

**Supporting Information for**  
**Direct Synthesis of Gold(III)-Annulated Perylene Diimides via**  
**Multiple C-H Auration**

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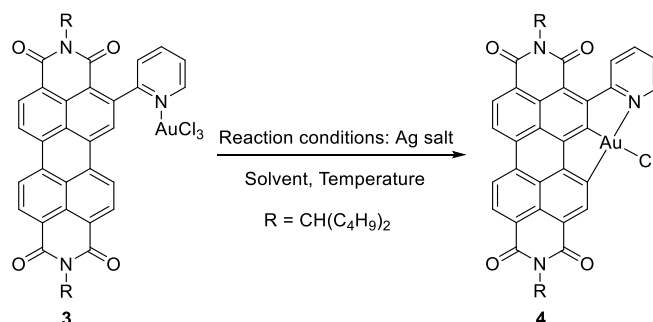
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## 1. General Information

Unless otherwise specified, reactions were performed under argon atmosphere employing standard Schlenk and glovebox techniques.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at a Bruker AV-400 or AV-500 spectrometer in  $\text{CDCl}_3$  or  $\text{CD}_2\text{Cl}_2$  at 298 K. Chemical shifts are given in ppm with reference to the residual solvent resonance of deuterated solvents. High-resolution mass spectrometry (HR-MS) analyses were recorded on a FT-MS instrument or a QTOF (Agilent 1290-G6545XT) instrument using ESI or APCI technique. UV-Vis absorption spectra and fluorescence spectra were obtained on a Hitachi U-3900 spectrophotometer and Hitachi F-7000, respectively. UV/vis/NIR absorption spectra were measured using an Agilent Cary 5000 UV/Vis/NIR spectrometer. The absolute quantum yields and fluorescence lifetimes were measured using an Edinburgh Instruments FLS1000 fluorescence spectrometer at room temperature. Transient PL measurements were performed using the HPL-TCSPC 510 nm laser as the excitation source. Cyclic voltammetry (CV) measurements were performed on a Bio-Logic-Science Instrument (EC-LAB SP-200). And the electrochemical measurements were carried out in dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate ( $^n\text{Bu}_4\text{NPF}_6$ ) as the supporting electrolyte at room temperature. Glassy carbon working electrode, platinum wire counter electrode and Ag/AgCl leakfree reference electrode. Single crystal X-ray diffraction data were collected on XtaLAB Synergy (Dualflex, HyPix) X-Ray single crystal diffractometer using  $\text{Cu K}\alpha$  ( $\lambda = 1.54184 \text{ \AA}$ ) micro-focus X-ray sources (PhotonJet (Cu) X-ray Source). The crystal was kept at 100 K during data collection. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimisation. The EPR measurements were conducted using a Bruker EMX-10/12 spectrometer. On the basis of crystal structures, the molecular orbitals were obtained by optimization and frequency analysis under gas phase conditions at B3LYP-D3(BJ)/def2-TZVP level,<sup>[1]</sup> and the imide substituents were replaced by methyl groups, as they hardly affect the molecular properties.<sup>[2]</sup>

Mechanochemical reactions were carried out using grinding vessels in a Retsch MM400 mill. Both jars (10 mL) and balls (1 mm) are made of stainless (SUS400B and SUS420J2, respectively). A heat gun QUICK 2020D+ with a temperature control function was used for high-temperature ball-milling reactions. After the ball-milling jar was closed, the jar was placed in the ball mill and a heat gun was placed directly above the ball-milling jar (distance between the heat gun and ball milling jar is ca. 1 cm) and fixed with clamps.<sup>[3]</sup> The mechanochemical cross-coupling reactions were conducted while applying heated air to the outside of the milling jar (preset temperature: 160 °C).

## 2. Reaction Optimization



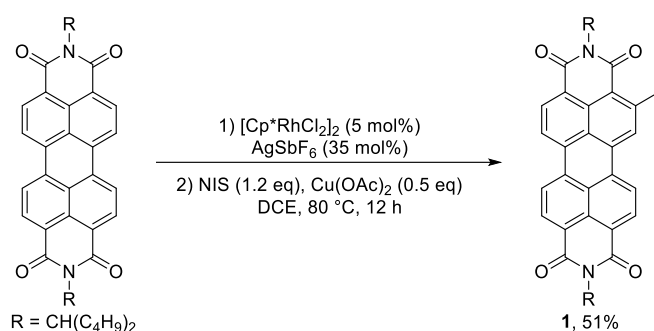
**Table S1.** Optimization of reaction conditions<sup>a</sup>

Entry	[Ag]	Solvent	Temp. (°C)	Yield of <b>4</b> <sup>b</sup> (%)
1	AgSbF <sub>6</sub>	DCM	60	26
2	AgSbF <sub>6</sub>	Et <sub>2</sub> O	60	25
3	AgSbF <sub>6</sub>	DCE	60	25
4	AgSbF <sub>6</sub>	Toluene	60	N.D.
5	AgSbF <sub>6</sub>	CH <sub>3</sub> CN	60	N.D.
6	AgSbF <sub>6</sub>	Acetone	60	N.D.
7	AgSbF <sub>6</sub>	DCE	100	26
8 <sup>c</sup>	AgSbF <sub>6</sub>	Et <sub>2</sub> O	60	N.D.
9 <sup>d</sup>	AgSbF <sub>6</sub>	Et <sub>2</sub> O	60	N.D.
10 <sup>e</sup>	AgSbF <sub>6</sub>	Et <sub>2</sub> O	60	7
11	AgBF <sub>4</sub>	DCM	60	29
12	AgPF <sub>6</sub>	DCM	60	33

13	AgOTs	DCM	60	N.D.
14	AgNTf <sub>2</sub>	DCM	60	57
15	AgNTf <sub>2</sub>	DCE	60	61

<sup>a</sup>Reactions conditions: 0.03 mmol **3**, Ag salt (2.2 equiv), 24 h, argon. <sup>b</sup>Isolated yields of **4**. <sup>c</sup>Additive: KO<sup>t</sup>Bu (2.0 eq). <sup>d</sup>Additive: Cy<sub>2</sub>NH (2.0 eq). <sup>e</sup>Additive: Cy<sub>2</sub>NH (20 mol%). N.D. = Not Detected.

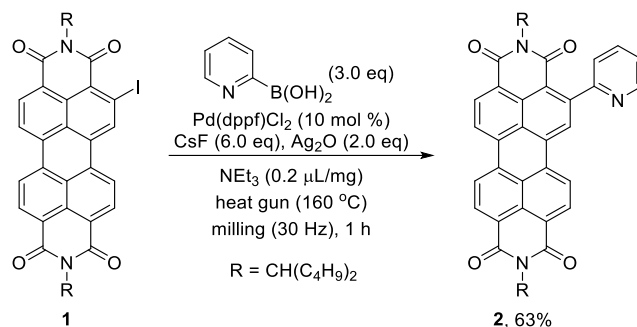
### 3. Procedures and Characterization Data



**Synthesis of 1.**<sup>[4]</sup> In a 15 mL Schlenk tube, a mixture of [Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> (0.0025 mmol, 1.6 mg) and AgSbF<sub>6</sub> (0.0175 mmol, 6.0 mg) was stirred at room temperature in 0.2 mL of DCE for 5 minutes under argon. Subsequently, the parent PDI (0.05 mmol, 32.1 mg), NIS (0.06 mmol, 13.5 mg), Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (0.025 mmol, 5.0 mg), and 1.3 mL of DCE were added sequentially. The tube was then sealed, and the mixture was stirred at 80 °C for 12 hours. After cooling to room temperature, the reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub>, washed with saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution and brine. The organic layer was collected, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The residue was purified by silica gel column chromatography using a DCM/PE eluent. After recrystallization from DCM/MeOH, compound **1** was obtained in 51% yield (19.6 mg).

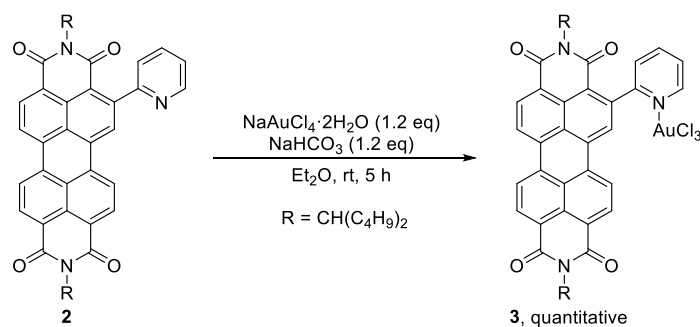
**1**: red solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.89 (s, 1H), 8.60 (d, *J* = 6.9 Hz, 1H), 8.55 (d, *J* = 7.9 Hz, 2H), 8.43 (d, *J* = 8.1 Hz, 1H), 8.40 (d, *J* = 8.1 Hz, 1H), 8.34 (d, *J* = 8.1 Hz, 1H), 5.26 – 5.07 (m, 2H), 2.32 – 2.14 (m, 4H), 1.99 – 1.83 (m, 4H), 1.43 – 1.18 (m, 16H), 0.87 (m, 12H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 164.5, 163.4, 162.8, 161.9, 137.7, 134.5, 133.9, 133.5, 132.7, 132.0, 131.9, 131.6, 131.3, 131.0, 130.7, 129.4, 126.1, 126.0,

123.3, 123.1, 122.9, 55.5, 54.9, 32.2, 32.1, 29.4, 29.3, 22.8, 14.2. HR-MS (ESI)  $m/z$   $[M+Na]^+$  calcd for  $C_{42}H_{45}N_2O_4INa^+$  791.2316; Found 791.2307.



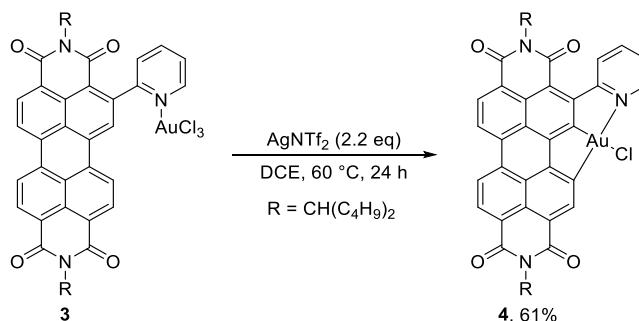
**Synthesis of 2.** Compound **1** (0.06 mmol, 46.2 mg), 2-pyridineboronic acid (0.18 mmol, 22.2 mg),  $\text{Pd(dppf)Cl}_2$  (0.006 mmol, 4.4 mg),  $\text{CsF}$  (0.36 mmol, 55.0 mg),  $\text{Ag}_2\text{O}$  (0.12 mmol, 28.0 mg), and dry  $\text{NEt}_3$  (31  $\mu\text{L}$ , 0.2  $\mu\text{L/mg}$ ) were placed in a milling jar (10 mL) with 70 balls (1 mm diameter) under an argon atmosphere. The jar was then sealed and placed in a ball mill (Retsch MM 400) set to run for 60 minutes at 30 Hz, with a heat gun (the preset temperature at 160 °C). After milling, the jar was cooled and opened, and the mixture was passed through a pad of Celite eluting with  $\text{CH}_2\text{Cl}_2$ . The crude material was then purified by flash column chromatography (using  $\text{SiO}_2$  and an eluent of  $\text{EtOAc/CH}_2\text{Cl}_2/\text{PE}$ ) to yield product **2** (63%, 27.2 mg).

**2:** red solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.78 (d,  $J = 4.5$  Hz, 1H), 8.66 – 8.44 (m, 7H), 7.84 (t,  $J = 7.3$  Hz, 1H), 7.48 (d,  $J = 7.8$  Hz, 1H), 7.43 (dd,  $J = 7.0, 5.2$  Hz, 1H), 5.15 (m, 2H), 2.31 – 2.05 (m, 4H), 1.94 – 1.74 (m, 4H), 1.29 (m, 16H), 0.96 – 0.75 (m, 12H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.6, 163.5, 159.4, 149.4, 145.7, 136.2, 134.4, 134.2, 134.0, 133.5, 131.9, 131.7, 131.2, 130.9, 130.2, 129.5, 126.8, 126.3, 126.2, 124.0, 123.4, 123.2, 122.9, 54.8, 32.2, 32.0, 29.3, 29.2, 22.75, 22.7, 14.2. HR-MS (ESI)  $m/z$   $[M+Na]^+$  calcd for  $C_{47}H_{49}N_3O_4Na^+$  742.3615; Found 742.3609.



**Synthesis of 3.** In a Schlenk tube, a mixture of **2** (0.030 mmol, 22.0 mg), sodium tetrachloroaurate dihydrate (0.036 mmol, 14.3 mg), and sodium bicarbonate (0.036 mmol, 3.0 mg) was dissolved in Et<sub>2</sub>O. The reaction mixture was stirred at 25 °C for 5 hours. Then the reaction mixture was diluted with distilled water and the organic compound was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic phases were combined and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the product **3** was obtained in a quantitative yield (30.7 mg).

