

## Experimental Section

**General Procedures.** All reagents were obtained from commercial suppliers and were used without further purification. All reactions were performed under an atmosphere of argon, unless otherwise specified. Electronic absorption spectra were obtained using a Perkin Elmer Lambda 6 UV/VIS Spectrophotometer. Elemental analyses were performed by Desert Analytics, Tucson, Arizona. Conductance measurements were performed at 23°C in dry acetonitrile on  $1 \times 10^{-3}$  M samples using an YSI Scientific model 35 conductance meter.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded using a Bruker DRX400, a Bruker DRX500, or a Bruker DMX500 Fourier transform spectrometer, as indicated for each substrate. Chemical shifts,  $\delta$ , are reported in ppm, referenced to tetramethylsilane (TMS), and coupling constants,  $J$ , are reported in hertz. Melting points are uncorrected. Acetonitrile was dried over  $\text{CaH}_2$ , tetrahydrofuran was dried over potassium/benzophenone ketyl, diethyl ether was dried over sodium/benzophenone ketyl, and methylene chloride was dried over  $\text{CaH}_2$ . Thin layer chromatography was carried out using precoated silica gel (Whatman PE SIL G/UV) or precoated aluminum oxide (J. T. Baker, aluminum oxide IB-F). Silica gel 60 Å (Merck, 230–400 mesh) and aluminum oxide 58 Å (either activated, basic, Brockman I or activated, neutral, Brockman I) were used for chromatography as indicated. Celite is J.T. Baker Celite 503.  $[\mathbf{9} (\text{L} = \text{CH}_3\text{CN})_2](\text{PF}_6)_4$  was prepared as previously described (1).

**Pyridine-2-carboxylic Acid Anthracen-9-yl Methyl Ester (pic-anth).** A 200-ml flask equipped with a condenser was flame dried under a continuous stream of argon. The flask was charged with a solution of picolinic acid (1.50 g, 12.2 mmol) in tetrahydrofuran (100 ml), and 1,1'-carbonyldiimidazole (2.07 g, 12.8 mmol) was added in a single portion. Slow bubbling occurred as the reaction was stirred at room temperature for 30 min. The reaction mixture was then heated to 80°C in an oil bath and maintained at this temperature for 2.5 h, during which time bubbling continued at a moderate pace. At the end of this period, bubbling ceased and the reaction was permitted to cool to 23°C. 9-Anthracenemethanol (2.66 g, 12.8 mmol) and sodium methoxide (32 mg, 0.592 mmol) were added to the colorless solution of the imidizolide. The reaction was stirred for 2 h with periodic sonication and heating to reflux. The solvent was then removed under reduced pressure. The resulting yellow oil was dissolved into methylene chloride (50 ml) and was washed with saturated  $\text{NaHCO}_3$  solution (25 ml) and brine (25 ml). The organic layer was

collected and dried over  $\text{MgSO}_4$ . Filtration followed by removal of the solvent yielded the crude product as a yellow oil that slowly crystallized. The solid was chromatographed through 81 g of silica using as the eluant first 4:1 hexanes/tetrahydrofuran, then 3:2 tetrahydrofuran/hexanes, and finally 95:5 tetrahydrofuran/triethylamine. The product was collected as the first bright yellow band from the tetrahydrofuran/triethylamine eluant. Removal of the solvent yielded a yellow oil (3.80 g) that was crystallized by the addition of ether and cooling. The product was collected by filtration and was washed with cold ether followed by pentane, yielding fine pale yellow crystals of the ester (3.63 g, 95.1%) mp 148.5°C.  $^1\text{H}$  NMR ( $(\text{CD}_3)_2\text{CO}$ , 500 MHz):  $\delta$  8.70 (s, 1H), 8.59 (m, 1H), 8.55 (dd,  $J_1 = 8.95$ ,  $J_2 = 0.72$ , 2H), 8.15 (d,  $J = 8.48$ , 2H), 8.03 (dt,  $J_1 = 7.9$ ,  $J_2 = 1.02$ , 1H), 7.90 (td,  $J_1 = 7.8$ ,  $J_2 = 1.74$ , 1H), 7.64 (ddd,  $J_1 = 6.55$ ,  $J_2 = 8.92$ ,  $J_3 = 1.34$ , 2H), 7.57 – 7.51 (m, 3H), 6.48 (s, 2H).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 100 MHz):  $\delta$  60.16, 124.19, 125.49, 126.23, 127.09, 127.14, 129.42, 129.69, 131.45, 131.71, 137.12, 148.33, 150.15, 165.58. Analysis calculated for  $\text{C}_{25}\text{H}_{19}\text{N}_3\text{O}$ : C, 80.49; H, 4.82; N, 4.47. Found: C, 80.36; H, 4.98; N, 4.42.

**[9 (L = pic-anth)(L =  $\text{CH}_3\text{CN}$ )]( $\text{PF}_6$ )<sub>4</sub> (16).** A 25-ml flask was charged with [9 (L =  $\text{CH}_3\text{CN}$ )<sub>2</sub>]( $\text{PF}_6$ )<sub>4</sub> (174 mg, 96.2  $\mu\text{mol}$ ) dissolved in acetonitrile (8 ml). To this yellow solution was added pyridine-2-carboxylic acid anthracen-9-yl methyl ester (30.2 mg, 96.2  $\mu\text{mol}$ ). Upon addition, the color of the reaction changed to light orange. The reaction mixture was stirred at room temperature for 6 h with little apparent change after the initial color change. The solution was then filtered through Celite and the volume was reduced to 9 ml of acetonitrile. The reaction was layered with ether and the product precipitated as a yellow-orange powder. The solid was collected by filtration and washed with ether (5 ml) followed by pentane (5 ml). This yielded the product as a yellow-orange solid (188 mg, 93.9%). Dilution experiments in  $(\text{CD}_3)_2\text{CO}$  showed no changes in the resonances with varying concentration, suggesting that the binding process is not intermolecular.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ , 16°C, 500 MHz):  $\delta$  9.28 (d,  $J = 1.92$ , 1H), 9.24 (d,  $J = 1.99$ , 1H), 9.19 (dd,  $J_1 = 5.51$ ,  $J_2 = 0.89$ , 1H), 8.83 (dd,  $J_1 = 8.19$ ,  $J_2 = 1.19$ , 1H), 8.52 (td,  $J_1 = 7.98$ ,  $J_2 = 1.42$ , 1H), 8.10 (d,  $J = 5.15$ , 2H), 8.05 (s, 2H), 7.98 – 8.03 (m, 3H), 7.93 – 7.97 (m, 3H), 7.90 (s, 2H), 7.83 (d,  $J = 7.72$ , 2H), 7.80 (dd,  $J_1 = 7.75$ ,  $J_2 = 2.01$ , 1H), 7.75 (dd,  $J_1 = 7.82$ ,  $J_2 = 1.95$ , 1H), 7.73 (d,  $J = 8.96$ , 2H), 7.69 (d,  $J = 7.43$ , 2H), 7.66 (d,  $J = 8.17$ , 1H), 7.64 (d,  $J = 7.96$ , 1H), 7.63 (t,  $J = 1.81$ , 1H), 7.50 (d,  $J = 8.43$ , 2H), 7.45 – 7.48 (m, 2H), 7.30 – 7.32 (m, 2H), 7.25 (d,  $J = 1.80$ , 2H), 7.18 (dd,  $J_1 = 5.354$ ,  $J_2 = 1.00$ , 2H), 6.92 (m, 2H),

6.57 (m, 2H), 6.51 (s, 2H), 3.09 (m, 4H), 2.91 (m, 4H), 1.95 (s, 3H), 1.42 (s, 18H).  $\Lambda_M(\text{acetonitrile}) = 457 \text{ } \Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ ,  $\Lambda_M(\text{acetone}) = 277 \text{ } \Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ . Analysis calculated for  $\text{C}_{88}\text{H}_{73}\text{F}_{24}\text{N}_9\text{O}_2\text{P}_4\text{Pd}_2$ : C, 50.78; H, 3.54; N, 6.06. Found: C, 50.12; H, 3.46; N, 5.79.

**[9 (L = pic-anth)<sub>2</sub>](PF<sub>6</sub>)<sub>4</sub> (17)**. A 25-ml flask was charged with **16** (104 mg, 50.0  $\mu\text{mol}$ ) dissolved in acetone (5.5 ml). To this was added pyridine-2-carboxylic acid anthracen-9-yl methyl ester (15.7 mg, 50.0  $\mu\text{mol}$ ). Upon addition, the color of the orange solution became more red. The reaction mixture was stirred for 5 h at room temperature and then was filtered through Celite. The volume of the red-orange solution was reduced to 5 ml. The solution was then layered with ether. The product was deposited as an orange powder, which was recovered by filtration and was washed with ether (5 ml) followed by pentane (5 ml). This yielded the product as an orange powder (110 mg, 93.2%). Crystals suitable for x-ray diffraction were grown by methanol diffusion into methyl ethyl ketone solutions of the bis-ester complex. Dilution experiments in  $(\text{CD}_3)_2\text{CO}$  showed no changes in the resonances with varying concentration, suggesting that the binding process is not intermolecular. Addition of excess added pyridine-2-carboxylic acid anthracen-9-yl methyl ester to solutions of the complex showed unchanged complex and free ligand in the  $^1\text{H}$  NMR, indicating that the picolinic ester ligand was not exchanging on an NMR timescale.  $^1\text{H}$  NMR ( $(\text{CD}_3)_2\text{CO}$ , 16°C, 500 MHz):  $\delta$  9.70 (d,  $J = 5.25$ , 2H), 9.18 (d,  $J = 1.95$ , 2H), 8.94 (dd,  $J_1 = 8.21$ ,  $J_2 = 1.08$ , 2H), 8.74 (td,  $J_1 = 8.02$ ,  $J_2 = 1.40$ , 2H), 8.34 (m, 2H), 8.22 (s, 2H), 8.10 (dd,  $J_1 = 7.69$ ,  $J_2 = 1.93$ , 2H), 8.07 (s, 4H), 7.87 (t,  $J = 7.64$ , 4H), 7.81 (d,  $J = 7.73$ , 2H), 7.77 (d,  $J = 8.91$ , 4H), 7.75 (t,  $J = 7.76$ , 4H), 7.72 (t,  $J = 1.79$ , 1H), 7.68 (d,  $J = 8.38$ , 4H), 7.48 (dd,  $J_1 = 5.49$ ,  $J_2 = 0.96$ , 4H), 7.35 (m, 4H), 7.33 (d,  $J = 1.78$ , 2H), 7.12 (m, 4H), 6.75 (m, 4H), 6.35 (s, 4H), 3.17 (m, 4H), 3.03 (m, 4H), 1.47 (s, 18H).  $\Lambda_M(\text{acetone}) = 242 \text{ } \Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ . Analysis calculated for  $\text{C}_{107}\text{H}_{85}\text{F}_{24}\text{N}_9\text{O}_4\text{P}_4\text{Pd}_2$ : C, 54.60; H, 3.64; N, 5.36. Found: C, 54.35; H, 3.51; N, 5.26.

