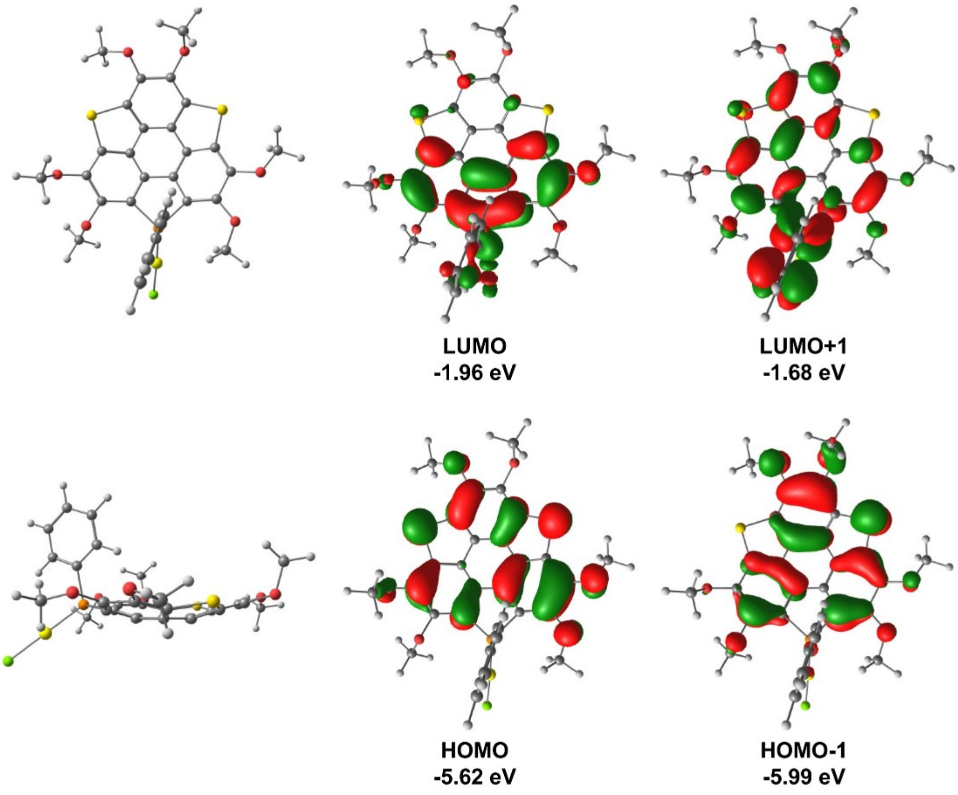


Fig. S30 Calculated molecular orbitals of compound (**1’**)•AuCl.

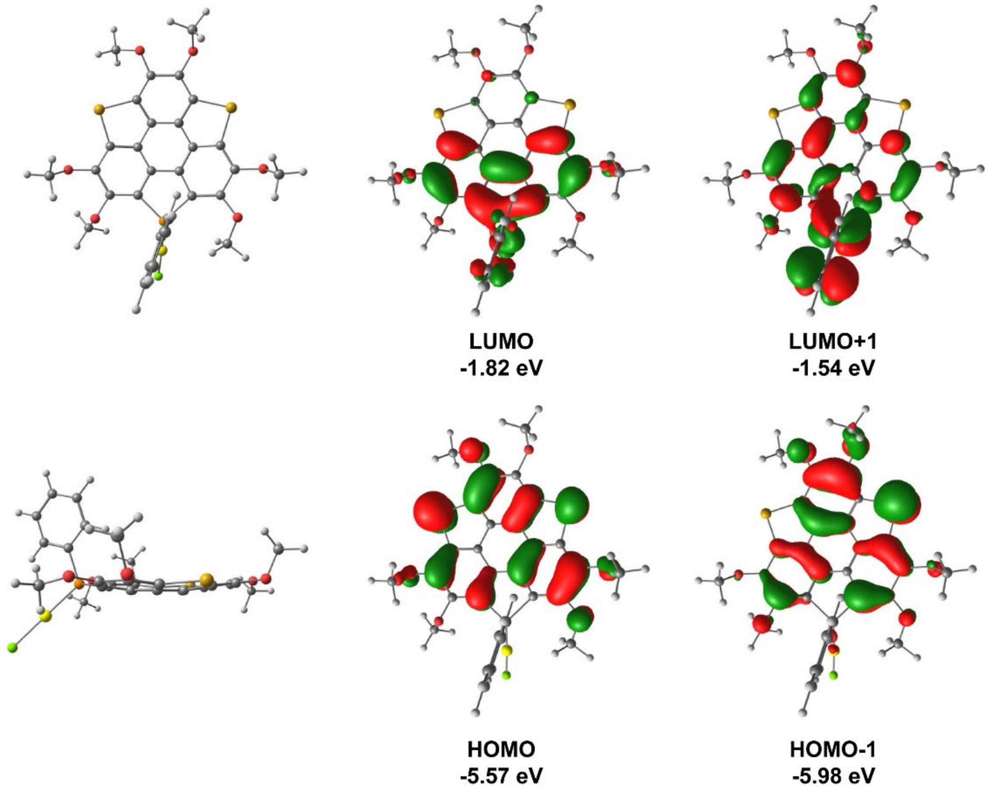


Fig. S31 Calculated molecular orbitals of compound (**2’**)•AuCl.

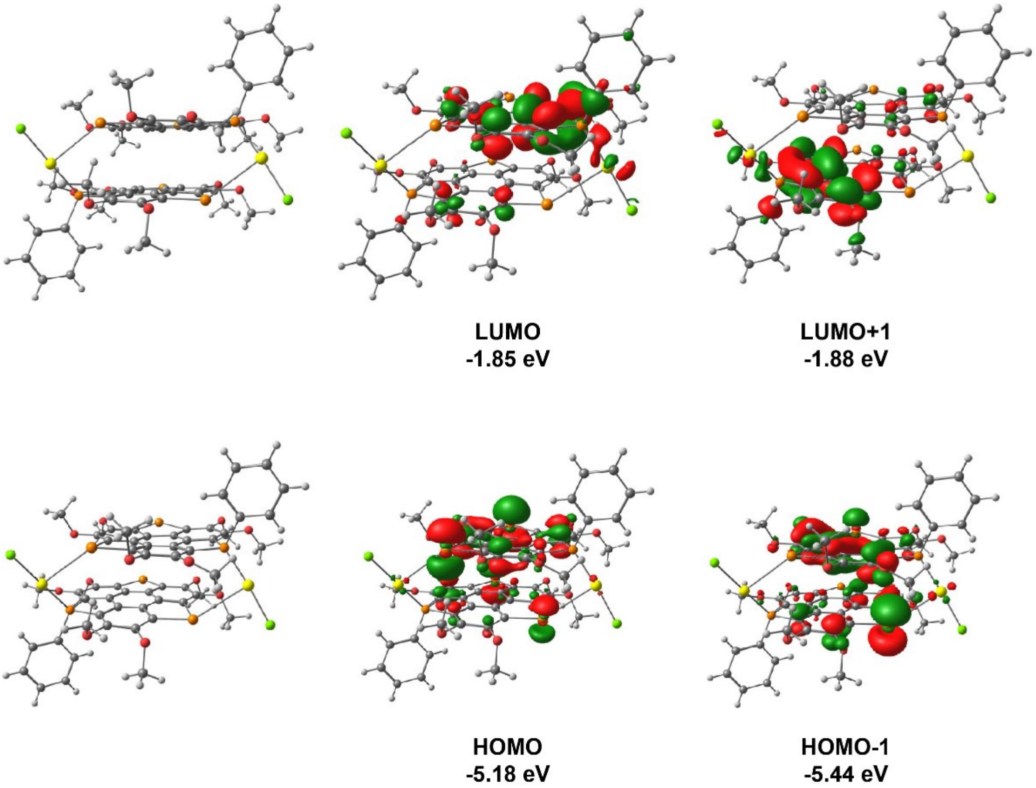


Fig. S32 Calculated molecular orbitals of compound ($\mathbf{3'}$)$_2$•(AuCl)$_2$.

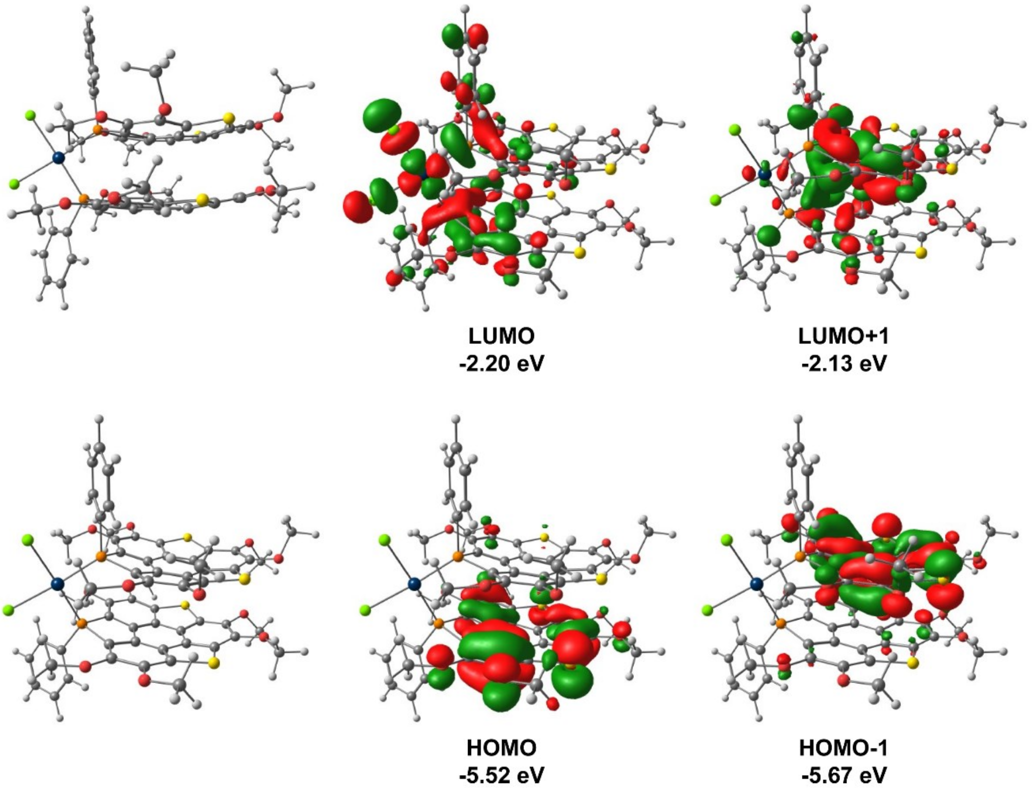


Fig. S33 Calculated molecular orbitals of compound ($\mathbf{1}$')$_2$•PtCl$_2$.

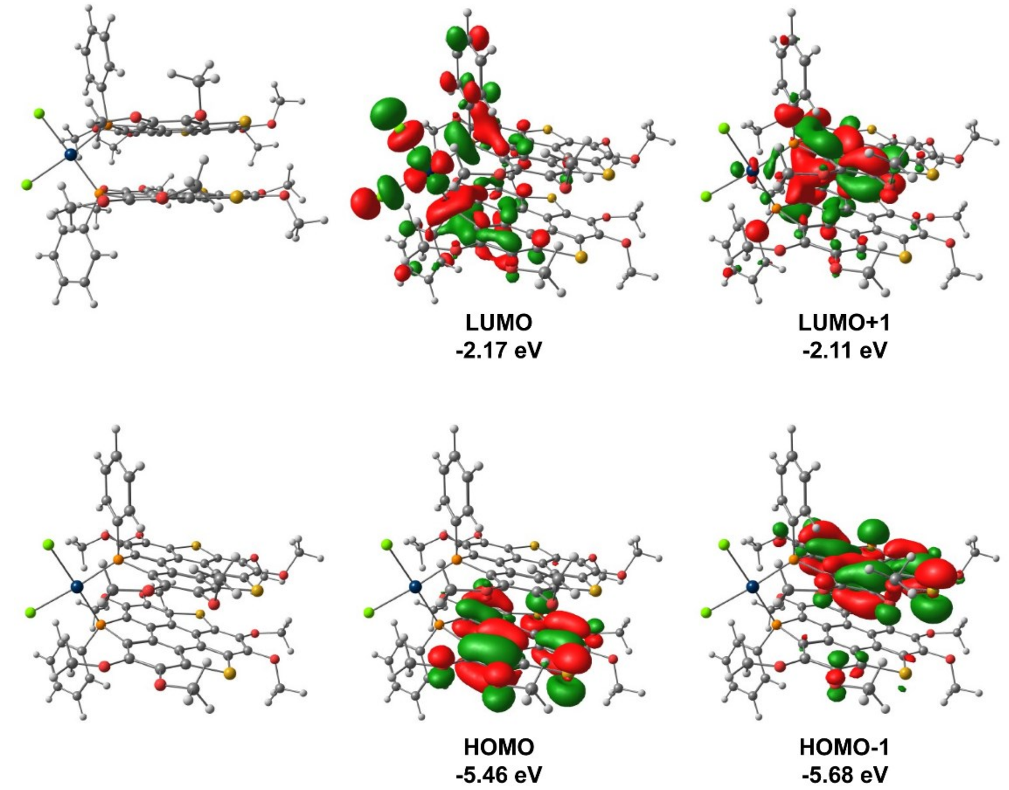


Fig. S34 Calculated molecular orbitals of compound ($\mathbf{2}$')$_2$•PtCl$_2$.

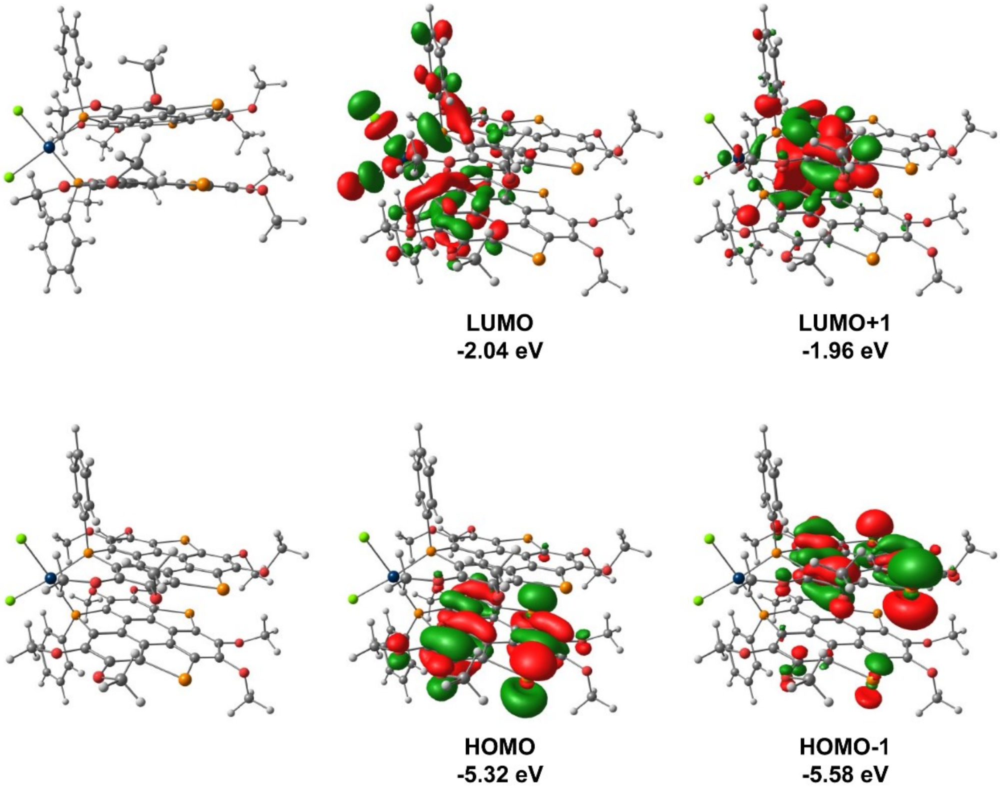


Fig. S35 Calculated molecular orbitals of compound (**3'**)$_2$•PtCl$_2$.

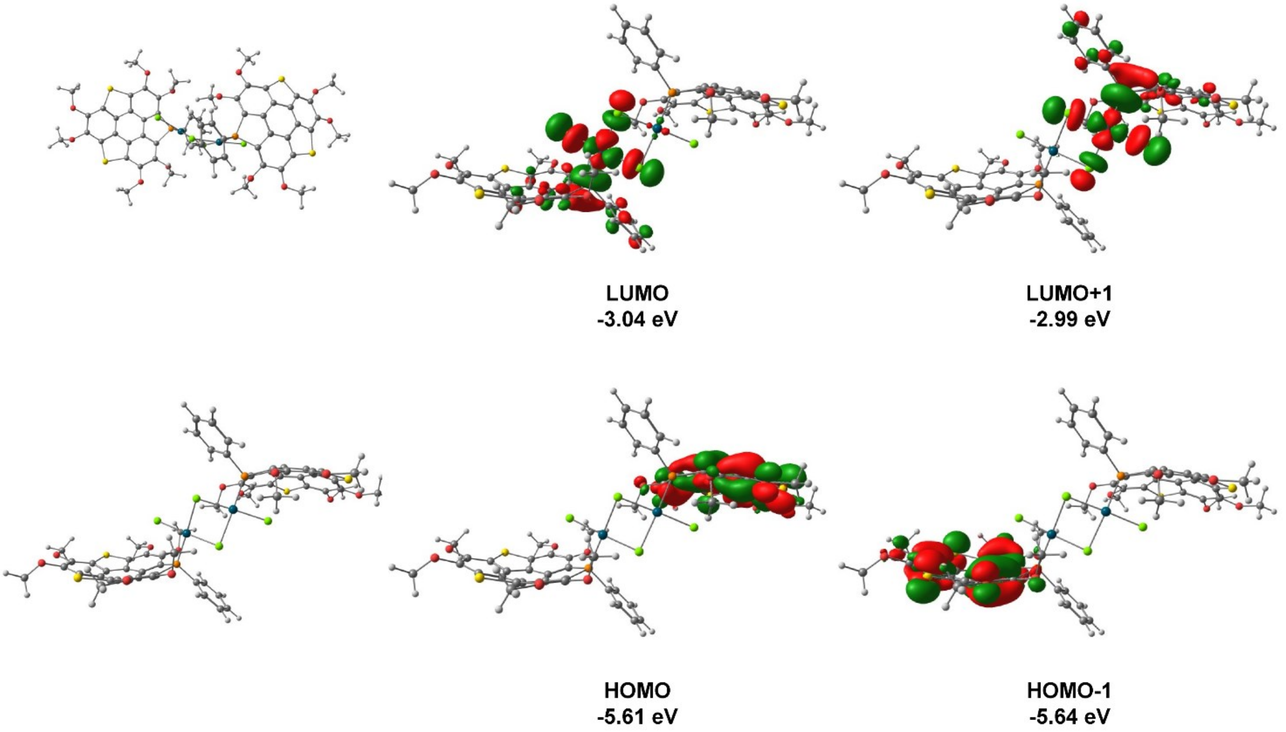
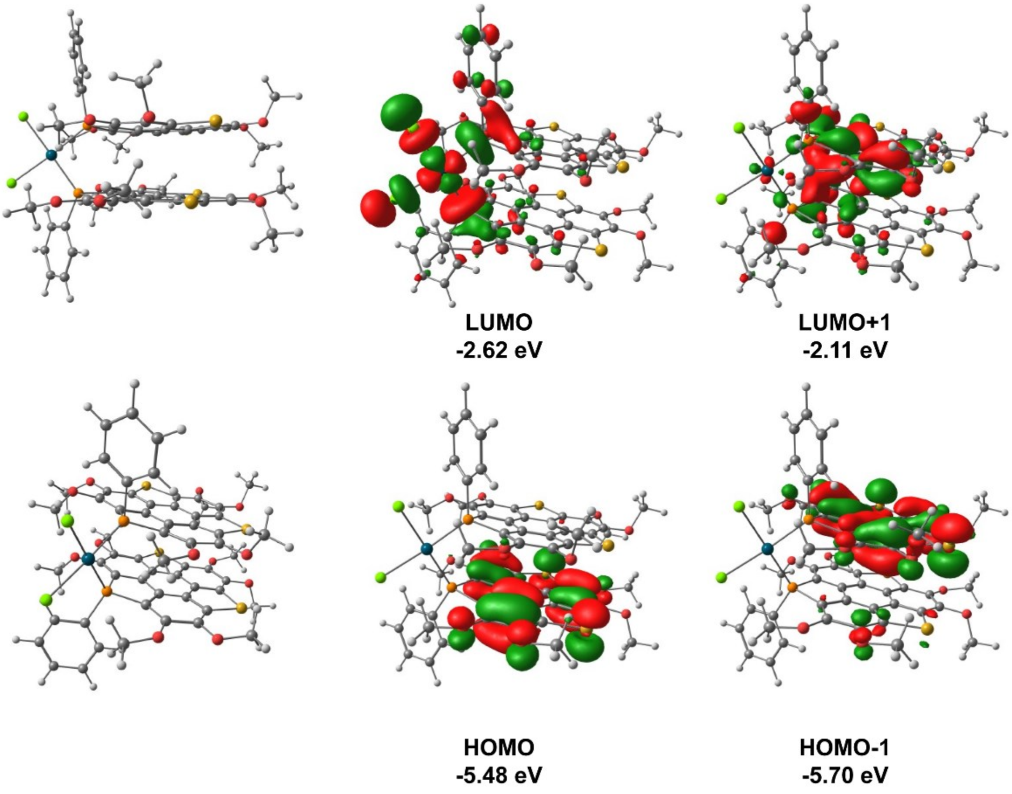


Fig. S36 Calculated molecular orbitals of compound (**1'**)$_2$•(PdCl$_2$)$_2$.



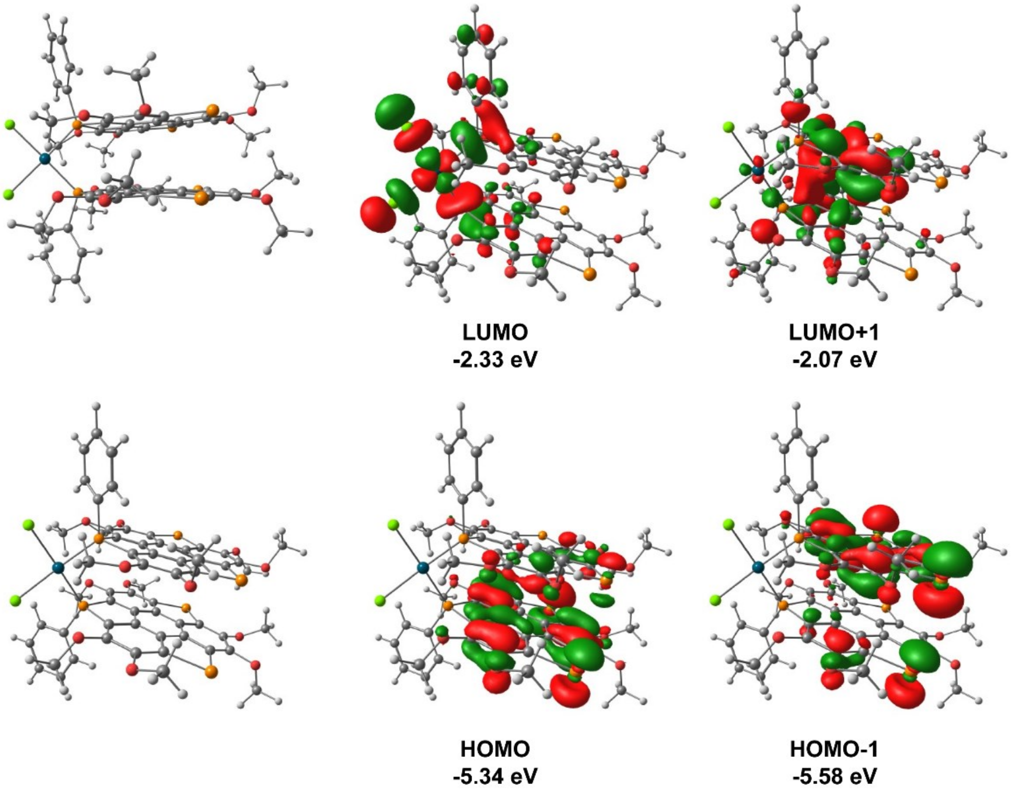
LUMO
-2.62 eV

LUMO+1
-2.11 eV

HOMO
-5.48 eV

HOMO-1
-5.70 eV

Fig. S37 Calculated molecular orbitals of compound (**2’**)$_2$•PdCl$_2$.



LUMO
-2.33 eV

LUMO+1
-2.07 eV

HOMO
-5.34 eV

HOMO-1
-5.58 eV

Fig. S38 Calculated molecular orbitals of compound (**3’**)$_2$•PdCl$_2$.

