Supporting Information

Bimetallic Reductive Elimination from Dinuclear Pd(III) Complexes.

David C. Powers, Diego Benitez, Ekaterina Tkatchouk, William A. Goddard, III, and Tobias Ritter*

Department of Chemistry and Chemical Biology, Harvard University

12 Oxford Street, Cambridge, Massachusetts 02138

Materials and Process Simulation Center, California Institute of Technology, Pasadena, California 91125

E-mail: ritter@chemistry.harvard.edu

Table of Contents

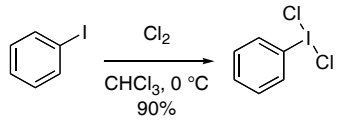
Materials and Methods

Reactions were carried out under ambient atmosphere unless otherwise specified. Anhydrous solvents were obtained either by filtration through drying columns[1] (ether, CH_2Cl_2) on an mBraun system or by distillation over sodium (ether, pentane). Purified compounds were further dried under high vacuum (0.01–0.05 Torr). Yields refer to purified and spectroscopically pure compounds. Melting points were measured on a Buchi 510 apparatus. All melting points were measured in open capillaries and are uncorrected. NMR spectra were recorded on either a Varian Unity/Inova 500 spectrometer operating at 500 MHz and 125 MHz for ^{1}H and ^{13}C acquisitions, respectively, or a Varian Mercury 400 spectrometer operating at 400 HMz and 375 MHz for ^{1}H and ^{19}F acquisitions, respectively. Chemical shifts are reported in ppm with the solvent resonace as the internal standard. Data is reported as follows: s = singlet, br = broad, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constants in Hz; integration. UV-VIS spectra were obtained on a Varian Cary 50 Probe UV-visible spectrophotometer. High-resolution mass spectra were obtained on Jeol AX-505 or SX-102 spectrometers at the Harvard University Mass Spectrometry Facilities. $Pd(OAc)_2$ was purchased from Strem. XeF_2 was purchased from Frontier Scientific. Benzo[*h*]quinoline (**8**) was obtained from TCI America. Acetic acid-*d4* and xylylene dibromide were purchased from Alfa Aesar. All chemicals were used without purification.

In the manuscript, compound **1** is identical to compound **18a** and compound **2** is identical to compound **19a**.

Synthesis and Thermolysis of 1 (Data Pertaining to Eq 1 and Figure 1)

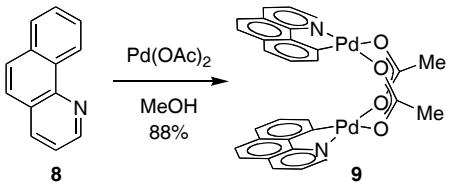
Iodobenzene Dichloride



A solution of iodobenzene (5.44 g, 26.7 mmol, 1.00 equiv) in $CHCl_3$ (30 mL) was cooled to 0 ºC. Chlorine gas was vigorously bubbled through the solution for one hour after which time a thick slurry was observed. The solid was isolated by filtration and washed with hexanes (20 mL) to afford 6.60 g of the title compound as a pale yellow solid (90% yield). The title compound was stored at –20 °C in the dark.

^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 8.19 (dd, J = 8.2 Hz, 1.3 Hz, 2H), 7.60 (tt, J = 6.7 Hz, J = 0.9 Hz, 1H), 7.48 (td, J = 7.3 Hz, J = 1.4 Hz, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 133.79, 132.08, 131.55, 125.30. Mass Spectrometry: LRMS-FIA (m/z): 238.91 [$C_6H_5ClI^+$]. These spectroscopic data are consistent with those reported in the literature.[2]

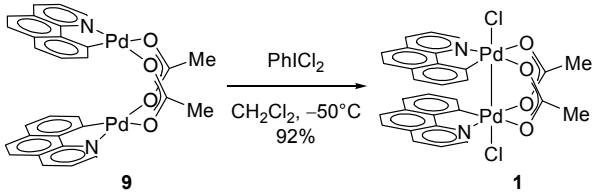
Benzo[*h*]quinolinyl palladium(II) acetate dimer (9)



To benzo[*h*]quinoline (**8**) (1.00 g, 5.58 mmol, 1.00 equiv) in MeOH (75 mL) at 23 ºC was added $Pd(OAc)_2$ (1.25 g, 5.58 mmol, 1.00 equiv). After eight hours, the precipitate was isolated by filtration and washed with MeOH (50 mL) and Et_2O (50 mL), sequentially, to afford 1.68 g of the title compound as a yellow solid (88% yield).

^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.82 (dd, J = 5.0 Hz, J = 1.1 Hz, 2H), 7.44 (dd, J = 8.0 Hz, J = 1.1 Hz, 2H), 7.25–7.20 (m, 6H), 7.09 (dd, J = 6.9 Hz, J = 1.1 Hz, 2H), 6.98 (d, J = 8.7 Hz, 2H), 6.48 (dd, J = 8.0 Hz, J = 5.0 Hz, 2H), 2.38 (s, 6H). ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 182.25, 152.92, 148.60, 148.52, 139.74, 135.00, 132.18, 128.71, 127.59, 127.42, 124.70, 122.62, 121.81, 119.52, 24.92. These spectroscopic data correspond to those reported in the literature.[3] UV-VIS Spectroscopy (CH_2Cl_2, 23 ˚C): 425 nm (ε = 2.00 × 10^3 M^{-1} cm^{-1}); 376 nm (ε = 4.30 × 10^3 M^{-1} cm^{-1}); 346 nm (ε = 4.18 × 10^3 M^{-1} cm^{-1}). Mass Spectrometry: LRMS-APCI (m/z): 686.0 [$C_{30}H_{22}N_2O_4Pd_2^+$]. Cyclic voltammogram included in Electrochemical Data Section. X-ray data included in X-Ray Data Analysis Section.

Benzo[*h*]quinolinyl chloro palladium(III) acetate dimer (1)

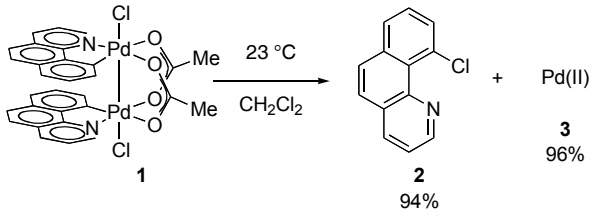


To a solution of benzo[*h*]quinolinyl palladium acetate dimer (**9**) (72.0 mg, 0.105 mmol, 1.00 equiv) in CH_2Cl_2 (2.5 mL) at –50˚C was added $PhICl_2$ (28.8 mg, 0.105 mmol, 1.00 equiv). The color of the solution immediately changed from pale yellow to dark red-brown. After stirring at –50˚C for 10 minutes, solvent was removed *in vacuo* at –50˚C. The residue was washed with cold Et_2O (–50˚C) three times. The remaining solid was dried under vacuum to afford 73.1 mg of the title compound as a dark red solid (92% yield.). X-ray quality crystals were obtained by layering a concentrated CH_2Cl_2 solution with pentane at –35˚C. Crystallization experiments were carried out in a dry box.

^{1}H-NMR (500 MHz, CD_2Cl_2, –50 ºC, δ): 7.71 (bs, 2H), 7.58 (d, J = 7.8 Hz, 2H), 7.45 (dd, J = 7.3 Hz, J = 7.3 Hz, 2H), 7.35 (d, J = 7.8 Hz, 2H), 7.22 (d, J = 8.8 Hz, 2H), 7.18 (d, J = 7.8 Hz, 2H), 7.03 (d, J = 8.3

Hz, 2H), 6.71 (bs, 2H), 2.69 (s, 6H).[1] UV-VIS Spectroscopy (CH_2Cl_2, 0 °C): 582 nm ($\varepsilon = 2.99 \times 10^3$ M^{-1} cm^{-1}); 491 nm ($\varepsilon = 7.39 \times 10^3$ M^{-1} cm^{-1}); 417 nm ($\varepsilon = 2.61 \times 10^4$ M^{-1} cm^{-1}); 270 nm ($\varepsilon = 3.69 \times 10^4$ M^{-1} cm^{-1}). X-ray data included in X-Ray Data Analysis Section. Thermal instability prevented both mass spectral as well as elemental analysis from being obtained. ^{13}C NMR could not be obtained due to low solubility of **1** at temperatures at which **1** is stable.

Thermolysis of 1



Isolation of **2**

A solution of benzo[*h*]quinolinyl chloro palladium acetate dimer (**1**) (33.6 mg, 0.0444 mmol, 1.00 equiv) in CH_2Cl_2 (3mL) was prepared at –50 ºC. The solution was warmed to 23 ºC. After stirring for three hours at 23 ºC, the solution was yellow. Solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel eluting with hexanes / diethyl ether (9:1) to afford 8.9 mg of the title compound as a colorless solid (94% yield).[2]

R_f = 0.32 (hexanes/Et_2O 9:1 (v/v)). ^1H-NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 9.12 (dd, *J* = 4.4 Hz, *J* = 2.0 Hz, 1H), 8.19 (dd, *J* = 8.3 Hz, *J* = 2.0 Hz, 1H), 7.84 (td, *J* = 7.3 Hz, *J* = 1.0 Hz, 2H), 7.80 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.59–7.55 (m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 147.63, 146.49, 136.32, 135.65, 132.34, 131.53, 128.14, 127.67, 127.60, 127.55, 127.54, 126.62, 121.71. Mass Spectrometry: HRMS-FIA (m/z): calcd for [$C_{13}H_8NCl$+H], 214.0418. Found, 214.0418. These spectroscopic data correspond to those reported in the literature[3] and are identical with those of an authentic sample prepared as described below.

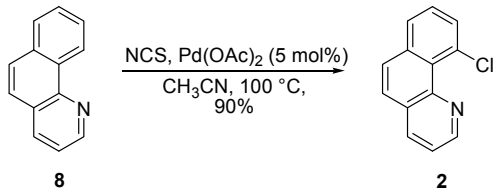
For discussion of the constitution of **3**, please see 'Analysis of the Pd Containing Byproducts of Reductive Elimination' below.

---

[1] Previously, we suggested that chloride for acetate positional exchange in **1** was observed at –10 ºC. Re-examination of the temperature-dependent ^1H NMR of **1** has failed to confirm the original assignment; the observed changes in the ^1H NMR sample were a result of adventitious water, not positional exchange.

[2] Chlorination of benzo[*h*]quinolinyl palladium acetate dimer (**9**) was also carried out with excess $PhICl_2$ according to the procedures outlines above. Treatment of **9** (100 mg, 0.145 mmol, 1.00 equiv) with $PhICl_2$ (100 mg, 0.364 mmol, 2.50 equiv) at 23 °C afforded 29.1 mg of **2** (94% yield). The observation of >100% yield would suggest that compound **1** could oxidized beyond the Pd(III) oxidation state by $PhICl_2$.

10-Chlorobenzo[*h*]quinoline (2)

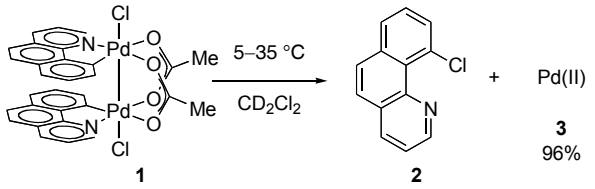


An authentic sample of 10-chlorobenzo[*h*]quinoline (**2**) was prepared according to literature procedures.[3] *N*-Chlorosuccinimide (101 mg, 0.758 mmol, 1.20 equiv) was added to a solution of benzo[*h*]quinoline (**8**) (113 mg, 0.632 mmol, 1.00 equiv) and $Pd(OAc)_2$ (7.1 mg, 0.032 mmol, 0.050 equiv) in CH_3CN (5.0 mL). The reaction was heated to 100 ˚C for 50 hours. The reaction was cooled and solvent was removed *in vacuo*. The residue was purified by chromatography on silica gel eluting with hexanes / benzene (1:1) to afford 121 mg of the title compound (90% yield).

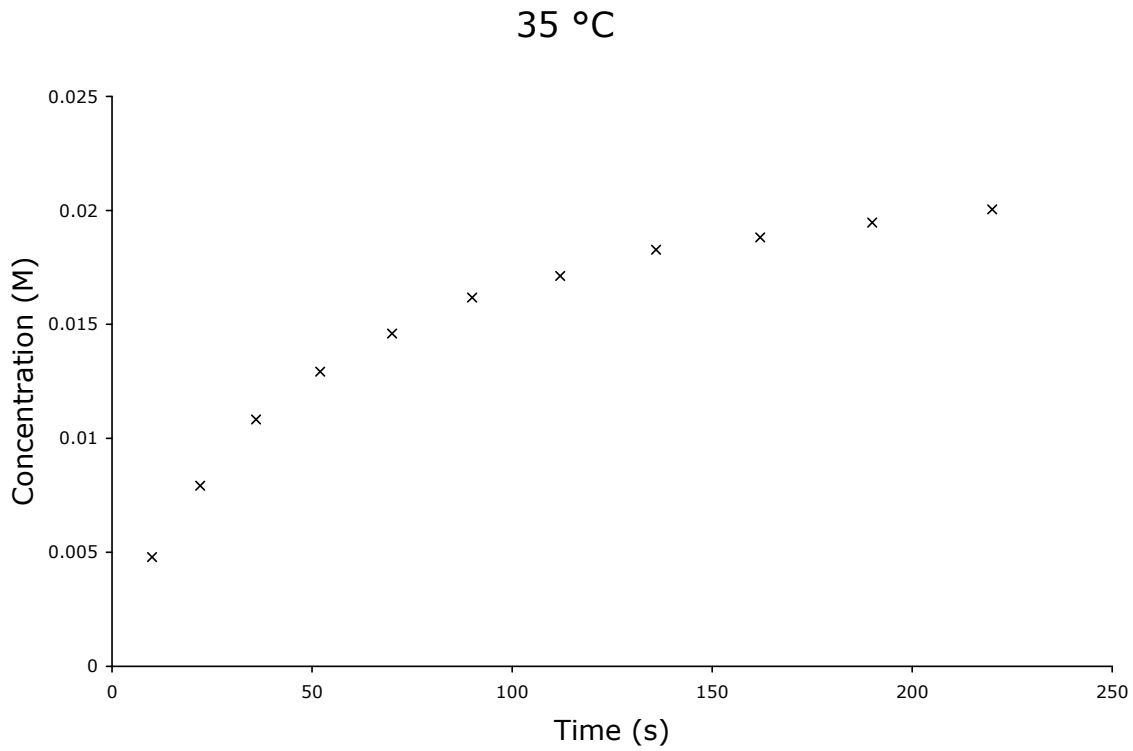
Spectral properties are identical to those reported above.

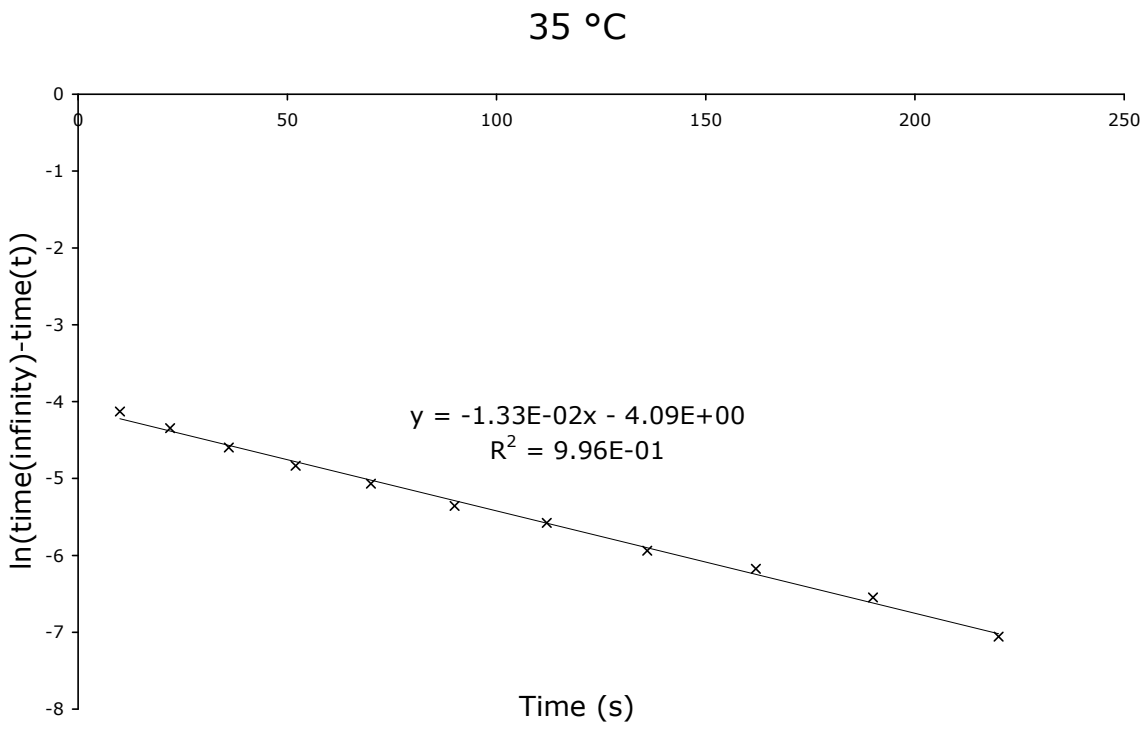
Thermal Decomposition of 1

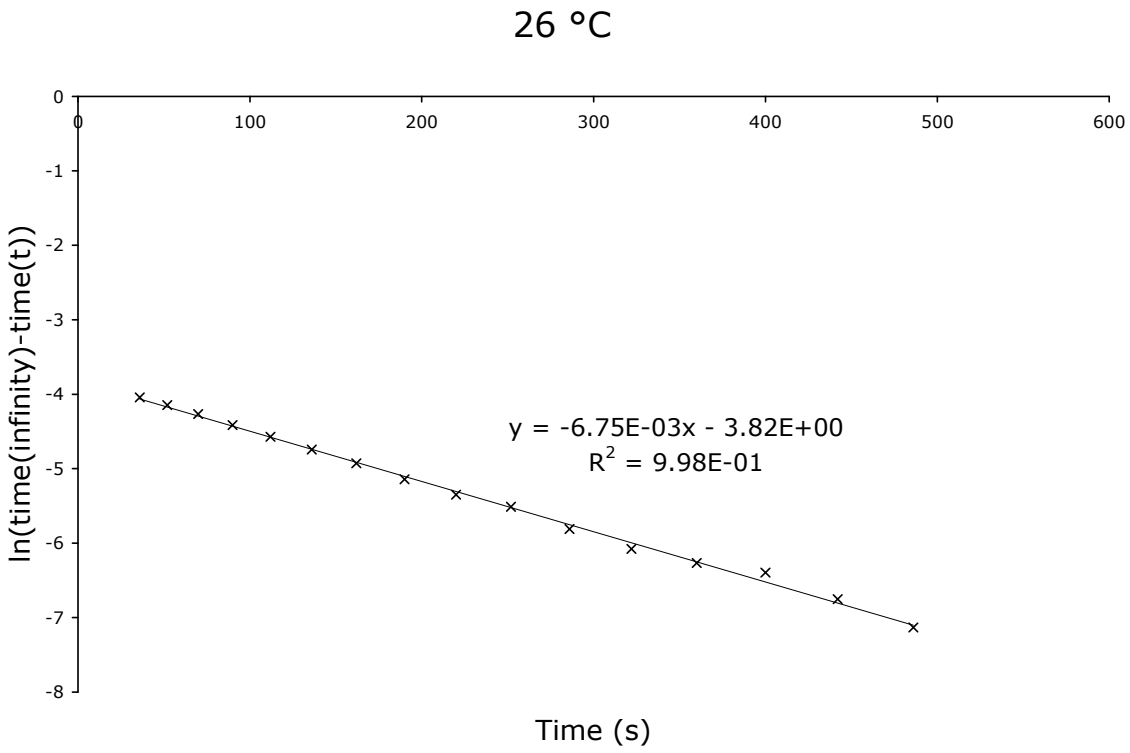
Rate of C–Cl Reductive Elimination from 1 as a Function of Temperature

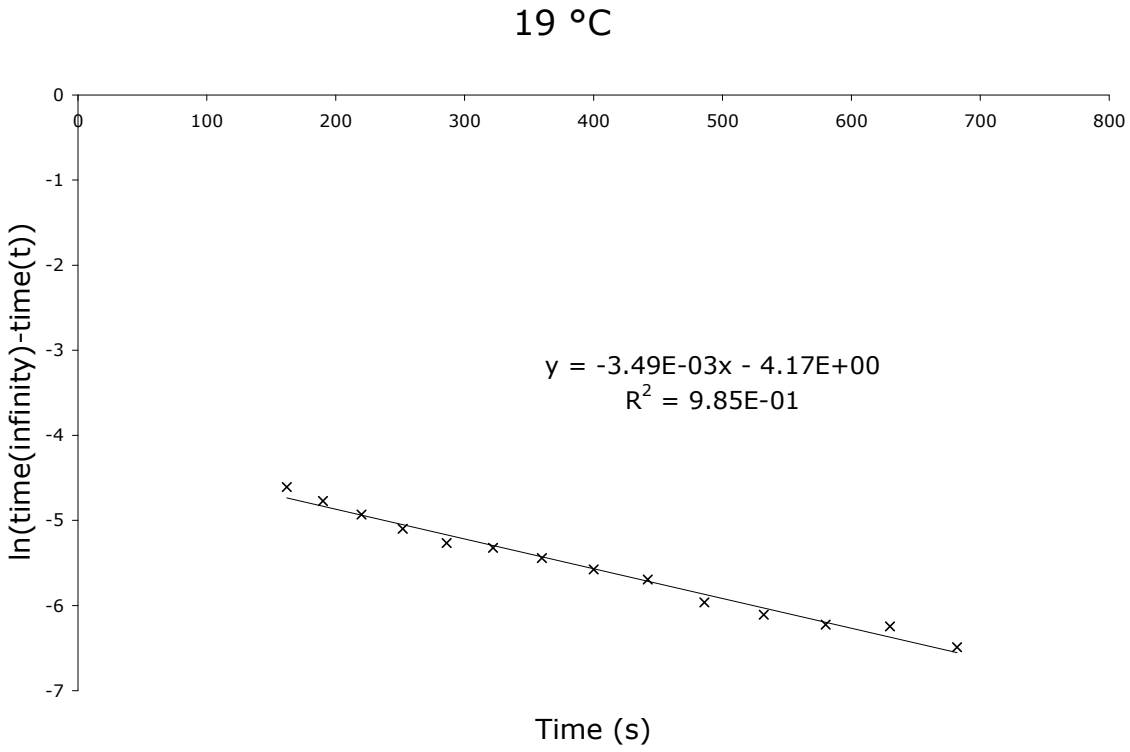


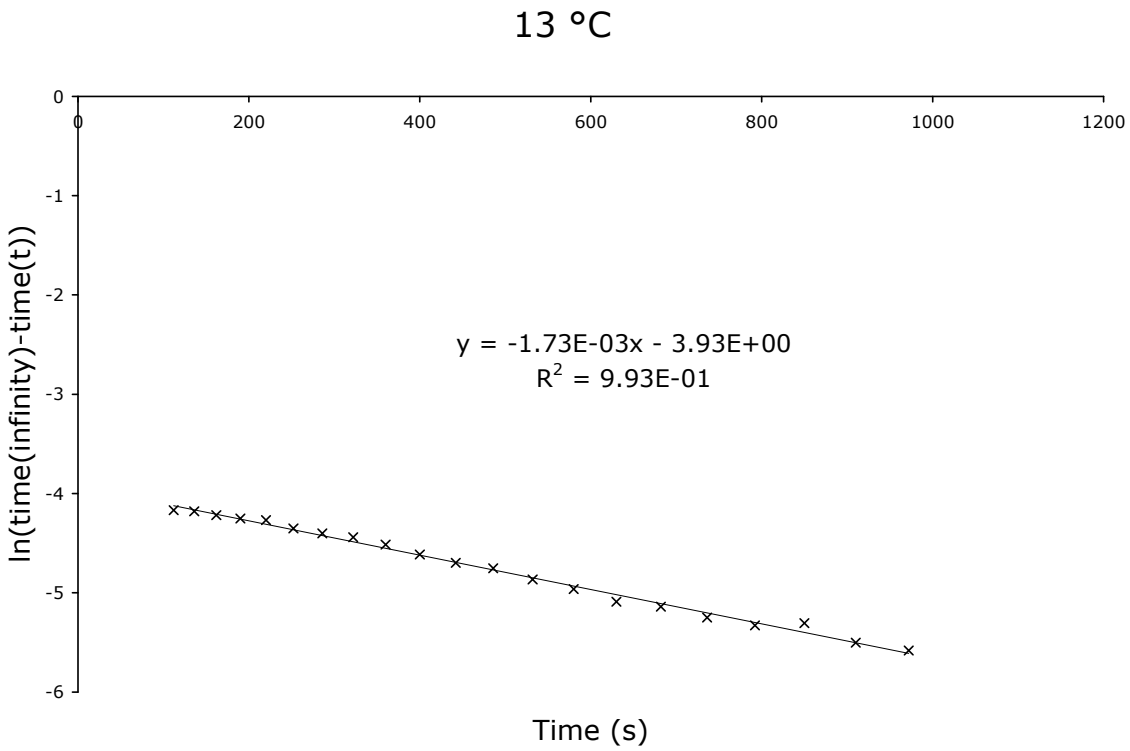
Solutions (20 mM) of compound **9** and $PhICl_2$ in CD_2Cl_2 were prepared and stored at –30 ˚C. An NMR tube was purged with N_2 and cooled to –45 ˚C. Compound **9** in CD_2Cl_2 (300 μL) and $PhICl_2$ in CD_2Cl_2 (300 μL) were combined. ^{1}H NMR spectra were obtained; the disappearance of **1** was monitored by the ^{1}H NMR signal at 2.70 ppm while the evolution of **2** was monitored by the ^{1}H NMR signal at 9.12 ppm. These signals were integrated relative the residual proton signal from CD_2Cl_2. These ratios were converted to concentrations based on the integration of a 20 mM solution of **2** in CD_2Cl_2. Since evolution of product was measured, linear natural log plots were obtained by using an infinite time point set to 100% yield (20 mM in **2**). In each case, the reactions were followed to greater than 3 half-lives. Data were fitted to a first order regression; plots, slopes, and R^2 values are reported below.

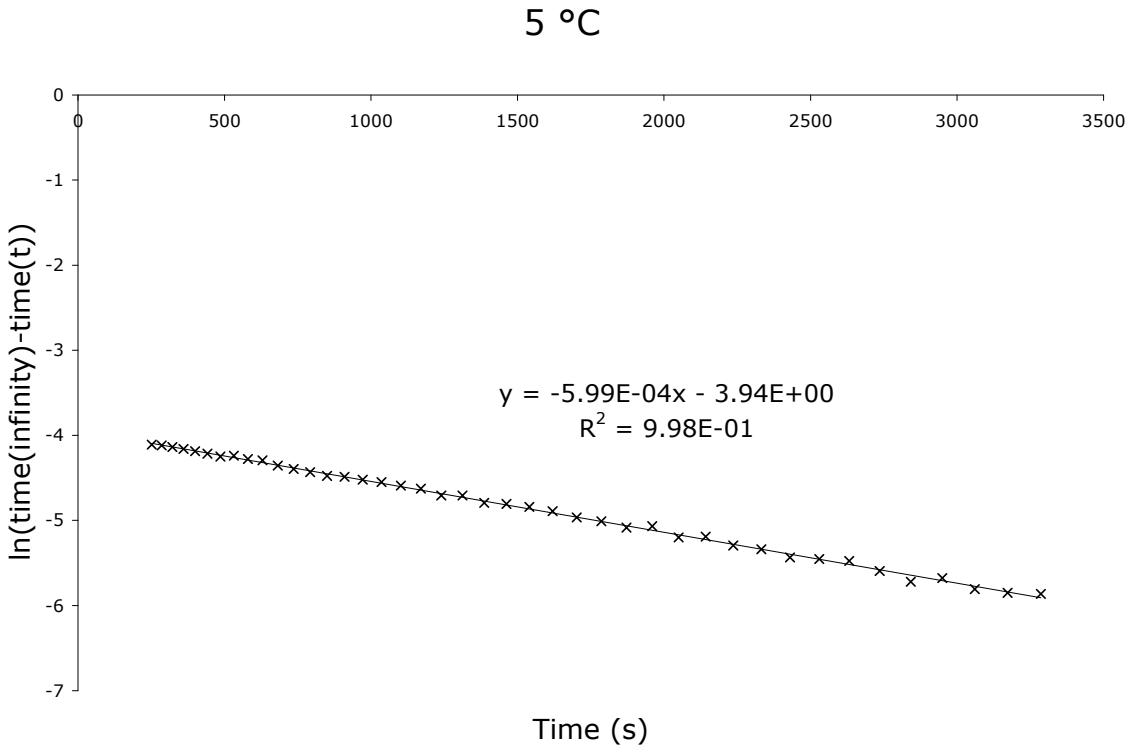

35 °C
Concentration (M)
0.025
0.02
0.015
0.01
0.005
0
0
50
100
150
200
250
Time (s)


35 °C
ln(time(infinity)-time(t))
0
-1
-2
-3
-4
-5
-6
-7
-8
0
50
100
150
200
250
y = -1.33E-02x - 4.09E+00
R2 = 9.96E-01
Time (s)


26 °C
ln(time(infinity)-time(t))
Time (s)
y = -6.75E-03x - 3.82E+00
R2 = 9.98E-01
0
100
200
300
400
500
600
-1
-2
-3
-4
-5
-6
-7
-8

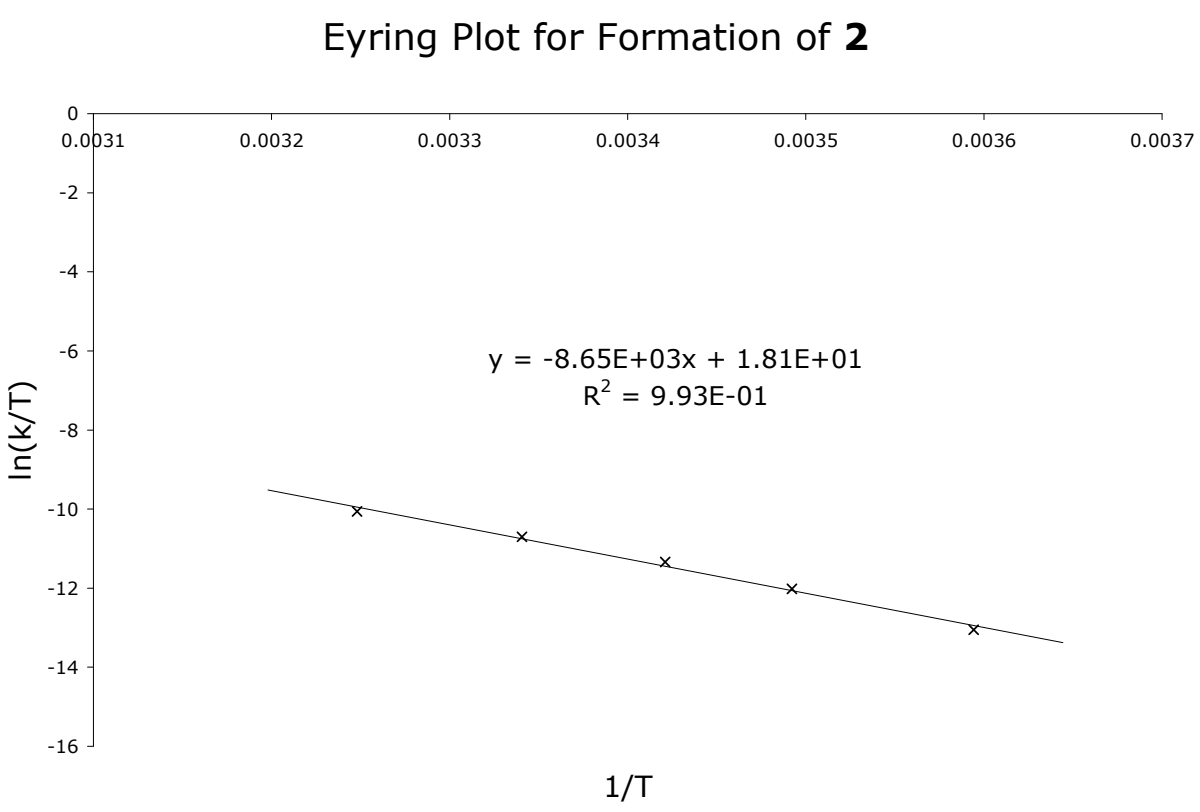

19 °C
ln(time(infinity)-time(t))
Time (s)
y = -3.49E-03x - 4.17E+00
R2 = 9.85E-01
0
100
200
300
400
500
600
700
800
-1
-2
-3
-4
-5
-6
-7


13 °C
ln(time(infinity)-time(t))
Time (s)
y = -1.73E-03x - 3.93E+00
R2 = 9.93E-01
0
-1
-2
-3
-4
-5
-6
0
200
400
600
800
1000
1200


5 °C
ln(time(infinity)-time(t))
Time (s)
y = -5.99E-04x - 3.94E+00
R2 = 9.98E-01
0
-1
-2
-3
-4
-5
-6
-7
0
500
1000
1500
2000
2500
3000
3500

Eyring Analysis

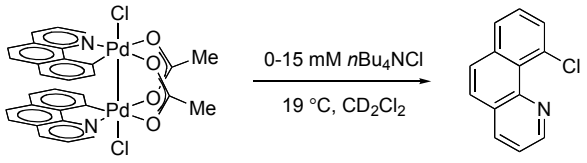
Temperature (K)	k (s^{-1}), R^2
278.37	5.99×10^{-4}; 0.998
286.50	1.73×10^{-3}; 0.993
292.46	3.49×10^{-3}; 0.985
299.50	6.75×10^{-3}; 0.998
308.03	1.32×10^{-2}; 0.997



Error Analysis for Eyring Data

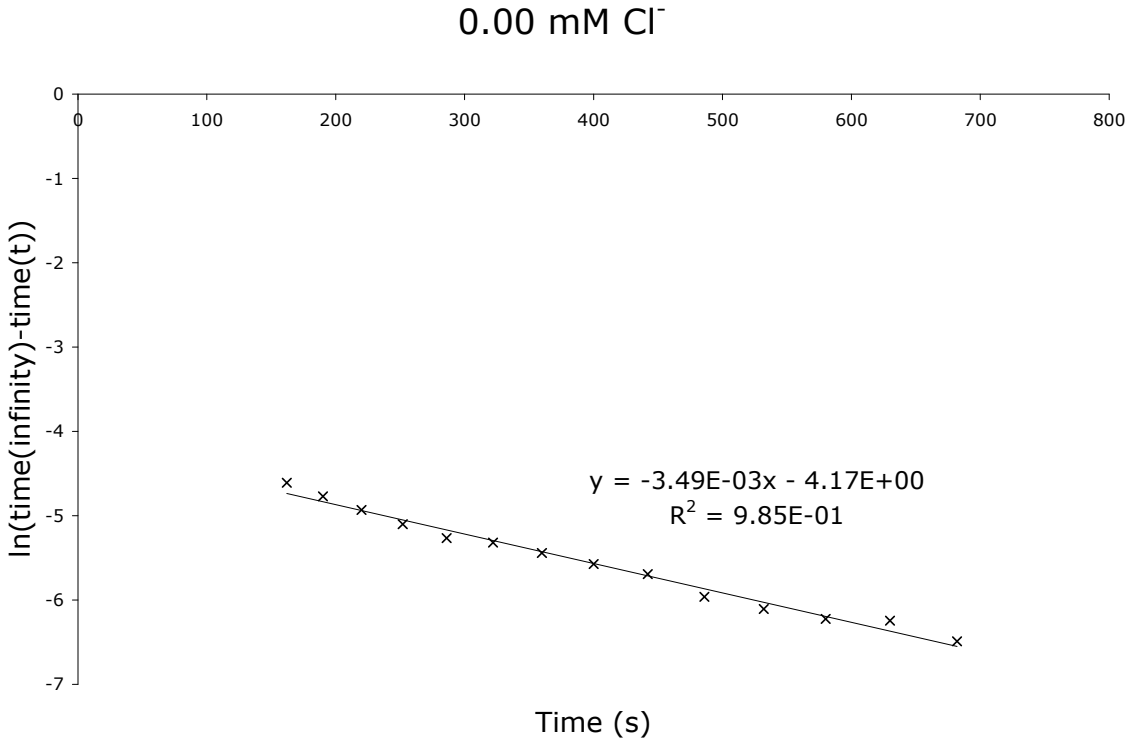
	Slope	Intercept	$\Delta H^{‡}$	Difference	$\Delta S^{‡}$	Difference	$\Delta G^{‡}$	Difference
calcd + error	–7271	13.43	14.5	–2.7	–20.5	–9.3	20.4	–0.1
calcd	–8647	18.13	17.2	0.0	–11.2	0.0	20.5	0.0
calcd – error	–10022	22.84	19.9	2.7	–1.8	9.4	20.6	0.1

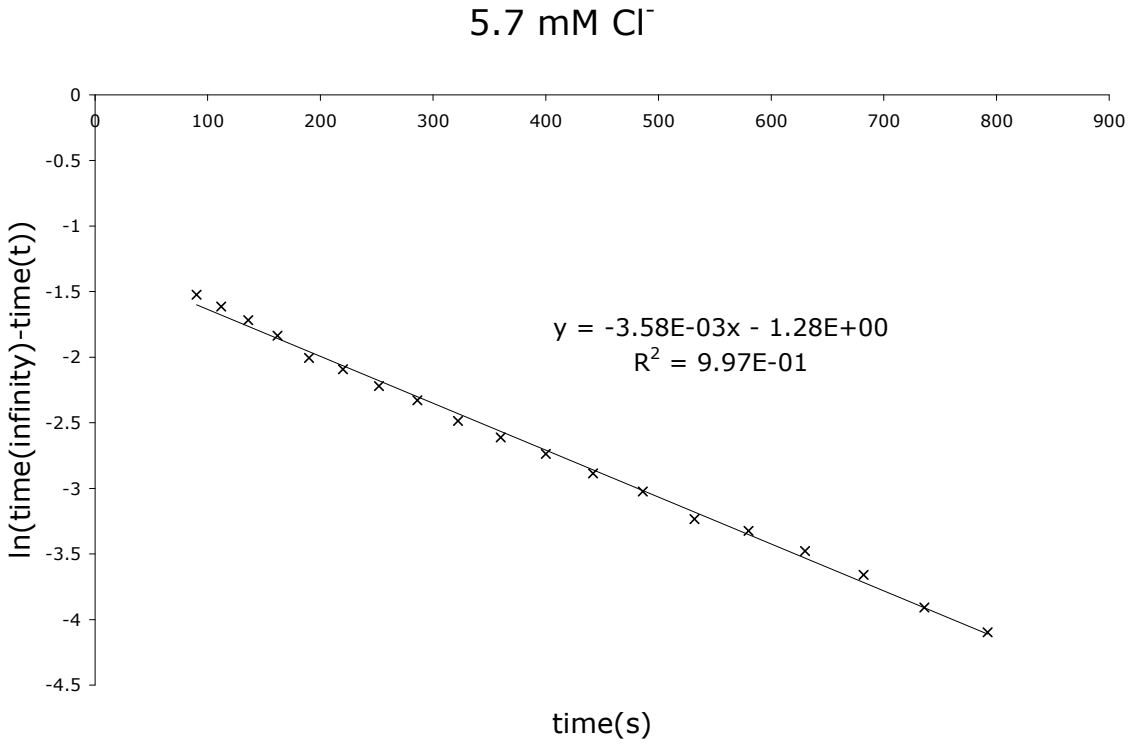
Rate of C–Cl Reductive Elimination from 1 as a Function of [Cl$^-$]

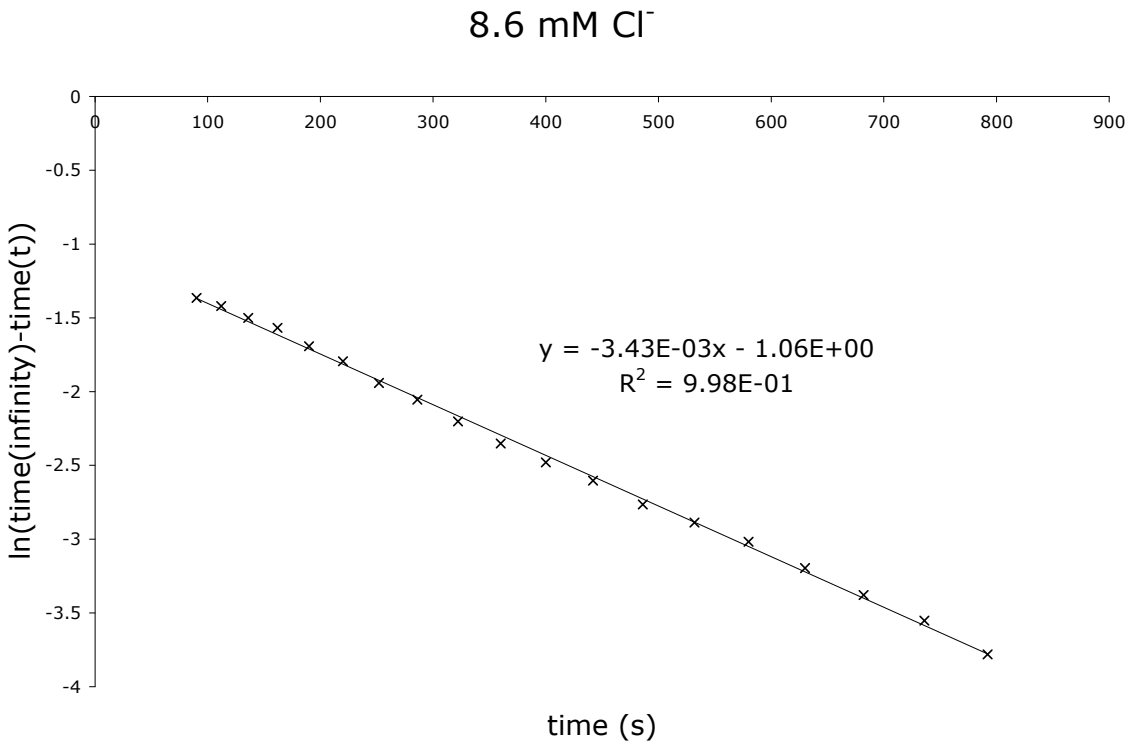


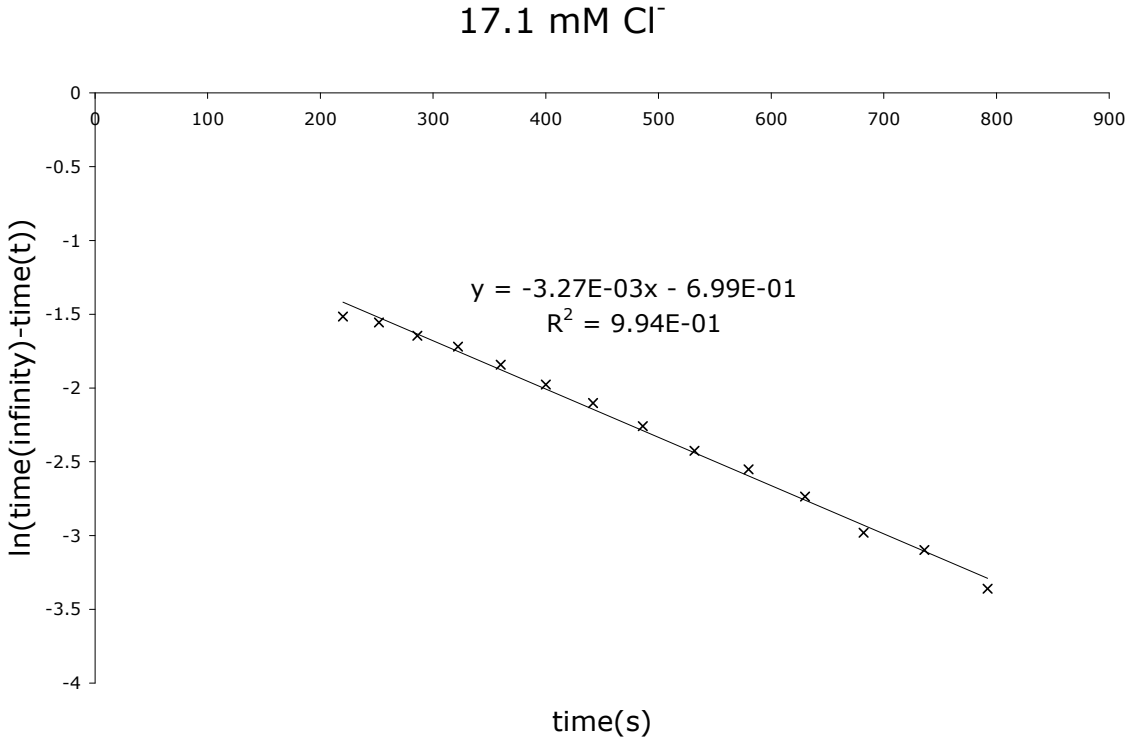
1 **2**

Stock solutions of compound **9** (29.2 mM) and nBu$_4$NCl (80.0 mM) were prepared in CD_2Cl_2. In a nitrogen-filled dry box, compound **9** (350 μL) was diluted with n μL CD_2Cl_2 in an NMR tube before 350–n μL nBu$_4$N$_4$Cl was added to the NMR tube. $PhICl_2$ (2.8 mg, 1.0 equiv) was added to the NMR tube as a solid. ^{1}H NMR spectra were obtained; the evolution of **2** was monitored by the ^{1}H NMR signal at 9.12 ppm. These signals were integrated relative the residual proton signal from CD_2Cl_2. Since evolution of product was measured, linear natural log plots were obtained by using an infinite time point set to 100% yield. In each case, the reactions were followed to greater than 3 half-lives. Data were fitted to a first order regression; plots, slopes, and R^2 values are reported below.