**[9 (L = py)(L = CH<sub>3</sub>CN)](PF<sub>6</sub>)<sub>4</sub>**. A 25 ml flask was charged with **[9 (L = CH<sub>3</sub>CN)]<sub>2</sub>(PF<sub>6</sub>)<sub>4</sub>** (100 mg, 55.3  $\mu\text{mol}$ ) dissolved in acetonitrile (6 ml). To this yellow solution was added pyridine (4.50  $\mu\text{l}$ , 55.3  $\mu\text{mol}$ ). Upon addition, the color lightened slightly. The reaction mixture was stirred at room temperature for 4.5 h before being concentrated to 4.5 ml. The reaction mixture was then vapor diffused with ether, crystallizing

the product as a fine yellow-orange powder. The product was collected by filtration and washed with ether (5 ml) followed by pentane (5 ml) (96.0 mg, 94.1%).  $^1\text{H NMR}$  ( $\text{CD}_3\text{CN}$ ,  $62^\circ\text{C}$ , 500 MHz):  $\delta$  9.27 (d,  $J = 1.86$ , 2H), 9.02 (d,  $J = 4.95$ , 2H), 8.63 (s, 4H), 8.41 – 8.32 (m, 11H), 8.00 (dd,  $J_1 = 7.85$ ,  $J_2 = 2.00$ , 2H), 7.93 – 7.74 (m, 6H), 7.64 – 7.62 (m, 5H), 7.17 (d,  $J = 1.80$ , 2H), 3.06 (m, 4H), 2.81 (m, 4H), 1.95 (s, 3H), 1.41 (s, 18H).  $\Lambda_{\text{M}}(\text{acetonitrile}) = 406 \text{ } \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ ,  $\Lambda_{\text{M}}(\text{acetone}) = 236 \text{ } \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ . Analysis calculated for  $\text{C}_{72}\text{H}_{63}\text{F}_{24}\text{N}_9\text{P}_4\text{Pd}_2$ : C, 46.82; H, 3.44; N, 6.83. Found: C, 46.63; H, 3.39; N, 6.56.

**[9 (L = py) $_2$ ](PF $_6$ ) $_4$ . (15).** A 10 ml flask was charged with [9 (L = py)(L = CH $_3$ CN)](PF $_6$ ) $_4$  (50.0 mg, 27.1  $\mu\text{mol}$ ) dissolved in acetone (3 ml). To this yellow solution was added pyridine (2.21  $\mu\text{l}$ , 27.1  $\mu\text{mol}$ ). Upon addition, the solution became pale yellow. The reaction mixture was stirred at room temperature for 6 h. The solution was then filtered through Celite and was again concentrated to 3 ml. The solution was then vapor diffused with ether, crystallizing the product as a fine yellow needles. The product was collected by filtration and washed with ether (5 ml) followed by pentane (5 ml) (47.3 mg, 92.7%).  $^1\text{H NMR}$  ( $(\text{CD}_3)_2\text{CO}$ ,  $16^\circ\text{C}$ , 500 MHz):  $\delta$  9.34 (d,  $J = 4.95$ , 4H), 9.17 (d,  $J = 1.86$ , 2H), 9.12 (s, 4H), 8.85 (d,  $J = 7.92$ , 4H), 8.52 – 8.44 (m, 6H), 8.15 (dd,  $J_1 = 7.71$ ,  $J_2 = 1.92$ , 2H), 8.04 (m, 4H), 7.85 – 7.83 (m, 8H), 7.66 (d,  $J = 7.87$ , 2H), 7.64 (t,  $J = 1.76$ , 1H), 7.22 (d,  $J = 1.73$ , 2H), 3.05 (m, 4H), 2.84 (m, 4H), 1.41 (s, 18H).  $\Lambda_{\text{M}}(\text{acetone}) = 245 \text{ } \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ . Analysis calculated for  $\text{C}_{75}\text{H}_{65}\text{F}_{24}\text{N}_9\text{P}_4\text{Pd}_2$ : C, 47.79; H, 3.48; N, 6.69. Found: C, 47.45; H, 3.35; N, 6.56.

**Host-Guest Interaction of [9 (L = py) $_2$ ](PF $_6$ ) $_4$  with 9-Methylanthracene (9-MA).** A series of 5.00 mM solutions of **15** in  $(\text{CD}_3)_2\text{CO}$  containing various amounts of 9-methylanthracene, ranging from 0.5 mM to 50 mM, were prepared. The solutions were permitted to equilibrate for at least 2 h before they were examined by  $^1\text{H NMR}$  and spectrophotometry. The host alone is yellow and the guest alone is nearly colorless. The host/guest mixtures varied from slightly golden at low concentrations of guest to orange-red at high concentrations of guest. The maximum chemical shift change for any proton of the host was 0.68 ppm. Several other protons of the host had maximum changes of approximately 0.2 – 0.6 ppm. The maximum chemical shift change observed for the guest was 0.28 ppm, with several other chemical shifts changing by about 0.2 ppm. The spectrophotometry results do not obey Beer's law. The stoichiometry

was determined by the “mole ratio” method to be two guest molecules per one host molecule, by plotting the change in chemical shift versus the mole ratio of guest to host for several protons of each, Fig. 5 (2). The 2:1 stoichiometry was also suggested by examining the spectrometry data. Equilibrium constants were determined using a previously described algorithm (1, 3). This procedure yielded values of  $K_1 = 400 \pm 50 \text{ M}^{-1}$  and  $K_2 = 100 \pm 50 \text{ M}^{-1}$ .

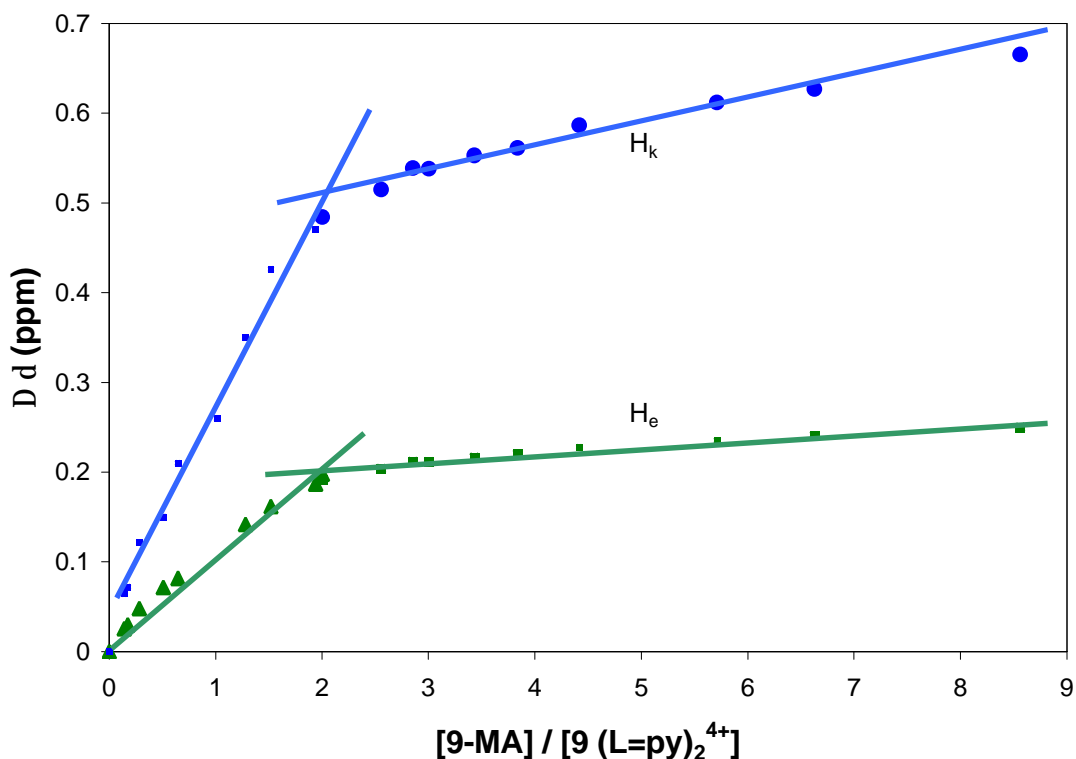


Fig. 5. <sup>1</sup>H NMR determination of the stoichiometry of the adducts formed by [9 (L = py)<sub>2</sub>](PF<sub>6</sub>)<sub>4</sub> with 9-MA. The protons are as defined in Fig. 9.

**Variable-Temperature Experiments for [(L<sub>R</sub>)Pd<sub>2</sub>(pic-anth)<sub>2</sub>](PF<sub>6</sub>)<sub>4</sub> (17).** Variable-temperature experiments permit the determination of relevant kinetic parameters for this system (4 – 7). The temperature was varied in 10°C increments between 20°C and –90°C for 5.00 mM solutions of the complex in (CD<sub>3</sub>)<sub>2</sub>CO. All of the resonances have temperature dependant chemical shifts. All of the resonances exhibit temperature dependent line broadening. A coalescence temperature is observed between –50°C and –65°C for the proton resonances. The resonances resolve once again by –90°C. However, when they have

resolved, many of the proton resonances are overlapped and interpretation is possible with only a few of the resonances.

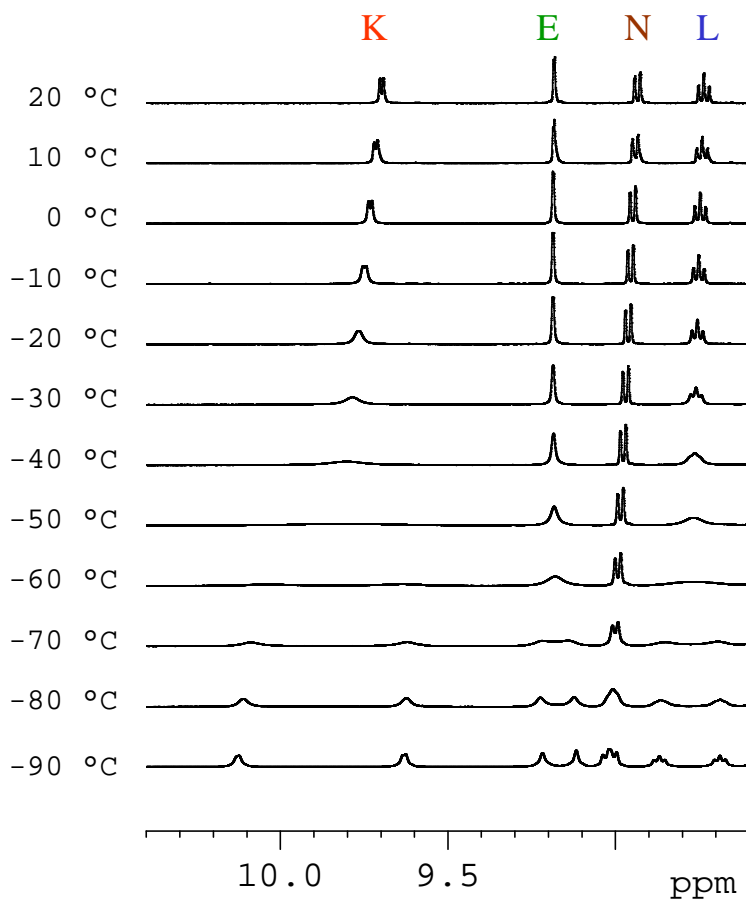


Fig. 6. A portion of the temperature-dependent  $^1\text{H}$  NMR spectrum of  $[\mathbf{9} (\text{L} = \text{pic-anth})_2](\text{PF}_6)_4$  ( $\mathbf{17}$ ). The protons are as defined on Fig. 15.