8.2 Bowl to Bowl Inversion Energy

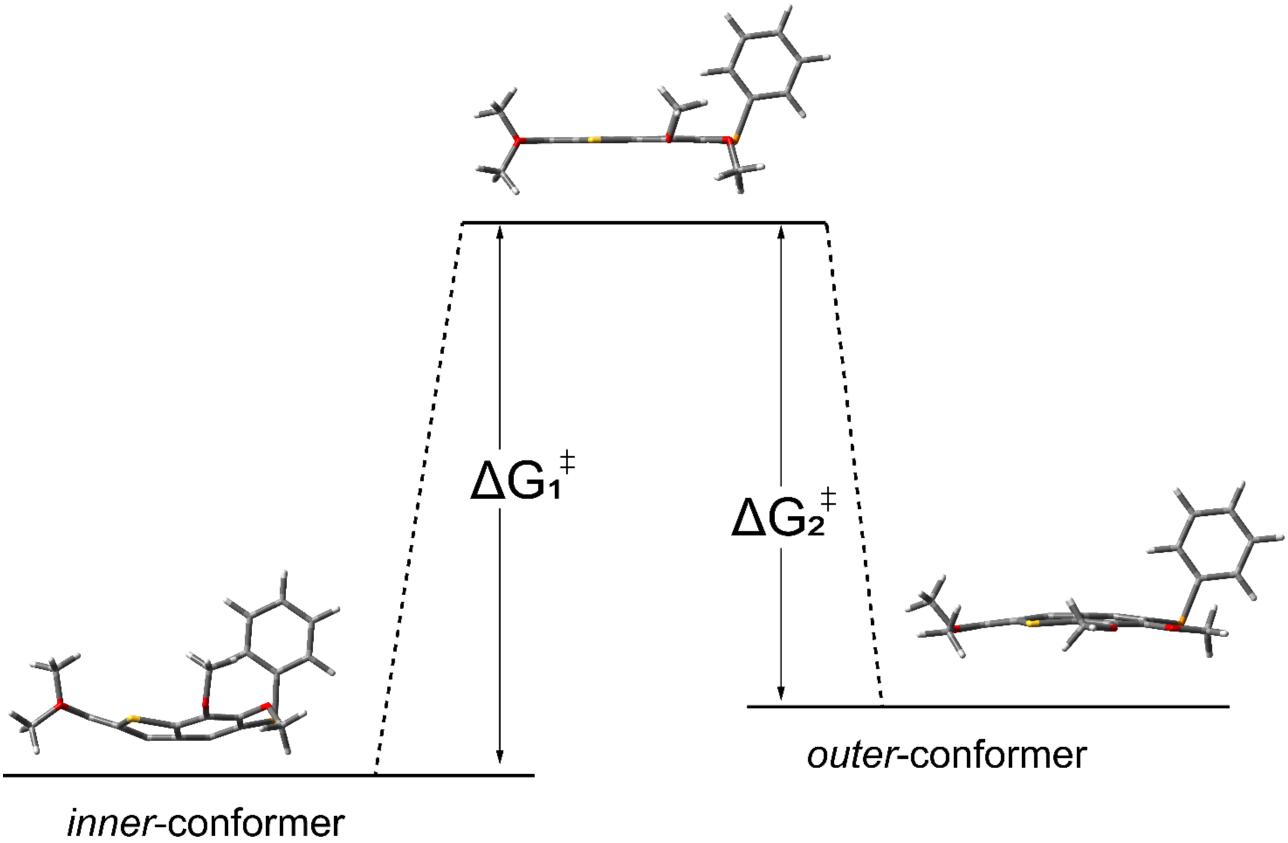
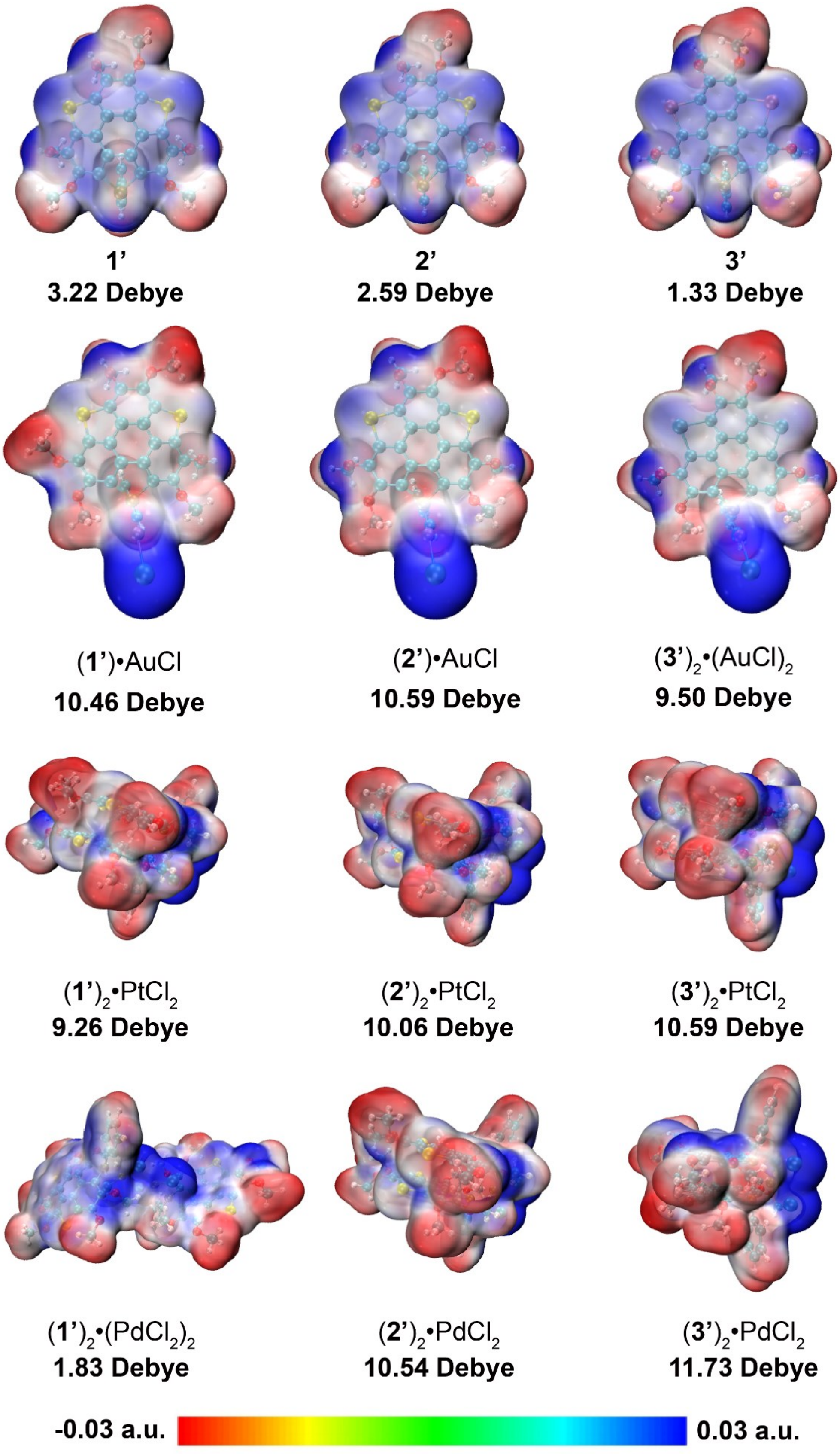


Fig. S39 Bowl-to-bowl inversion energy of **1’** calculated at the B3LYP/def2-TZVP level.

Table S12 Bowl inversion energy of **1’**, (**1’**)•AuCl and (**1’**)•($PdCl_2$)•CH_3CN.

comp.	**conformer**	**inversion energy** **ΔG‡（kcal / mol）**
1’	*inner*	4.44
	outer	2.95
(**1’**)•AuCl	*inner*	7.02
	outer	2.87
(**1’**)•($PdCl_2$)•CH_3CN	*inner*	4.74
	outer	1.81

8.3 Molecular Electrostatic Potential Surfaces and Dipole Moments



1’
3.22 Debye

2’
2.59 Debye

3’
1.33 Debye

(**1’**)•AuCl
10.46 Debye

(**2’**)•AuCl
10.59 Debye

(**3’**)$_2$•(AuCl)$_2$
9.50 Debye

(**1’**)$_2$•PtCl$_2$
9.26 Debye

(**2’**)$_2$•PtCl$_2$
10.06 Debye

(**3’**)$_2$•PtCl$_2$
10.59 Debye

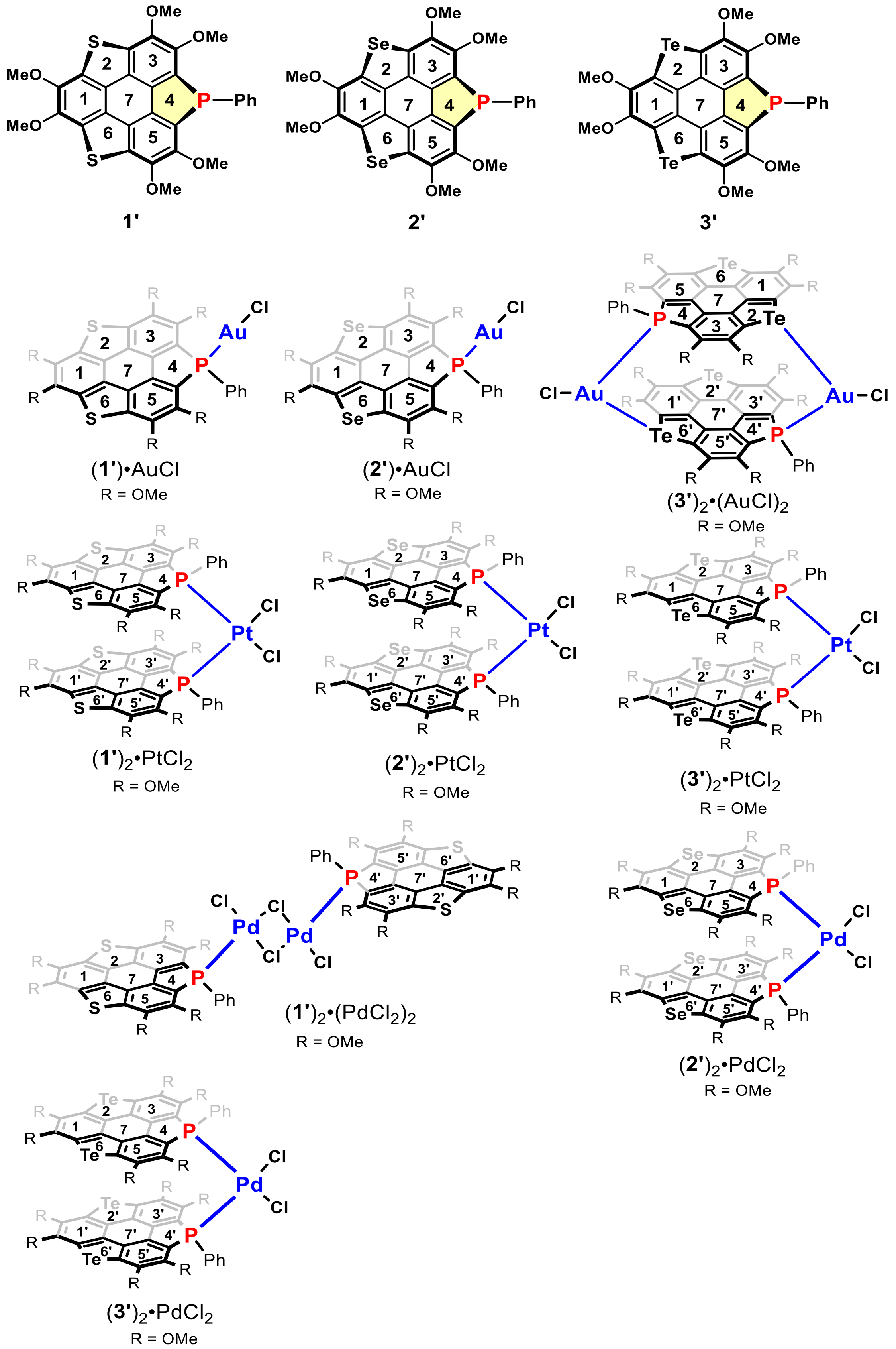
(**1’**)$_2$•(PdCl$_2$)$_2$
1.83 Debye

(**2’**)$_2$•PdCl$_2$
10.54 Debye

(**3’**)$_2$•PdCl$_2$
11.73 Debye

Fig. S40 Calculated electrostatic potential surfaces and dipole moments.

8.4 Aromaticity Calculations



Scheme S6 The chemical structures of calculated compounds (R=OBu).

Table S13 Calculated nucleus independent chemical shift (NICS).

Comp.	1 ring	2 ring	3 ring	4 ring	5 ring	6 ring	7 ring
1’	-12.74	-5.72	-11.44	1.47	-11.45	-5.87	-0.51
2’	-12.25	-4.80	-11.10	1.61	-11.13	-4.91	-1.12
3’	-11.54	-4.05	-10.66	1.45	-10.67	-4.08	-1.49
(**1’**)•AuCl	-12.49	-5.15	-9.73	2.18	-11.06	-5.71	-2.02
(**2’**)•AuCl	-11.99	-4.05	-9.76	2.56	-10.72	-4.68	-2.35
(**3’**)$_2$•(AuCl)$_2$	-12.14	-4.85	-11.43	2.00	-10.13	-5.28	-3.99
(**1’**)$_2$•PtCl$_2$	-13.99	-7.36	-12.70	0.48	-12.34	-6.68	-4.94
(**2’**)$_2$•PtCl$_2$	-13.43	-6.52	-12.09	1.08	-11.76	-5.54	-4.62
(**3’**)$_2$•PtCl$_2$	-12.44	-5.72	-11.43	1.03	-11.18	-4.60	-4.37
(**1’**)$_2$•(PdCl$_2$)$_2$	-12.35	-5.24	-10.21	2.04	-10.17	-5.54	-1.92
(**2’**)$_2$•PdCl$_2$	-13.46	-6.55	-12.08	0.95	-11.72	-5.54	-4.64
(**3’**)$_2$•PdCl$_2$	-12.44	-5.97	-11.90	1.28	-10.25	-4.57	-3.92

Table S14 Calculated nucleus independent chemical shift (NICS).

Comp.	1’ ring	2’ ring	3’ ring	4’ ring	5’ ring	6’ ring	7’ ring
(**3’**)$_2$•(AuCl)$_2$	-13.14	-4.51	-10.19	1.95	-10.94	-5.42	-3.30
(**1’**)$_2$•PtCl$_2$	-14.15	-6.46	-10.45	1.75	-12.44	-7.27	-4.17
(**2’**)$_2$•PtCl$_2$	-13.47	-5.49	-10.09	1.47	-12.31	-6.98	-4.31
(**3’**)$_2$•PtCl$_2$	-12.44	-4.42	-9.52	1.33	-11.86	-6.09	-4.37
(**1’**)$_2$•(PdCl$_2$)$_2$	-12.35	-5.26	-10.27	2.01	-10.18	-5.54	-1.83
(**2’**)$_2$•PdCl$_2$	-13.48	-7.01	-12.33	1.18	-10.07	-5.47	-4.36
(**3’**)$_2$•PdCl$_2$	-12.57	-5.89	-11.27	0.96	-11.18	-4.65	-4.30

9. References

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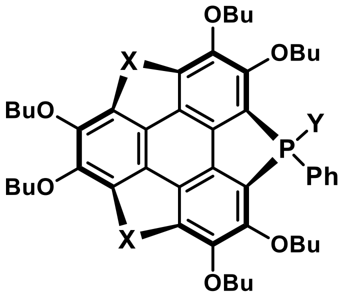
10. ^{1}H NMR, ^{31}P NMR, C NMR, IR Spectra of Products

10.1 ^{31}P NMR of P^{III}-doped heterasumanenes and their coordination complexes

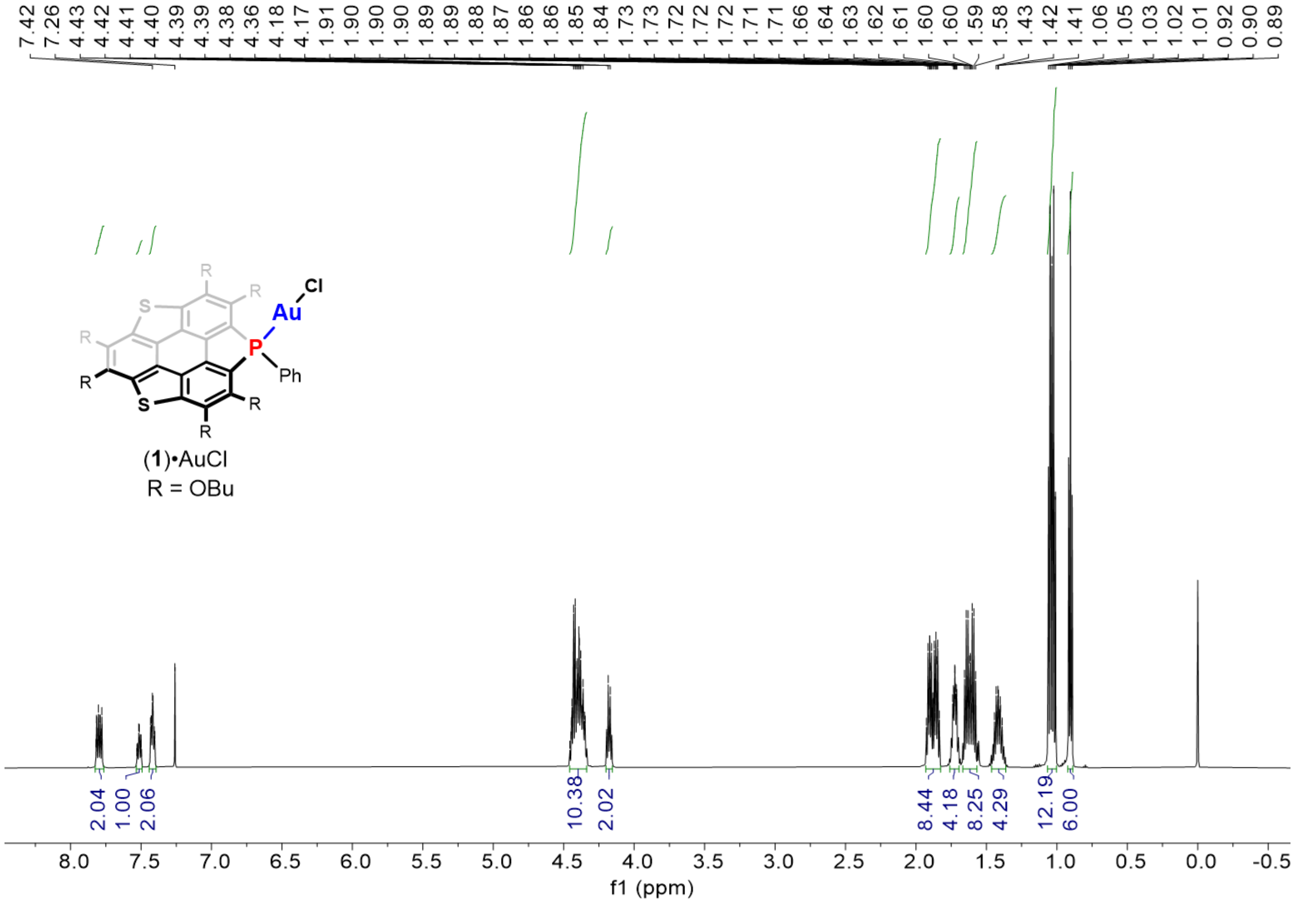


1 : X = S; Y= lone pair
2 : X = Se; Y= lone pair
3 : X = Te; Y= lone pair

	1	(**1'**)•AuCl	(**1**)$_2$•(PdCl$_2$)$_2$	(**1**)$_2$•PtCl$_2$
	Y = lone pair	Y = Au	Y = Pd	Y = Pt
^{31}P NMR (ppm)	21.48	41.32	50.94	31.61

	2	(**2'**)•AuCl	(**2**)$_2$•PdCl$_2$	(**2**)$_2$•PtCl$_2$
	Y = lone pair	Y = Au	Y = Pd	Y = Pt
^{31}P NMR (ppm)	23.10	42.92	47.29	27.11

	3	(**3'**)$_2$•(AuCl)$_2$	(**3**)$_2$•PdCl$_2$	(**3**)$_2$•PtCl$_2$
	Y = lone pair	Y = Au	Y = Pd	Y = Pt
^{31}P NMR (ppm)	14.09	36.72	39.47	19.80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1.60
1.59
1.58
1.43
1.42
1.41
1.06
1.05
1.03
1.02
1.01
0.92
0.90
0.89
R
S
Au
Cl
P
Ph
(1)•AuCl
R = OBu
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1.00
2.06
10.38
2.02
8.44
4.18
8.25
4.29
12.19
6.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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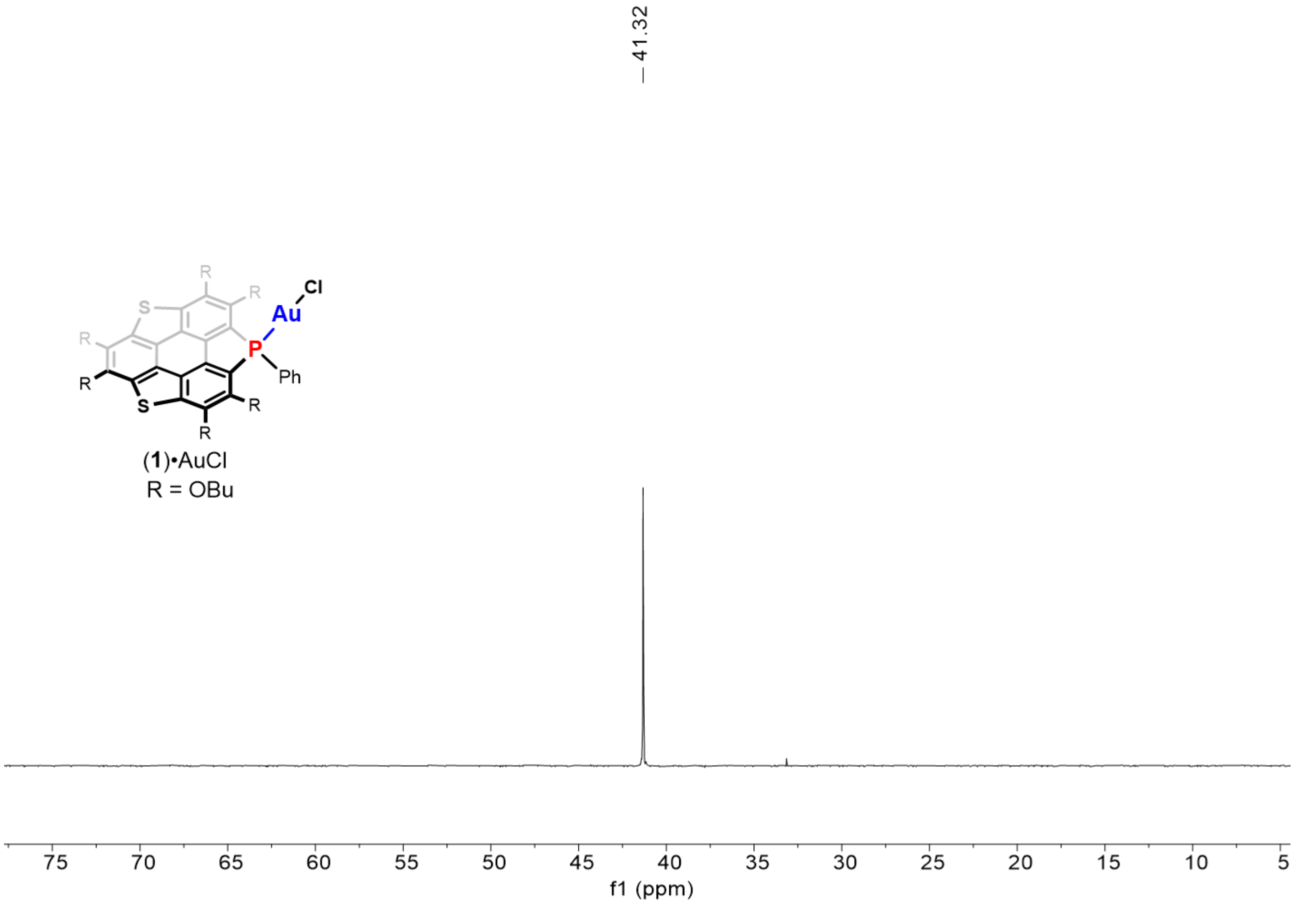
f1 (ppm)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Au
Cl
P
Ph
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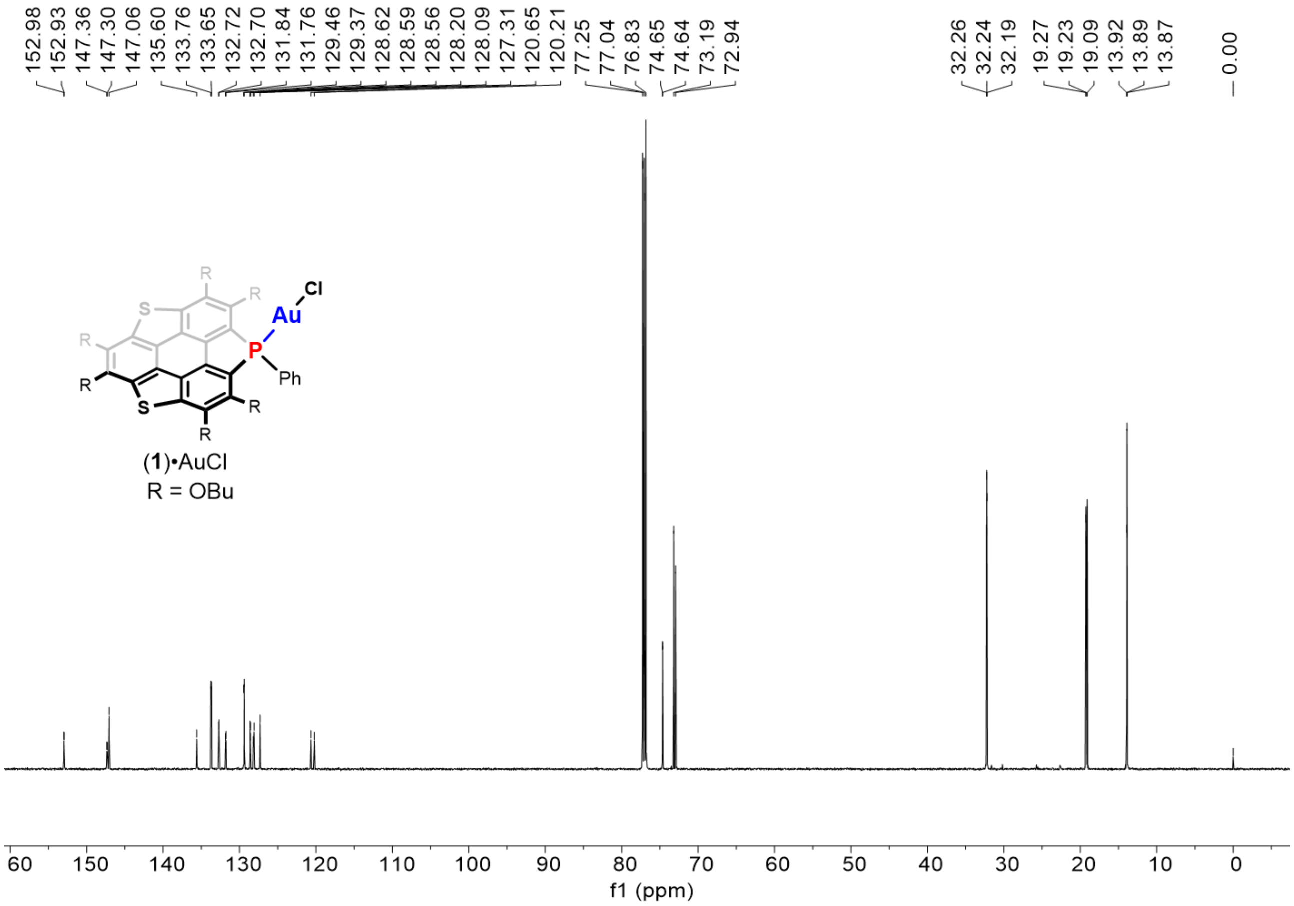
f1 (ppm)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73.19
72.94
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32.19
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19.23
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R = OBu
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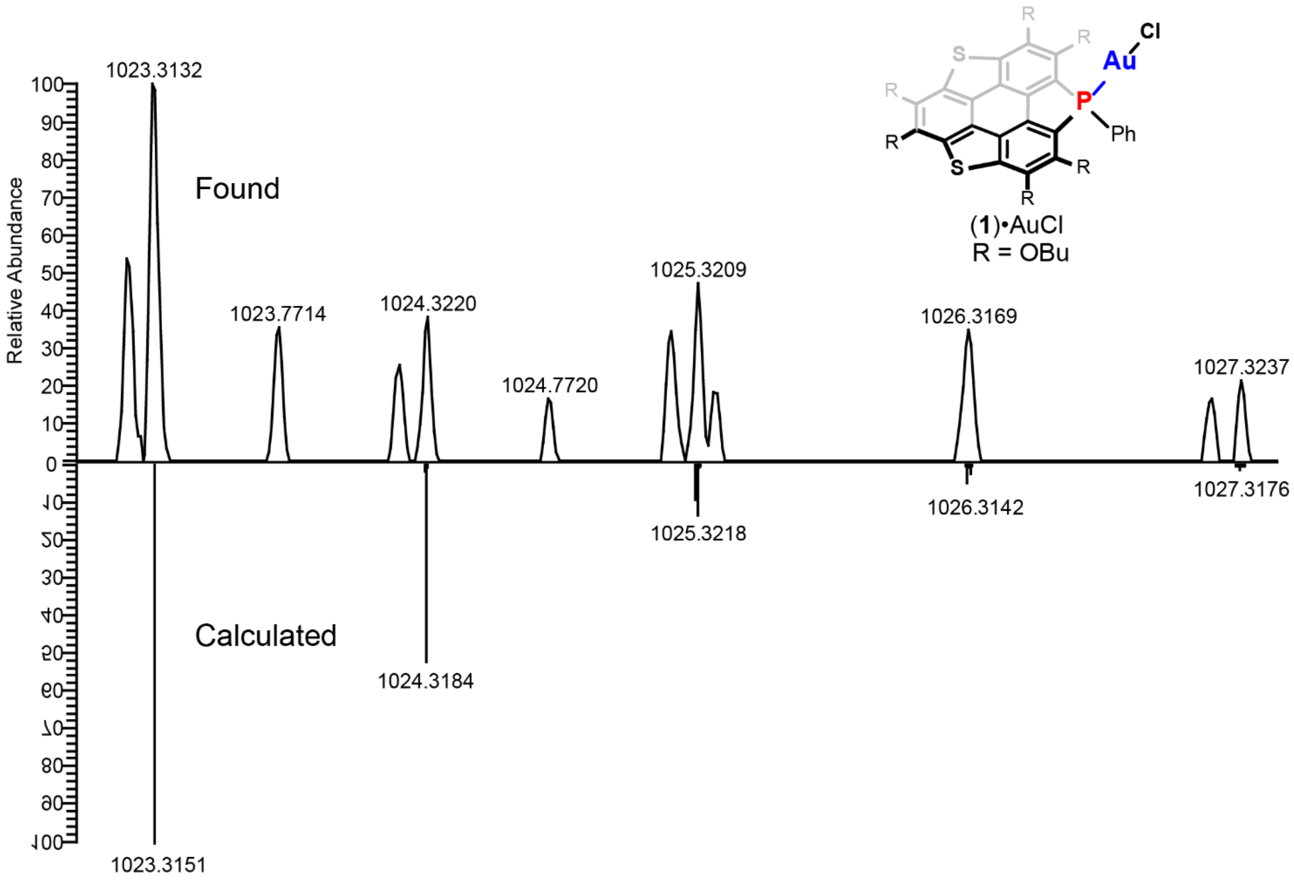
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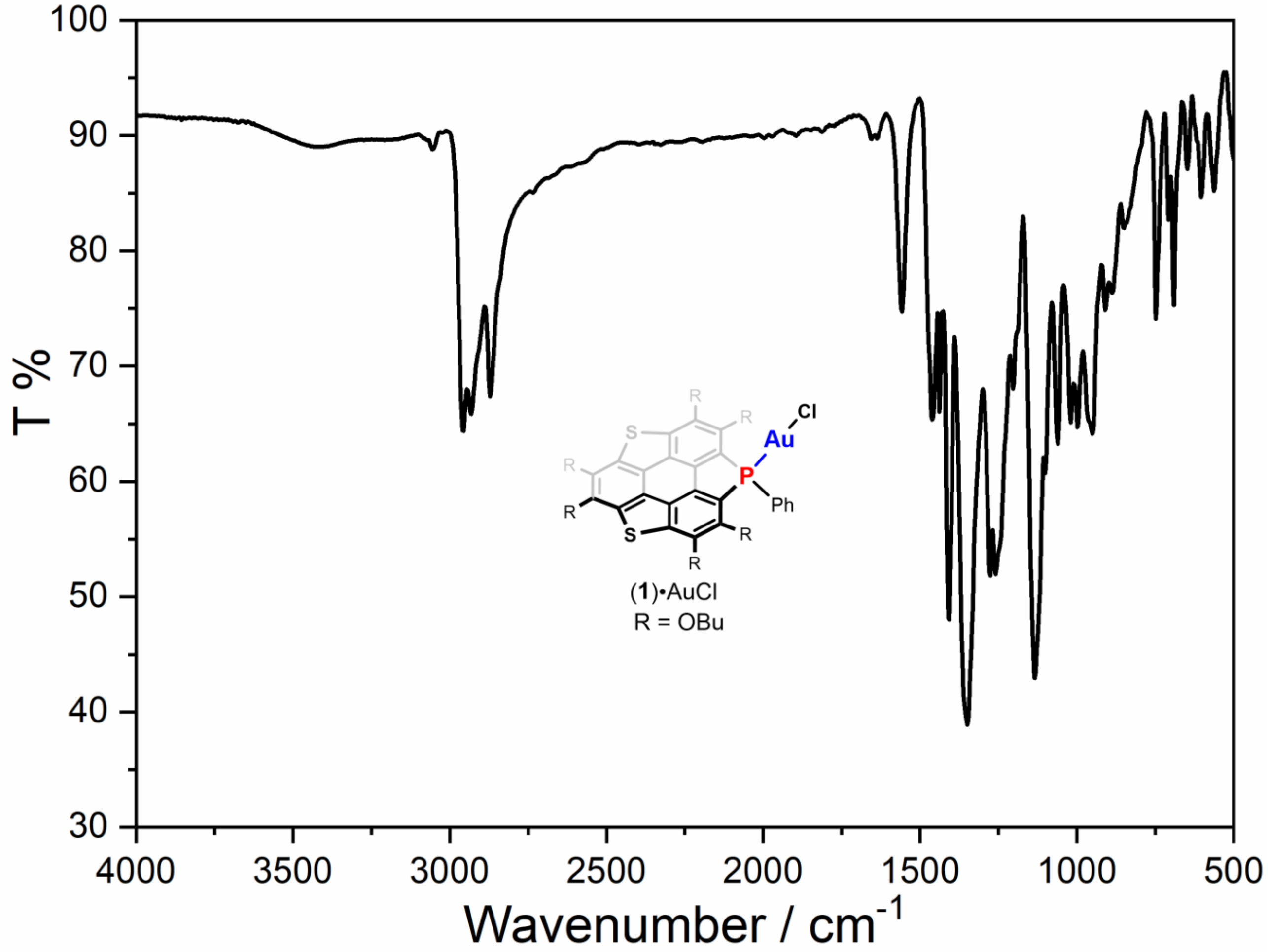
R = OBu