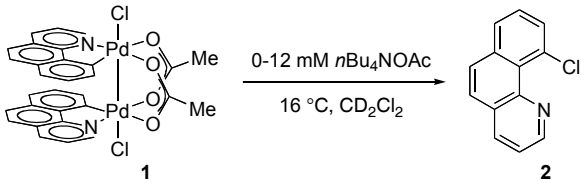

5.7 mM Cl-
ln(time(infinity)-time(t))
time(s)
y = -3.58E-03x - 1.28E+00
R2 = 9.97E-01
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
-4.5
0
100
200
300
400
500
600
700
800
900


8.6 mM Cl-
ln(time(infinity)-time(t))
time (s)
y = -3.43E-03x - 1.06E+00
R2 = 9.98E-01
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
0
100
200
300
400
500
600
700
800
900



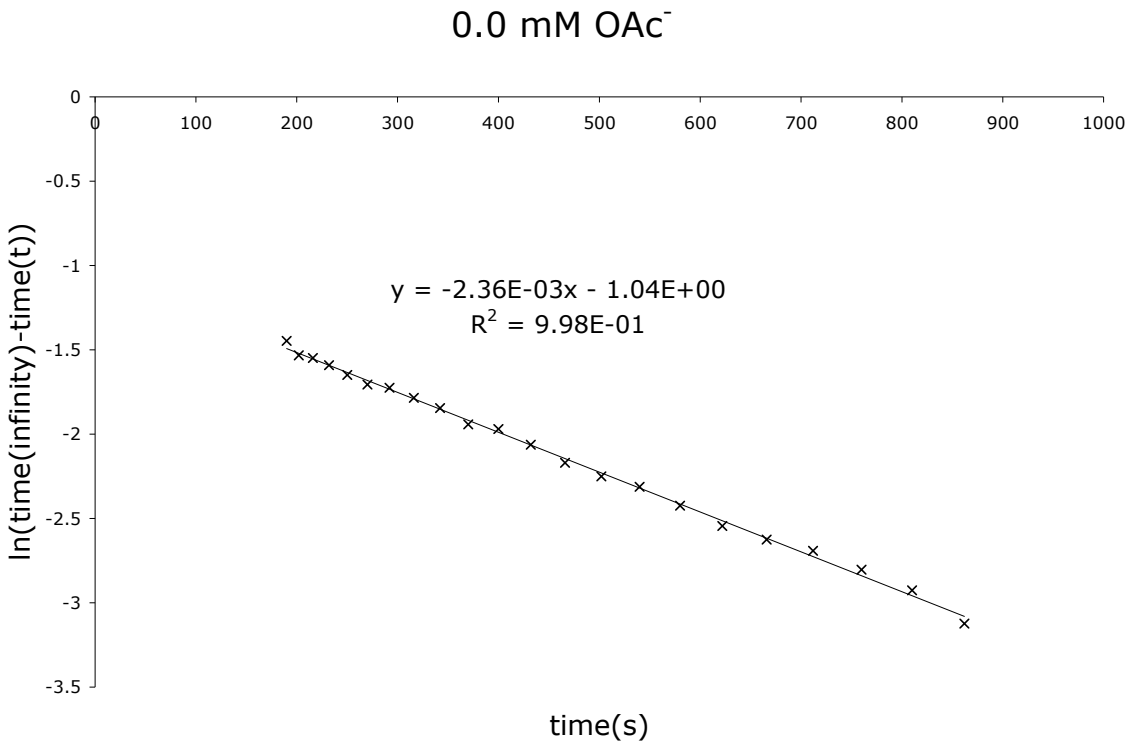
[Cl^-] (mM)	k (s^{-1}), R^2
0.0	3.49×10^{-3}; 0.985
5.7	3.58×10^{-3}; 0.997
8.6	3.43×10^{-3}; 0.998
17.1	3.27×10^{-3}; 0.994

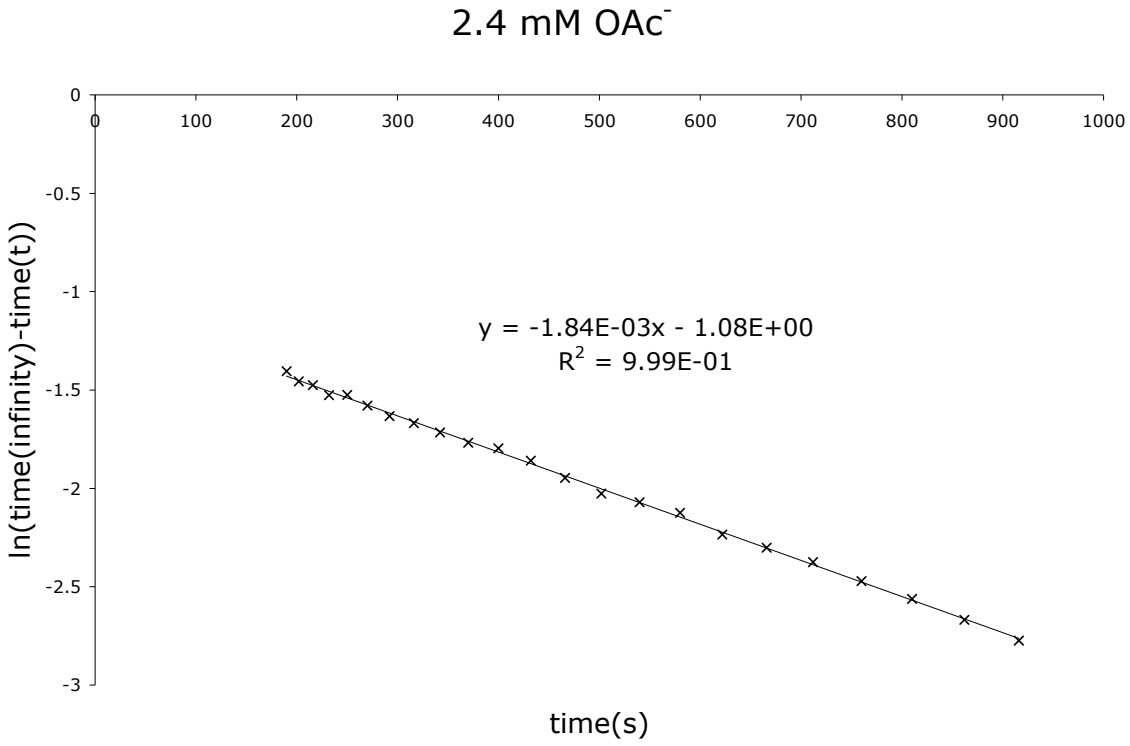
Rate of C–Cl Reductive Elimination from 1 as a Function of [OAc^-]

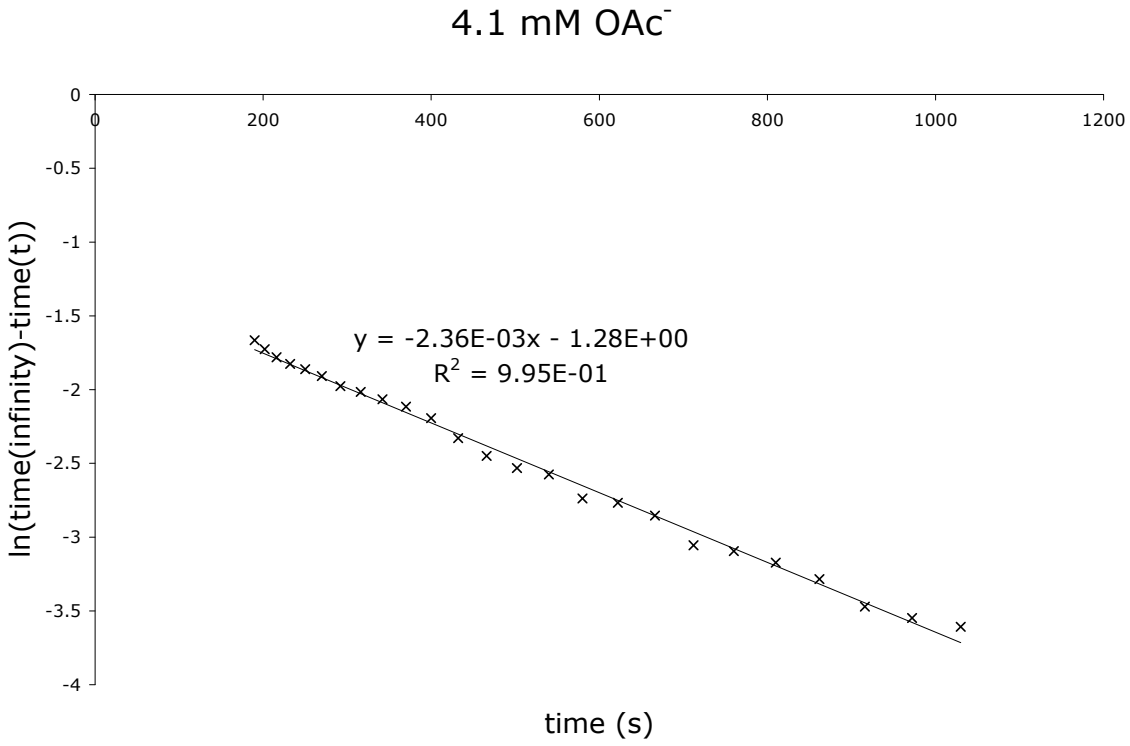


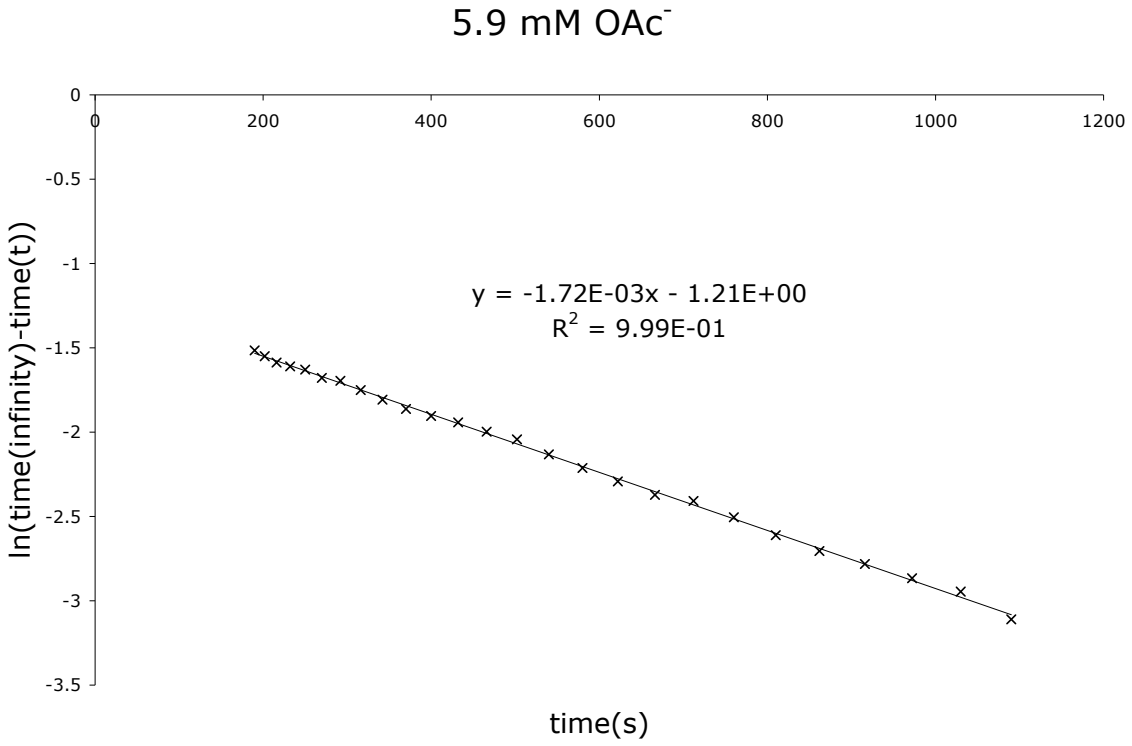
Stock solutions of compound **9** (29.9 mM) and $n$$Bu_4NOAc$ (82.8 mM) were prepared in CD_2Cl_2. In a nitrogen-filled dry box, compound **9** (350 μL) was diluted with n μL CD_2Cl_2 in an NMR tube before (350 – n) μL $n$$Bu_4N_4OAc$ was added to the NMR tube. $PhICl_2$ (2.8 mg, 1.0 equiv) was added to the NMR tube as a solid. ^1H NMR spectra were obtained; the evolution of **2** was monitored by the ^1H NMR signal at 9.12 ppm. These signals were integrated relative the residual proton signal from CD_2Cl_2. Since evolution

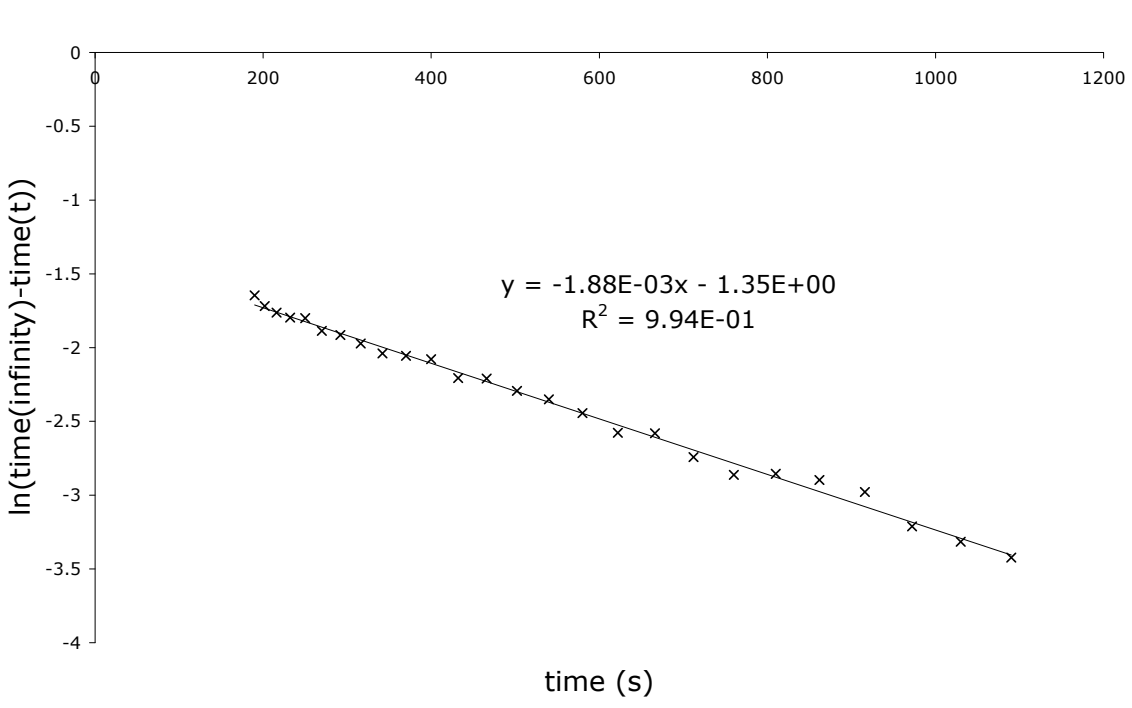
of product was measured, linear natural log plots were obtained by using an infinite time point set to 100% yield. In each case, the reactions were followed to greater than 3 half-lives. Data were fitted to a first order regression; plots, slopes, and R^2 values are reported below.




2.4 mM OAc-
ln(time(infinity)-time(t))
time(s)
y = -1.84E-03x - 1.08E+00
R2 = 9.99E-01
0
-0.5
-1
-1.5
-2
-2.5
-3
0
100
200
300
400
500
600
700
800
900
1000


4.1 mM OAc-
ln(time(infinity)-time(t))
time (s)
y = -2.36E-03x - 1.28E+00
R2 = 9.95E-01
0
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
0
200
400
600
800
1000
1200

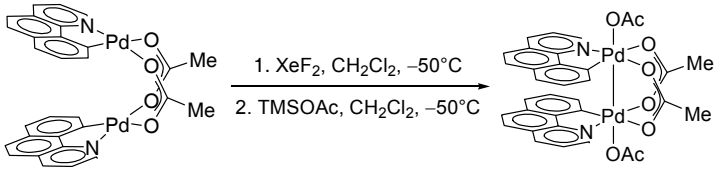

5.9 mM OAc-
y = -1.72E-03x - 1.21E+00
R2 = 9.99E-01
ln(time(infinity)-time(t))
time(s)
0
200
400
600
800
1000
1200
-0.5
-1
-1.5
-2
-2.5
-3
-3.5


11.8 mM OAc-
y = -1.88E-03x - 1.35E+00
R2 = 9.94E-01
ln(time(infinity)-time(t))
time (s)
0
200
400
600
800
1000
1200
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4

[OAc^-] (mM)	k (s^{-1}), R^2
0.0	2.36×10^{-3}; 0.998
2.4	1.84×10^{-3}; 0.999
4.1	2.36×10^{-3}; 0.995
5.9	1.72×10^{-3}; 0.999
11.8	1.88×10^{-3}; 0.994

Synthesis and Thermolysis of 10 (Data Pertaining to Scheme 1)

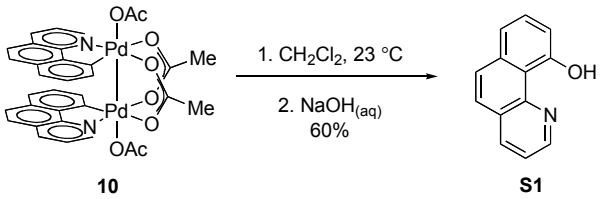
$[Pd(bhq)(OAc)_2]_2$ (10)



This reaction was carried out in a dry box. To a solution of benzo[*h*]quinolinyl palladium acetate dimer (**9**) (61.3 mg, 8.92×10^{-5} mol, 1.00 equiv) in CH_2Cl_2 (2.0mL) was added XeF_2 (15.1 mg, 8.92×10^{-5} mol, 1.00 equiv) at –50 ºC. The reaction mixture immediately became dark red. After stirring for five minutes at –50 ºC, TMSOAc (40.1 μL, 2.68×10^{-4} mol, 3.00 equiv) was added in one portion. After 15 minutes, solvent was removed *in vacuo* at –50 ºC. The dark red residue was washed with pre-cooled (–50 ºC) Et_2O (2 × 3 mL) and dried at –50 ºC to afford 63.9 mg of the title compound (89% yield) as a 15:1 mixture of isomers (benzo[*h*]quinolinyl ligand head to tail vs. head to head). The title compound is a moisture sensitive dark red solid.

^{1}H-NMR (500 MHz, CD_2Cl_2, –30 ºC, δ): Head to Tail Isomer: 7.89 (d, J = 5.4 Hz, 2H), 7.62 (d, J = 7.3 Hz, 2H), 7.47–7.41 (m, 4H), 7.31 (d, J = 8.8 Hz, 2H), 7.24 (d, J = 7.3 Hz, 2H), 7.12 (d, J = 8.8 Hz, 2H), 6.71 (dd, J = 7.8 Hz, 5.4 Hz, 2H), 2.71 (s, 6H), 1.47 (s, 6H). Head to Head Isomer: 8.26 (d, J = 5.2 Hz, 2H), 7.84 (d, 7.8 Hz, 2H), 6.88 (d, J = 7.3 Hz, 2H). ^{13}C-NMR (125 MHz, CD_2Cl_2, –30 ºC, δ): Head to Tail Isomer: 187.41, 175.91, 157.38, 150.57, 149.85, 136.82, 136.69, 133.38, 130.36, 127.38, 126.28, 125.60, 124.76, 124.53, 121.20, 25.05, 23.00. X-ray data included in X-Ray Data Analysis Section. Thermal instability prevented either mass spectral or elemental analysis from being obtained.

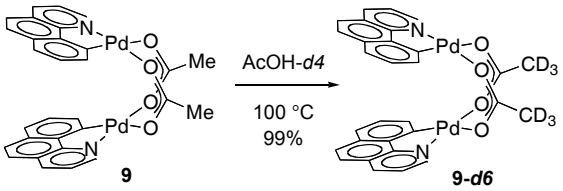
Benzo[*h*]quinolin-10-ol (S1)



All manipulations involving $[Pd(bhq)(OAc)_2]_2$ (**10**) were carried out in a dry box. A solution of $[Pd(bhq)(OAc)_2]_2$ (**10**) (133 mg, 0.0138 mmol, 1.00 equiv) in CH_2Cl_2 (3.0 mL) was stirred at 23 ˚C for four hours. Solvent was removed *in vacuo*. The residue was dissolved in MeOH (5.0 mL) and NaOH (27.5 mg, 0.0689 mmol, 5.00 equiv) was added. The solution was stirred for three hours before concentrated $HCl_{(aq)}$ was added until pH 7. Solvent was removed *in vacuo*. The residue was dissolved in EtOAc (8 mL) and washed with H_2O (2 × 5 mL). The phases were separated and the organic phase was concentrated. The residue was purified by chromatography on silica gel eluting with hexanes/benzene (1:1) to afford 16.1 mg of the title compound (60% yield) as a pale yellow solid.

R_f = 0.25 (benzene/hexanes 1:1 (v/v)). ^{1}H-NMR (600 MHz, $CDCl_3$, 23 ºC, δ): 8.85 (dd, *J* = 4.7 Hz, *J* = 1.8 Hz, 1H), 8.27 (dd, *J* = 8.1 Hz, *J* = 1.8 Hz, 1H), 7.82 (d, *J* = 8.9 Hz, 1H), 7.66–7.62 (m, 2H), 7.58 (dd, *J* = 7.9 Hz, *J* = 4.5 Hz 1H), 7.43 (dd, *J* = 7.9 Hz, *J* = 0.7 Hz, 1H), 7.25 (dd, *J* = 8.6 Hz, *J* = 1.2 Hz, 1H), –1.08 (s, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 159.44, 148.42, 145.04, 136.19, 135.05, 129.89, 129.15, 126.28, 124.54, 120.80, 118.07, 115.96, 113.96. Mass Spectrometry: HRMS-FIA (m/z): calcd for $[C_{13}H_9NO+H]$, 196.0760. Found, 196.0761. These spectroscopic data correspond to those reported in the literature[3] and are identical with those of an authentic sample prepared as described below.

Benzo[*h*]quinolinyl palladium acetate dimer-*d6* (9-*d6*)

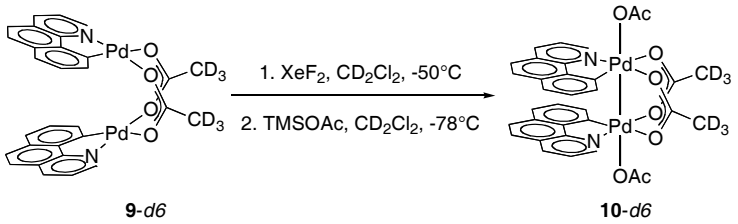


A solution of benzo[*h*]quinolinyl palladium acetate dimer (**9**) (198 mg, 0.288 mmol, 1.00 equiv) in acetic acid-*d4* (5.0 mL) was heated to 100 ºC for 3 hours at which time the suspension was cooled to room temperature and solvent was removed *in vacuo*. The solid residue was dissolved in $CHCl_3$ and filtered through celite. The filtrate was concentrated *in vacuo*. The residue was triturated with Et_2O to afford 199 mg of the title compound as a yellow solid (99% yield).

^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.82 (dd, *J* = 5.4 Hz, *J* = 1.0 Hz, 2H), 7.44 (dd, *J* = 8.3 Hz, *J* = 1.5 Hz, 2H), 7.25–7.20 (m, 6H), 7.08 (dd, *J* = 7.3 Hz, *J* = 1.5 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.48 (dd, *J* = 8.3 Hz, *J* = 5.4 Hz, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 152.99, 148.65, 148.56, 139.80, 135.02, 132.21, 128.77, 127.63, 127.46, 124.74, 122.64, 121.82, 119.55. These spectroscopic data correspond to

those reported above for compound **9** without the resonance for the bridging acetate ligands at 2.38 ppm**.**

[Pd(bhq)(OAc)(O_2CCD_3)]$_2$ (10-*d6*)



9-*d6* **10**-*d6*

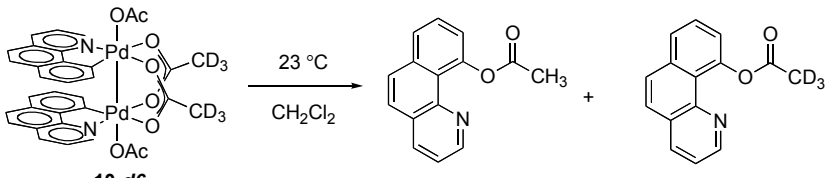
This reaction was carried out in a dry box. To a solution of benzo[*h*]quinolinyl palladium acetate-*d6* dimer (**9-*d6***) (39.7 mg, 5.73×10^{-5} mol, 1.00 equiv) in CD_2Cl_2 (1.0mL) was added XeF_2 (9.7 mg, 5.7×10^{-5} mol, 1.0 equiv) at –50 ºC. The reaction mixture immediately became dark red. The reaction solution was transferred to an NMR tube and cooled to –78 ºC. TMSOAc (17.2 μL, 1.15×10^{-4} mol, 2.00 equiv) was added in one portion. The ^{1}H NMR was observed at –60 ºC. Upon warming to –30 ºC, exchange between the bridging and apical acetate groups was observed. See "Ligand Exchange" section for details of this process.

^{1}H-NMR (500 MHz, CD_2Cl_2, –60 ºC, δ): 7.86 (d, *J* = 5.4 Hz, 2H), 7.61 (d, *J* = 7.8 Hz, 2H), 7.47–7.42 (m, 4H), 7.31 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 7.3 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 6.68 (dd, *J* = 7.8 Hz, *J* = 5.9 Hz, 2H), 1.48 (s, 6H). These spectroscopic data correspond to those reported for compound **10** above except for the absence of the resonance at 2.71 ppm.

Ligand Exchange

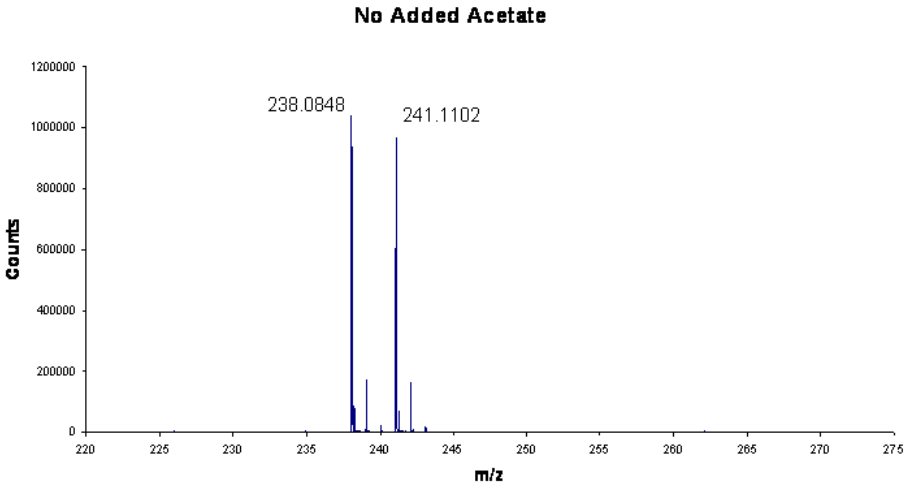
Exchange with Exogenous Acetate

Thermolysis of 10-*d6*

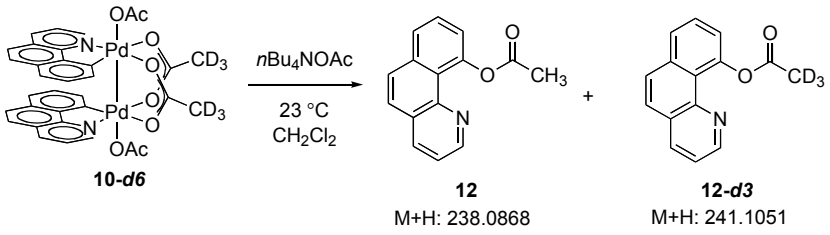


10-*d6* **12** M+H: 238.0868 **12-*d3*** M+H: 241.1051

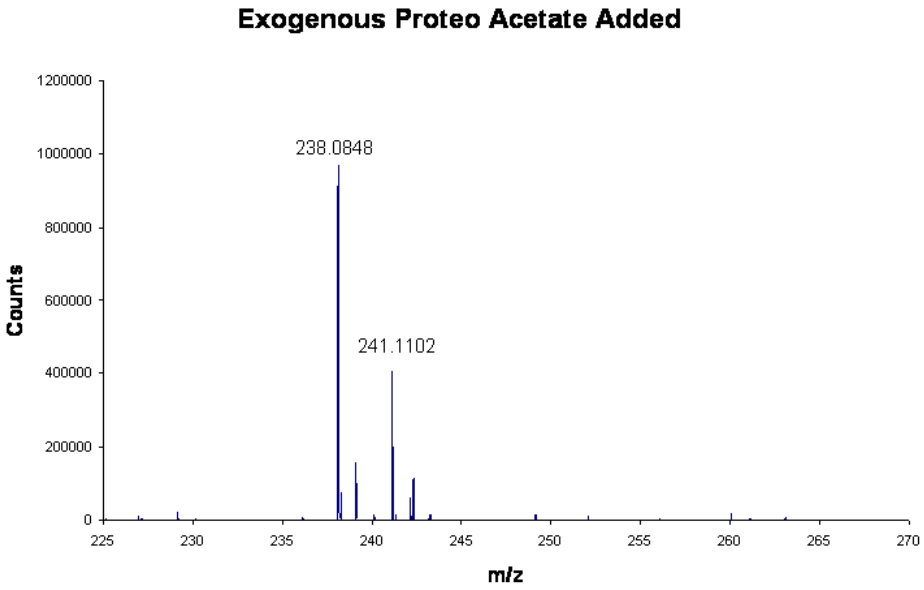
A solution of **10-*d6*** (46.6 mg, 5.73×10^{-5} mol, 1.00 equiv) in CH_2Cl_2 (2.20 mL) at –50 ˚C was warmed to 23 ˚C. The solution was stirred for three hours at 23 ˚C at which time, the crude reaction mixture was analyzed by mass spectrometry. The ratio of **12** (238.0868 amu) to **12-*d3*** (241.1051 amu) was determined to be 1.02 based on the area under the peaks corresponding to the respective products.



Thermolysis of 10-*d6* in the Presence of Exogenous Acetate

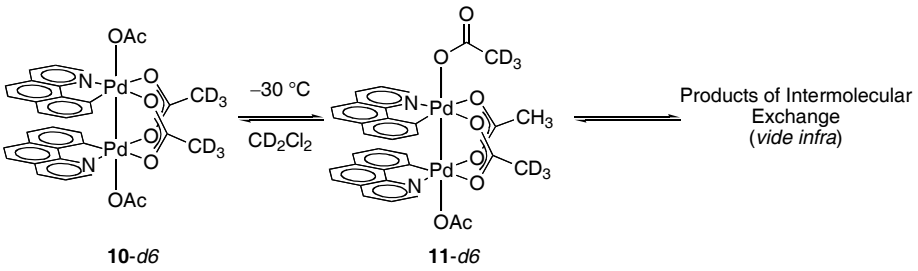


To a solution of **10-*d6*** (29.3 mg, 3.60×10^{-5} mol, 1.00 equiv) in CH_2Cl_2 (1.20 mL) at –50 ˚C was added *n*-Bu_4N·OAc (21.8 mg, 7.20×10^{-5} mol, 2.00 equiv) and the solution was warmed to 23 ˚C. The solution was stirred for three hours at 23 ˚C. The solution was passed through a plug of SiO_2 to remove tetrabutylammonium acetate residue, after which time, the crude reaction mixture was analyzed by mass spectrometry. The ratio of **12** (238.0868 amu) to **12-*d3*** (241.1051 amu) was determined to be 2.38 based on the area under the peaks corresponding to the respective products.



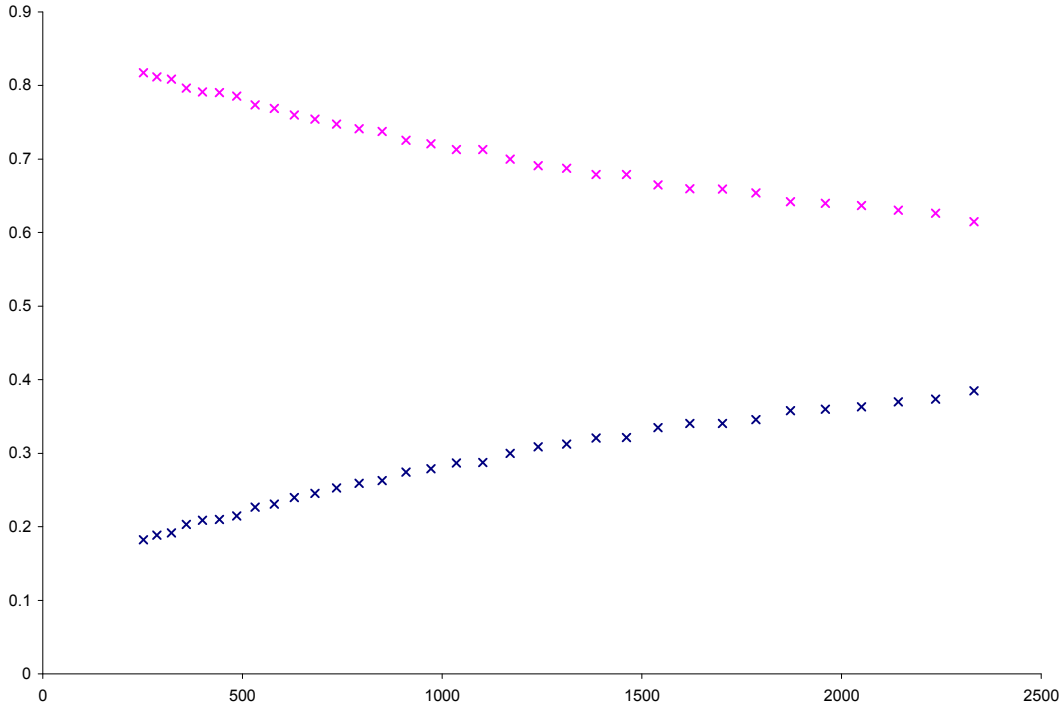
	12	**12-*d3***	**12:12-*d3***
No Added Acetate	2.65×10^6	2.60×10^6	1.02
Added Acetate	3.12×10^6	1.31×10^6	2.38

Exchange in the Absence of Exogenous Acetate



10-*d6* **11**-*d6*

This reaction was carried out in a dry box. To a solution of **9-*d6*** (39.7 mg, 5.73×10^{-5} mol, 1.00 equiv) in CD_2Cl_2 (1.0mL) was added XeF_2 (9.7 mg, 5.7×10^{-5} mol, 1.0 equiv) at –50 ºC. The reaction mixture immediately becomes dark red. The reaction solution was transferred to an NMR tube and cooled to –78 ºC. TMSOAc (17.2 µL, 1.15×10^{-4} mol, 2.00 equiv) was added in one portion. Upon warming to –30 ºC, exchange between the bridging and apical acetate groups was observed. ^{1}H NMR spectra were obtained; the exchange of the acetate ligands could be followed by the relative integration of the signals at 1.48 and 2.71 ppm. These signals were integrated relative the residual proton signal from CD_2Cl_2.



Using the software package SigmaPlot10.0, nonlinear regression analysis was carried out. The decay of excess proteo-acetate in the apical position was fitted with the following function:

$y = y_0 + ae^{-bx} - c(1-e^{-bx})$.

The following values were determined to fit the experimental data most closely:

$y_0 = 0.6408$

$a = 0.2209$

$b = 0.00058$

$c = 0.1068$

The regression analysis is appended below:

Nonlinear Regression

Data Source: Data 1 in isomerization

Equation: User-Defined, ModifiedDouble, 5 Parameter

f=y0+a*exp(-b*x)-c*(1-exp(-b*x))

R	Rsqr	Adj Rsqr	Standard Error of Estimate
0.9992	0.9983	0.9981	0.0027

	Coefficient	Std. Error	t	P	VIF
y0	0.6408	15342.6826	4.1763E-005	1.0000	1.0928E+015<
a	0.2209	15342.6824	1.4396E-005	1.0000	3.7446E+014<
b	0.0006	2.9641E-005	19.4690	<0.0001	122.0754<
c	0.1068	15342.6823	6.9641E-006	1.0000	2.5407E+014<

Analysis of Variance:

Uncorrected for the mean of the observations:

	DF	SS	MS
Regression	4	17.0313	4.2578

Residual	29	0.0002	7.1086E-006		
Total	33	17.0315	0.5161		

Corrected for the mean of the observations:

	DF	SS	MS	F	P
Regression	3	0.1224	0.0408	5741.2248	<0.0001
Residual	29	0.0002	7.1086E-006		
Total	32	0.1226	0.0038		

Statistical Tests:

PRESS	0.0003	
Durbin-Watson Statistic	2.3132	Passed
Normality Test	Passed	(P = 0.6141)
K-S Statistic = 0.1288	Significance Level = 0.6141	
Constant Variance Test	Passed	(P = 0.1289)

Power of performed test with alpha = 0.0500: 1.0000

The evolution of proteo-acetate in the bridging position was fitted with the following function:

$y = y_0 + ae^{-bx} - c(1-e^{-bx})$.

The following values were determined to fit the experimental data most closely:

$y_0 = 0.3592$

a = -0.2209

b = 0.00058

c = -0.1068

The regression analysis is appended below:

Nonlinear Regression

Data Source: Data 1 in isomerization good

Equation: User-Defined, ModifiedDouble, 5 Parameter

f=y0+a*exp(-b*x)-c*(1-exp(-b*x))

R	Rsqr	Adj Rsqr	Standard Error of Estimate
0.9992	0.9983	0.9981	0.0027

	Coefficient	Std. Error	t	P	VIF
y0	0.3592	26973.9434	1.3318E-005	1.0000	3.3777E+015<
a	-0.2209	26973.9428	-8.1883E-006	1.0000	1.1574E+015<
b	0.0006	3.0438E-005	18.9589	<0.0001	128.7321<
c	-0.1068	26973.9412	-3.9612E-006	1.0000	7.8529E+014<

Analysis of Variance:

Uncorrected for the mean of the observations:

	DF	SS	MS
Regression	4	2.7876	0.6969
Residual	29	0.0002	7.1086E-006
Total	33	2.7878	0.0845

Corrected for the mean of the observations:

	DF	SS	MS	F	P
Regression	3	0.1224	0.0408	5741.2248	<0.0001
Residual	29	0.0002	7.1086E-006		
Total	32	0.1226	0.0038		

Statistical Tests:
PRESS 0.0003
Durbin-Watson Statistic 2.3132 Passed
Normality Test Passed (P = 0.6141)
K-S Statistic = 0.1288 Significance Level = 0.6141
Constant Variance Test Passed (P = 0.1289)
Power of performed test with alpha = 0.0500: 1.0000

Comparison of Acetate Scrambling Rate with Rate of C–Cl Reductive Elimination

The rate of acetate scrambling was observed at –30 ˚C and was determined to be 5.8×10^{-4} s^{-1}.

The rate of C–Cl reductive elimination was extrapolated from the Arrhenius equation generated for this reaction:

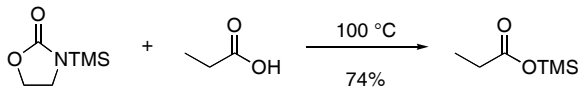
$$\ln(k/T) = -8.65 \times 10^{3}(1/T) + 18.1.$$

At –30 ˚C, the calculated rate of C–Cl reductive elimination is 6.14×10^{-6} s^{-1}.

Based on these calculations, acetate scrambling between **10-*d6*** and **11-*d6*** is 94 times faster than is C–Cl reductive elimination from **1**.

Observation of Intermolecular Ligand Exchange

Trimethylsilylpropionate (S2)

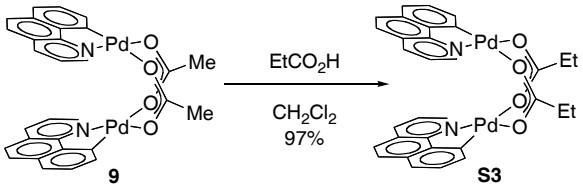


S2

Under N_2, 3-(trimethylsilyl)oxazolidin-2-one (6.50 mL, 6.79 g, 42.7 mmol, 1.00 equiv) and propionic acid (3.75 mL, 3.71 g, 50.1 mmol, 1.17 equiv) were combined and heated to 100 °C. After 30 minutes at 100 °C, the reaction was cooled to room temperature at which time a white precipitate was observed. The title compound was obtained as a colorless oil by distillation under N_2 at 120 °C. **S2** prepared in this manner was contaminated by ~2% propionic acid (determined by ^{1}H NMR spectroscopy).

^{1}H-NMR (500 MHz, CD_2Cl_2, 23 ºC, δ): 2.29, (q, *J* = 7.3 Hz, 2H), 1.06 (t, *J* = 7.3 Hz, 3H), 0.26 (s, 12H). ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 175.18, 29.42, 9.30, –0.25. These spectroscopic data correspond to those reported in the literature.[4]

Benzo[*h*]quinolinyl palladium propionate dimer (S3)

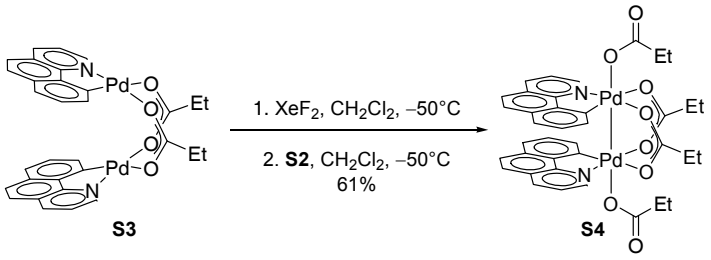


9 **S3**

To a solution of benzo[*h*]quinolinyl palladium acetate dimer (**9**) (550 mg, 0.800 mmol, 1.00 equiv) in CH_2Cl_2 (10 mL) at 23 °C was added propionic acid (1.00 mL, 0.990 g, 13.4 mmol, 16.7 equiv) and the reaction solution was stirred at 23 °C for 15 minutes. Saturated $NaHCO_{3(aq)}$ (10 mL) was added and the layers were separated. The organic layer was washed with sat. $NaHCO_{3(aq)}$ (2 × 10 mL) and brine (1 × 10 mL). The organic layer was dried with Na_2SO_4 before solvent was removed in vacuo to afford 572 mg of the title complex as a yellow solid (97 % yield) in a 17:1 ratio of isomers (benzo[*h*]quinolinyl ligands head to tail vs. head to head).

^{1}H-NMR (500 MHz, CD_2Cl_2, 23 ºC, δ): Major Isomer : 7.77 (dd, *J* = 5.4 Hz, *J* = 1.5 Hz, 2H), 7.49 (dd, *J* = 7.8 Hz, *J* = 1.0 Hz, 2H), 7.27–7.24 (m, 4H), 7.18 (dd, *J* = 7.3 Hz, *J* = 7.3 Hz, 2H), 7.03–6.99 (m, 4H), 6.52 (dd, *J* = 8.3 Hz, *J* = 5.4 Hz, 2H), 2.59 (q, *J* = 7.3 Hz, 4H), 1.32 (t, *J* = 7.3 Hz, 6H). Minor Isomer: 8.07 (dd, *J* = 4.9 Hz, *J* = 1.0 Hz, 2H), 7.06 (d, *J* = 8.3 Hz, 4H), 6.95 (dd, *J* = 7.8 Hz, *J* = 4.9 Hz, 2H), 6.88–6.86 (m, 4H), 6.72 (d, *J* = 7.3 Hz, 2H). ^{13}C-NMR (125 MHz, CD_2Cl_2, 23 ºC, δ): Major Isomer: 185.38, 153.24, 148.90, 140.06, 135.68, 132.60, 128.80, 127.93, 127.79, 125.19, 123.19, 122.25, 120.18, 31.81, 11.19.

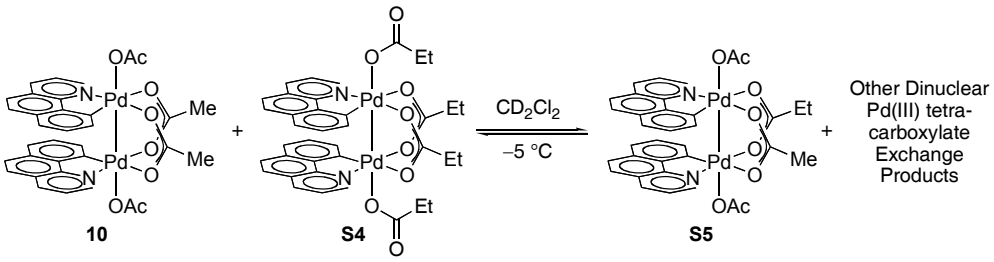
Benzo[*h*]quinolinyl propionate palladium(III) propionate dimer (S4)



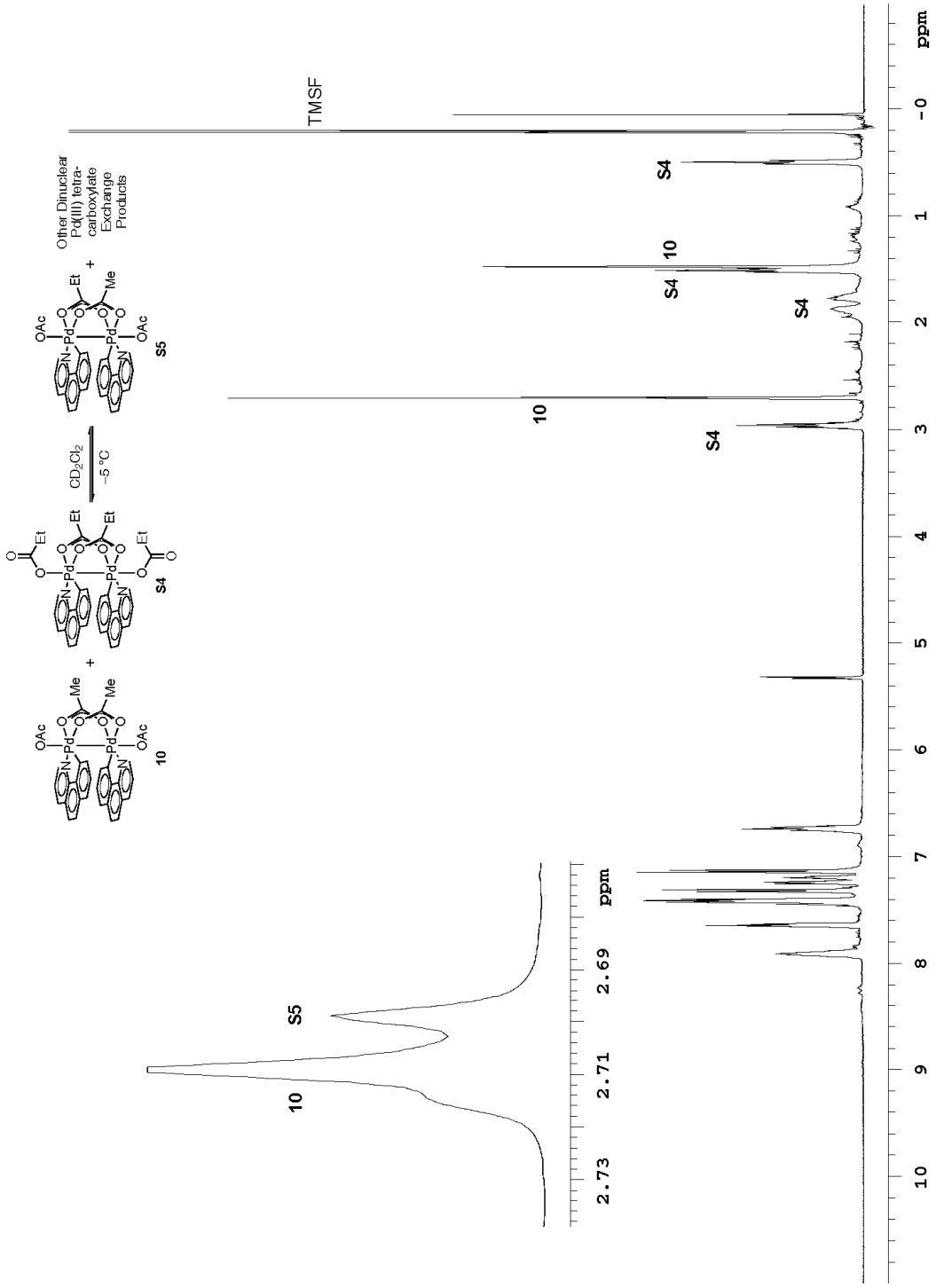
This reaction was carried out in a dry box. To a solution of benzo[*h*]quinolinyl palladium propionate dimer (**S3**) (85.5 mg, 0.120 mmol, 1.00 equiv) in CH_2Cl_2 (2.0mL) was added XeF_2 (20.2 mg, 0.120 mmol, 1.00 equiv) at –50 ºC. The reaction mixture immediately became dark red. After stirring for 15 minutes at –50 ºC, trimethylsilylpropionate (**S2**) (36.0 mg, 0.246 mmol, 2.05 equiv) was added in one portion. The resulting solution was layered with pentane. After 24 hours, 63.0 mg of the title complex (61%) was obtained as a dark red crystalline solid by decanting the solvent followed by drying in vacuo. The title compound was isolated as a single isomer and is a moisture and temperature sensitive dark red solid.

^{1}H-NMR (500 MHz, CD_2Cl_2, –20 ºC, δ): Head to Tail Isomer: 7.89 (dd, *J* = 5.9 Hz, *J* = 1.0 Hz, 2H), 7.66 (dd, *J* = 6.8 Hz, *J* = 1.0 Hz, 2H), 7.43–7.40 (m, 4H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.18 (dd, *J* = 5.4 Hz, *J* = 3.4 Hz, 2H), 7.15 (d, *J* = 8.8 Hz, 2H), 6.75 (dd, *J* = 8.3 Hz, *J* = 5.9 Hz, 2H), 2.98–2.93 (m, 4H), 1.90–1.86 (m, 2H), 1.79–1.73 (m, 2H), 1.50 (t, *J* = 7.8 Hz, 6H), 0.47 (t, *J* = 7.8 Hz, 6H).