Three proton resonances, K, E, and L as defined on Fig. 15, are interpretable (Fig. 6). The coalescence temperatures,  $T_c$ , for these protons are listed in Table 3 along with the peak separation at  $T_c$  and an estimate of  $\Delta G^\ddagger$ , the activation free energy, at the coalescence temperature.  $\Delta G^\ddagger$  of the process is estimated using the Eyring equation:

$$\Delta G^\ddagger = RT_c \left[ 22.96 + \ln \left( \frac{T_c}{\Delta \mathbf{u}_{T_c}} \right) \right]$$

where  $R$  is the gas constant, and  $\Delta \mathbf{u}_{T_c}$  is the chemical shift difference (in Hz) of an exchanging proton at the coalescence temperature.

Table 3. Estimation of kinetic parameters			
$\Delta \mathbf{n}$	$T_c$	$\Delta G^\ddagger$	$\Delta G^\ddagger$
Hz	K	J/mol	kcal/mol
248.65	223	42370	10.1
50.53	208	42150	10.1
90.53	213	42170	10.1

The rate constants for the process at and below the coalescence temperature can be estimated by using the following equations:

$$k_{(T < T_c)} = \frac{P}{\sqrt{2}} \left( \Delta \mathbf{u}_o^2 - \Delta \mathbf{u}_{\text{obs.}}^2 \right)^{\frac{1}{2}}$$

$$k_{T_c} = \frac{P \Delta \mathbf{u}_o}{\sqrt{2}}$$

where  $k_{(T < T_c)}$  is the rate constant for the exchange process below the coalescence temperature,  $k_{T_c}$  is the rate constant for the exchange process at the coalescence temperature,  $\Delta \mathbf{n}_o$  is the maximum chemical shift difference of an exchanging proton (in Hz) for a particular, exchanging proton, and  $\Delta \mathbf{n}_{\text{obs.}}$  is the chemical shift difference of an exchanging proton (in Hz) for a proton at a particular temperature. Since there are several temperatures below the coalescence temperature where  $^1\text{H}$  NMR spectra were recorded, the rates for protons k, e, and l can be determined at each of the temperatures. Using these experimental values, an Eyring plot (Fig. 7) can be constructed for a linearized Eyring equation:

$$\ln \left( \frac{k}{T} \right) = \frac{-\Delta H^\ddagger}{R} \left( \frac{1}{T} \right) + \left( 23.76 + \frac{\Delta S^\ddagger}{R} \right)$$

where  $k$  is the rate,  $T$  is temperature,  $\Delta H^\ddagger$  is the activation enthalpy,  $R$  is the gas constant, and  $\Delta S^\ddagger$  is the activation entropy.

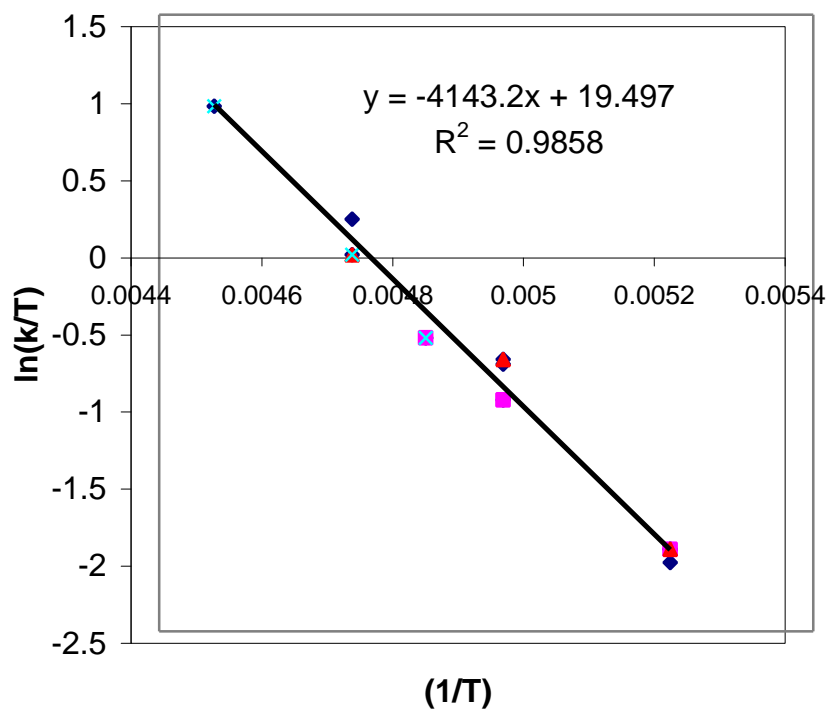
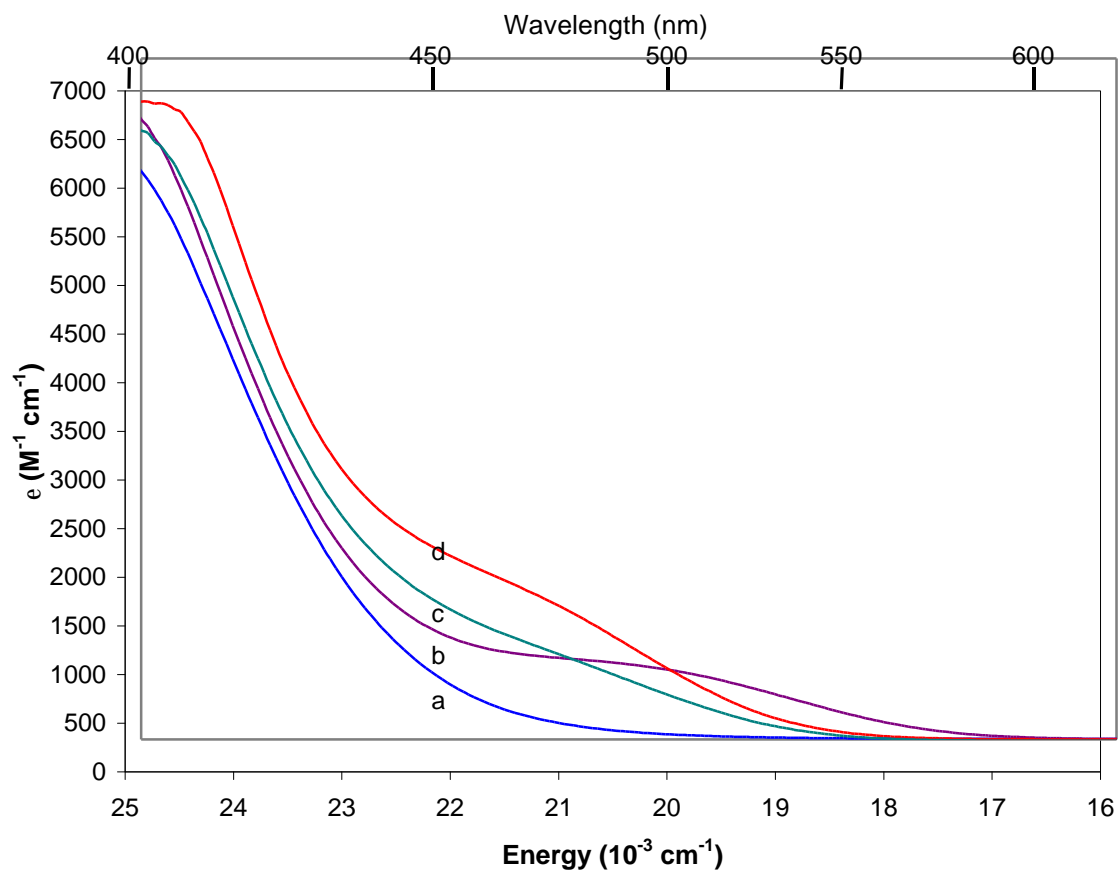


Fig. 7. Linearized Eyring plot.

Ten points from three different resonances were used to construct this plot. From the slope and the intercept of a linear fit of the data, the values of the activation enthalpy,  $\Delta H^\ddagger$ , and the activation entropy,  $\Delta S^\ddagger$ , can be determined. The value of  $\Delta H^\ddagger$  was found to be 8.2 kcal/mol and the value of  $\Delta S^\ddagger$  was found to be -8.5 cal/mol·K. These values are in agreement with the earlier estimated value of  $\Delta G^\ddagger$  at the coalescence temperature. Using these values, the rate constant,  $k$ , and the site residency time (life-time),  $\tau = 1/k$ , can be calculated.



Absorption spectra were recorded for the inter- and intramolecular host-guest systems (Fig. 8). All spectra were recorded at 21°C in  $(\text{CD}_3)_2\text{CO}$  solution.



**Fig. 8.** Absorption spectra for (a)  $[\mathbf{9}(\text{L} = \text{py})_2](\text{PF}_6)_4$  (5.00 mM), (b) **9-MA**, (10.0 mM) and  $[\mathbf{9}(\text{L} = \text{py})_2](\text{PF}_6)_4$  (5.00 mM), (c)  $[\mathbf{9}(\text{L} = \text{pic-anth})(\text{L} = \text{CH}_3\text{CN})](\text{PF}_6)_4$  (5.00 mM), and (d)  $[\mathbf{9}(\text{L} = \text{pic-anth})_2](\text{PF}_6)_4$  (5.00 mM).

1. Sommer, R. D., Rheingold, A. L., Goshe, A. J. & Bosnich, B. (2001) *J. Am Chem. Soc.* **123**, 3940-3952.
2. Meyer, A. S. & Ayres, G. H. (1957) *J. Am. Chem. Soc.* **79**, 49-53.
3. Kneeland, D. M., Ariga, K., Lynch, V. M., Huang, C. -Y. & Anslyn, E. V. (1993) *J. Am. Chem. Soc.* **115**, 10042-10055.
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6. Schneider, H. -J. & Yatsimirsky, A. K. (2000) in *Principles and Methods in Supramolecular Chemistry* (Wiley, Chichester U. K.), pp. 259-263.
7. Binsch, G. (1968) in *Topics in Stereochemistry*, eds. Eliel, E. L & Allinger, N. L. (Interscience, New York), Vol. 3, pp. 97-185.