(**1**)•AuCl
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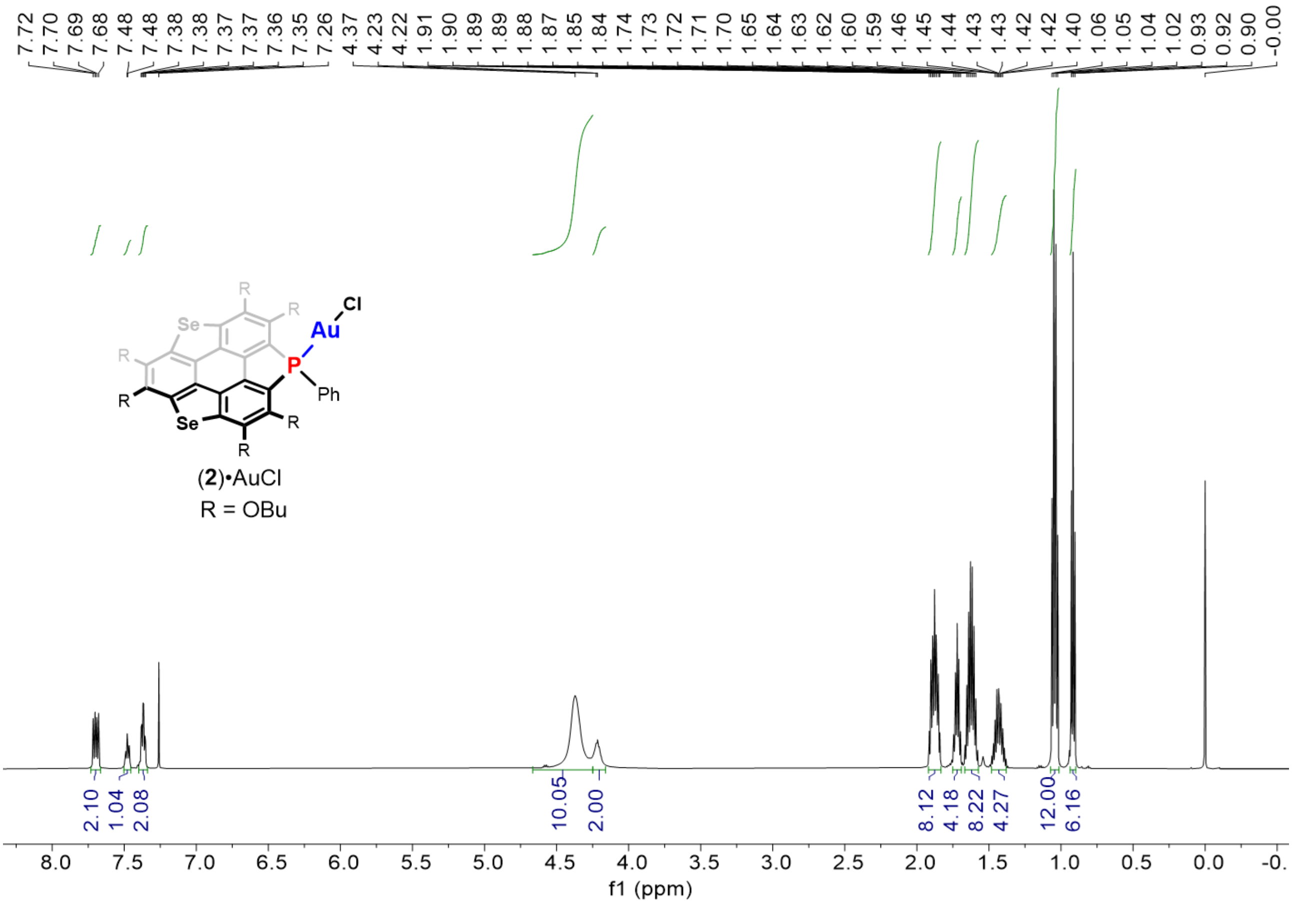

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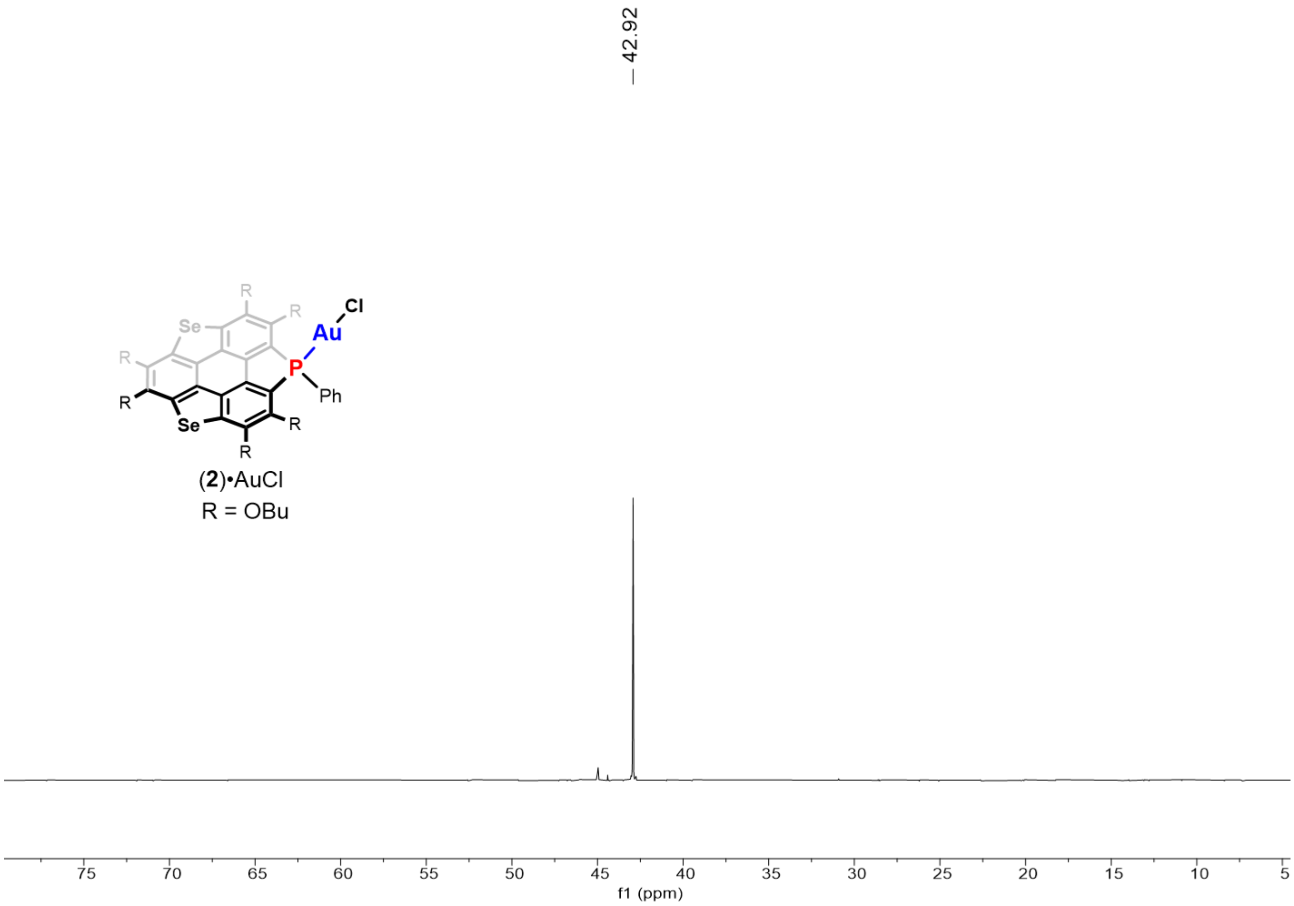
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P
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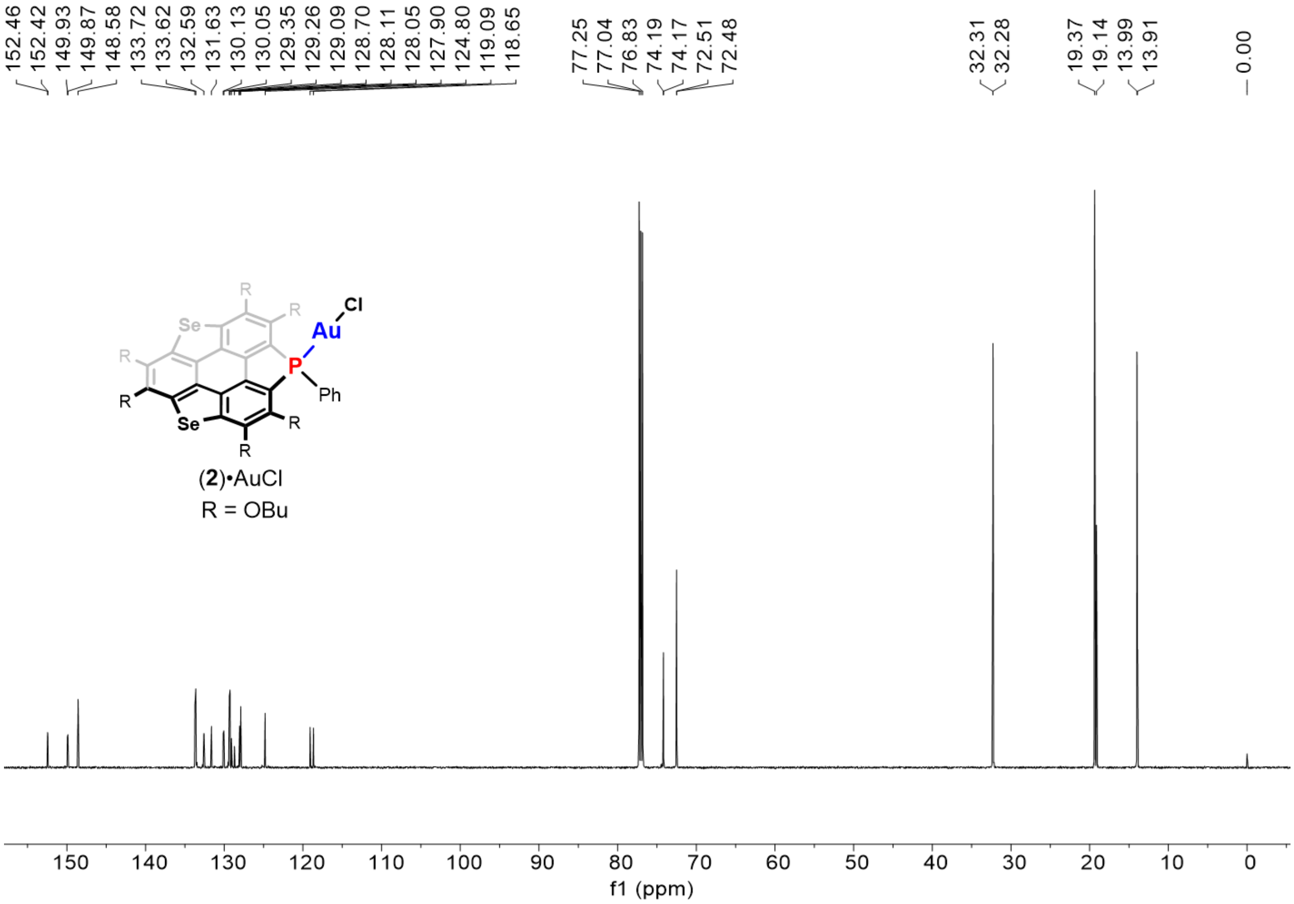
f1 (ppm)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32.31
32.28
19.37
19.14
13.99
13.91
0.00
Se
Se
R
Au
Cl
P
Ph
(2)•AuCl
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90
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50
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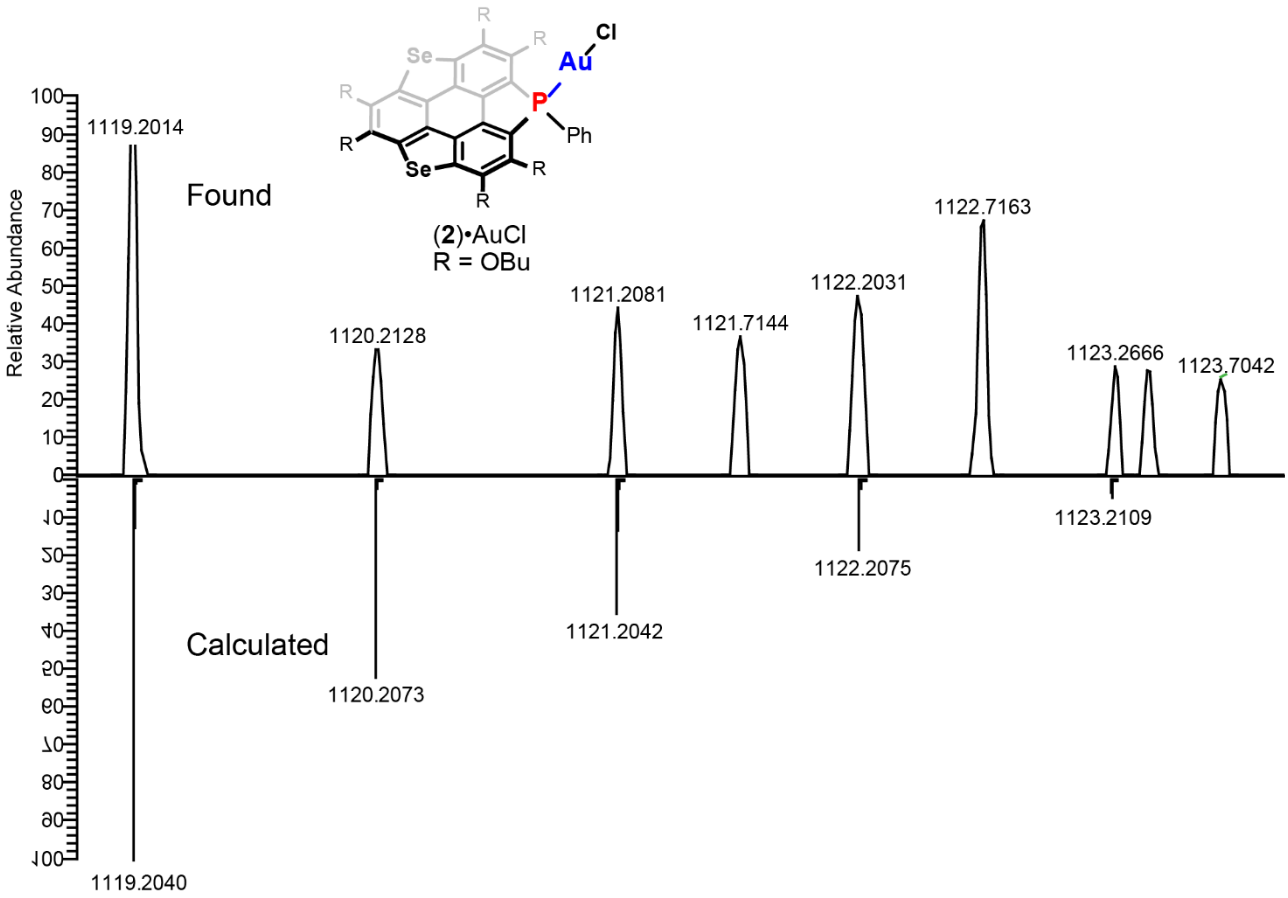
f1 (ppm)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1122.2075
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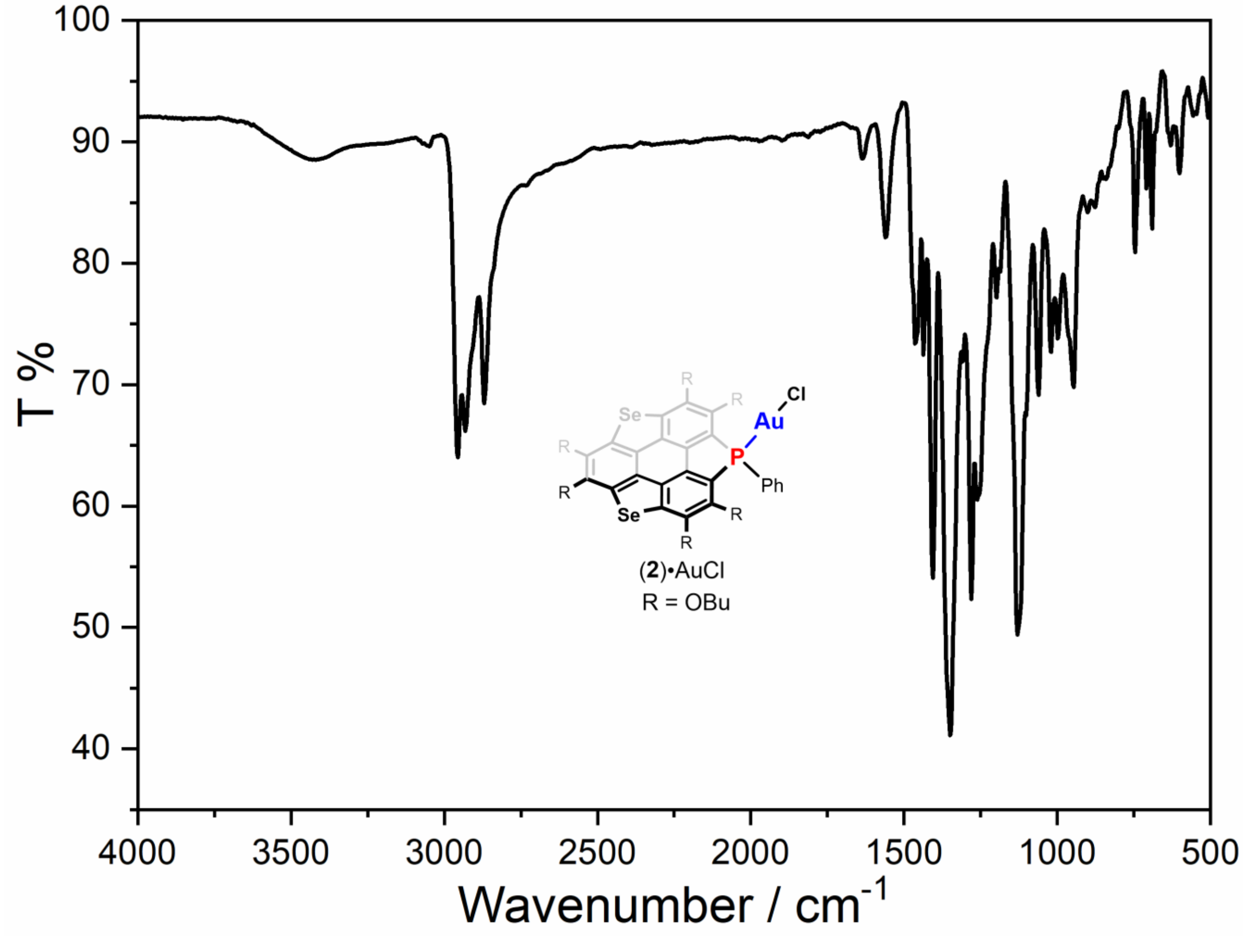
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R
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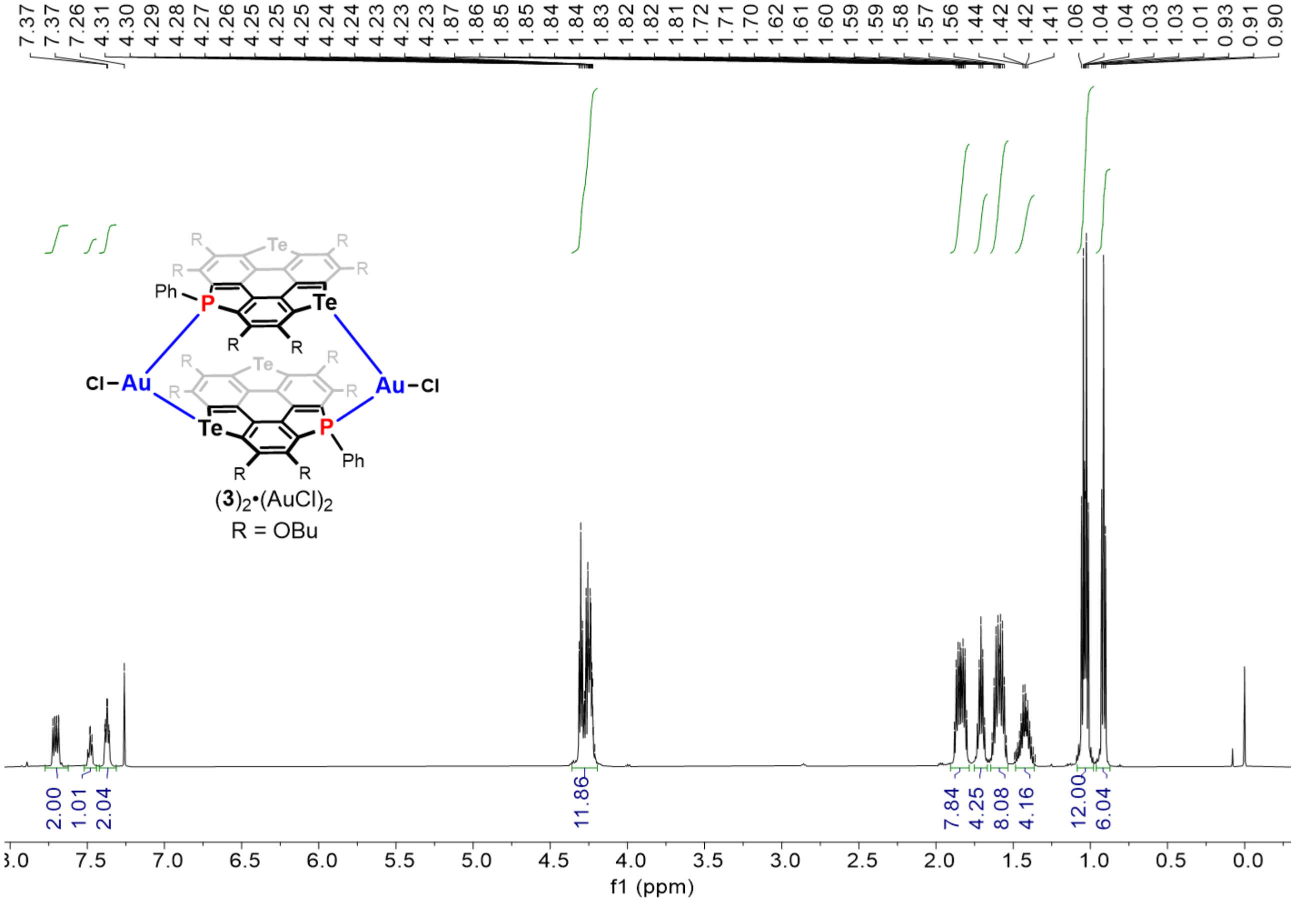
Cl
P
Ph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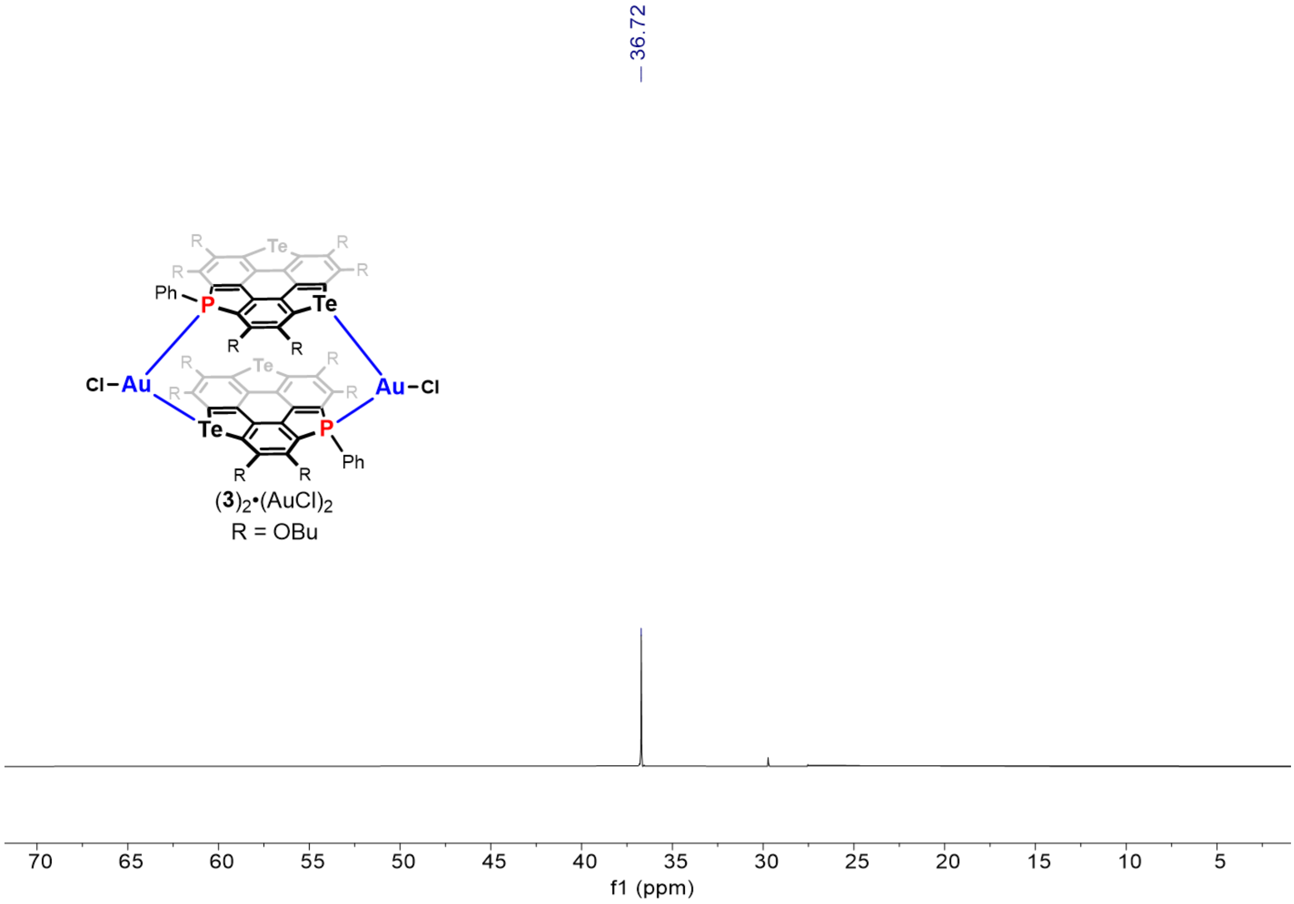
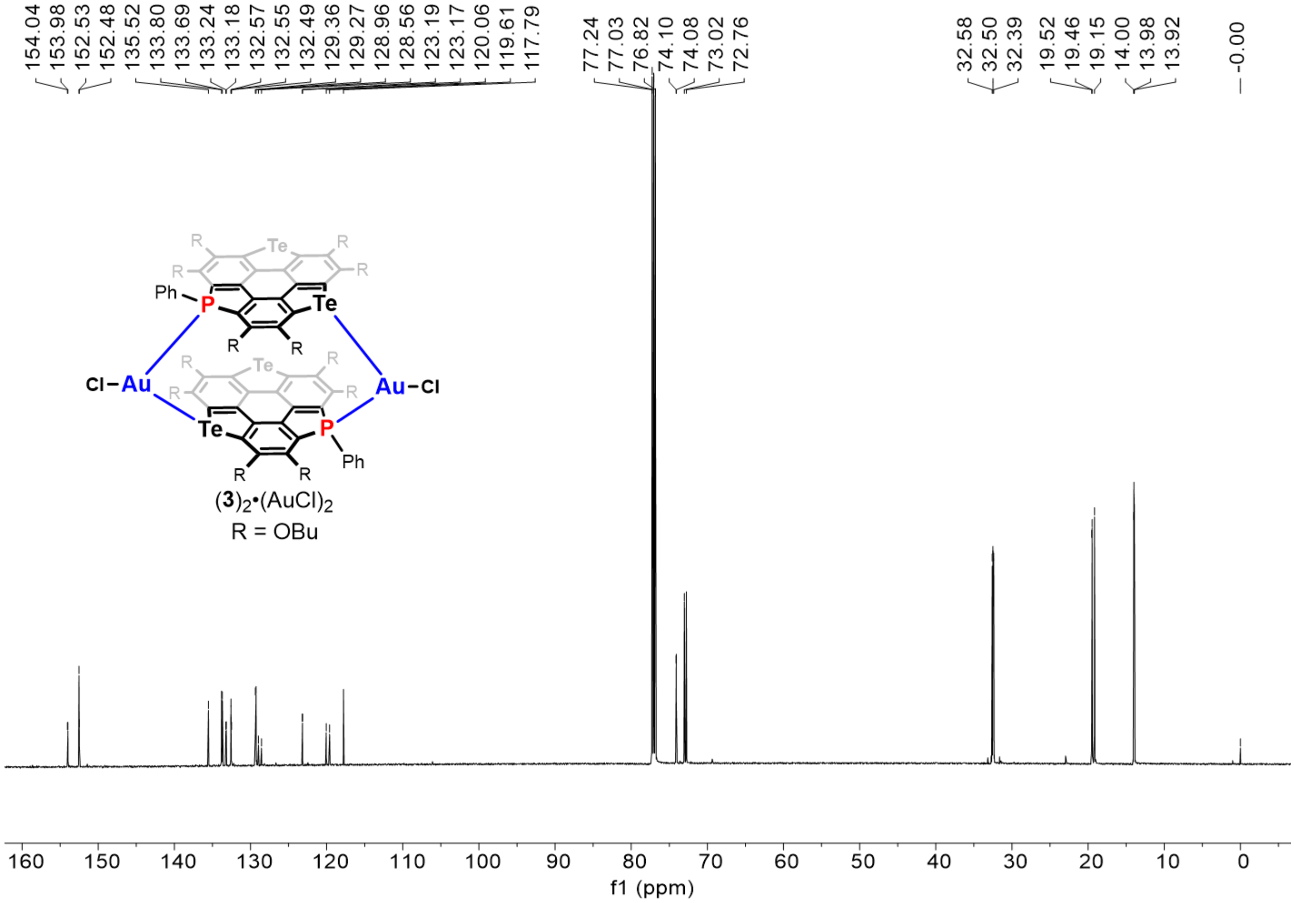
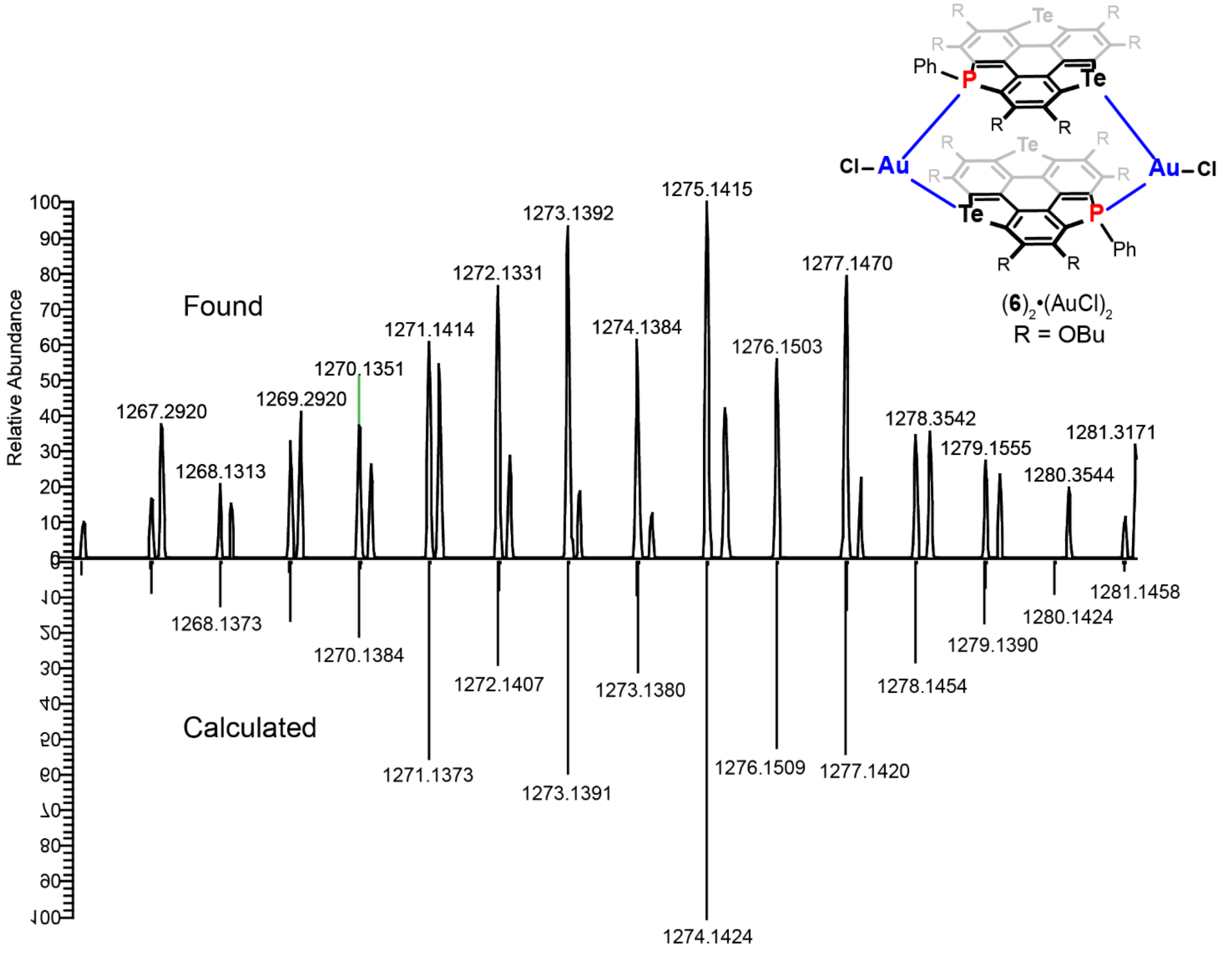
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