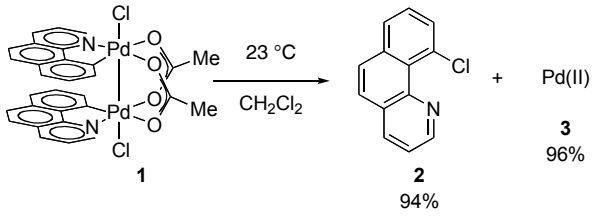
Ligand exchange between 10 and S4



This reaction was carried out in a dry box. To a solution of benzo[*h*]quinolinyl propionate palladium(III) propionate dimer (**S4**) (9.0 mg, 0.010 mmol, 1.0 equiv) in CD_2Cl_2 (0.5 mL) was a solution of benzo[*h*]quinolinyl acetate palladium(III) acetate dimer (**10**) (8.4 mg, 0.010 mmol, 1.0 equiv) in CD_2Cl_2 (0.5 mL) at –50 ºC. A ^{1}H NMR spectrum obtained at –50 ºC showed complexes **10** and **S4**. The reaction mixture was warmed to –5 ºC in the NMR spectrometer, at which temperature a signal at 2.69 ppm was observed to increase in intensity as a function of time. This peak was assigned as a new complex with one bridging acetate and one bridging propionate ligand (for example **S5**). The relevant ^{1}H NMR spectrum is reproduced below.


TMSF
S4
10
S4
S4
10
S4
S4
Other Dinuclear Pd(III) tetra-carboxylate Exchange Products
S5
CD_2Cl_2
−5 °C
S4
10
S5
10
2.73
2.71
2.69
ppm
ppm

Analysis of the Pd Containing Byproducts of Reductive Elimination (Data Pertaining to Scheme 2)



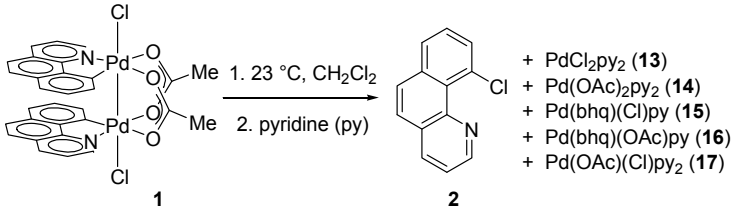
Isolation of **3**

A solution of benzo[*h*]quinolinyl chloro palladium acetate dimer (**1**) (37.5 mg, 0.0495 mmol, 1.00 equiv) in CH_2Cl_2 (3mL) was prepared at −50 ºC. The solution was warmed to 23 ºC. After stirring for three hours at 23 ºC, the solution was yellow. Solvent was removed *in vacuo.* Trituration with Et_2O to remove compound **2** and PhI afforded 25.9 mg of **3** as a yellow solid (96% yield based on empirical formula: $[Pd_2(bhq)(OAc)_2Cl]$).

The crude mixture **3**, prior to trituration has been analyzed by elemental analysis. Anal: calcd for $[Pd_2(bhq)(OAc)_2Cl\cdot$Compound $\mathbf{2}\cdot C_6H_5I]$: C, 44.93; H, 2.83; N, 2.91; found: C, 44.63; H, 2.55; N, 3.40.

Single crystals of **3a** are obtained by layering the crude CH_2Cl_2 solution of mixture **3** with pentane and manual separation of the crystals from non-crystalline solids (data included in X-ray Data Analysis Section). Compound **3a** was not isolated in bulk and thus was not characterized further; isolation of a single crystal was only used to assign the oxidation state of the palladium nuclei. We have not determined what fraction of mixture **3** is constituted by compound **3a**.

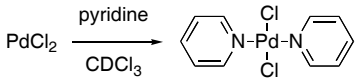
Derivatization of Pd Containing Byproducts (3) with Pyridine



A solution of benzo[*h*]quinolinyl chloro palladium acetate dimer (**1**) (61.1 mg, 8.06×10^{-5} mol, 1.00 equiv) in CH_2Cl_2 (4.0 mL) was prepared at –50 °C and was allowed to warm to 23 °C. After stirring at 23 °C for 5 h, solvent was removed *in vacuo*. The crude residue was taken up in 3.0 mL $CDCl_3$ and pyridine (80 μL, 78.6 mg, 0.993 mmol, 12.3 equiv) was added resulting in the formation of a yellow solution. ^{1}H NMR analysis of this solution revealed the presence of six species, which have been assigned as 10-chlorobenzo[*h*]quinoline (**2**), $PdCl_2py_2$ (**13**), $Pd(OAc)_2py_2$ (**14**), Pd(bhq)(OAc)py (**15**), Pd(bhq)Clpy (**16**), and $Pd(OAc)(Cl)py_2$ (**17**). All species were assigned based on comparison with the ^{1}H NMR spectra of authentic samples (prepared below; ^{1}H NMR data for the crude reaction mixture following reductive elimination as well as following treatment with pyridine are reproduced below; ^{1}H NMR of the authentic

samples of **13**, **14**, **15**, **16**, and **17** are reproduced below for comparison). The combined yield of compounds **13**–**17** was determined to be 99% by comparison of the integration of the ^{1}H NMR signal for **2** (9.12 ppm; 92% yield based on **1** as determined by isolation above) with the integrations of the ^{1}H NMR signals of **13** (8.83 ppm), **14** and **17** (overlapping signal at 8.67 ppm), **15** (9.21 ppm), and **16** (9.06 ppm).

***Trans*-dichloro bis(pyridine)palladium(II) (13)**

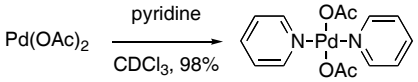


13

To a suspension of $PdCl_2$ (20.9 mg, 0.118 mmol, 1.00 equiv) in $CDCl_3$ (1.5 mL) at 23 °C was added pyridine (9.5 μL, 9.3 mg, 0.12 mmol, 2.0 equiv). The title complex was observed by ^{1}H NMR in the presence of pyridine and was not isolated.

^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 8.83 (dd, J = 6.4 Hz, J = 1.0 Hz, 4H), 7.77 (tt, J = 6.4 Hz, J = 1.2 Hz, 2H), 7.33 (ddd, J = 6.6 Hz, J = 5.1 Hz, J = 1.5 Hz, 4H). These spectroscopic data correspond to those reported in the literature.[5]

***Trans*-diacetato bis(pyridine)palladium(II) (14)**

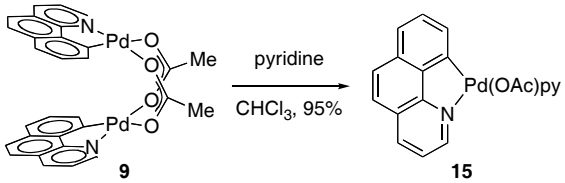


14

To a suspension of $Pd(OAc)_2$ (18.7 mg, 8.33×10^{-5} mol, 1.00 equiv) in $CDCl_3$ (0.6 mL) at 23 °C was added pyridine (13.5 μL, 13.2 mg, 0.167 mmol, 2.00 equiv) resulting in the formation of a pale yellow solution. Solvent was removed in vacuo to afford 31.2 mg of the title compound as a pale yellow solid (98% yield).

^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC, δ): Major Isomer : 8.67 (ddd, J = 6.0 Hz, J = 1.2 Hz, J = 1.2 Hz, 4H), 7.76 (tt, J = 7.8 Hz, J = 1.6 Hz, 2H), 7.31 (ddd, J = 6.4 Hz, J = 5.0 Hz, J = 1.1 Hz, 4H), 1.81 (s, 6H). ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 178.15, 151.59, 138.45, 124.75, 23.14. These spectroscopic data correspond to those reported in the literature.[6]

Acetato benzo[*h*]quinolinyl-(pyridyl)-palladium(II) (15)

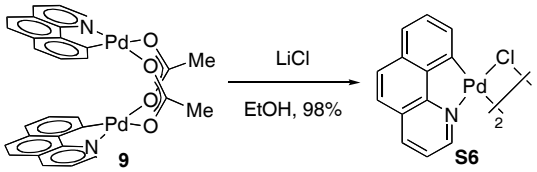


9 **15**

To a solution of benzo[*h*]quinolinyl palladium acetate dimer (**9**) (15.7 mg, 2.28×10^{-5} mol, 1.00 equiv) in $CHCl_3$ (0.6 mL) at 23 °C was added pyridine (3.7 μL, 3.6 mg, 4.6×10^{-5} mol, 2.0 equiv). Solvent was removed in vacuo to afford 18.5 mg of the title compound as a pale yellow solid (95% yield).

^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 9.21 (ddd, J = 4.8 Hz, J = 1.6 Hz, J = 1.6 Hz, 2H), 8.76 (dd, J = 5.3 Hz, J = 1.4 Hz, 1H), 8.28 (dd, J = 8.0 Hz, J = 1.4 Hz, 1H), 7.92 (tt, J = 7.8 Hz, J = 1.6 Hz, 1H), 7.74 (d, J = 8.7 Hz, 1H), 7.60 (d, J = 8.7 Hz, 1H), 7.56 (d, J = 7.8 Hz, 1H), 7.52–7.50 (m, 3H), 7.29–7.28 (m, 1H), 6.47 (dd, J = 7.3 Hz, J = 0.7 Hz, 1H), 2.07 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 178.15, 155.06, 153.66, 150.65, 148.55, 141.75, 138.02, 137.17, 133.20, 130.44, 128.87, 128.35, 126.58, 125.31, 123.26, 122.67, 121.19, 25.00.

Benzo[*h*]quinolinyl palladium(II) chloride dimer (S6)

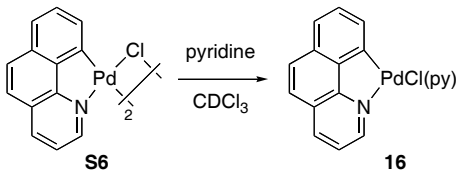


9 **S6**

To a solution of benzo[*h*]quinolinyl palladium acetate dimer (**9**) (4.27 g, 12.4 mmol, 1.00 equiv) in EtOH (100 mL) at 0 °C was added lithium chloride (10.5 g, 24.8 mmol, 20.0 equiv). The reaction was warmed to 23 °C and stirred for 1.0 h. The precipitate was isolated by vacuum filtration and was washed with water (3 × 100 mL), MeOH (2 × 100 mL), and Et_2O (100 mL) to afford 3.89 g of the title compound[7] as a pale yellow solid (98% yield).

^{1}H-NMR (500 MHz, DMSO-d_6, 23 ºC, δ): 9.44 (d, J = 4.5 Hz, 1H), 8.72 (br), 8.67 (d, J = 7.5 Hz, 1H), 8.61 (br), 8.22 (d, J = 7.0 Hz, 1H), 7.91 (d, J = 9.0 Hz, 1H), 7.86–7.74 (m, 3H), 7.73 (br), 7.60 (br), 7.53 (dd, J = 7.5 Hz, J = 7.0, 1H), 7.38 (br). ^{13}C-NMR (125 MHz, DMSO-d_6, 23 ºC, δ): 153.9, 152.2, 150.7, 150.6, 148.0, 141.7, 139.9, 134.4, 130.8, 129.6, 129.4, 127.5, 125.1, 124.4, 123.0, 122.9. Note: The ^{1}H and ^{13}C NMR spectra are more complicated than expected, probably due to a mixture of the title compound with a solvated adduct. The title compound is not soluble in non-coordinating solvents.

Chloro benzo[*h*]quinolinyl-(pyridyl)-palladium(II) (16)

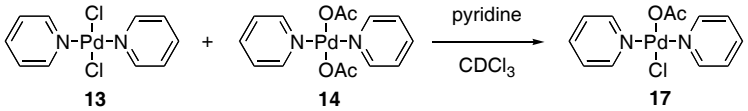


S6 **16**

To a suspension of benzo[*h*]quinolinyl palladium chloride dimer (**S6**) (21.9 mg, 3.42×10^{-5} mol, 1.00 equiv) in $CDCl_3$ (2.0 mL) at 23 °C was added pyridine (31.0 μL, 30.4 mg, 3.84×10^{-4} mol, 11.3 equiv). The title complex[8] was observed by ^{1}H NMR in the presence of pyridine and was not isolated; evaporation of solvent afforded mixtures of **16** with benzo[*h*]quinolinyl palladium chloride dimer **S6**.

^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 9.58 (dd, *J* = 5.4 Hz, *J* = 1.0 Hz, 1H), 9.06 (d, *J* = 4.9 Hz, 2H), 8.82 (dd, *J* = 6.3 Hz, *J* = 1.5 Hz, 2H), 8.27 (dd, *J* = 8.3 Hz, *J* = 1.0 Hz, 1H), 7.91 (dd, *J* = 7.8 Hz, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 8.3 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.52–7.47 (m, 3H), 6.42 (d, *J* = 7.3 Hz, 1H).

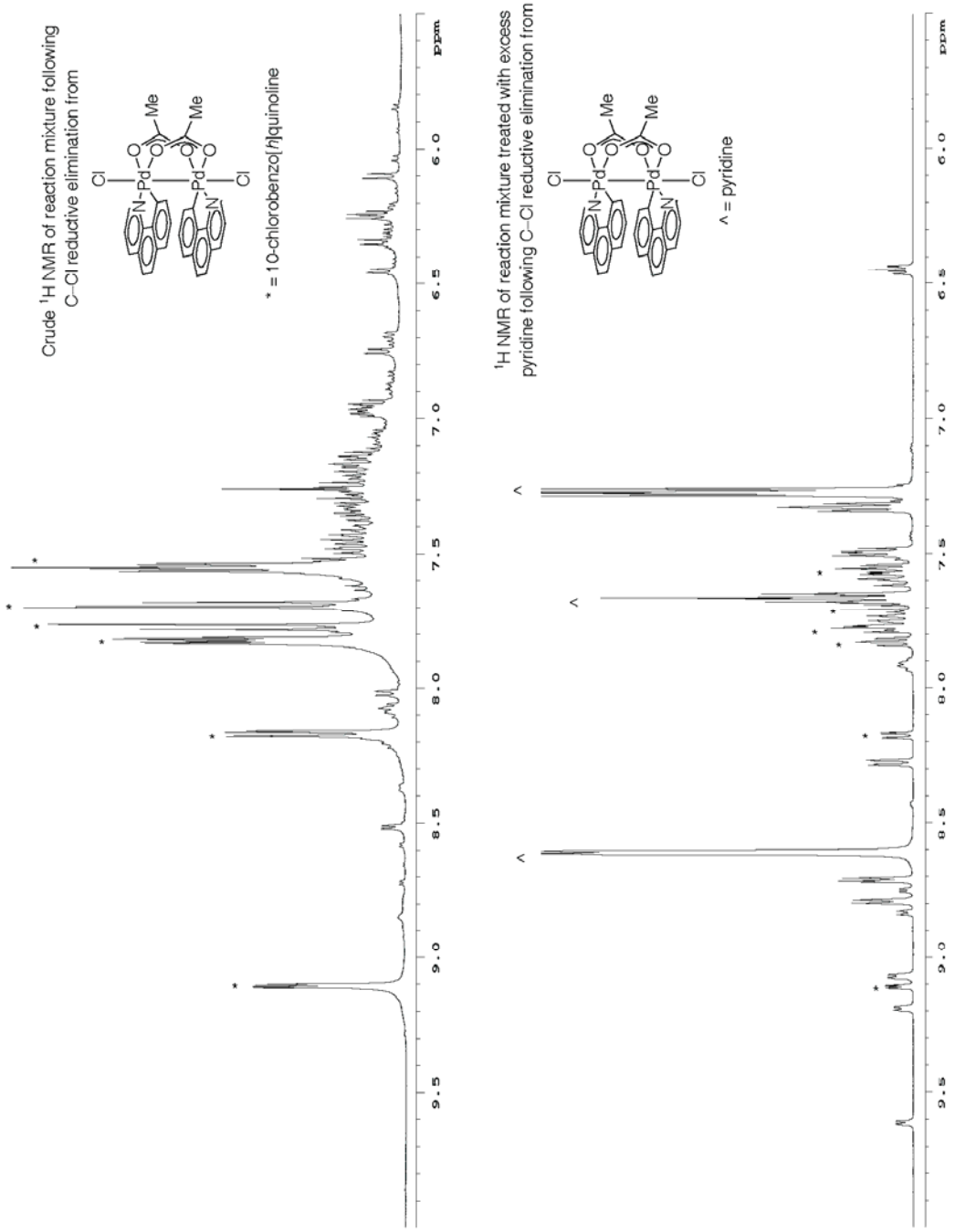
***Trans*-chloro-acetato bis(pyridine)palladium(II) (17)**



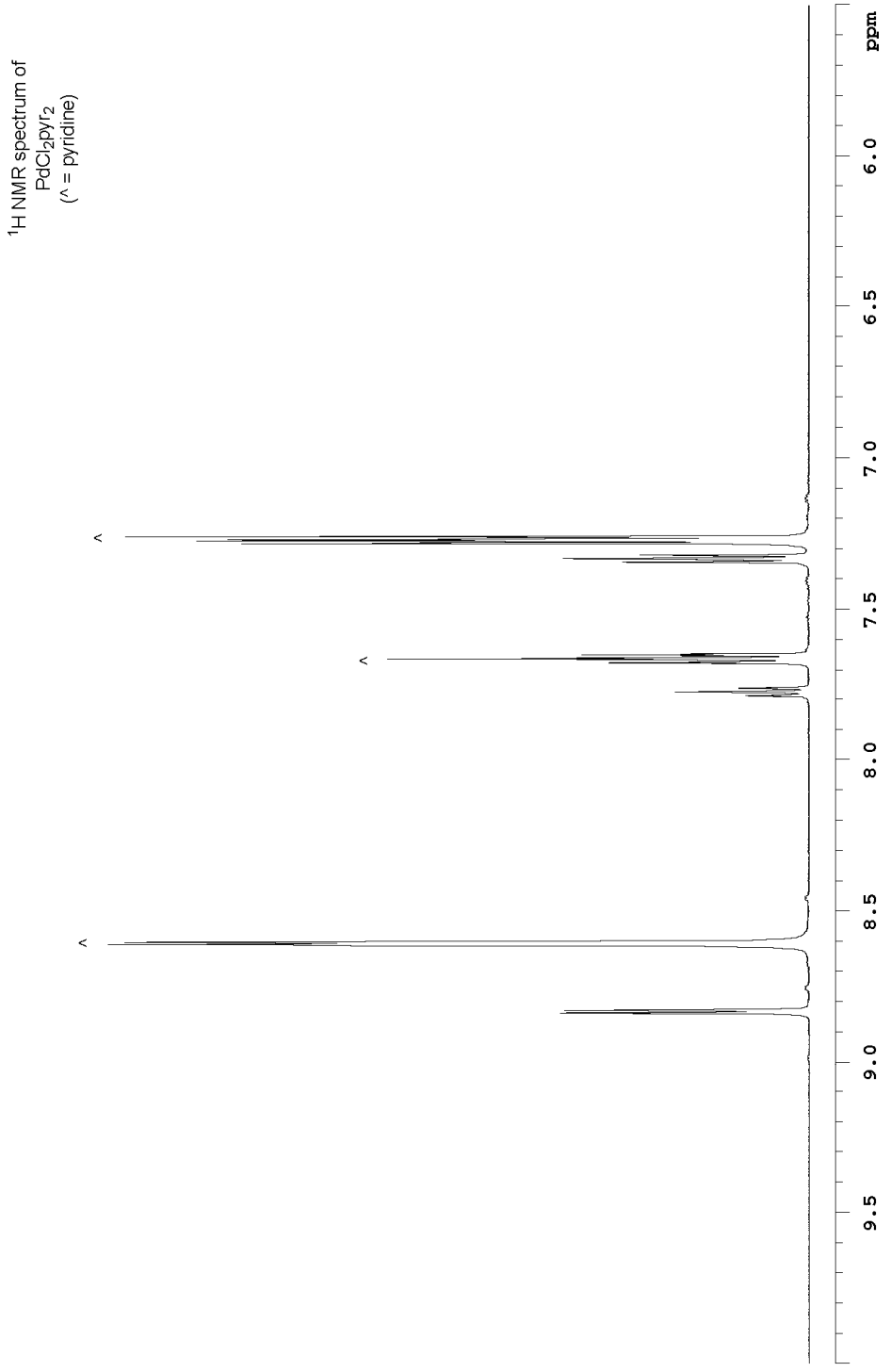
To a suspension of *trans*-dichloro bis(pyridine) palladium(II) (**13**) (29.6 mg, 8.82×10^{-5} mol, 1.00 equiv) in $CDCl_3$ (2.0 mL) and pyridine (70 μL) was added *trans*-diacetato bis(pyridine) palladium(II) (**14**) (33.8 mg, 8.82×10^{-5} mol, 1.00 equiv) in $CDCl_3$ (2.0 mL) and pyridine (70 μL) at 23 °C. The title complex was observed by ^{1}H NMR in a mixture which also included **13** and **14**.

^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 1.82 (s, 3H). Other ^{1}H NMR signals were not differentiable from those of **13** and **14**.

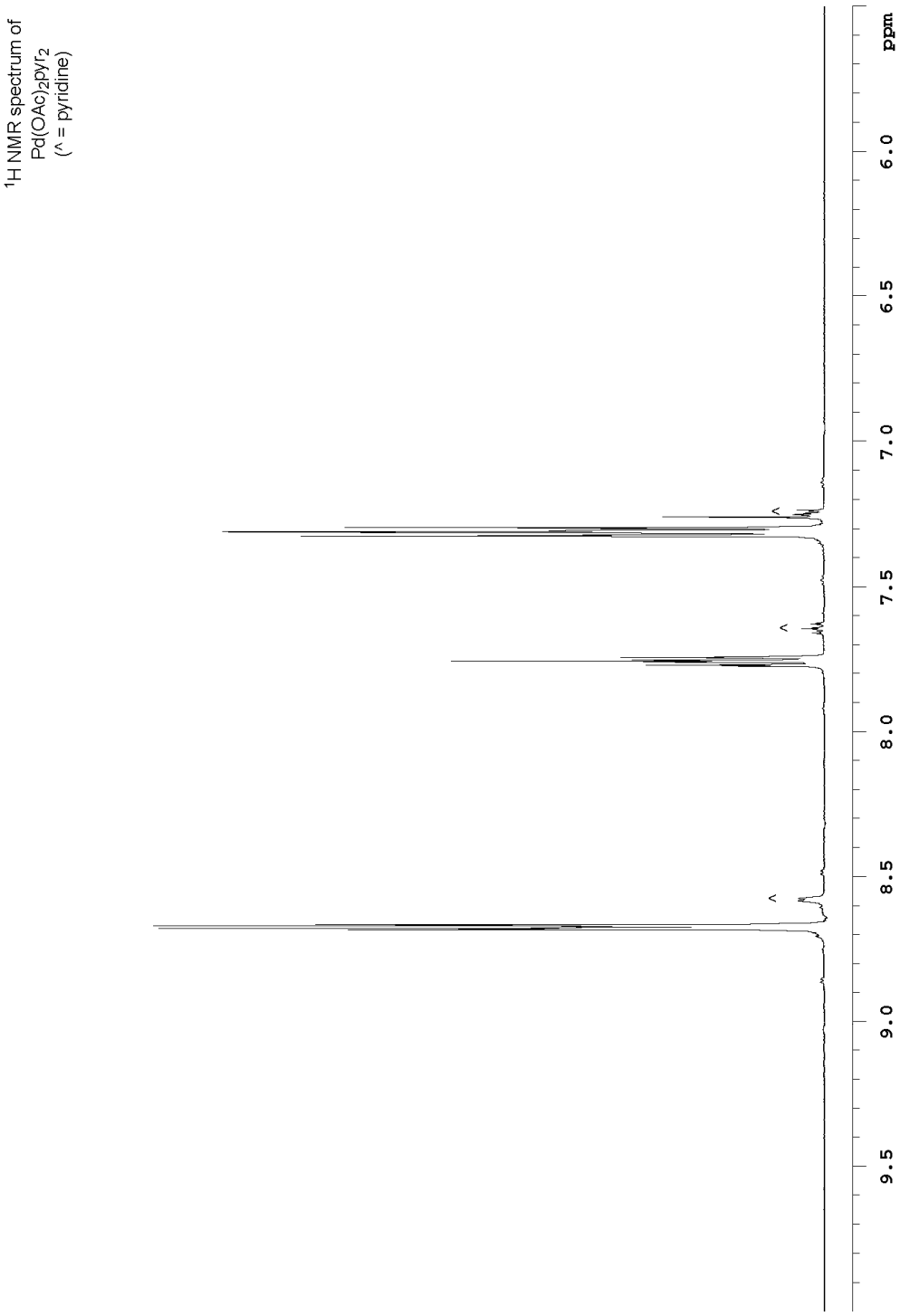
[1]H NMR Data for Assignment of Palladium Containing Byproducts of Reductive Elimination



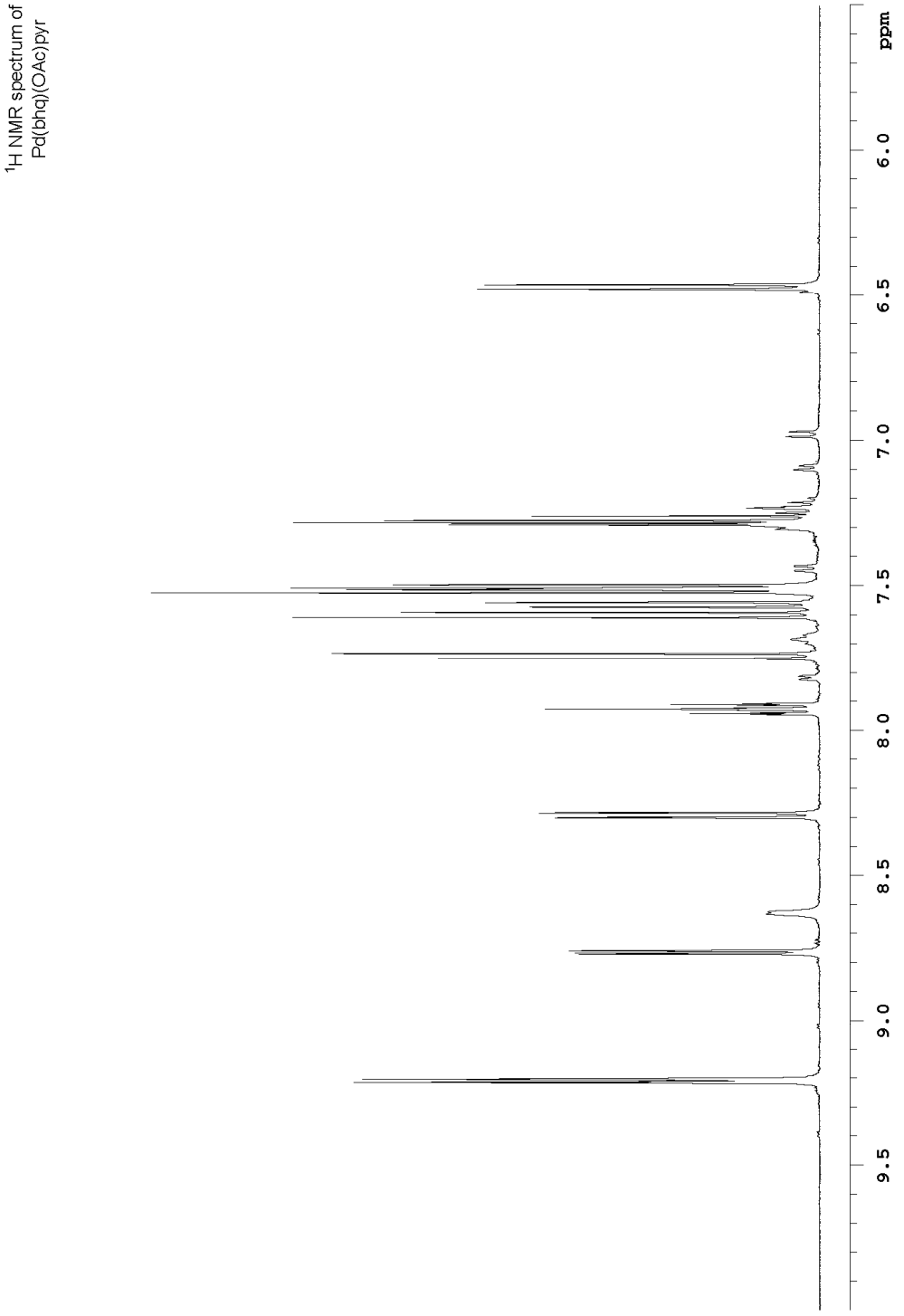
[1]H NMR spectra of the crude reaction mixture following reductive elimination from **1** (top) and after treatment with excess pyridine (bottom) in $CDCl_3$ at 23 °C.



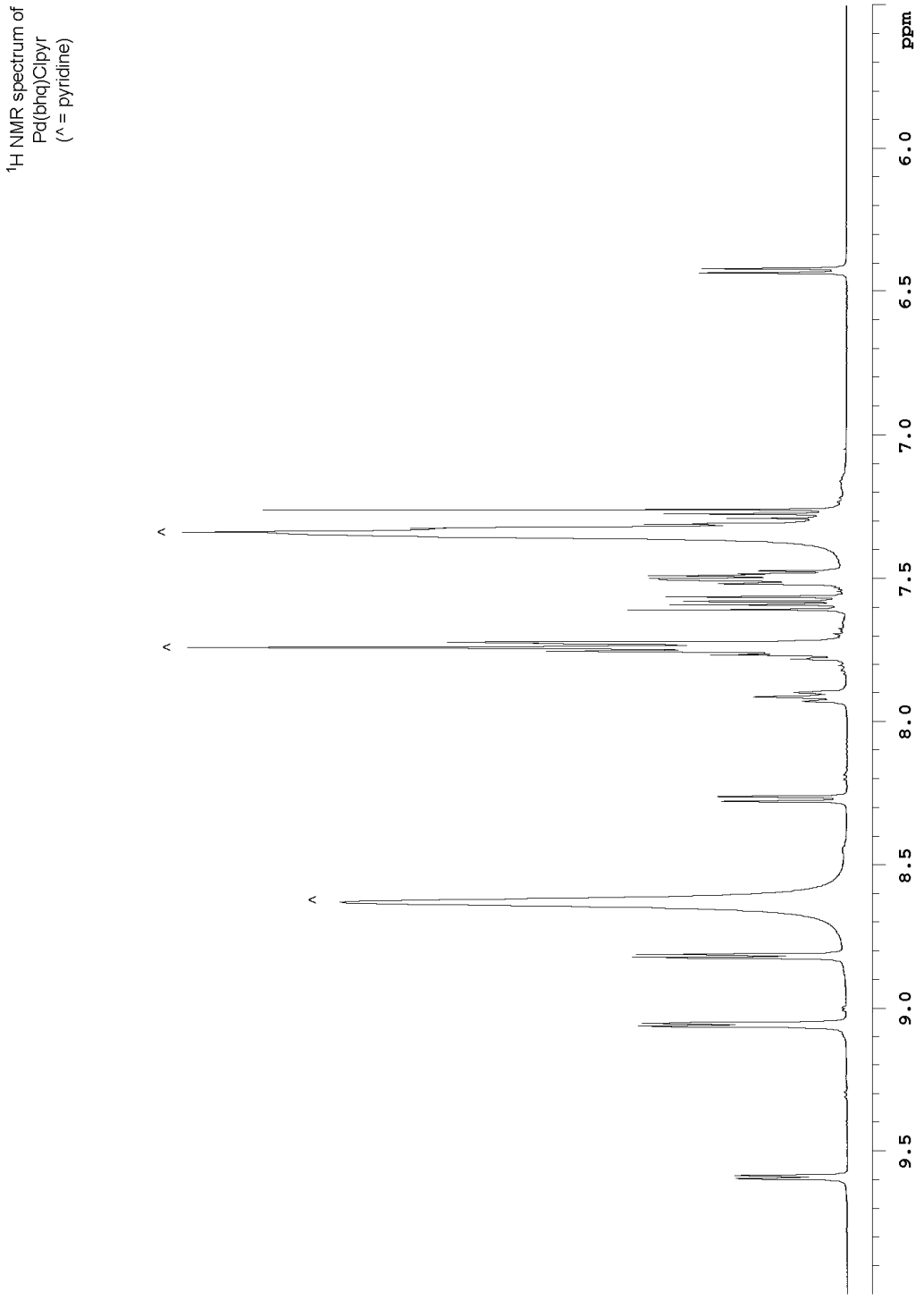
^{1}H NMR spectrum of $PdCl_2py_2$ (**13**) and pyridine in $CDCl_3$ at 23 °C.



^{1}H NMR spectrum of $Pd(OAc)_2py_2$ (**14**) and pyridine in $CDCl_3$ at 23 °C.

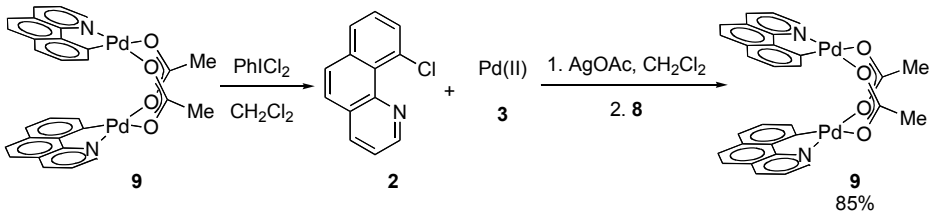


^{1}H NMR spectrum of Pd(bhq)(OAc)py (**15**) in $CDCl_3$ at 23 °C.



^{1}H NMR spectrum of Pd(bhq)Clpy (**16**) and pyridine in $CDCl_3$ at 23 °C.

Conversion of Pd-Containing Mixture 3 to 9:



Additional information about the constitution of the palladium-containing byproducts of reductive elimination was obtained by sequential treatment of the palladium-containing byproducts (**3**) with AgOAc and benzo[*h*]quinoline (**8**) to reform **9**. Details of this sequence are presented below.

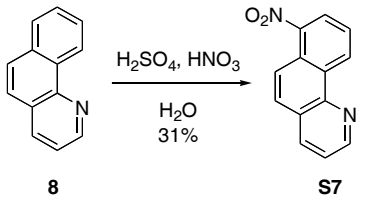
To a solution of benzo[*h*]quinolinyl palladium acetate dimer (**9**) (100 mg, 0.0145 mmol, 1.00 equiv) in CH_2Cl_2 (4mL) was added $PhICl_2$ (40.0 mg, 0.0145 mmol, 1.00 equiv) at 23 ºC. The mixture immediately turned dark red. After stirring for three hours at 23 ºC, the solution was yellow. Solvent was removed *in vacuo*. The residue was triturated with Et_2O to remove **2** and PhI. The residue obtained by filtration was dissolved in CH_2Cl_2. AgOAc (97.1 mg, 0.0582 mmol, 4.00 equiv) was added and the reaction was stirred for three hours. Solids were removed by filtration through celite before benzo[*h*]quinoline (**8**) (19.5 mg, 0.0109 mmol, 1.50 equiv) was added to the filtrate. The solution was stirred for 16 hours at 23 ºC. Solvent was removed *in vacuo* and the residue was triturated with Et_2O to afford 85.0 mg of compound as a yellow solid (85% yield from **9**).

Spectral properties are identical to those reported above.

Hammett Analysis Based on Substitution of Benzo[*h*]quinolinyl Ligand (Data Pertaining to Figure 2)

Synthesis of 7-Substituted Benzo[*h*]quinolines

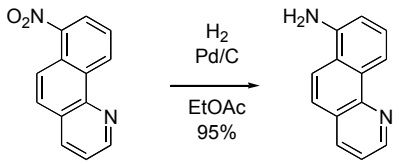
7-Nitrobenzo[*h*]quinoline (S7)



Under air, benzo[*h*]quinoline (**8**) (5.45 g, 30.4 mmol, 1.00 equiv) was dissolved in concentrated H_2SO_4 (11 mL) at 23 ºC. The reaction mixture was cooled to 0 ºC and the mixture of concentrated H_2SO_4 (3.6 mL) and HNO_3 (5.8 mL) (prepared by combining H_2SO_4 and HNO_3 at 0 ºC) was added dropwise over 20 min. The reaction mixture was stirred at 0 °C for 15 min and was subsequently poured onto water (300 mL). The precipitate was filtered, dried and purified by chromatography on silica gel eluting with CH_2Cl_2/hexanes 1:1 (v/v) to afford 2.11 g of the title compound[9] as a pale yellow solid (31% yield).

R_f = 0.78 (CH_2Cl_2). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 9.65 (d, *J* = 8.0 Hz, 1H), 9.03 (dd, *J* = 4.5 Hz, *J* = 2.0 Hz, 1H), 8.43 (d, *J* = 9.5 Hz, 1H), 8.32 (dd, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H), 8.21 (dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 7.88 (d, *J* = 9.0 Hz, 1H), 7.77 (dd, *J* = 8.0 Hz, *J* = 8.0 Hz, 1H), 7.61 (dd, *J* = 8.0 Hz, *J* = 4.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 149.9, 146.9, 145.3, 135.9, 132.9, 130.4, 129.0, 125.9, 125.6, 125.6, 125.1, 123.0, 121.3. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{13}H_8N_2O_2$ + H], 225.06585. Found, 225.06650. These data correspond to those reported in the literature.[10]

7-Aminobenzo[*h*]quinoline (S8)

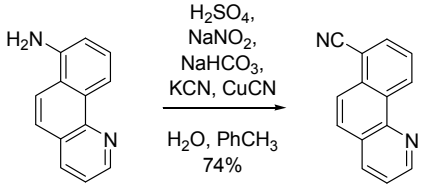


S7 **S8**

To 7-nitrobenzo[*h*]quinoline (**S7**) (400 mg, 1.78 mmol, 1.00 equiv) in EtOAc (30 mL) at 23 ºC was added 10% Pd/C (197 mg). H_2 gas (1 atm) was introduced using a balloon and the reaction mixture was stirred for 1.0 hr at 23 ºC. The reaction mixture was filtered through a pad of celite and the filtrate was concentrated to afford 328 mg of the title compound as a brown solid (95% yield).

R_f = 0.30 (CH_2Cl_2). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ) : 8.99 (dd, *J* =4.0 Hz, *J* = 1.5 Hz, 1H), 8.79 (d, *J* = 8.5 Hz, 1H), 8.13 (dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 7.82 (d, *J* = 9.0 Hz, 1H), 7.62 (d, *J* = 9.5 Hz, 1H), 7.54 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H), 7.49 (dd, *J* = 8.0 Hz, *J* = 4.5 Hz, 1H), 7.02 (dd, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H), 4.19 (br s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 146.8, 146.7, 142.4, 135.7, 132.5, 127.5, 126.1, 124.0, 122.4, 121.7, 120.5, 115.3, 113.5. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{13}H_{10}N_2$ + H], 195.09222. Found, 195.09235. These data correspond to those reported in the literature.[10]

7-Cyanobenzo[*h*]quinoline (S9)



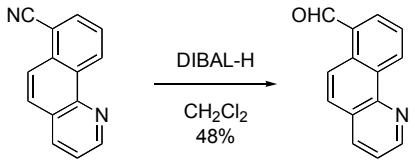
S8 **S9**

Under air, to 7-aminobenzo[*h*]quinoline (**S8**) (202 mg, 1.04 mmol, 1.00 equiv) in H_2O (4.0 mL), concentrated sulfuric acid (110 μL, 2.08 mmol, 2.00 equiv) was added dropwise at 0 ºC. After stirring for 10 min, a solution of $NaNO_2$ (86.1 mg, 1.25 mmol, 1.20 equiv) in H_2O (2.0 mL) was added dropwise and the reaction mixture was stirred for 30 min at 0 ºC. $NaHCO_3$ (350 mg, 4.16 mmol, 4.00 equiv), H_2O (5.0

mL), and toluene (5.0 mL) were added and the reaction mixture was warmed to 23 ºC over 15 min. A solution of KCN (464 mg, 7.12 mmol, 6.85 equiv) and CuCN (233 mg, 2.60 mmol, 2.50 equiv) in H_2O (2.0 mL) was added dropwise. The reaction mixture was warmed to 70 ºC, stirred for 2.0 hr, and cooled to 23 ºC. The cooled mixture was extracted with EtOAc (3 x 15 mL). The combined organic phases were washed with brine, dried ($MgSO_4$), and concentrated in vacuo. The crude product was purified by chromatography on silica gel eluting with EtOAc/hexanes 1:9 (v/v) to afford 155 mg of the title compound as a brown solid (74% yield).

R_f = 0.15 (hexanes/EtOAc 14 :1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 9.55 (d, *J* = 8.5 Hz, 1H), 9.05 (d, *J* = 4.5 Hz, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 8.20 (d, *J* = 9.0 Hz, 1H), 8.07 (d, *J* = 7.5 Hz, 1H), 7.90 (d, *J* = 9.0 Hz, 1H), 7.77 (ddd, *J* = 8.0 Hz, *J* = 8.0 Hz, *J* = 1.0 Hz, 1H), 7.61 (ddd, *J* = 8.0 Hz, *J* = 4.0 Hz, *J* = 2.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 149.8, 145.7, 136.1, 133.8, 133.4, 131.7, 129.6, 128.5, 126.4, 126.3, 123.9, 122.8, 117.9, 110.1. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{14}H_8N_2$ + H], 205.07657. Found, 205.07669. These data correspond to those reported in the literature.[10]

7-Formylbenzo[*h*]quinoline (S10)

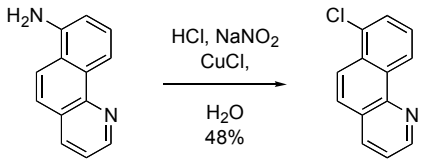


S9 **S10**

To 7-cyanobenzo[*h*]quinoline (**S9**) (84.6 mg, 0.414 mmol, 1.00 equiv) in CH_2Cl_2 (5.0 mL) at –78 ºC, diisobutylaluminum hydride (1.0 M in hexanes, 0.83 mL, 0.83 mmol, 2.0 equiv) was added dropwise and the reaction mixture was stirred for 1.5 hr. An additional equivalent of diisobutylaluminum hydride (1.0 M in hexanes, 0.42 mL, 0.42 mmol, 1.0 equiv) was added dropwise. The reaction mixture was stirred for 30 min and warmed to 23 ºC. The reaction was quenched with 1N HCl (5.0 mL), and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were washed with $NaHCO_3$ (aq) and brine, dried ($MgSO_4$), and concentrated in vacuo. The crude mixture was filtered through a plug of silica gel eluting with CH_2Cl_2 and concentrated in vacuo to afford 41.3 mg of the title compound as a tan solid (48 % yield).

R_f = 0.33 (hexanes/EtOAc 5:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 10.51 (s, 1H), 9.68 (d, *J* = 8.5 Hz, 1H), 9.26 (d, *J* = 9.5 Hz, 1H), 9.05 (dd, *J* = 4.5 Hz, *J* = 1.5 Hz, 1H), 8.25 (dd, *J* = 8.0 Hz, *J* = 2.0 Hz, 1H), 8.19 (dd, *J* = 7.0 Hz, *J* = 1.0 Hz, 1H), 7.93–7.89 (m, 2H), 7.60 (dd, *J* = 8.0 Hz, *J* = 4.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 193.6, 149.4, 145.8, 137.2, 135.8, 132.2, 131.7, 131.2, 131.1, 128.7, 126.3, 126.2, 123.5, 122.5. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{14}H_9NO$ + H], 208.07624. Found, 208.07655. These data correspond to those reported in the literature.[10]

7-Chlorobenzo[*h*]quinoline (S11)

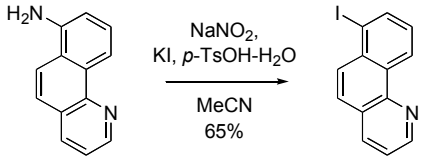


S8 **S11**

Under air, 7-aminobenzo[*h*]quinoline (**S8**) (123 mg, 0.633 mmol, 1.00 equiv) was dissolved in 2N HCl (3.8 mL) at 0 ºC. To the reaction mixture was added a solution of $NaNO_2$ (52.4 mg, 0.760 mmol, 1.20 equiv) in H_2O (1.6 mL) dropwise over 2 min. The reaction mixture was stirred for 30 min at 0 ºC and a solution of CuCl (62.7 mg, 0.633 mmol, 1.00 equiv) in concentrated HCl (1.6 mL) was added dropwise over 2 min. The reaction mixture was warmed to 23 ºC and further stirred for 1.0 hr before aqueous $NaHCO_3$ (10 mL) was added. To the reaction mixture was added CH_2Cl_2 (10 mL) and the phases were separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phases were washed with brine (10 mL) and dried (Na_2SO_4). The filtrate was concentrated in vacuo and the residue was purified by chromatography on silica gel eluting with hexanes/CH_2Cl_2 1:2 (v/v) to afford 65.2 mg of the title compound as a pale-yellow solid (48% yield).

R_f = 0.79 (CH_2Cl_2). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 9.26 (d, *J* = 8.5 Hz, 1H), 9.02 (dd, *J* = 4.5 Hz, *J* = 2.0 Hz, 1H), 8.27 (d, *J* = 9.5 Hz, 1H), 8.19 (dd, *J* = 8.0 Hz, *J* = 2.0 Hz, 1H), 7.79–7.76 (m, 2H), 7.64 (dd, *J* = 8.5 Hz, *J* = 8.5 Hz, 1H), 7.55 (dd, *J* = 8.0 Hz, *J* = 4.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 149.3, 146.1, 135.9, 133.1, 131.9, 130.8, 128.6, 127.0, 126.5, 126.2, 123.4, 123.4, 122.3. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{13}H_8ClN$ + H], 214.04235. Found, 214.04200. These data correspond to those reported in the literature.[10]

7-Iodobenzo[*h*]quinoline (S12)



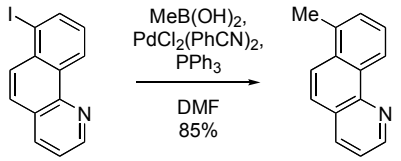
S8 **S12**

To a solution of *p*–toluenesulfonic acid monohydrate (896 mg, 4.71 mmol, 3.00 equiv) in acetonitrile (6.0 mL) under air was added 7-aminobenzo[*h*]quinoline (**S8**) (305 mg, 1.57 mmol, 1.00 equiv). The reaction mixture was cooled to 10 ºC and a solution of $NaNO_2$ (217 mg, 3.14 mmol, 2.00 equiv) and KI (652 mg, 3.93 mmol, 2.50 equiv) in H_2O (1.0 mL) was added dropwise, and the reaction was stirred for 10 min, warmed to 23 ºC, and stirred for an additional 1.5 hr. H_2O (15 mL), $Na_2S_2O_3$ (2 mL) and sat. $NaHCO_3$ (aq) were added to basify the solution. The reaction mixture was extracted with EtOAc (10 mL) and CH_2Cl_2 (2 × 15 mL). The combined organic phases were dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by chromatography on silica gel eluting with CH_2Cl_2/ hexanes 2:1 (v/v) to afford 311

mg of the title compound as a light yellow crystalline solid (65% yield).

R_f = 0.52 (CH_2Cl_2/hexanes 2:1 (v/v)). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 9.37 (dd, *J* = 9.5 Hz, *J* = 1.0 Hz, 1H), 9.03 (dd, *J* = 4.5 Hz, *J* = 1.5 Hz, 1H), 8.28 (dd, *J* = 7.5 Hz, *J* = 1.5 Hz, 1H), 8.22 (dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 8.13 (d, *J* = 9.5 Hz, 1H), 7.79 (d, *J* = 9.5 Hz, 1H), 7.57 (dd, *J* = 8.5 Hz, *J* = 4.5 Hz, 1H), 7.44 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 149.5, 146.2, 139.7, 136.0, 134.7, 132.9, 131.5, 128.2, 127.2, 126.2, 125.3, 122.5, 99.4. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{13}H_8IN$ + H], 305.97797. Found, 305.97765. These data correspond to those reported in the literature.[10]

7-Methylbenzo[*h*]quinoline (S13)



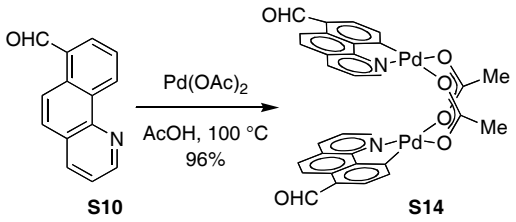
S12 **S13**

Under air, to 7-iodobenzo[*h*]quinoline (**S12**) (289 mg, 0.950 mmol, 1.00 equiv), methylboronic acid (623 mg, 2.84 mmol, 3.00 equiv), $PdCl_2(PhCN)_2$ (36.0 mg, 0.095 mmol, 0.100 equiv), PPh_3 (50.0 mg, 0.190 mmol, 0.200 equiv), and potassium carbonate (393 mg, 2.84 mmol, 3.00 equiv), was added DMF (7.2 mL). The reaction mixture was heated to 110 ºC for 5.5 hr. After cooling to 23 ºC, the reaction mixture was diluted with H_2O (10 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were dried with Na_2SO_4 and concentrated in vacuo. The crude product was purified by chromatography on silica gel eluting with CH_2Cl_2 to afford 155 mg of the title compound as a light yellow solid (85% yield).