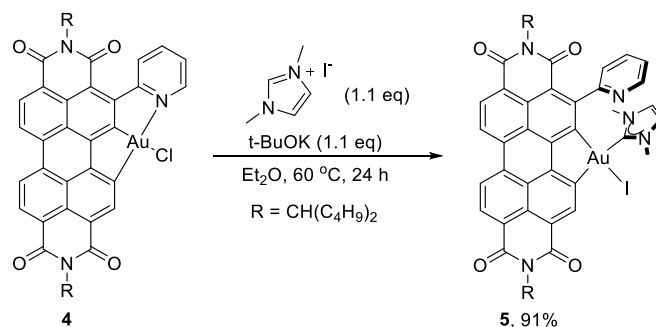
**3:** red solid; <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.88 (d, *J* = 5.9 Hz, 1H), 8.81 – 8.60 (m, 7H), 8.24 (t, *J* = 7.5 Hz, 1H), 7.92 (d, *J* = 7.5 Hz, 1H), 7.89 – 7.84 (m, 1H), 5.21 – 4.80 (m, 2H), 2.30 – 1.99 (m, 4H), 1.90 – 1.69 (m, 4H), 1.37 – 1.14 (m, 16H), 0.86 (m, 12H). <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 164.8, 164.3, 163.8, 163.7, 163.0, 162.7, 160.9, 149.5, 141.1, 139.7, 139.3, 135.4, 135.0, 134.3, 133.6, 132.8, 132.1, 131.6, 130.9, 130.5, 129.8, 127.8, 127.2, 126.8, 126.3, 124.8, 124.6, 124.2, 122.4, 121.9, 55.2, 54.9, 54.3, 54.1, 53.8, 53.6, 53.4, 32.4, 32.4, 32.3, 29.6, 29.5, 23.0, 14.2. HR-MS (ESI) *m/z* [M+Na]<sup>+</sup> calcd for C<sub>47</sub>H<sub>49</sub>AuCl<sub>3</sub>N<sub>3</sub>O<sub>4</sub>Na<sup>+</sup> 1044.2346; Found 1044.2353.



**Synthesis of 4.** In a glove box, a mixture of **3** (0.05 mmol, 51.0 mg) and silver bis(trifluoromethanesulfonyl)imide (0.11 mmol, 43.0 mg) was dissolved in dry DCE in a Schlenk tube. The reaction mixture was stirred for 24 hours at 60 °C. The resulting solution was filtered through a pad of Celite and washed with CH<sub>2</sub>Cl<sub>2</sub>. After concentration under reduced pressure, the solid was washed successively with MeOH and PE until the eluate was colorless. The resulting solid was then vacuum-dried to obtain blue solid **4** (61%, 29.0 mg).

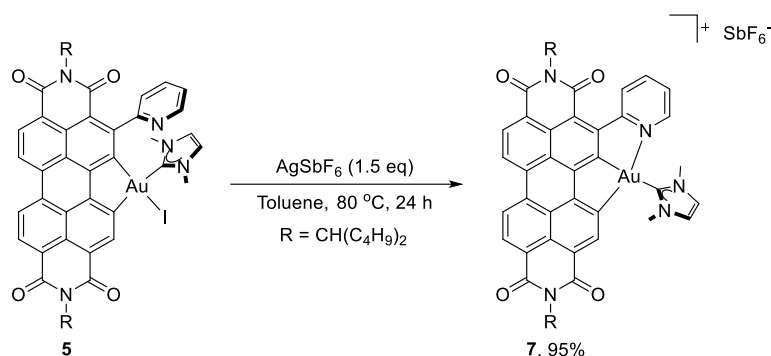
**4:** blue solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.77 (br, 1H), 8.19 (br, 1H), 7.88 (br, 1H), 7.78 (br, 1H), 7.57 (br, 1H), 7.43 (br, 1H), 7.37 (br, 1H), 7.17 (br, 1H), 6.89 (br, 1H),

4.91 (br, 2H), 2.04 (br, 4H), 1.96 (br, 4H), 1.42 (br, 16H), 0.97 (br, 12H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.9, 163.4, 162.6, 161.1, 151.8, 151.5, 148.2, 146.1, 141.4, 140.5, 134.1, 133.7, 131.3, 130.4, 129.0, 128.7, 127.4, 126.4, 124.6, 124.4, 122.5, 122.1, 120.0, 55.4, 54.5, 32.3, 29.6, 29.6, 22.9, 14.4, 14.3. HR-MS (ESI)  $m/z$   $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{47}\text{H}_{47}\text{AuClN}_3\text{O}_4\text{Na}^+$  972.2813; Found 972.2800.



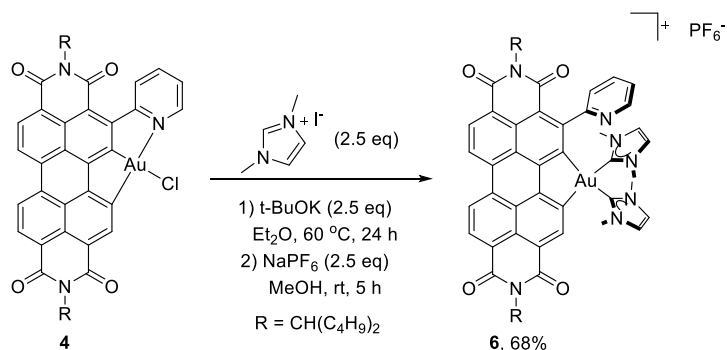
**Synthesis of 5.** A mixture of **4** (0.063 mmol, 60.0 mg), potassium tert-butoxide (0.070 mmol, 8.0 mg) and 1,3-dimethyl-1H-imidazol-3-ium iodide (0.070 mmol, 16.0 mg) in  $\text{Et}_2\text{O}$  was heated to 60 °C for 24 h. The solvent was then removed under vacuum, and the residue was dissolved in  $\text{CH}_2\text{Cl}_2$ . The mixture was filtered through a pad of Celite. After concentration under reduced pressure, it was purified by column chromatography on silica gel with  $\text{EtOAc}/\text{CH}_2\text{Cl}_2$  as eluent, and purple solid **5** was obtained (91%, 65.4 mg).

**5:** purple solid;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  10.10 (d,  $J = 15.1$  Hz, 1H), 8.58 – 8.35 (m, 5H), 7.55 (t,  $J = 6.4$  Hz, 1H), 7.13 (d,  $J = 7.6$  Hz, 1H), 7.06 – 7.02 (m, 1H), 6.72 (s, 1H), 6.67 (s, 1H), 4.98 (m, 2H), 3.59 (s, 3H), 3.45 (s, 3H), 2.14 (m, 4H), 1.90 – 1.66 (m, 4H), 1.29 (m, 16H), 0.87 – 0.76 (m, 12H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  172.4, 165.1, 164.1, 161.3, 160.8, 155.3, 153.8, 153.4, 149.1, 143.4, 142.7, 136.5, 135.3, 135.1, 132.1, 131.6, 130.8, 129.5, 127.9, 126.6, 126.4, 123.9, 123.3, 122.6, 122.6, 122.3, 122.2, 54.6, 38.2, 32.4, 32.1, 32.0, 29.8, 29.3, 29.1, 22.8, 22.7, 14.2, 14.2. HR-MS (ESI)  $m/z$   $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{52}\text{H}_{55}\text{AuIN}_5\text{O}_4\text{Na}^+$  1160.2856; Found 1160.2841.



**Synthesis of 7.** In a glove box, a mixture of **5** (0.046 mmol, 52.0 mg) and silver hexafluoroantimonate (0.069 mmol, 24.0 mg) was dissolved in dry toluene in a Schlenk tube. The reaction mixture was stirred for 24 hours at 80 °C. The solvent was then removed under vacuum, the residue was dissolved in  $\text{CH}_2\text{Cl}_2$ , and the mixture was filtered through a pad of Celite. After concentration under reduced pressure, slow diffusion of *n*-hexane into the residue solution resulted in the formation of purple crystals of **7** (95%, 54.5 mg).

**7:** purple solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  9.35 (d,  $J = 8.3$  Hz, 1H), 8.61 – 8.54 (m, 2H), 8.48 (s, 1H), 8.43 (d,  $J = 7.9$  Hz, 2H), 8.37 – 8.29 (m, 1H), 7.80 (t,  $J = 6.0$  Hz, 2H), 7.52 (s, 2H), 5.17 (m, 2H), 4.03 (s, 6H), 2.31 – 2.09 (m, 4H), 1.97 – 1.87 (m, 2H), 1.85 – 1.75 (m, 2H), 1.38 – 1.21 (m, 16H), 0.89 – 0.81 (m, 12H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  177.8, 175.4, 165.2, 164.7, 163.4, 156.3, 153.5, 149.4, 147.8, 145.5, 142.8, 136.3, 135.8, 135.0, 133.3, 132.6, 130.9, 130.0, 129.5, 128.9, 126.9, 126.3, 125.6, 124.6, 124.4, 123.7, 123.0, 121.0, 55.7, 54.9, 38.4, 32.5, 29.6, 29.5, 23.0, 14.2, 14.2. HR-MS (ESI)  $m/z$   $[\text{M}]^+$  calcd for  $\text{C}_{52}\text{H}_{55}\text{AuN}_5\text{O}_4^+$  1010.3914; Found 1010.3906.

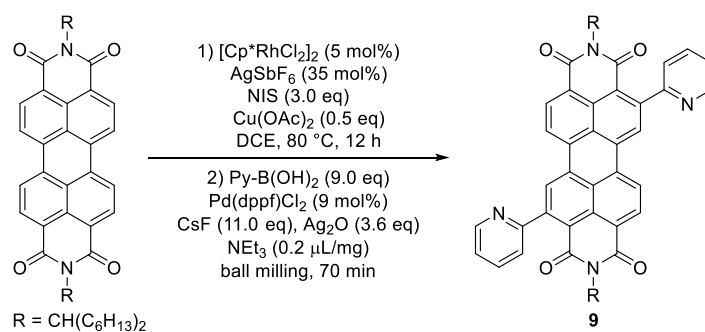


**Synthesis of 6.** A mixture of **4** (0.032 mmol, 30.4 mg), potassium tert-butoxide (0.080 mmol, 9.0 mg) and 1,3-dimethyl-1H-imidazol-3-ium iodide (0.080 mmol, 18.0 mg) in



Et<sub>2</sub>O was heated to 60 °C for 24 h. The solvent was then removed under vacuum, the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, and the mixture was filtered through a pad of Celite. The reaction mixture was concentrated and subjected to a metathesis reaction with sodium hexafluorophosphate (0.080 mmol, 14.0 mg) in methanol. After extracting the crude product into dichloromethane layer, it was purified by column chromatography on silica gel with MeOH/CH<sub>2</sub>Cl<sub>2</sub> as eluent, and purple solid **6** was obtained (68%, 27.4 mg).

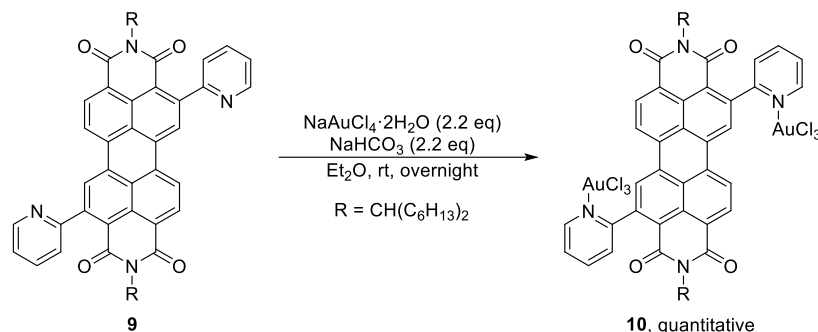
**6**: purple solid; <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.49 (m, 4H), 8.38 (d, *J* = 4.0 Hz, 1H), 7.66 (br, 1H), 7.39 (s, 3H), 7.20 (d, *J* = 6.3 Hz, 1H), 7.10 (br, 1H), 6.86 (s, 2H), 5.18 – 4.63 (m, 2H), 3.70 (s, 6H), 3.46 (s, 6H), 2.13 (m, 4H), 1.72 (m, 4H), 1.26 (m, 16H), 0.86 – 0.80 (m, 12H). <sup>13</sup>C NMR (101 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 175.4, 170.0, 168.1, 164.9, 164.3, 163.7, 162.4, 160.3, 157.8, 155.9, 155.2, 149.6, 136.1, 135.8, 135.4, 132.5, 132.1, 131.8, 130.3, 130.1, 129.8, 129.1, 128.1, 126.9, 126.7, 125.6, 124.6, 124.0, 123.5, 123.3, 122.8, 122.5, 114.2, 54.8, 38.2, 38.0, 36.1, 32.5, 32.3, 30.2, 30.1, 29.9, 29.7, 29.6, 29.5, 29.4, 27.6, 25.9, 23.0, 23.0, 14.2. HR-MS (ESI) *m/z* [M]<sup>+</sup> calcd for C<sub>57</sub>H<sub>63</sub>AuN<sub>7</sub>O<sub>4</sub><sup>+</sup> 1106.4602; Found 1106.4600.