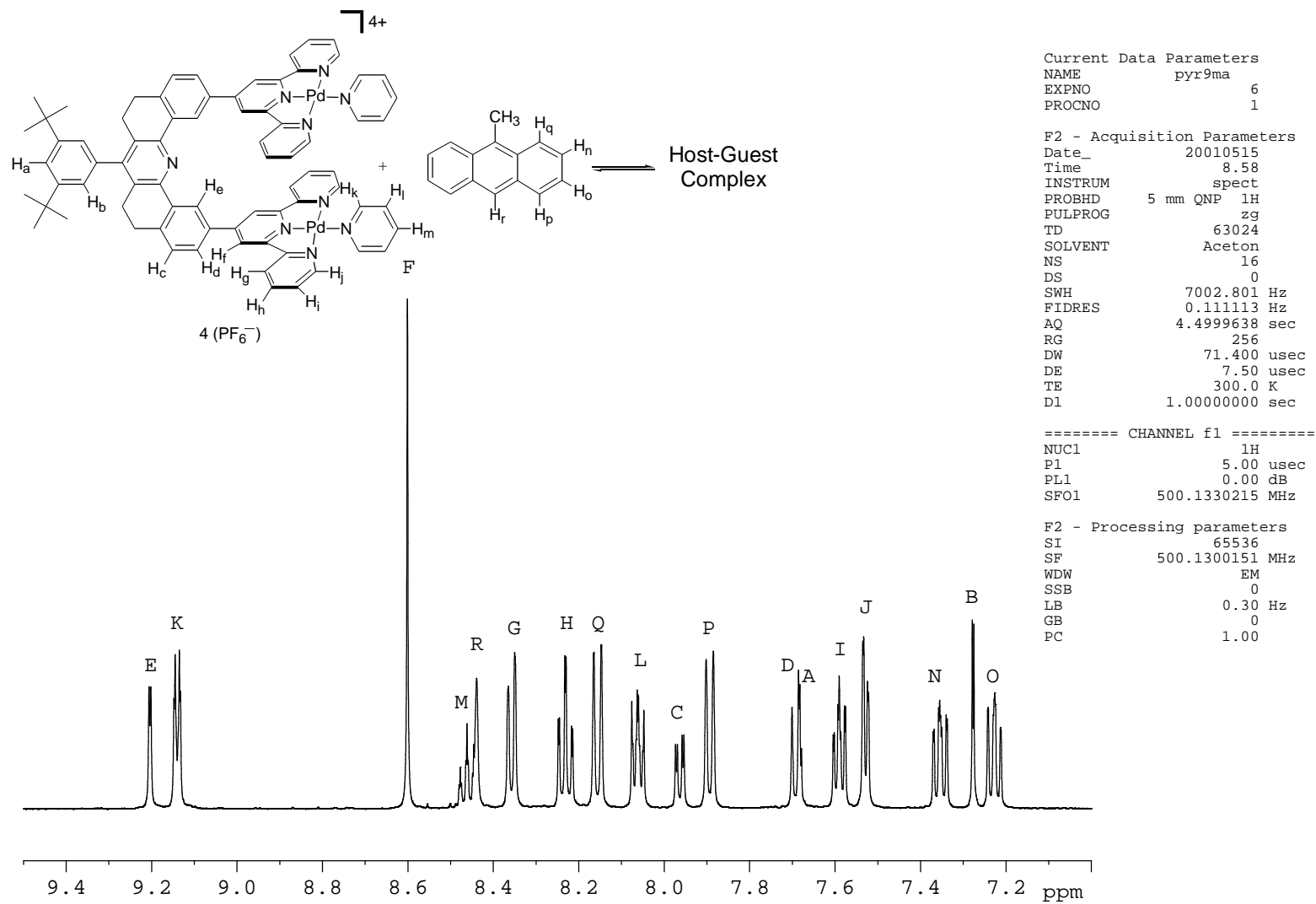
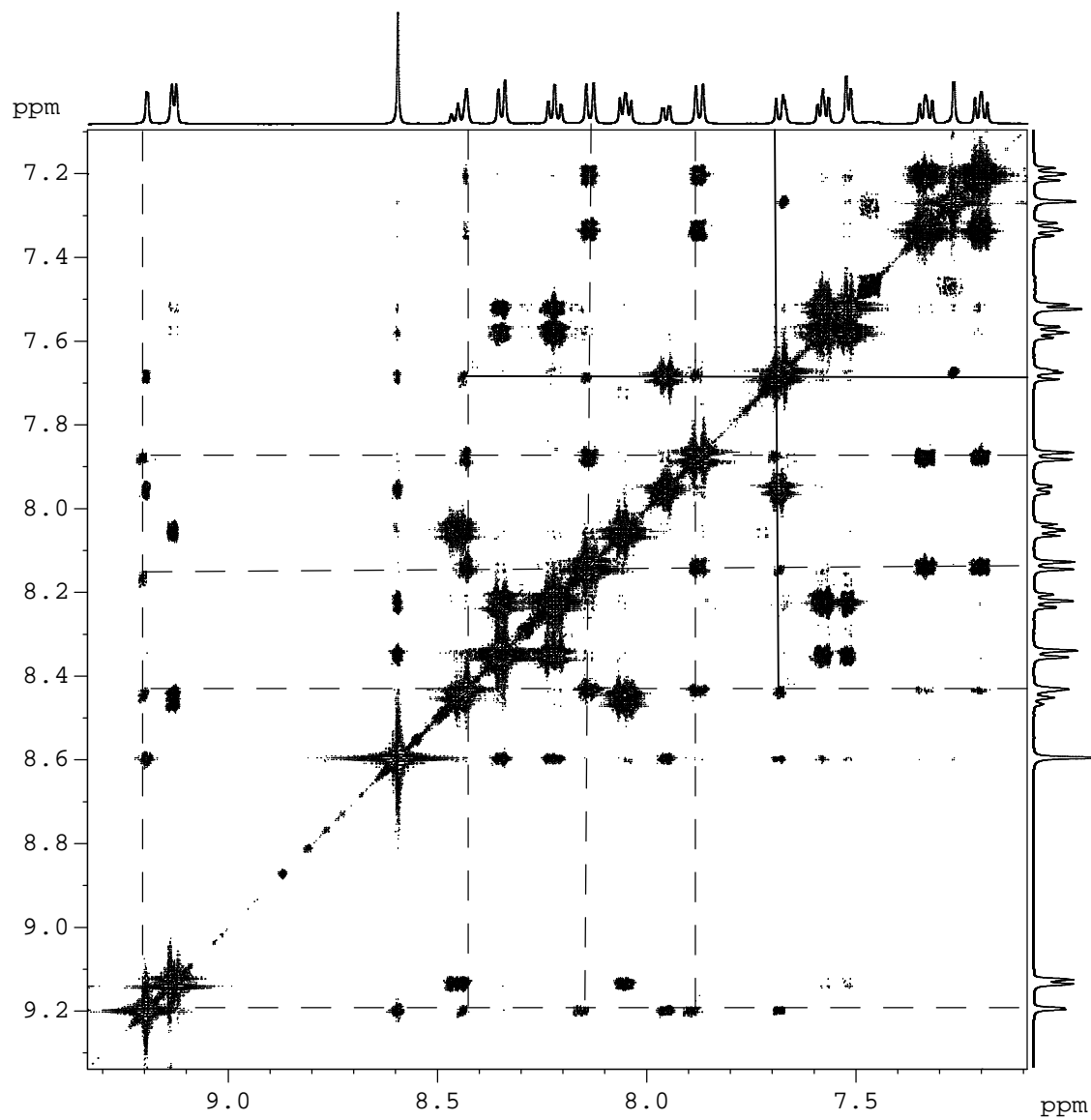


Fig. 9. <sup>1</sup>H NMR spectrum of a 2:1 solution of 9-methylanthracene and [9(L=py)<sub>2</sub>](PF<sub>6</sub>)<sub>4</sub> (**15**).



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DS            16
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RG            161.4
DW            240.000 usec
DE            7.50 usec
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D1            3.50000000 sec
d12           0.00002000 sec
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P15           50000.00 usec
PL1           0.00 dB
PL11          24.00 dB
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F1 - Acquisition parameters
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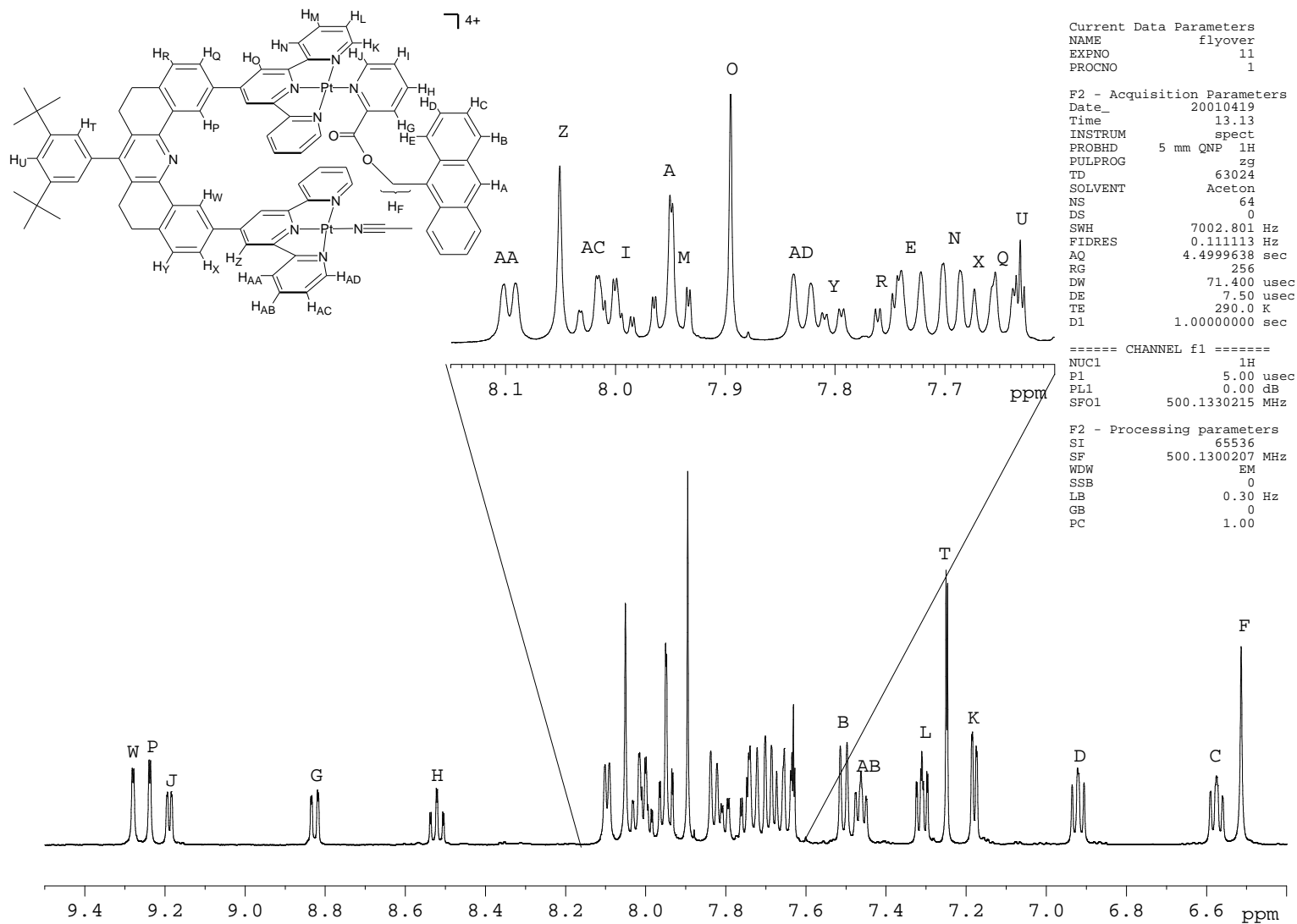
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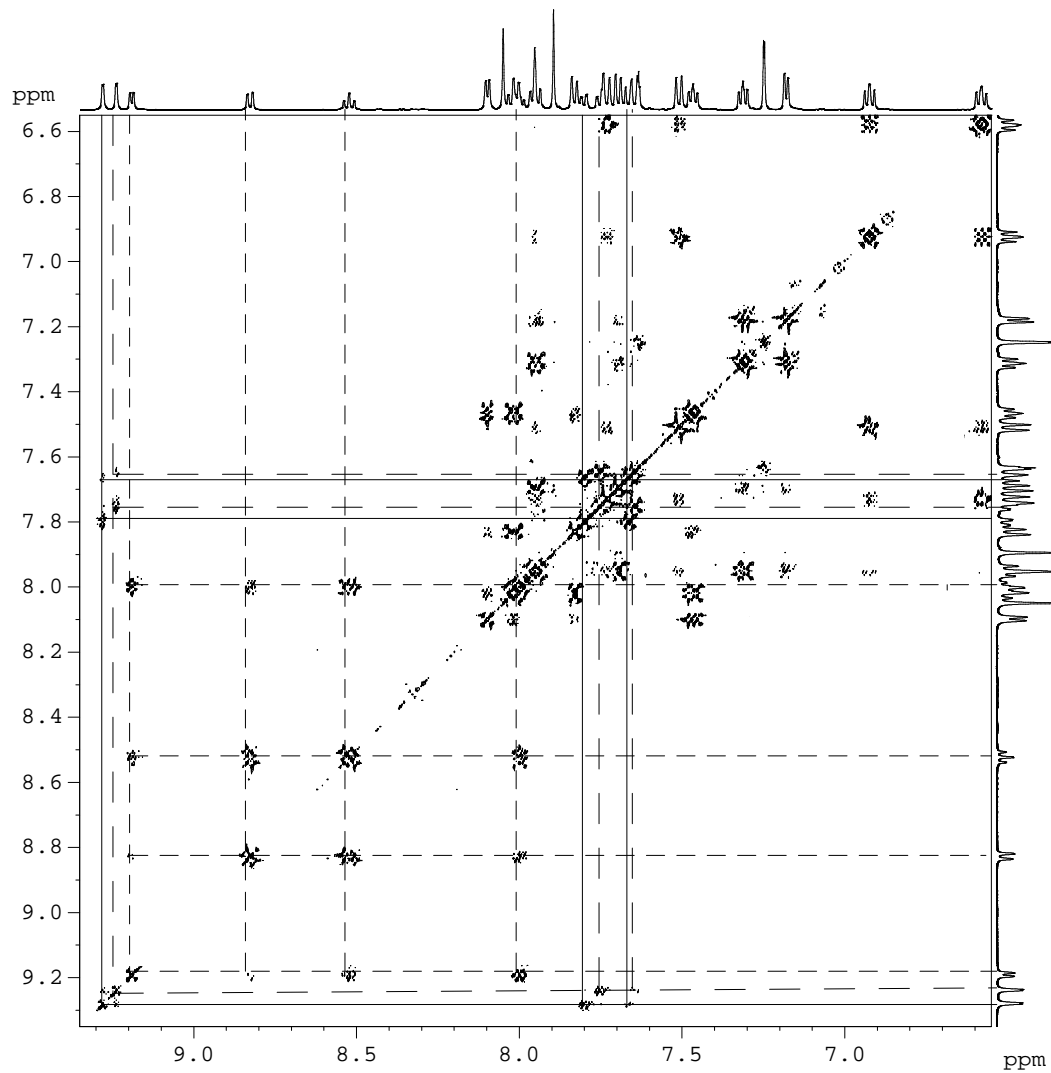
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Fig. 10. <sup>1</sup>H ROESY spectrum of a 2:1 solution of 9-methylanthracene and [9(L=py)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (15).