R_f = 0.57 (CH_2Cl_2). NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$ 25 ºC, δ): 9.22 (d, *J* = 8.0 Hz, 1H), 9.01 (dd, *J* = 4.5 Hz, *J* = 2.0 Hz, 1H), 8.18 (dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 8.03 (d, *J* = 9.5 Hz, 1H), 7.73 (d, *J* = 9.5 Hz, 1H), 7.64 (dd, *J* = 8.0 Hz, *J* = 7.0 Hz, 1H), 7.56–7.51 (m, 2H), 2.78 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, δ): 149.0, 147.0, 135.9, 134.4, 132.6, 131.8, 129.5, 126.8, 126.1, 125.2, 124.0, 122.7, 121.8, 19.9. Mass Spectrometry: HRMS-FIA (m/z): Calcd for [$C_{14}H_{11}N$ + H], 194.09697. Found, 194.09667. These data correspond to those reported in the literature.[10]

Synthesis of 7-Substituted Benzo[*h*]quinolinyl palladium acetate dimers

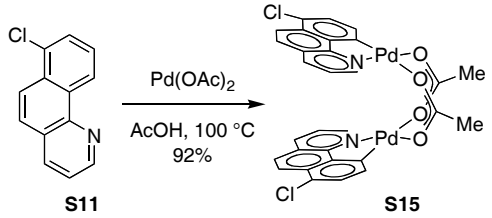
7-Formylbenzo[*h*]quinolinyl palladium acetate dimer (S14)



To a suspension of 7-formylbenzo[*h*]quinoline (**S10**) (102 mg, 0.490 mmol, 1.00 equiv) in AcOH (3.0 mL) at 23 °C was added $Pd(OAc)_2$ (110 mg, 0.490 mmol, 1.00 equiv) and the reaction mixture was heated to 100 °C for 10 minutes. After cooling to 23 °C, the reaction mixture was concentrated in vacuo and the residue was triturated with Et_2O (3 × 1 mL) to afford 175 mg of the title compound as a yellow solid (96% yield) in a 6:1 ratio of isomers (7-formylbenzo[*h*]quinolinyl ligands head to tail vs. head to head).

Melting Point: >250 ˚C. ^{1}H-NMR (600 MHz, CD_2Cl_2, 23 ºC, δ): Major Isomer : 10.19 (s, 2H), 8.63 (d, *J* = 8.9 Hz, 2H), 7.95 (dd, *J* = 5.1 Hz, *J* = 1.3 Hz, 2H), 7.65 (dd, *J* = 8.1 Hz, *J* = 1.3 Hz, 2H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.28 (d, 8.9 Hz, 2H), 7.24 (d, *J* = 7.5 Hz, 2H), 6.68 (dd, *J* = 8.1 Hz, *J* = 5.3 Hz, 2H), 2.37 (s, 6H). Minor Isomer : 10.00 (s, 2H), 8.56 (d, *J* = 8.9 Hz, 2H), 8.16 (dd, *J* = 5.1 Hz, *J* = 1.3 Hz, 2H), 7.87 (dd, *J* = 7.9 Hz, *J* = 1.3 Hz, 2H), 7.31 (d, *J* = 8.9, 2H), 7.07 (dd, *J* = 8.1 Hz, *J* = 5.1 Hz, 2H), 6.98 (d, *J* = 7.5 Hz, 2H). ^{13}C-NMR (125 MHz, CD_2Cl_2, 23 ºC, δ): Major Isomer: 193.13, 182.82, 160.59, 152.42, 149.35, 140.12, 136.50, 136.25, 129.92, 129.02, 127.51, 126.50, 125.65, 125.38, 121.24, 25.00. Minor Isomer: 192.83, 160.19, 153.50, 152.42, 147.98, 136.72, 136.03, 130.45, 126.16, 121.48. UV-VIS Spectroscopy (CH_2Cl_2, 23 ˚C): 420 nm (ε = 3.11 × 10^3 M^{-1} cm^{-1}); 379 nm (ε = 5.80 × 10^3 M^{-1} cm^{-1}); 340 nm (ε = 1.94 × 10^4 M^{-1} cm^{-1}); 300 nm (ε = 3.01 × 10^4 M^{-1} cm^{-1}). Mass Spectrometry: LRMS-FIA (m/z): calcd for $[C_{14}H_8NOPd+C_2H_3N]^+$, 352.9901. Found, 353.9928.

7-Chlorobenzo[*h*]quinolinyl palladium acetate dimer (S15)

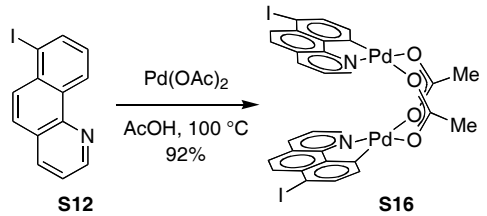


To a suspension of 7-chlorobenzo[*h*]quinoline (**S11**) (65.2 mg, 0.305 mmol, 1.00 equiv) in AcOH (3.0 mL) at 23 °C was added $Pd(OAc)_2$ (68.5 mg, 0.305 mmol, 1.00 equiv) and the reaction mixture was heated to 100 °C for 10 minutes. After cooling to 23 °C, the reaction mixture was concentrated in vacuo and the residue was triturated with Et_2O (3 × 1 mL) to afford 106 mg of the title compound as a yellow solid (92% yield) in a 14:1 ratio of isomers (7-chlorobenzo[*h*]quinolinyl ligands head to tail vs. head to

head).

Melting Point: >250 ˚C (decomp.). ^{1}H-NMR (600 MHz, $CDCl_3$, 23 ºC, δ): Major Isomer : 7.92 (d, *J* = 5.1 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.9 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 7.14 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 7.8 Hz, 2H), 6.74 (dd, *J* = 8.1 Hz, *J* = 5.1 Hz, 2H), 2.37 (s, 6H). Minor Isomer : 8.12 (d, *J* = 5.1 Hz, 2H), 7.77 (d, *J* = 7.9 Hz, 2H), 7.00 (d, *J* = 7.8 Hz, 2H), 6.96 (dd, *J* = 7.8, *J* = 5.3 Hz, 2H), 6.68 (d, *J* = 7.9 Hz, 2H). ^{13}C-NMR (125 MHz, CD_2Cl_2, 23 ºC, δ): Major Isomer: 182.43, 152.50, 148.97, 146.62, 140.31, 135.29, 129.31, 129.18, 127.28, 126.23, 125.18, 124.08, 124.05, 120.71, 24.91. UV-VIS Spectroscopy (CH_2Cl_2, 23 ˚C): 384 nm (ε = 4.58 × 10^3 M^{-1} cm^{-1}); 291 nm (ε = 1.98 × 10^4 M^{-1} cm^{-1}). Mass Spectrometry: LRMS-FIA (m/z): calcd for $[C_{13}H_7ClNPd+C_2H_3N]^+$, 358.9562. Found, 358.9580.

7-Iodobenzo[*h*]quinolinyl palladium acetate dimer (S16)

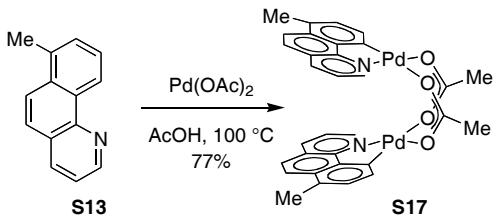


S12 **S16**

To a suspension of 7-iodobenzo[*h*]quinoline (**S12**) (85.0 mg, 0.279 mmol, 1.00 equiv) in AcOH (2.0 mL) at 23 °C was added $Pd(OAc)_2$ (62.5 mg, 0.279 mmol, 1.00 equiv) and the reaction mixture was heated to 100 °C for 10 minutes. After cooling to 23 °C, the reaction mixture was concentrated in vacuo and the residue was triturated with Et_2O (3 × 1 mL) to afford 120 mg of the title compound as a dark yellow solid (92% yield) in a 19:1 ratio of isomers (7-iodobenzo[*h*]quinolinyl ligands head to tail vs. head to head).

Melting Point: >250 ˚C (decomp.). ^{1}H-NMR (500 MHz, CD_2Cl_2, 23 ºC, δ): Major Isomer : 7.93 (d, *J* = 5.1 Hz, 2H), 7.80 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.39 (d, *J* = 8.9 Hz, 2H), 7.19 (d, 8.9 Hz, 2H), 6.83 (dd, *J* = 8.1 Hz, *J* = 5.1 Hz, 2H), 6.66 (d, *J* = 7.6 Hz, 2H), 2.31 (s, 6H). Minor Isomer : 8.10 (d, *J* = 5.4 Hz, 2H), 7.49 (d, *J* = 9.1 Hz, 2H), 7.44 (d, *J* = 7.8 Hz, 2H), 6.99 (dd, *J* = 8.1, *J* = 5.0 Hz, 2H), 6.48 (d, *J* = 7.6 Hz, 2H). ^{13}C-NMR (125 MHz, CD_2Cl_2, 23 ºC, δ): Major Isomer: 182.54, 152.90, 149.54, 149.34, 140.55, 137.95, 135.85, 133.53, 131.41, 131.00, 125.56, 125.13, 121.54, 91.96, 25.03. UV-VIS Spectroscopy (CH_2Cl_2, 23 ˚C): 383 nm (ε = 4.65 × 10^3 M^{-1} cm^{-1}); 321 nm (ε = 1.15 × 10^4 M^{-1} cm^{-1}); 295 nm (ε = 2.17 × 10^4 M^{-1} cm^{-1}). Mass Spectrometry: LRMS-FIA (m/z): calcd for $[C_{13}H_7INPd+C_2H_3N]^+$, 450.8918. Found, 450.8912.

7-Methylbenzo[*h*]quinolinyl palladium acetate dimer (S17)

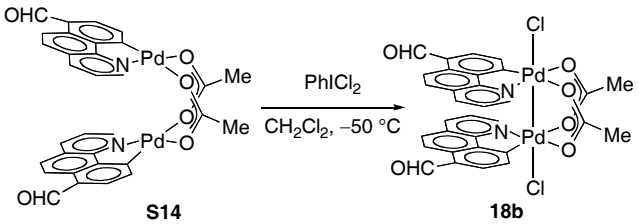


S13 **S17**

To a suspension of 7-methylbenzo[*h*]quinoline (**S13**) (97.0 mg, 0.502 mmol, 1.00 equiv) in AcOH (3 mL) at 23 °C was added $Pd(OAc)_2$ (113 mg, 0.502 mmol, 1.00 equiv) and the reaction mixture was heated to 100 °C for 10 minutes. After cooling to 23 °C, the reaction mixture was concentrated in vacuo and the residue was triturated with Et_2O (3 × 1 mL) to afford 138 mg of the title compound as a yellow solid (77% yield) in a 7:1 ratio of isomers (7-methylbenzo[*h*]quinolinyl ligands head to tail vs. head to head).

Melting Point: >250 ˚C. ^{1}H-NMR (500 MHz, CD_2Cl_2, 23 ºC, δ): Major Isomer : 7.80 (d, *J* = 5.0 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.7 Hz, 2H), 7.04 (d, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 7.3 Hz, 2H), 6.84 (d, *J* = 7.3 Hz, 2H), 6.54 (dd, *J* = 7.8 Hz, *J* = 5.0 Hz, 2H), 2.50 (s, 6H), 2.31 (s, 6H). Minor Isomer : 8.06 (d, *J* = 5.0 Hz, 2H), 7.76 (d, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 8.7 Hz, 2H), 6.93 (dd, *J* = 7.8, *J* = 5.0 Hz, 2H), 6.69 (d, *J* = 7.3 Hz, 2H), 6.56 (d, *J* = 7.3 Hz, 2H), 2.41 (s, 6H). ^{13}C-NMR (125 MHz, CD_2Cl_2, 23 ºC, δ): Major Isomer: 182.22, 153.31, 149.02, 145.82, 139.85, 135.01, 131.59, 129.17, 128.94, 128.79, 125.25, 124.71, 122.99, 120.26. Minor Isomer: 147.36, 125.52, 121.97, 120.38, 114.39. UV-VIS Spectroscopy (CH_2Cl_2, 23 ˚C): 393 nm (ε = 4.26 × 10^3 M^{-1} cm^{-1}); 326 nm (ε = 7.27 × 10^3 M^{-1} cm^{-1}); 296 nm (ε = 1.65 × 10^4 M^{-1} cm^{-1}). Mass Spectrometry: LRMS-FIA (m/z): calcd for $[C_{14}H_{10}NPd+C_2H_3N]^+$, 339.0108. Found, 339.0117.

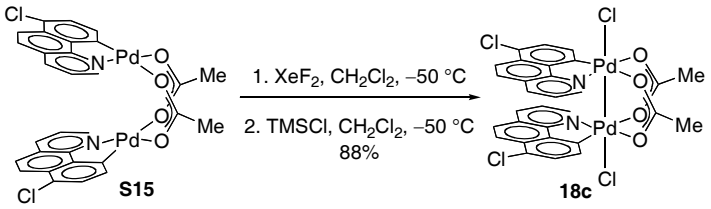
7-Formylbenzo[*h*]quinolinyl chloro palladium(III) acetate dimer (18b)



This reaction was carried out in a nitrogen-filled dry box. To a solution of of 7-formylbenzo[*h*]quinolinyl palladium acetate dimer (**S14**) (16.0 mg, 2.16 × 10^{-5} mol, 1.00 equiv) in CH_2Cl_2 (1.5 mL) at –50 °C was added $PhICl_2$ (6.0 mg, 2.2 × 10^{-5} mol, 1.00 equiv). The reaction mixture immediately turned from yellow to dark red. ^{1}H NMR analyis of the crude reaction product indicated a mixture of complexes and the ^{1}H NMR spectrum was too complicated for assignment of signals. Subsequent thermolysis of the crude mixture **18b** produced 7-formylbenzo[*h*]quinoline (**19b**) in 91% yield (*vide infra*). Further evidence that the crude reaction mixture is composed on complexes related to **18b** as drawn above is that the rate of formation of **19b** is measured to be as expected based on the σ-value of the formyl substituent (*vide infra*).

UV-VIS Spectroscopy (CH_2Cl_2, 0 ˚C): 496 nm (ε = 9.14 × 10^3 M^{-1} cm^{-1}); 420 nm (ε = 2.48 × 10^4 M^{-1} cm^{-1}).

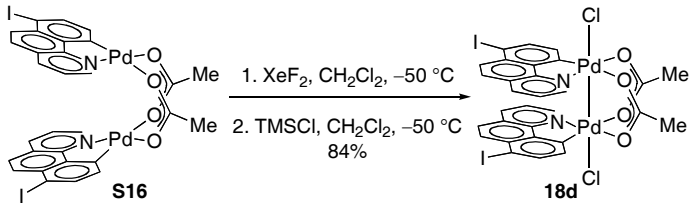
7-Chlorobenzo[*h*]quinolinyl chloro palladium(III) acetate dimer (18c)



This reaction was carried out in a nitrogen-filled dry box.[3] To a suspension of 7-chlorobenzo[*h*]quinolinyl palladium acetate dimer (**S15**) (22.7 mg, 3.00×10^{-5} mol, 1.00 equiv) in CH_2Cl_2 (1.5 mL) at –50 °C was added XeF_2 (5.1 mg, 3.0×10^{-5} mol, 1.0 equiv) in one portion. The reaction mixture was stirred for 10 minutes before TMSCl (7.80 μL, 6.68 mg, 6.15×10^{-5} mol, 2.05 equiv) was added. The reaction mixture was stirred at –50 °C for 5 minutes before solvent was removed in vacuo at –50 °C to afford 21.8 mg of the title compound as a dark red solid (88% yield) in a 10:1 ratio of isomers (7-chlorobenzo[*h*]quinolinyl ligands head to tail vs. head to head).

^{1}H-NMR (500 MHz, CD_2Cl_2, –50 ºC, δ): Major Isomer : 7.89–7.85 (m, 4H), 7.61 (d, J = 8.3 Hz, 2H), 7.50 (d, J = 7.8 Hz, 2H), 7.29 (d, J = 8.3 Hz, 2H), 7.09 (d, J = 8.3 Hz, 2H), 7.04 (dd, J = 5.4 Hz, J = 5.4 Hz, 2H), 2.69 (s, 6H). Minor Isomer : 2.62 (s, 6H). UV-VIS Spectroscopy (CH_2Cl_2, 0 ˚C): 612 nm ($\varepsilon = 2.64 \times 10^3$ M^{-1} cm^{-1}); 498 nm ($\varepsilon = 6.17 \times 10^3$ M^{-1} cm^{-1}); 422 nm ($\varepsilon = 2.64 \times 10^4$ M^{-1} cm^{-1}).

7-Iodobenzo[*h*]quinolinyl chloro palladium(III) acetate dimer (18d)



This reaction was carried out in a nitrogen-filled dry box.[4] To a suspension of 7-iodobenzo[*h*]quinolinyl palladium acetate dimer (**S16**) (18.1 mg, 1.93×10^{-5} mol, 1.00 equiv) in CD_2Cl_2 (1.5 mL) at –50 °C was added XeF_2 (5.1 mg, 3.0×10^{-5} mol, 1.0 equiv) in one portion. The reaction mixture was stirred for 10 minutes before TMSCl (7.80 μL, 6.68 mg, 6.15×10^{-5} mol, 2.05 equiv) was added. The reaction mixture was stirred at –50 °C for 5 minutes before solvent was removed in vacuo at –50 °C to afford 16.4 mg of the title compound as a dark red solid (84% yield) in a 15:1 ratio of isomers (7-iodobenzo[*h*]quinolinyl ligands head to tail vs. head to head). In solution, **18d** is both thermally and photochemically unstable;

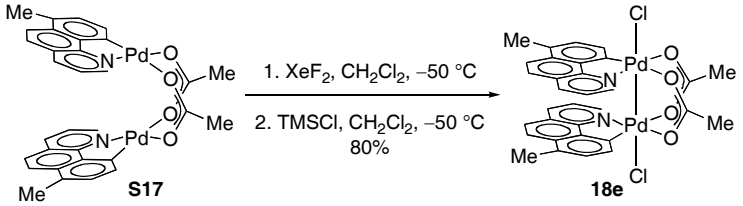
[3] Oxidation was carried out with XeF_2 in lieu of $PhICl_2$ to simplify purification of **18c**.

[4] Oxidation was carried out with XeF_2 in lieu of $PhICl_2$ because the byproducts of oxidation with XeF_2 do not overlap with the aromatic resonances of **18d**, which simplified analysis of the resulting ^{1}H NMR spectrum.

characterization has been accomplished on unpurified samples of **18d** because we have been unable to handle **18d** for sufficient times to purify.

^{1}H-NMR (500 MHz, CD_2Cl_2, –50 ºC, δ): Major Isomer : 7.89 (d, J = 4.9 Hz, 2H), 7.83–7.80 (m, 4H), 7.33 (d, J = 8.8 Hz, 2H), 7.19 (d, J = 9.3 Hz, 2H), 7.03 (dd, J = 8.3 Hz, J = 5.9Hz, 2H), 6.87 (d, J = 8.3 Hz, 2H), 2.68 (s, 6H). Minor Isomer : 8.05 (d, J = 5.9 Hz, 2H), 7.43 (d, J = 8.8 Hz, 2H), 6.69 (d, J = 8.3 Hz, 2H), 2.66 (s, 6H). UV-VIS Spectroscopy (CH_2Cl_2, 0 ˚C): 600 nm (ε = 3.69 × 10^3 M^{-1} cm^{-1}); 496 nm (ε = 8.27 × 10^3 M^{-1} cm^{-1}); 420 nm (ε = 3.28 × 10^4 M^{-1} cm^{-1}); 318 nm (ε = 2.53 × 10^4 M^{-1} cm^{-1}).

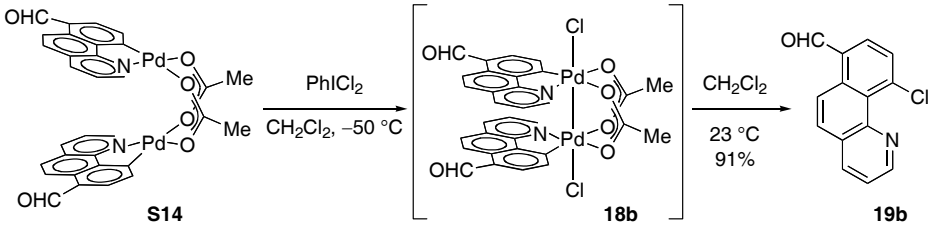
7-Methylbenzo[*h*]quinolinyl chloro palladium(III) acetate dimer (18e)



This reaction was carried out in a nitrogen-filled dry box.[5] To a suspension of 7-methylbenzo[*h*]quinolinyl palladium acetate dimer (**S17**) (22.5 mg, 3.15 × 10^{-5} mol, 1.00 equiv) in CH_2Cl_2 (1.5 mL) at –50 °C was added XeF_2 (5.3 mg, 3.2 × 10^{-5} mol, 1.0 equiv) in one portion. The reaction mixture was stirred for 10 minutes before TMSCl (8.20 μL, 7.02 mg, 6.46 × 10^{-5} mol, 2.05 equiv) was added. The reaction mixture was stirred at –50 °C for 5 minutes before solvent was removed in vacuo at –50 °C. The resulting solid was triturated with pre-cooled Et_2O (–50 °C) to afford 19.8 mg of the title compound as a dark red solid (80% yield) in a 8:1 ratio of isomers (7-methylbenzo[*h*]quinolinyl ligands head to tail vs. head to head).

^{1}H-NMR (500 MHz, CD_2Cl_2, 23 ºC, δ): Major Isomer : 7.75 (d, J = 4.9 Hz, 2H), 7.67 (d, J = 7.8 Hz, 2H), 7.38 (d, J = 8.8 Hz, 2H), 7.27 (d, J = 7.8 Hz, 2H), 7.13 (d, J = 8.8 Hz, 2H), 7.05 (d, J = 8.3 Hz, 2H), 6.77 (dd, J = 7.3 Hz, J = 5.9 Hz, 2H), 2.68 (s, 6H), 2.54 (s, 6H). Minor Isomer : 7.84 (d, J = 7.8 Hz, 2H), 7.61 (d, J = 8.8 Hz, 2H), 7.00 (d, J = 8.3 Hz, 2H), 2.70 (s, 6H), 2.61 (s, 6H). UV-VIS Spectroscopy (CH_2Cl_2, 0 ˚C): 622 nm (ε = 3.00 × 10^3 M^{-1} cm^{-1}); 498 nm (ε = 7.37 × 10^3 M^{-1} cm^{-1}); 414 nm (ε = 3.74 × 10^4 M^{-1} cm^{-1}).

10-chlorobenzo[*h*]quinoline-7-carbaldehyde (19b)

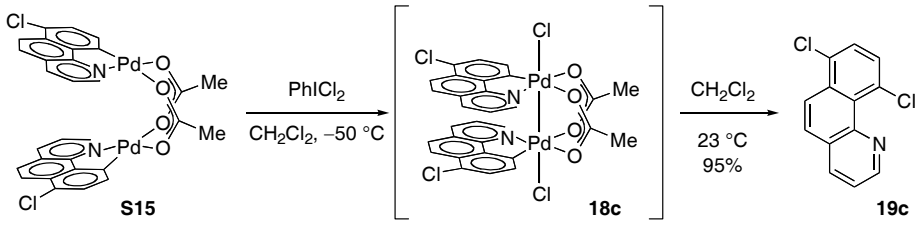


[5] Oxidation was carried out with XeF_2 in lieu of $PhICl_2$ to simplify purification of **18e**.

This reaction was carried out in a nitrogen-filled dry box. To a solution of 7-formylbenzo[*h*]quinolinyl palladium acetate dimer (**S14**) (44.2 mg, 5.95×10^{-5} mol, 1.00 equiv) in CH_2Cl_2 (3.0 mL) at –50 °C was added $PhICl_2$ (16.3 mg, 5.95×10^{-5} mol, 1.00 equiv) in one portion. The reaction mixture was stirred at –50 °C for 5 minutes before being warmed to 23 °C, at which time the reaction mixture was stirred for 6 hours. Solvent was removed in vacuo and the residue was purified by chromatography on silica gel eluting with hexanes / EtOAc (6:1 (v/v)) to afford 13.1 mg of the title compound as a colorless solid (91% yield).

R_f = 0.18 (hexanes / EtOAc (9 / 1, v / v)). ^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 10.48 (s, 1H), 9.29 (d, *J* = 9.2 Hz, 1H), 9.14 (d, *J* = 2.3 Hz, 1H), 8.24 (d, *J* = 6.9 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 9.2 Hz, 1H), 7.63 (dd, *J* = 7.8 Hz, 4.1 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 192.35, 148.07, 145.95, 139.66, 135.64, 135.48, 134.59, 130.98, 129.94, 129.86, 128.01, 127.29, 123.05, 122.46. Mass Spectrometry: HRMS-FIA (m/z): calcd for $[C_{14}H_8NOCl+H]^+$, 242.0367. Found, 242.0372.

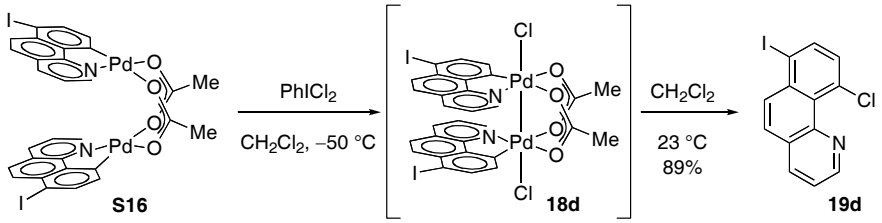
7,10-dichlorobenzo[*h*]quinoline (19c)



This reaction was carried out in a nitrogen-filled dry box. To a solution of 7-chlorobenzo[*h*]quinolinyl palladium acetate dimer (**S15**) (33.0 mg, 4.36×10^{-5} mol, 1.00 equiv) in CH_2Cl_2 (3.0 mL) at –50 °C was added $PhICl_2$ (12.0 mg, 4.36×10^{-5} mol, 1.00 equiv) in one portion. The reaction mixture was stirred at –50 °C for 5 minutes before being warmed to 23 °C, at which time the reaction mixture was stirred for 6 hours. Solvent was removed in vacuo and the residue was purified by chromatography on silica gel eluting with hexanes / EtOAc (6:1 (v/v)) to afford 10.3 mg of the title compound as a colorless solid (95% yield).

R_f = 0.41 (hexanes / EtOAc (9 / 1, v / v)). ^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 9.14 (dd, *J* = 4.1 Hz, *J* = 1.4 Hz, 1H), 8.35 (d, *J* = 9.2 Hz, 1H), 8.23 (dd, *J* = 8.2 Hz, *J* = 1.8 Hz, 1H), 7.84 (d, *J* = 9.2 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.61 (dd, *J* = 8.2 Hz, 4.6 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 148.99, 146.18, 135.74, 132.99, 131.24, 131.12, 128.89, 128.16, 127.91, 127.41, 123.85, 122.31. Mass Spectrometry: LRMS-FIA (m/z): calcd for $[C_{13}H_7NCl_2+H]^+$, 248.0028. Found, 228.0022.

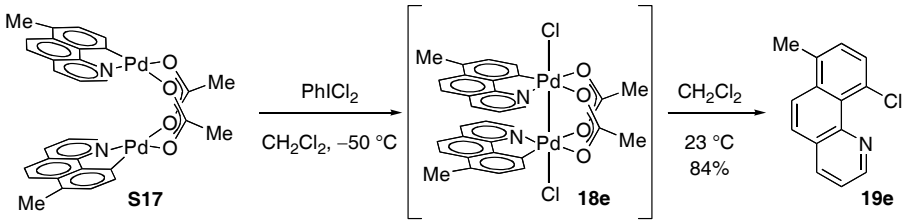
10-chloro-7-iodobenzo[*h*]quinoline (19d)



This reaction was carried out in a vial wrapped in electrical tape to exclude light and in a nitrogen-filled dry box. To a solution of 7-iodobenzo[*h*]quinolinyl palladium acetate dimer (**S16**) (35.5 mg, 3.78×10^{-5} mol, 1.00 equiv) in CH_2Cl_2 (1.5 mL) at –50 °C was added $PhICl_2$ (10.4 mg, 3.78×10^{-5} mol, 1.00 equiv) in one portion. The reaction mixture was stirred at –50 °C for 5 minutes before being warmed to 23 °C, at which time the reaction mixture was stirred for 6 hours. Solvent was removed in vacuo and the residue was purified by chromatography on silica gel eluting with hexanes / EtOAc (6:1 (v/v)) to afford 11.4 mg of the title compound as a colorless solid (89% yield). Compound **19d** gradually turns from colorless to red upon exposure to light and thus was stored in the dark.

R_f = 0.41 (hexanes / EtOAc (9 / 1, v / v)). ^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 9.13 (dd, J = 4.1 Hz, J = 1.4 Hz, 1H), 8.22 (dd, J = 8.2 Hz, J = 1.8 Hz, 1H), 8.19 (d, J = 9.2 Hz, 1H), 8.15 (d, J = 8.2 Hz, 1H), 7.79 (d, J = 9.2 Hz, 1H), 7.59 (dd, J = 8.2 Hz, J = 4.6 Hz, 1H), 7.54 (d, J = 8.2 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 147.97, 146.13, 138.93, 136.42, 135.69, 133.57, 132.29, 132.22, 128.32, 127.27, 122.27, 110.67, 98.00. Mass Spectrometry: LRMS-FIA (m/z): calcd for $[C_{13}H_7NICl+H]^+$, 339.9385. Found, 339.9390.

10-chloro-7-methylbenzo[*h*]quinoline (19e)

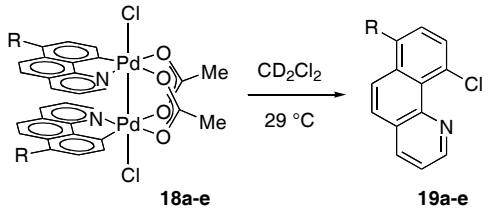


This reaction was carried out in a nitrogen-filled dry box. To a solution of 7-methylbenzo[*h*]quinolinyl palladium acetate dimer (**S17**) (19.2 mg, 2.68×10^{-5} mol, 1.00 equiv) in CH_2Cl_2 (2.0 mL) at –50 °C was added $PhICl_2$ (7.4 mg, 2.7×10^{-5} mol, 1.0 equiv) in one portion. The reaction mixture was stirred at –50 °C for 5 minutes before being warmed to 23 °C, at which time the reaction mixture was stirred for 6 hours. Solvent was removed in vacuo and the residue was purified by chromatography on silica gel eluting with hexanes / EtOAc (6:1 (v/v)) to afford 5.1 mg of the title compound as a colorless solid (84% yield).

R_f = 0.32 (hexanes / EtOAc (9 / 1, v / v)). ^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 9.11 (dd, J = 4.4 Hz, J = 2.0 Hz, 1H), 8.19 (dd, J = 8.3 Hz, J = 1.9 Hz, 1H), 8.01 (d, J = 9.3 Hz, 1H), 7.75 (d, J = 9.3 Hz, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.56 (dd, J = 8.3 Hz, J = 4.4 Hz, 1H), 7.43 (d, J = 7.8 Hz, 1H), 2.75 (s, 3H). ^{13}C-

NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 147.51, 146.73, 135.49, 134.83, 133.63, 130.98, 130.17, 129.08, 127.57, 125.10, 126.36, 124.01, 121.66, 20.19. Mass Spectrometry: HRMS-FIA (m/z): calcd for $[C_{14}H_{10}NCl+H]^+$, 228.0575. Found, 228.0585.

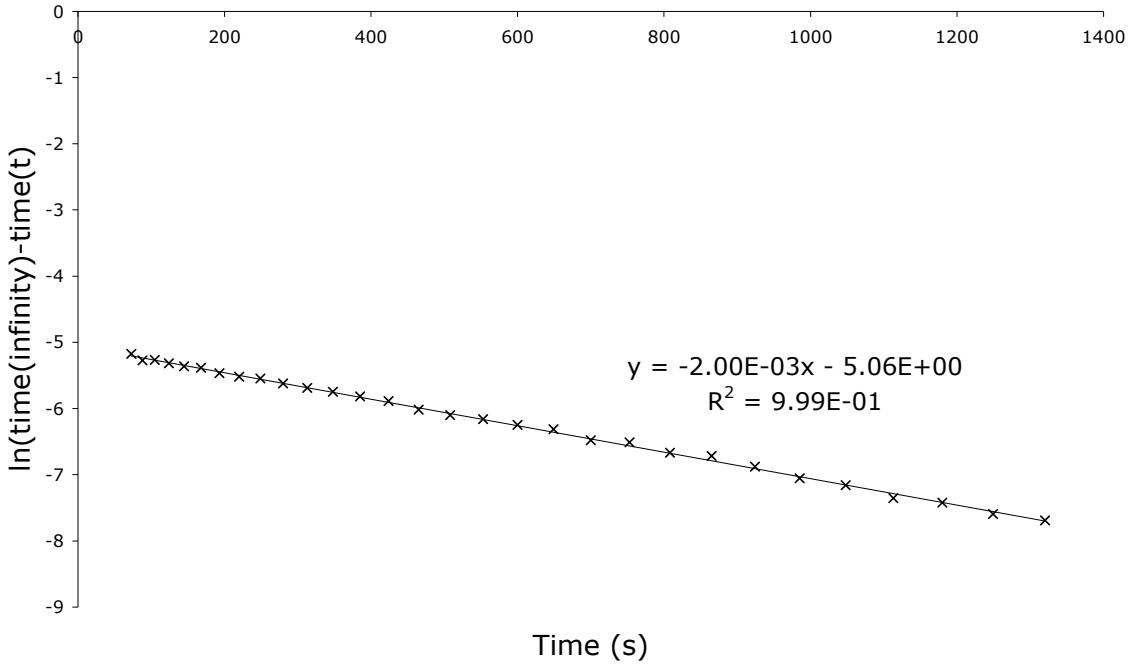
Hammett Study Based on Benzo[*h*]quinolinyl Ligand Substitution



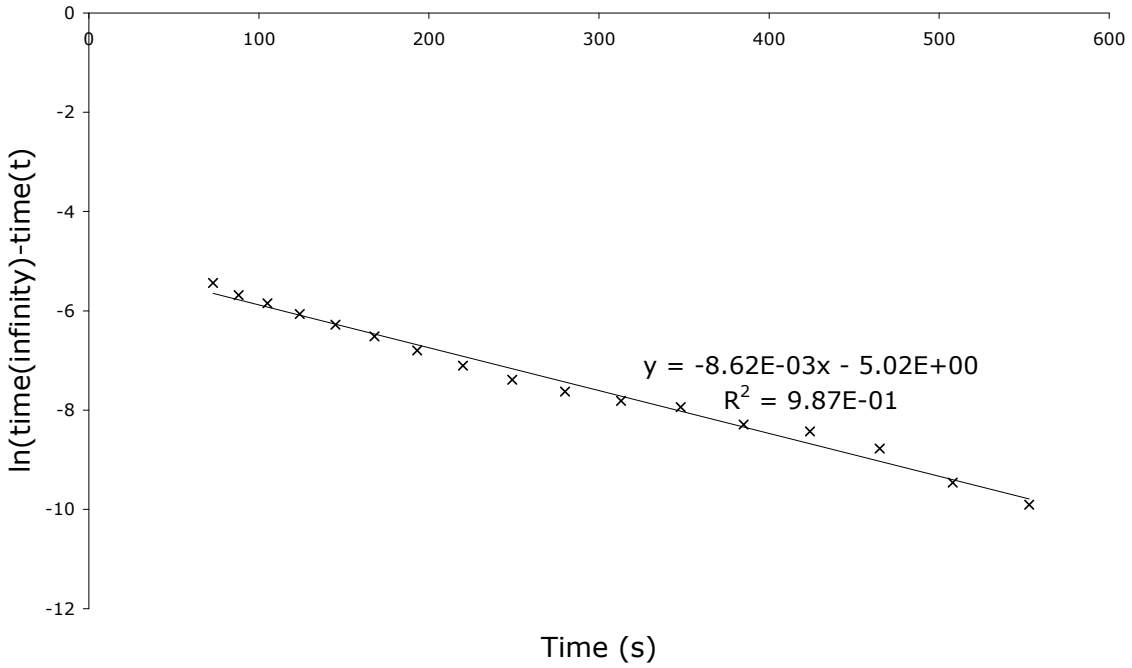
18a-e **19a-e**

Stock solutions of compounds **9**, **S14**, **S15**, **S16**, and **S17** (22.0 mM) and $PhICl_2$ (22.0 mM) were prepared in CD_2Cl_2. Samples were prepared by combining the appropriate palladium containing solution (200 μL), $PhICl_2$ solution (200 μL), and CD_2Cl_2 (300 μL) in a nitrogen-purged NMR tube. ^1H NMR spectra were obtained; the evolution of compounds **19a-e** was monitored by the ^1H NMR signals (R = H, 9.12 ppm; R = CHO, 9.14 ppm; R = Cl, 9.14 ppm; R = I, 9.13 ppm; R = Me, 9.11 ppm). These signals were integrated relative the residual proton signal from CD_2Cl_2. Time points were excluded for those spectra in which the monitored peak overlapped with other peaks. Since evolution of product was measured, linear natural log plots were obtained by using an infinite time point set to 100% yield. In each case, the reactions were followed to greater than 3 half-lives. Data were fitted to a first order regression; plots, slopes, and R^2 values are reported below.

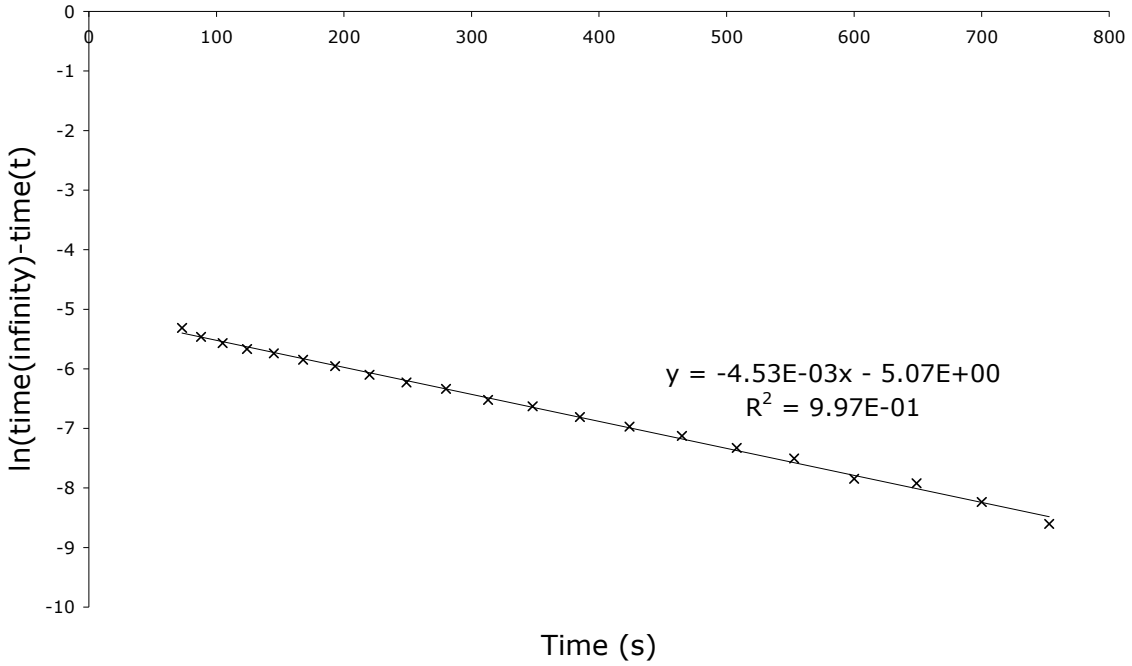
Formation of **19a** (R = H)



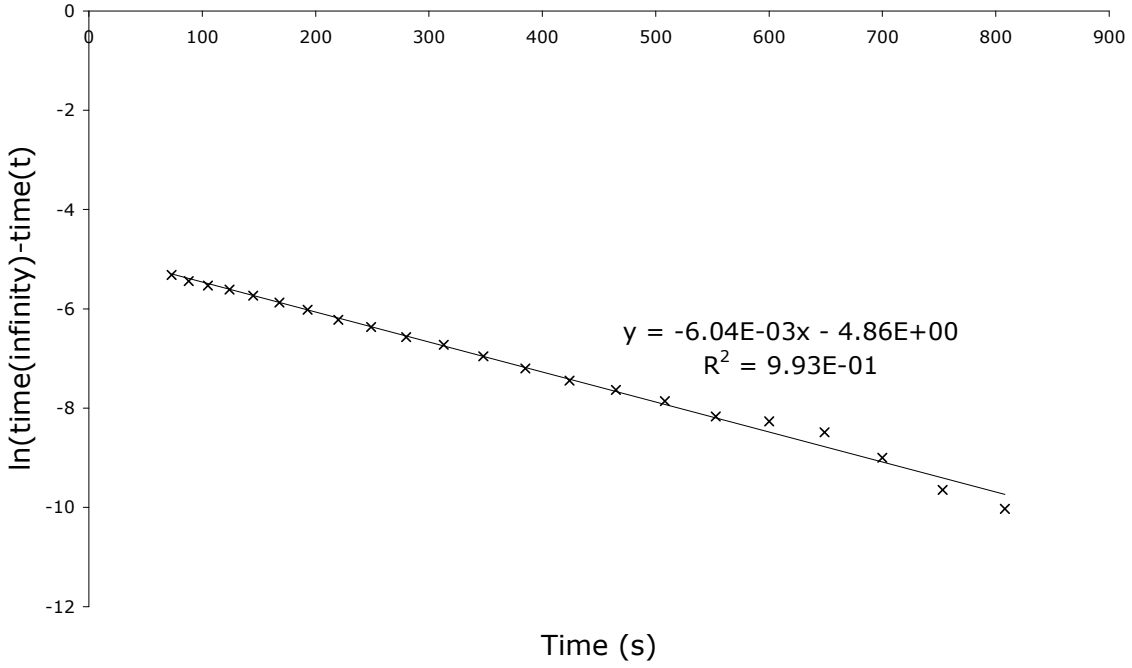
Formation of **19b** (R = CHO)

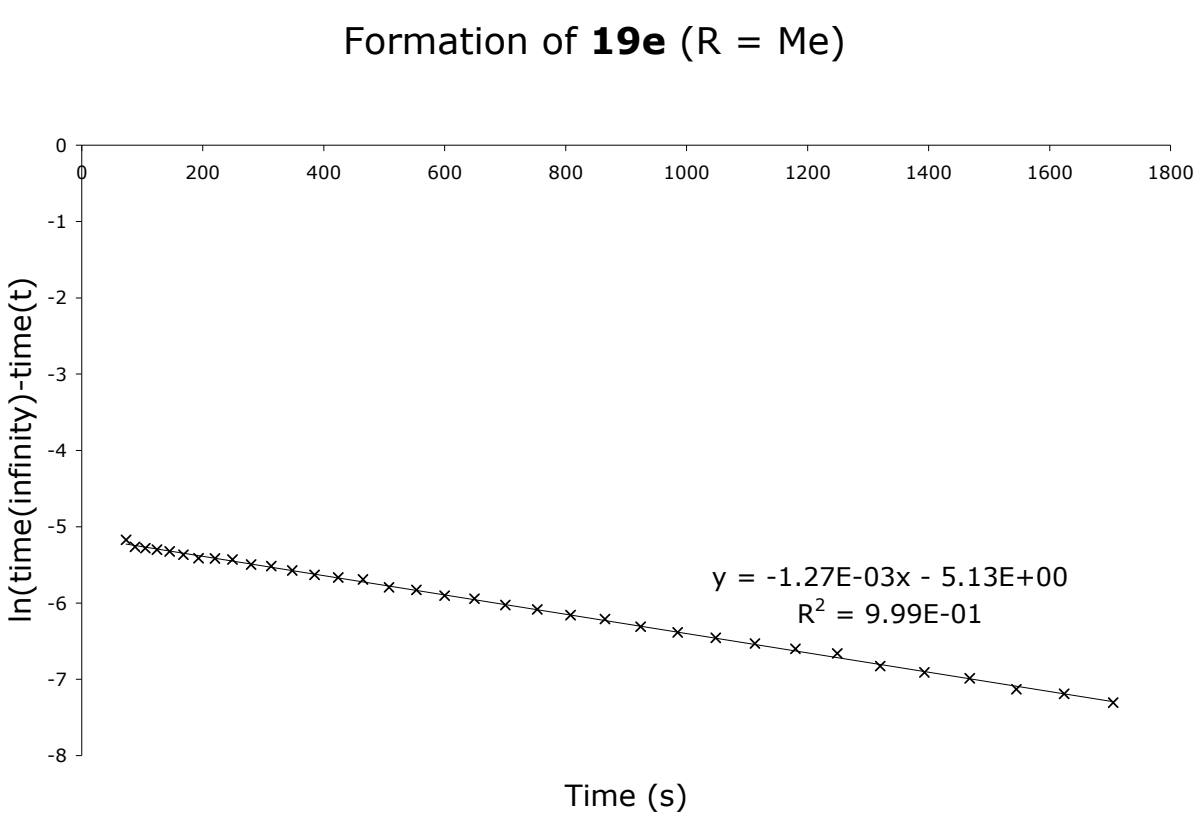


Formation of **19c** (R = Cl)

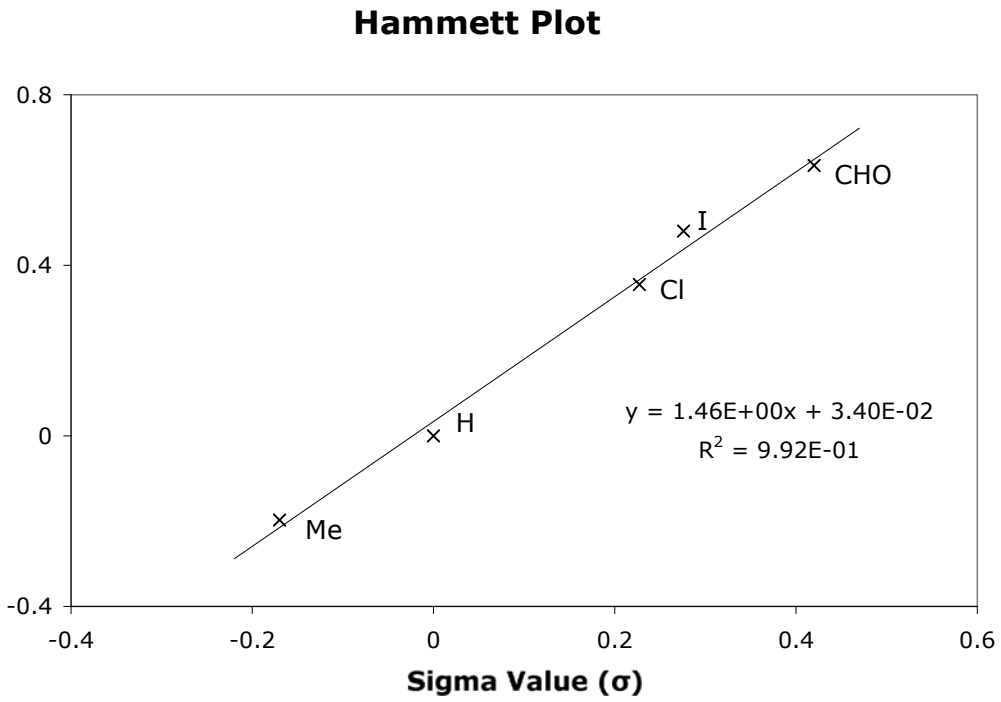


Formation of **19d** (R = I)



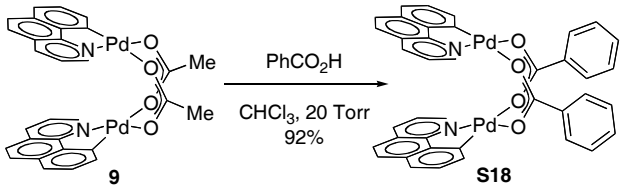


Substituent (R)	σ	k (s^{-1})
CHO	0.42	8.62×10^{-3}
I	0.276	6.04×10^{-3}
Cl	0.227	4.53×10^{-3}
H	0.0	2.00×10^{-3}
CH_3	–0.17	1.27×10^{-3}



Hammett Analysis Based on Substitution of Bridging Carboxylate Ligand (Data Pertaining to Figure 3)

Benzo[h]quinolinyl palladium benzoate dimer (S18)

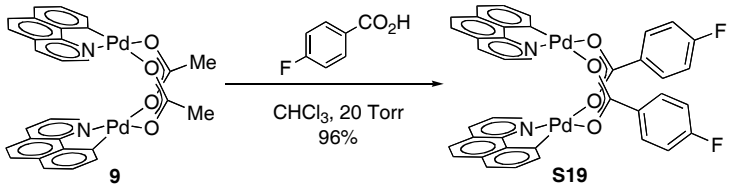


To a suspension of benzo[*h*]quinolinyl palladium acetate dimer (**9**) (306 mg, 0.445 mmol, 1.00 equiv) in $CHCl_3$ (15 mL) at 23 °C was added benzoic acid (109 mg, 0.890 mmol, 2.00 equiv) and the reaction mixture was stirred at 23 °C for 1h. Solvent was removed in vacuo. The residue was taken up in $CHCl_3$ (15 mL) and solvent was removed in vacuo four times, sequentially in order to remove all AcOH. The residue was triturated in Et_2O (10 mL) to afford 332 mg of the title compound as a yellow solid (92% yield) in a 20:1 ratio of isomers (benzo[*h*]quinolinyl ligands head to tail vs. head to head).