**Synthesis of 9.** In a Schlenk tube, a mixture of [Cp<sup>\*</sup>RhCl<sub>2</sub>]<sub>2</sub> (0.05 mmol, 31.0 mg) and AgSbF<sub>6</sub> (0.35 mmol, 121.0 mg) was stirred at room temperature in DCE (5.0 mL) for 5 minutes under argon. And then, followed by adding the parent PDI (1.00 mmol, 755.0 mg), NIS (3.00 mmol, 675.0 mg), Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (0.50 mmol, 100.0 mg), and DCE (15.0 mL) in succession, the mixture was stirred at 80 °C for 12 hours. After cooling down to room temperature, the reaction mixture was purified by silica gel column chromatography using DCM/hexane (2:5) as eluent to afford a mixture of PDI-I<sub>2</sub> (**8**) and PDI-I<sub>3</sub> (197.3 mg) as a red solid. The mixture (113.3 mg), 2-pyridineboronic acid

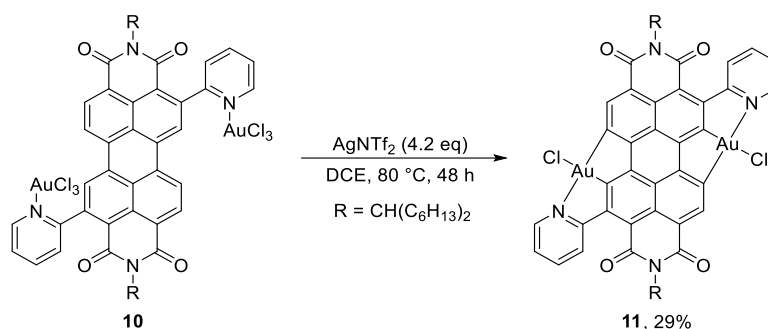
(1.00 mmol, 123.0 mg), Pd(dppf)Cl<sub>2</sub> (0.01 mmol, 7.3 mg), CsF (1.20 mmol, 182.3 mg), Ag<sub>2</sub>O (0.40 mmol, 92.7 mg) and dry NEt<sub>3</sub> (105.0 μL, 0.2 μL/mg) were placed in a milling jar (10 mL) with 70 balls (1 mm, diameter) under argon atmosphere. After the jar was closed, the jar was placed in the ball mill (Retsch MM 400, 70 min, 30 Hz) with a heat gun (the preset temperature at 160 °C). After ball milling, the jar was then cooled down and opened. The mixture was passed through a pad of Celite eluting with CH<sub>2</sub>Cl<sub>2</sub>. The crude material was purified by flash column chromatography (SiO<sub>2</sub>, EtOAc/CH<sub>2</sub>Cl<sub>2</sub>/PE) to give the product **9** (25%, 24.7 mg).

**9**: red solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.78 (d, *J* = 4.6 Hz, 2H), 8.60 (m, 6H), 7.84 (t, *J* = 7.2 Hz, 2H), 7.49 (d, *J* = 7.8 Hz, 2H), 7.45 – 7.40 (m, 2H), 5.02 (m, 2H), 2.16 (br, 4H), 1.77 (br, 4H), 1.28 – 1.21 (m, 32H), 0.83 (t, *J* = 6.7 Hz, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 164.0, 163.3, 159.5, 149.3, 145.7, 136.3, 133.9, 133.7, 132.2, 132.1, 131.5, 130.2, 128.6, 127.1, 126.3, 124.1, 123.7, 122.9, 54.8, 32.3, 31.9, 29.8, 29.3, 27.0, 22.7, 14.2. HR-MS (ESI) *m/z* [M+Na]<sup>+</sup> calcd for C<sub>60</sub>H<sub>68</sub>N<sub>4</sub>O<sub>4</sub>Na<sup>+</sup> 931.5133; Found 931.5117.



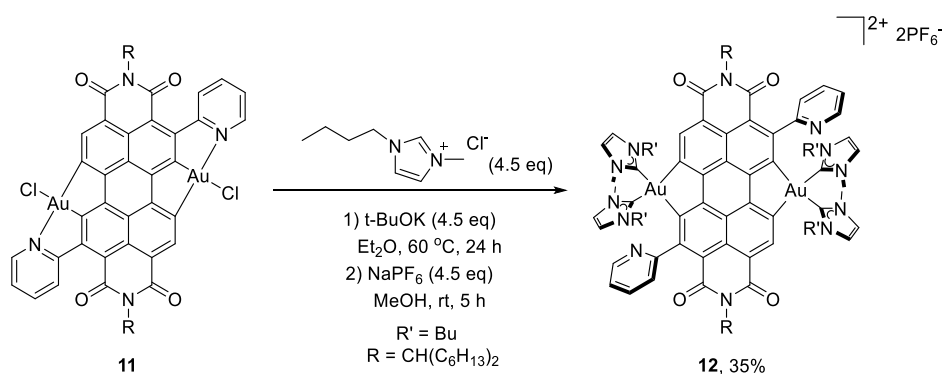
**Synthesis of 10.** In a Schlenk tube, a mixture of **9** (0.027 mmol, 24.5 mg), sodium tetrachloroaurate dihydrate (0.060 mmol, 24.0 mg) and sodium bicarbonate (0.060 mmol, 5.0 mg) were dissolved in Et<sub>2</sub>O. The reaction mixture was stirred at 25 °C overnight. Then the reaction mixture was diluted with distilled water and organic compound was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic phases were combined and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the product **10** was obtained in a quantitative yield (40.5 mg).

**10**: red solid;  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.95 – 8.76 (m, 8H), 8.25 (m, 2H), 7.96 – 7.83 (m, 4H), 5.19 – 4.76 (m, 2H), 2.09 (m, 4H), 1.77 (m, 4H), 1.23 (m, 32H), 0.87 – 0.81 (m, 12H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  164.1, 163.8, 162.9, 162.5, 160.7, 149.6, 149.5, 141.3, 141.1, 139.8, 139.4, 134.5, 134.2, 133.9, 133.1, 130.9, 130.8, 130.4, 127.9, 127.3, 127.0, 126.0, 125.9, 125.7, 124.8, 122.9, 122.4, 55.4, 32.6, 32.3, 32.2, 32.1, 30.1, 29.8, 29.6, 27.3, 23.0, 23.0, 14.2. HR-MS (ESI)  $m/z$   $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{60}\text{H}_{68}\text{Au}_2\text{Cl}_6\text{N}_4\text{O}_4\text{Na}^+$  1535.2595; Found 1535.2582.



**Synthesis of 11.** In a glove box, a mixture of **10** (0.16 mmol, 242.6 mg) and silver bis(trifluoromethanesulfonyl)imide (0.67 mmol, 260.7 mg) was dissolved in dry DCE in a Schlenk tube. The reaction mixture was stirred for 48 hours at 80 °C. The solvent was removed under vacuum,  $\text{CH}_2\text{Cl}_2$  was added to the residue, and the mixture was filtered until the filtrate became colorless. Finally, the filter cake was washed successively with water and methanol to obtain dark green solid **11** (29%, 63.6 mg).

**11**: dark green solid; due to its low solubility in common deuterated solvents, **11** did not yield a sufficient signal-to-noise ratio for  $^1\text{H}$  NMR spectroscopy.



**Synthesis of 12.** A mixture of **11** (0.046 mmol, 63.0 mg), potassium tert-butoxide (0.207 mmol, 23.2 mg) and 1-butyl-3-methylimidazolium chloride (0.207 mmol, 36.2 mg) in  $\text{Et}_2\text{O}$  was heated to 60 °C for 24 h. The solvent was then removed under vacuum,

the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, and the mixture was filtered through a pad of Celite. The reaction mixture was concentrated and subjected to a metathesis reaction with sodium hexafluorophosphate (0.207 mmol, 35.0 mg) in methanol. After extracting the crude product into dichloromethane layer, it was purified by column chromatography on silica gel with MeOH/CH<sub>2</sub>Cl<sub>2</sub> as eluent, and blue solid **12** was obtained (35%, 34.2 mg).

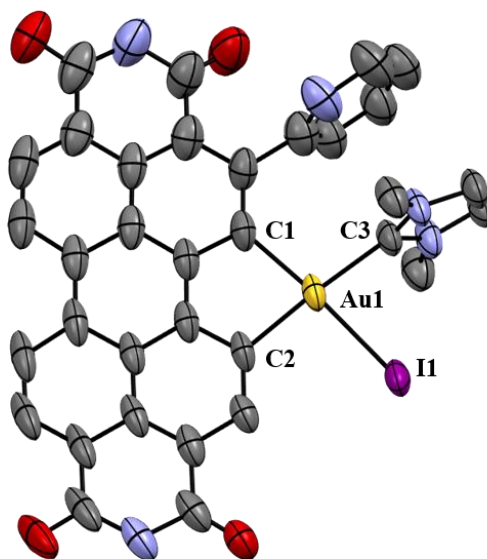
**12**: blue solid; <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.33 (s, 2H), 7.65 (s, 2H), 7.45 (d, *J* = 14.6 Hz, 2H), 7.35 (s, 2H), 7.17 (m, 6H), 6.99 – 6.80 (m, 4H), 4.74 (m, 2H), 3.98 – 3.47 (m, 20H), 2.01 – 1.71 (m, 8H), 1.28 – 1.10 (m, 48H), 0.90 – 0.75 (m, 24H). Due to the weak <sup>13</sup>C NMR signal of **12**, a clear carbon peak spectrum could not be obtained. HR-MS (ESI) *m/z* [*M*]<sup>2+</sup> calcd for C<sub>92</sub>H<sub>120</sub>Au<sub>2</sub>N<sub>12</sub>O<sub>4</sub><sup>2+</sup> 925.9455; Found 925.9442.

#### 4. Crystallographic Data

Single crystal X-ray diffraction data were collected at room temperature on XtaLAB Synergy (Dualflex, HyPix). X-Ray single crystal diffractometer using Cu Kα ( $\lambda$  = 1.54184 Å) micro-focus X-ray sources (PhotonJet (Cu) X-ray Source). The raw data were collected and reduced by CrysAlisPro software. The structures were solved by the SHELXT with Intrinsic Phasing and refined on *F*<sup>2</sup> by full-matrix least-squares methods with the SHELXL and OLEX2 was used as GUI.

Refinement details: All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions using the riding model and refined isotropically. The instructions AFIX 23 and AFIX 43 were used for the hydrogen atoms on the secondary -CH<sub>2</sub>- and the aromatic C-H, respectively, with the parameter of Uiso = 1.2 Ueq. The instruction AFIX 33 was used for the hydrogen atoms on the highly disordered terminal -CH<sub>3</sub> groups with the parameter of Uiso=1.5 Ueq.

For **5** (exp\_14612, CCDC 2349582), the flexible alkyl chains, solvent molecules and pyridine ring are expected to be highly disordered. Therefore, necessary Shelx restraints (i.e., DELU, DANG, SIMU, ISOR and DFIX) were applied to the alkyl chains, solvent molecules and pyridine ring to result in a reasonable model.

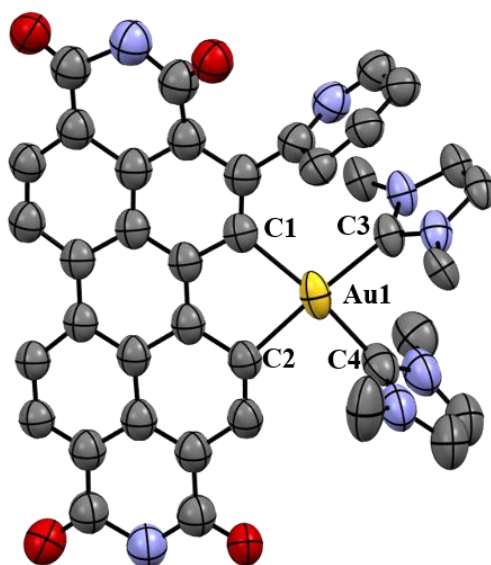


**Fig. S1.** X-ray crystal structure of **5** (50% probability thermal ellipsoids). Hydrogen atoms, alkyl chains on nitrogen atoms are omitted for clarity.

**Table S2.** Selected bond lengths and angles of **5**.

Selected bond lengths (Å)			
Au1-C1	2.102(6)	Au1-C3	2.093(5)
Au1-C2	2.081(5)	Au1-I1	2.654(4)
Selected bond angles (°)			
C1-Au1-C2	82.4(2)	C3-Au1-I1	82.6(2)
C1-Au1-C3	101.6(2)	C2-Au1-I1	93.4(2)

For **6**, BASF/TWIN refinement was performed on the data. Moreover, the PDI structure expected to be highly disordered. Therefore, necessary Shelx restraints (i.e., DELU, DANG, SIMU, ISOR, FLAT and DFIX) were applied to PDI to result in a reasonable model. A satisfactory disorder model for the solvent molecules was not found, therefore the OLEX2 Solvent Mask routine (similar to PLATON/SQUEEZE) was used to mask out the disordered density.

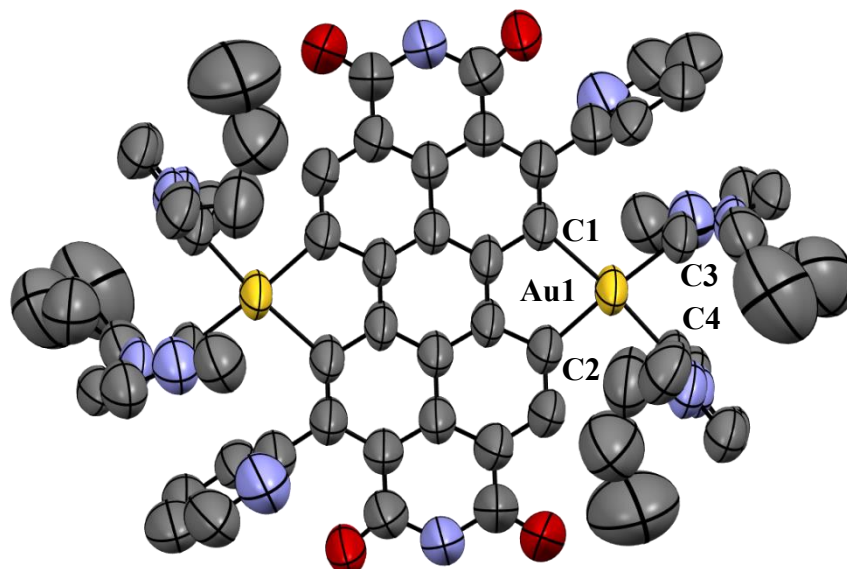


**Fig. S2.** X-ray crystal structure of **6** (50% probability thermal ellipsoids). Hydrogen atoms, alkyl chains on nitrogen atoms and  $\text{PF}_6^-$  counterion are omitted for clarity.