Fig. 11.  $^1\text{H}$  NMR spectrum of **19** ( $\text{L} = \text{pic-antH}$ )( $\text{L} = \text{CH}_3\text{CN}$ )( $\text{PF}_6$ )<sub>4</sub> (**16**).





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NUC1          1H
P1            5.70 usec
PL1           0.00 dB
SFO1          500.1340380 MHz

```

```

F1 - Acquisition parameters
ND0           2
TD            512
SFO1          500.134 MHz
FIDRES        5.029251 Hz
SW            4.495 ppm

```

```

F2 - Processing parameters
SI            2048
SF            500.1300624 MHz
WDW           SINE
SSB           0
LB            0.00 Hz
GB            0
PC            1.00

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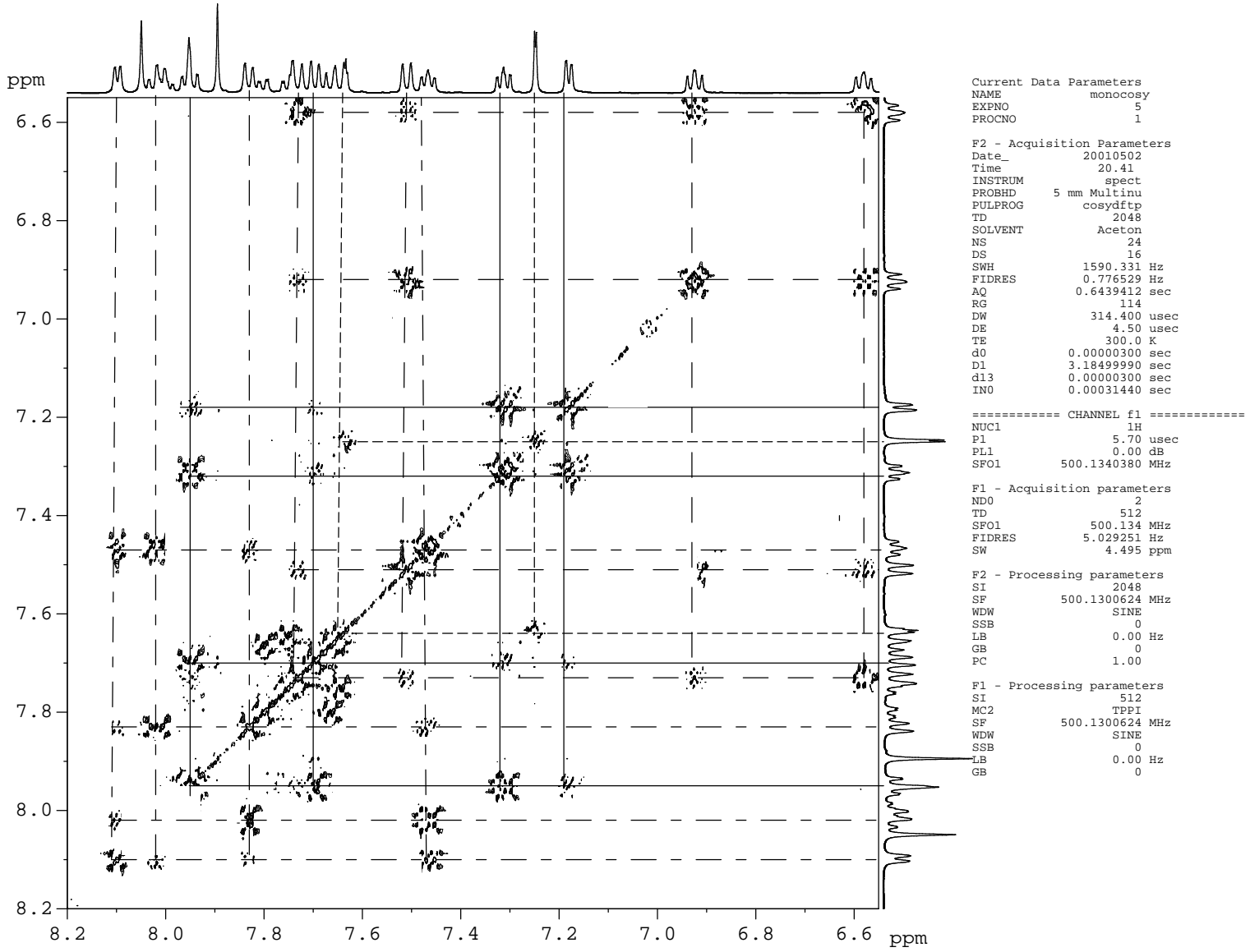
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F1 - Processing parameters
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MC2           TPPI
SF            500.1300624 MHz
WDW           SINE
SSB           0
LB            0.00 Hz
GB            0

```