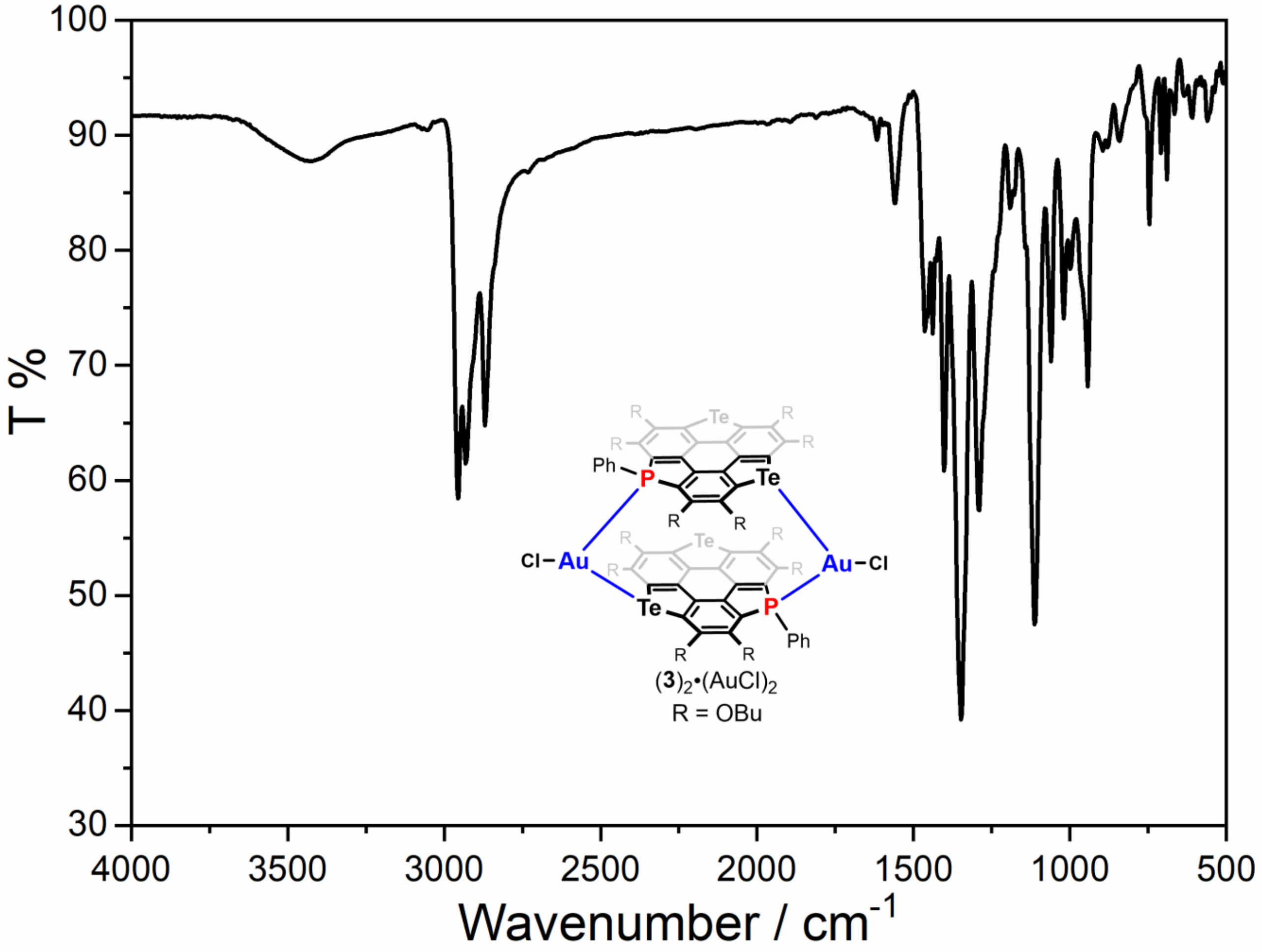

36.72
Ph
P
Te
Te
R
Cl
Au
Au
Cl
(3)2•(AuCl)2
R = OBu
70
65
60
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)

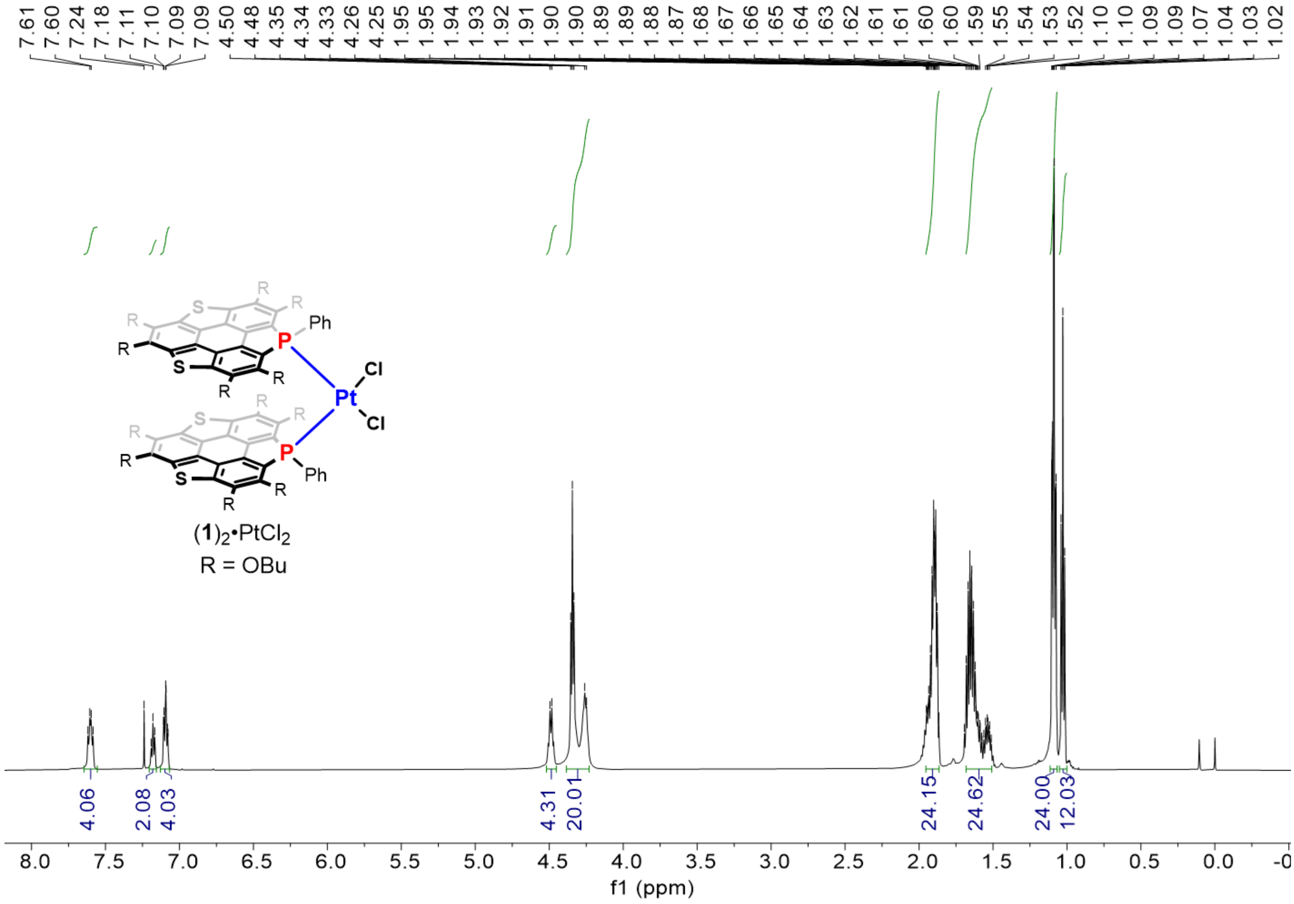


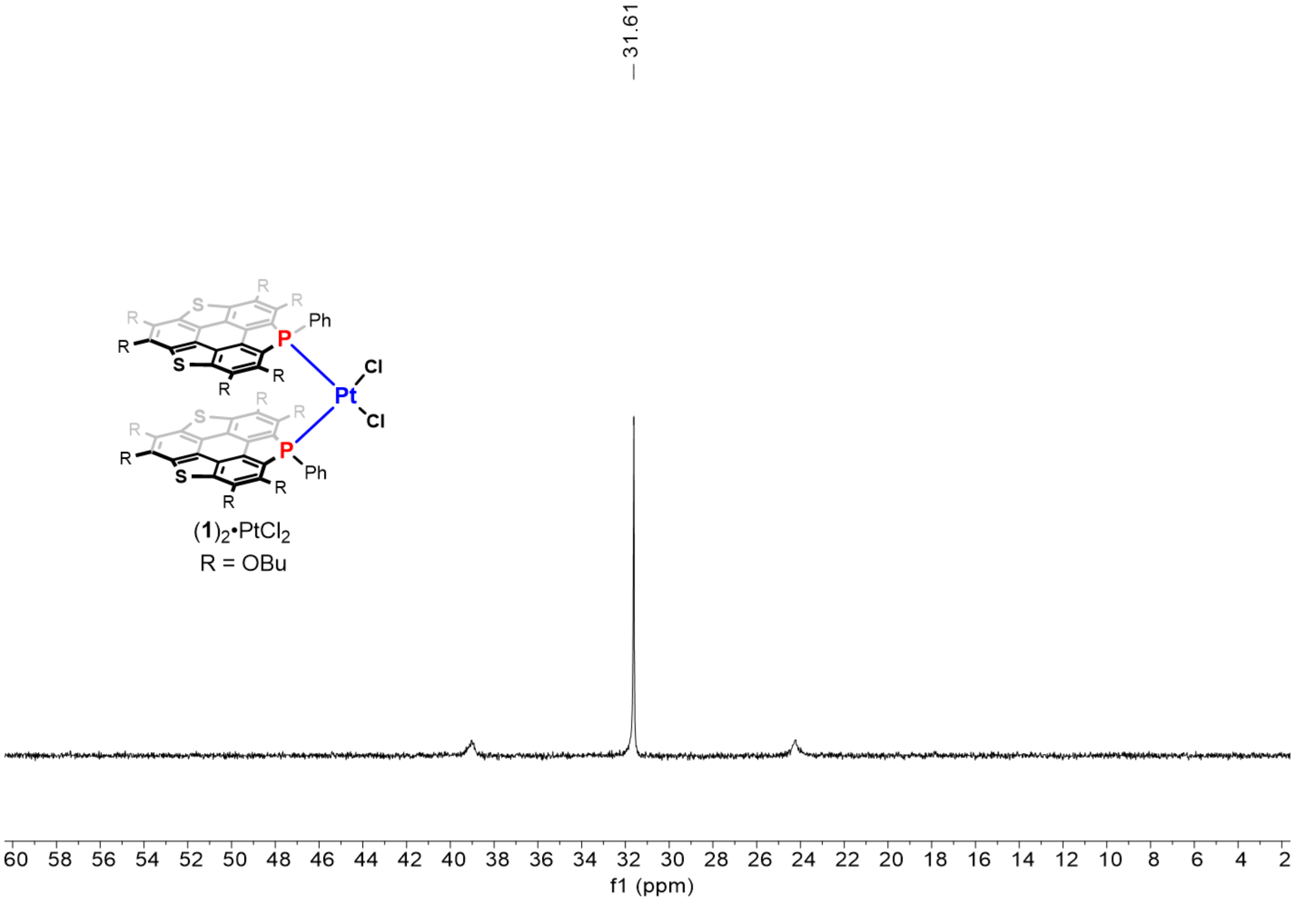
($\mathbf{3}$)$_2$•(AuCl)$_2$
R = OBu

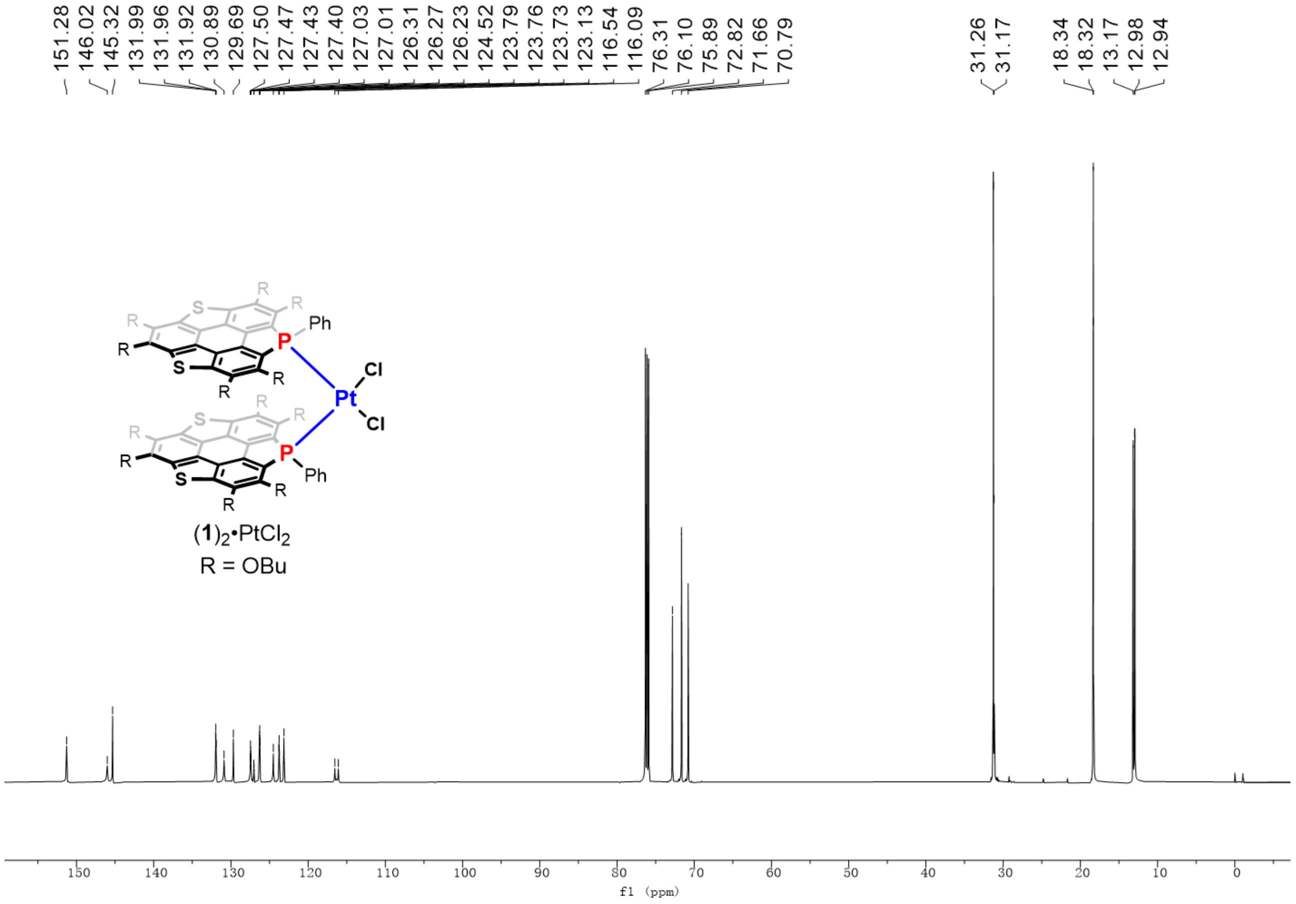


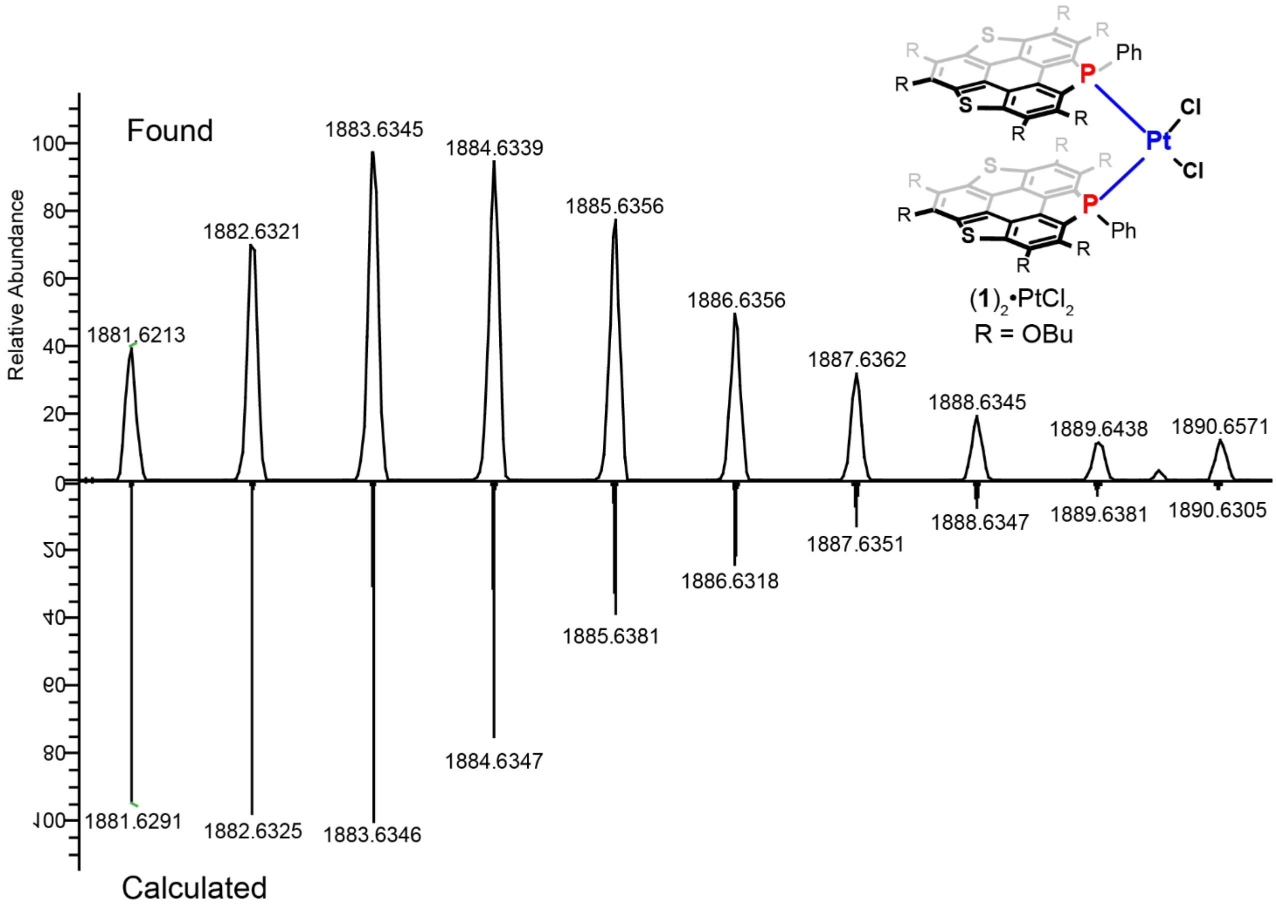
($\mathbf{6}$)$_2$•(AuCl)$_2$
R = OBu

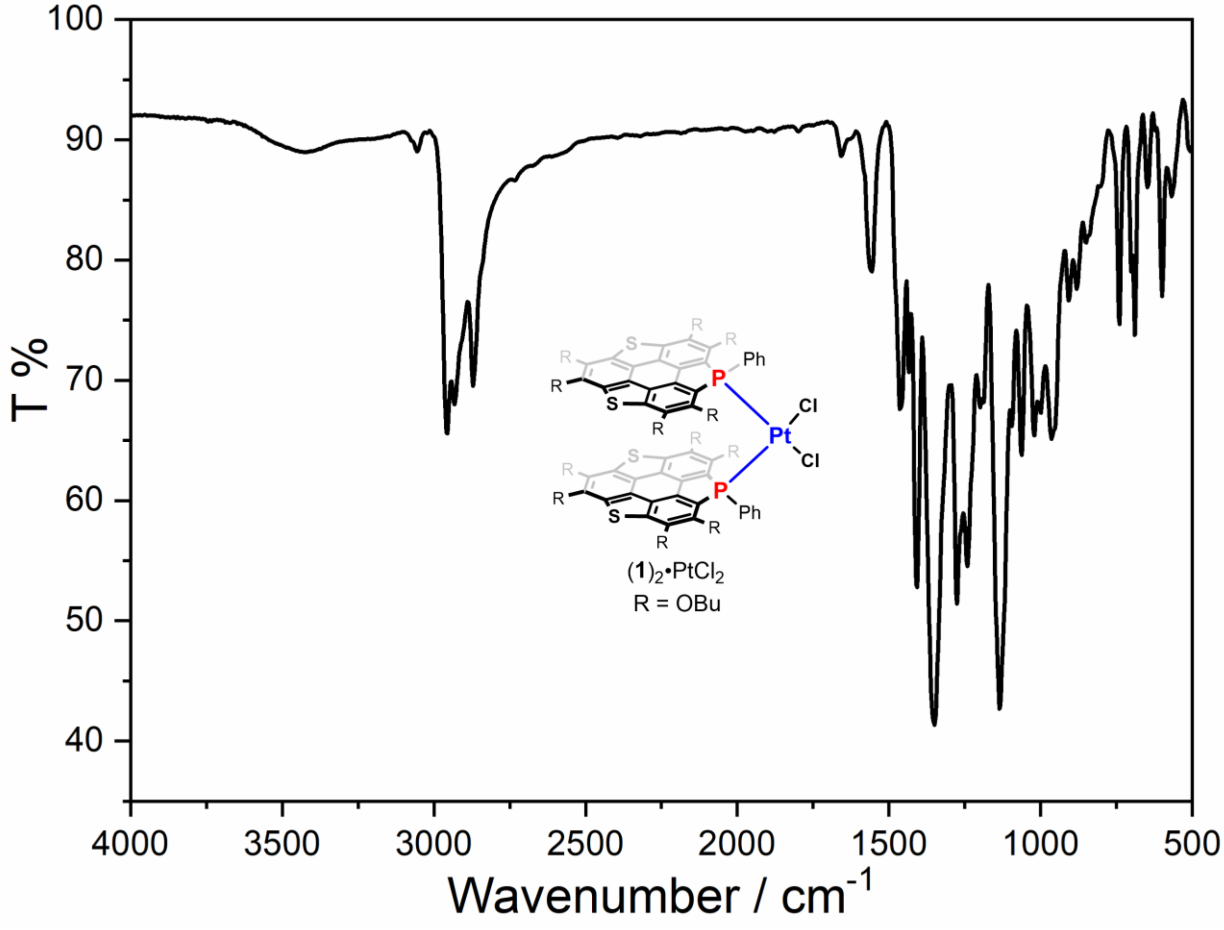

T %
100
90
80
70
60
50
40
30
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber / cm^{-1}
Ph
P
Te
R
Au
Cl
$(\mathbf{3})_2$•$(AuCl)_2$
R = OBu

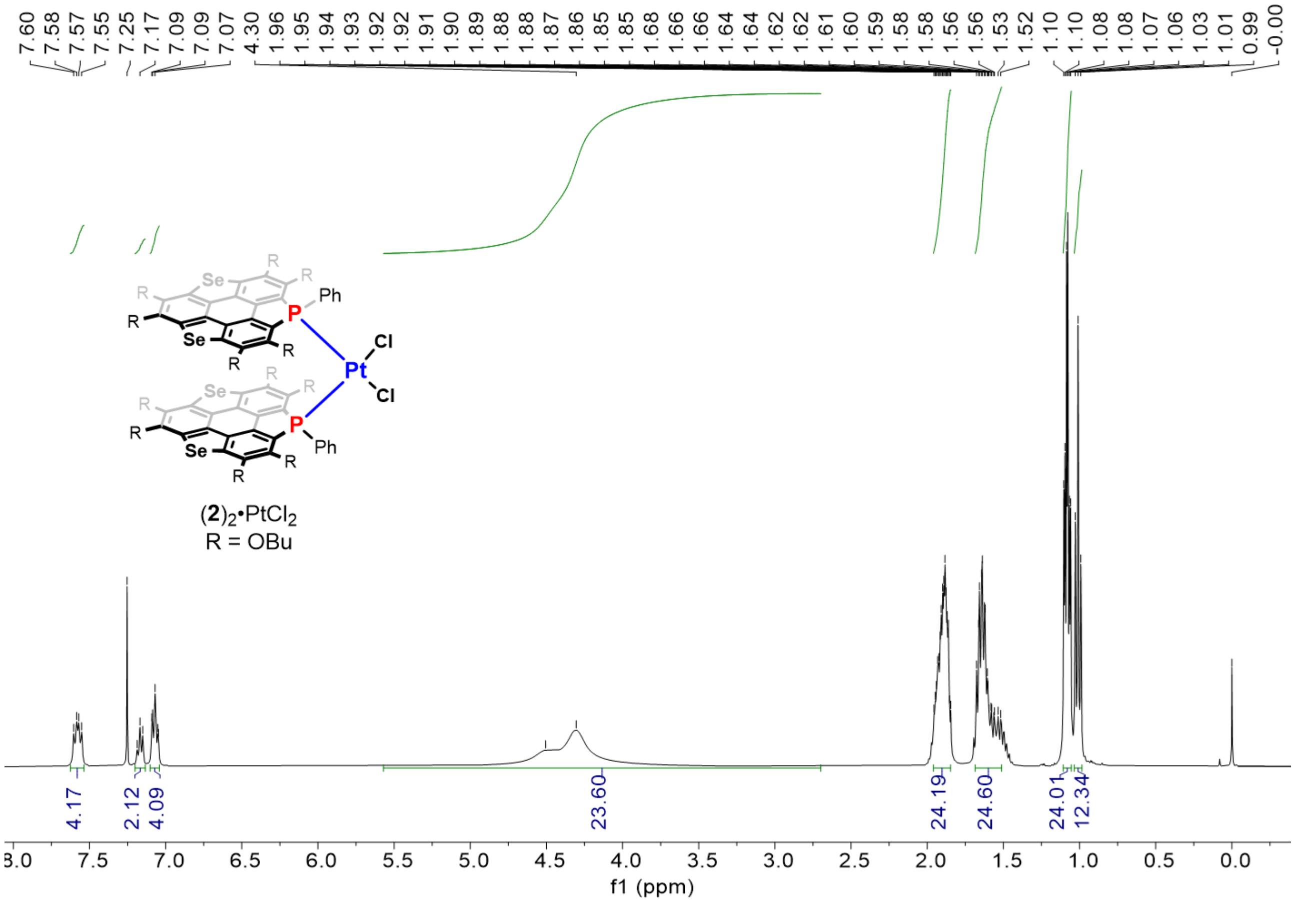

7.61
7.60
7.24
7.18
7.11
7.10
7.09
7.09
4.50
4.48
4.35
4.34
4.33
4.26
4.25
1.95
1.95
1.94
1.93
1.92
1.91
1.90
1.90
1.89
1.89
1.88
1.87
1.68
1.67
1.66
1.65
1.64
1.63
1.62
1.61
1.61
1.60
1.60
1.59
1.55
1.54
1.53
1.52
1.10
1.10
1.09
1.09
1.07
1.04
1.03
1.02
4.06
2.08
4.03
4.31
20.01
24.15
24.62
24.00
12.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)
S
R
P
Ph
Pt
Cl
$(\mathbf{1})_2$•$PtCl_2$
R = OBu