**Table S3.** Selected bond lengths and angles of **6**.

Selected bond lengths (Å)			
Au1-C1	2.140(20)	Au1-C3	2.047(18)
Au1-C2	2.070(20)	Au1-C4	2.057(12)
Selected bond angles (°)			
C1-Au1-C2	82.7(10)	C2-Au1-C4	95.4(8)
C1-Au1-C3	95.7(10)	C3-Au1-C4	86.2(7)

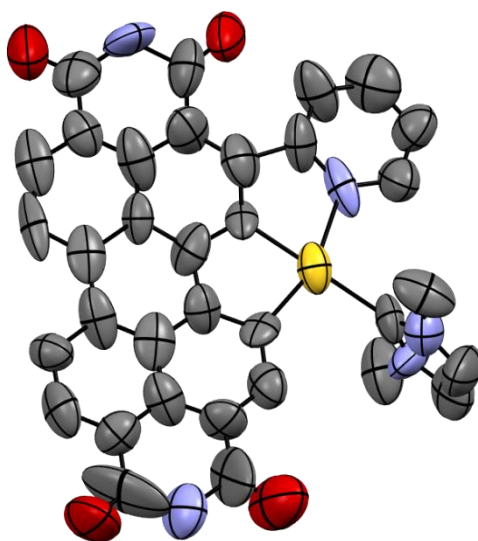
The crystal of **12** is anisotropically diffracted, at some orientation, crystal can only diffract to 1.1 Å, while other sides, the resolution can reach 0.86 Å. This leads to so many reflections in the high-resolution range, their intensity is negative. Also the structure model can be observed with disorder at same orientation. Therefore, necessary Shelx restraints (i.e., DELU, SADI, RIGU, SIMU, ISOR and DFIX) were applied to the structure model. A satisfactory disorder model for the solvent molecules was not found, therefore the OLEX2 Solvent Mask routine (similar to PLATON/SQUEEZE) was used to mask out the disordered density.



**Fig. S3.** X-ray crystal structure of **12** (50% probability thermal ellipsoids). Hydrogen atoms, alkyl chains on nitrogen atoms and  $\text{PF}_6^-$  counterion are omitted for clarity.

**Table S4.** Selected bond lengths and angles of **12**.

Selected bond lengths (Å)			
Au1-C1	2.151(12)	Au1-C3	2.019(15)
Au1-C2	2.021(15)	Au1-C4	2.031(15)
Selected bond angles (°)			
C1-Au1-C2	83.7(5)	C4-Au1-C3	86.7(6)
C2-Au1-C4	90.2(6)	C3-Au1-C1	99.6(6)



**Fig. S4.** X-ray crystal structure of **7** (50% probability thermal ellipsoids). Hydrogen atoms, alkyl chains on nitrogen atoms and  $\text{SbF}_6^-$  counterion are omitted for clarity. The crystal quality is insufficient to obtain reliable data; only the primary structure is discernible.

**Table S5.** Crystal data and structure refinement for **5**.

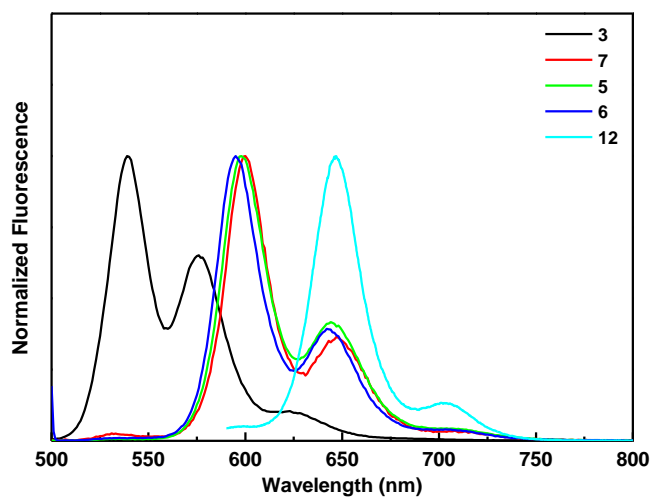
Identification code	<b>5</b> (CCDC 2349582)
Empirical formula	$\text{C}_{53.5}\text{H}_{58.5}\text{AuIN}_5\text{O}_4$
Formula weight	1159.42
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
$a/\text{\AA}$	7.87150(10)
$b/\text{\AA}$	20.7417(3)
$c/\text{\AA}$	29.2003(3)
$\alpha/^\circ$	98.8440(10)
$\beta/^\circ$	90.2900(10)
$\gamma/^\circ$	95.7940(10)
Volume/ $\text{\AA}^3$	4685.71(10)
Z	4



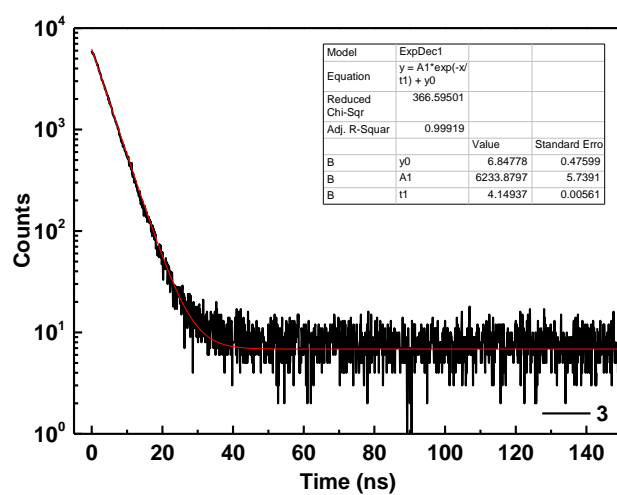
$\rho_{\text{calc}}/\text{cm}^3$	1.644
$\mu/\text{mm}^{-1}$	11.484
F(000)	2314.0
Crystal size/ $\text{mm}^3$	$0.25 \times 0.15 \times 0.1$
Radiation	CuK $\alpha$ ( $\lambda = 1.54184$ )
$2\Theta$ range for data collection/ $^\circ$	4.334 to 150.328
Index ranges	$-9 \leq h \leq 8, -25 \leq k \leq 26, -36 \leq l \leq 36$
Reflections collected	56949
Independent reflections	18349 [ $R_{\text{int}} = 0.0362, R_{\text{sigma}} = 0.0373$ ]
Data/restraints/parameters	18349/1889/1698
Goodness-of-fit on $F^2$	1.043
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0445, wR_2 = 0.1234$
Final R indexes [all data]	$R_1 = 0.0524, wR_2 = 0.1295$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	1.70/-1.49

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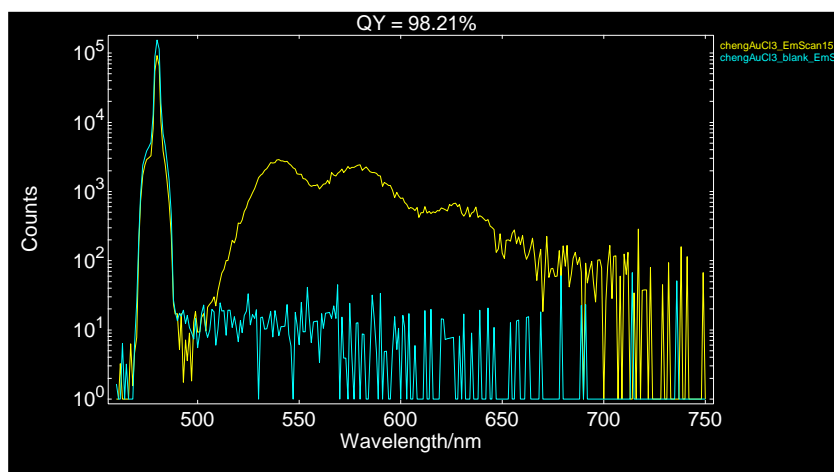
## 5. Optical Measurements



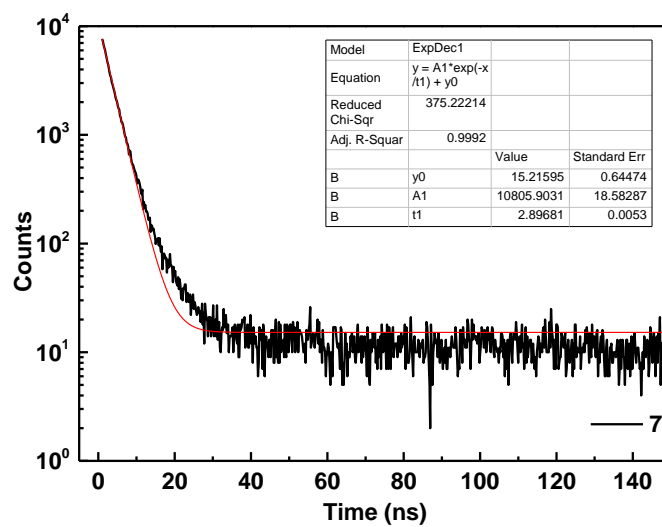
**Fig. S5.** Normalized fluorescence spectra of compounds **3**, **5**, **6**, **7**, and **12** in DCM ( $c=10 \mu\text{M}$ ,  $\lambda_{\text{ex}}=490 \text{ nm}$ ;  $\lambda_{\text{ex}}=580 \text{ nm}$  for **12**).



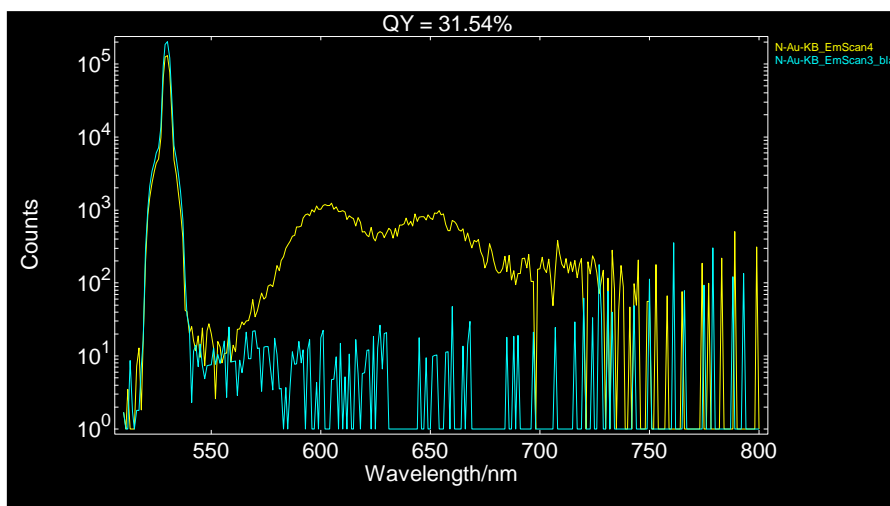
**Fig. S6.** Time-resolved fluorescence decay curve of **3**. ( $c = 5 \mu\text{M}$ , DCM).



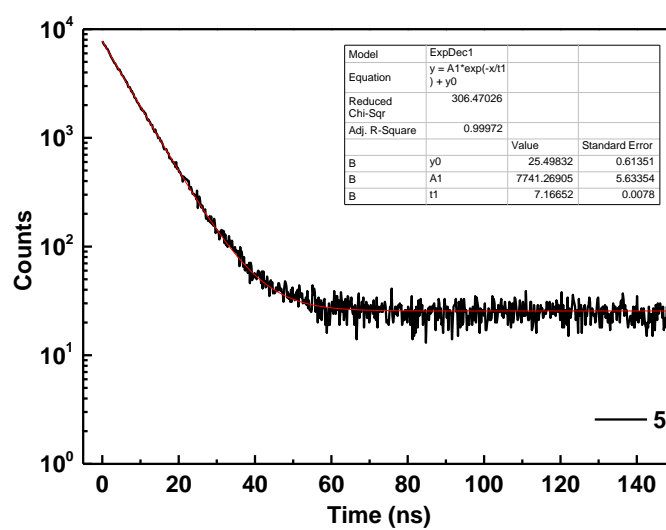
**Fig. S7.** The image of quantum yield of **3**. ( $c = 5 \mu\text{M}$ , DCM).



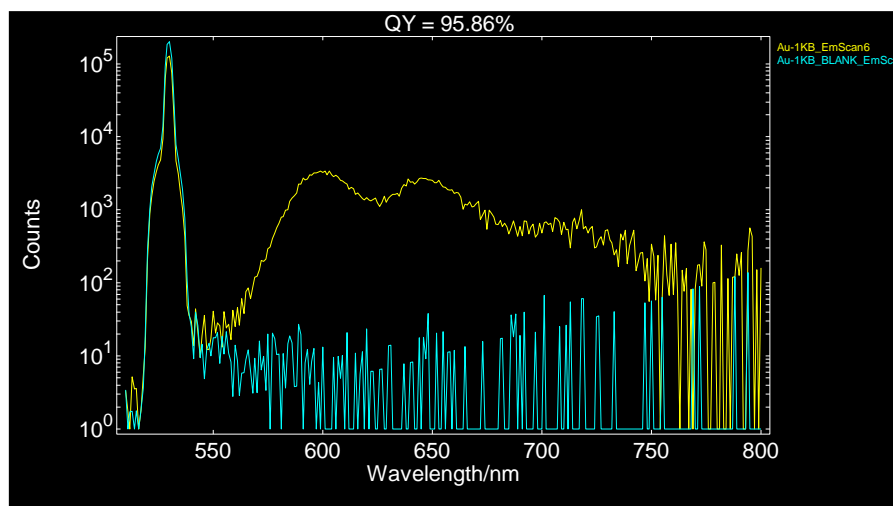
**Fig. S8.** Time-resolved fluorescence decay curve of **7**. ( $c = 5 \mu\text{M}$ , DCM).