Melting Point: >250 ˚C. ^{1}H-NMR (600 MHz, $CDCl_3$, 23 ºC, δ): Major Isomer : 8.36 (d, *J* = 8.2 Hz, 4H), 7.92 (d, *J* = 5.1 Hz, 2H), 7.53 (ddd, *J* = 6.7 Hz, *J* = 6.7 Hz, *J* = 1.3 Hz, 2H), 7.48–7.46 (m, 6H), 7.25 (d, *J* = 8.8 Hz, 2H), 7.21 (t, *J* = 4.4 Hz, 2H), 7.10 (d, *J* = 4.2 Hz, 4H), 7.00 (d, *J* = 8.6 Hz, 2H), 6.47 (dd, *J* = 8.1 Hz, *J* = 5.3 Hz, 2H). Minor Isomer: 8.18 (d, *J* = 5.6 Hz, 2H), 7.72 (d, *J* = 7.9 Hz, 2H), 7.03 (d, *J* = 8.6 Hz, 2H), 6.97 (d, *J* = 6.9 Hz, 2H). 6.87–6.81 (m, 4H). ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC, δ): Major

Isomer: 176.16, 153.13, 148.92, 148.72, 139.81, 135.51, 135.07, 132.15, 131.32, 130.26, 128.88, 127.86, 127.69, 127.46, 124.76, 122.64, 121.75, 119.69. UV-VIS Spectroscopy (CH_2Cl_2, 23 ˚C): 377 nm ($\varepsilon = 4.54 \times 10^3$ M^{-1} cm^{-1}); 291 nm ($\varepsilon = 2.01 \times 10^4$ M^{-1} cm^{-1}); 273 nm ($\varepsilon = 2.26 \times 10^4$ M^{-1} cm^{-1}).

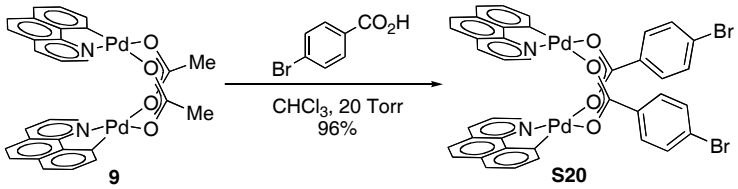
Benzo[*h*]quinolinyl palladium *para*-fluorobenzoate dimer (S19)



To a suspension of benzo[*h*]quinolinyl palladium acetate dimer (**9**) (300 mg, 0.436 mmol, 1.00 equiv) in $CHCl_3$ (25 mL) at 23 °C was added *para*-fluorobenzoic acid (122 mg, 0.872 mmol, 2.00 equiv) and the reaction mixture was stirred at 23 °C for 1h. Solvent was removed in vacuo. The residue was taken up in $CHCl_3$ (25 mL) and solvent was removed in vacuo four times, sequentially in order to remove all AcOH. The residue was triturated in Et_2O (10 mL) to afford 355 mg of the title compound as a yellow solid (96% yield) in a 16:1 ratio of isomers (benzo[*h*]quinolinyl ligands head to tail vs. head to head).

Melting Point: >250 ˚C. ^{1}H-NMR (600 MHz, CD_2Cl_2, 23 ºC, δ): Major Isomer : 8.36 (dd, J = 5.6 Hz, J = 2.1 Hz, 4H), 7.88 (dd, J = 5.3 Hz, J = 1.3 Hz, 2H), 7.47 (dd, J = 8.1 Hz, J = 1.2 Hz, 2H), 7.26 (d, J = 8.6 Hz, 2H), 7.22 (d, J = 7.9 Hz, 2H), 7.14–7.10 (m, 6H), 7.04 (d, J = 7.2 Hz, 2H), 7.01 (d, J = 8.6 Hz, 2H), 6.47 (dd, J = 5.3 Hz, J = 1.2 Hz, 2H). Minor Isomer : 8.38 (dd, J = 5.6 Hz, J = 2.1 Hz, 4H), 8.14 (d, J = 5.1 Hz, 2H), 7.73 (d, J = 7.9 Hz, 2H), 7.44 (d, J = 8.1 Hz, J = 7.2 Hz, 2H), 6.88 (dd, J = 7.9 Hz, J = 5.1 Hz, 2H), 6.83 (dd, J = 7.6 Hz, J = 7.6 Hz, 4H), 6.78 (d, J = 7.6 Hz, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC, δ): Major Isomer: 175.48, 166.42, 164.42, 153.37, 149.04, 148.80, 140.10, 135.88, 132.76 (d, J = 9.2 Hz), 132.17, 129.00, 128.05, 127.88, 125.33, 123.29, 122.24, 120.34, 115.14 (d, J = 22.0 Hz). Minor Isomer: 147.43, 130.45, 120.60. ^{19}F-NMR (375 MHz, $CDCl_3$, 23 ºC, δ): –109.53. UV-VIS Spectroscopy (CH_2Cl_2, 23 ˚C): 377 nm ($\varepsilon = 3.63 \times 10^3$ M^{-1} cm^{-1}); 290 nm ($\varepsilon = 1.59 \times 10^4$ M^{-1} cm^{-1}).

Benzo[h]quinolinyl palladium *para*-bromobenzoate dimer (S20)

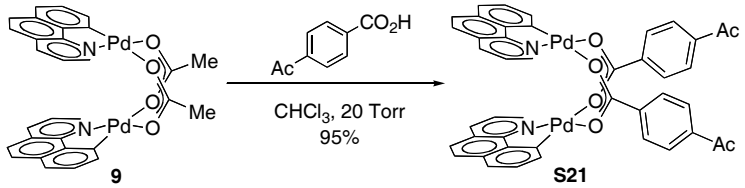


To a suspension of benzo[*h*]quinolinyl palladium acetate dimer (**9**) (209 mg, 0.304 mmol, 1.00 equiv) in $CHCl_3$ (25 mL) at 23 °C was added *para*-bromobenzoic acid (122 mg, 0.608 mmol, 2.00 equiv) and the reaction mixture was stirred at 23 °C for 1h. Solvent was removed in vacuo. The residue was taken up in $CHCl_3$ (50 mL) and solvent was removed in vacuo four times, sequentially in order to remove all AcOH. The residue was triturated in Et_2O (10 mL) to afford 262 mg of the title compound as a yellow solid (96%

yield) in a 26:1 ratio of isomers (benzo[*h*]quinolinyl ligands head to tail vs. head to head).

Melting Point: >250 ˚C. ^{1}H-NMR (600 MHz, $CDCl_3$, 23 ºC, δ): Major Isomer : 8.21 (d, *J* = 8.3 Hz, 4H), 7.86 (d, *J* = 5.3 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 4H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.10 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 2H), 7.02–7.00 (m, 4H), 6.48 (dd, *J* = 7.9 Hz, *J* = 5.1 Hz, 2H). Minor Isomer : 8.11 (d, *J* = 5.5 Hz, 2H), 7.74 (d, *J* = 5.3 Hz, 2H). Compound **S22** is insufficiently soluble in organic solvents which do not displace a bridging acetate for ^{13}C-NMR to be obtained. UV-VIS Spectroscopy (CH_2Cl_2, 23 ˚C): 376 nm (ε = 4.22 × 10^3 M^{-1} cm^{-1}); 293 nm (ε = 1.82 × 10^4 M^{-1} cm^{-1}).

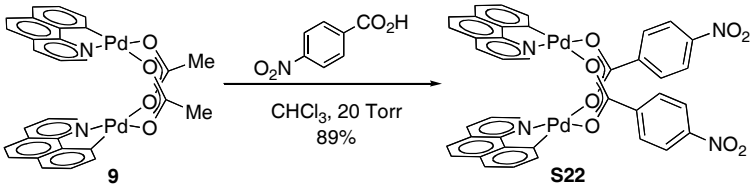
Benzo[*h*]quinolinyl palladium *para*-acetylbenzoate dimer (S21)



To a suspension of benzo[*h*]quinolinyl palladium acetate dimer **9** (347 mg, 0.505 mmol, 1.00 equiv) in $CHCl_3$ (25 mL) at 23 °C was added *para*-acetylbenzoic acid (166 mg, 1.01 mmol, 2.00 equiv) and the reaction mixture was stirred at 23 °C for 1h. Solvent was removed in vacuo. The residue was taken up in $CHCl_3$ (50 mL) and solvent was removed in vacuo four times, sequentially in order to remove all AcOH. The residue was triturated in Et_2O (10 mL) to afford 430 mg of the title compound as a yellow solid (95% yield) in a 27:1 ratio of isomers (benzo[*h*]quinolinyl ligands head to tail vs. head to head).

Melting Point: >250 ˚C. ^{1}H-NMR (600 MHz, CD_2Cl_2, 23 ºC, δ): Major Isomer : 8.43 (d, *J* = 8.2 Hz, 4H), 8.05 (d, *J* = 8.1 Hz, 4H), 7.88 (d, *J* = 5.1 Hz, 2H), 7.48 (d, *J* = 7.9 Hz, 2H), 7.27 (d, *J* = 8.9 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.11 (dd, *J* = 7.5 Hz, *J* = 7.5 Hz, 2H), 7.03–7.01 (m, 4H), 6.44 (dd, *J* = 7.9 Hz, *J* = 5.1 Hz, 2H), 2.67 (s, 6H). Minor Isomer : 8.46 (d, *J* = 8.2 Hz, 4H), 8.08 (d, *J* = 7.9 Hz, 4H), 7.75 (d, *J* = 5.7 Hz, 2H), 6.90–6.87 (m, 4H), 6.82 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 2H) 6.75 (d, *J* = 7.3 Hz, 2H). ^{13}C-NMR (125 MHz, CD_2Cl_2, 23 ºC, δ): Major Isomer: 198.04, 149.05, 139.69, 135.95, 132.81, 130.56, 129.01, 128.30, 127.93, 123.37, 122.55, 120.48. UV-VIS Spectroscopy (CH_2Cl_2, 23 ˚C): 377 nm (ε = 4.61 × 10^3 M^{-1} cm^{-1}); 290 nm (ε = 2.71 × 10^4 M^{-1} cm^{-1}).

Benzo[*h*]quinolinyl palladium *para*-nitrobenzoate dimer (S22)

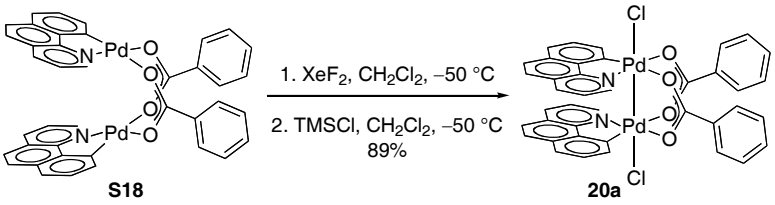


To a suspension of benzo[*h*]quinolinyl palladium acetate dimer (**9**) (182 mg, 0.265 mmol, 1.00 equiv) in

$CHCl_3$ (10 mL) at 23 °C was added *para*-nitrobenzoic acid (88.6 mg, 0.530 mmol, 2.00 equiv) and the reaction mixture was stirred at 23 °C for 1h. Solvent was removed in vacuo. The residue was taken up in $CHCl_3$ (20 mL) and solvent was removed in vacuo four times, sequentially in order to remove all AcOH. The residue was triturated in Et_2O (10 mL) to afford 213 mg of the title compound as a yellow solid (89% yield). A single isomer (benzo[*h*]quinolinyl ligands head to tail) was observed by ^{1}H NMR.

Melting Point: >250 ˚C. ^{1}H-NMR (500 MHz, CD_2Cl_2, 23 ºC, δ): Major Isomer : 8.47 (d, J = 8.7 Hz, 4H), 8.32 (d, J = 8.7 Hz, 4H), 7.83 (d, J = 5.0 Hz, 2H), 7.55 (d, J = 7.8 Hz, 2H), 7.31 (d, J = 8.7 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 7.11 (dd, J = 7.3 Hz, J = 7.3 Hz, 2H), 7.07 (d, J = 8.7 Hz, 2H), 6.95 (d, J = 7.3 Hz, 2H), 6.53 (dd, J = 8.2 Hz, J = 5.5 Hz, 2H). Compound **S24** is insufficiently soluble in organic solvents which do not displace a bridging acetate for ^{13}C-NMR to be obtained. UV-VIS Spectroscopy (CH_2Cl_2, 23 ˚C): 375 nm (ε = 4.82 × 10^3 M^{-1} cm^{-1}); 272 nm (ε = 4.60 × 10^4 M^{-1} cm^{-1}).

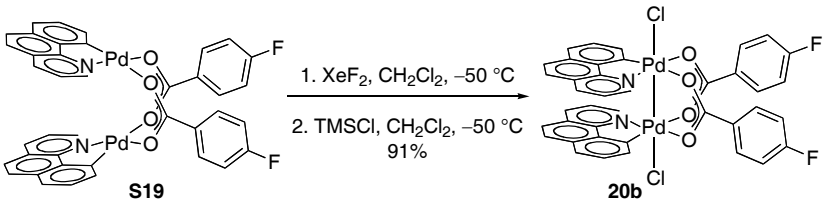
Benzo[*h*]quinolinyl chloro palladium(III) benzoate dimer (20a)



This reaction was carried out in a nitrogen-filled dry box. To a suspension of benzo[*h*]quinolinyl palladium benzoate dimer (**S18**) (12.0 mg, 1.48 × 10^{-5} mol, 1.00 equiv) in CH_2Cl_2 (1.0 mL) at –50 °C was added XeF_2 (2.5 mg, 1.5 × 10^{-5} mol, 1.0 equiv) in one portion. After stirring at –50 °C for 10 minutes, TMSCl (3.9 μL, 3.0 × 10^{-5} mol, 2.1 equiv) was added. After stirring for 10 minutes, solvent was removed in vacuo and the residue was triturated with Et_2O (1 × 1 mL) to afford 11.6 mg of the title compound as a dark red solid (89% yield) as a 14 : 1 mixture of isomers (benzo[*h*]quinolinyl ligand head-to-tail versus head-to-head). Upon isolation as a solid, compound **20a** would not redissolve in any common organic solvent and thus **20a** was characterized by ^{1}H NMR and UV-vis without removal of solvent or purification of the reaction mixture.

^{1}H-NMR (500 MHz, CD_2Cl_2, 23 ºC, δ): Major Isomer : 8.44, (d, J = 6.8 Hz, 4H), 7.88 (d, J = 5.4 Hz, 2H), 7.72 (d, J = 7.3 Hz, 2H), 7.69 (d, J = 7.8 Hz, 2H), 7.57 (dd, J = 7.8 Hz, J = 7.8 Hz, 4H), 7.41–7.34 (m, 6H), 7.20 (d, J = 8.8 Hz, 2H), 7.14 (d, J = 7.8 Hz, 2H), 6.81 (dd, J = 7.8 Hz, J = 5.9 Hz, 2H). Minor Isomer : 8.48 (d, J = 6.8 Hz, 4H), 8.07 (d, J = 7.8 Hz, 2H), 7.50 (dd, J = 7.8 Hz, J = 7.8 Hz, 4H), 7.31 (d, J = 5.0, 2H), 6.90 (d, J = 7.8 Hz, 2H). UV-VIS Spectroscopy (CH_2Cl_2, 0 ˚C): 586 nm (ε = 9.34 × 10^2 M^{-1} cm^{-1}); 496 nm (ε = 2.17 × 10^3 M^{-1} cm^{-1}); 418 nm (ε = 7.78 × 10^3 M^{-1} cm^{-1}).

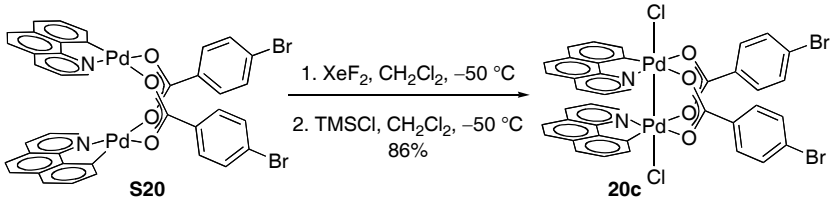
Benzo[*h*]quinolinyl chloro palladium(III) *para*-fluorobenzoate dimer (20b)



This reaction was carried out in a nitrogen-filled dry box. To a suspension of benzo[*h*]quinolinyl palladium *para*-fluorobenzoate dimer (**S19**) (15.5 mg, 1.83×10^{-5} mol, 1.00 equiv) in CH_2Cl_2 (1.0 mL) at –50 °C was added XeF_2 (3.1 mg, 1.83×10^{-5} mol, 1.00 equiv) in one portion. After stirring at –50 °C for 10 minutes, TMSCl (4.8 μL, 3.75×10^{-5} mol, 2.05 equiv) was added. After stirring for 10 minutes, solvent was removed in vacuo and the residue was triturated with Et_2O (1 × 1 mL) to afford 15.3 mg of the title compound as a dark red solid (91% yield) as a 15 : 1 ratio of isomers (benzo[*h*]quinolinyl ligand head-to-tail versus head-to-head). Upon isolation as a solid, compound **20b** would not redissolve in any common organic solvent and thus **20b** was characterized by ^{1}H NMR and UV-vis without removal of solvent or purification of the reaction mixture.

^{1}H-NMR (500 MHz, CD_2Cl_2, –50 ºC, δ): Major Isomer : 8.47 (dd, J = 8.8 Hz, J = 5.9 Hz, 4H), 7.85 (d, J = 5.4 Hz, 2H), 7.71–7.68 (m, 2H), 7.40–7.33 (m, 6H), 7.25 (dd, J = 8.8 Hz, J = 8.8 Hz, 4H), 7.19 (d, J = 8.8 Hz, 2H), 7.12 (d, J = 8.8 Hz, 2H), 6.80 (dd, J = 8.3 Hz, J = 5.9 Hz, 2H). Minor Isomer : 8.10 (d, J = 5.9 Hz, 2H), 6.87 (d, J = 7.8 Hz, 2H). UV-VIS Spectroscopy (CH_2Cl_2, 0 ˚C): 590 nm ($\varepsilon = 1.91 \times 10^3$ M^{-1} cm^{-1}); 492 nm ($\varepsilon = 4.61 \times 10^3$ M^{-1} cm^{-1}); 418 nm ($\varepsilon = 1.54 \times 10^4$ M^{-1} cm^{-1}).

Benzo[*h*]quinolinyl chloro palladium(III) *para*-bromobenzoate dimer (20c)

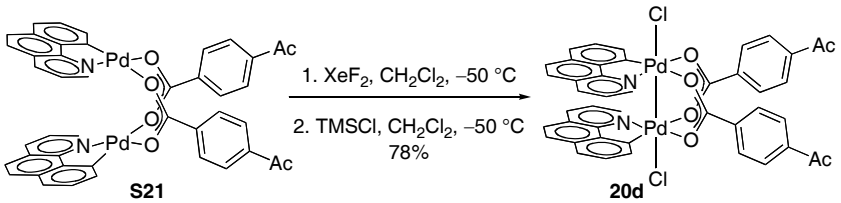


This reaction was carried out in a nitrogen-filled dry box. To a suspension of benzo[*h*]quinolinyl palladium *para*-bromobenzoate dimer (**S20**) (11.8 mg, 1.22×10^{-5} mol, 1.00 equiv) in CH_2Cl_2 (1.0 mL) at –50 °C was added XeF_2 (2.1 mg, 1.2×10^{-5} mol, 1.0 equiv) in one portion. After stirring at –50 °C for 10 minutes, TMSCl (3.2 μL, 2.5×10^{-5} mol, 2.1 equiv) was added. After stirring for 10 minutes, solvent was removed in vacuo and the residue was triturated with Et_2O (1 × 1 mL) to afford 10.9 mg of the title compound as a dark red solid (86% yield) as a single isomer. Upon isolation as a solid, compound **20c** would not redissolve in any common organic solvent and thus **20c** was characterized by ^{1}H NMR and UV-vis without removal of solvent or purification of the reaction mixture.

^{1}H-NMR (500 MHz, CD_2Cl_2, –50 ºC, δ): 8.32 (d, J = 7.8 Hz, 2H), 7.83 (br s, 2H), 7.72–7.70 (m, 6H), 7.38–7.33 (m, 6H), 7.17 (d, J = 8.3 Hz, 2H), 7.08 (d, J = 7.3 Hz, 2H), 6.80 (br s, 2H). UV-VIS

Spectroscopy (CH_2Cl_2, 0 ˚C): 590 nm (ε = 3.02 × 10^3 M^{-1} cm^{-1}); 500 nm (ε = 6.72 × 10^3 M^{-1} cm^{-1}); 418 nm (ε = 2.53 × 10^4 M^{-1} cm^{-1}).

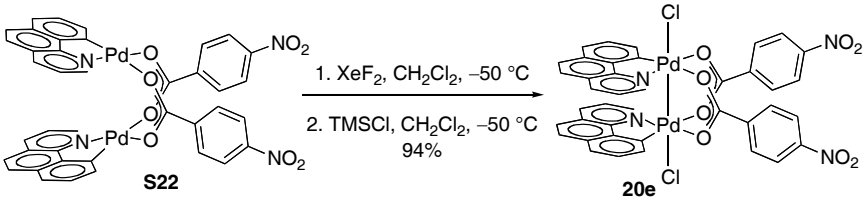
Benzo[*h*]quinolinyl chloro palladium(III) *para*-acetylbenzoate dimer (20d)



This reaction was carried out in a nitrogen-filled dry box. To a suspension of benzo[*h*]quinolinyl palladium *para*-acetylbenzoate dimer (**S21**) (16.4 mg, 1.83 × 10^{-5} mol, 1.00 equiv) in CH_2Cl_2 (1.0 mL) at –50 °C was added XeF_2 (3.1 mg, 1.8 × 10^{-5} mol, 1.0 equiv) in one portion. After stirring at –50 °C for 10 minutes, TMSCl (4.8 μL, 3.8 × 10^{-5} mol, 2.1 equiv) was added. After stirring for 10 minutes, solvent was removed in vacuo and the residue was triturated with Et_2O (1 × 1 mL) to afford 13.8 mg of the title compound as a dark red solid (78% yield). Upon isolation as a solid, compound **19d** would not redissolve in any common organic solvent and thus **20d** was characterized by ^{1}H NMR and UV-vis without removal of solvent or purification of the reaction mixture.

^{1}H-NMR (500 MHz, CD_2Cl_2, –50 ºC, δ): Major Isomer : 8.53 (d, *J* = 8.3 Hz, 4H), 8.16 (d, *J* = 8.8 Hz, 4H), 7.84 (br s, 2H), 7.66 (d, *J* = 7.3 Hz, 2H), 7.41–7.29 (m, 6H), 7.12 (d, *J* = 8.8 Hz, 2H), 7.09 (d, *J* = 7.3 Hz, 2H), 6.79 (br s, 2H), 2.69 (s, 6H). Minor Isomer : 7.98 (d, *J* = 8.8 Hz, 4H), 7.49 (dd, *J* = 7.8 Hz, *J* = 7.8 Hz, 2H), 7.023 (d, *J* = 7.3 Hz, 2H), 2.62 (s, 6H). UV-VIS Spectroscopy (CH_2Cl_2, 0 ˚C): 596 nm (ε = 3.10 × 10^3 M^{-1} cm^{-1}); 494 nm (ε = 7.03 × 10^3 M^{-1} cm^{-1}); 420 nm (ε = 2.25 × 10^4 M^{-1} cm^{-1}).

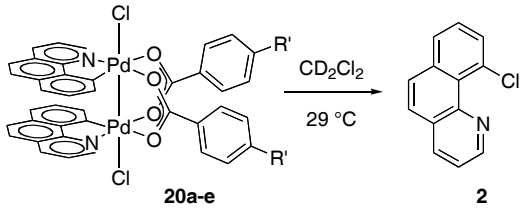
Benzo[*h*]quinolinyl chloro palladium(III) *para*-nitrobenzoate dimer (20e)



This reaction was carried out in a nitrogen-filled dry box. To a suspension of benzo[*h*]quinolinyl palladium *para*-nitrobenzoate dimer (**S22**) (12.8 mg, 1.42 × 10^{-5} mol, 1.00 equiv) in CH_2Cl_2 (1.0 mL) at –50 °C was added XeF_2 (2.4 mg, 1.4 × 10^{-5} mol, 1.0 equiv) in one portion. After stirring at –50 °C for 10 minutes, TMSCl (3.6 μL, 1.5 × 10^{-5} mol, 2.1 equiv) was added. After stirring for 10 minutes, solvent was removed in vacuo and the residue was triturated with Et_2O (1 × 1 mL) to afford 13.0 mg of the title compound as a dark red solid (94% yield). Upon isolation as a solid, compound **20e** would not redissolve in any common organic solvent and thus **20e** was characterized by ^{1}H NMR and UV-vis without removal of solvent or purification of the reaction mixture.

^{1}H-NMR (500 MHz, CD_2Cl_2, –50 ºC, δ): Major Isomer : 8.64 (d, *J* = 8.3 Hz, 2H), 8.40 (d, *J* = 8.8 Hz, 2H), 8.32 (d, *J* = 8.8 Hz, 2H), 8.26 (d, *J* = 9.1 Hz, 2H), 7.87 (d, *J* = 5.4 Hz, 2H), 7.78 (d, *J* = 7.8 Hz, 2H), 7.46–7.37 (m, 6H), 7.25 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 7.3 Hz, 2H), 7.86 (dd, *J* = 7.8 Hz, *J* = 5.0 Hz, 2H). UV-VIS Spectroscopy (CH_2Cl_2, 0 ˚C): 600 nm (ε = 1.28 × 10^3 M^{-1} cm^{-1}); 500 nm (ε = 2.98 × 10^3 M^{-1} cm^{-1}); 422 nm (ε = 1.14 × 10^4 M^{-1} cm^{-1}).

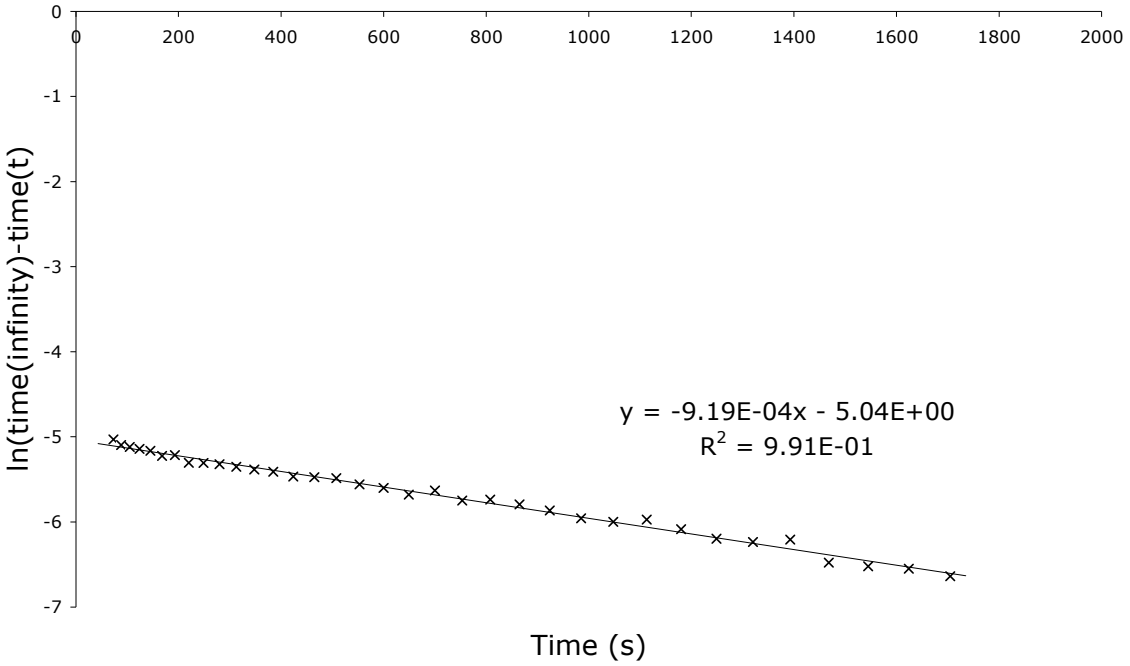
Hammett Study Based on Bridging Benzoate Substitution



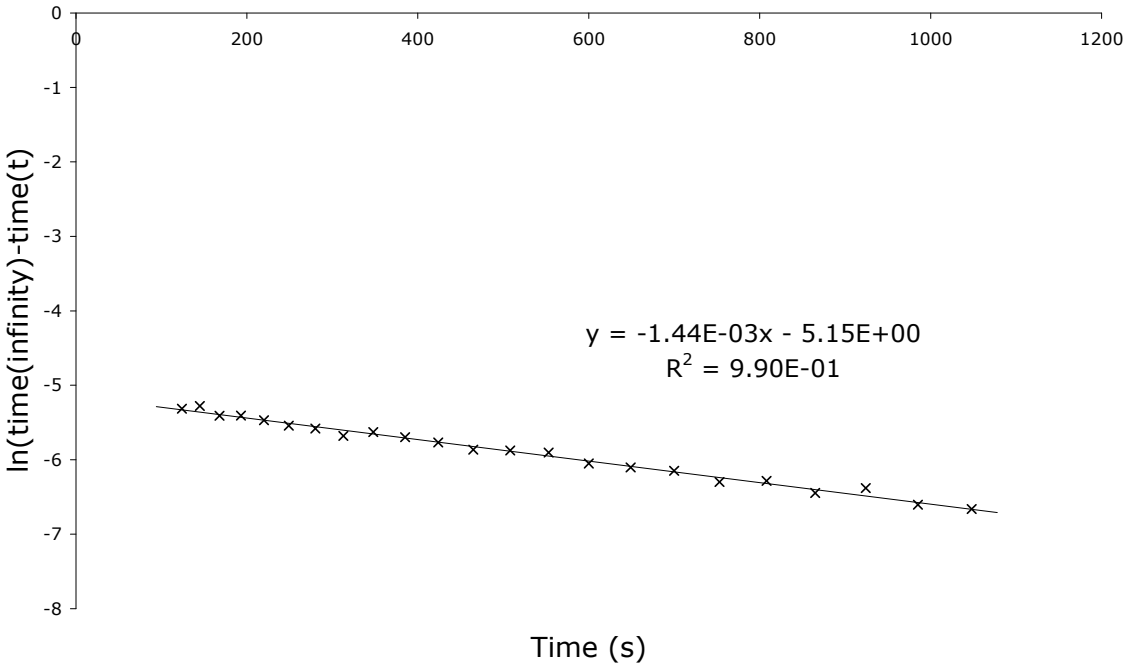
20a-e **2**

10-Chlorobenzo[*h*]quinoline (**2**) was observed upon warming solutions of compounds **20a-e** to 23 °C. Yields were as follows: from **20a**, 91%; from **20b**, 94%; from **20c**, 92%; from **20d**, 96%; and from **20e**, 91%. The rate of formation of 10-chlorobenzo[*h*]quinoline (**2**) was determined by the following procedure. Stock solutions of compounds **S18**–**22** (22.0 mM) and $PhICl_2$ (44.0 mM) were prepared in CD_2Cl_2. Samples were prepared by combining the relevant compound (**S18**–**22**) solution (200 μL), $PhICl_2$ solution (100 μL), and CD_2Cl_2 (400 μL) in a nitrogen-purged NMR tube. ^{1}H NMR spectra were obtained; the evolution of compound **2** was monitored by the ^{1}H NMR signal at 9.12 ppm. These signals were integrated relative the residual proton signal from CD_2Cl_2. Time points were excluded for those spectra in which the monitored peak overlapped with other peaks. Since evolution of product was measured, linear natural log plots were obtained by using an infinite time point set to 100% yield. In each case, the reactions were followed to greater than 3 half-lives. Data were fitted to a first order regression; plots, slopes, and R^2 values are reported below.

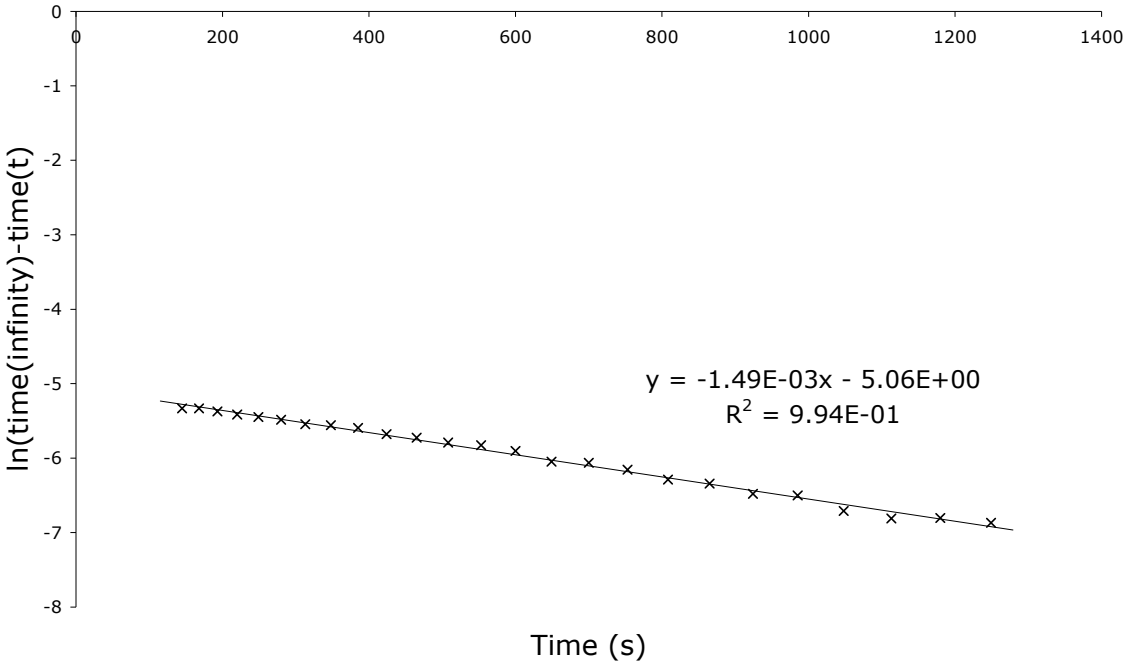
Formation of **2** from **20a** (R = H)



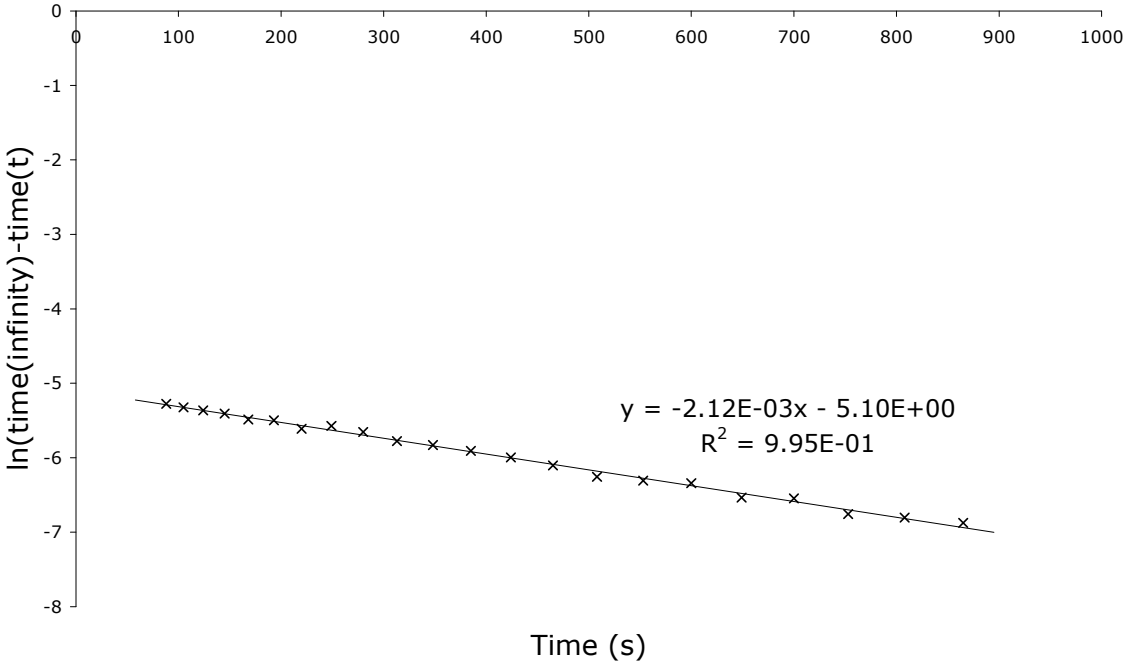
Formation of **2** from **20b** (R = F)

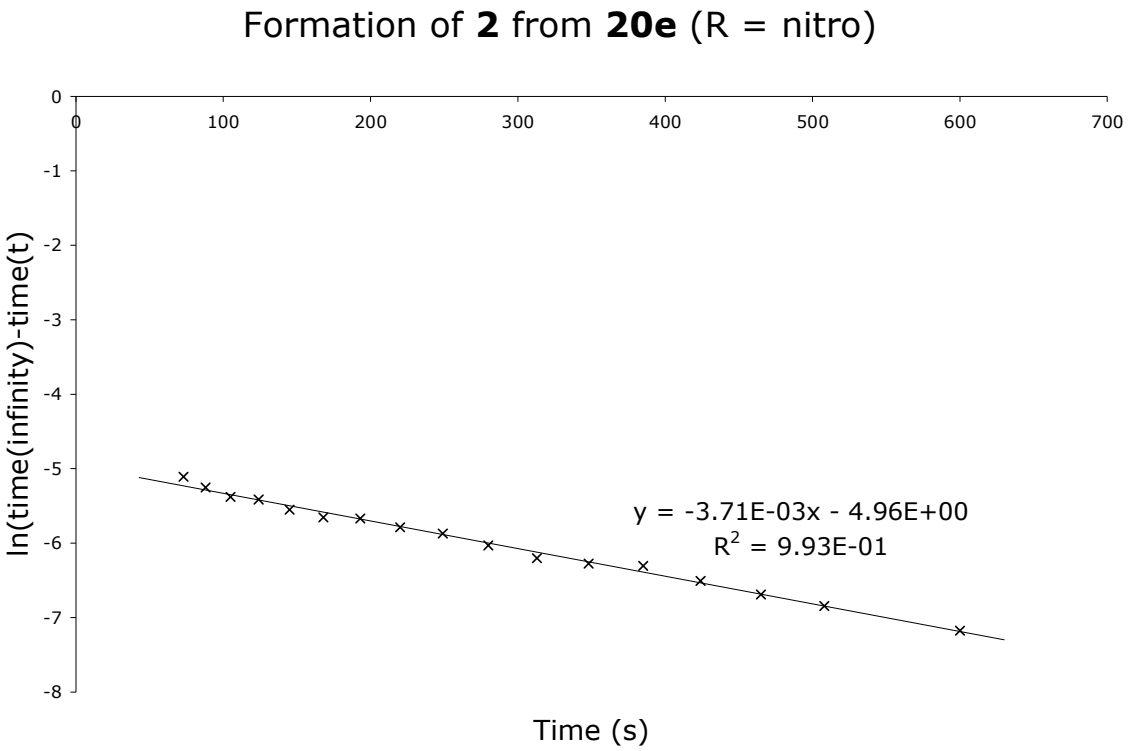


Formation of **2** from **20c** (R = Br)

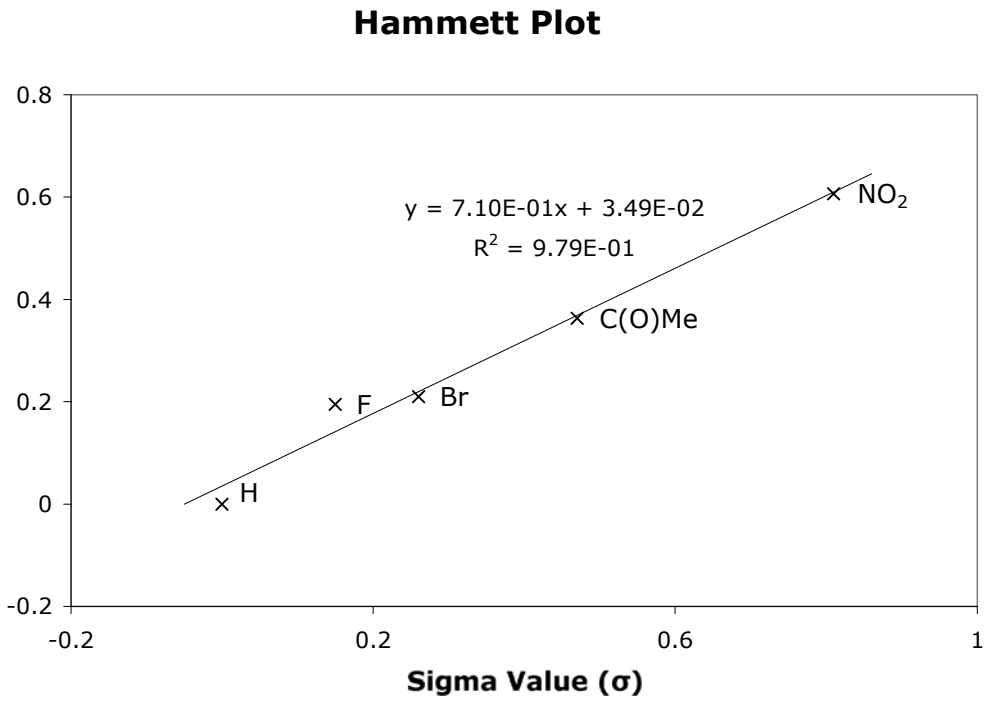


Formation of **2** from **20d** (R = Ac)

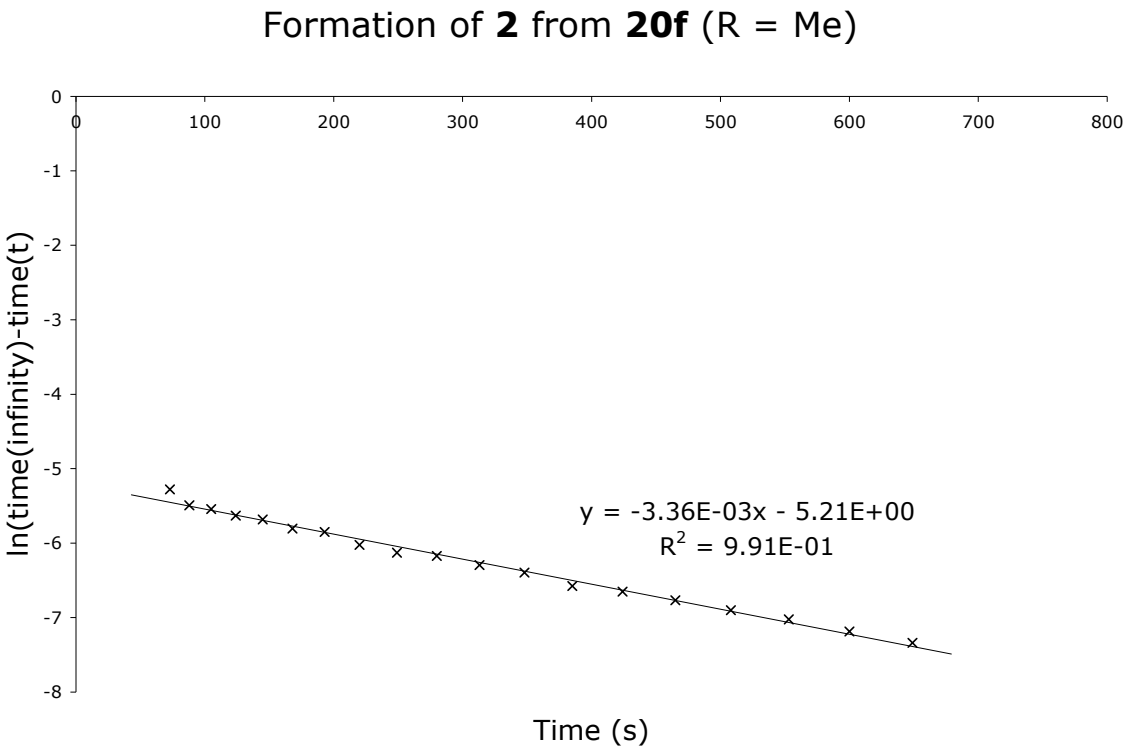


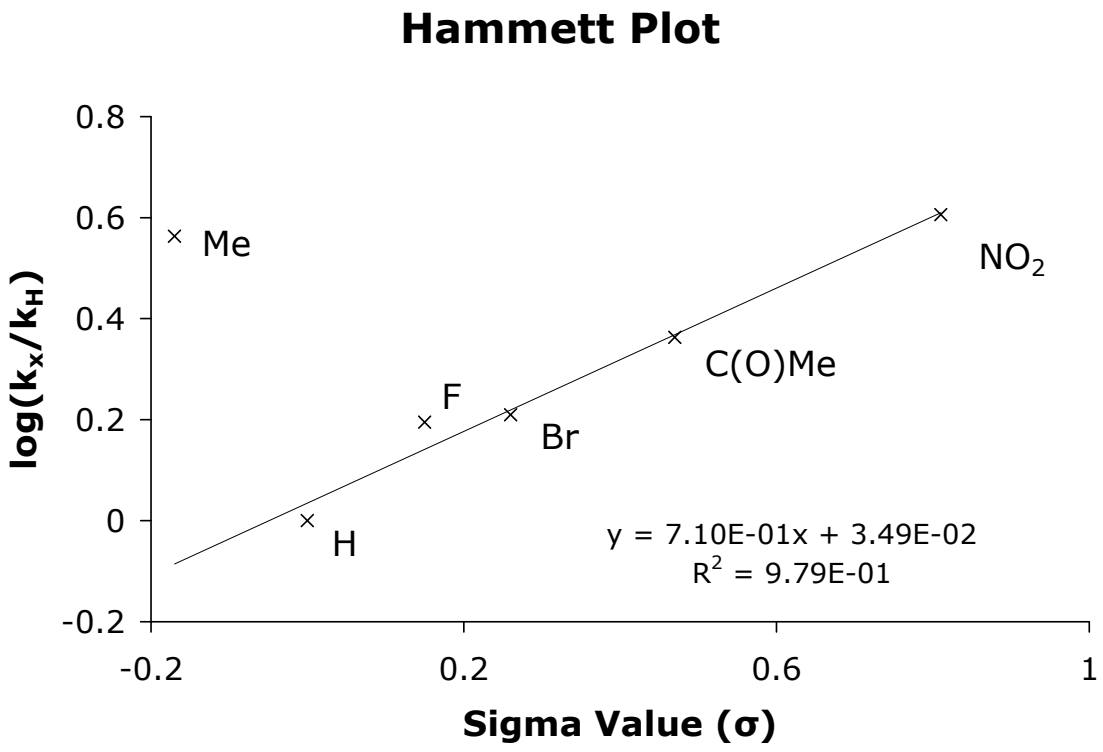


Substituent (R)	σ	k (s^{-1})
NO_2	0.81	3.71×10^{-3}
Ac	0.47	2.12×10^{-3}
Br	0.26	1.49×10^{-3}
F	0.15	1.44×10^{-3}
H	0.00	9.19×10^{-4}



Decomposition of complexes **20f** (*p*-Me) and **20g** (*p*-OMe) with bridging benzoate ligands substituted with electron donating ligands was not linearly correlated with Hammett σ-value. Complex **20g** decomposed too rapidly for accurate determination of rate under the conditions used to evaluate decomposition of **20a**–**f**. Kinetics of the decomposition of **20f** are shown below with a Hammett plot showing the non-linear behavior of rate of decomposition when **20f** is included.