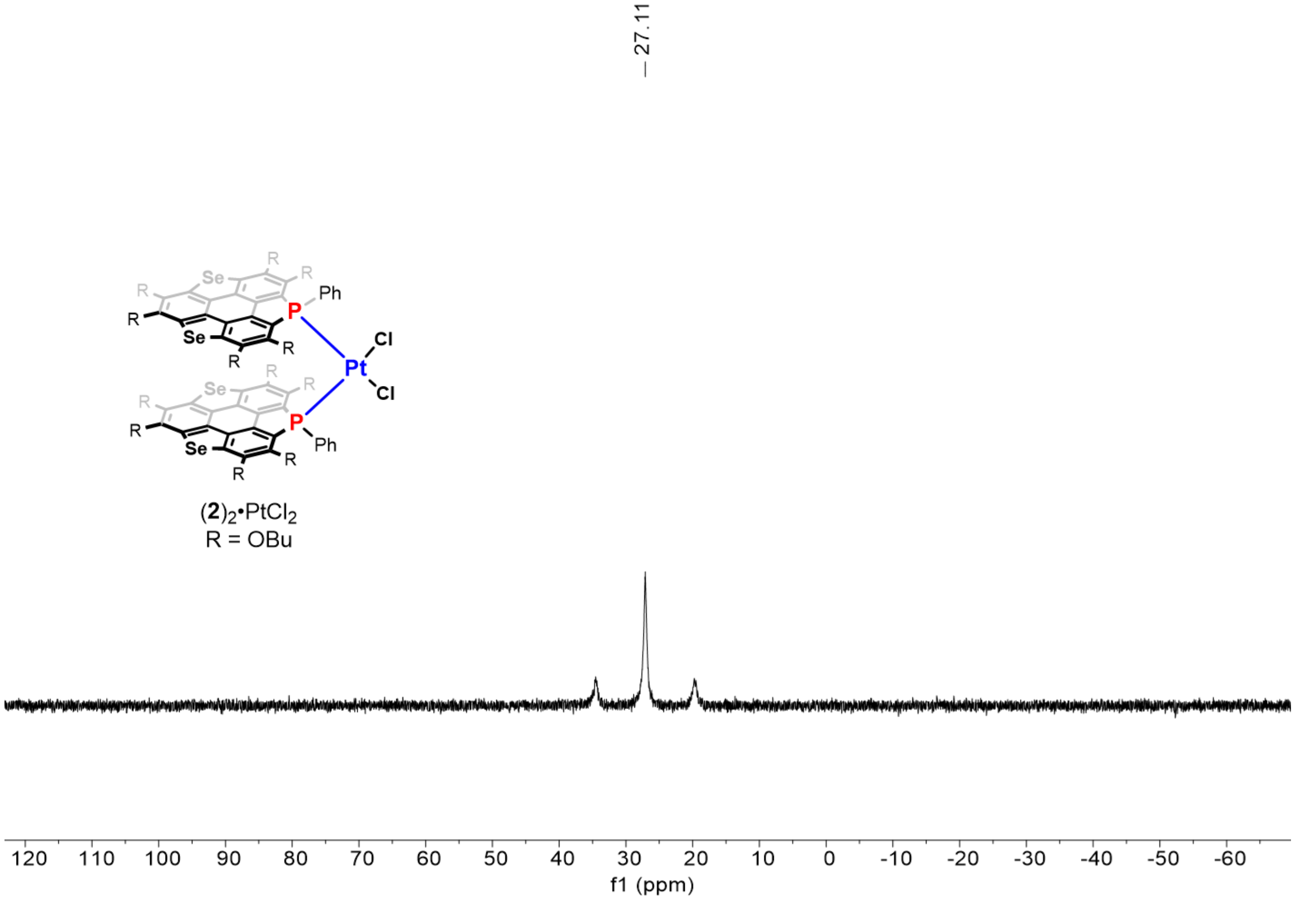

31.61
(1)2•PtCl2
R = OBu
S
R
Ph
P
Pt
Cl
60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2
f1 (ppm)

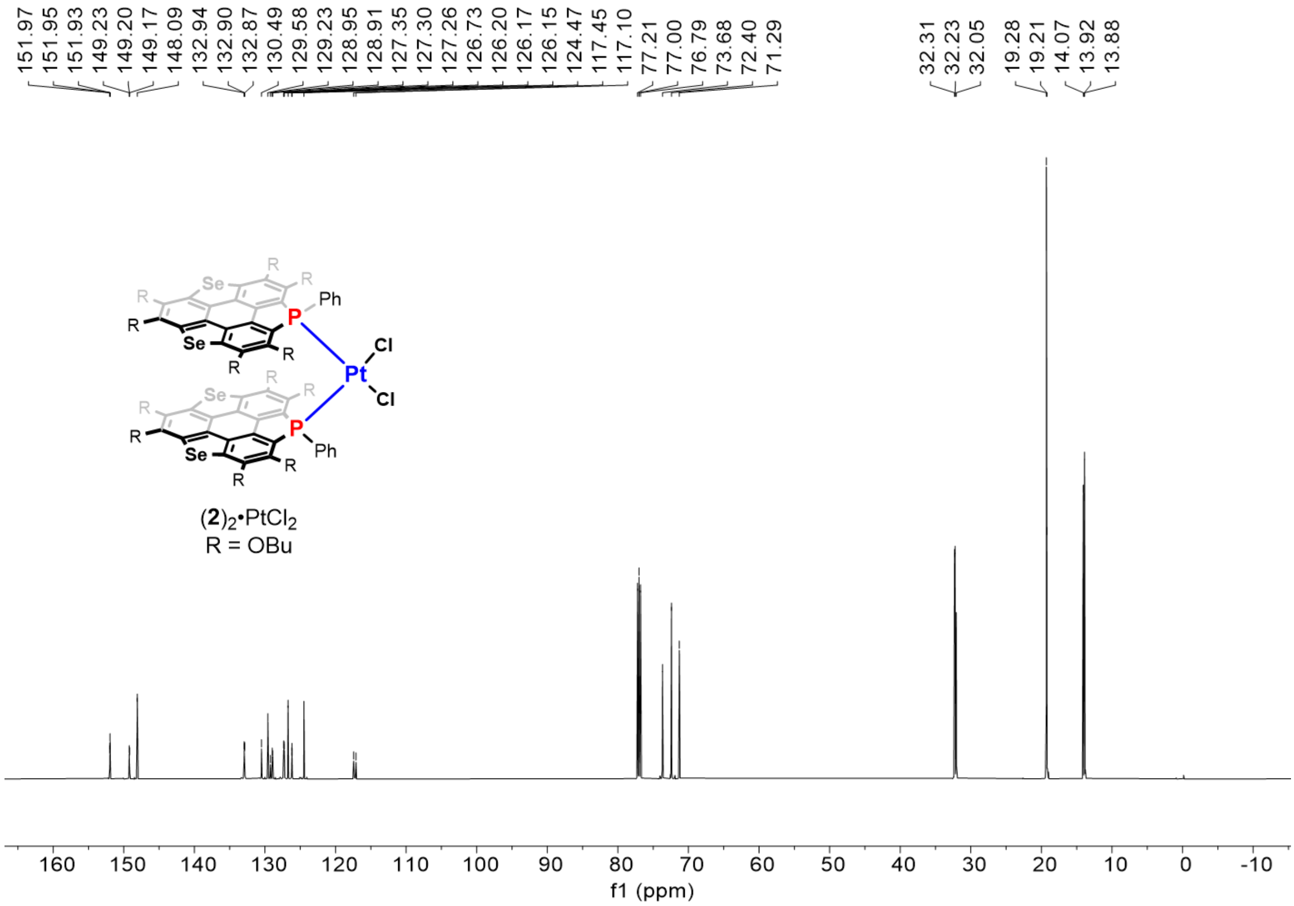

151.28
146.02
145.32
131.99
131.96
131.92
130.89
129.69
127.50
127.47
127.43
127.40
127.03
127.01
126.31
126.27
126.23
124.52
123.79
123.76
123.73
123.13
116.54
116.09
76.31
76.10
75.89
72.82
71.66
70.79
31.26
31.17
18.34
18.32
13.17
12.98
12.94
(1)2•PtCl2
R = OBu
S
R
Ph
P
Pt
Cl
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

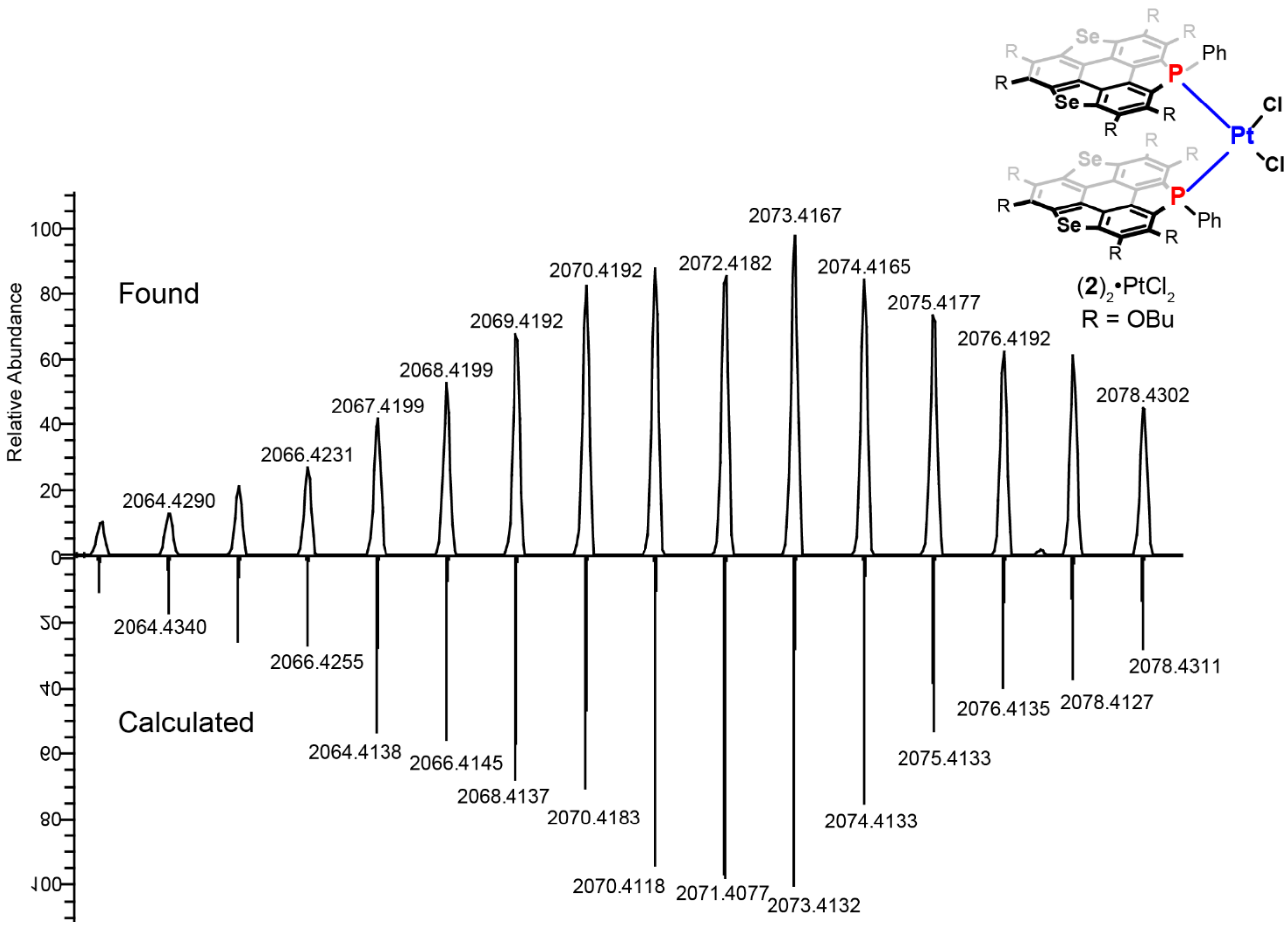

Found
Calculated
Relative Abundance
100
80
60
40
20
0
20
40
60
80
100
1881.6213
1882.6321
1883.6345
1884.6339
1885.6356
1886.6356
1887.6362
1888.6345
1889.6438
1890.6571
1881.6291
1882.6325
1883.6346
1884.6347
1885.6381
1886.6318
1887.6351
1888.6347
1889.6381
1890.6305
R
S
P
Ph
Pt
Cl
Cl
(1)2•PtCl2
R = OBu

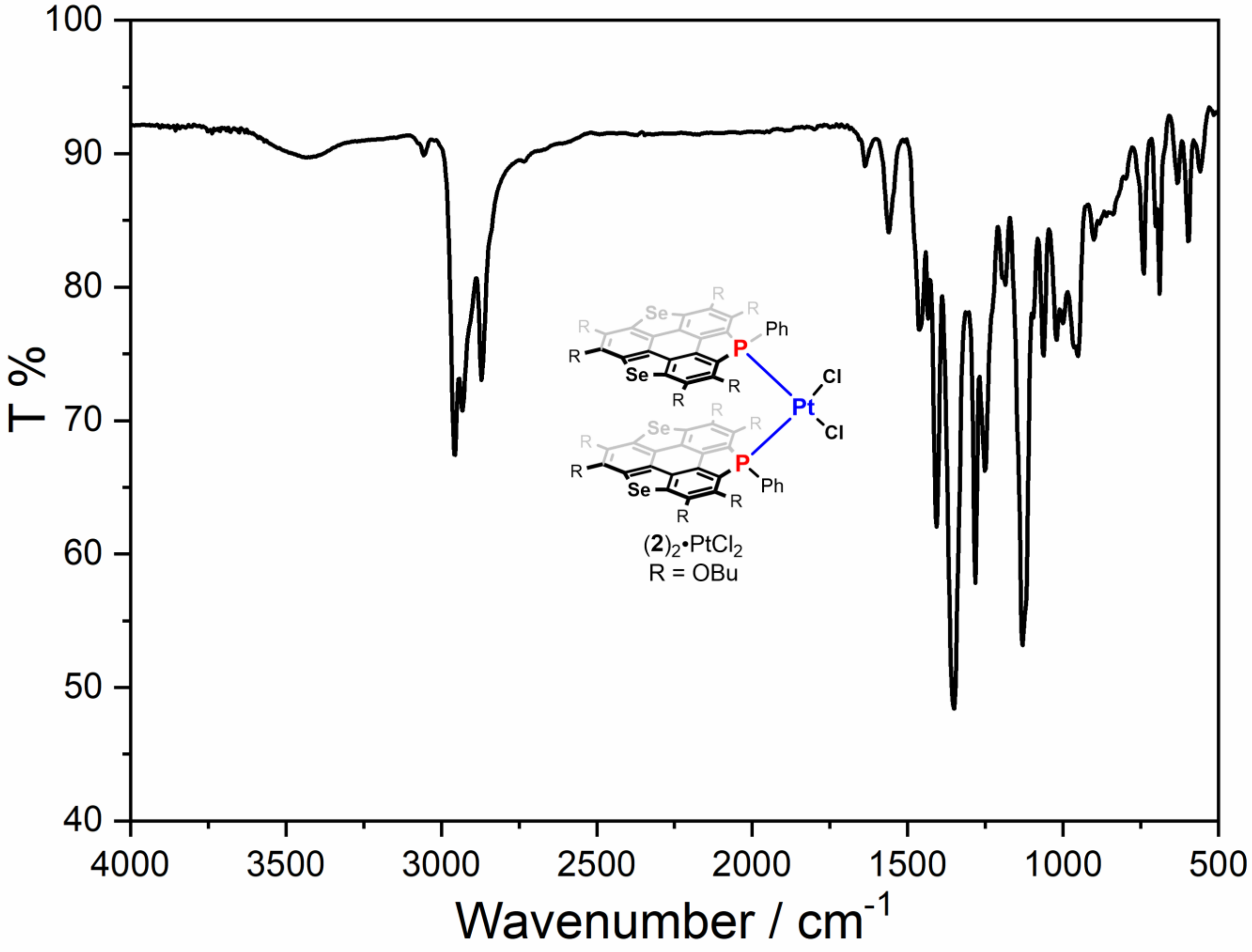

T %
100
90
80
70
60
50
40
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber / cm-1
R
S
P
Ph
Pt
Cl
Cl
(1)2•PtCl2
R = OBu