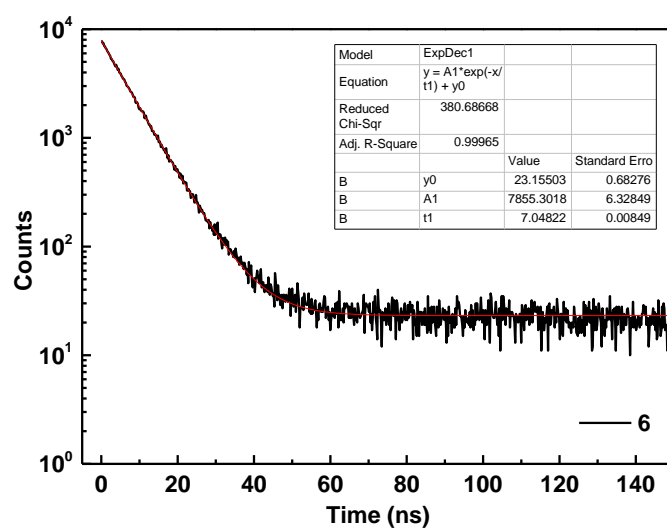
**Fig. S9.** The image of quantum yield of **7**. ( $c = 5 \mu\text{M}$ , DCM).



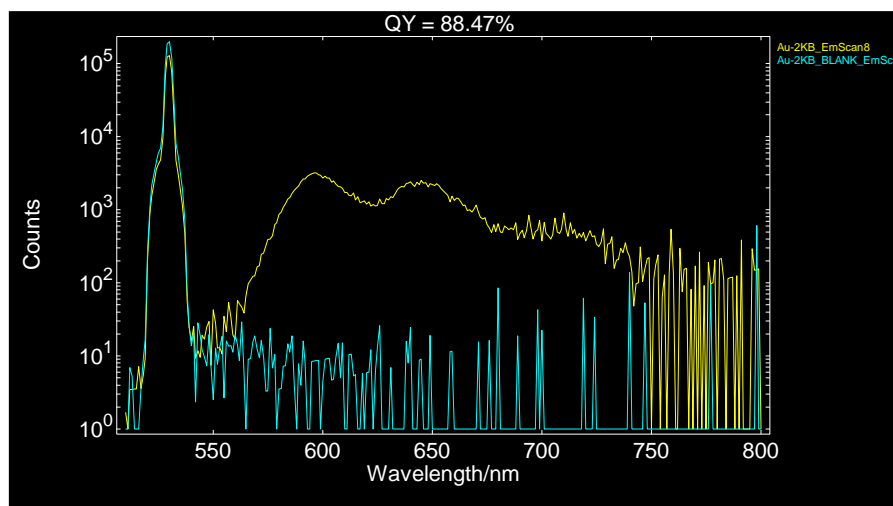
**Fig. S10.** Time-resolved fluorescence decay curve of **5**. ( $c = 5 \mu\text{M}$ , DCM).



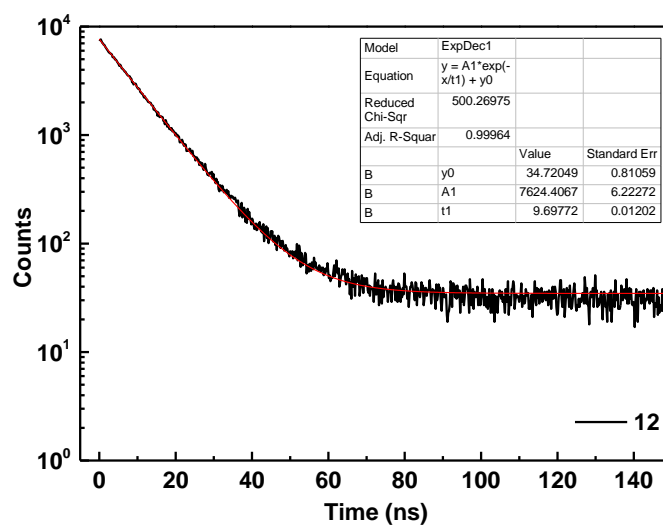
**Fig. S11.** The image of quantum yield of **5**. ( $c = 5 \mu\text{M}$ , DCM).



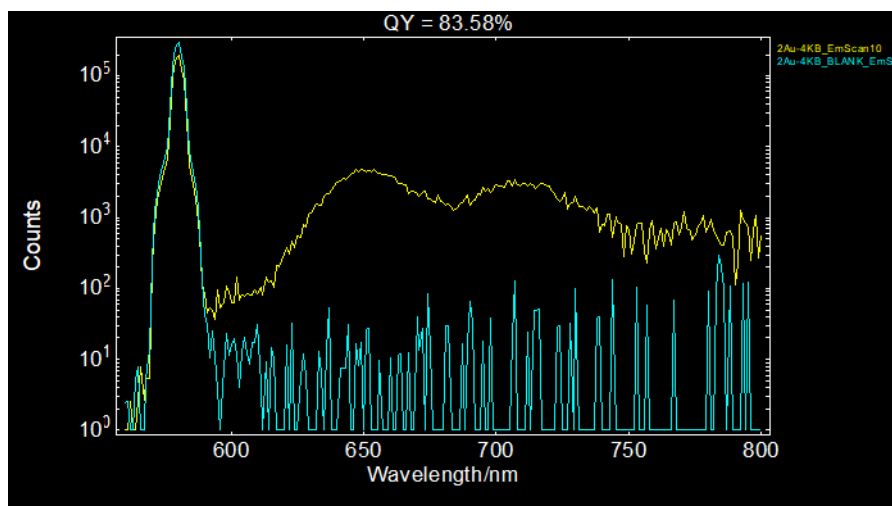
**Fig. S12.** Time-resolved fluorescence decay curve of **6**. ( $c = 5 \mu\text{M}$ , DCM).



**Fig. S13.** The image of quantum yield of **6**. ( $c = 5 \mu\text{M}$ , DCM).



**Fig. S14.** Time-resolved fluorescence decay curve of **12**. ( $c = 5 \mu\text{M}$ , DCM).

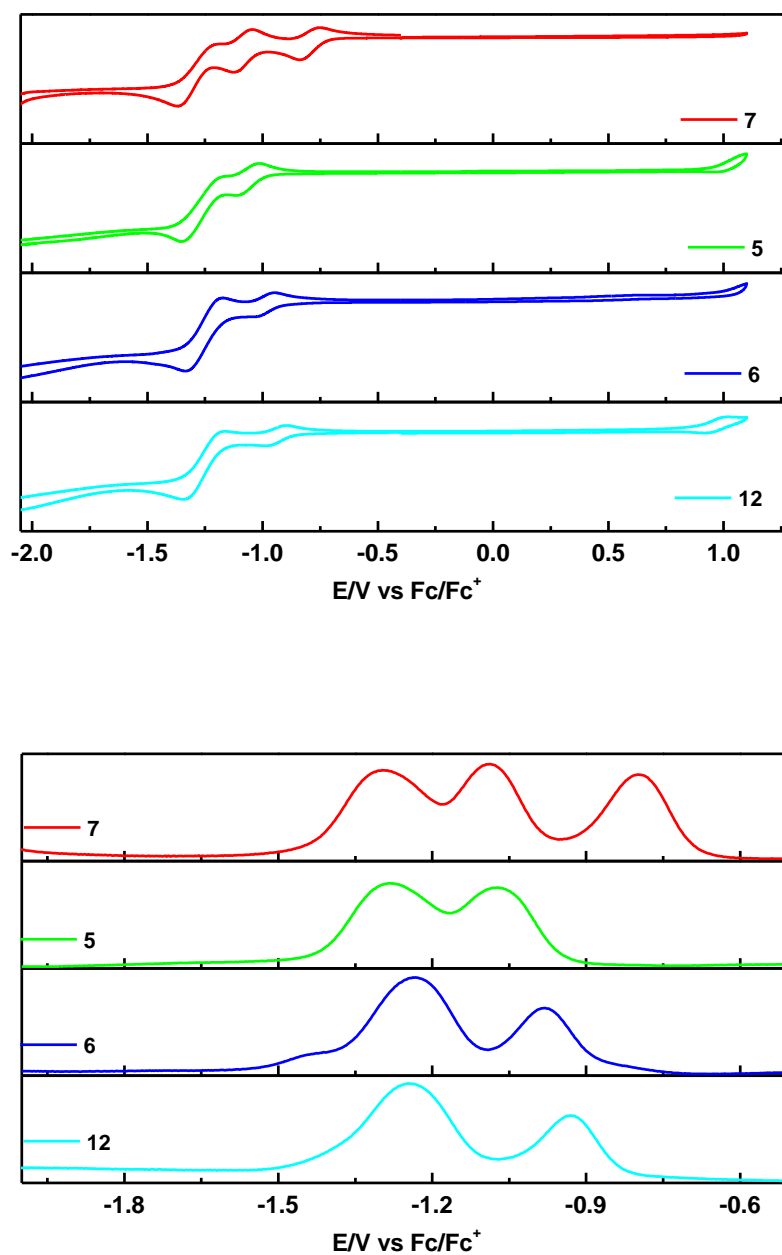


**Fig. S15.** The image of quantum yield of **12**. ( $c = 5 \mu\text{M}$ , DCM).

**Table S6.** Summary of quantum yield and fluorescence lifetime.

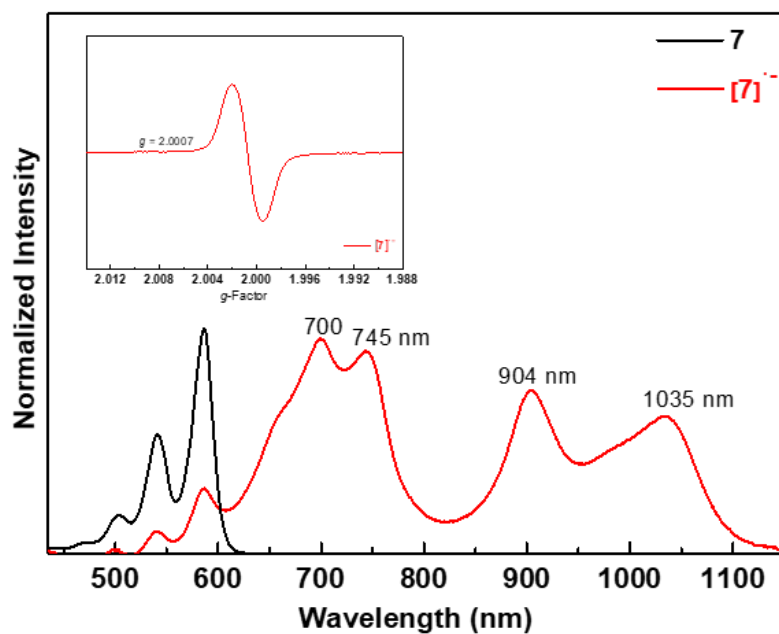
Compounds	$\Phi$ (%)	$\tau$ (ns)
<b>3</b>	98.21	4.15
<b>7</b>	31.54	2.90
<b>5</b>	95.86	7.17
<b>6</b>	88.47	7.05
<b>12</b>	83.58	9.70

## 6. Electrochemical Measurements

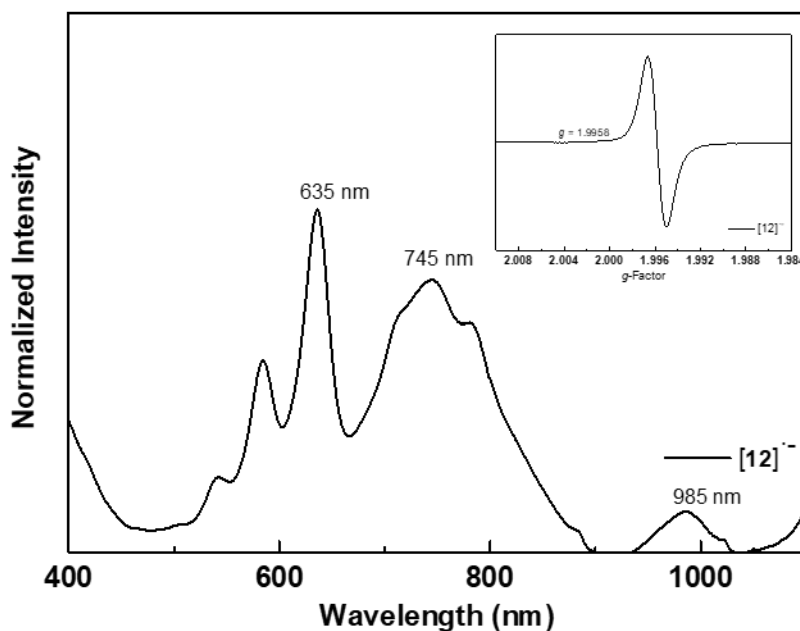


**Fig. S16.** Cyclic voltammograms and square wave voltammograms of **5**, **6**, **7**, and **12**.  
( $c = 2 \times 10^{-3}$  M, 0.1 M TBAHFP, DCM)