Fig. 12. <sup>1</sup>H COSY spectrum of **9** (L = pic-anth)(L = CH<sub>3</sub>CN)(PF<sub>6</sub>)<sub>4</sub> (**16**).

Fig. 13. Expanded view of the <sup>1</sup>H COSY spectrum of [9 (L = pic-anth)(L = CH<sub>3</sub>CN)](PF<sub>6</sub>)<sub>4</sub> (16) for the region between 6.6 and 8.2 ppm.



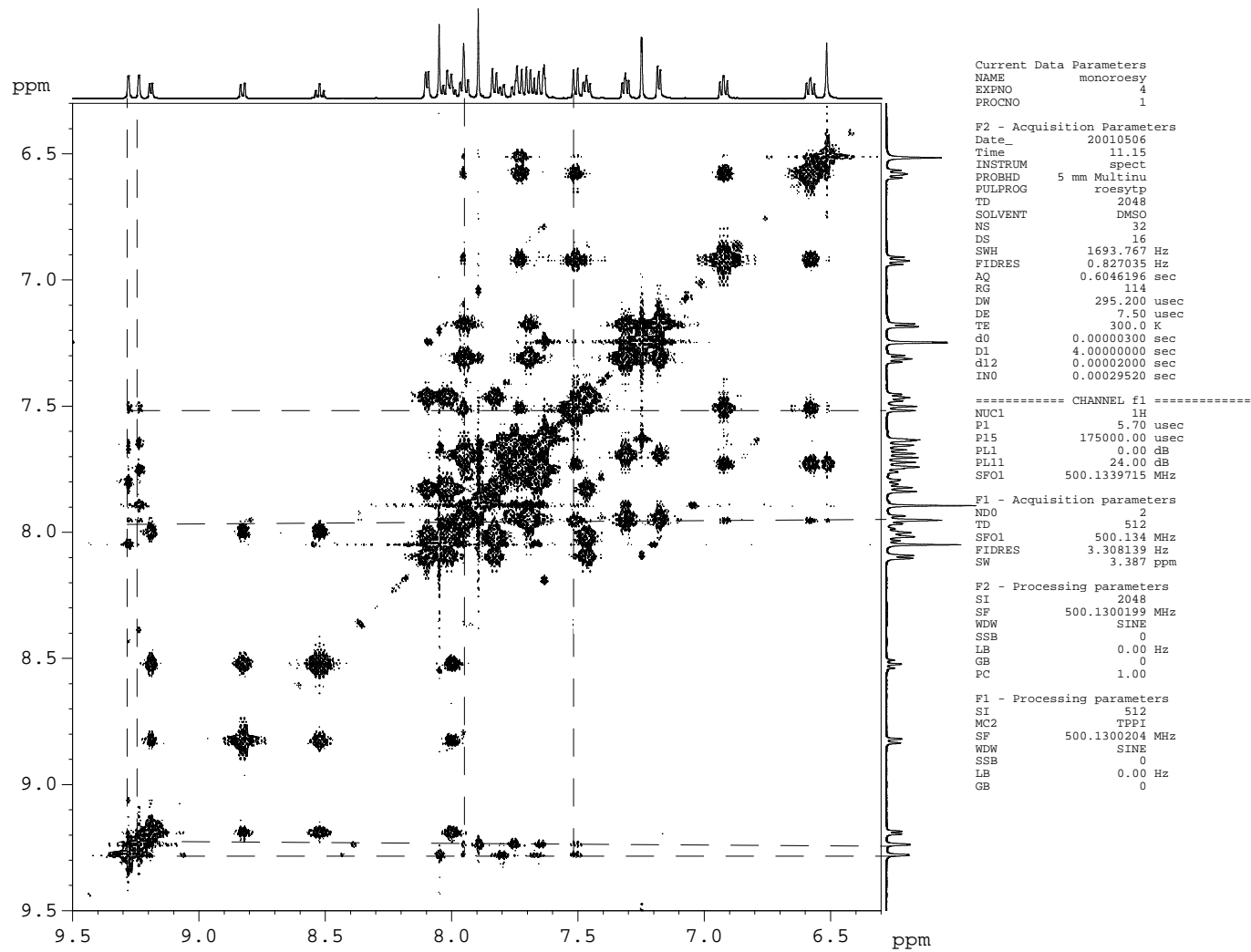


Fig. 14.  $^1\text{H}$  ROESY spectrum of **19** ( $\text{L} = \text{pic-antH}$ )( $\text{L} = \text{CH}_3\text{CN}$ )( $\text{PF}_6$ )<sub>4</sub> (**16**).



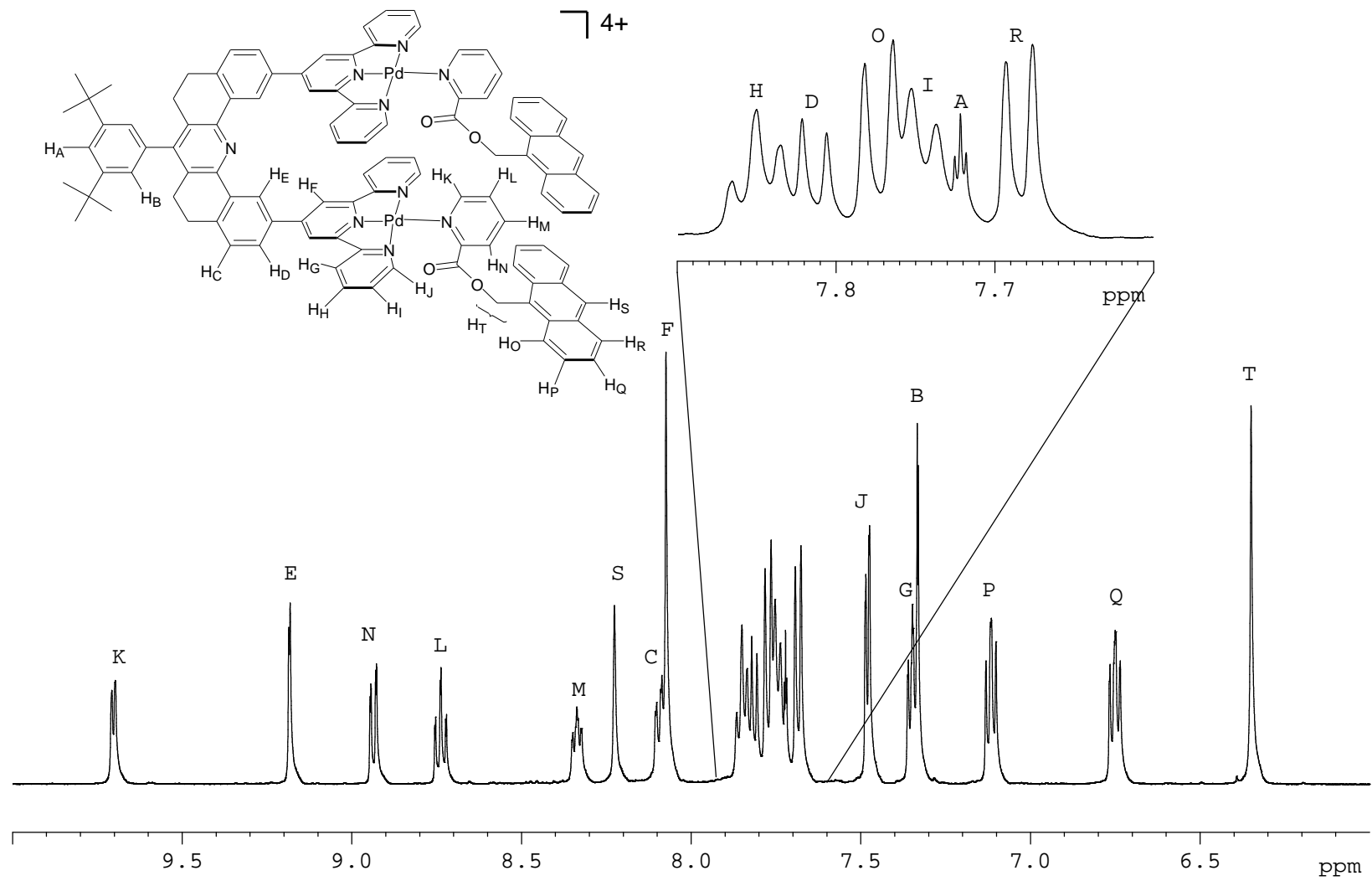


Fig. 15. <sup>1</sup>H NMR spectrum of [9] (L = pic-anth)<sub>2</sub>[(PF<sub>6</sub>)<sub>4</sub>] (17).

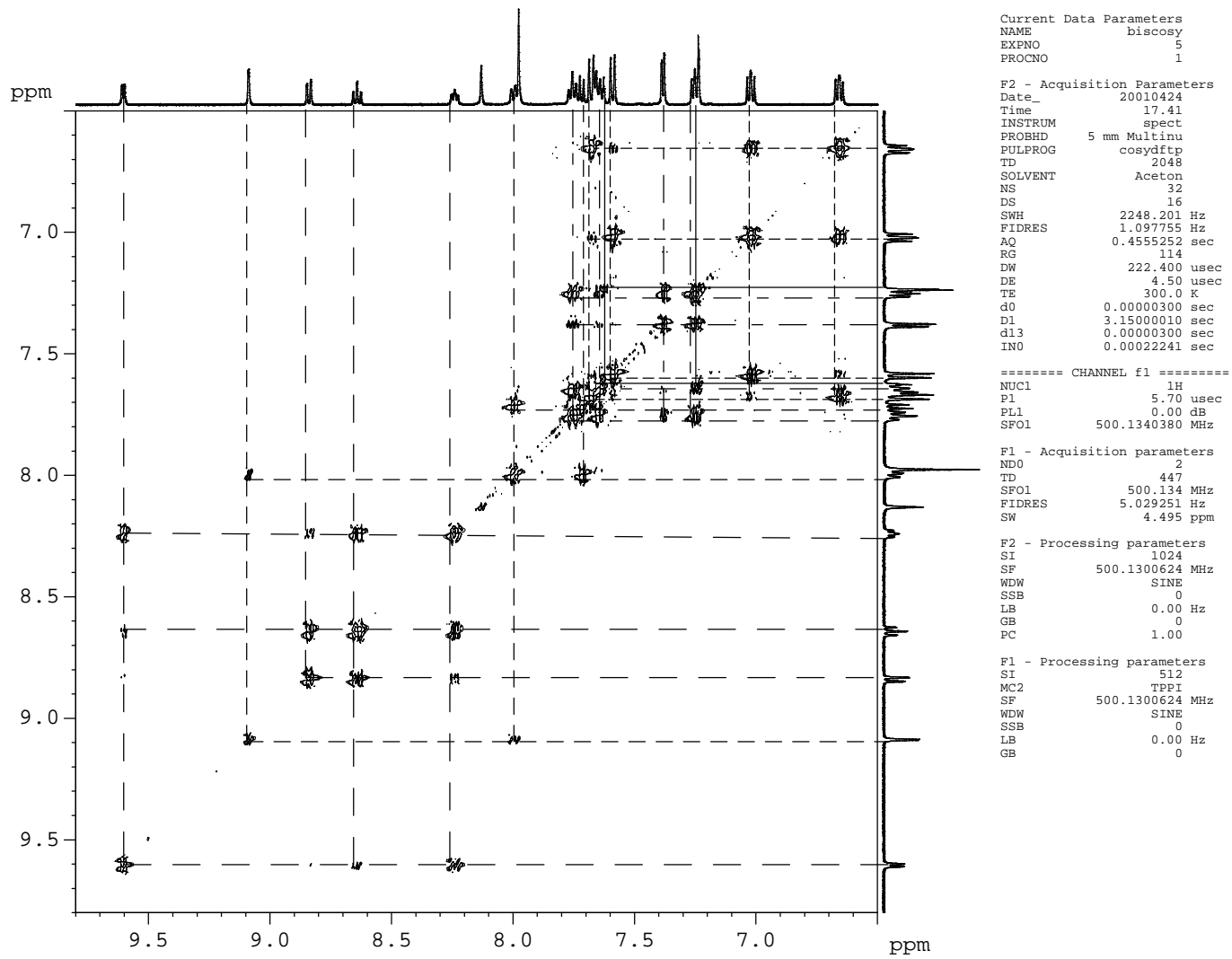
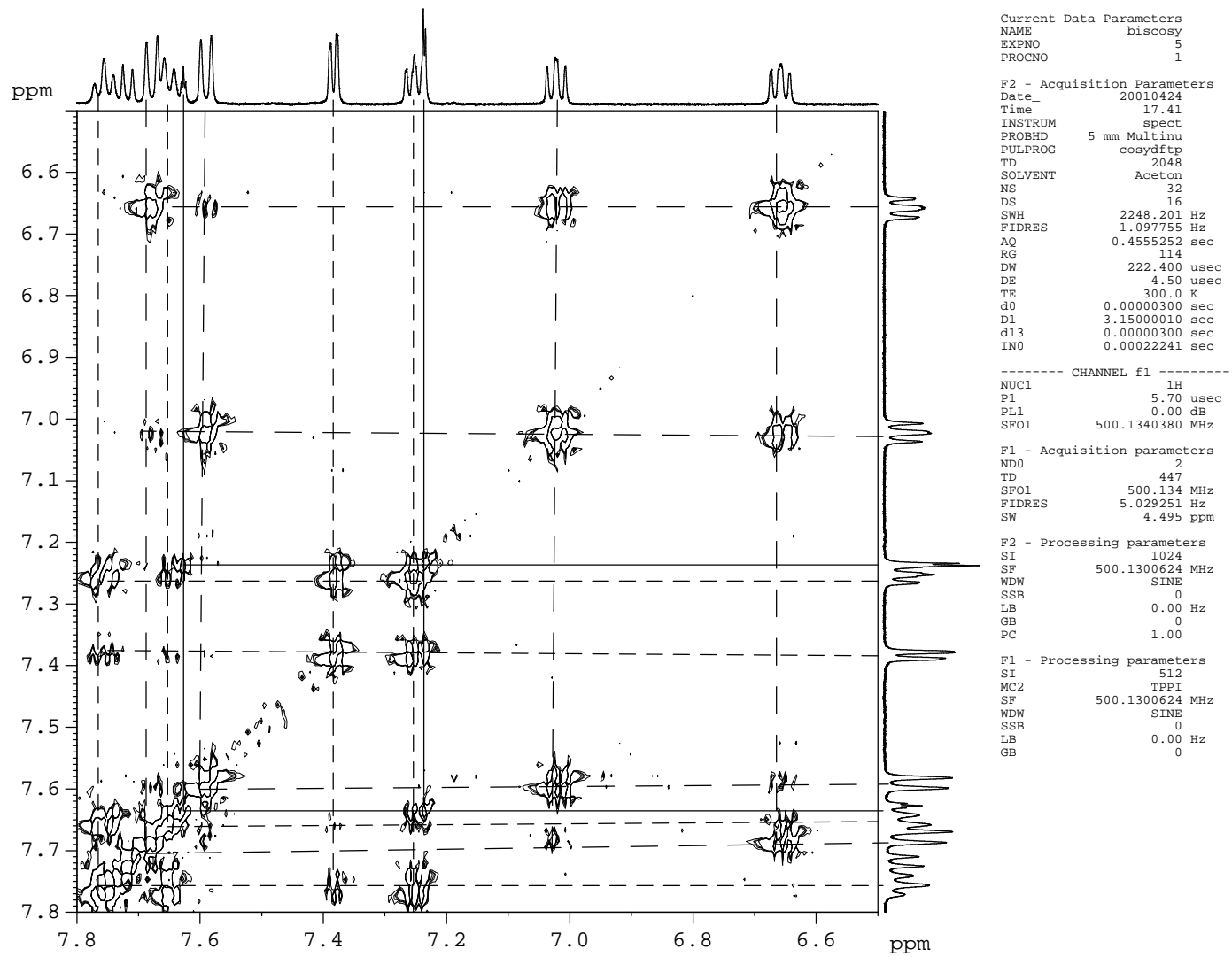
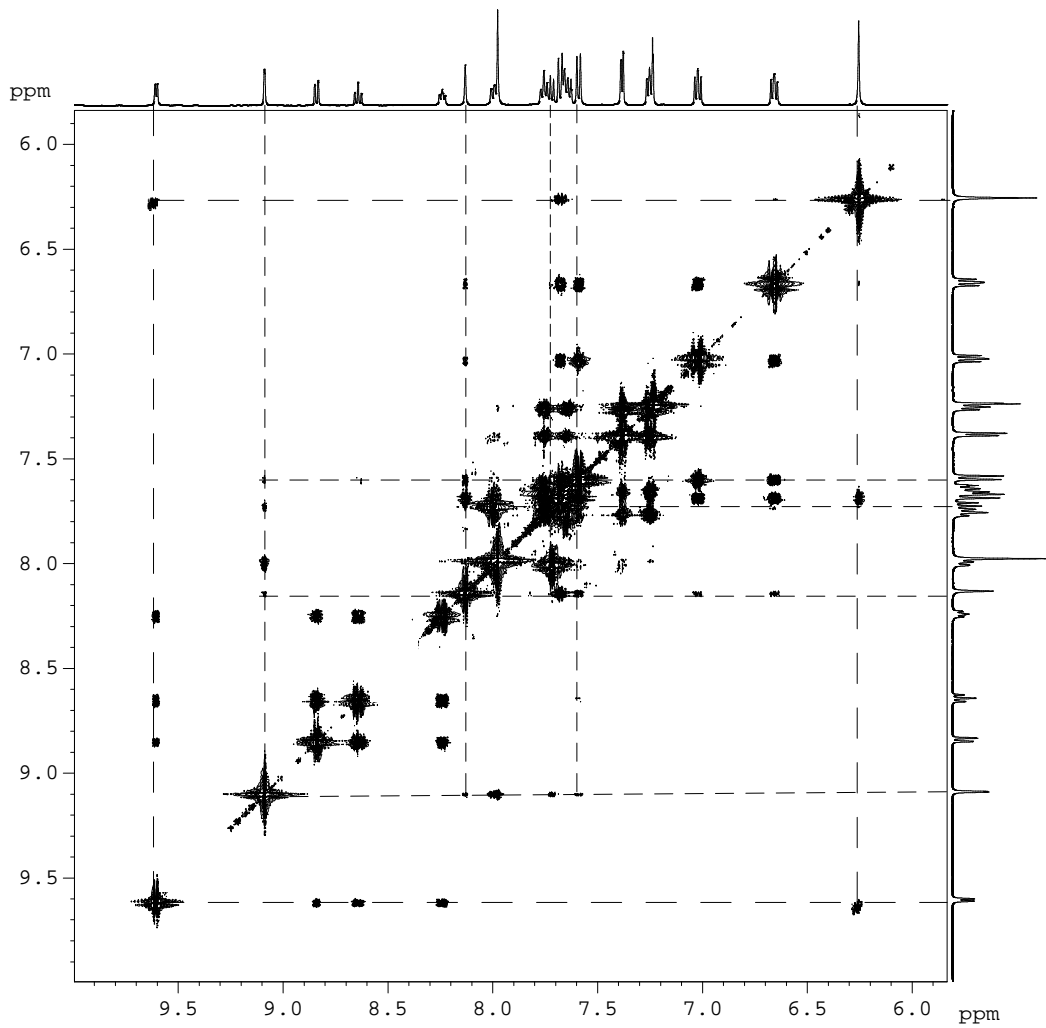
Fig. 16.  $^1\text{H}$  COSY spectrum of [9 (L = pic-anth) $_2$ ](PF $_6$ ) $_4$  (17).

Fig. 17. Expanded view of the  $^1\text{H}$  COSY spectrum of [9(L = pic-anth) $_2$ ](PF $_6$ ) $_4$  (17) for the region between 6.5 and 7.8 ppm.