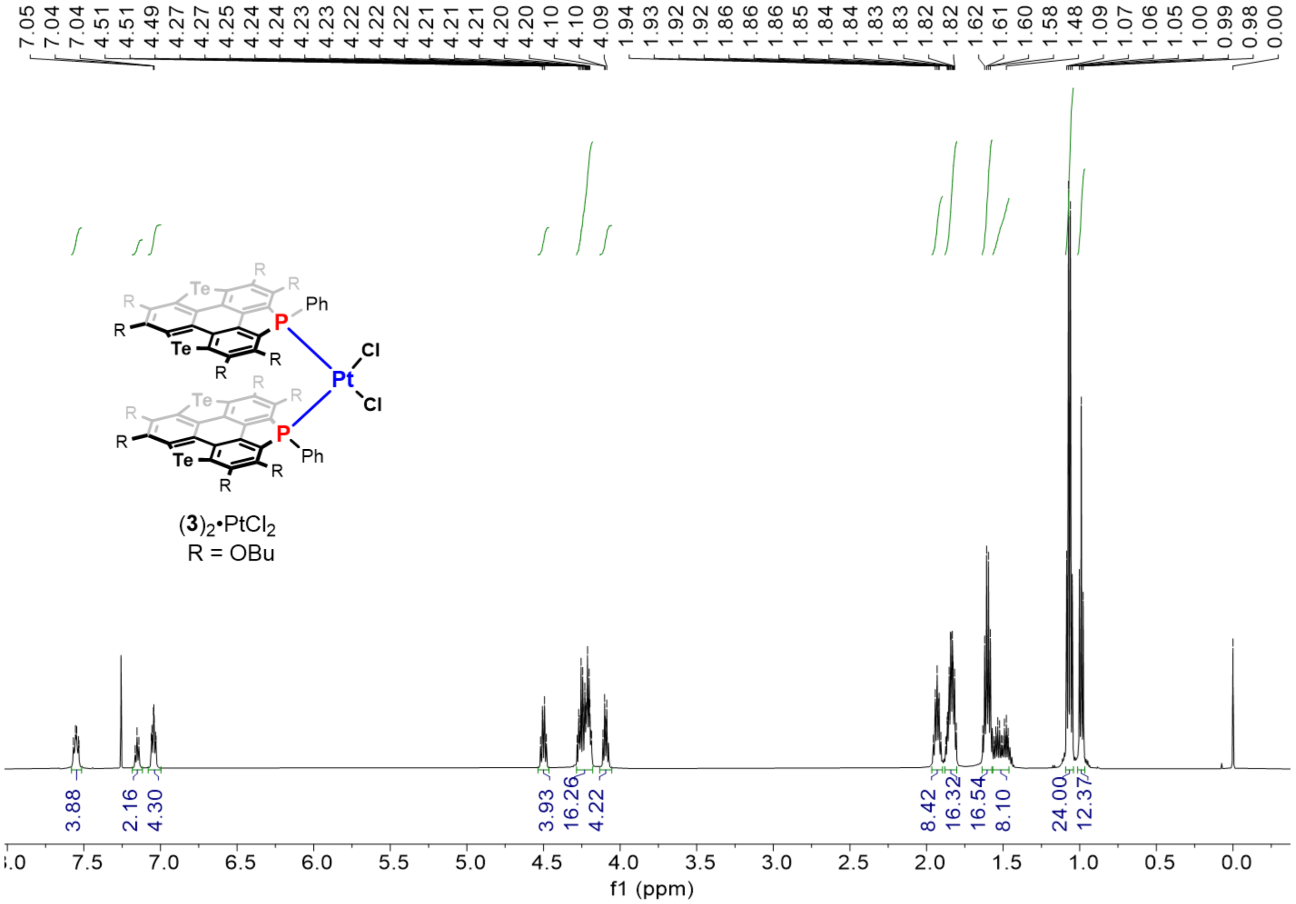

7.60
7.58
7.57
7.55
7.25
7.17
7.09
7.09
7.07
4.30
1.96
1.95
1.94
1.93
1.92
1.92
1.91
1.90
1.89
1.88
1.88
1.87
1.86
1.85
1.85
1.68
1.66
1.66
1.64
1.64
1.62
1.62
1.61
1.60
1.59
1.58
1.58
1.56
1.56
1.53
1.52
1.10
1.10
1.08
1.08
1.07
1.06
1.03
1.01
0.99
-0.00
Se
R
Ph
P
Pt
Cl
Cl
Ph
$(\mathbf{2})_2$•$PtCl_2$
R = OBu
4.17
2.12
4.09
23.60
24.19
24.60
24.01
12.34
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

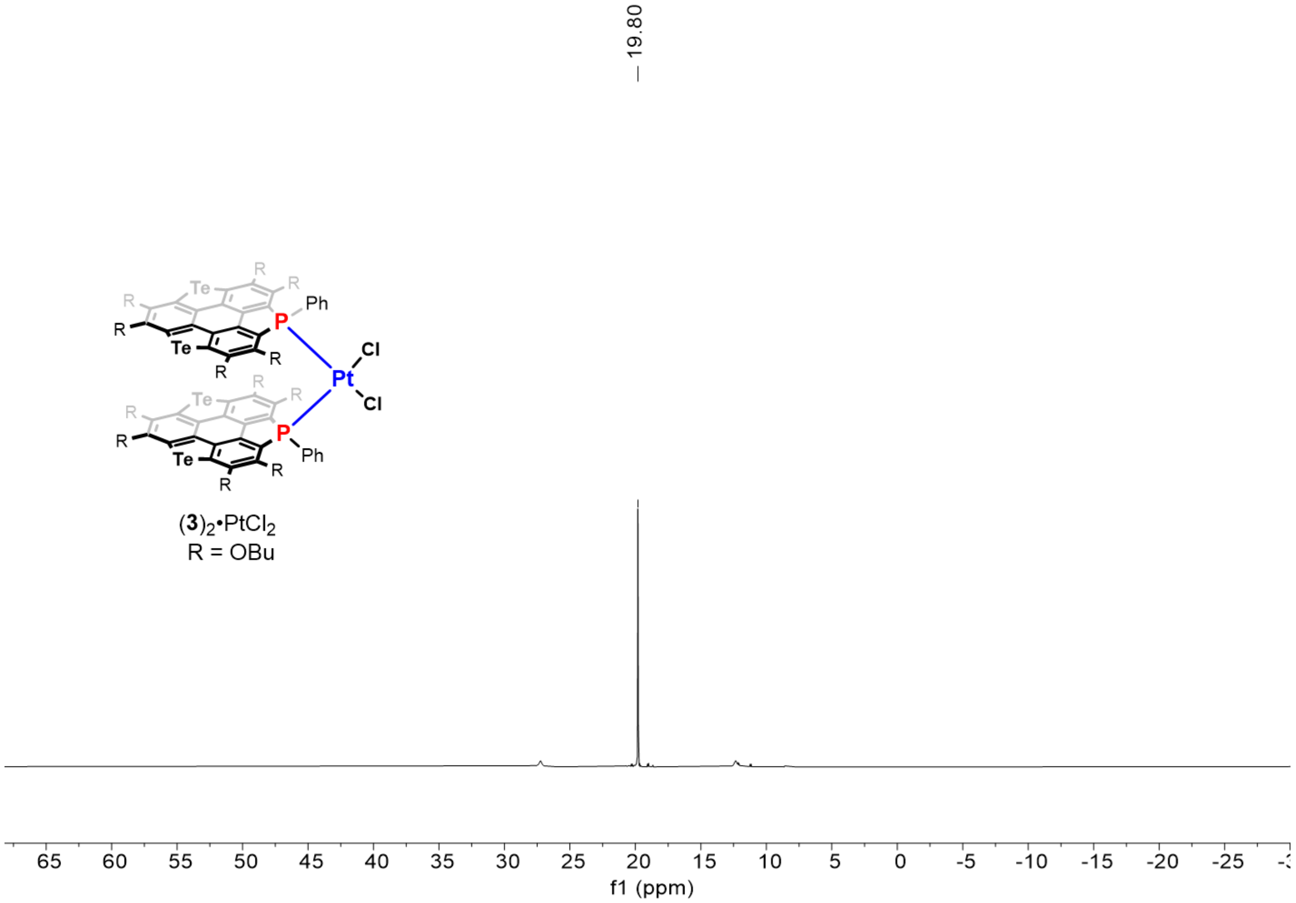

27.11
Se
R
Ph
P
Pt
Cl
Cl
Ph
$(\mathbf{2})_2$•$PtCl_2$
R = OBu
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
f1 (ppm)

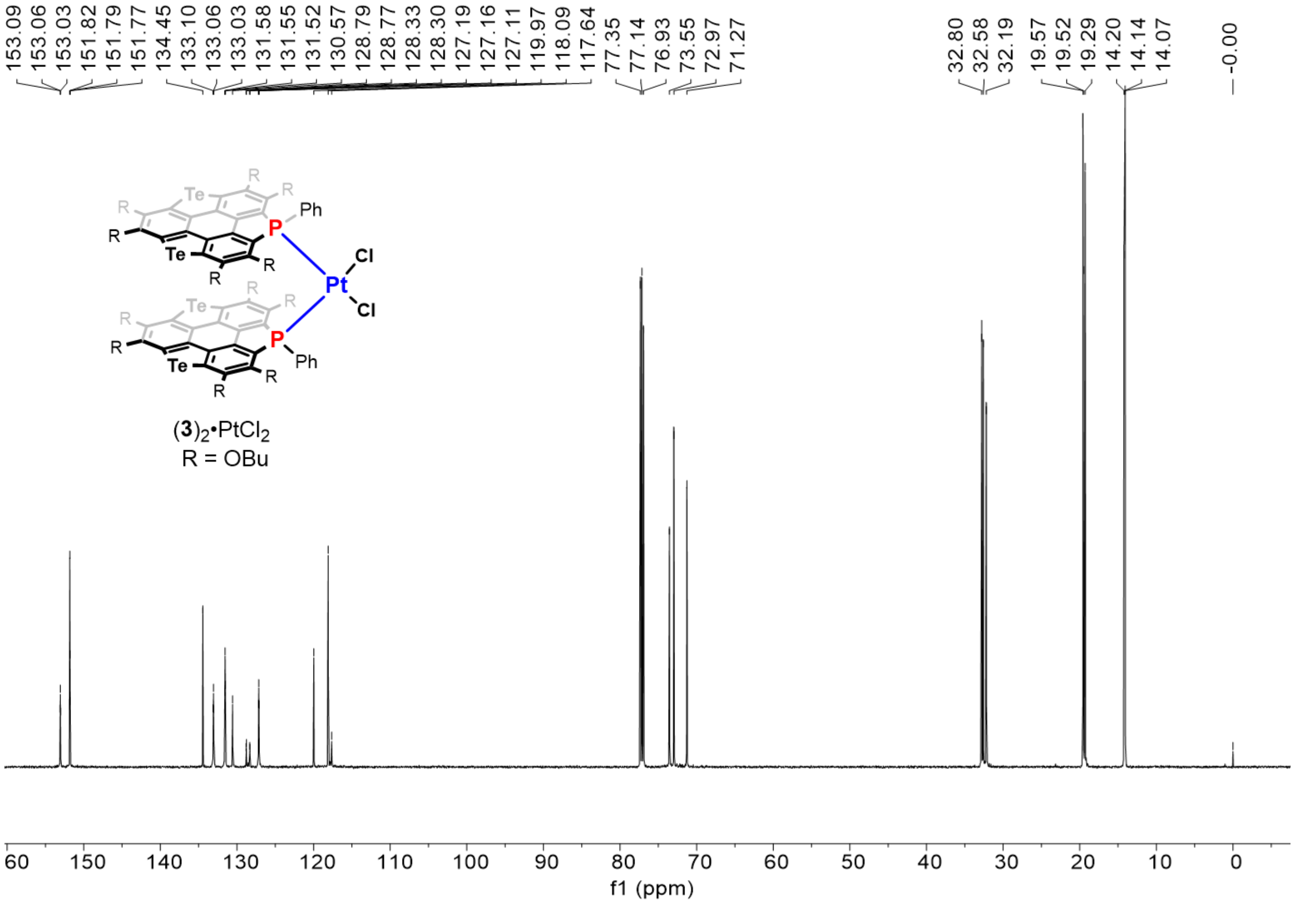

151.97
151.95
151.93
149.23
149.20
149.17
148.09
132.94
132.90
132.87
130.49
129.58
129.23
128.95
128.91
127.35
127.30
127.26
126.73
126.20
126.17
126.15
124.47
117.45
117.10
77.21
77.00
76.79
73.68
72.40
71.29
32.31
32.23
32.05
19.28
19.21
14.07
13.92
13.88
Se
R
Ph
P
Cl
Pt
(2)2•PtCl2
R = OBu
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

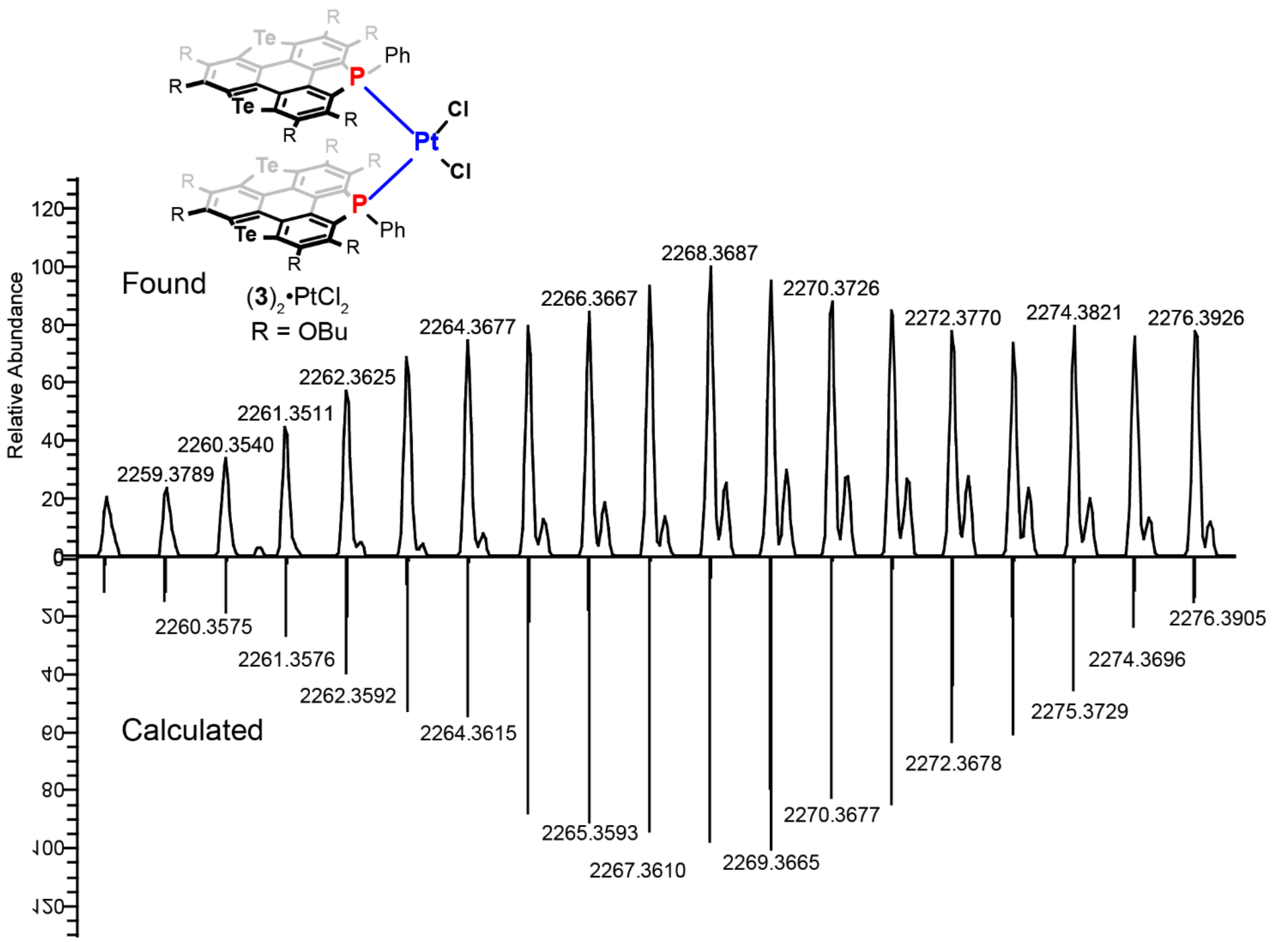

Relative Abundance
Found
Calculated
100
80
60
40
20
0
2064.4290
2066.4231
2067.4199
2068.4199
2069.4192
2070.4192
2072.4182
2073.4167
2074.4165
2075.4177
2076.4192
2078.4302
2064.4340
2066.4255
2064.4138
2066.4145
2068.4137
2070.4183
2070.4118
2071.4077
2073.4132
2074.4133
2075.4133
2076.4135
2078.4127
2078.4311
Se
R
Ph
P
Cl
Pt
(2)2•PtCl2
R = OBu

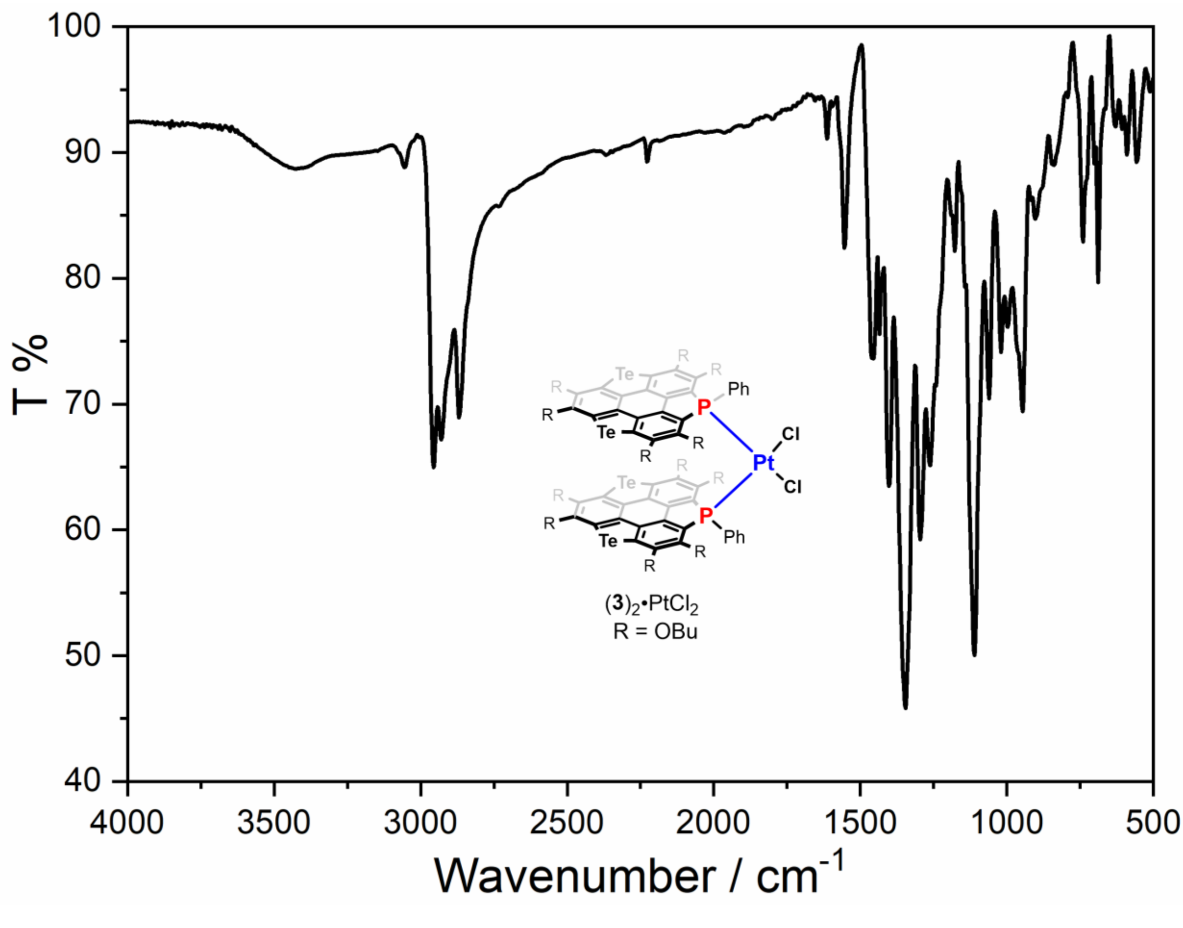

T %
100
90
80
70
60
50
40
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber / cm^{-1}
Se
Se
R
Ph
P
Cl
Pt
Cl
R = OBu
$(\mathbf{2})_2$•PtCl$_2$

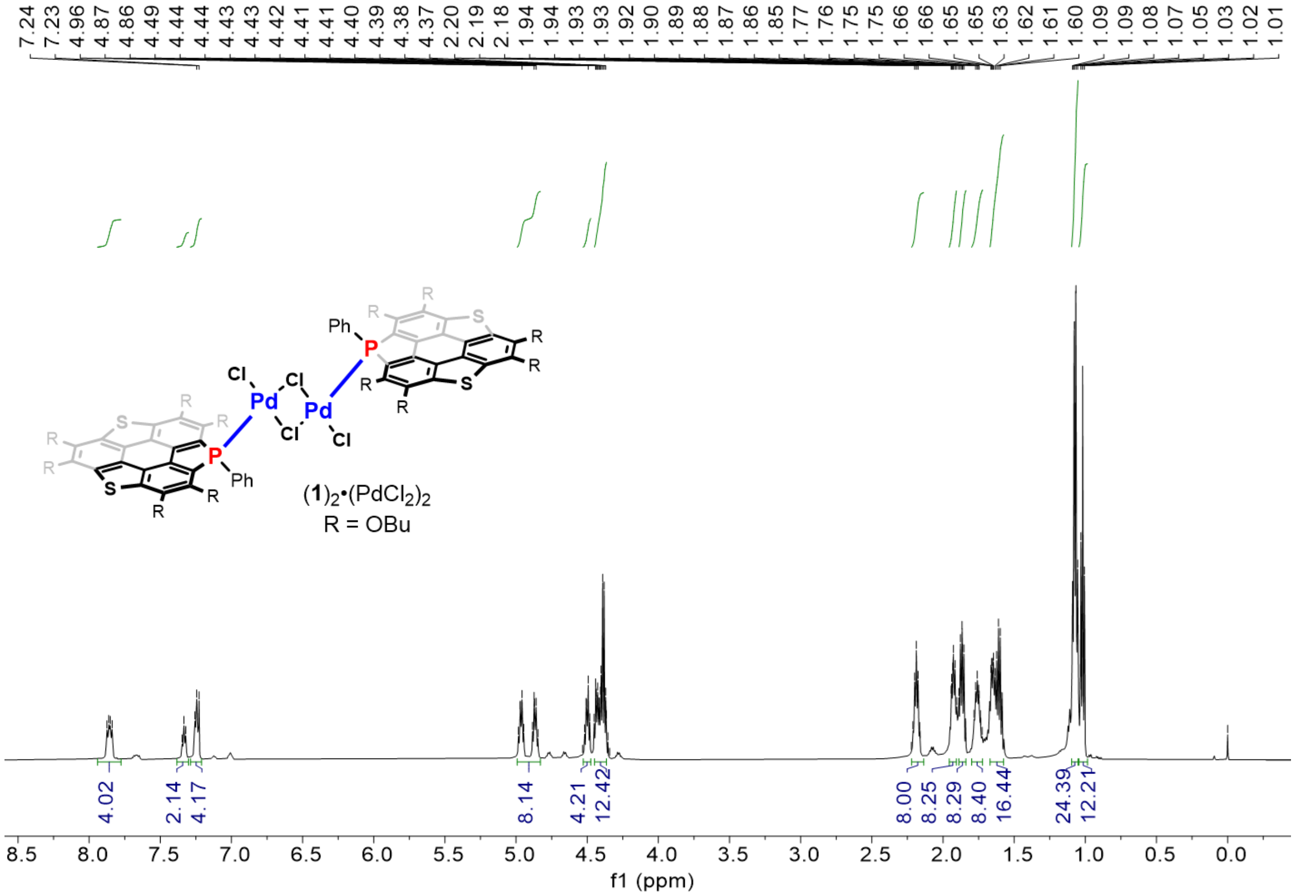

7.05
7.04
7.04
4.51
4.51
4.49
4.27
4.27
4.25
4.24
4.24
4.23
4.23
4.22
4.22
4.22
4.21
4.21
4.21
4.20
4.20
4.10
4.10
4.09
1.94
1.93
1.92
1.92
1.86
1.86
1.85
1.84
1.84
1.83
1.83
1.82
1.82
1.62
1.61
1.60
1.58
1.48
1.09
1.07
1.06
1.05
1.00
0.99
0.98
0.00
Te
Te
R
Ph
P
Cl
Pt
Cl
$(\mathbf{3})_2$•PtCl$_2$
R = OBu
3.88
2.16
4.30
3.93
16.26
4.22
8.42
16.32
16.54
8.10
24.00
12.37
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

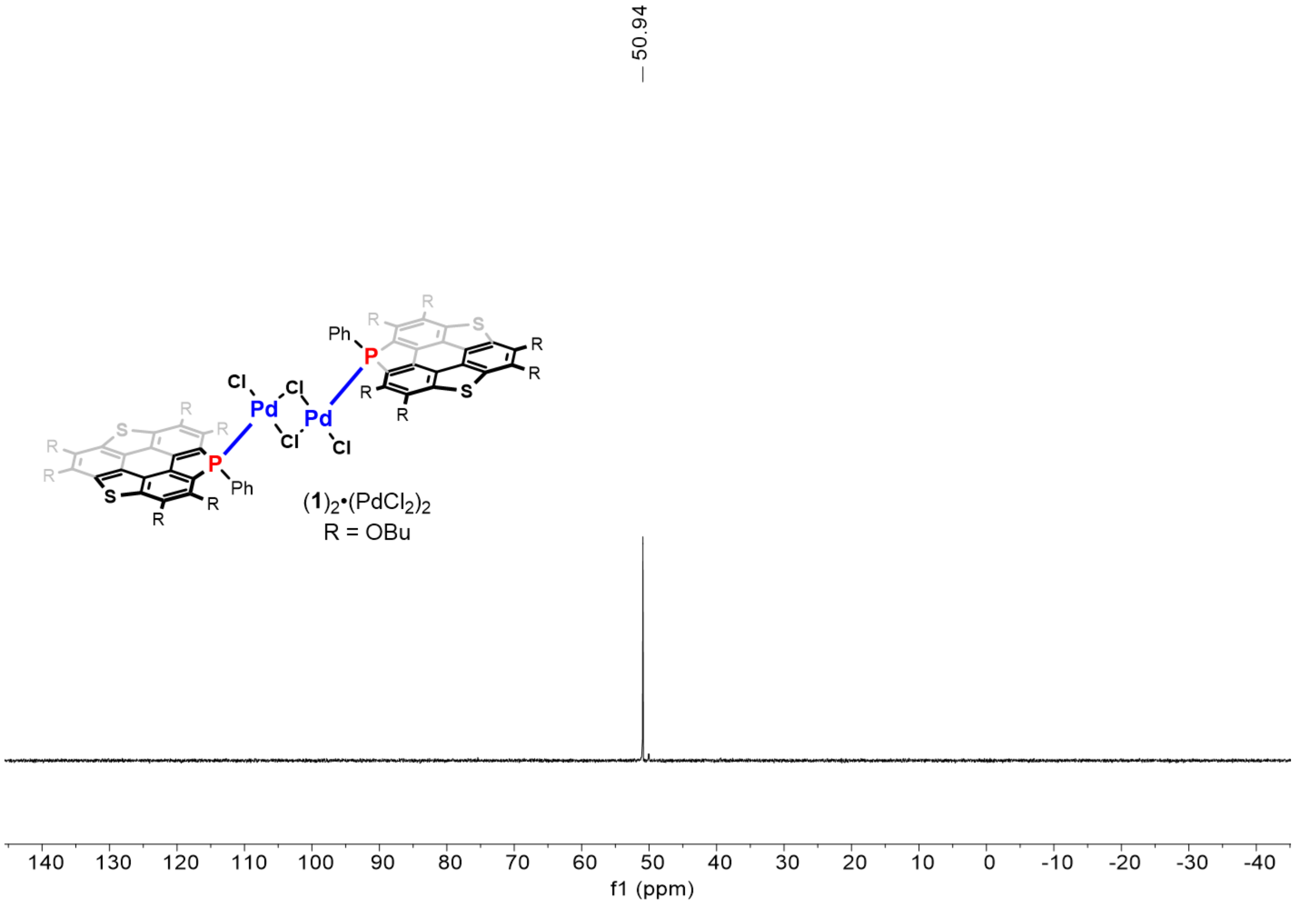

19.80
(3)2•PtCl2
R = OBu
Te
R
Ph
P
Pt
Cl
65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25
f1 (ppm)