## 7. Chemical Reduction and EPR Experiment



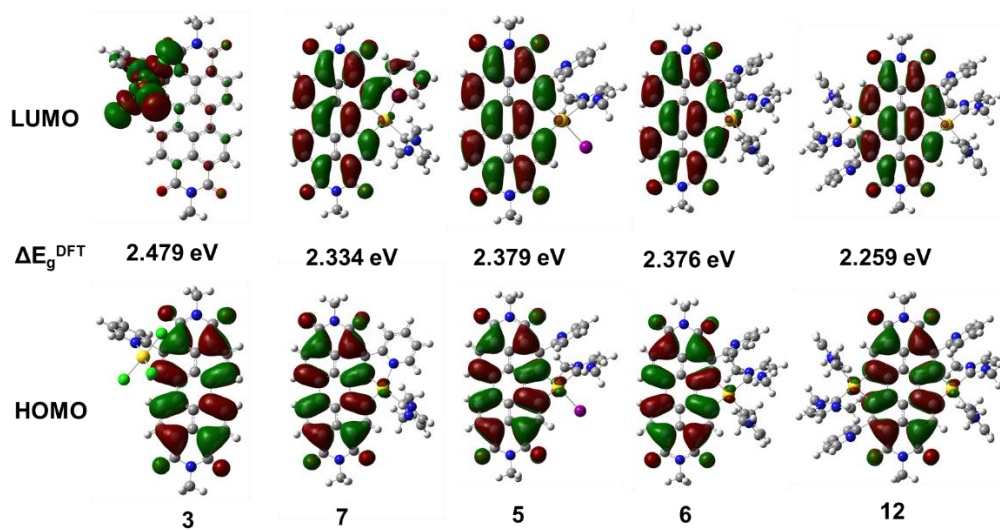
**Fig. S17.** Normalized UV/Vis-NIR absorption spectra of  $[7]^{\bullet-}$  in DCM, insert: EPR spectra of  $[7]^{\bullet-}$  ( $c = 5 \times 10^{-5}$  M)



**Fig. S18.** Normalized UV/Vis-NIR absorption spectra of  $[12]^{\bullet-}$  in DCM, insert: EPR spectra of  $[12]^{\bullet-}$  ( $c = 5 \times 10^{-5}$  M)



## 8. Theoretical Investigation

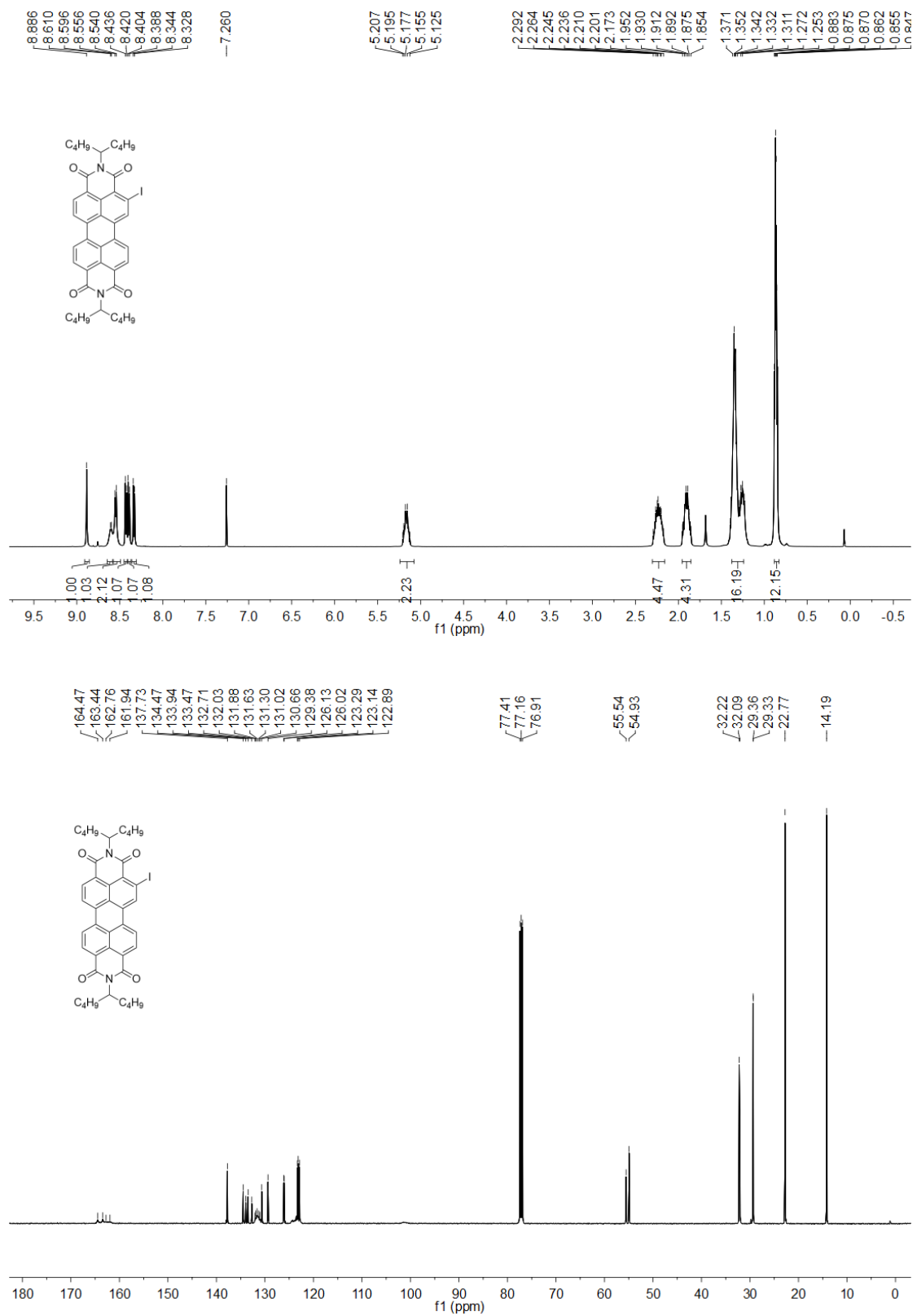


**Fig. S19.** Molecular orbitals of **3**, **5**, **6**, **7** and **12**.

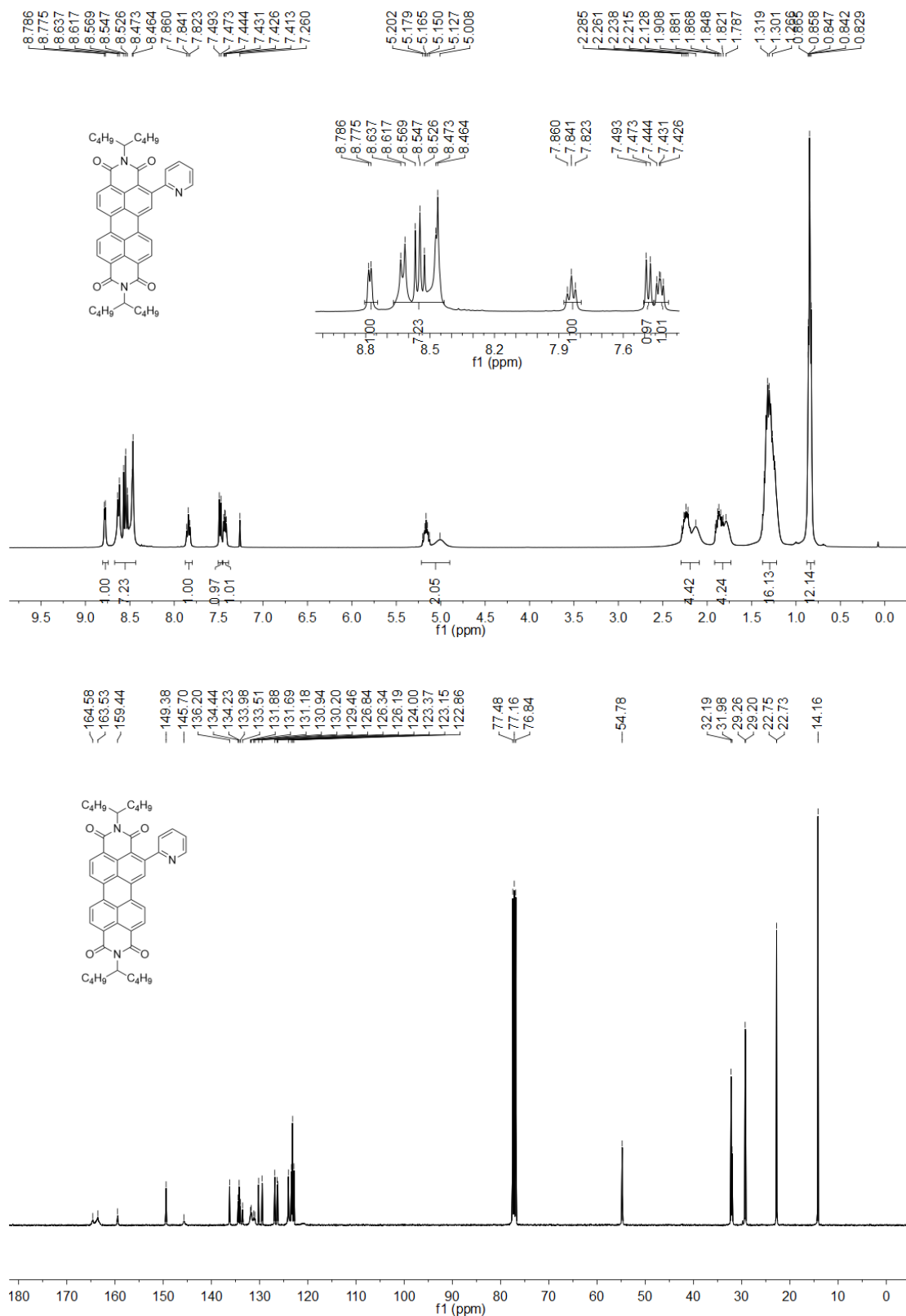
**Table S7.** Summary of optical and theoretically calculated energy gaps.

Compounds	$\Delta E_g^{\text{Opt}}$ (eV)	$\Delta E_g^{\text{DFT}}$ (eV)
<b>3</b>	2.29	2.479
<b>7</b>	2.06	2.334
<b>5</b>	2.07	2.379
<b>6</b>	2.07	2.376
<b>12</b>	1.91	2.259

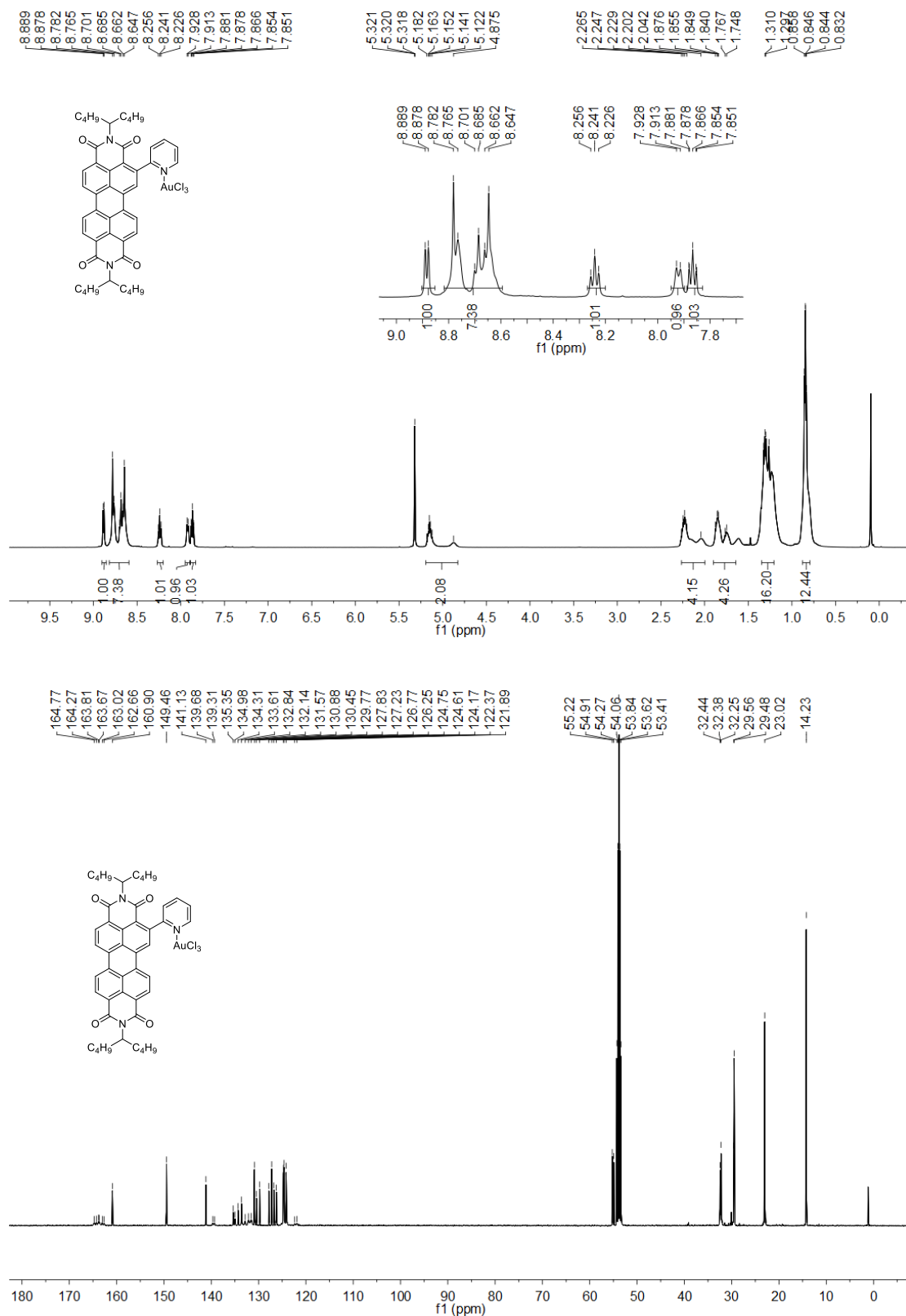
## 9. $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra