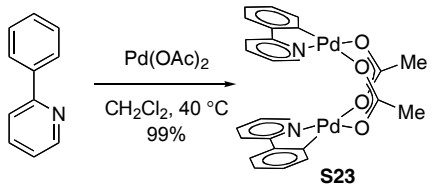


The non-linear relationship between rate of C–Cl bond formation and Hammett σ-value for

complexes bearing electron-rich benzoate ligands may be a reflection of the ligand fluxionality that we have documented at carboxylate-bridged dinuclear Pd(III) complexes. The equilibrium distribution of carboxylate in the bridging versus apical positions is dictated by the differing electronic roles of these two positions (in complex **10**, the partial charge on the oxygen atoms in the bridging acetate ligands are calculated to be –0.64862 and –0.69649, while the partial charges on the oxygen atoms of the apical acetate ligands are calculated to be –0.69832 and –0.70219). Changing the electronics of the carboxylates from electron-poor to electron-rich may alter the distribution of apical versus bridging carboxylate and give rise to the observed non-linearity.

Apical Ligand Experiment (Data Pertaining to Schemes 3, 4, and 5)

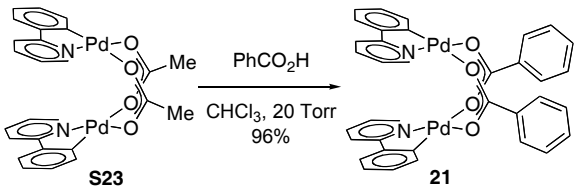
2-Phenylpyridyl palladium acetate dimer (S23)



To a solution of 2-phenylpyridine (3.46 g, 22.3 mmol, 1.00 equiv) in CH_2Cl_2 (220 mL) at 23 °C is added palladium acetate (5.00 g, 22.3 mmol, 1.00 equiv). After stirring for 3 h, the orange solution is concentrated in vacuo and the solid residue is triturated with Et_2O (70 mL). The solid isolated by vacuum filtration and washed with Et_2O (2 × 30 mL) to afford 7.07 g of the title compound as an orange-yellow solid (99% yield).

NMR Spectroscopy: ^{1}H NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.89–7.88 (m, 1H), 7.39–7.36 (m, 1H), 7.08 (d, J = 7.8 Hz, 1H), 6.93–6.79 (m, 4H), 6.46–6.43 (m, 1H), 2.27 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 181.6, 150.0, 137.4, 131.8, 128.4, 123.8, 122.3, 121.0, 117.1, 24.9. These spectroscopic data correspond to the reported data.[11]

(2-phenylpyridyl) palladium benzoate dimer (21)

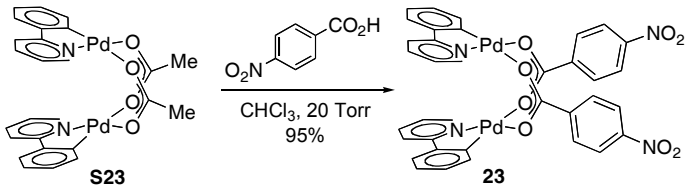


To a suspension of (2-phenylpyridyl) palladium acetate dimer (**S23**) (901 mg, 1.41 mmol, 1.00 equiv) in $CHCl_3$ (50 mL) at 23 °C was added benzoic acid (344 mg, 2.82 mmol, 2.00 equiv) and the reaction mixture was stirred at 23 °C for 1h. Solvent was removed in vacuo. The residue was taken up in $CHCl_3$ (50 mL) and solvent was removed in vacuo three times, sequentially in order to remove all AcOH. The residue was triturated in Et_2O (25 mL) to afford 1.03 g of the title compound as a yellow solid (96%

yield) in a 10:1 ratio of isomers (2-phenylpyridyl ligands head to tail vs. head to head).

Melting Point: >250 ˚C. ^{1}H-NMR (600 MHz, CD_2Cl_2, 23 ºC, δ): Major Isomer : 8.28 (ddd, *J* = 8.2 Hz, *J* = 1.3 Hz, *J* = 0.6 Hz, 4H), 7.98 (ddd, *J* = 5.7 Hz, *J* = 0.7 Hz, *J* =0.7 Hz, 2H), 7.49 (tt, *J* = 7.6 Hz, *J* = 1.3 Hz, 2H), 7.42 (dd, *J* = 7.9 Hz, *J* = 7.9 Hz, 4H), 7.38 (ddd, *J* = 7.6 Hz, *J* = 7.6 Hz, *J* = 1.5 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 6.96 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 2H), 6.90 (dd, *J* = 7.6 Hz, *J* = 1.5 Hz, 2H), 6.80 (ddd, *J* = 7.3 Hz, *J* = 7.3 Hz, *J* = 1.2 Hz, 2H), 6.75 (ddd, *J* = 7.3 Hz, *J* = 7.3 Hz, *J* = 1.5 Hz, 2H), 6.44 (ddd, *J* = 5.7 Hz, *J* = 5.7 Hz, *J* = 1.3 Hz, 2H). Minor Isomer : 8.14 (d, *J* = 6.6 Hz, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 6.67 (dd, *J* = 6.9 Hz, *J* = 6.9 Hz, 2H), 6.61 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC, δ): Major Isomer: 175.48, 164.32, 152.30, 150.09, 144.40, 137.46, 135.51, 131.92, 131.21, 130.19, 128.44, 127.79, 123.79, 122.21, 121.11, 117.08. UV-VIS Spectroscopy (CH_2Cl_2, 23 ˚C): 405 nm (ε = 1.82 × 10^3 M^{-1} cm^{-1}); 343 nm (ε = 4.13 × 10^3 M^{-1} cm^{-1}); 317 nm (ε = 5.70 × 10^3 M^{-1} cm^{-1}); 306 nm (ε = 7.24 × 10^3 M^{-1} cm^{-1}). Mass Spectrometry: LRMS-FIA (m/z): calcd for $[C_{36}H_{26}N_2O_4Pd_2–C_7H_5O_2]^+$, 640.967. Found, 640.969.

(2-phenylpyridyl) palladium *p*-nitrobenzoate dimer (23)

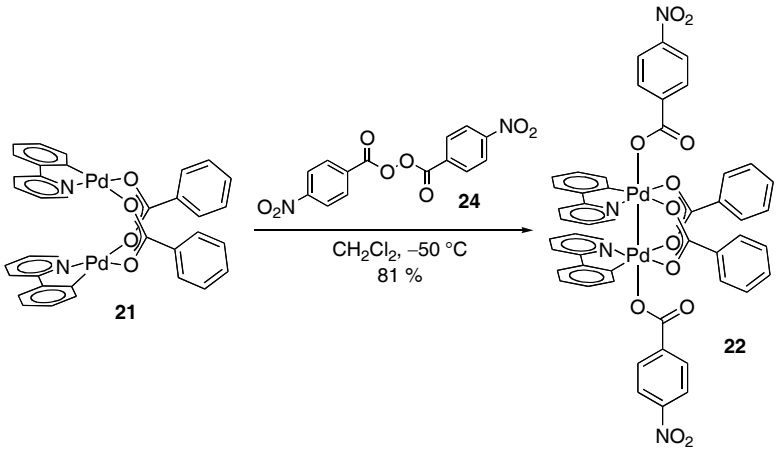


S23 **23**

To a suspension of (2-phenylpyridyl) palladium acetate dimer (**S23**) (1.09 g, 1.70 mmol, 1.00 equiv) in $CHCl_3$ (70 mL) at 23 °C was added *p*-nitrobenzoic acid (568 mg, 3.40 mmol, 2.00 equiv) and the reaction mixture was stirred at 23 °C for 1h. Solvent was removed in vacuo. The residue was taken up in $CHCl_3$ (50 mL) and solvent was removed in vacuo three times, sequentially in order to remove all AcOH. The residue was triturated in Et_2O (25 mL) to afford 1.38 g of the title compound as a yellow solid (95% yield) in a 11:1 ratio of isomers (2-phenylpyridyl ligands head to tail vs. head to head).

Melting Point: >250 ˚C. ^{1}H-NMR (600 MHz, $CDCl_3$, 23 ºC, δ): Major Isomer : 8.40 (d, *J* = 8.8 Hz, 4H), 8.26 (d, *J* = 8.8 Hz, 4H), 7.90 (dd, *J* = 5.7 Hz, *J* = 0.9 Hz, 2H), 7.43 (ddd, *J* = 8.1 Hz, *J* = 8.1 Hz, *J* = 1.6 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 6.93 (dd, *J* = 7.8 Hz, *J* = 1.2 Hz, 2H), 6.85–6.82 (m, 4H), 6.77 (ddd, *J* = 7.0 Hz, *J* = 7.0 Hz, *J* = 1.5 Hz, 2H), 6.49 (ddd, *J* = 7.2 Hz, *J* = 5.6 Hz, *J* = 1.3 Hz, 2H). Minor Isomer : 8.05 (d, *J* = 5.8 Hz, 2H), 7.53 (ddd, *J* = 6.3 Hz, *J* = 6.3 Hz, *J* = 1.6 Hz, 2H), 7.23 (d, *J* = 7.3 Hz, 2H), 6.72 (ddd, *J* = 5.7, *J* = 5.7 Hz, *J* = 5.7 Hz, 2H), 6.68 (d, *J* = 7.8 Hz, 2H), 6.62 (ddd, *J* = 7.5 Hz, *J* = 7.5 Hz, *J* = 1.5 Hz, 2H). ^{13}C-NMR (125 MHz, CD_2Cl_2, 23 ºC, δ): Major Isomer: 173.95, 164.60, 151.57, 150.21, 150.16, 144.90, 141.08, 138.51, 131.77, 131.30, 128.97, 124.72, 123.50, 123.08, 121.90, 117.97. UV-VIS Spectroscopy (CH_2Cl_2, 23 ˚C): 398 nm (ε = 3.36 × 10^3 M^{-1} cm^{-1}); 341 nm (ε = 8.33 × 10^3 M^{-1} cm^{-1}); 317 nm (ε = 1.50 × 10^4 M^{-1} cm^{-1}). Mass Spectrometry: LRMS-FIA (m/z): calcd for $[C_{36}H_{24}N_4O_8Pd_2–C_7H_4NO_4]$, 685.95. Found, 685.94.

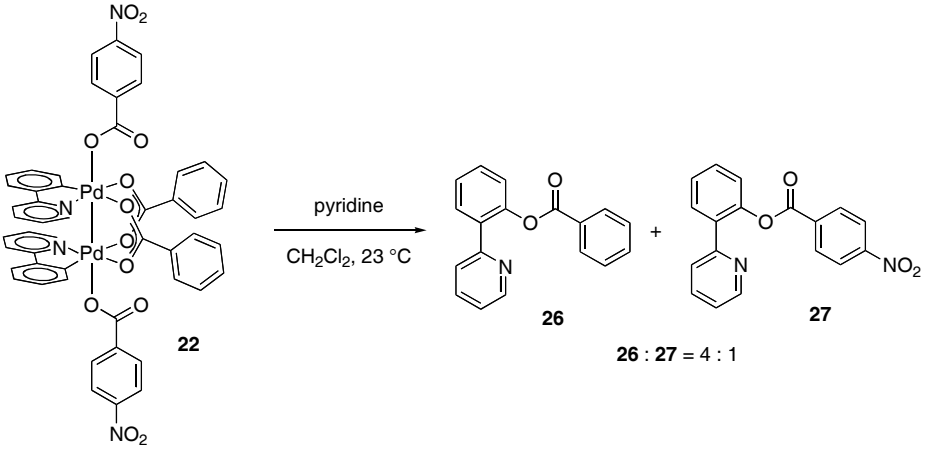
(2-phenylpyridyl) palladium (III) benzoate *p*-nitrobenzoate dimer (22)



This reaction was carried out in a nitrogen-filled dry box. To a solution of (2-phenylpyridyl) palladium benzoate dimer (**21**) (24.4 mg, 3.20×10^{-5} mol, 1.00 equiv) in CH_2Cl_2 (2.0 mL) at –50 °C was added bis(*p*-nitrobenzoyl) peroxide (**24**) (10.6 mg, 3.20×10^{-5} mol, 1.00 equiv) in one portion. The reaction mixture was stirred at –50 °C for 1 h. Solvent was removed in vacuo and the residue was triturated with Et_2O at –50 °C. The residue was dried in vacuo at –50 °C to afford 28.4 mg of the title compound as a dark red solid (81% yield) in a 10:1 ratio of isomers (2-phenylpyridyl ligands head to tail vs. head to head).

^{1}H-NMR (500 MHz, CD_2Cl_2, –50 °C, δ): Major Isomer : 8.38 (dd, J = 7.3 Hz, J = 1.5 Hz, 4H), 8.11 (dd, J = 5.9 Hz, J = 1.0 Hz, 2H), 8.08 (d, J = 8.8 Hz, 4H), 7.92 (d, J = 9.3 Hz, 4H), 7.71–7.65 (m, 4H), 7.54 (dd, J = 7.8 Hz, J = 7.8 Hz, 4H), 7.32 (d, J = 8.3 Hz, 2H), 7.12 (dd, J = 7.8 Hz, J = 1.0 Hz, 2H), 7.05–6.97 (m, 6H), 6.71 (ddd, J = 5.9 Hz, J = 1.0 Hz, J = 1.0 Hz, 2H). Minor Isomer : 8.58 (d, 4H), 7.75–7.71 (m), 7.24 (dd, J = 7.8 Hz, J = 7.8 Hz, 4H). UV-VIS Spectroscopy (CH_2Cl_2, 0 °C): 434 nm ($\varepsilon = 2.09 \times 10^4$ M^{-1} cm^{-1}).

Thermolysis of (2-phenylpyridyl) palladium (III) benzoate *p*-nitrobenzoate dimer (22)

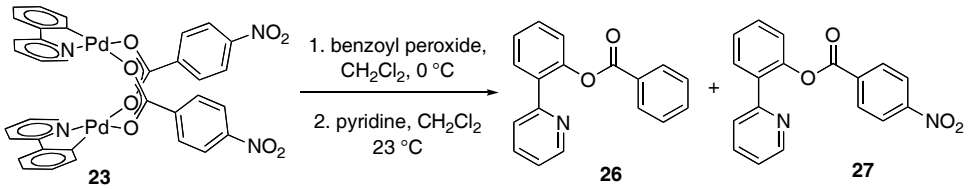


This reaction was carried out in a nitrogen-filled dry box. To a solution of (2-phenylpyridyl) palladium (III) benzoate *p*-nitrobenzoate dimer (**22**) (95.9 mg, 8.75×10^{-5} mol, 1.00 equiv) in CH_2Cl_2 (6.0 mL) at –50 °C was added pyridine (141 μL, 1.75 mmol, 20.0 equiv) in one portion. The reaction mixture was allowed to warm to 23 °C, at which time the reaction mixture was stirred for 2 hours. Solvent was removed in vacuo. The residue was passed through a plug of silica gel eluting with hexanes / EtOAc (1:1 (v/v)). Solvent was removed in vacuo and ^{1}H NMR of the residue indicated a 4 : 1 mixture of **26** and **27**. Separation of **26** and **27** was achieved by chromatography on silica gel eluting with hexanes / EtOAc (4:1 (v/v)) to afford 12.0 mg of **26** (50% yield) and 3.3 mg of **27** (12% yield).

2-(pyridin-2-yl)phenyl benzoate (**26**): R_f = 0.19 (hexanes / EtOAc (4 / 1)). ^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 8.60 (d, *J* = 4.1 Hz, 1H), 8.08 (d, *J* = 7.8 Hz, 2H), 7.78 (dd, *J* = 7.8 Hz, *J* = 1.4 Hz, 1H), 7.64–7.56 (m, 3H), 7.50–7.45 (m, 3H), 7.41 (ddd, *J* = 7.8 Hz, *J* = 7.8 Hz, *J* = 0.9 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.16 (dd, *J* = 7.3 Hz, *J* = 6.0 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 165.16, 155.58, 149.62, 136.13, 133.43, 133.33, 130.92, 130.17, 129.71, 129.50, 128.48, 126.40, 123.70, 123.31, 122.12, 110.67. Mass Spectrometry: HRMS-FIA (m/z): calcd for $[C_{18}H_{13}NO_2+H]^+$, 276.1019 Found, 276.1019. These spectroscopic data correspond to those reported in the literature.[12]

2-(pyridin-2-yl)phenyl 4-nitrobenzoate (**27**): R_f = 0.11 (hexanes / EtOAc (4 / 1)). ^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 8.49 (d, *J* = 4.1 Hz, 1H), 8.30 (d, *J* = 8.7 Hz, 2H), 8.24 (d, *J* = 8.7 Hz, 2H), 7.74 (dd, *J* = 7.8 Hz, *J* = 1.4 Hz, 1H), 7.67 (ddd, *J* = 7.8 Hz, *J* = 7.8 Hz, *J* = 1.4 Hz, 1H), 7.54–7.50 (m, 2H), 7.44 (dd, *J* = 7.3 Hz, 7.3 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.17 (dd, *J* = 6.9 Hz, 5.0 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 163.46, 155.60, 150.74, 149.45, 147.93, 136.41, 135.05, 132.97, 131.25, 130.87, 129.90, 126.87, 123.60, 123.43, 123.19, 122.31. Mass Spectrometry: HRMS-FIA (m/z): calcd for $[C_{18}H_{12}N_2O_4+H]^+$, 321.0870 Found, 321.0873. These spectroscopic data correspond to those reported in the literature.[12]

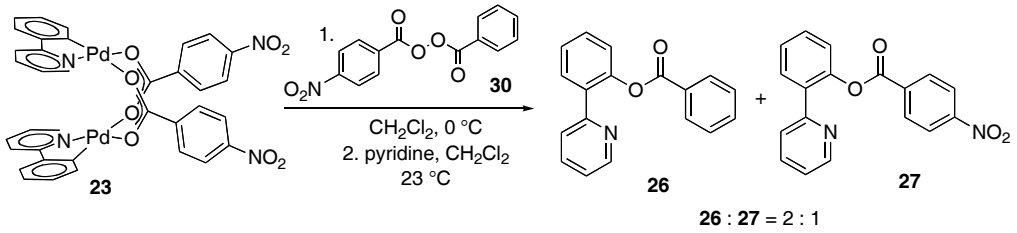
Reaction of (2-phenylpyridyl) palladium *p*-nitrobenzoate dimer (23) with benzoyl peroxide (25)



This reaction was carried out in a nitrogen-filled dry box. To a solution of (2-phenylpyridyl) palladium *p*-nitrobenzoate dimer (**23**) (32.8 mg, 3.84×10^{-5} mol, 1.00 equiv) in CH_2Cl_2 (3.0 mL) at 0 °C was added benzoyl peroxide (**25**) (9.3 mg, 3.8×10^{-5} mol, 1.0 equiv) in one portion. The reaction mixture was stirred at 0 °C for 5 minutes, at which time the reaction mixture was dark red. Pyridine (62.0 μL, 7.68×10^{-4} mol, 20.0 equiv) was added in one portion and the reaction mixture was allowed to warm to 23 °C, at which time the reaction mixture was stirred for 1.5 hours. Solvent was removed in vacuo. The residue was passed through a plug of silica gel elting with hexanes / EtOAc (1:1 (v/v)). Solvent was removed in vacuo and ^{1}H NMR of the residue indicated a 4 : 1 mixture of **26** and **27**.

The spectroscopic data of **26** and **27** correspond to those reported above.

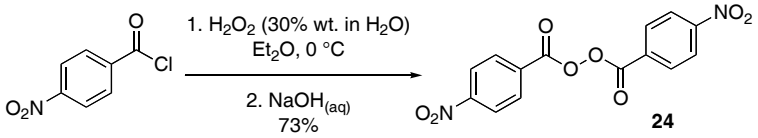
Reaction of (2-phenylpyridyl) palladium *p*-nitrobenzoate dimer (23) with benzoyl(nitrobenzoyl) peroxide (30)



This reaction was carried out in a nitrogen-filled dry box. To a solution of (2-phenylpyridyl) palladium *p*-nitrobenzoate dimer (**23**) (36.0 mg, 4.22×10^{-5} mol, 1.00 equiv) in CH_2Cl_2 (4.0 mL) at –50 °C was added benzoyl(*p*-nitrobenzoyl) peroxide (**30**) (12.1 mg, 4.22×10^{-5} mol, 1.00 equiv) in one portion. The reaction mixture was stirred at –50 °C for 45 minutes, at which time the reaction mixture was dark red. Pyridine (68.0 μL, 8.44×10^{-4} mol, 20.0 equiv) was added in one portion and the reaction mixture was allowed to warm to 23 °C, at which time the reaction mixture was stirred for 2 hours. Solvent was removed in vacuo. The residue was passed through a plug of silica gel elting with hexanes / EtOAc (1:1 (v/v)). Solvent was removed in vacuo and ^{1}H NMR of the residue indicated a 2 : 1 mixture of **26** and **27**.

The spectroscopic data of **26** and **27** correspond to those reported above.

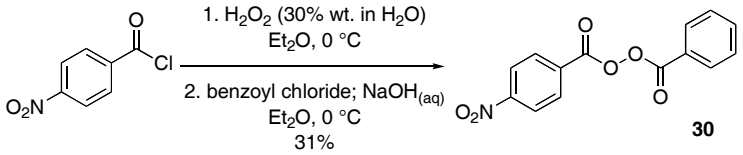
Bis(*p*-nitrobenzoyl) peroxide (24)



To a solution of 4-nitrobenzoyl chloride (5.66 g, 30.5 mmol, 1.00 equiv) in Et_2O (10 mL) at 0 °C was added 30% $H_2O_{2(aq)}$ (1.95 mL, 2.16 g, 19.1 mmol, 0.626 equiv) dropwise over 10 minutes. After stirring for 10 minutes, NaOH (1.5 g, 37.5 mmol, 1.23 equiv) in H_2O (10mL) was added dropwise over 20 minutes. The resulting precipitate was isolated by vacuum filtration, washed with H_2O (3 × 10 mL) and Et_2O (3 × 10 mL), and dried to afford 4.61 g of the title compound as a colorless solid (91% yield).

R_f = 0.35 (hexanes : EtOAc (4 : 1)). ^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 8.40 (d, J = 8.7 Hz, 4H), 8.28 (d, J = 8.7 Hz, 4H). ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 161.07, 151.39, 131.11, 130.61, 124.11. These spectroscopic data correspond to those reported in the literature.[13]

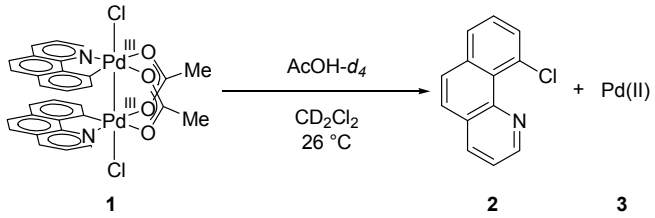
Benzoyl(*p*-nitrobenzoyl) peroxide (30)



To a solution of 4-nitrobenzoyl chloride (2.80 g, 15.0 mmol, 1.00 equiv) in Et_2O (10 mL) at 0 °C was added 30% $H_2O_{2(aq)}$ (1.70 mL, 1.89 g, 16.6 mmol, 1.10 equiv) dropwise over 10 minutes. After stirring for 15 minutes, a solution of benzoyl chloride (1.75 mL, 2.12 g, 15.0 mmol, 1.00 equiv) was added at 0 °C. After stirring for 5 minutes, $NaOH_{(aq)}$ (1.50 g, 37.5 mmol, 2.50 equiv) in H_2O (10 mL) was added dropwise over 20 minutes. The resulting precipitate was isolated by vacuum filtration and washed with H_2O (3 × 10 mL) and Et_2O (3 × 10 mL). The residue was purified by two sequential chromatographic separations (to remove byproduct **24**) on silica gel eluting with hexanes / EtOAc (19:1 (v/v)) to afford 1.34 g of the title compound[14] as a colorless solid (31% yield).

R_f = 0.50 (hexanes : EtOAc (4 : 1)). ^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 8.37 (d, *J* = 8.7 Hz, 2H), 8.27 (d, *J* = 8.7 Hz, 2H), 8.07 (d, *J* = 7.8 Hz, 2H), 7.69 (t, *J* = 7.3 Hz, 1H), 7.54 (dd, *J* = 7.8 Hz, *J* = 7.8 Hz, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 162.74, 161.34, 151.21, 134.59, 131.16, 131.04, 129.82, 128.98, 125.10, 123.98.

Reactivity of 1 in the Presence of Exogenous AcOH (Data Pertaining to Figure 4)[6]

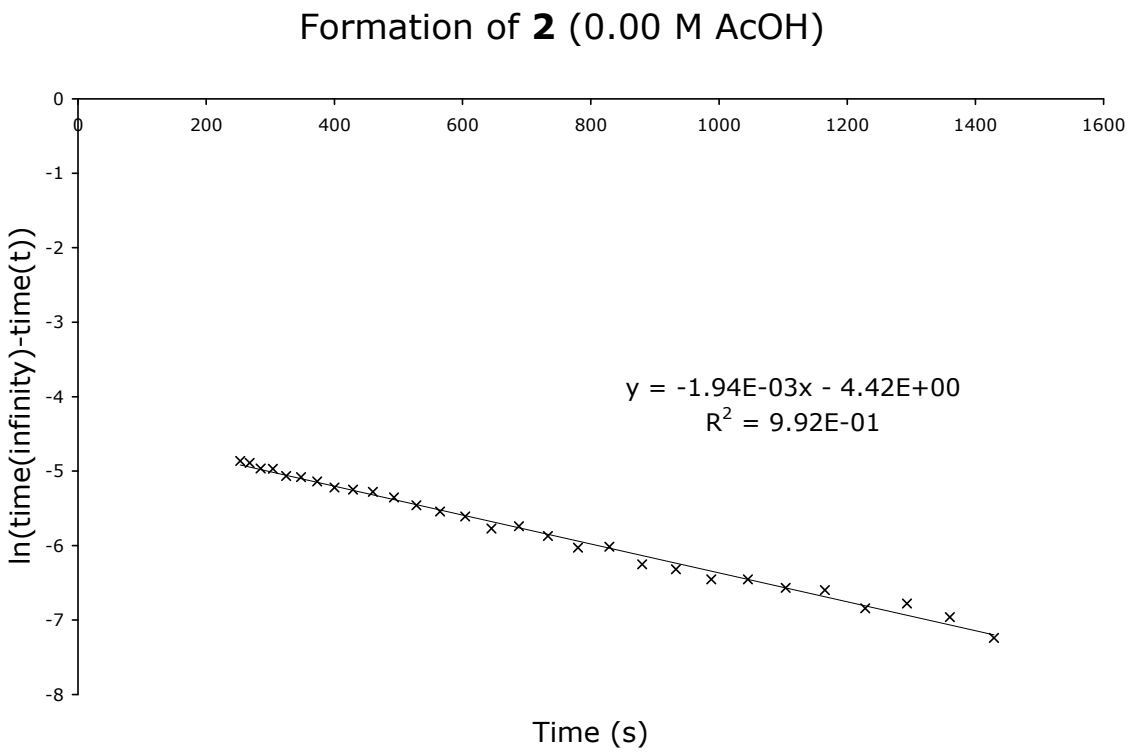


Stock solutions of compound **9** (20.2 mM) and $PhICl_2$ (20.2 mM) were prepared in CD_2Cl_2. Under N_2, to the solution of compound **9** (350 μL) was added *n* μL AcOH-d_4.[7] To the resulting solution was added the

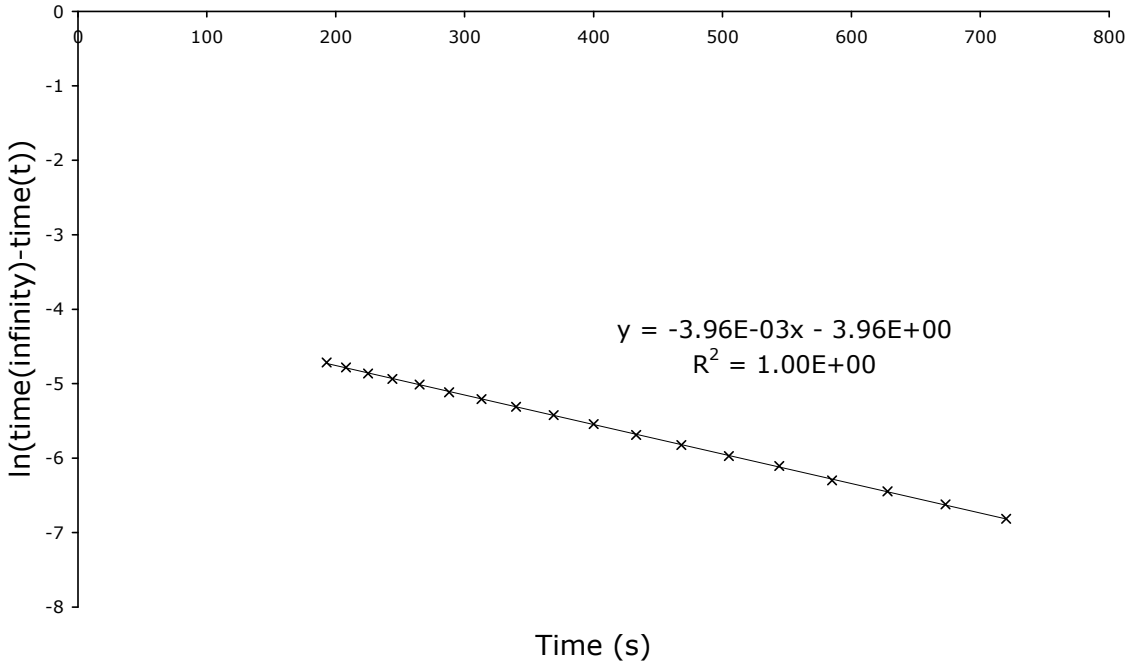
[6] Previously, we have reported rate enhancement for the formation of **2** from **1** at 23 °C in the presence of **8**. Based on extensive re-examination of this rate effect, we have revised our original proposal that **8** acts as a ligand for **1** and now provide evidence that the observed acceleration is due to acid, not *N*-ligation. We believe that acid generated by metallation of **8** by **3** is responsible for the acceleration observed in the presence of **8**. For the original data regarding the effect of **8** on the rate of C–Cl reductive elimination, see Appendix E.

[7] At high concentrations of AcOH (data obtained of 0.94 and 1.16 M AcOH, a small amount (<10 %) of **12** was observed during the course of the reaction. The peak corresponding to **12** (9.14 ppm was observed to increase at early times before being completely consumed at later times in the reaction. This observation is consistent with our earlier observations that the product of C–O reductive elimination can be consumed by the Pd-containing byproducts of reductive elimination.

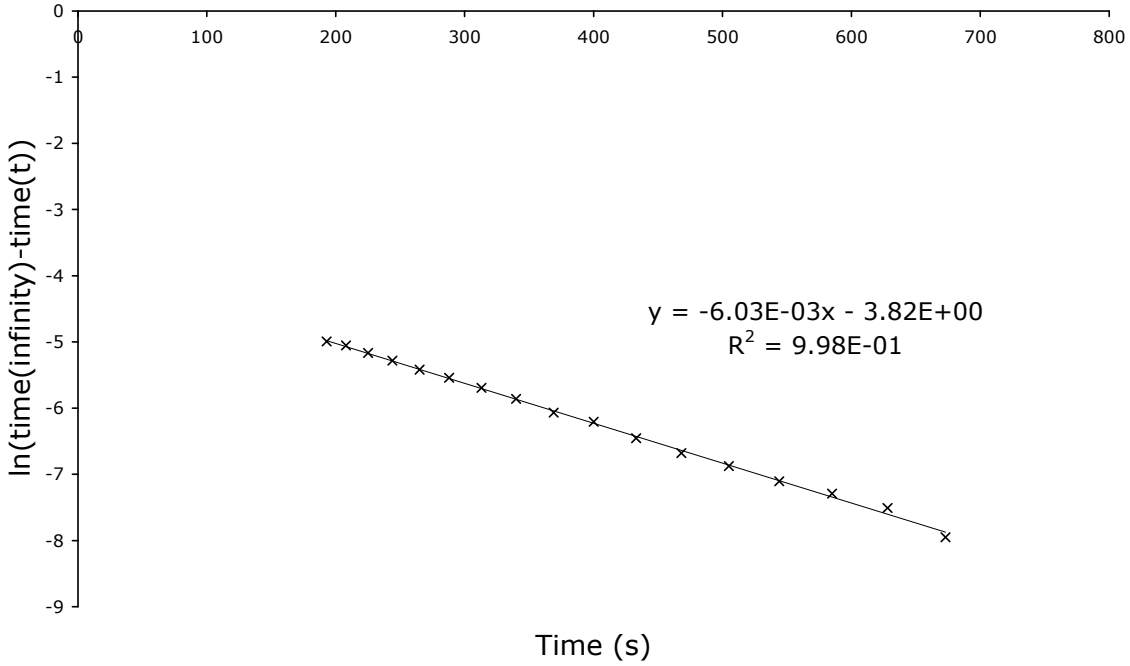
$PhICl_2$ solution (350 μL). ^1H NMR spectra were obtained; the evolution of **2** was monitored by the ^1H NMR signal at 9.12 ppm. These signals were integrated relative the residual proton signal from CD_2Cl_2. Since evolution of product was measured, linear natural log plots were obtained by using an infinite time point set to 100% yield. In each case, the reactions were followed to greater than 3 half-lives. Data were fitted to a first order regression; plots, slopes, and R^2 values are reported below.

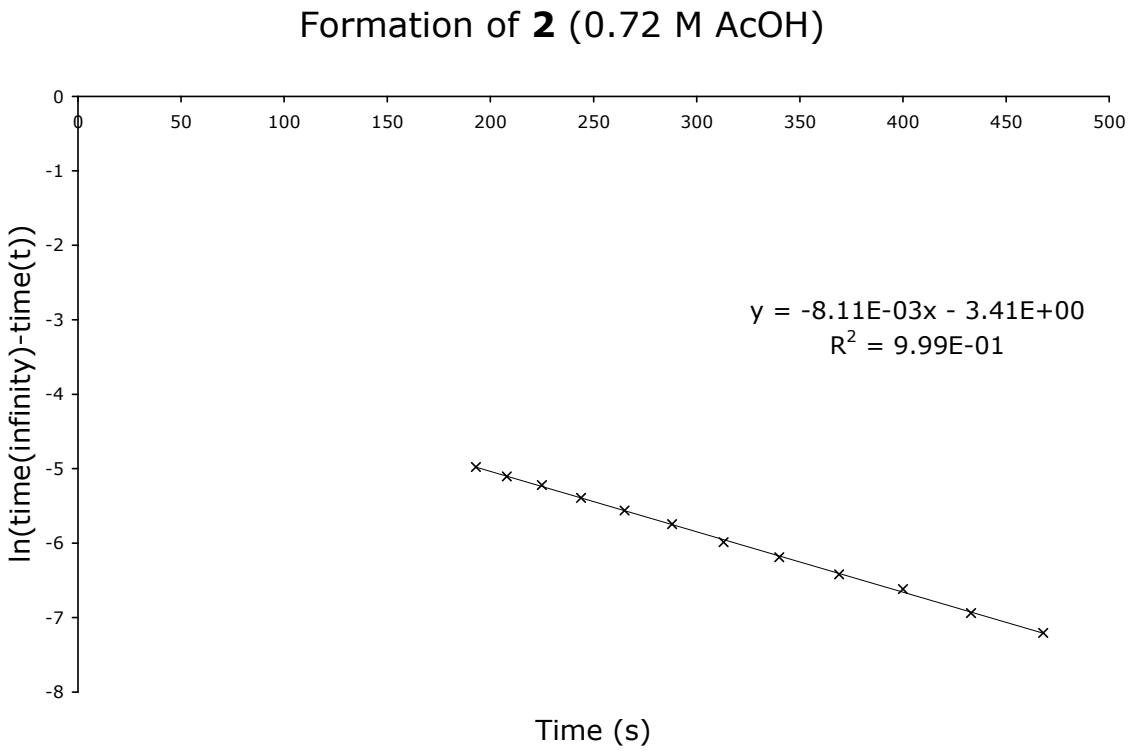


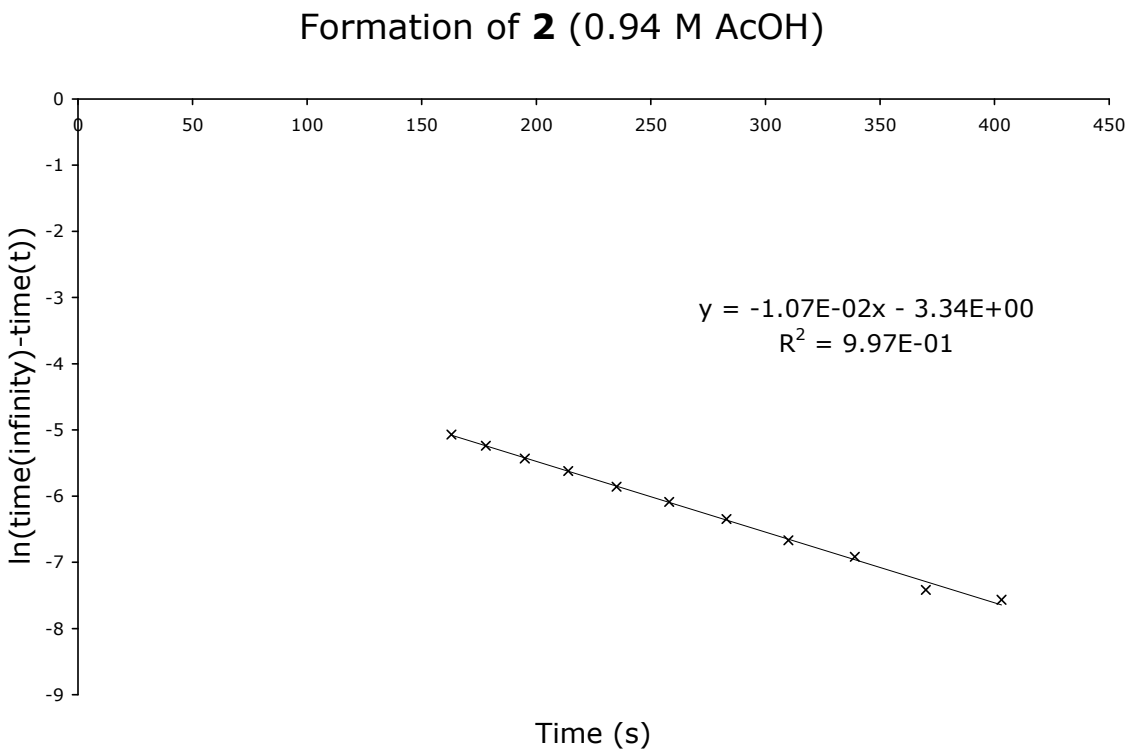
Formation of **2** (0.25 M AcOH)

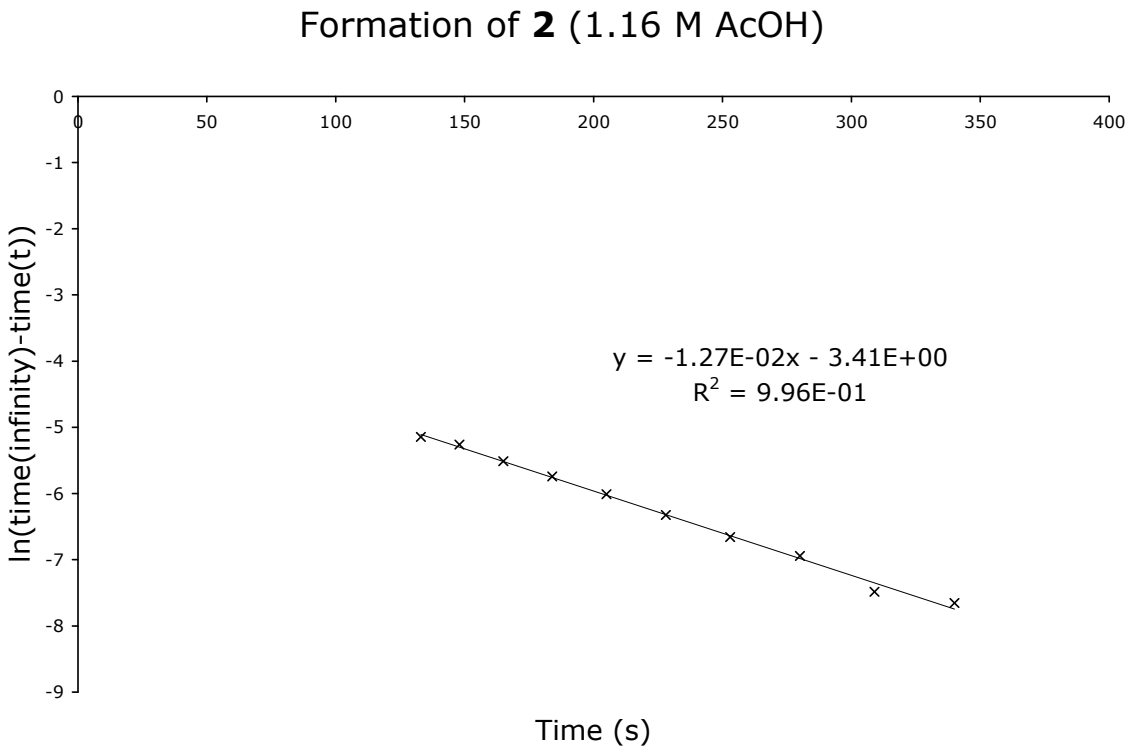


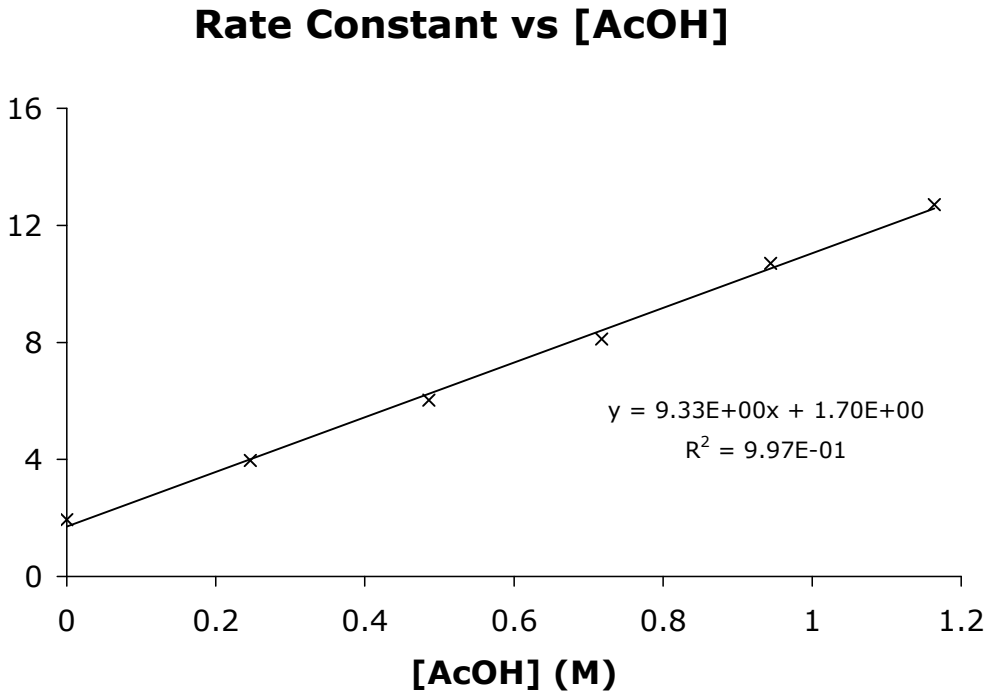
Formation of **2** (0.49 M AcOH)




Formation of **2** (0.72 M AcOH)
ln(time(infinity)-time(t))
Time (s)
y = -8.11E-03x - 3.41E+00
R2 = 9.99E-01
0
-1
-2
-3
-4
-5
-6
-7
-8
0
50
100
150
200
250
300
350
400
450
500


Formation of **2** (0.94 M AcOH)
ln(time(infinity)-time(t))
Time (s)
y = -1.07E-02x - 3.34E+00
R2 = 9.97E-01
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
0
50
100
150
200
250
300
350
400
450


Formation of **2** (1.16 M AcOH)
ln(time(infinity)-time(t))
Time (s)
y = -1.27E-02x - 3.41E+00
R2 = 9.96E-01
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
0
50
100
150
200
250
300
350
400


Rate Constant vs [AcOH]
[AcOH] (M)
y = 9.33E+00x + 1.70E+00
R2 = 9.97E-01
16
12
8
4
0
0
0.2
0.4
0.6
0.8
1
1.2

Computational Details

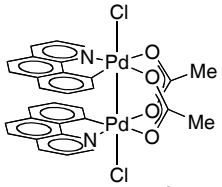
Computational Methods

Calculations were performed using density functional theory (DFT) with the M06 functional,[15] as implemented in Jaguar 7.6.110[16] All calculations used the Hay and Wadt small core-valence relativistic effective-core-potential[17] (ECP) for Pd. The LACV3P** basis set was used for all geometry optimizations and LACV3P++**(2f) for energies. LACV3P++**(2f) utilizes the LACV3P++** basis set as implemented in Jaguar plus a double-zeta f-shell with exponents from Martin and Sundermann.[18] All electrons were described for all other atoms using the 6-31G** (except Cl using 6-311G** for geometry optimizations) or 6-311++G** basis sets for electronic energies.[19,20] For each optimized structure, the M06 analytic Hessian was calculated to obtain the vibrational frequencies, which in turn were used to obtain the zero point energies and free energy corrections (without translational or rotational components). Solvent corrections were based on single point self-consistent Poisson-Boltzmann continuum solvation calculations (using the LACVP** basis set) for CH_2Cl_2 ($\varepsilon = 8.93$ and $R_0 = 2.33$ Å using the PBF[21] module in Jaguar.

Natural Bond Orbital[22,23] analyses were performed using the NBO 5.0 code[24] as implemented in Jaguar 7.6.110 on M06/LACV3P++**(2f) wavefunctions. We obtained the NBO orbital energies for the 4s orbitals of Pd directly from the NBO output and converted the energies from Eh to eV by multiplying the Eh value by 27.211. Given that an effective-core potential basis set (LACV3P) is used for our calculations, the 1s to 3d electrons are described by a pseudopotential, and therefore unavailable for the NBO program. We chose the energies of the natural 4s orbital as a spherical descriptor for the electronic changes in the valence shell. We believe that the change in energy of the 4s natural orbital is a good "gauge" for the electric field in each Pd atom and will therefore follow changes in oxidation state.

All computed structures in the manuscript are designated by compound letters, not numbers.

Structural Method Validation and Method Comparison



1

Method Comparison using structure **1**

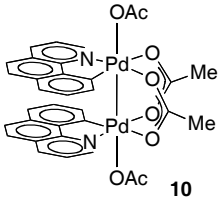
Method=	Pd-Pd(Å)	Pd-N(Å)	Pd-C(Å)	Pd-Cl(Å)	[bhq]-[bhq]*(Å)
M06	2.62	2.05	1.99	2.43	4.2

B3LYP	2.67	2.05	2.00	2.45	4.9
X-Ray	**2.57**	2.02	1.99	2.42	4.1

*Distance measured between the C5-C6 midbond points of each benzo[*h*]quinolinyl ligand. This geometrical parameter describes the interaction between the aromatic ligands. As observed, B3LYP leads to 0.8 Å too long, which is consistent with the repulsive nature of the functional at medium-range.

All geometry optimizations used LACV3P** for Pd, 6-311G** for Cl and 6-31G** for all other atoms.

Method Comparison using structure **10**

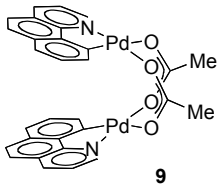


10

Method=	**Pd-Pd(Å)**	**Pd-N(Å)**	**Pd-C(Å)**	**Pd-OAc(Å)**
M06	2.59	2.04	1.99	2.13
M06-L	2.64	2.05	1.99	2.17
B3LYP	2.70	2.04	1.99	2.13
X-Ray	**2.55**	**2.00**	**1.99**	**2.14**

All geometry optimizations used LACV3P** for Pd and 6-31G** for all other atoms.