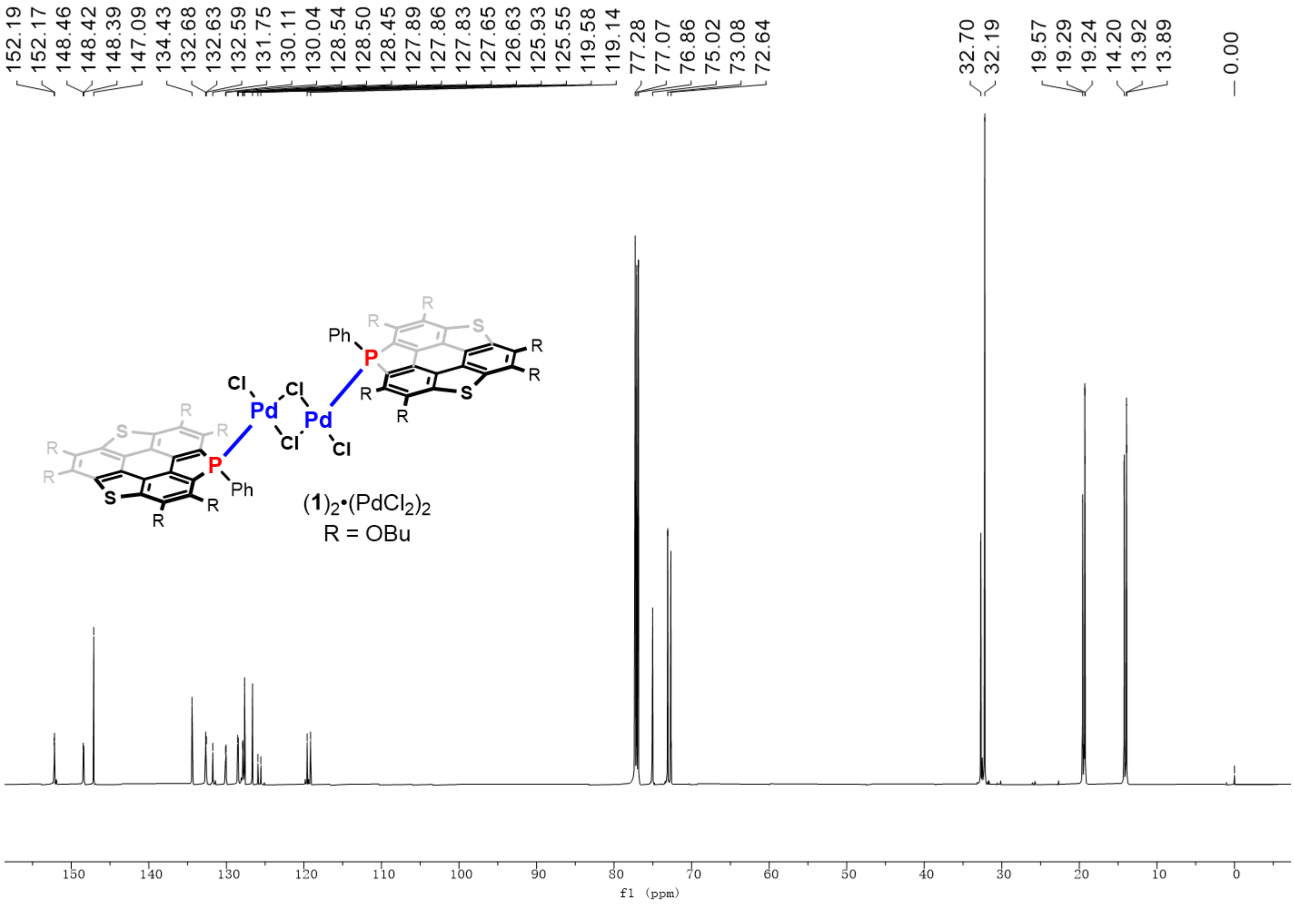

153.09
153.06
153.03
151.82
151.79
151.77
134.45
133.10
133.06
133.03
131.58
131.55
131.52
130.57
128.79
128.77
128.33
128.30
127.19
127.16
127.11
119.97
118.09
117.64
77.35
77.14
76.93
73.55
72.97
71.27
32.80
32.58
32.19
19.57
19.52
19.29
14.20
14.14
14.07
-0.00
(3)2•PtCl2
R = OBu
Te
R
Ph
P
Pt
Cl
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

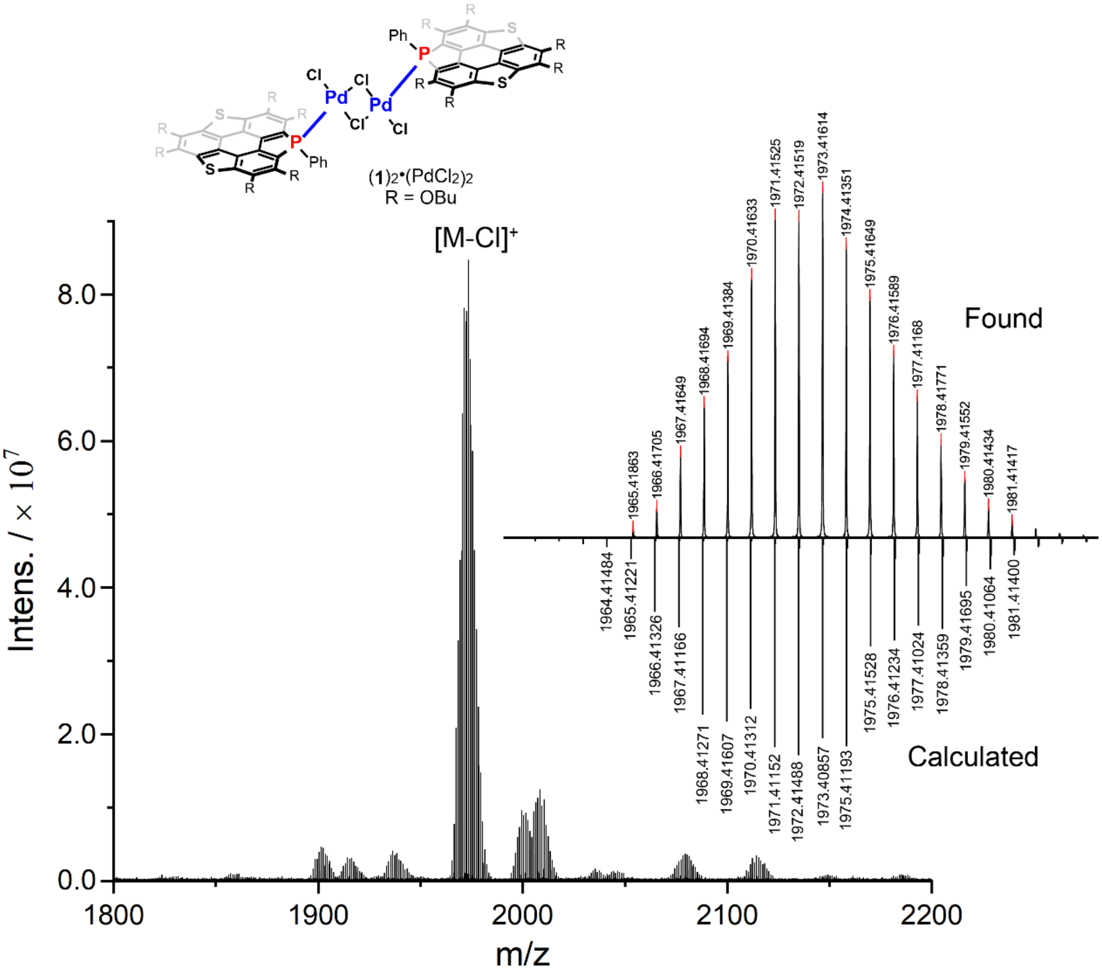

Found
Calculated
(3)2•PtCl2
R = OBu
Relative Abundance
2259.3789
2260.3540
2261.3511
2262.3625
2264.3677
2266.3667
2268.3687
2270.3726
2272.3770
2274.3821
2276.3926
2260.3575
2261.3576
2262.3592
2264.3615
2265.3593
2267.3610
2269.3665
2270.3677
2272.3678
2275.3729
2274.3696
2276.3905
0
20
40
60
80
100
120

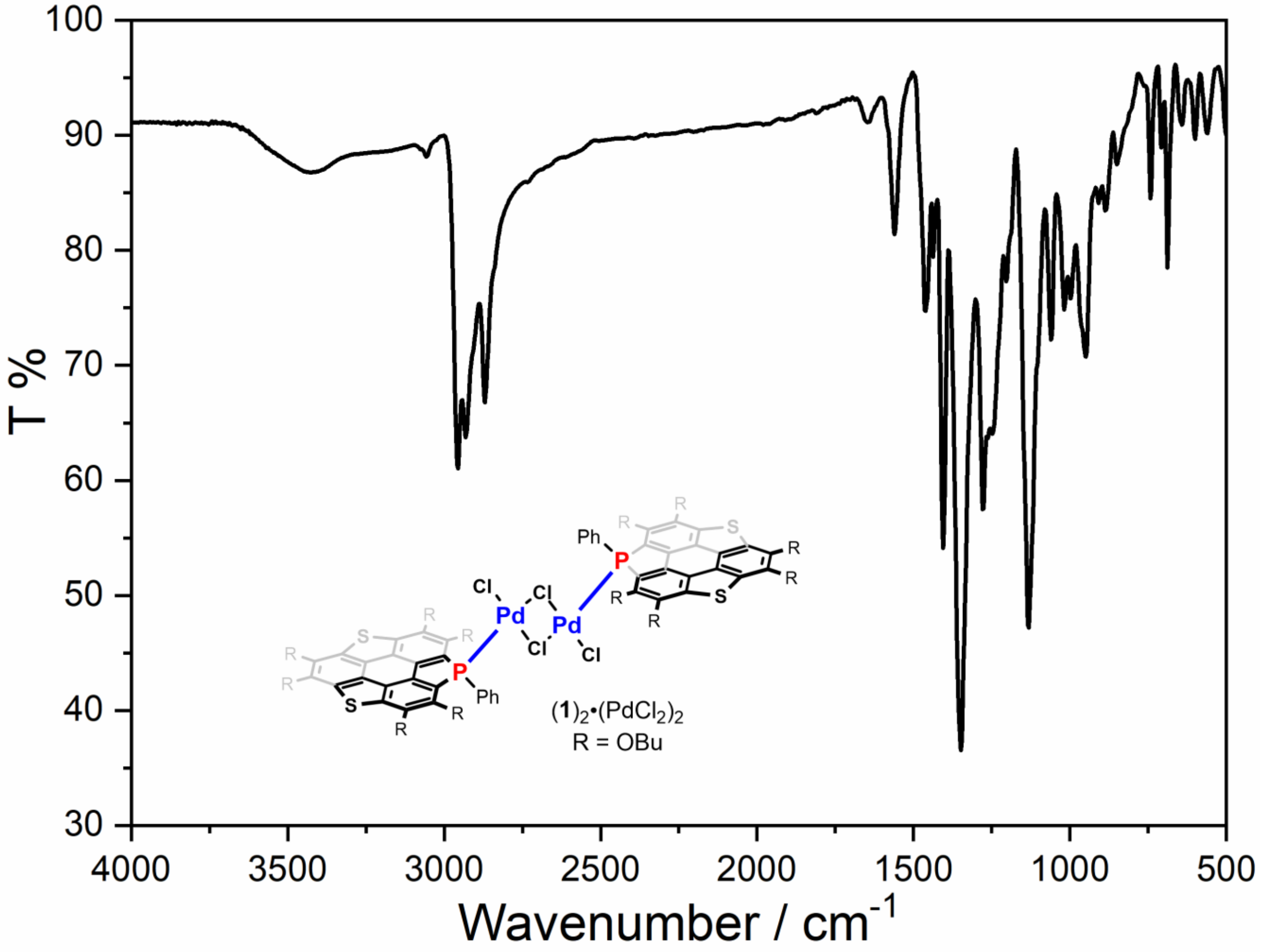

T %
Wavenumber / cm-1
(3)2•PtCl2
R = OBu
100
90
80
70
60
50
40
4000
3500
3000
2500
2000
1500
1000
500

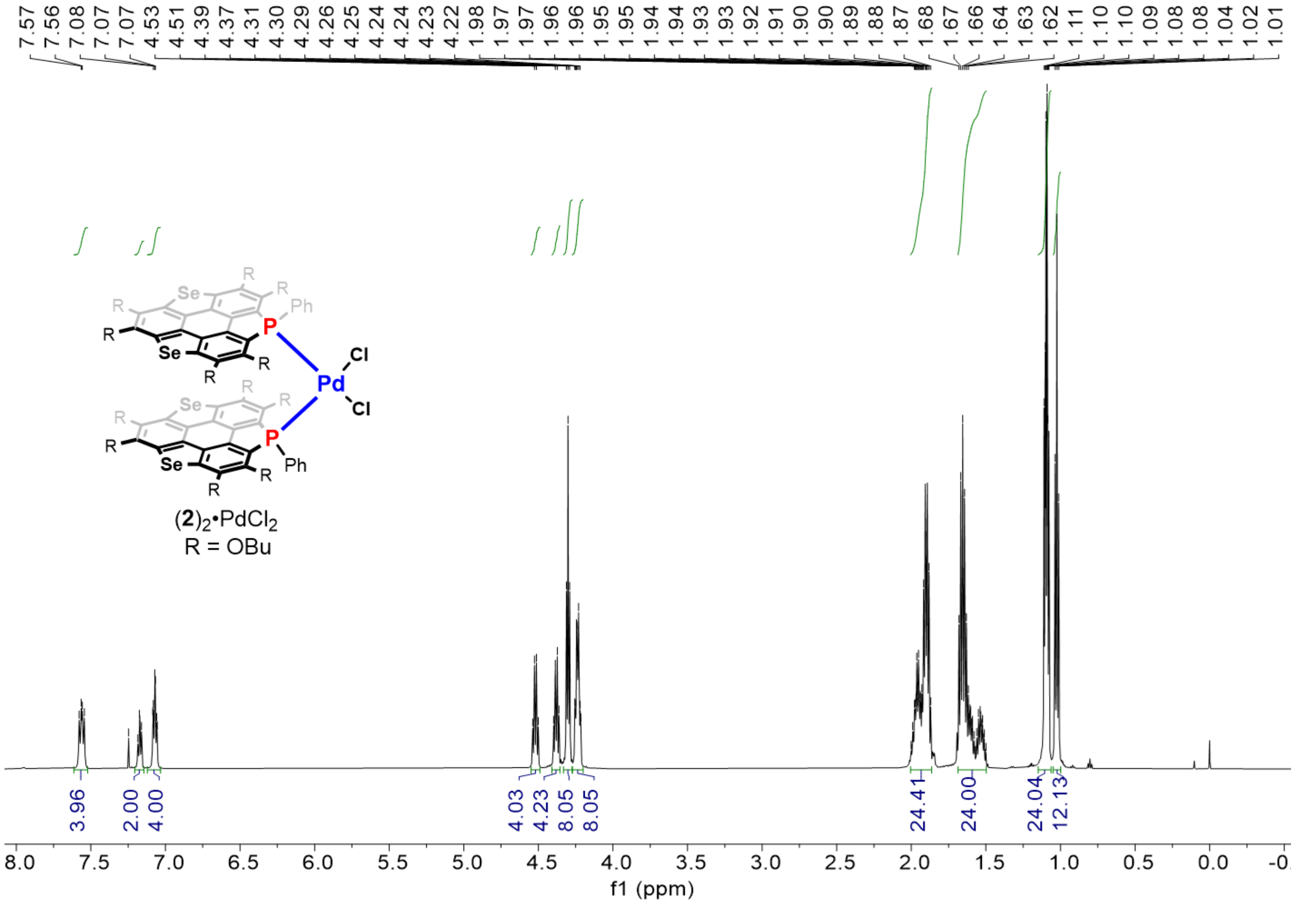

7.24
7.23
4.96
4.87
4.86
4.49
4.44
4.44
4.43
4.43
4.42
4.41
4.41
4.40
4.39
4.38
4.37
2.20
2.19
2.18
1.94
1.94
1.93
1.93
1.92
1.90
1.89
1.88
1.87
1.86
1.85
1.77
1.76
1.75
1.75
1.66
1.66
1.65
1.65
1.63
1.62
1.61
1.60
1.09
1.09
1.08
1.07
1.05
1.03
1.02
1.01
Ph
P
R
S
Cl
Pd
Cl
Pd
Cl
Cl
P
Ph
(1)2•(PdCl2)2
R = OBu
4.02
2.14
4.17
8.14
4.21
12.42
8.00
8.25
8.29
8.40
16.44
24.39
12.21
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

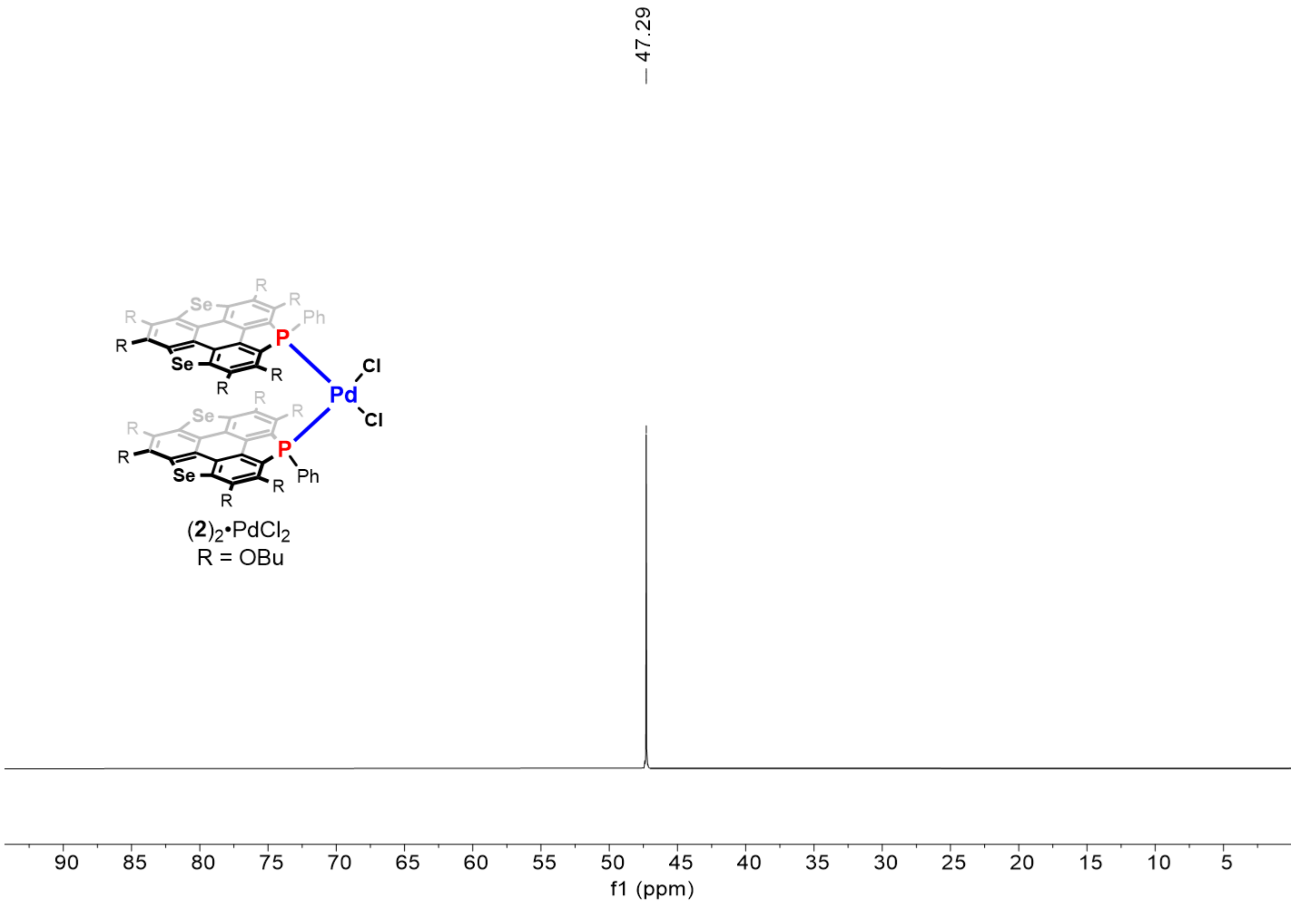

50.94
Ph
P
R
S
Cl
Pd
Cl
Pd
Cl
Cl
P
Ph
(1)2•(PdCl2)2
R = OBu
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)


152.19
152.17
148.46
148.42
148.39
147.09
134.43
132.68
132.63
132.59
131.75
130.11
130.04
128.54
128.50
128.45
127.89
127.86
127.83
127.65
126.63
125.93
125.55
119.58
119.14
77.28
77.07
76.86
75.02
73.08
72.64
32.70
32.19
19.57
19.29
19.24
14.20
13.92
13.89
0.00
Ph
P
Cl
Pd
Cl
Pd
Cl
Cl
P
Ph
S
S
R
R = OBu
(1)2•(PdCl2)2
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

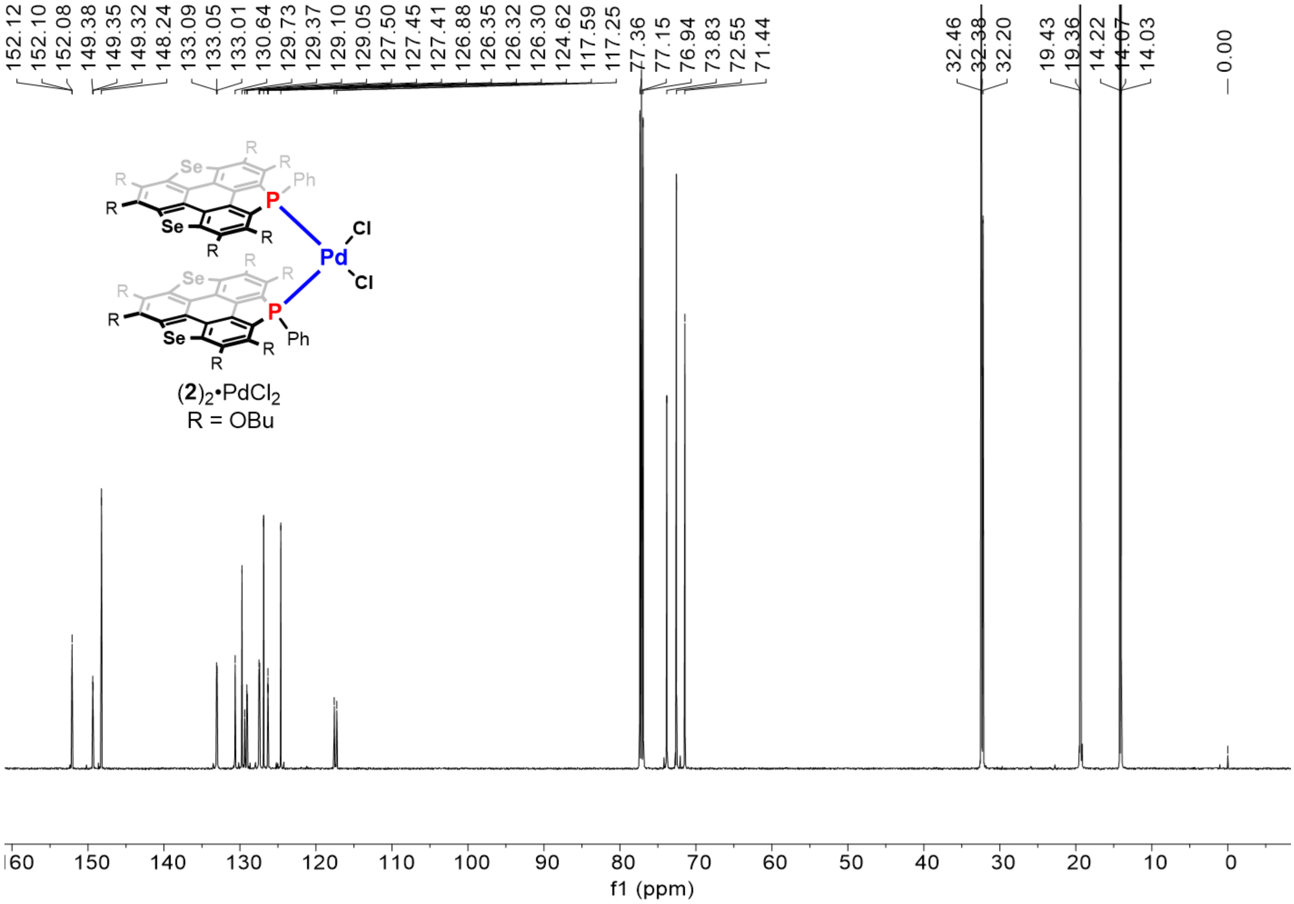

Ph
P
Cl
Pd
Cl
Pd
Cl
Cl
S
R
(1)2•(PdCl2)2
R = OBu
[M-Cl]+
Found
Calculated
1965.41863
1966.41705
1967.41649
1968.41694
1969.41384
1970.41633
1971.41525
1972.41519
1973.41614
1974.41351
1975.41649
1976.41589
1977.41168
1978.41771
1979.41552
1980.41434
1981.41417
1964.41484
1965.41221
1966.41326
1967.41166
1968.41271
1969.41607
1970.41312
1971.41152
1972.41488
1973.40857
1975.41193
1975.41528
1976.41234
1977.41024
1978.41359
1979.41695
1980.41064
1981.41400
Intens. / × 10^7
8.0
6.0
4.0
2.0
0.0
1800
1900
2000
2100
2200
m/z


100
90
80
70
60
50
40
30
T %
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber / cm^{-1}
Ph
P
R
S
Pd
Cl
Cl
Pd
Cl
Cl
P
Ph
S
(**1**)$_2$•(PdCl$_2$)$_2$
R = OBu