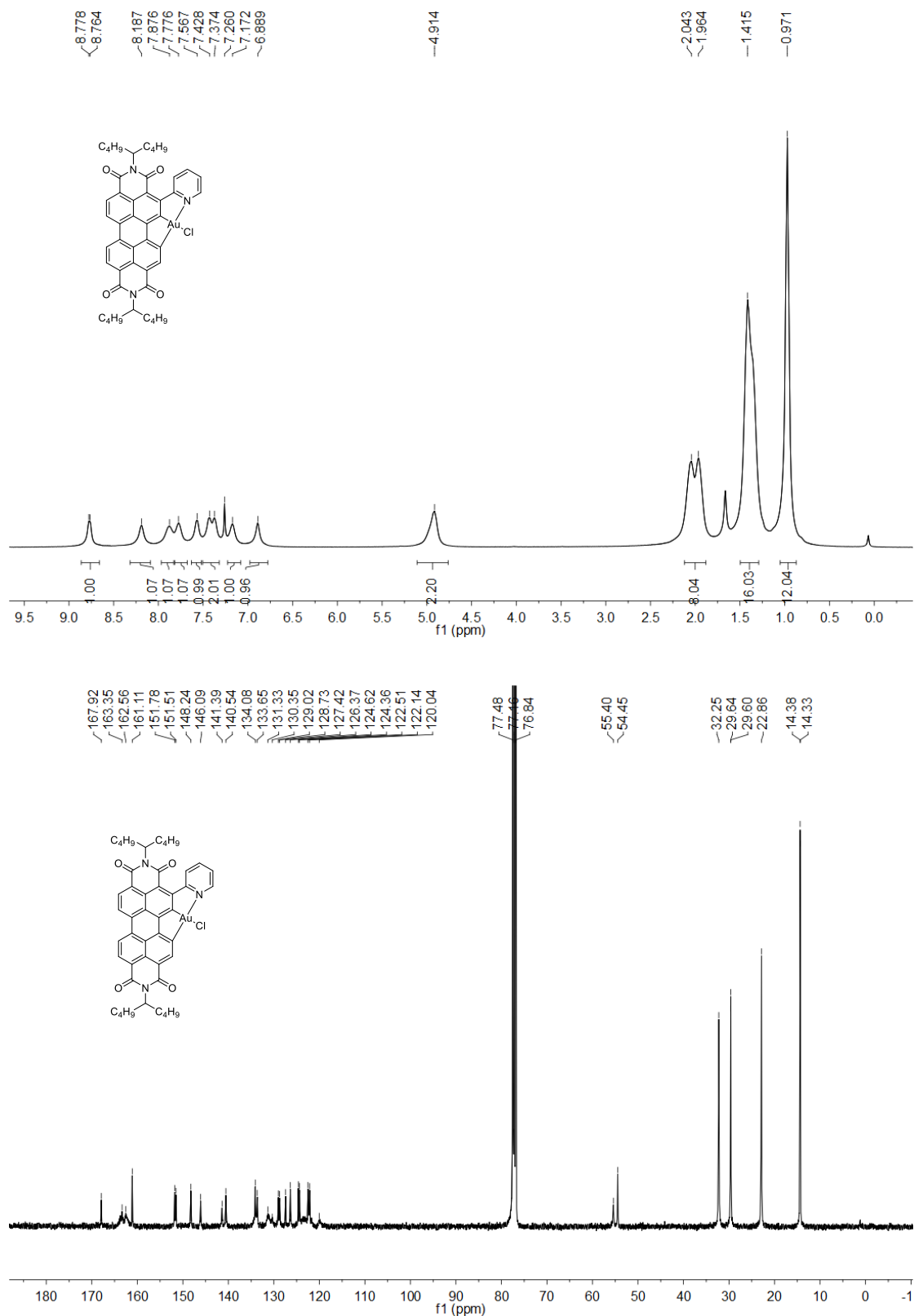
**Fig. S20.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectrum of **1** in CDCl<sub>3</sub>.



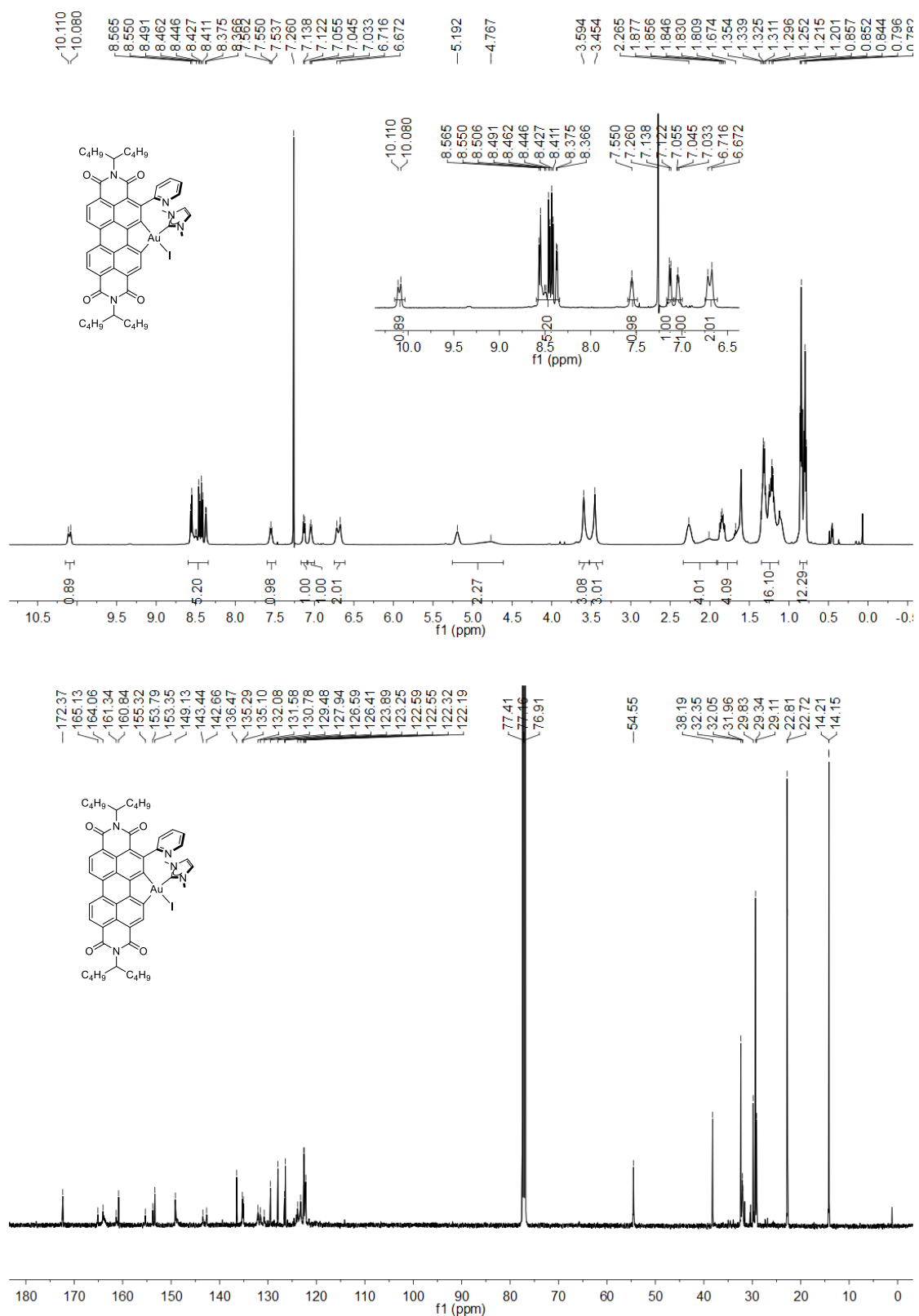
**Fig. S21.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectrum of **2** in CDCl<sub>3</sub>.



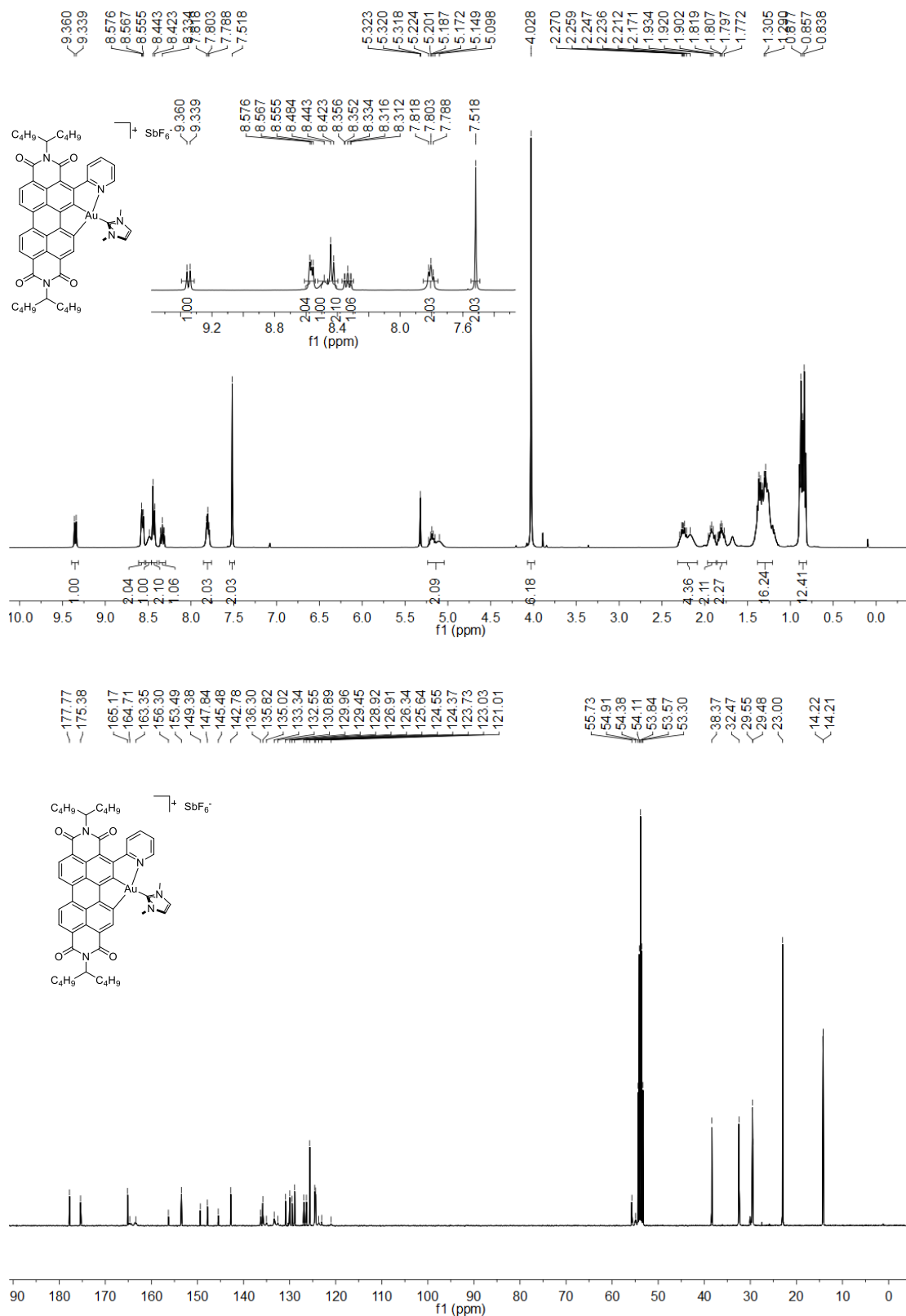
**Fig. S22.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectrum of **3** in CD<sub>2</sub>Cl<sub>2</sub>.