Method Validation using structure 9



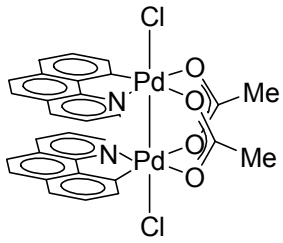
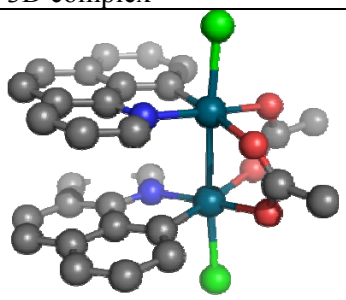
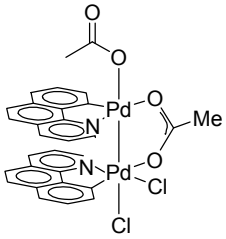
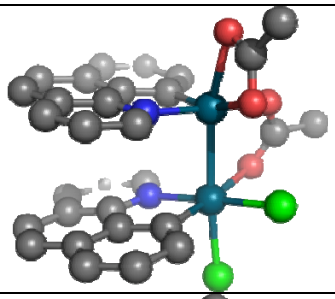
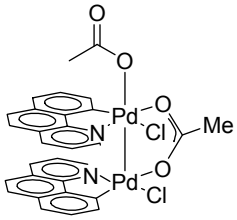
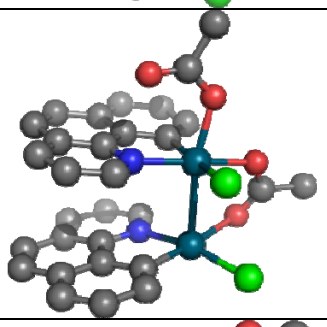
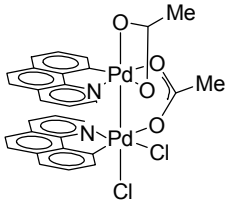
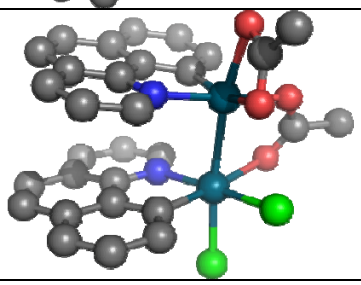
9

Method=	**Pd-Pd(Å)**	**Pd-N(Å)**	**Pd-C(Å)**
M06	2.87	2.066	1.98
X-Ray	**2.84**	**2.00**	**2.00**

All geometry optimizations used LACV3P** for Pd and 6-31G** for all other atoms.

Evaluation of stability of isomers of 1

We investigated the positional exchange of the chloride and acetate ligands of complex **1** computationally using the M06/LACVP** method. We found three additional isomers **1A**, **1B**, and **1C** shown below. We find that complex **1** is the most stable isomer by >10 kcal/mol (free energy at 298 K).

Complex	3D complex	ΔG (kcal·mol^{-1})	ΔH (kcal·mol^{-1})
 **A**		**0.0**	**0.0**
 **SA1**		**9.74**	**10.85**
 **SA2**		**17.62**	**19.45**
 **SA3**		**8.88**	**10.43**

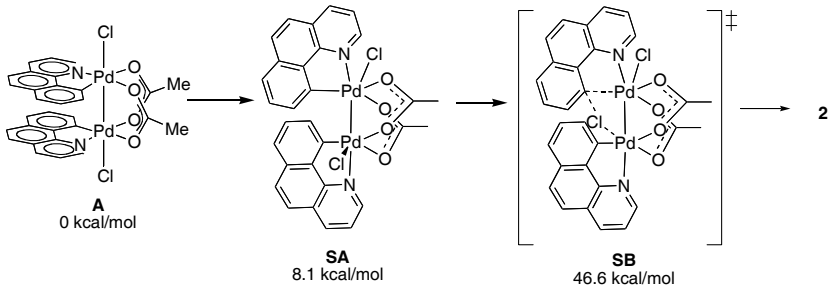
1,2-Reductive Elimination

We have computationally investigated the energetic barrier of a 1,2-reductive elimination employing **SA**, in which one of the benzo[*h*]quinolinyl ligands is rotated 90° with respect to its position in **A**. The thermodynamic stability of **SA** evaluated with respect to **A**. We found that the isomerization is 8.1 kcal/mol uphill. We did not calculate any transition state relevant to the isomerization and cannot make any assertion with respect to the kinetic feasibility of such transformation.

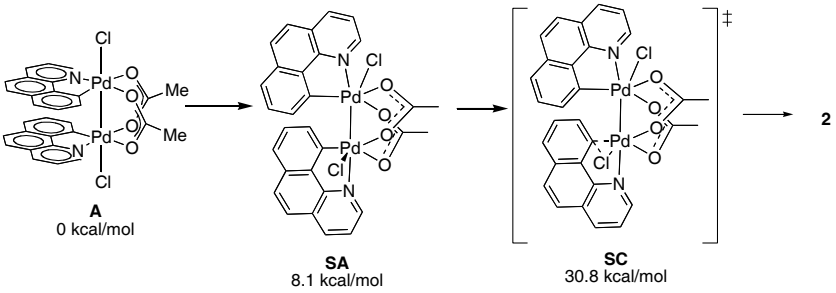
We considered 1,2-reductive elimination happening across the Pd–Pd core. We find a transition state for such transformation at 46.6 kcal/mol higher in energy than **A**, likely a consequence of the relatively long distance between the C and Cl atoms bound to the different Pd centers. We also examined the 1,1-reductive elimination reactions that are possible from each of the metal centers in **SA**. We find that C-Cl

reductive elimination occurring from the same metal center (from the isomerized fragment (**SC**) or from the fragment similar to complex **A** (**SD**)) is very close in energy at roughly 30~31 kcal/mol. This is at least 10 kcal/mol higher in energy than the barrier for reductive elimination from **1**. Energies are electronic energies with solvation corrections for CH_2Cl_2 (no thermodynamic corrections).

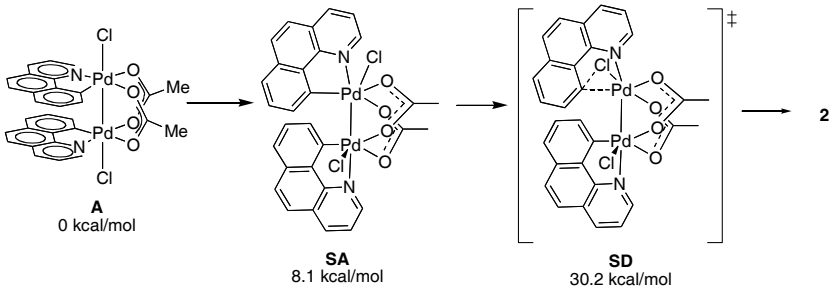
1,2-Reductive Elimination Pathway



1,1-Reductive Elimination Pathway #1



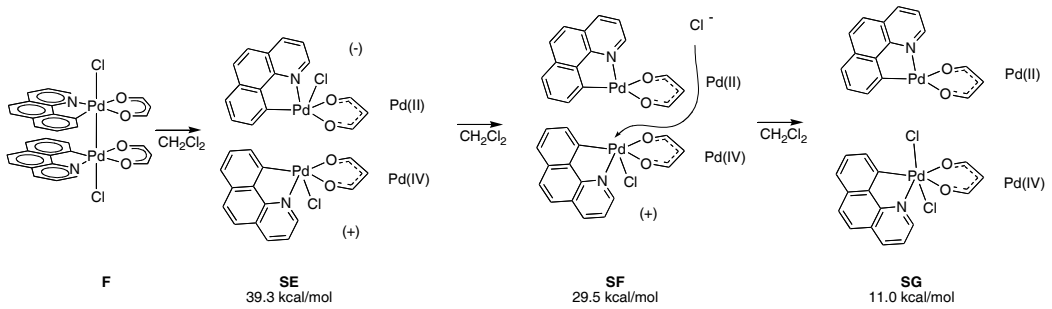
1,1-Reductive Elimination Pathway #2



Computed Kinetic Barrier to Disproportionation

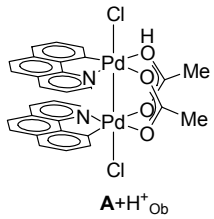
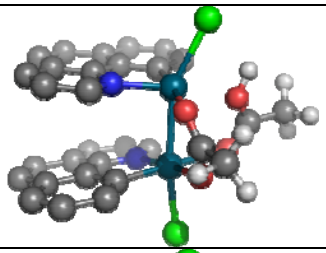
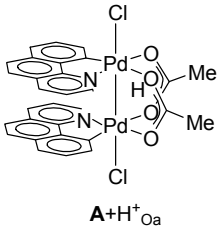
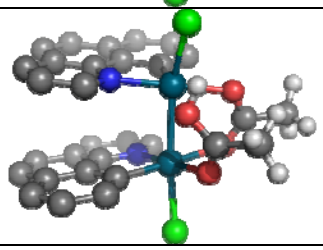
We have computed a heterolytic cleavage mechanism occurring by simple elongation of the Pd–Pd bond. The vertical process generates two fragments: one cationic, one anionic. This ion-pair (**SE**) is calculated to be 39.3 kcal/mol higher in energy than **F**. Dissociation of chloride from the anionic fragment of **SE** lowers the potential energy by ~10 kcal/mol (**SF**). The solvated chloride coordinated to the Pd(IV) fragment (**SG**), predicted to be 18.5 kcal/mol lower in potential energy. Except for the vertical Pd-Pd heterolysis, all structures are stationary points and reflect thermodynamic stability of the complexes (no

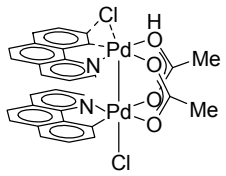
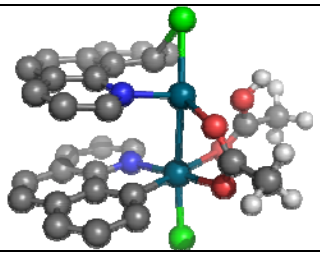
activation barriers were calculated). Therefore, we believe that the adiabatic process will incur at least 29.5 kcal/mol which is ~10 kcal/mol higher than the reductive elimination from **1**. Energies are electronic energies with solvation corrections for CH_2Cl_2 (no thermodynamic corrections).



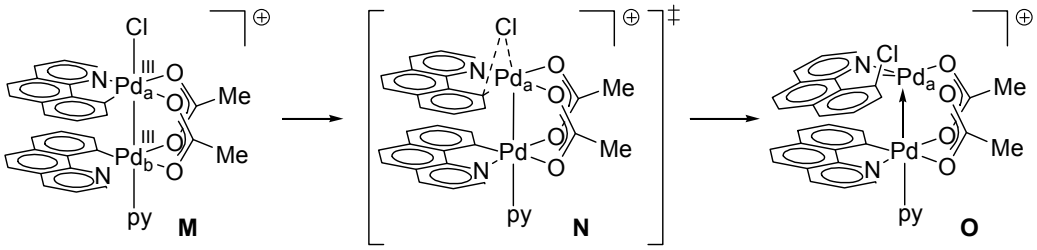
Computed Reductive Elimination in the Presence of Acid

We investigated the protonation of complex **1** and found that protonation at the acetate oxygen trans to the carbon atom (**A** + H^+_{Oa}) coordination is 0.9 kcal/mol more stable (electronic energy in CH_2Cl_2) than protonation at the acetate oxygen trans to the nitrogen atom (**A** + H^+_{Ob}) coordination. We were also able to locate a transition state for a protonated complex. We investigated all four possible oxygen protonation sites and found that the only available pathway involves protonation at the oxygen trans to the nitrogen atom bound to the Pd atom that is involved in reductive elimination (Pda). All other protonated isomers of the transition state led to acetate de-coordination, followed by significant structural reorganization, at higher electronic energy than **B** + H^+_{Ob}. Reductive elimination via **B** + H^+_{Ob} is bimetallic: the EBEs of the 4s orbitals of **A** + H^+_{ob} are Pd_a: 93.8425389 and Pd_b: 94.1312517; the EBEs of the 4s orbitals of **B** + H^+_{ob} are Pd_a: 93.0887836 and Pd_b: 93.6580458.

Complex	Structure	ΔE (kcal/mol)
 **A**+H^+_{Ob}		0.9
 **A**+H^+_{Oa}		0.0

 **B**+H^+_{Ob}		20.05

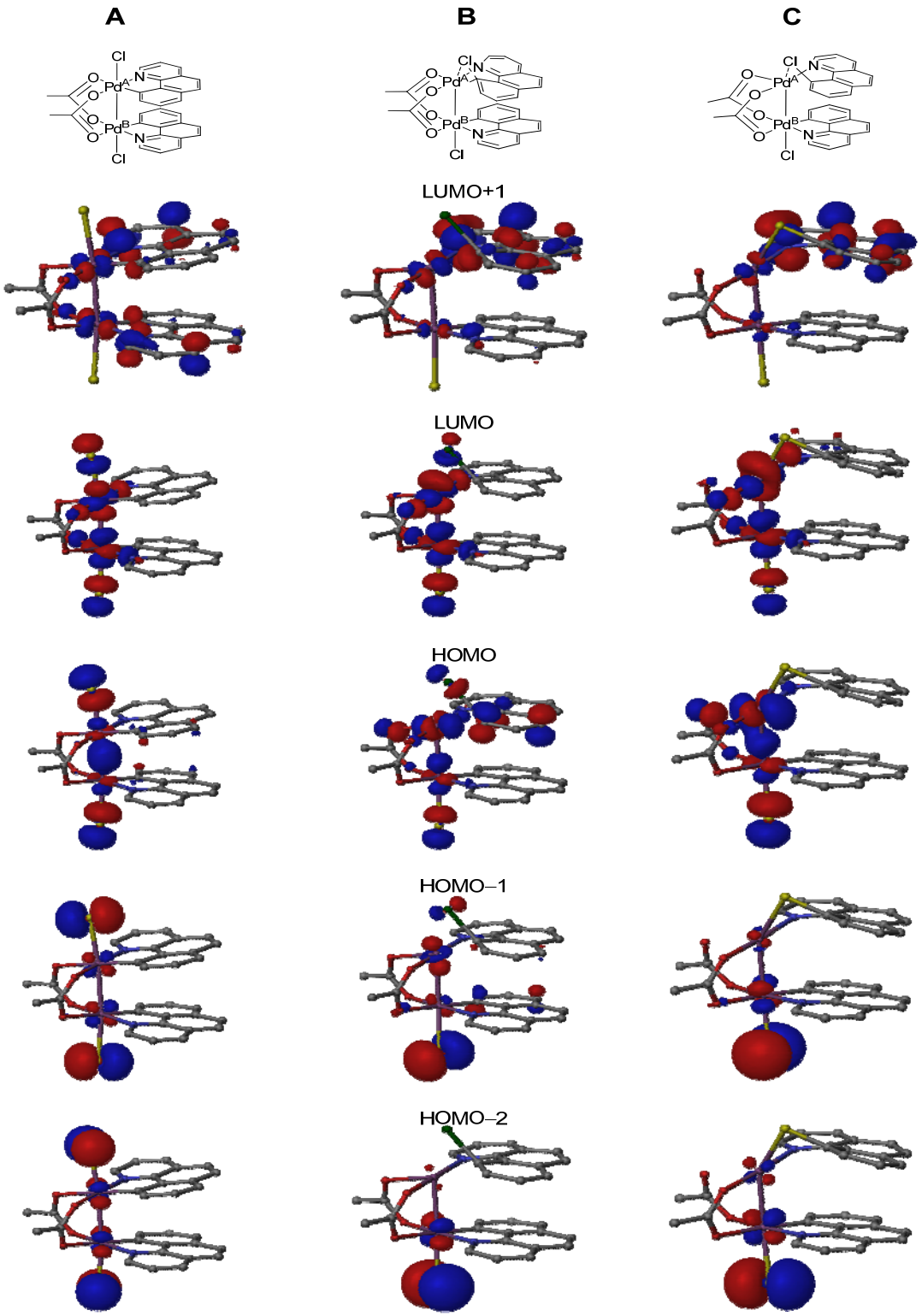
Computational Investigation of Reductive Elimination from Cation Complex M



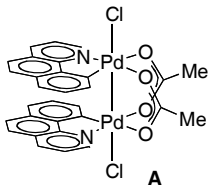
Electron Binding Energies	**M**	**N**	**O**
Pd_a	93.66287143	93.36245537	92.91836206
Pd_b	93.31891681	92.94067557	92.53712754

See below for x,y,z coordinates and energies for **M**, **N**, and **O**.

Selected Molecular Orbitals of A



XYZ coordinates and selected NBO output: NAO, type, occupation, energy



A

H1	-3.7833091881	0.5696857129	0.2825308408
C2	-2.7153423657	0.3593179966	0.3015480670
H3	-2.5646215694	0.2616318689	-1.8419851903
C4	-2.0381047002	0.1886172461	-0.8920292442
C5	-0.7189326575	0.0160412077	1.5738789762
C6	-0.6641339382	-0.1178896782	-0.8830448712
C7	-2.0703127843	0.2635252782	1.5535261675
C8	-0.0232665565	-0.1959098891	0.3701168897
C9	0.1225645599	-0.3788509160	-2.0540884668
H10	-2.6290913653	0.3751503009	2.4799177433
C11	1.4336598401	-0.7390293943	-1.9731418639
H12	-0.3613569597	-0.3016648563	-3.0267432934
H13	2.0056980881	-0.9525959403	-2.8743194450
C14	2.0900494631	-0.8649546475	-0.7053614543
C15	3.4158829381	-1.2848791066	-0.5092285097
C16	1.3428744267	-0.5596445503	0.4443642837
C17	3.9174741445	-1.4009900508	0.7727594229
H18	4.0353327009	-1.5301641705	-1.3703463093
H19	4.9312680104	-1.7457470549	0.9507377523
C20	3.1096998064	-1.0704253618	1.8663388865
H21	3.4500227616	-1.1588190079	2.8954459179
N22	1.8702388310	-0.6344286633	1.6918355930
Pd23	0.5007579008	-0.1441599387	3.1399043988
Pd24	1.1801451363	2.3901590695	3.2898447250
H25	4.8679816245	2.2270767525	-0.3655362694
C26	3.8235964984	2.4118174924	-0.1201071161
H27	3.2915846202	2.8592100403	-2.1548970588
C28	2.9447038348	2.7656856757	-1.1271035092
C29	2.0930517562	2.5054601129	1.5260294029
C30	1.5978167229	3.0382064308	-0.8236711962
C31	3.4149178807	2.2874898635	1.2246970674
C32	1.1944798059	2.8992555151	0.5192789313
C33	0.6151375159	3.4670047750	-1.7770953659
H34	4.1290925225	2.0349658775	2.0047932897
C35	-0.6564805875	3.7827190539	-1.4047288874
H36	0.9142972553	3.5546502816	-2.8206932244
H37	-1.3807074288	4.1240549455	-2.1422305014
C38	-1.0707551253	3.6929427857	-0.0357005836
C39	-2.3344454425	4.0506000387	0.4614887195
C40	-0.1310231525	3.2220737796	0.8961287503
C41	-2.5936965708	3.9519300666	1.8148352807

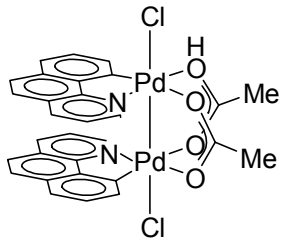
H42	-3.0975140225	4.4174046301	-0.2230653378
H43	-3.5547458244	4.2445941642	2.2259736364
C44	-1.6044990879	3.4666029229	2.6771278248
H45	-1.7515055658	3.3830541344	3.7513845934
N46	-0.4224281679	3.0868310182	2.2137084000
C47	-0.8247303627	1.3197755841	5.2701939265
O48	0.0020872578	2.2516682710	5.1414455120
O49	-0.9645309978	0.3245296948	4.4800753766
C50	2.8519728765	0.6196722665	4.8691910830
O51	2.0014418745	-0.2906919627	4.7427448309
O52	2.8591042406	1.7340651094	4.2428319282
C53	-1.7593295210	1.3327946178	6.4464190981
H54	-1.8939138723	2.3509989786	6.8173790797
H55	-1.3142390352	0.7272957487	7.2433852598
H56	-2.7167342202	0.8767420000	6.1835207314
C57	3.9901718153	0.4294943757	5.8310962770
H58	4.9051959542	0.8757829338	5.4336452205
H59	4.1325092766	-0.6295909182	6.0544098828
H60	3.7475096579	0.9582669461	6.7589195938
Cl61	1.8142372927	4.7027919074	3.6747208526
Cl62	-0.0819620829	-2.5013288355	3.2532183990

367	Pd 23	s	Cor(4s)	1.99339	-3.33249
368	Pd 23	s	Val(5s)	0.36692	0.58991
369	Pd 23	s	Ryd(6s)	0.00203	1.32276
370	Pd 23	s	Ryd(11s)	0.00090	21.56905
371	Pd 23	s	Ryd(7s)	0.00037	2.49036
372	Pd 23	s	Ryd(8s)	0.00003	13.96494
373	Pd 23	s	Ryd(9s)	0.00001	14.20085
374	Pd 23	s	Ryd(10s)	0.00000	18.36333
375	Pd 23	px	Cor(4p)	1.99617	-2.12585
376	Pd 23	px	Ryd(5p)	0.00387	1.39094
377	Pd 23	px	Ryd(7p)	0.00149	2.01626
378	Pd 23	px	Ryd(8p)	0.00052	2.92586
379	Pd 23	px	Ryd(6p)	0.00024	1.92190
380	Pd 23	px	Ryd(9p)	0.00001	7.79856
381	Pd 23	px	Ryd(10p)	0.00000	11.02085
382	Pd 23	py	Cor(4p)	1.99772	-2.12662
383	Pd 23	py	Ryd(7p)	0.01505	1.60778
384	Pd 23	py	Ryd(5p)	0.00361	1.23196
385	Pd 23	py	Ryd(8p)	0.00017	3.12426
386	Pd 23	py	Ryd(6p)	0.00020	1.37807
387	Pd 23	py	Ryd(9p)	0.00001	8.66206
388	Pd 23	py	Ryd(10p)	0.00000	11.04897
389	Pd 23	pz	Cor(4p)	1.99569	-2.12783
390	Pd 23	pz	Ryd(6p)	0.00355	2.06841
391	Pd 23	pz	Ryd(7p)	0.00134	2.35571
392	Pd 23	pz	Ryd(8p)	0.00055	2.89914
393	Pd 23	pz	Ryd(5p)	0.00049	1.40346

394	Pd 23	pz	Ryd(9p)	0.00001	7.93210
395	Pd 23	pz	Ryd(10p)	0.00000	11.02576
396	Pd 23	dxy	Val(4d)	1.89346	-0.33748
397	Pd 23	dxy	Ryd(6d)	0.00364	1.09582
398	Pd 23	dxy	Ryd(5d)	0.00114	0.92565
399	Pd 23	dxy	Ryd(7d)	0.00004	2.84264
400	Pd 23	dxz	Val(4d)	1.31969	-0.32112
401	Pd 23	dxz	Ryd(6d)	0.00095	1.96592
402	Pd 23	dxz	Ryd(5d)	0.00109	0.84650
403	Pd 23	dxz	Ryd(7d)	0.00006	2.75318
404	Pd 23	dyz	Val(4d)	1.91689	-0.33941
405	Pd 23	dyz	Ryd(6d)	0.00323	1.06303
406	Pd 23	dyz	Ryd(5d)	0.00157	0.78143
407	Pd 23	dyz	Ryd(7d)	0.00002	2.77142
408	Pd 23	dx2y2	Val(4d)	1.74727	-0.33627
409	Pd 23	dx2y2	Ryd(6d)	0.00464	1.41261
410	Pd 23	dx2y2	Ryd(5d)	0.00093	1.24328
411	Pd 23	dx2y2	Ryd(7d)	0.00009	2.73997
412	Pd 23	dz2	Val(4d)	1.85885	-0.34212
413	Pd 23	dz2	Ryd(6d)	0.00315	1.25823
414	Pd 23	dz2	Ryd(5d)	0.00079	0.70399
415	Pd 23	dz2	Ryd(7d)	0.00007	2.63729
416	Pd 23	f(0)	Ryd(4f)	0.00036	1.63454
417	Pd 23	f(0)	Ryd(5f)	0.00001	4.42492
418	Pd 23	f(c1)	Ryd(4f)	0.00090	1.85411
419	Pd 23	f(c1)	Ryd(5f)	0.00004	4.59355
420	Pd 23	f(s1)	Ryd(4f)	0.00037	1.57419
421	Pd 23	f(s1)	Ryd(5f)	0.00001	4.36817
422	Pd 23	f(c2)	Ryd(4f)	0.00080	1.78639
423	Pd 23	f(c2)	Ryd(5f)	0.00003	4.53971
424	Pd 23	f(s2)	Ryd(4f)	0.00053	1.61989
425	Pd 23	f(s2)	Ryd(5f)	0.00001	4.39964
426	Pd 23	f(c3)	Ryd(4f)	0.00039	1.63256
427	Pd 23	f(c3)	Ryd(5f)	0.00001	4.42133
428	Pd 23	f(s3)	Ryd(4f)	0.00044	1.62953
429	Pd 23	f(s3)	Ryd(5f)	0.00001	4.40887
430	Pd 24	s	Cor(4s)	1.99335	-3.33214
431	Pd 24	s	Val(5s)	0.36698	0.58970
432	Pd 24	s	Ryd(6s)	0.00205	1.24125
433	Pd 24	s	Ryd(11s)	0.00093	21.64574
434	Pd 24	s	Ryd(7s)	0.00037	2.39417
435	Pd 24	s	Ryd(8s)	0.00003	14.08603
436	Pd 24	s	Ryd(9s)	0.00001	14.58689
437	Pd 24	s	Ryd(10s)	0.00000	19.30408
438	Pd 24	px	Cor(4p)	1.99690	-2.12617
439	Pd 24	px	Ryd(5p)	0.00396	1.28487
440	Pd 24	px	Ryd(7p)	0.00152	1.87952
441	Pd 24	px	Ryd(8p)	0.00054	3.10675
442	Pd 24	px	Ryd(6p)	0.00026	1.78116

443	Pd 24	px	Ryd(9p)	0.00001	7.66953
444	Pd 24	px	Ryd(10p)	0.00000	11.01170
445	Pd 24	py	Cor(4p)	1.99772	-2.12710
446	Pd 24	py	Ryd(7p)	0.01531	1.57173
447	Pd 24	py	Ryd(5p)	0.00351	1.28496
448	Pd 24	py	Ryd(8p)	0.00020	3.26698
449	Pd 24	py	Ryd(6p)	0.00020	1.44256
450	Pd 24	py	Ryd(9p)	0.00001	8.34282
451	Pd 24	py	Ryd(10p)	0.00000	11.03369
452	Pd 24	pz	Cor(4p)	1.99493	-2.12686
453	Pd 24	pz	Ryd(6p)	0.00345	2.15722
454	Pd 24	pz	Ryd(7p)	0.00148	2.48511
455	Pd 24	pz	Ryd(8p)	0.00052	3.02192
456	Pd 24	pz	Ryd(5p)	0.00052	1.09029
457	Pd 24	pz	Ryd(9p)	0.00001	8.13171
458	Pd 24	pz	Ryd(10p)	0.00000	11.04090
459	Pd 24	dxy	Val(4d)	1.81247	-0.33487
460	Pd 24	dxy	Ryd(6d)	0.00349	1.21788
461	Pd 24	dxy	Ryd(5d)	0.00117	0.97553
462	Pd 24	dxy	Ryd(7d)	0.00004	2.87034
463	Pd 24	dxz	Val(4d)	1.50615	-0.32650
464	Pd 24	dxz	Ryd(6d)	0.00171	1.71963
465	Pd 24	dxz	Ryd(5d)	0.00114	0.72438
466	Pd 24	dxz	Ryd(7d)	0.00005	2.67109
467	Pd 24	dyz	Val(4d)	1.90970	-0.33973
468	Pd 24	dyz	Ryd(6d)	0.00281	1.05900
469	Pd 24	dyz	Ryd(5d)	0.00169	0.75141
470	Pd 24	dyz	Ryd(7d)	0.00002	2.75554
471	Pd 24	dx2y2	Val(4d)	1.74605	-0.33606
472	Pd 24	dx2y2	Ryd(6d)	0.00497	1.42583
473	Pd 24	dx2y2	Ryd(5d)	0.00098	1.27855
474	Pd 24	dx2y2	Ryd(7d)	0.00009	2.72771
475	Pd 24	dz2	Val(4d)	1.76161	-0.33964
476	Pd 24	dz2	Ryd(6d)	0.00276	1.34337
477	Pd 24	dz2	Ryd(5d)	0.00089	0.73048
478	Pd 24	dz2	Ryd(7d)	0.00008	2.67286
479	Pd 24	f(0)	Ryd(4f)	0.00056	1.67714
480	Pd 24	f(0)	Ryd(5f)	0.00002	4.45994
481	Pd 24	f(c1)	Ryd(4f)	0.00073	1.80697
482	Pd 24	f(c1)	Ryd(5f)	0.00003	4.55999
483	Pd 24	f(s1)	Ryd(4f)	0.00037	1.60453
484	Pd 24	f(s1)	Ryd(5f)	0.00001	4.39541
485	Pd 24	f(c2)	Ryd(4f)	0.00061	1.70417
486	Pd 24	f(c2)	Ryd(5f)	0.00002	4.46690
487	Pd 24	f(s2)	Ryd(4f)	0.00054	1.64256
488	Pd 24	f(s2)	Ryd(5f)	0.00002	4.41797
489	Pd 24	f(c3)	Ryd(4f)	0.00040	1.62497
490	Pd 24	f(c3)	Ryd(5f)	0.00001	4.41510
491	Pd 24	f(s3)	Ryd(4f)	0.00058	1.67396

492 Pd 24 f(s3) Ryd(5f) 0.00002 4.44045



A+H^+_{Ob}

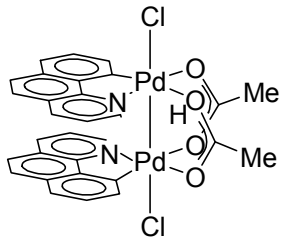
Pd1	6.8057630819	3.7576372946	5.9174916173
Pd2	6.6280627856	1.0839298361	6.0347599021
O3	5.1546258863	3.4747375059	4.4683088024
O4	4.4087144214	1.5759237069	5.2772169202
C5	4.1573102326	2.5830400076	4.6485745429
C6	2.8488746979	2.9250644640	4.0293315688
H7	2.9533819252	2.9315899635	2.9384460469
H8	2.5272295974	3.9289205004	4.3308073954
H9	2.0986579502	2.1879635860	4.3155022925
N10	8.2940193119	3.7858965550	7.3149222781
N11	6.0210480976	1.0023478921	8.0122124443
C12	5.6664283456	4.2005159143	7.5136085466
C13	4.3223357706	4.4740782548	7.5721094096
H14	3.7072042843	4.5418081096	6.6777213063
C15	3.7419408766	4.7309309366	8.8346015805
H16	2.6778126755	4.9520055969	8.8813803209
C17	4.4886891522	4.7379778526	9.9966607286
H18	4.0156294595	4.9580373941	10.9515918290
C19	5.8750884271	4.4965114961	9.9472873295
C20	6.4421482331	4.2275183183	8.6858540688
C21	7.8341048344	4.0226320914	8.5696522503
C22	8.6935797231	4.0881564719	9.6768844313
C23	10.0671552226	3.9228798038	9.4259795860
H24	10.7740276794	3.9642315169	10.2528551082
C25	10.5135227487	3.7227916950	8.1332126309
H26	11.5702237728	3.6033442703	7.9148710923
C27	9.5934083638	3.6557096343	7.0801282927
H28	9.8852673648	3.4825846583	6.0466136689
C29	8.4134308649	0.6262832184	6.8295012068
C30	9.5666755931	0.3181232999	6.1624492338
H31	9.6048656923	0.2547809116	5.0785261633
C32	10.7122094028	0.0463191479	6.9470854064
H33	11.6418180990	-0.1919140077	6.4351144859
C34	10.6745103686	0.0487567423	8.3276229056
H35	11.5695216351	-0.1876187929	8.8992567090
C36	9.4650796591	0.3010375834	9.0068030864
C37	8.3259499344	0.5880316658	8.2272521489
C38	7.0667135811	0.7711350405	8.8440206306
C39	6.9092480816	0.6728014067	10.2349202060
C40	5.6028190491	0.8139871376	10.7366152753
H41	5.4283172289	0.7435673075	11.8087283157
C42	4.5490574246	1.0211666004	9.8676349384
H43	3.5308128435	1.1184117708	10.2308945590
C44	4.7903070638	1.1051863844	8.4907890572
H45	3.9941392816	1.2597646986	7.7658830606
C46	8.0820929485	0.4198309808	11.0186205293
H47	7.9765258474	0.3497242194	12.0992444477
C48	9.2990361445	0.2445530663	10.4308556793
H49	10.1732628759	0.0297963828	11.0428247110
C50	6.7529884951	4.5230836269	11.0830299948

H51	6.3220843558	4.7226793160	12.0626263506
C52	8.0963101185	4.3318311103	10.9570095057
H53	8.7448269699	4.3768421106	11.8291815400
O54	7.3719691767	1.1173125110	4.1298939818
Cl55	6.2643096666	-1.2546347363	5.8645394959
O56	8.1759086555	3.2213055985	4.2805409163
C57	8.0157932519	2.1345600979	3.6833739423
C58	8.6515107364	1.9388449005	2.3376669937
H59	8.1781858547	1.1220760862	1.7906333040
H60	8.6096099981	2.8707026103	1.7694580748
H61	9.7084601196	1.6885463875	2.4884529438
Cl62	6.2264450490	6.0506828295	5.0734072771
H63	4.9615033201	4.4155389767	4.2131577387

NAO	Atom	No	lang	Type(AO)	Occupancy	Energy
1	Pd	1	s	Cor(4s)	1.99354	-3.44865
2	Pd	1	s	Val(5s)	0.35260	0.44378
3	Pd	1	s	Ryd(6s)	0.00200	1.18265
4	Pd	1	s	Ryd(11s)	0.00102	22.67702
5	Pd	1	s	Ryd(7s)	0.00033	2.30094
6	Pd	1	s	Ryd(8s)	0.00002	11.24691
7	Pd	1	s	Ryd(9s)	0.00000	13.74832
8	Pd	1	s	Ryd(10s)	0.00000	15.33564
9	Pd	1	px	Cor(4p)	1.99520	-2.23526
10	Pd	1	px	Ryd(5p)	0.00327	1.19896
11	Pd	1	px	Ryd(7p)	0.00118	1.98132
12	Pd	1	px	Ryd(8p)	0.00051	3.17996
13	Pd	1	px	Ryd(6p)	0.00032	1.97845
14	Pd	1	px	Ryd(9p)	0.00001	7.01019
15	Pd	1	px	Ryd(10p)	0.00000	10.90905
16	Pd	1	py	Cor(4p)	1.99758	-2.23269
17	Pd	1	py	Ryd(7p)	0.01588	1.61345
18	Pd	1	py	Ryd(6p)	0.00294	1.12825
19	Pd	1	py	Ryd(8p)	0.00025	3.33119
20	Pd	1	py	Ryd(5p)	0.00016	0.98815
21	Pd	1	py	Ryd(9p)	0.00002	8.44090
22	Pd	1	py	Ryd(10p)	0.00000	10.99424
23	Pd	1	pz	Cor(4p)	1.99614	-2.23670
24	Pd	1	pz	Ryd(6p)	0.00375	1.89754
25	Pd	1	pz	Ryd(7p)	0.00165	2.17479
26	Pd	1	pz	Ryd(8p)	0.00056	2.84161
27	Pd	1	pz	Ryd(5p)	0.00031	1.08316
28	Pd	1	pz	Ryd(9p)	0.00001	7.65741
29	Pd	1	pz	Ryd(10p)	0.00000	10.96568
30	Pd	1	dxy	Val(4d)	1.96336	-0.44898
31	Pd	1	dxy	Ryd(6d)	0.00311	0.89836
32	Pd	1	dxy	Ryd(5d)	0.00100	0.71785
33	Pd	1	dxy	Ryd(7d)	0.00004	2.73790
34	Pd	1	dxz	Val(4d)	1.32607	-0.43071
35	Pd	1	dxz	Ryd(6d)	0.00142	1.72719
36	Pd	1	dxz	Ryd(5d)	0.00101	0.87118
37	Pd	1	dxz	Ryd(7d)	0.00006	2.67113
38	Pd	1	dyz	Val(4d)	1.90411	-0.44916
39	Pd	1	dyz	Ryd(6d)	0.00301	0.94703
40	Pd	1	dyz	Ryd(5d)	0.00202	0.73074
41	Pd	1	dyz	Ryd(7d)	0.00004	2.78809
42	Pd	1	dx2y2	Val(4d)	1.74178	-0.44453
43	Pd	1	dx2y2	Ryd(6d)	0.00392	1.35865

44	Pd	1	dx2y2	Ryd(5d)	0.00187	1.18481
45	Pd	1	dx2y2	Ryd(7d)	0.00007	2.68128
46	Pd	1	dz2	Val(4d)	1.88741	-0.45198
47	Pd	1	dz2	Ryd(6d)	0.00300	1.14613
48	Pd	1	dz2	Ryd(5d)	0.00127	0.62928
49	Pd	1	dz2	Ryd(7d)	0.00007	2.58228
50	Pd	1	f(0)	Ryd(4f)	0.00028	1.51303
51	Pd	1	f(0)	Ryd(5f)	0.00001	4.30021
52	Pd	1	f(c1)	Ryd(4f)	0.00064	1.71756
53	Pd	1	f(c1)	Ryd(5f)	0.00003	4.46066
54	Pd	1	f(s1)	Ryd(4f)	0.00027	1.48567
55	Pd	1	f(s1)	Ryd(5f)	0.00001	4.27844
56	Pd	1	f(c2)	Ryd(4f)	0.00069	1.66893
57	Pd	1	f(c2)	Ryd(5f)	0.00003	4.42570
58	Pd	1	f(s2)	Ryd(4f)	0.00042	1.48958
59	Pd	1	f(s2)	Ryd(5f)	0.00001	4.26956
60	Pd	1	f(c3)	Ryd(4f)	0.00027	1.47729
61	Pd	1	f(c3)	Ryd(5f)	0.00001	4.26582
62	Pd	1	f(s3)	Ryd(4f)	0.00028	1.53081
63	Pd	1	f(s3)	Ryd(5f)	0.00001	4.32186
64	Pd	2	s	Cor(4s)	1.99357	-3.45926
65	Pd	2	s	Val(5s)	0.36706	0.43828
66	Pd	2	s	Ryd(6s)	0.00256	2.34445
67	Pd	2	s	Ryd(11s)	0.00094	20.09213
68	Pd	2	s	Ryd(7s)	0.00036	2.40940
69	Pd	2	s	Ryd(8s)	0.00002	12.59189
70	Pd	2	s	Ryd(10s)	0.00001	16.76315
71	Pd	2	s	Ryd(9s)	0.00000	16.06707
72	Pd	2	px	Cor(4p)	1.99309	-2.24762
73	Pd	2	px	Ryd(6p)	0.00340	1.53841
74	Pd	2	px	Ryd(7p)	0.00148	2.30672
75	Pd	2	px	Ryd(8p)	0.00041	3.05804
76	Pd	2	px	Ryd(5p)	0.00031	1.49010
77	Pd	2	px	Ryd(9p)	0.00001	7.41647
78	Pd	2	px	Ryd(10p)	0.00000	11.04276
79	Pd	2	py	Cor(4p)	1.99741	-2.25112
80	Pd	2	py	Ryd(7p)	0.01283	1.37062
81	Pd	2	py	Ryd(5p)	0.00453	1.03299
82	Pd	2	py	Ryd(8p)	0.00016	3.47026
83	Pd	2	py	Ryd(6p)	0.00017	1.09014
84	Pd	2	py	Ryd(9p)	0.00001	8.16818
85	Pd	2	py	Ryd(10p)	0.00000	11.05720
86	Pd	2	pz	Cor(4p)	1.99737	-2.24926
87	Pd	2	pz	Ryd(6p)	0.00396	1.65305
88	Pd	2	pz	Ryd(7p)	0.00142	1.87417
89	Pd	2	pz	Ryd(8p)	0.00058	3.35652
90	Pd	2	pz	Ryd(5p)	0.00037	1.08447
91	Pd	2	pz	Ryd(9p)	0.00001	7.47015
92	Pd	2	pz	Ryd(10p)	0.00000	11.01943
93	Pd	2	dxy	Val(4d)	1.92578	-0.46241
94	Pd	2	dxy	Ryd(6d)	0.00264	0.88904
95	Pd	2	dxy	Ryd(5d)	0.00175	0.67336
96	Pd	2	dxy	Ryd(7d)	0.00002	2.72182
97	Pd	2	dxz	Val(4d)	1.69099	-0.45350
98	Pd	2	dxz	Ryd(6d)	0.00226	1.36339
99	Pd	2	dxz	Ryd(5d)	0.00106	0.57474
100	Pd	2	dxz	Ryd(7d)	0.00004	2.53986

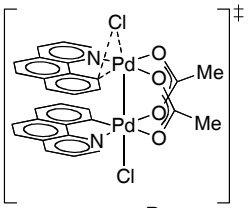
101	Pd	2	dyz	Val(4d)	1.96611	-0.46294
102	Pd	2	dyz	Ryd(6d)	0.00336	0.87805
103	Pd	2	dyz	Ryd(5d)	0.00221	0.67814
104	Pd	2	dyz	Ryd(7d)	0.00003	2.66388
105	Pd	2	dx2y2	Val(4d)	1.65355	-0.46055
106	Pd	2	dx2y2	Ryd(6d)	0.00360	1.33832
107	Pd	2	dx2y2	Ryd(5d)	0.00099	1.25206
108	Pd	2	dx2y2	Ryd(7d)	0.00010	2.74051
109	Pd	2	dz2	Val(4d)	1.51677	-0.44667
110	Pd	2	dz2	Ryd(6d)	0.00207	1.54981
111	Pd	2	dz2	Ryd(5d)	0.00100	0.76743
112	Pd	2	dz2	Ryd(7d)	0.00007	2.59262
113	Pd	2	f(0)	Ryd(4f)	0.00075	1.67005
114	Pd	2	f(0)	Ryd(5f)	0.00003	4.40743
115	Pd	2	f(c1)	Ryd(4f)	0.00072	1.60320
116	Pd	2	f(c1)	Ryd(5f)	0.00003	4.36319
117	Pd	2	f(s1)	Ryd(4f)	0.00044	1.44641
118	Pd	2	f(s1)	Ryd(5f)	0.00001	4.25207
119	Pd	2	f(c2)	Ryd(4f)	0.00047	1.54608
120	Pd	2	f(c2)	Ryd(5f)	0.00002	4.32668
121	Pd	2	f(s2)	Ryd(4f)	0.00023	1.42056
122	Pd	2	f(s2)	Ryd(5f)	0.00001	4.22647
123	Pd	2	f(c3)	Ryd(4f)	0.00046	1.50621
124	Pd	2	f(c3)	Ryd(5f)	0.00001	4.29581
125	Pd	2	f(s3)	Ryd(4f)	0.00052	1.55530
126	Pd	2	f(s3)	Ryd(5f)	0.00002	4.34584



A+H^+_{Oa}

Pd1	6.8252902392	3.6931175682	5.9512042631
Pd2	6.5616514881	1.0435993327	6.0728152962
O3	5.2710568940	3.5645625528	4.6026755669
O4	4.5281956403	1.5749551298	5.3558929718
C5	4.4174997844	2.6023950664	4.6551834185
C6	3.2160887781	2.7751911747	3.7726201149
H7	3.4925681429	2.5134932297	2.7449964182
H8	2.8880197285	3.8178288956	3.7679747367
H9	2.4125786110	2.1090532739	4.0911734628
N10	8.2810496122	3.7985690994	7.4236107361
N11	5.9909258379	1.0226175862	8.0166924975
C12	5.6240442989	4.1838218607	7.4677643179
C13	4.2897234810	4.4900141866	7.4071099350
H14	3.7394313338	4.4973040123	6.4710317154
C15	3.6465138282	4.8342816360	8.6188759257
H16	2.5870054585	5.0784706753	8.5878338409
C17	4.3211149464	4.8807349302	9.8226590925
H18	3.7950582177	5.1569588754	10.7342416415
C19	5.7025000707	4.6090356636	9.8753491219
C20	6.3452039609	4.2657275112	8.6689437826
C21	7.7444845479	4.0631632066	8.6410816479
C22	8.5276237888	4.1736566055	9.8005628375

C23	9.9144018771	3.9982722161	9.6496439401
H24	10.5642411929	4.0715246477	10.5198140006
C25	10.4438182948	3.7504211720	8.3977211724
H26	11.5121709464	3.6236121155	8.2532396802
C27	9.5926193468	3.6612140921	7.2900598900
H28	9.9674077410	3.4667250860	6.2876532954
C29	8.3616421075	0.6064963132	6.8653498944
C30	9.5318179816	0.3133522834	6.2183792932
H31	9.5912831924	0.2511401090	5.1347726796
C32	10.6740760051	0.0558883386	7.0136544202
H33	11.6112565414	-0.1726844847	6.5109176112
C34	10.6273194331	0.0585885469	8.3947378598
H35	11.5204104730	-0.1674378054	8.9735588213
C36	9.4103357082	0.3069888810	9.0607624304
C37	8.2826669901	0.5844956342	8.2651139411
C38	7.0229270705	0.7891544157	8.8654056307
C39	6.8385432658	0.7171162050	10.2541284245
C40	5.5239934445	0.8769644019	10.7273144626
H41	5.3275096555	0.8264954369	11.7967340306
C42	4.4866266974	1.0772418327	9.8354241746
H43	3.4627723874	1.1867515706	10.1787974355
C44	4.7474850454	1.1416577921	8.4613625288
H45	3.9746708303	1.2970426933	7.7117910419
C46	8.0011528173	0.4652458594	11.0548466214
H47	7.8827855289	0.4119979014	12.1351515261
C48	9.2243217035	0.2726917695	10.4840754839
H49	10.0887848262	0.0639396534	11.1118628956
C50	6.5074653814	4.6847568912	11.0609808542
H51	6.0181772709	4.9378493223	11.9998806870
C52	7.8529737853	4.4740582515	11.0287985872
H53	8.4454574626	4.5534520956	11.9375481748
O54	7.1769017866	1.1157168664	3.9886239438
Cl55	6.2792258260	-1.3265144870	5.9128026074
O56	8.2441234596	3.0326440632	4.1695559597
C57	7.6198057919	2.1143099099	3.4294261503
C58	7.4826110263	2.3693452373	1.9755538425
H59	7.0681097573	1.4924048544	1.4781930244
H60	6.7980654165	3.2204079570	1.8512111126
H61	8.4428441474	2.6464785904	1.5301059000
Cl62	7.5961528987	5.8091833078	4.8721146841
H63	8.2917719725	3.9513478835	3.7926912282



B

H1	-3.8680994531	0.5471944474	0.3715008669
C2	-2.7959872114	0.3563787274	0.3732343287
H3	-2.6781783820	0.2626958188	-1.7727904631
C4	-2.1347204493	0.2003456082	-0.8310007306
C5	-0.7737113738	0.0346460071	1.6085068273
C6	-0.7557116689	-0.0788062259	-0.8471482679
C7	-2.1285679907	0.2623150002	1.6115131838
C8	-0.0890559071	-0.1495694539	0.3932016966