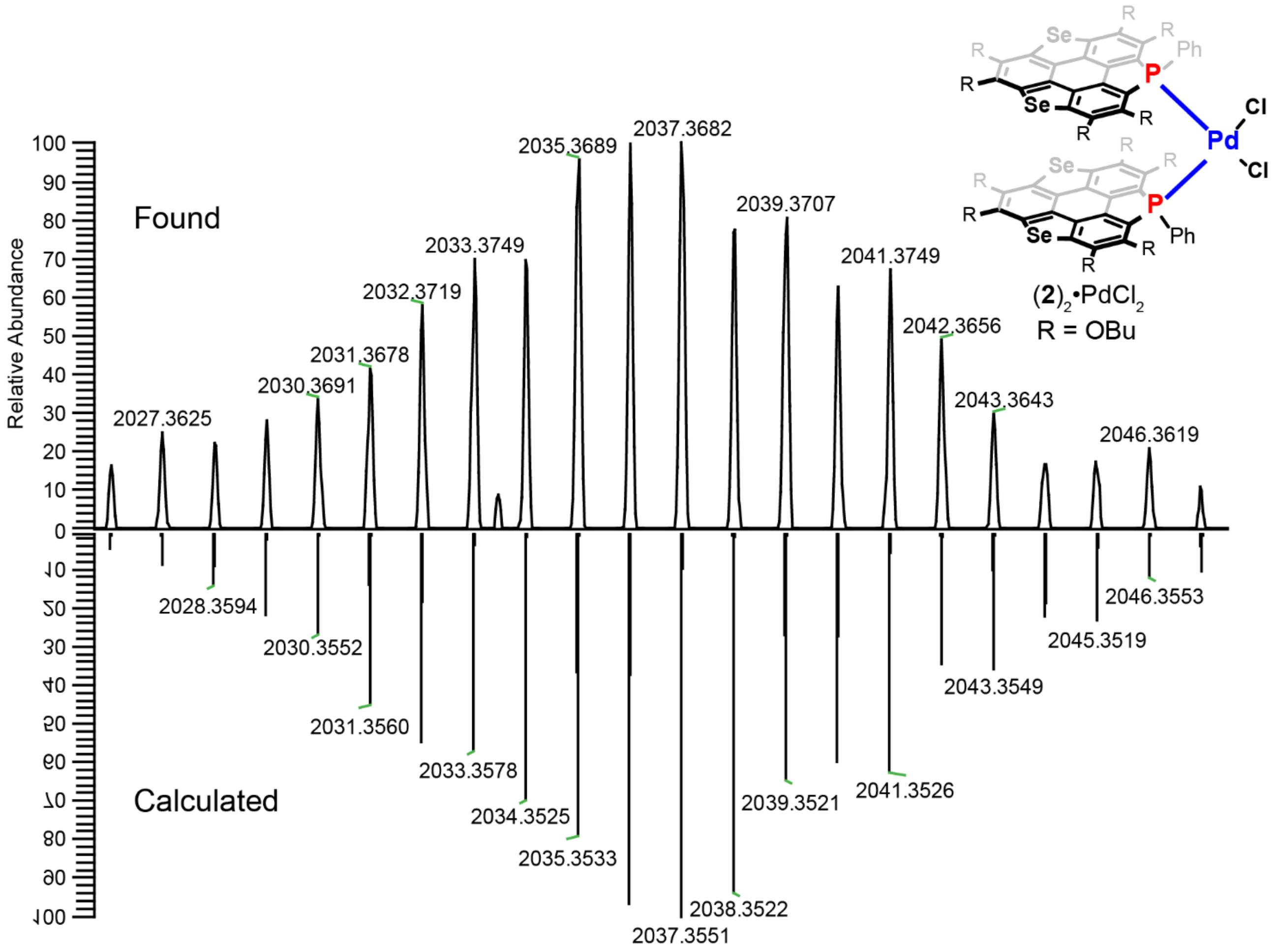

7.57
7.56
7.08
7.07
7.07
4.53
4.51
4.39
4.37
4.31
4.30
4.29
4.26
4.25
4.24
4.24
4.23
4.22
1.98
1.97
1.97
1.96
1.96
1.95
1.95
1.94
1.94
1.93
1.93
1.92
1.91
1.90
1.90
1.89
1.88
1.87
1.68
1.67
1.66
1.64
1.63
1.62
1.11
1.10
1.10
1.09
1.08
1.08
1.04
1.02
1.01
Se
R
P
Ph
Pd
Cl
Cl
(**2**)$_2$•PdCl$_2$
R = OBu
3.96
2.00
4.00
4.03
4.23
8.05
8.05
24.41
24.00
24.04
12.13
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

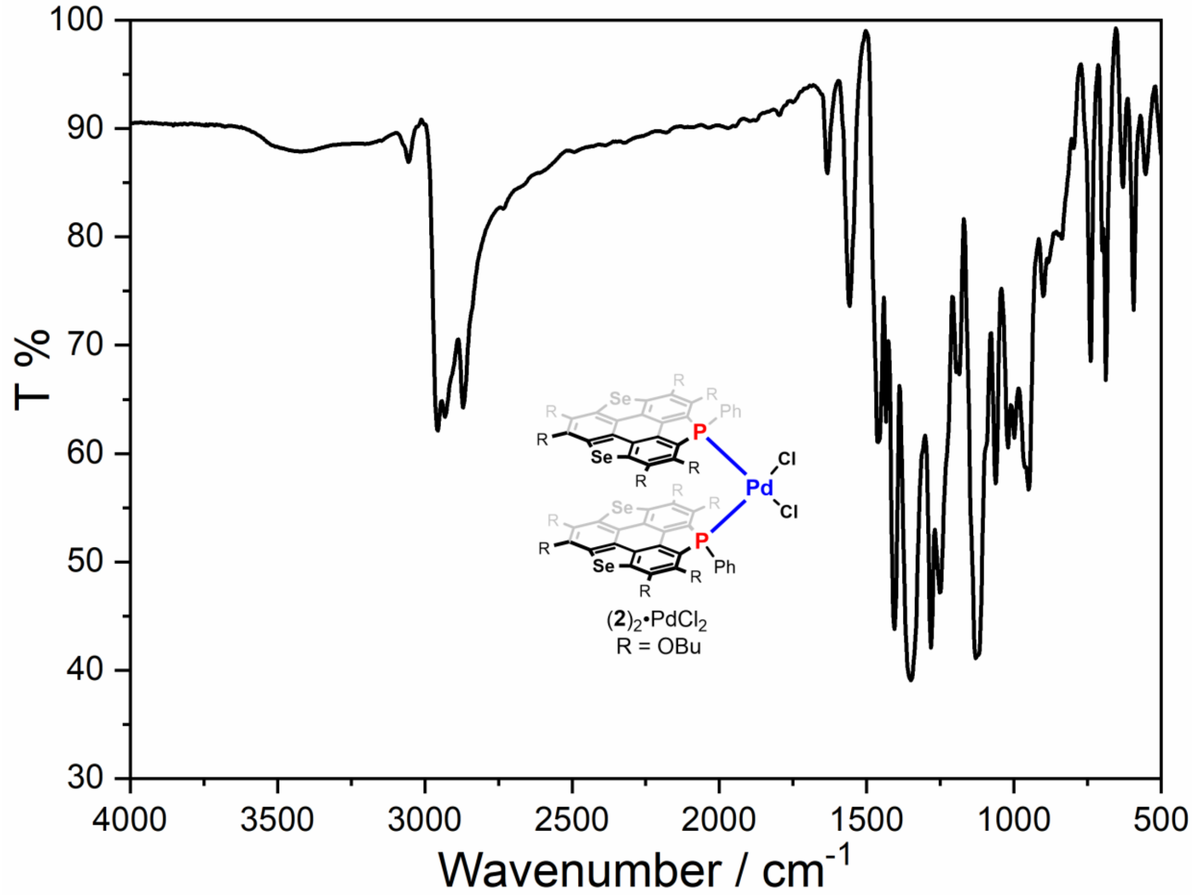


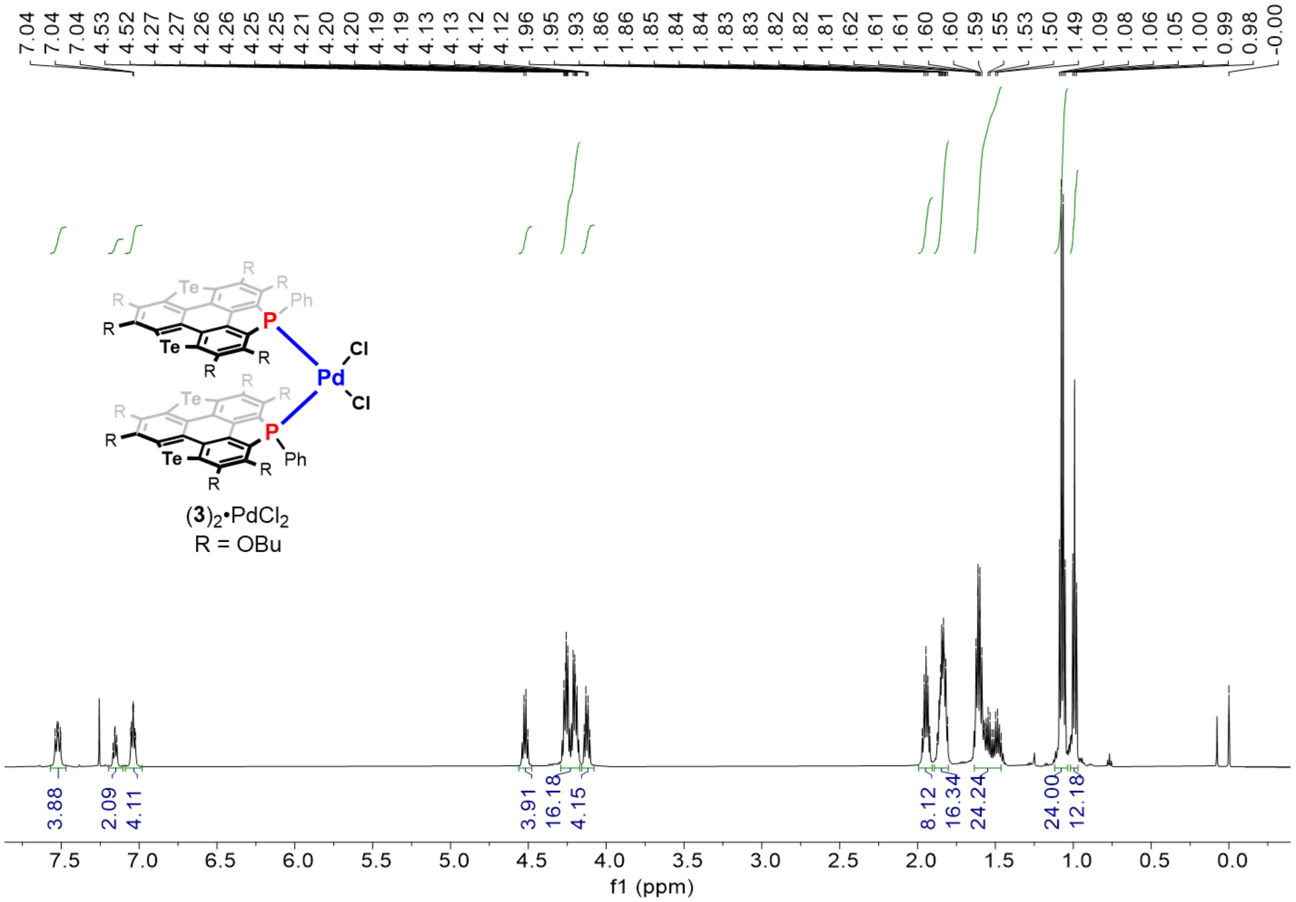
47.29
Se
R
R
Ph
R
P
Pd
Cl
Cl
Se
R
R
(2)2•PdCl2
R = OBu
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)

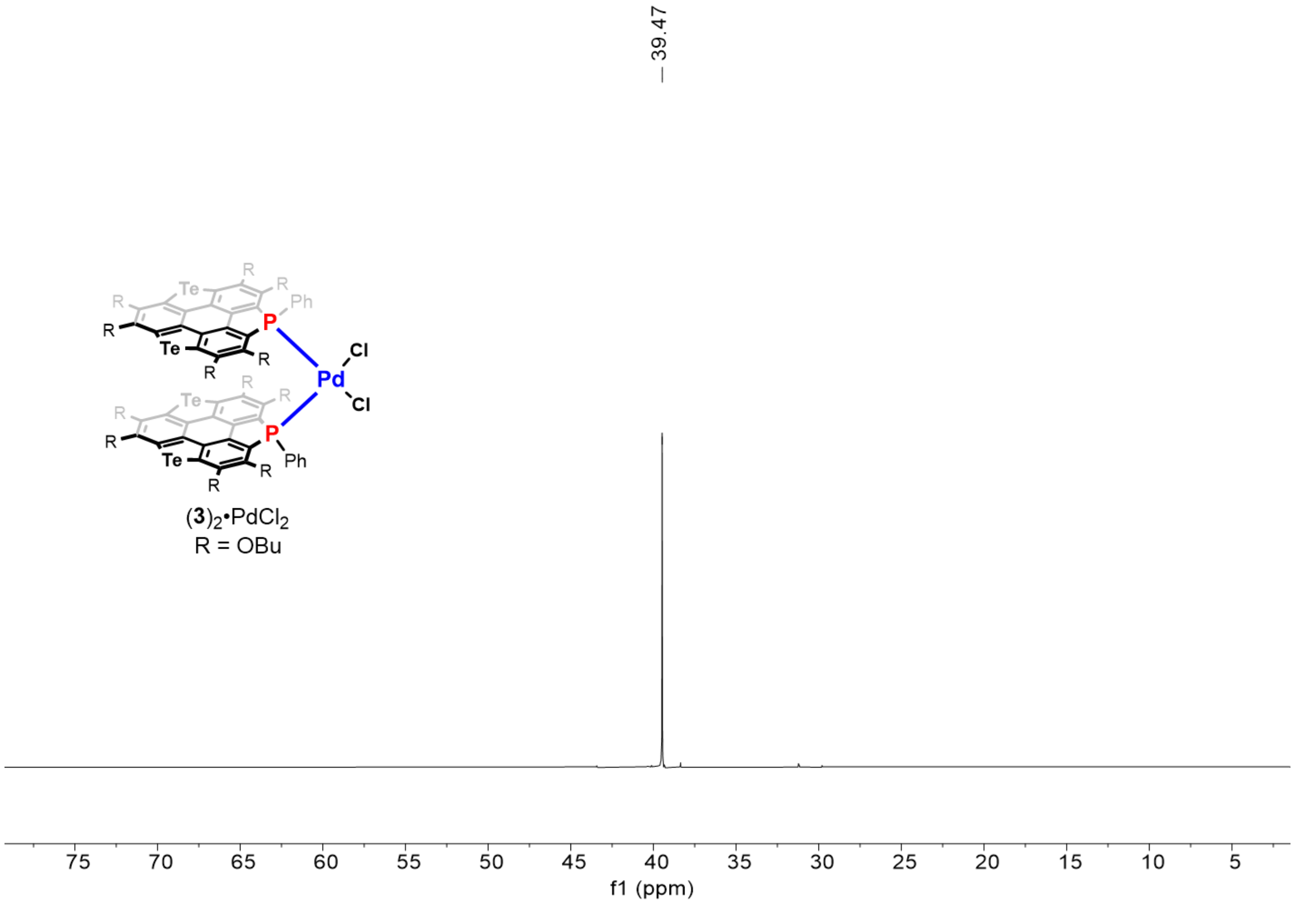


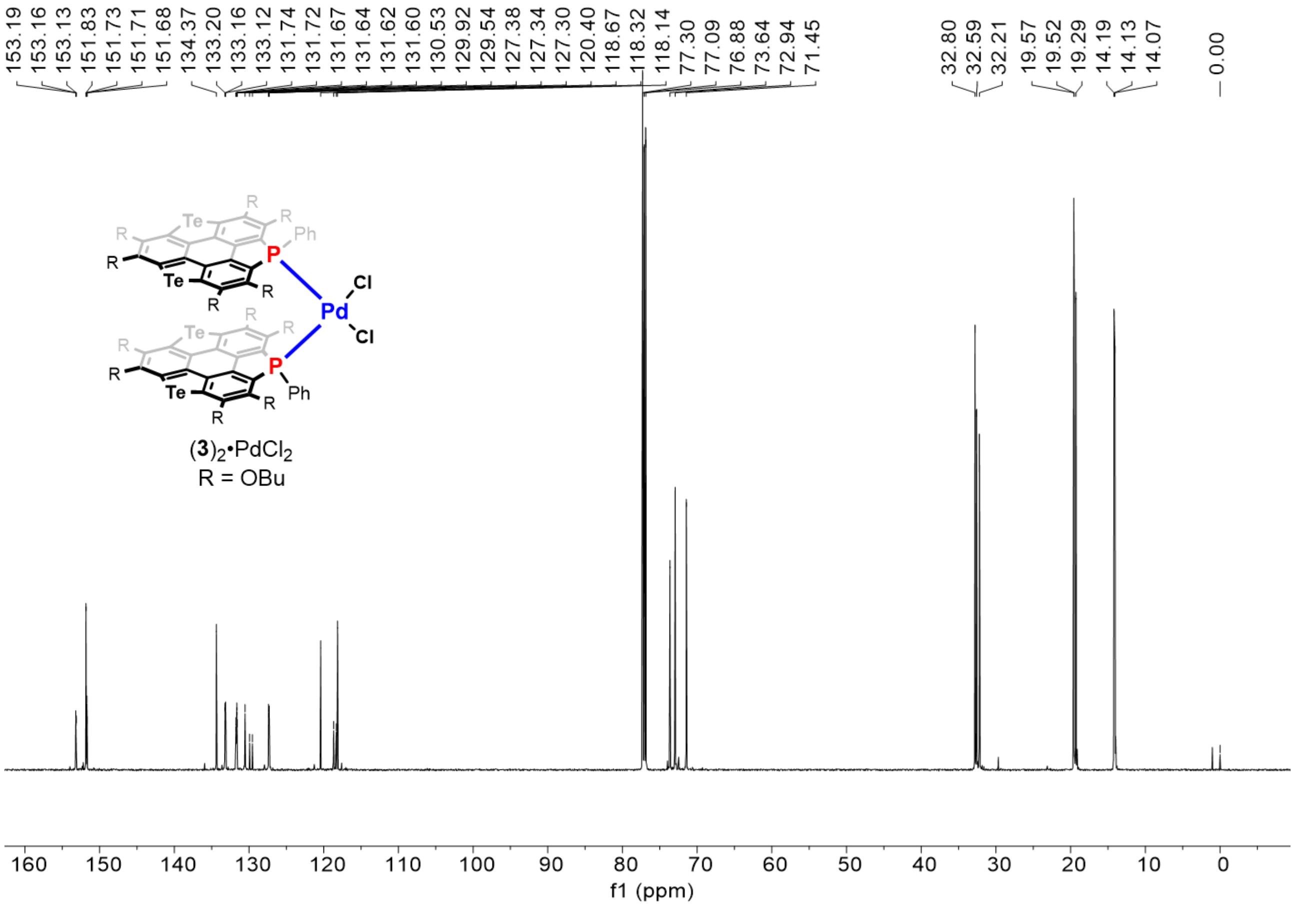
152.12
152.10
152.08
149.38
149.35
149.32
148.24
133.09
133.05
133.01
130.64
129.73
129.37
129.10
129.05
127.50
127.45
127.41
126.88
126.35
126.32
126.30
124.62
117.59
117.25
77.36
77.15
76.94
73.83
72.55
71.44
32.46
32.38
32.20
19.43
19.36
14.22
14.07
14.03
0.00
Se
R
Ph
P
Pd
Cl
Cl
(2)2•PdCl2
R = OBu
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

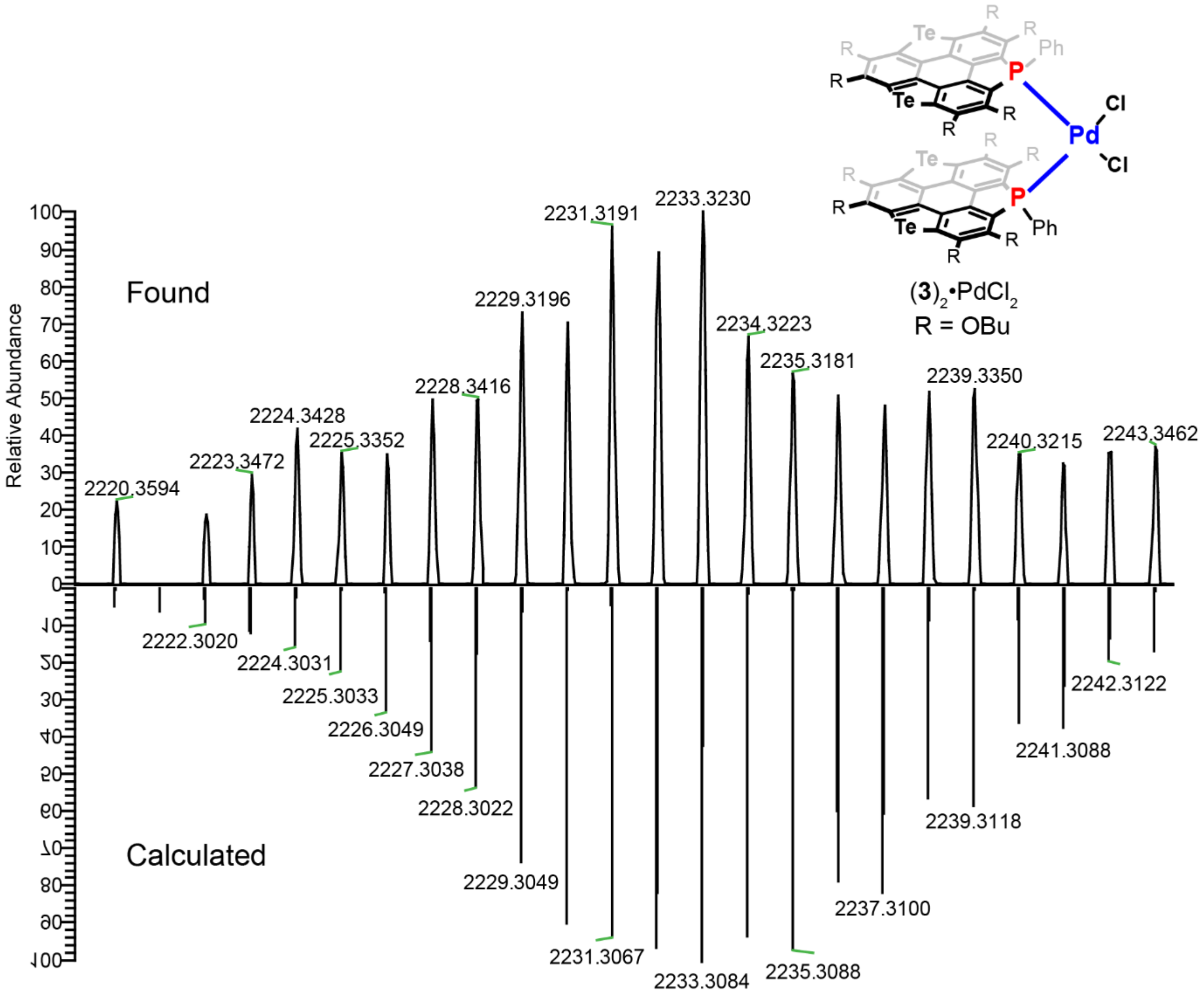

Relative Abundance
100
90
80
70
60
50
40
30
20
10
0
Found
Calculated
2027.3625
2030.3691
2031.3678
2032.3719
2033.3749
2035.3689
2037.3682
2039.3707
2041.3749
2042.3656
2043.3643
2046.3619
2028.3594
2030.3552
2031.3560
2033.3578
2034.3525
2035.3533
2037.3551
2038.3522
2039.3521
2041.3526
2043.3549
2045.3519
2046.3553
Se
R
Ph
P
Pd
Cl
(2)2•PdCl2
R = OBu

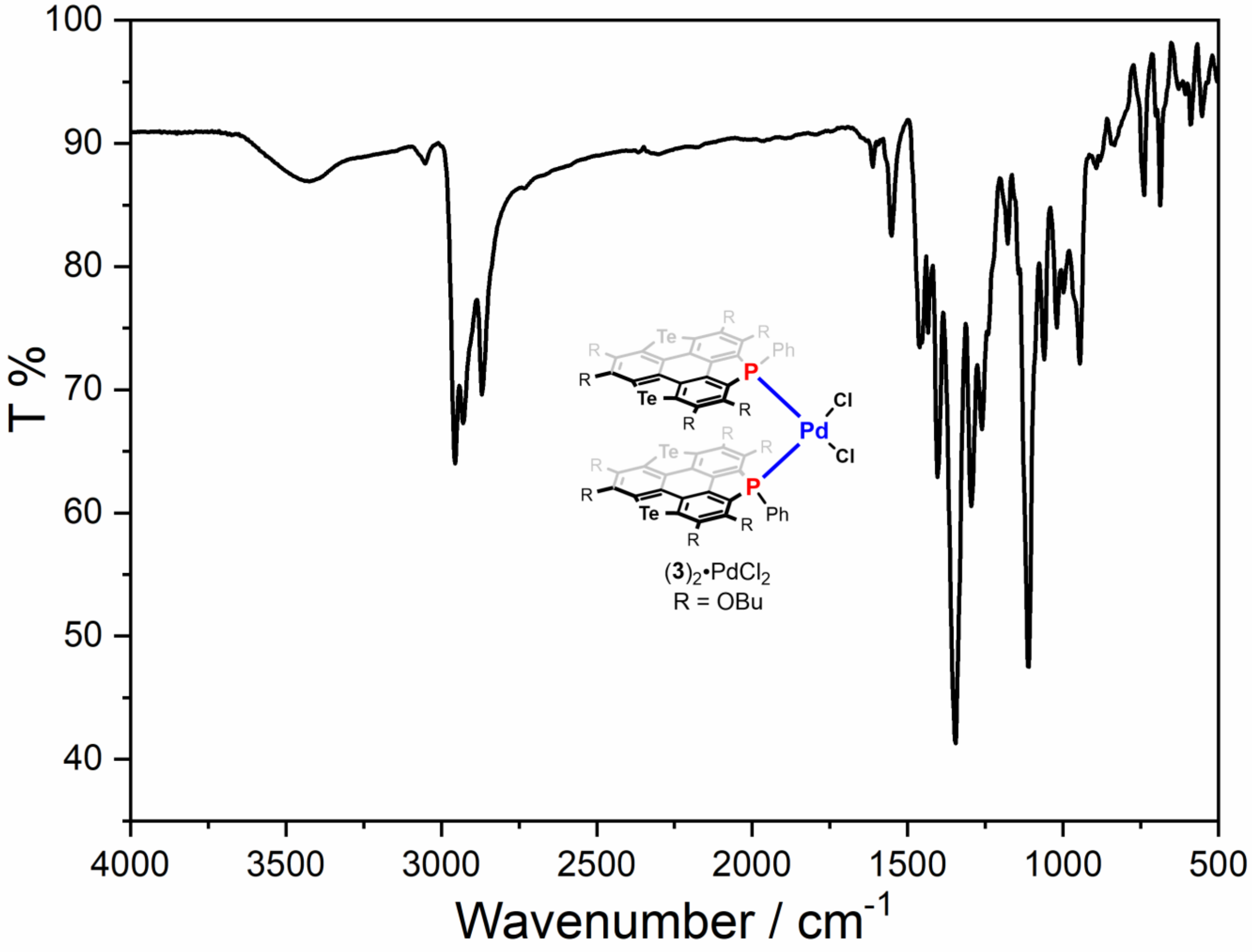

T %
100
90
80
70
60
50
40
30
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber / cm-1
Se
R
Ph
P
Pd
Cl
(2)2•PdCl2
R = OBu


7.04
7.04
7.04
4.53
4.52
4.27
4.27
4.26
4.26
4.25
4.25
4.21
4.20
4.20
4.19
4.19
4.13
4.13
4.12
4.12
1.96
1.95
1.93
1.86
1.86
1.85
1.84
1.84
1.83
1.83
1.82
1.82
1.81
1.62
1.61
1.61
1.60
1.60
1.59
1.55
1.53
1.50
1.49
1.09
1.08
1.06
1.05
1.00
0.99
0.98
-0.00
Te
R
Ph
P
Cl
Pd
Cl
OBu
(3)2•PdCl2
R = OBu
3.88
2.09
4.11
3.91
16.18
4.15
8.12
16.34
24.24
24.00
12.18
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


39.47
Te
R
Ph
P
Cl
Pd
Cl
(3)2•PdCl2
R = OBu
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)


153.19
153.16
153.13
151.83
151.73
151.71
151.68
134.37
133.20
133.16
133.12
131.74
131.72
131.67
131.64
131.62
131.60
130.53
129.92
129.54
127.38
127.34
127.30
120.40
118.67
118.32
118.14
77.30
77.09
76.88
73.64
72.94
71.45
32.80
32.59
32.21
19.57
19.52
19.29
14.19
14.13
14.07
0.00
Te
R
Ph
P
Cl
Pd
(3)2•PdCl2
R = OBu
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Te
R
Ph
P
Cl
Pd
(3)2•PdCl2
R = OBu
Relative Abundance
Found
Calculated
100
90
80
70
60
50
40
30
20
10
0
2220.3594
2223.3472
2224.3428
2225.3352
2228.3416
2229.3196
2231.3191
2233.3230
2234.3223
2235.3181
2239.3350
2240.3215
2243.3462
2222.3020
2224.3031
2225.3033
2226.3049
2227.3038
2228.3022
2229.3049
2231.3067
2233.3084
2235.3088
2237.3100
2239.3118
2241.3088
2242.3122


100
90
80
70
60
50
40
T %
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber / cm-1
Te
R
P
Ph
Pd
Cl
Cl
(3)2•PdCl2
R = OBu