```

Current Data Parameters
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EXPNO         4
PROCNO        1

F2 - Acquisition Parameters
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Time          17.17
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PROBHD        5 mm Multinu
PULPROG       roesytp
TD            2048
SOLVENT       DMSO
NS            32
DS            16
SWH           2083.333 Hz
FIDRES        1.017253 Hz
AQ            0.4915700 sec
RG            161.4
DW            240.000 usec
DE            7.50 usec
TE            300.0 K
d0            0.0000300 sec
d1            3.5000000 sec
d12           0.0002000 sec
IN0           0.0002400 sec

===== CHANNEL f1 =====
NUC1          1H
P1            6.10 usec
P15           50000.00 usec
PL1           0.00 dB
PL11          24.00 dB
SFO1          500.1340210 MHz

F1 - Acquisition parameters
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TD            489
SFO1          500.134 MHz
FIDRES        4.260396 Hz
SW            4.166 ppm

F2 - Processing parameters
SI            1024
SF            500.1300000 MHz
WDW           SINE
SSB           0
LB            0.00 Hz
GB            0
PC            1.00

F1 - Processing parameters
SI            512
MC2           TPPI
SF            500.1300000 MHz
WDW           SINE
SSB           0
LB            0.00 Hz
GB            0

```

Fig. 18. <sup>1</sup>H ROESY spectrum of [9 (L = pic-anth)<sub>2</sub>](PF<sub>6</sub>)<sub>4</sub> (**17**).

## Crystallographic Experimental Section

**Data Collection.** An approximately square plate crystal of [9 (L = pic-anth)<sub>2</sub>](PF<sub>6</sub>)<sub>4</sub> (**17**) (0.24 × 0.20 × 0.06 mm, large face = (001)) was selected while immersed in Fluorolube oil to minimize possible reaction with air. The crystal was mounted on a Bruker SMART APEX system at 100 K. Rotation and still images showed the reflections to be slightly diffuse with diffraction seldom beyond 2θ = 40°. Visual observation of the crystals left at room temperature in the oil showed modification possibly resulting from solvent loss within 1 h.

A full sphere of data was obtained because of the triclinic symmetry to a resolution of 0.84 Å using 0.3° steps in ω and a scan time per frame of 90 sec. Integration of intensities and refinement of cell parameters were done using SAINT (1). Absorption corrections were applied using SADABS (1).

**Structure Solution and Refinement.** The space group was assigned as *P1* based on systematic absences and intensity statistics. The Pd atoms were located from a Patterson synthesis. Repeated difference Fourier maps allowed recognition of the expected structural units but only with difficulty. PF<sub>6</sub> groups were evident, although the geometry was only poorly octahedral for two of these molecules. Methyl ethyl ketone was present, but disorder made only approximate modeling possible. N and O assignments were made based on knowledge of the synthesis. The acentric space group *P1* was confirmed using PLATON and distinct absence of inversional relationships among the potentially related parts of the structure. Following location of all atoms in the main molecule and PF<sub>6</sub> groups, hydrogen positions were calculated. At this point isotropic refinement gave an R value of approximately 0.16. All refinements were done in BLOCK mode to accommodate the ~2700 parameters. Because the solvent “volume” was large and the solvent apparently was disordered, program SQUEEZE was applied to the data to attempt to correct for disordered solvent. Using the HKL file output from SQUEEZE, the isotropic R value was approximately 0.11 with no obvious residual electron density within the void space. Anisotropic refinement of all nonhydrogen atoms resulted in several nonpositive definite atoms. The two PF<sub>6</sub> units that are not close to any Pd complex show clear deviations from octahedral geometry and large thermal parameters.