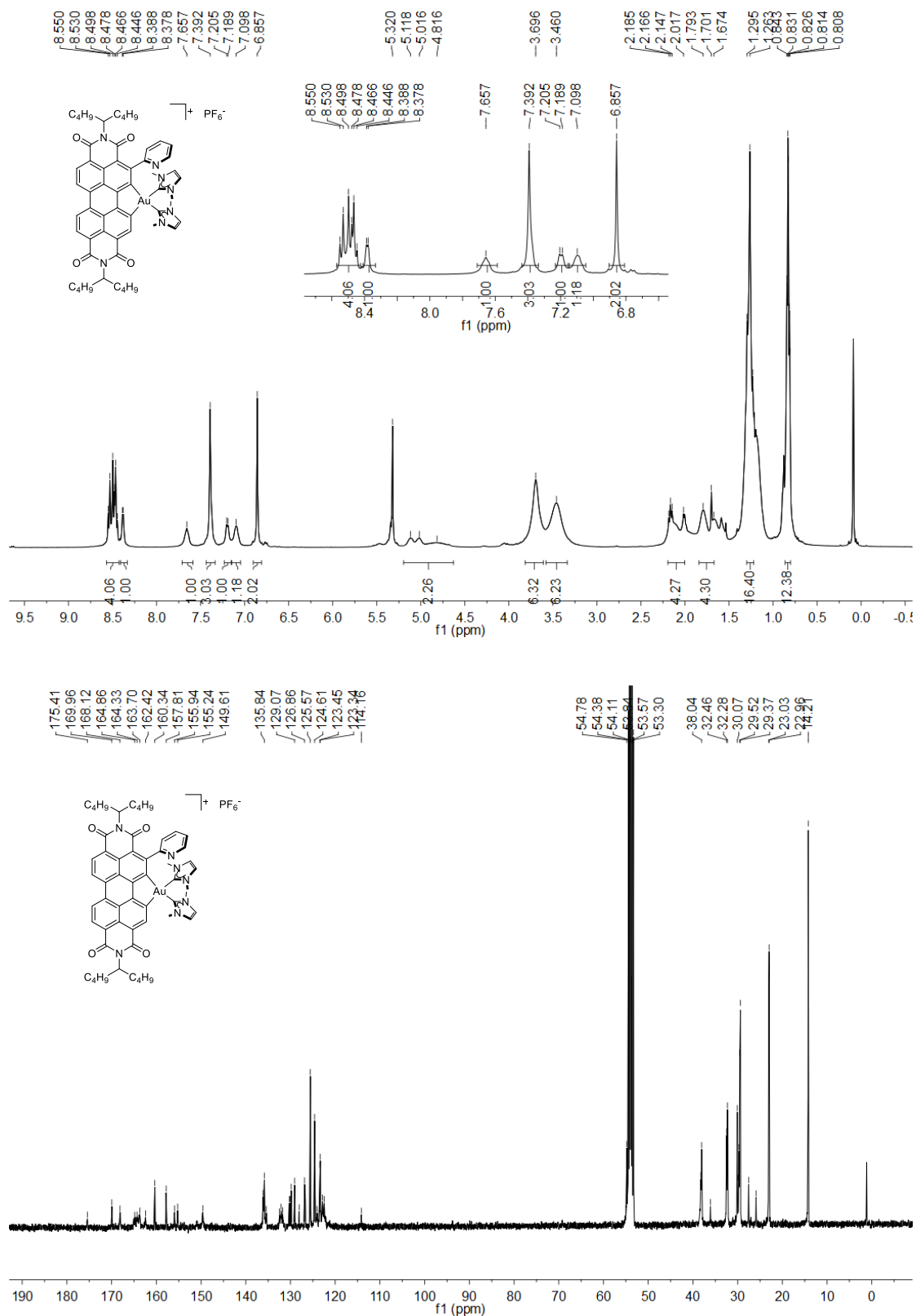
**Fig. S23.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectrum of **4** in CDCl<sub>3</sub>.



**Fig. S24.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectrum of **5** in CDCl<sub>3</sub>.

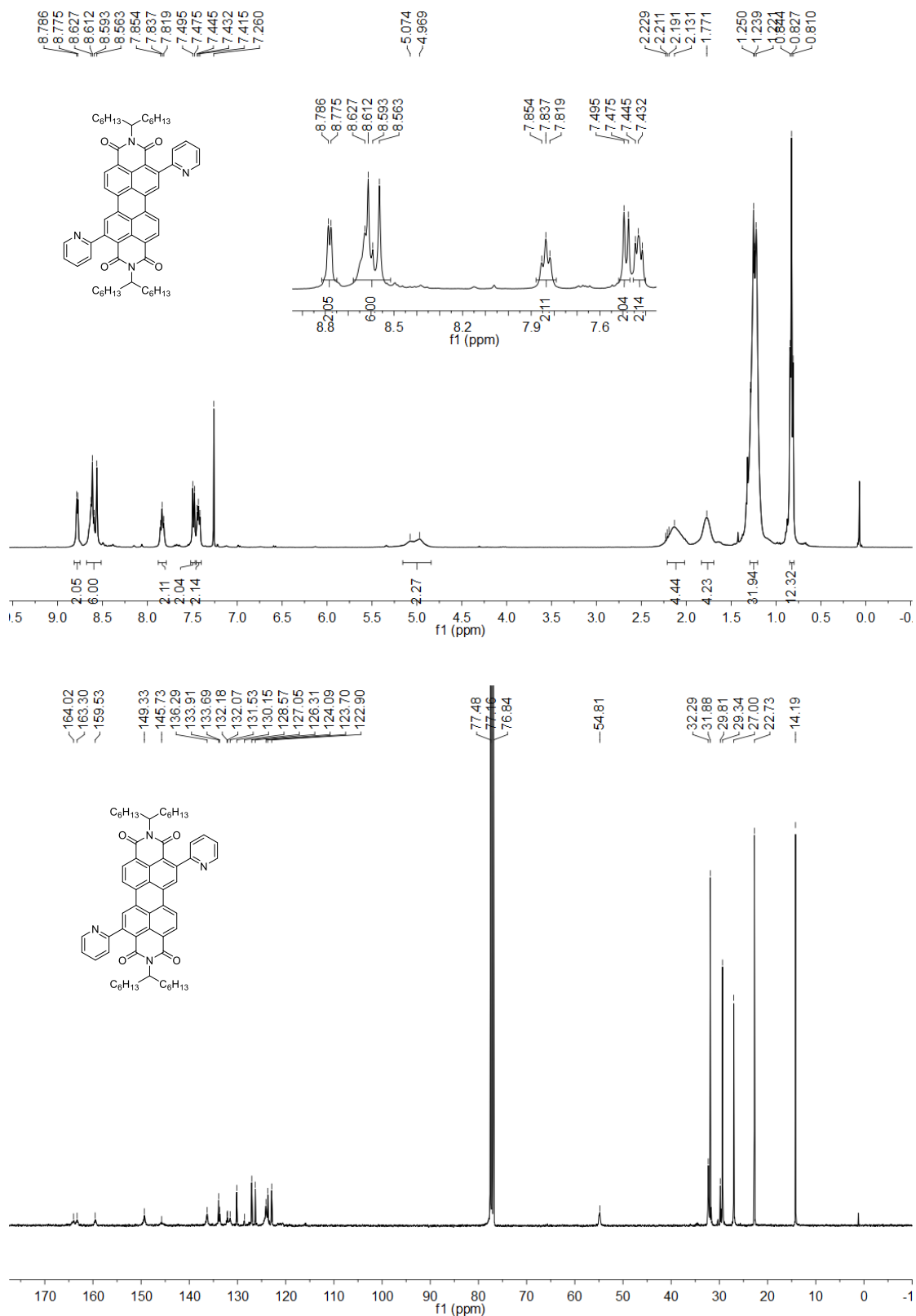


**Fig. S25.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectrum of **7** in CD<sub>2</sub>Cl<sub>2</sub>.

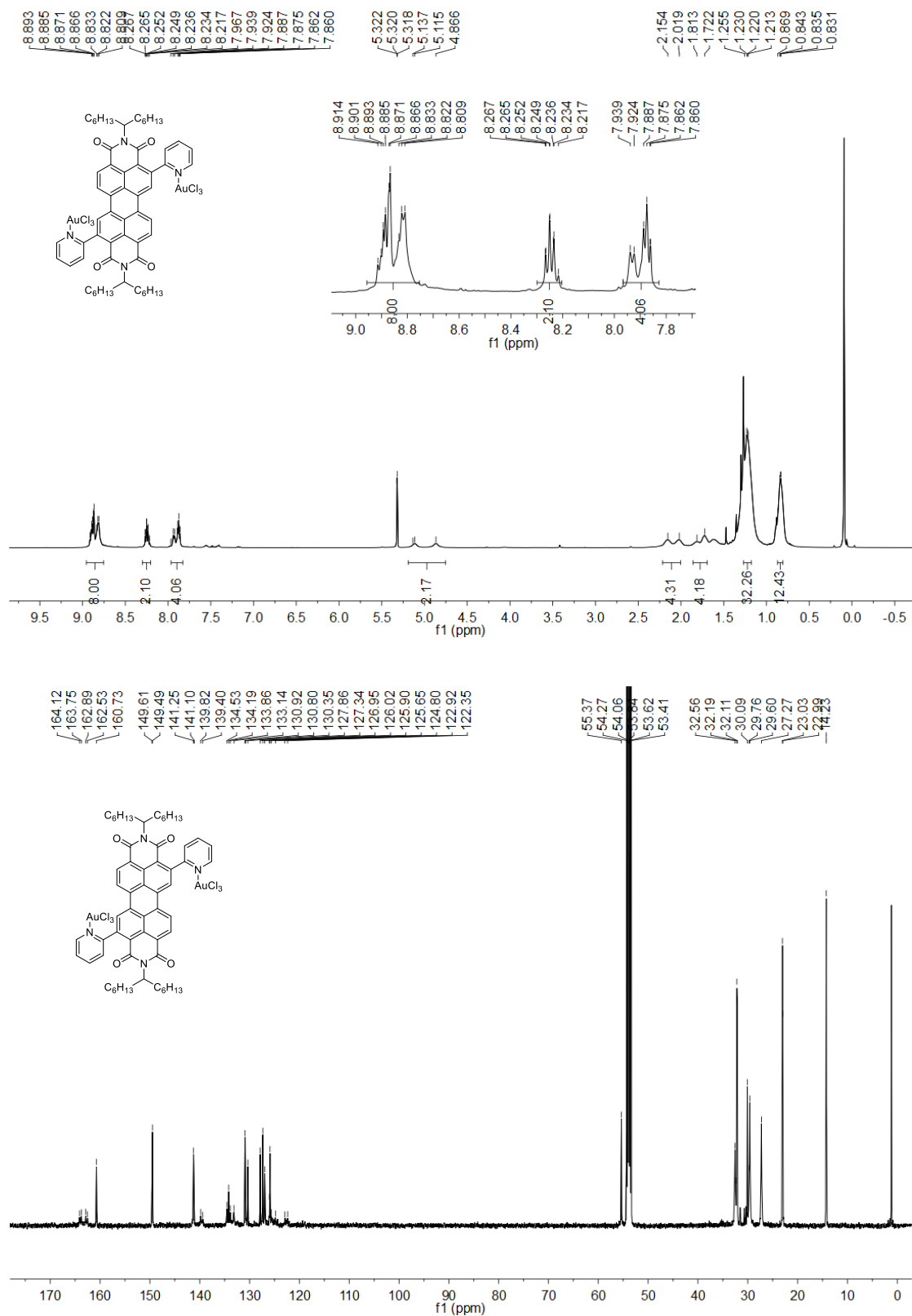


**Fig. S26.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectrum of **6** in CD<sub>2</sub>Cl<sub>2</sub>.

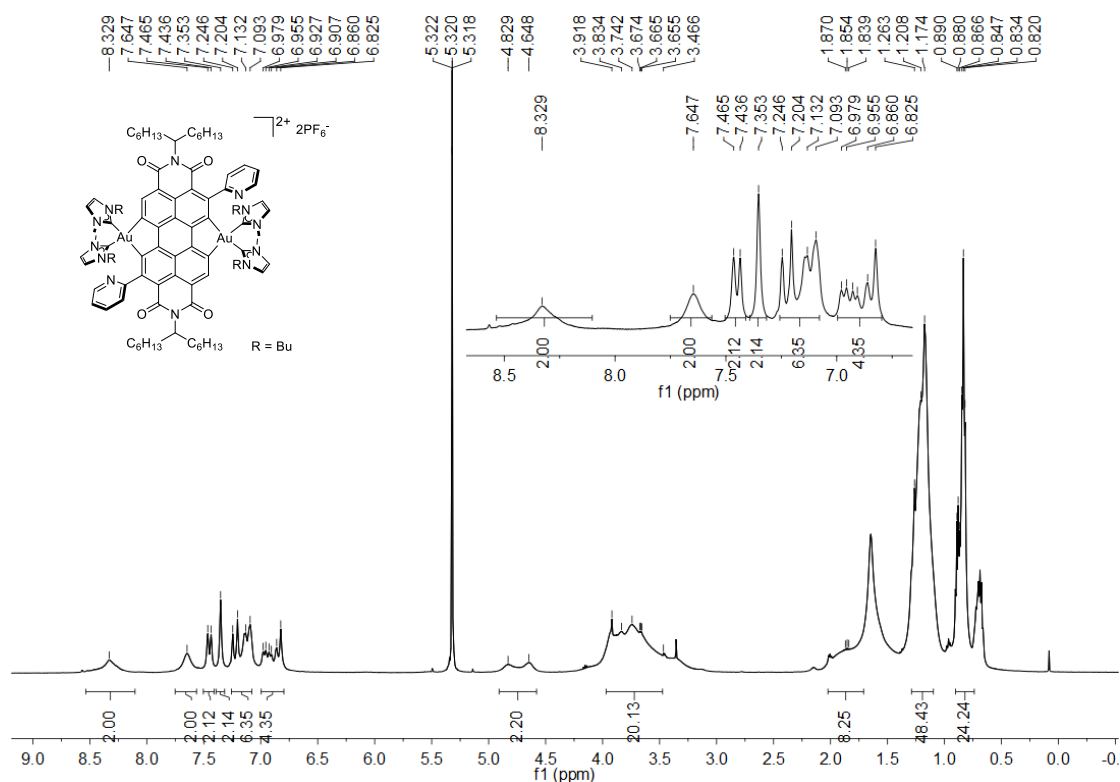




**Fig. S27.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectrum of **9** in CDCl<sub>3</sub>.



**Fig. S28.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectrum of **10** in CD<sub>2</sub>Cl<sub>2</sub>.



**Fig. S29.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectrum of **12** in CD<sub>2</sub>Cl<sub>2</sub>.

## 10. References

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