Intensity statistics reveal that reflections with odd-*h* index are significantly weaker than those with even-*h* index. The average values of  $I/\sigma(I)$  for odd-*h* and even-*h* reflections are 3.3 and 10.9, respectively. This results from the pseudosymmetry operator ( $\frac{1}{2} + x, y, z$ ) being applied to at least some of the atoms in the structure. It is apparent by inspection of the atomic coordinates and thermal parameters that the palladium and phosphorus atoms are translationally related in pairs by this pseudosymmetry operator. The many problems encountered during structure refinement have certainly been exacerbated in part by this pseudosymmetry.

**Equations of interest:**

$$R_{\text{int}} = \Sigma |F_o^2 - \langle F_o^2 \rangle| / \Sigma |F_o^2|$$

$$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

$$wR2 = [\Sigma [w (F_o^2 - F_c^2)^2] / \Sigma [w (F_o^2)^2]]^{1/2}$$

$$\text{GooF} = S = [\Sigma [w (F_o^2 - F_c^2)^2] / (n - p)]^{1/2}$$

where  $w = q / \sigma^2 (F_o^2) + (aP)^2 + bP$ ;

$n$  = number of independent reflections;

$q, a, b, P$  as defined in (1).

$p$  = number of parameters refined.

(1) All software and sources of scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI).

Table 4. Crystal and structure refinement for [9 (L = pic-anth)<sub>2</sub>](PF<sub>6</sub>)<sub>4</sub> (17)

Identification code	Andy01	
Empirical formula	C <sub>107</sub> H <sub>85</sub> N <sub>9</sub> O <sub>4</sub> Pd <sub>2</sub> + 4PF <sub>6</sub>	
Formula weight	2353.52	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	$a = 14.755(3) \text{ \AA}$	$a = 76.974(3)^\circ$
	$b = 16.781(3) \text{ \AA}$	$b = 89.164(3)^\circ$
	$c = 30.397(6) \text{ \AA}$	$\beta = 64.047(3)^\circ$
Volume	6563(2) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.191 Mg/m <sup>3</sup>	
Absorption coefficient	0.402 mm <sup>-1</sup>	
$F(000)$	2380	
Crystal size, color, habit	0.24 × 0.20 × 0.06 mm, pale yellow, plate	
Theta range for data collection	1.54 – 25.03°	
Index ranges	-17 ≤ $h$ ≤ 17, -19 ≤ $k$ ≤ 19, -36 ≤ $l$ ≤ 36	
Reflections collected	63,047	
Independent reflections	45,489 ( $R_{\text{int}} = 0.0396$ )	
Absorption correction	SADABS based on redundant diffractions	
Max. and min. transmission	1.0, 0.814	
Refinement method	Full-matrix least squares on $F^2$	
Weighting scheme	$w = q [\sigma^2 (F_o^2) + (aP)^2 + bP]^{-1}$ where $P = (F_o^2 + 2 F_c^2)/3$ , $a = 0.1113$ , $b = 0.0$ , $q = 1$	
Data/restraints/parameters	45489/3/2634	
Goodness-of-fit on $F^2$	1.065	
Final $R$ indices [ $I > 2 \sigma(I)$ ]	$R1 = 0.0874$ , $wR2 = 0.207$	
$R$ indices (all data)	$R1 = 0.1067$ , $wR2 = 0.218$	
Largest diff. peak and hole	2.497, -2.204 e·Å <sup>-3</sup>	

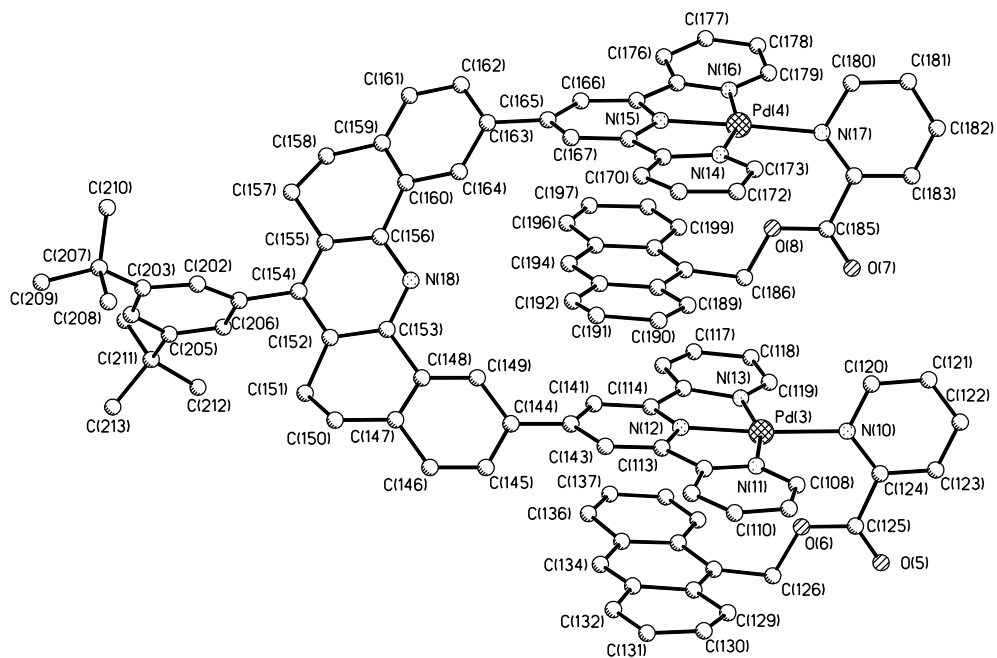


Fig. 19.  $[9 (L = \text{pic-anth})_2]^{4+}$  (**17**) “side” view of one of the molecules in the unit cell. The counterions and solvent have been removed for clarity.

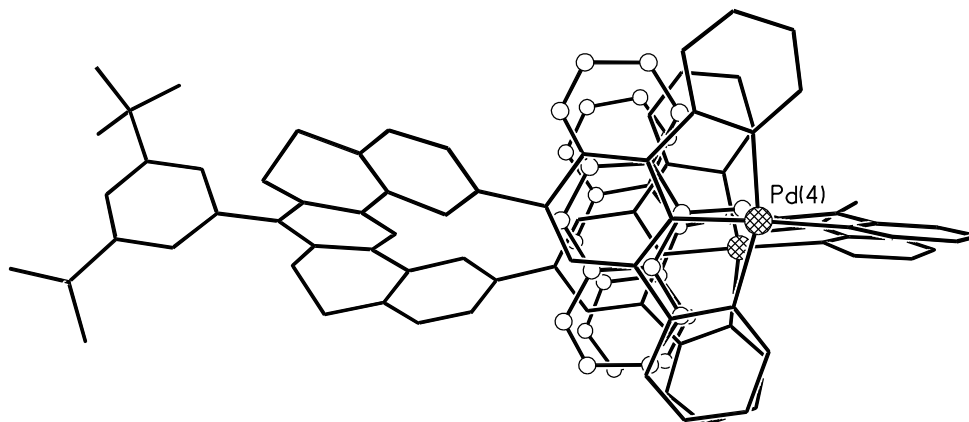


Fig. 20.  $[9 (L = \text{pic-anth})_2]^{4+}$  (**17**) “top” view of one of the molecules in the unit cell. The counterions and solvent have been removed for clarity.



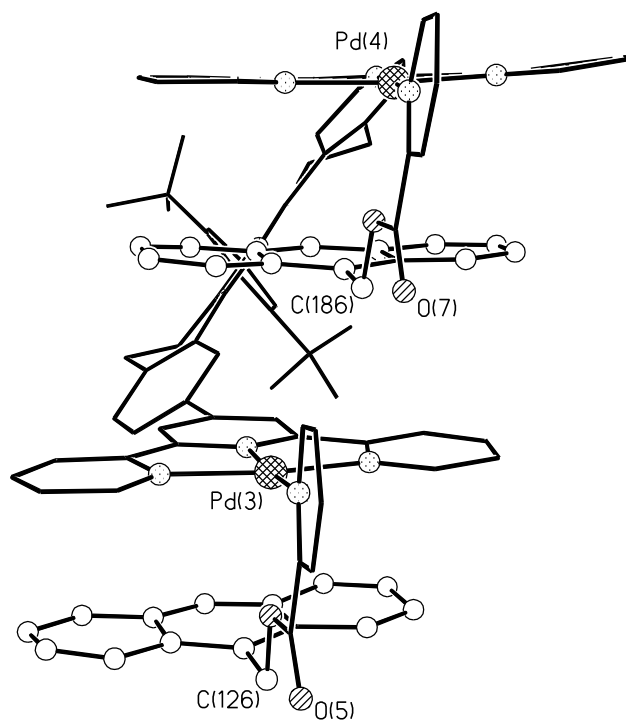


Fig. 21.  $[9(L = \text{pic-anth})_2]^{4+}$  (**17**) “front” view of one of the molecules in the unit cell. The counterions and solvent have been removed for clarity.

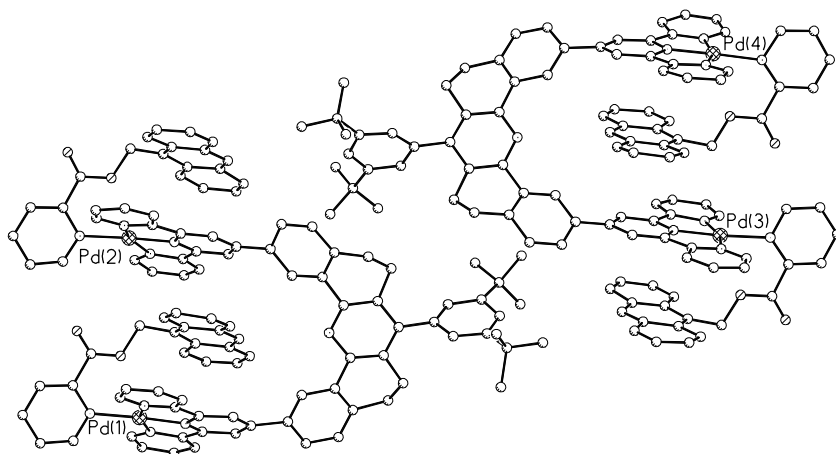


Fig. 22.  $[9(L = \text{pic-anth})_2](\text{PF}_6)_4$  (**17**) “view of the unit cell.” The counterions and solvent have been removed for clarity.

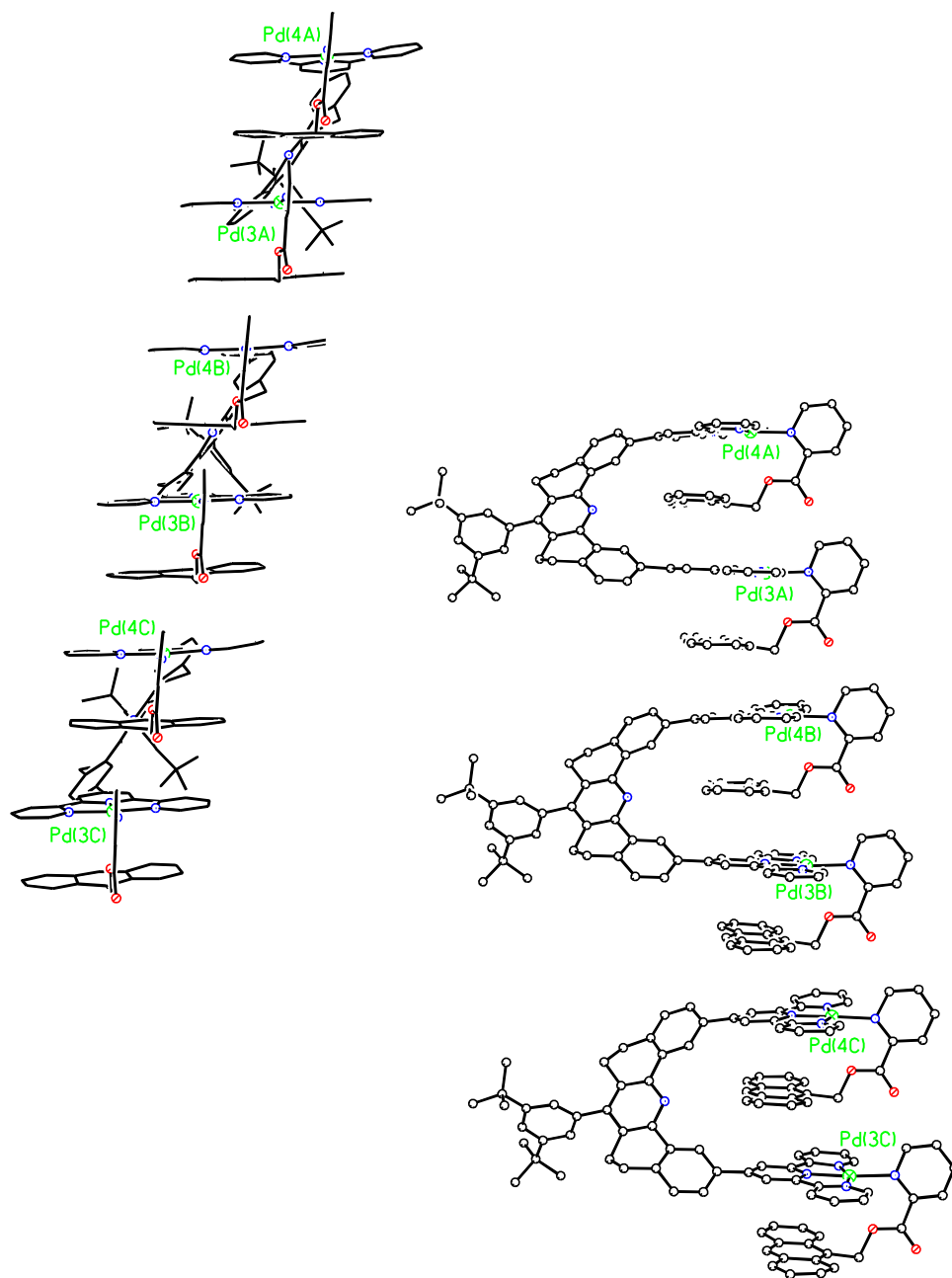


Fig. 23. Stacking views for three molecules that belong to an infinite stack of molecules in the crystal [9 (L = pic-anth)<sub>2</sub>]<sup>4+</sup> (**17**). The counterions and solvent have been removed for clarity.