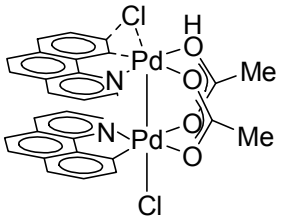
C9	0.0057214918	-0.3364539238	-2.0352562910
H10	-2.6711220369	0.3502230981	2.5498976281
C11	1.3207642876	-0.6860908076	-1.9834414286
H12	-0.5033437372	-0.2688495622	-2.9957589826
H13	1.8743001117	-0.9006576664	-2.8963777725
C14	2.0060394184	-0.7979591601	-0.7301916615
C15	3.3427477932	-1.1965215463	-0.5693425749
C16	1.2843235189	-0.4971996634	0.4376323808
C17	3.8837460761	-1.2923130413	0.6977310283
H18	3.9401195494	-1.4386026483	-1.4474011337
H19	4.9088798422	-1.6164826008	0.8491473955
C20	3.0972059414	-0.9733827639	1.8105518673
H21	3.4655826393	-1.0600524191	2.8300881766
N22	1.8439264849	-0.5666831864	1.6715190435
Pd23	0.4472582779	-0.1800543846	3.1721296697
Pd24	1.2175891783	2.3504819807	3.3142177739
H25	4.8372415455	1.9093357190	-0.4339229137
C26	3.8448272644	2.2700804489	-0.1684317930
H27	3.1566930988	2.3215650062	-2.2149233180
C28	2.9078207562	2.4882280787	-1.1683959310
C29	2.3177013165	3.0258176109	1.5405953797
C30	1.6174089887	2.9244061341	-0.8241640535
C31	3.5796472174	2.5587072030	1.1719106947
C32	1.3037272361	3.1218796277	0.5387878001
C33	0.5864841658	3.1672596580	-1.7937475327
H34	4.3588241918	2.4846109633	1.9268026798
C35	-0.6656059335	3.5544013429	-1.4321196817
H36	0.8390536146	3.0396133199	-2.8458565838
H37	-1.4264648148	3.7550300513	-2.1847943477
C38	-1.0359939977	3.6303250904	-0.0509967481
C39	-2.3330805293	3.8862151687	0.4164731489
C40	-0.0472805654	3.3417045661	0.9112589391
C41	-2.6064809997	3.8144216764	1.7694707395
H42	-3.1211100746	4.1204222669	-0.2979973083
H43	-3.6023917577	4.0096410770	2.1552983546
C44	-1.5962344757	3.4149876016	2.6483687874
H45	-1.7699029105	3.2654222149	3.7119955447
N46	-0.3645563290	3.1664438745	2.2217509570
C47	-0.9458617961	1.2423802097	5.3060428360
O48	-0.1183945582	2.1679463299	5.2429759859
O49	-1.0528670751	0.2450188464	4.5077082642
C50	2.8231707256	0.4879366414	4.9109828728
O51	1.9579545213	-0.4027393776	4.7653821044
O52	2.8599308386	1.6135074013	4.3096000724
C53	-1.9654633573	1.2292698642	6.4193320274
H54	-2.0458449241	2.2178461717	6.8757575244
H55	-1.6371188292	0.5115964120	7.1783834670
H56	-2.9355205529	0.8868647484	6.0500859670
C57	3.9513464859	0.2360226331	5.8756222560

H58	4.8103582701	0.8709954606	5.6488985213
H59	4.2286305636	-0.8212203440	5.8608935035
H60	3.6034518382	0.4745668371	6.8864080383
Cl61	2.4370207308	4.5354877243	2.7982931542
Cl62	-0.1491265467	-2.5585063023	3.1572621587

367	Pd 23 s	Cor(4s)	1.99308	-3.32001
368	Pd 23 s	Val(5s)	0.36087	0.58622
369	Pd 23 s	Ryd(6s)	0.00204	1.16148
370	Pd 23 s	Ryd(11s)	0.00097	20.52464
371	Pd 23 s	Ryd(7s)	0.00040	2.67426
372	Pd 23 s	Ryd(9s)	0.00003	14.46000
373	Pd 23 s	Ryd(8s)	0.00001	11.04868
374	Pd 23 s	Ryd(10s)	0.00000	16.80926
375	Pd 23 px	Cor(4p)	1.99640	-2.11112
376	Pd 23 px	Ryd(5p)	0.00367	1.29662
377	Pd 23 px	Ryd(7p)	0.00130	2.09338
378	Pd 23 px	Ryd(8p)	0.00054	2.77359
379	Pd 23 px	Ryd(6p)	0.00025	1.59922
380	Pd 23 px	Ryd(9p)	0.00001	8.10667
381	Pd 23 px	Ryd(10p)	0.00000	11.17560
382	Pd 23 py	Cor(4p)	1.99787	-2.11128
383	Pd 23 py	Ryd(7p)	0.01203	1.62649
384	Pd 23 py	Ryd(5p)	0.00335	1.21314
385	Pd 23 py	Ryd(8p)	0.00017	2.95797
386	Pd 23 py	Ryd(6p)	0.00022	1.30314
387	Pd 23 py	Ryd(9p)	0.00001	8.82701
388	Pd 23 py	Ryd(10p)	0.00000	11.21489
389	Pd 23 pz	Cor(4p)	1.99572	-2.11338
390	Pd 23 pz	Ryd(6p)	0.00354	1.84571
391	Pd 23 pz	Ryd(7p)	0.00121	2.55007
392	Pd 23 pz	Ryd(8p)	0.00057	2.76999
393	Pd 23 pz	Ryd(5p)	0.00047	1.26002
394	Pd 23 pz	Ryd(9p)	0.00001	8.24686
395	Pd 23 pz	Ryd(10p)	0.00000	11.16920
396	Pd 23 dxy	Val(4d)	1.90913	-0.32346
397	Pd 23 dxy	Ryd(6d)	0.00353	1.07326
398	Pd 23 dxy	Ryd(5d)	0.00115	1.04427
399	Pd 23 dxy	Ryd(7d)	0.00004	2.82375
400	Pd 23 dxz	Val(4d)	1.30700	-0.30490
401	Pd 23 dxz	Ryd(6d)	0.00102	1.90296
402	Pd 23 dxz	Ryd(5d)	0.00112	0.93302
403	Pd 23 dxz	Ryd(7d)	0.00005	2.63624
404	Pd 23 dyz	Val(4d)	1.92586	-0.32480
405	Pd 23 dyz	Ryd(6d)	0.00328	1.00798
406	Pd 23 dyz	Ryd(5d)	0.00160	0.75644
407	Pd 23 dyz	Ryd(7d)	0.00002	2.76908
408	Pd 23 dx2y2	Val(4d)	1.74551	-0.32075
409	Pd 23 dx2y2	Ryd(6d)	0.00418	1.39854

410	Pd 23	dx2y2	Ryd(5d)	0.00093	1.30611
411	Pd 23	dx2y2	Ryd(7d)	0.00008	2.77053
412	Pd 23	dz2	Val(4d)	1.86008	-0.32736
413	Pd 23	dz2	Ryd(6d)	0.00294	1.20541
414	Pd 23	dz2	Ryd(5d)	0.00070	0.74941
415	Pd 23	dz2	Ryd(7d)	0.00006	2.66051
416	Pd 23	f(0)	Ryd(4f)	0.00034	1.63826
417	Pd 23	f(0)	Ryd(5f)	0.00001	4.43226
418	Pd 23	f(c1)	Ryd(4f)	0.00086	1.86455
419	Pd 23	f(c1)	Ryd(5f)	0.00004	4.60020
420	Pd 23	f(s1)	Ryd(4f)	0.00036	1.57129
421	Pd 23	f(s1)	Ryd(5f)	0.00001	4.37255
422	Pd 23	f(c2)	Ryd(4f)	0.00076	1.80595
423	Pd 23	f(c2)	Ryd(5f)	0.00003	4.55163
424	Pd 23	f(s2)	Ryd(4f)	0.00045	1.61386
425	Pd 23	f(s2)	Ryd(5f)	0.00001	4.39661
426	Pd 23	f(c3)	Ryd(4f)	0.00038	1.64603
427	Pd 23	f(c3)	Ryd(5f)	0.00001	4.44123
428	Pd 23	f(s3)	Ryd(4f)	0.00040	1.61043
429	Pd 23	f(s3)	Ryd(5f)	0.00001	4.39875
430	Pd 24	s	Cor(4s)	1.99494	-3.31579
431	Pd 24	s	Val(5s)	0.34813	0.46462
432	Pd 24	s	Ryd(9s)	0.00138	11.58833
433	Pd 24	s	Ryd(7s)	0.00049	5.76185
434	Pd 24	s	Ryd(8s)	0.00043	7.43651
435	Pd 24	s	Ryd(6s)	0.00003	4.38217
436	Pd 24	s	Ryd(10s)	0.00000	12.92872
437	Pd 24	s	Ryd(11s)	0.00000	18.17934
438	Pd 24	px	Cor(4p)	1.99747	-2.08832
439	Pd 24	px	Ryd(6p)	0.00309	0.97858
440	Pd 24	px	Ryd(7p)	0.00095	1.42787
441	Pd 24	px	Ryd(5p)	0.00047	0.74243
442	Pd 24	px	Ryd(8p)	0.00037	3.53234
443	Pd 24	px	Ryd(9p)	0.00001	8.93549
444	Pd 24	px	Ryd(10p)	0.00000	11.30334
445	Pd 24	py	Cor(4p)	1.99736	-2.08975
446	Pd 24	py	Ryd(6p)	0.01028	1.25128
447	Pd 24	py	Ryd(7p)	0.00170	1.38068
448	Pd 24	py	Ryd(5p)	0.00036	0.79183
449	Pd 24	py	Ryd(8p)	0.00021	3.28790
450	Pd 24	py	Ryd(9p)	0.00001	9.11165
451	Pd 24	py	Ryd(10p)	0.00000	11.32994
452	Pd 24	pz	Cor(4p)	1.99649	-2.08131
453	Pd 24	pz	Ryd(7p)	0.00354	1.37358
454	Pd 24	pz	Ryd(6p)	0.00114	1.35795
455	Pd 24	pz	Ryd(5p)	0.00050	0.71666
456	Pd 24	pz	Ryd(8p)	0.00024	3.33813
457	Pd 24	pz	Ryd(9p)	0.00001	9.11404
458	Pd 24	pz	Ryd(10p)	0.00000	11.33040

459	Pd 24	dxy	Val(4d)	1.70864	-0.29927
460	Pd 24	dxy	Ryd(6d)	0.00266	1.33256
461	Pd 24	dxy	Ryd(5d)	0.00109	0.95658
462	Pd 24	dxy	Ryd(7d)	0.00004	2.85468
463	Pd 24	dxz	Val(4d)	1.59032	-0.28760
464	Pd 24	dxz	Ryd(6d)	0.00177	1.64361
465	Pd 24	dxz	Ryd(5d)	0.00086	0.86011
466	Pd 24	dxz	Ryd(7d)	0.00005	2.63916
467	Pd 24	dyz	Val(4d)	1.92226	-0.30605
468	Pd 24	dyz	Ryd(6d)	0.00260	1.29323
469	Pd 24	dyz	Ryd(5d)	0.00118	0.61233
470	Pd 24	dyz	Ryd(7d)	0.00005	2.70436
471	Pd 24	dx2y2	Val(4d)	1.80308	-0.30308
472	Pd 24	dx2y2	Ryd(6d)	0.00325	1.31290
473	Pd 24	dx2y2	Ryd(5d)	0.00102	1.01025
474	Pd 24	dx2y2	Ryd(7d)	0.00006	2.66149
475	Pd 24	dz2	Val(4d)	1.88578	-0.30165
476	Pd 24	dz2	Ryd(6d)	0.00204	1.17809
477	Pd 24	dz2	Ryd(5d)	0.00077	0.76687
478	Pd 24	dz2	Ryd(7d)	0.00005	2.70687
479	Pd 24	f(0)	Ryd(4f)	0.00035	1.65176
480	Pd 24	f(0)	Ryd(5f)	0.00002	4.43667
481	Pd 24	f(c1)	Ryd(4f)	0.00039	1.69714
482	Pd 24	f(c1)	Ryd(5f)	0.00001	4.47576
483	Pd 24	f(s1)	Ryd(4f)	0.00023	1.67303
484	Pd 24	f(s1)	Ryd(5f)	0.00001	4.46301
485	Pd 24	f(c2)	Ryd(4f)	0.00032	1.66333
486	Pd 24	f(c2)	Ryd(5f)	0.00002	4.44699
487	Pd 24	f(s2)	Ryd(4f)	0.00053	1.73545
488	Pd 24	f(s2)	Ryd(5f)	0.00002	4.49616
489	Pd 24	f(c3)	Ryd(4f)	0.00029	1.64705
490	Pd 24	f(c3)	Ryd(5f)	0.00001	4.44143
491	Pd 24	f(s3)	Ryd(4f)	0.00036	1.67634
492	Pd 24	f(s3)	Ryd(5f)	0.00002	4.44583



B+H^{+}_{Ob}

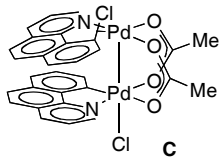
Pd1	6.7741204772	3.7328080636	5.8820442341
Pd2	6.6557108947	1.0809800861	5.9715085455
O3	5.0470581693	3.5301645058	4.3829257094
O4	4.4419745988	1.6012773962	5.2479222118
C5	4.1428025884	2.5275198246	4.5324146067
C6	2.8577281163	2.6856566052	3.7965174752
H7	3.0424267354	2.7055171709	2.7164930624
H8	2.3682080484	3.6268666289	4.0724922847
H9	2.2000774854	1.8484505590	4.0298988794

N10	8.2729839373	3.8319626592	7.3204448017
N11	6.0923155777	1.0959732341	7.9757711462
C12	5.6371613926	4.6923849928	7.4623726848
C13	4.2544218211	4.7427074784	7.5616390527
H14	3.6508190078	4.9652607311	6.6844001718
C15	3.6499650009	4.6597688132	8.8273761266
H16	2.5655320060	4.7188449922	8.8887395829
C17	4.3988489852	4.5979476394	9.9877900584
H18	3.9164477890	4.6207296694	10.9624973453
C19	5.8026277198	4.5156753122	9.9102149669
C20	6.4132427615	4.4858873705	8.6377076355
C21	7.7936962745	4.1762305810	8.5430161721
C22	8.6192352254	4.1363937975	9.6831626245
C23	9.9845694099	3.8722511887	9.4817477970
H24	10.6546649251	3.8431869032	10.3394488876
C25	10.4641713762	3.6367840585	8.2077551566
H26	11.5143193080	3.4281435071	8.0282370428
C27	9.5639910499	3.5923786048	7.1368245924
H28	9.8641649006	3.3226035812	6.1258587147
C29	8.4361999554	0.5997518485	6.7379667011
C30	9.5646987528	0.2473831064	6.0494384717
H31	9.5758085863	0.1805370172	4.9653146692
C32	10.7140186231	-0.0709599530	6.8093418470
H33	11.6235808549	-0.3448943162	6.2795726227
C34	10.7017254003	-0.0750187379	8.1901291902
H35	11.5969003205	-0.3510917619	8.7439717602
C36	9.5195521574	0.2303114163	8.8938261213
C37	8.3790780698	0.5703572617	8.1385263735
C38	7.1439499865	0.8131423414	8.7843412002
C39	7.0131816889	0.7152998035	10.1784761236
C40	5.7250300110	0.9040581477	10.7103276038
H41	5.5721918494	0.8300761324	11.7856532148
C42	4.6628425442	1.1627788488	9.8665955599
H43	3.6575187399	1.2983761777	10.2529145942
C44	4.8800056982	1.2512997678	8.4855316326
H45	4.0751364054	1.4516169902	7.7817970182
C46	8.1891596344	0.4056931026	10.9363307432
H47	8.1039279585	0.3358223855	12.0188646860
C48	9.3831113612	0.1770977017	10.3210117812
H49	10.2606822710	-0.0789872766	10.9121934837
C50	6.6485046587	4.4345423566	11.0666670765
H51	6.1800298247	4.4993718005	12.0473381680
C52	7.9985218097	4.3024411539	10.9615539683
H53	8.6257552967	4.2747090181	11.8500733427
O54	7.3335369543	1.0441276474	4.0437786766
Cl55	6.2263392719	-1.2675615900	5.8818439230
O56	8.2072331982	3.1236422590	4.1268606853
C57	8.0047077452	2.0366069089	3.5632305490
C58	8.5961911666	1.7584343821	2.2065436124
H59	7.9321456022	1.1284233487	1.6109311328
H60	8.8158911903	2.6952914126	1.6916338537
H61	9.5344344047	1.2075365929	2.3414813164
Cl62	6.2941803301	6.1732446110	6.1859637364
H63	4.7518477519	4.2762184039	3.8380874546

NAO	Atom	No	lang	Type(AO)	Occupancy	Energy
1	Pd	1	s	Cor(4s)	1.99469	-3.42095
2	Pd	1	s	Val(5s)	0.31603	0.35137
3	Pd	1	s	Ryd(8s)	0.00145	9.28677
4	Pd	1	s	Ryd(9s)	0.00058	10.68916
5	Pd	1	s	Ryd(6s)	0.00046	4.39028

6	Pd	1	s	Ryd(7s)	0.00002	9.03393
7	Pd	1	s	Ryd(10s)	0.00001	12.59475
8	Pd	1	s	Ryd(11s)	0.00000	16.18686
9	Pd	1	px	Cor(4p)	1.99633	-2.18831
10	Pd	1	px	Ryd(6p)	0.00308	0.81654
11	Pd	1	px	Ryd(7p)	0.00092	1.47816
12	Pd	1	px	Ryd(5p)	0.00035	0.72162
13	Pd	1	px	Ryd(8p)	0.00032	2.82344
14	Pd	1	px	Ryd(9p)	0.00000	9.33663
15	Pd	1	px	Ryd(10p)	0.00000	11.22706
16	Pd	1	py	Cor(4p)	1.99716	-2.19584
17	Pd	1	py	Ryd(7p)	0.01079	1.47499
18	Pd	1	py	Ryd(6p)	0.00216	1.26621
19	Pd	1	py	Ryd(5p)	0.00024	0.79253
20	Pd	1	py	Ryd(8p)	0.00015	2.94832
21	Pd	1	py	Ryd(9p)	0.00001	9.42778
22	Pd	1	py	Ryd(10p)	0.00000	11.23553
23	Pd	1	pz	Cor(4p)	1.99679	-2.18745
24	Pd	1	pz	Ryd(7p)	0.00291	1.44606
25	Pd	1	pz	Ryd(6p)	0.00111	1.37161
26	Pd	1	pz	Ryd(5p)	0.00040	0.64384
27	Pd	1	pz	Ryd(8p)	0.00031	2.93254
28	Pd	1	pz	Ryd(9p)	0.00000	9.28317
29	Pd	1	pz	Ryd(10p)	0.00000	11.22811
30	Pd	1	dxy	Val(4d)	1.94538	-0.41389
31	Pd	1	dxy	Ryd(6d)	0.00250	0.96670
32	Pd	1	dxy	Ryd(5d)	0.00083	0.63409
33	Pd	1	dxy	Ryd(7d)	0.00004	2.70896
34	Pd	1	dxz	Val(4d)	1.54448	-0.39213
35	Pd	1	dxz	Ryd(6d)	0.00174	1.62621
36	Pd	1	dxz	Ryd(5d)	0.00091	0.90978
37	Pd	1	dxz	Ryd(7d)	0.00005	2.59147
38	Pd	1	dyz	Val(4d)	1.93458	-0.41503
39	Pd	1	dyz	Ryd(6d)	0.00246	1.10618
40	Pd	1	dyz	Ryd(5d)	0.00116	0.51560
41	Pd	1	dyz	Ryd(7d)	0.00004	2.63612
42	Pd	1	dx2y2	Val(4d)	1.69712	-0.40767
43	Pd	1	dx2y2	Ryd(6d)	0.00323	1.32912
44	Pd	1	dx2y2	Ryd(5d)	0.00111	1.30435
45	Pd	1	dx2y2	Ryd(7d)	0.00008	2.72435
46	Pd	1	dz2	Val(4d)	1.89079	-0.41111
47	Pd	1	dz2	Ryd(6d)	0.00217	1.09348
48	Pd	1	dz2	Ryd(5d)	0.00076	0.62129
49	Pd	1	dz2	Ryd(7d)	0.00004	2.55677
50	Pd	1	f(0)	Ryd(4f)	0.00020	1.51349
51	Pd	1	f(0)	Ryd(5f)	0.00001	4.31071
52	Pd	1	f(c1)	Ryd(4f)	0.00037	1.63662
53	Pd	1	f(c1)	Ryd(5f)	0.00002	4.39950
54	Pd	1	f(s1)	Ryd(4f)	0.00023	1.55384
55	Pd	1	f(s1)	Ryd(5f)	0.00001	4.34844
56	Pd	1	f(c2)	Ryd(4f)	0.00038	1.61389
57	Pd	1	f(c2)	Ryd(5f)	0.00002	4.38869
58	Pd	1	f(s2)	Ryd(4f)	0.00028	1.53778
59	Pd	1	f(s2)	Ryd(5f)	0.00001	4.33372
60	Pd	1	f(c3)	Ryd(4f)	0.00023	1.47236
61	Pd	1	f(c3)	Ryd(5f)	0.00001	4.27264
62	Pd	1	f(s3)	Ryd(4f)	0.00030	1.58936
63	Pd	1	f(s3)	Ryd(5f)	0.00001	4.36928
64	Pd	2	s	Cor(4s)	1.99298	-3.44187
65	Pd	2	s	Val(5s)	0.36540	0.47572
66	Pd	2	s	Ryd(6s)	0.00248	1.64296
67	Pd	2	s	Ryd(11s)	0.00098	20.82702

68	Pd	2	s	Ryd(7s)	0.00038	2.37314
69	Pd	2	s	Ryd(8s)	0.00002	11.70282
70	Pd	2	s	Ryd(10s)	0.00001	16.30064
71	Pd	2	s	Ryd(9s)	0.00000	15.77080
72	Pd	2	px	Cor(4p)	1.99287	-2.23373
73	Pd	2	px	Ryd(6p)	0.00289	1.68456
74	Pd	2	px	Ryd(7p)	0.00145	2.27156
75	Pd	2	px	Ryd(8p)	0.00040	2.79530
76	Pd	2	px	Ryd(5p)	0.00026	1.27666
77	Pd	2	px	Ryd(9p)	0.00001	7.96891
78	Pd	2	px	Ryd(10p)	0.00000	11.03132
79	Pd	2	py	Cor(4p)	1.99734	-2.23545
80	Pd	2	py	Ryd(7p)	0.01211	1.37802
81	Pd	2	py	Ryd(5p)	0.00413	1.04615
82	Pd	2	py	Ryd(8p)	0.00016	3.21542
83	Pd	2	py	Ryd(6p)	0.00020	1.11130
84	Pd	2	py	Ryd(9p)	0.00001	8.58173
85	Pd	2	py	Ryd(10p)	0.00000	11.05238
86	Pd	2	pz	Cor(4p)	1.99742	-2.23382
87	Pd	2	pz	Ryd(6p)	0.00343	1.67038
88	Pd	2	pz	Ryd(7p)	0.00130	1.80216
89	Pd	2	pz	Ryd(8p)	0.00062	3.08037
90	Pd	2	pz	Ryd(5p)	0.00033	1.03367
91	Pd	2	pz	Ryd(9p)	0.00001	8.09254
92	Pd	2	pz	Ryd(10p)	0.00000	11.01982
93	Pd	2	dxy	Val(4d)	1.91612	-0.44776
94	Pd	2	dxy	Ryd(6d)	0.00247	0.89521
95	Pd	2	dxy	Ryd(5d)	0.00154	0.69879
96	Pd	2	dxy	Ryd(7d)	0.00002	2.77572
97	Pd	2	dxz	Val(4d)	1.71629	-0.44029
98	Pd	2	dxz	Ryd(6d)	0.00238	1.32302
99	Pd	2	dxz	Ryd(5d)	0.00080	0.64856
100	Pd	2	dxz	Ryd(7d)	0.00004	2.65278
101	Pd	2	dyz	Val(4d)	1.97102	-0.44778
102	Pd	2	dyz	Ryd(6d)	0.00328	0.88223
103	Pd	2	dyz	Ryd(5d)	0.00196	0.72844
104	Pd	2	dyz	Ryd(7d)	0.00003	2.68907
105	Pd	2	dx2y2	Val(4d)	1.65753	-0.44654
106	Pd	2	dx2y2	Ryd(5d)	0.00346	1.33303
107	Pd	2	dx2y2	Ryd(6d)	0.00102	1.38769
108	Pd	2	dx2y2	Ryd(7d)	0.00010	2.79465
109	Pd	2	dz2	Val(4d)	1.50224	-0.43111
110	Pd	2	dz2	Ryd(6d)	0.00202	1.60967
111	Pd	2	dz2	Ryd(5d)	0.00092	0.91331
112	Pd	2	dz2	Ryd(7d)	0.00007	2.63228
113	Pd	2	f(0)	Ryd(4f)	0.00078	1.70147
114	Pd	2	f(0)	Ryd(5f)	0.00003	4.43524
115	Pd	2	f(c1)	Ryd(4f)	0.00067	1.60403
116	Pd	2	f(c1)	Ryd(5f)	0.00003	4.37149
117	Pd	2	f(s1)	Ryd(4f)	0.00045	1.45574
118	Pd	2	f(s1)	Ryd(5f)	0.00001	4.26437
119	Pd	2	f(c2)	Ryd(4f)	0.00042	1.54648
120	Pd	2	f(c2)	Ryd(5f)	0.00002	4.33141
121	Pd	2	f(s2)	Ryd(4f)	0.00021	1.43538
122	Pd	2	f(s2)	Ryd(5f)	0.00001	4.24465
123	Pd	2	f(c3)	Ryd(4f)	0.00046	1.50887
124	Pd	2	f(c3)	Ryd(5f)	0.00001	4.29920
125	Pd	2	f(s3)	Ryd(4f)	0.00055	1.57180
126	Pd	2	f(s3)	Ryd(5f)	0.00002	4.36765



C

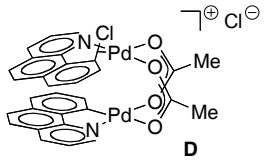
H1	-3.8784949058	0.5537249391	0.3334845847
C2	-2.8046241421	0.3876678682	0.3615038010
H3	-2.6368530729	0.2539269207	-1.7751097093
C4	-2.1155386271	0.2204746416	-0.8217749431
C5	-0.8098025002	0.1146641763	1.6542078791
C6	-0.7345348511	-0.0313091399	-0.7974101324
C7	-2.1652544790	0.3207992577	1.6127737621
C8	-0.0982940768	-0.0686670487	0.4569330820
C9	0.0621438572	-0.2779696434	-1.9619599568
H10	-2.7337780785	0.4006679272	2.5340714122
C11	1.3858847117	-0.5684239603	-1.8742895342
H12	-0.4251968565	-0.2443675898	-2.9338665433
H13	1.9695202847	-0.7694424182	-2.7691779602
C14	2.0433916225	-0.6412001095	-0.6054662242
C15	3.3894902211	-0.9761863041	-0.4128035245
C16	1.2799394859	-0.3763475473	0.5417511975
C17	3.8960564639	-1.0571643428	0.8655003571
H18	4.0189692045	-1.1862469080	-1.2740130429
H19	4.9282019121	-1.3332292317	1.0455442298
C20	3.0647611572	-0.7883791378	1.9548068973
H21	3.4209847598	-0.8590627223	2.9767215906
N22	1.8011395049	-0.4367216061	1.7907283213
Pd23	0.3389111672	-0.1465925046	3.2483562055
Pd24	1.3559215414	2.2556763780	3.4252123151
H25	4.8023509496	2.3582489876	-1.6022752393
C26	3.8716881295	2.6197822875	-1.1099718580
H27	2.6660443574	2.4023574511	-2.8647801738
C28	2.6902596555	2.6320428334	-1.8034440650
C29	2.7142451361	3.3382380224	0.8666677011
C30	1.4828091202	2.9587004944	-1.1626707480
C31	3.8884218555	3.0237874528	0.2272621683
C32	1.4540636373	3.2140242350	0.2344417043
C33	0.2896957000	3.0881699675	-1.9374188695
H34	4.8248801569	3.1304929290	0.7624994983
C35	-0.8707364825	3.4790007739	-1.3720002676
H36	0.3567332873	2.9038974084	-3.0058658826
H37	-1.7658542022	3.6318902909	-1.9678596106
C38	-0.9708593948	3.6141881734	0.0436729621
C39	-2.1974368596	3.8986182265	0.6602431880
C40	0.1566346810	3.3712173528	0.8593786159
C41	-2.2940427443	3.8918483568	2.0265433360
H42	-3.0635233890	4.0997745753	0.0354658687
H43	-3.2226105990	4.1136546324	2.5383134265
C44	-1.1807795934	3.4924460854	2.7618641437

H45	-1.2262075256	3.3438693852	3.8377319126
N46	-0.0094940706	3.2184207486	2.1992174924
C47	-1.1631853180	1.1732350027	5.4084473862
O48	-0.3479174378	2.0906324736	5.4804140846
O49	-1.2084091472	0.2427416895	4.5231745088
C50	2.5414941311	0.3222819218	5.2637032128
O51	1.6822591146	-0.5189508835	4.9431534889
O52	2.7422153816	1.4328448176	4.6784821429
C53	-2.2685709763	1.0448056875	6.4311710637
H54	-2.3825022666	1.9743959763	6.9895273732
H55	-1.9985726644	0.2430469363	7.1242222952
H56	-3.2084128217	0.7558972791	5.9571552824
C57	3.4296234377	0.0304963536	6.4385822231
H58	4.4174766367	0.4729796467	6.2994898173
H59	3.4997954701	-1.0441530901	6.6091472878
H60	2.9794047910	0.4910735716	7.3233008979
Cl61	2.9053267667	4.1040662649	2.4435064624
Cl62	-0.2798248816	-2.5189868713	3.0532474837

366	Pd 23 s	Cor(4s)	1.99273	-3.30409
367	Pd 23 s	Val(5s)	0.35943	0.57984
368	Pd 23 s	Ryd(6s)	0.00204	1.20922
369	Pd 23 s	Ryd(11s)	0.00091	20.96658
370	Pd 23 s	Ryd(7s)	0.00046	2.25597
371	Pd 23 s	Ryd(10s)	0.00004	15.43334
372	Pd 23 s	Ryd(8s)	0.00001	8.49028
373	Pd 23 s	Ryd(9s)	0.00000	14.55822
374	Pd 23 px	Cor(4p)	1.99655	-2.09923
375	Pd 23 px	Ryd(5p)	0.00420	1.30291
376	Pd 23 px	Ryd(7p)	0.00121	2.05781
377	Pd 23 px	Ryd(8p)	0.00053	2.39221
378	Pd 23 px	Ryd(6p)	0.00025	1.93959
379	Pd 23 px	Ryd(9p)	0.00001	8.36520
380	Pd 23 px	Ryd(10p)	0.00000	11.15919
381	Pd 23 py	Cor(4p)	1.99837	-2.09914
382	Pd 23 py	Ryd(6p)	0.01190	1.61094
383	Pd 23 py	Ryd(5p)	0.00331	1.14136
384	Pd 23 py	Ryd(8p)	0.00017	2.43844
385	Pd 23 py	Ryd(7p)	0.00023	1.80965
386	Pd 23 py	Ryd(9p)	0.00001	9.13640
387	Pd 23 py	Ryd(10p)	0.00000	11.21919
388	Pd 23 pz	Cor(4p)	1.99556	-2.10134
389	Pd 23 pz	Ryd(6p)	0.00345	1.73431
390	Pd 23 pz	Ryd(8p)	0.00118	2.51645
391	Pd 23 pz	Ryd(7p)	0.00051	2.37750
392	Pd 23 pz	Ryd(5p)	0.00049	1.66345
393	Pd 23 pz	Ryd(9p)	0.00001	8.45412
394	Pd 23 pz	Ryd(10p)	0.00000	11.16076
395	Pd 23 dxy	Val(4d)	1.90382	-0.31207

396	Pd 23	dxy	Ryd(5d)	0.00381	1.14204
397	Pd 23	dxy	Ryd(6d)	0.00100	1.55375
398	Pd 23	dxy	Ryd(7d)	0.00004	2.94572
399	Pd 23	dxz	Val(4d)	1.31581	-0.29402
400	Pd 23	dxz	Ryd(6d)	0.00118	1.91821
401	Pd 23	dxz	Ryd(5d)	0.00103	1.03229
402	Pd 23	dxz	Ryd(7d)	0.00005	2.68695
403	Pd 23	dyz	Val(4d)	1.92096	-0.31252
404	Pd 23	dyz	Ryd(6d)	0.00340	0.99425
405	Pd 23	dyz	Ryd(5d)	0.00135	0.88192
406	Pd 23	dyz	Ryd(7d)	0.00003	2.75795
407	Pd 23	dx2y2	Val(4d)	1.76128	-0.30870
408	Pd 23	dx2y2	Ryd(6d)	0.00386	1.38039
409	Pd 23	dx2y2	Ryd(5d)	0.00102	1.35036
410	Pd 23	dx2y2	Ryd(7d)	0.00007	2.81076
411	Pd 23	dz2	Val(4d)	1.85087	-0.31586
412	Pd 23	dz2	Ryd(6d)	0.00293	1.24464
413	Pd 23	dz2	Ryd(5d)	0.00062	0.91656
414	Pd 23	dz2	Ryd(7d)	0.00006	2.68011
415	Pd 23	f(0)	Ryd(4f)	0.00038	1.65843
416	Pd 23	f(0)	Ryd(5f)	0.00001	4.45037
417	Pd 23	f(c1)	Ryd(4f)	0.00090	1.87939
418	Pd 23	f(c1)	Ryd(5f)	0.00004	4.61748
419	Pd 23	f(s1)	Ryd(4f)	0.00036	1.57096
420	Pd 23	f(s1)	Ryd(5f)	0.00001	4.37756
421	Pd 23	f(c2)	Ryd(4f)	0.00077	1.81136
422	Pd 23	f(c2)	Ryd(5f)	0.00003	4.55968
423	Pd 23	f(s2)	Ryd(4f)	0.00046	1.62489
424	Pd 23	f(s2)	Ryd(5f)	0.00001	4.41074
425	Pd 23	f(c3)	Ryd(4f)	0.00040	1.65971
426	Pd 23	f(c3)	Ryd(5f)	0.00001	4.46403
427	Pd 23	f(s3)	Ryd(4f)	0.00040	1.58705
428	Pd 23	f(s3)	Ryd(5f)	0.00001	4.38366
429	Pd 24	s	Cor(4s)	1.99701	-3.29378
430	Pd 24	s	Val(5s)	0.36065	0.31316
431	Pd 24	s	Ryd(8s)	0.00130	6.75115
432	Pd 24	s	Ryd(9s)	0.00037	7.01646
433	Pd 24	s	Ryd(7s)	0.00018	4.11392
434	Pd 24	s	Ryd(6s)	0.00001	2.95839
435	Pd 24	s	Ryd(10s)	0.00000	10.24513
436	Pd 24	s	Ryd(11s)	0.00000	13.22437
437	Pd 24	px	Cor(4p)	1.99858	-2.05113
438	Pd 24	px	Ryd(7p)	0.00357	1.55006
439	Pd 24	px	Ryd(6p)	0.00125	1.40632
440	Pd 24	px	Ryd(5p)	0.00037	1.29525
441	Pd 24	px	Ryd(8p)	0.00035	2.50991
442	Pd 24	px	Ryd(9p)	0.00000	9.23979
443	Pd 24	px	Ryd(10p)	0.00000	11.44908
444	Pd 24	py	Cor(4p)	1.99736	-2.05333

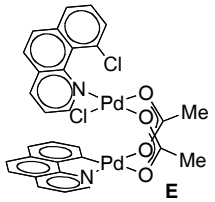
445	Pd 24	py	Ryd(6p)	0.00790	1.51166
446	Pd 24	py	Ryd(7p)	0.00098	1.58950
447	Pd 24	py	Ryd(5p)	0.00020	1.13301
448	Pd 24	py	Ryd(8p)	0.00020	2.49495
449	Pd 24	py	Ryd(9p)	0.00001	9.27469
450	Pd 24	py	Ryd(10p)	0.00000	11.44929
451	Pd 24	pz	Cor(4p)	1.99911	-2.04436
452	Pd 24	pz	Ryd(5p)	0.00462	1.13068
453	Pd 24	pz	Ryd(7p)	0.00111	1.19387
454	Pd 24	pz	Ryd(6p)	0.00032	1.18647
455	Pd 24	pz	Ryd(8p)	0.00020	2.48226
456	Pd 24	pz	Ryd(9p)	0.00000	9.26771
457	Pd 24	pz	Ryd(10p)	0.00000	11.45986
458	Pd 24	dxy	Val(4d)	1.63006	-0.26386
459	Pd 24	dxy	Ryd(6d)	0.00172	1.46368
460	Pd 24	dxy	Ryd(5d)	0.00075	0.97602
461	Pd 24	dxy	Ryd(7d)	0.00004	3.08698
462	Pd 24	dxz	Val(4d)	1.69894	-0.25531
463	Pd 24	dxz	Ryd(6d)	0.00196	1.72049
464	Pd 24	dxz	Ryd(5d)	0.00067	0.85813
465	Pd 24	dxz	Ryd(7d)	0.00004	2.79550
466	Pd 24	dyz	Val(4d)	1.86040	-0.26756
467	Pd 24	dyz	Ryd(6d)	0.00177	1.50875
468	Pd 24	dyz	Ryd(5d)	0.00062	0.66566
469	Pd 24	dyz	Ryd(7d)	0.00005	2.73238
470	Pd 24	dx2y2	Val(4d)	1.92728	-0.27442
471	Pd 24	dx2y2	Ryd(6d)	0.00162	1.16237
472	Pd 24	dx2y2	Ryd(5d)	0.00059	0.76169
473	Pd 24	dx2y2	Ryd(7d)	0.00006	2.60085
474	Pd 24	dz2	Val(4d)	1.95515	-0.26872
475	Pd 24	dz2	Ryd(6d)	0.00134	1.07516
476	Pd 24	dz2	Ryd(5d)	0.00060	0.79050
477	Pd 24	dz2	Ryd(7d)	0.00003	2.72145
478	Pd 24	f(0)	Ryd(4f)	0.00023	1.66535
479	Pd 24	f(0)	Ryd(5f)	0.00001	4.44985
480	Pd 24	f(c1)	Ryd(4f)	0.00027	1.69300
481	Pd 24	f(c1)	Ryd(5f)	0.00001	4.46132
482	Pd 24	f(s1)	Ryd(4f)	0.00016	1.68619
483	Pd 24	f(s1)	Ryd(5f)	0.00001	4.45310
484	Pd 24	f(c2)	Ryd(4f)	0.00021	1.65640
485	Pd 24	f(c2)	Ryd(5f)	0.00001	4.44368
486	Pd 24	f(s2)	Ryd(4f)	0.00059	1.77429
487	Pd 24	f(s2)	Ryd(5f)	0.00004	4.53003
488	Pd 24	f(c3)	Ryd(4f)	0.00022	1.70967
489	Pd 24	f(c3)	Ryd(5f)	0.00001	4.47342
490	Pd 24	f(s3)	Ryd(4f)	0.00024	1.68496
491	Pd 24	f(s3)	Ryd(5f)	0.00002	4.45911



D

C1	-2.196000	0.235000	-0.478000
C2	-1.428000	-0.244000	-1.523000
C3	-0.383000	-0.017000	1.087000
C4	-0.093000	-0.632000	-1.292000
C5	-1.687000	0.353000	0.834000
C6	0.406000	-0.500000	0.020000
C7	0.785000	-1.155000	-2.299000
C8	2.073000	-1.499000	-2.019000
C9	2.605000	-1.355000	-0.696000
C10	3.922000	-1.662000	-0.312000
C11	1.746000	-0.864000	0.302000
C12	4.313000	-1.485000	1.001000
C13	3.388000	-1.011000	1.939000
C14	-1.186000	1.200000	4.888000
C15	2.488000	0.491000	5.287000
C16	-2.332000	1.009000	5.840000
C17	2.790000	2.063000	-1.224000
C18	1.520000	2.334000	-1.669000
C19	2.192000	2.947000	0.924000
C20	0.553000	2.906000	-0.819000
C21	3.138000	2.398000	0.089000
C22	0.846000	3.177000	0.551000
C23	-0.715000	3.254000	-1.377000
C24	-1.640000	3.909000	-0.641000
C25	-1.422000	4.132000	0.749000
C26	-2.416000	4.757000	1.522000
C27	-0.230000	3.688000	1.380000
C28	-2.251000	4.905000	2.877000
C29	-1.121000	4.335000	3.458000
C30	3.406000	-0.006000	6.368000
N31	2.142000	-0.708000	1.594000
N32	-0.168000	3.733000	2.745000
O33	1.820000	-0.327000	4.626000
O34	2.477000	1.767000	5.151000
O35	-1.131000	0.447000	3.889000
O36	-0.358000	2.122000	5.199000
Cl37	2.853000	3.481000	2.484000
Pd38	0.603000	-0.045000	2.814000
Pd39	1.154000	2.656000	3.921000
H40	-3.229000	0.520000	-0.666000
H41	-1.851000	-0.343000	-2.521000
H42	-2.326000	0.712000	1.639000
H43	0.397000	-1.280000	-3.309000
H44	2.721000	-1.898000	-2.797000

H45	4.624000	-2.045000	-1.051000
H46	5.322000	-1.722000	1.324000
H47	3.639000	-0.888000	2.991000
H48	3.531000	1.620000	-1.884000
H49	1.238000	2.121000	-2.698000
H50	4.151000	2.250000	0.451000
H51	-0.891000	3.023000	-2.425000
H52	-2.581000	4.239000	-1.077000
H53	-3.316000	5.112000	1.025000
H54	-2.993000	5.393000	3.500000
H55	-0.995000	4.316000	4.537000
H56	-2.514000	1.905000	6.435000
H57	-2.078000	0.186000	6.518000
H58	-3.227000	0.714000	5.288000
H59	4.290000	0.630000	6.452000
H60	3.688000	-1.044000	6.176000
H61	2.876000	0.035000	7.325000



E

H1	-4.3357183022	-0.0705173485	1.8399906777
C2	-3.2858550271	-0.2609845083	1.6218226364
H3	-3.6948719075	-0.9739191205	-0.3682011944
C4	-2.9349380215	-0.7674205891	0.3840253396
C5	-0.9846059463	-0.2213139322	2.3641572279
C6	-1.5808985255	-1.0323829637	0.0960438908
C7	-2.3228078749	0.0152767763	2.6160453514
C8	-0.6321278286	-0.7546124620	1.1007096039
C9	-1.1095010615	-1.5577168969	-1.1528505821
H10	-2.6369592947	0.4112024224	3.5811289549
C11	0.2143385888	-1.7785418831	-1.3843378601
H12	-1.8421125176	-1.7787667766	-1.9279420535
H13	0.5505968678	-2.1737800165	-2.3413106978
C14	1.1971309173	-1.4964406220	-0.3811003633
C15	2.5848319200	-1.6712898988	-0.5283211314
C16	0.7433318562	-0.9960045475	0.8495849822
C17	3.4301184200	-1.3490038604	0.5127176436
H18	2.9810666547	-2.0546412978	-1.4676477694
H19	4.5057864608	-1.4620548594	0.4201671754
C20	2.8964422117	-0.8586339008	1.7122888112
H21	3.5157757308	-0.5804090591	2.5618874990
N22	1.5903669592	-0.7035773135	1.8709178892
Pd23	0.6206318601	0.1024592091	3.5041210374
Pd24	1.4925558215	2.9618796026	3.4329753158
H25	5.1222570991	7.7165725132	1.5780766322

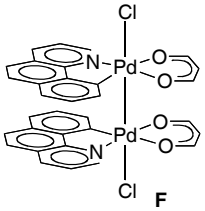
C26	4.2239891266	7.1215613006	1.4348018448
H27	4.4369564252	6.9812551703	-0.6971181230
C28	3.8543451976	6.7023907721	0.1788677932
C29	2.2665080290	6.0663699792	2.3644993382
C30	2.7022529642	5.9187798584	-0.0042671933
C31	3.3993974161	6.8377427234	2.5268418452
C32	1.9333842968	5.4880708875	1.1141112435
C33	2.2751403057	5.6118762877	-1.3344280034
H34	3.6205012125	7.2426107221	3.5099965965
C35	1.1287177974	4.9335093820	-1.5636021528
H36	2.8771996560	5.9874022551	-2.1594598452
H37	0.7649265190	4.7552129216	-2.5733938807
C38	0.4101747546	4.3587336096	-0.4716079692
C39	-0.7085161689	3.5403798689	-0.7003333718
C40	0.8741116674	4.5331115553	0.8570934282
C41	-1.3183569520	2.8949387609	0.3485120253
H42	-1.0660888881	3.4181513413	-1.7217580390
H43	-2.1862517120	2.2529202715	0.2198883681
C44	-0.7175202991	2.9931668029	1.6031005634
H45	-1.0854408487	2.4061502857	2.4389171928
N46	0.3589253168	3.7390917559	1.8386843009
C47	-0.6925599059	2.1431239662	5.2953463230
O48	-0.1486889002	3.1340639213	4.7285991104
O49	-0.5301054202	0.9154935123	5.0495510200
C50	2.9860838197	1.1439846565	5.1700541536
O51	2.4790034587	0.1336198477	4.6327273326
O52	2.6430470740	2.3562655383	4.9986569901
C53	-1.6536843199	2.4691416034	6.4102539380
H54	-2.0185669733	3.4939187174	6.3180991726
H55	-1.1249714786	2.3738987821	7.3648430799
H56	-2.4835638207	1.7577941590	6.4166224029
C57	4.1518929443	0.9502719701	6.1028850367
H58	5.0719443605	1.1362382541	5.5371892682
H59	4.1712627469	-0.0697173959	6.4913248509
H60	4.1148329444	1.6771350718	6.9177072903
Cl61	1.2104038074	5.9618650164	3.7523236527
Cl62	3.3151206457	2.6263637302	2.0012083368

370	Pd 23 s	Cor(4s)	1.99463	-3.27646
371	Pd 23 s	Val(5s)	0.37514	0.46249
372	Pd 23 s	Ryd(11s)	0.00156	18.74366
373	Pd 23 s	Ryd(6s)	0.00059	1.43825
374	Pd 23 s	Ryd(7s)	0.00037	1.57142
375	Pd 23 s	Ryd(8s)	0.00003	5.53042
376	Pd 23 s	Ryd(9s)	0.00000	7.42842
377	Pd 23 s	Ryd(10s)	0.00000	12.99567
378	Pd 23 px	Cor(4p)	1.99523	-2.06376
379	Pd 23 px	Ryd(5p)	0.00157	0.95089
380	Pd 23 px	Ryd(7p)	0.00026	2.50461

381	Pd 23	px	Ryd(8p)	0.00034	3.34009
382	Pd 23	px	Ryd(6p)	0.00021	1.04544
383	Pd 23	px	Ryd(9p)	0.00001	8.30494
384	Pd 23	px	Ryd(10p)	0.00000	11.35779
385	Pd 23	py	Cor(4p)	1.99806	-2.05150
386	Pd 23	py	Ryd(6p)	0.00302	1.30501
387	Pd 23	py	Ryd(7p)	0.00049	1.38203
388	Pd 23	py	Ryd(8p)	0.00022	2.85378
389	Pd 23	py	Ryd(5p)	0.00027	0.86701
390	Pd 23	py	Ryd(9p)	0.00000	9.23833
391	Pd 23	py	Ryd(10p)	0.00000	11.43951
392	Pd 23	pz	Cor(4p)	1.99723	-2.06101
393	Pd 23	pz	Ryd(6p)	0.00161	0.93344
394	Pd 23	pz	Ryd(7p)	0.00037	1.88576
395	Pd 23	pz	Ryd(8p)	0.00043	3.14906
396	Pd 23	pz	Ryd(5p)	0.00026	0.92203
397	Pd 23	pz	Ryd(9p)	0.00001	8.65166
398	Pd 23	pz	Ryd(10p)	0.00000	11.39011
399	Pd 23	dxy	Val(4d)	1.88189	-0.27334
400	Pd 23	dxy	Ryd(6d)	0.00231	1.10743
401	Pd 23	dxy	Ryd(5d)	0.00057	0.96863
402	Pd 23	dxy	Ryd(7d)	0.00002	2.87313
403	Pd 23	dxz	Val(4d)	1.37187	-0.25974
404	Pd 23	dxz	Ryd(6d)	0.00125	1.76261
405	Pd 23	dxz	Ryd(5d)	0.00054	0.90104
406	Pd 23	dxz	Ryd(7d)	0.00005	2.60303
407	Pd 23	dyz	Val(4d)	1.90444	-0.27418
408	Pd 23	dyz	Ryd(6d)	0.00197	1.25717
409	Pd 23	dyz	Ryd(5d)	0.00051	0.59061
410	Pd 23	dyz	Ryd(7d)	0.00004	2.81950
411	Pd 23	dx2y2	Val(4d)	1.87899	-0.27474
412	Pd 23	dx2y2	Ryd(6d)	0.00284	1.46873
413	Pd 23	dx2y2	Ryd(5d)	0.00050	0.82625
414	Pd 23	dx2y2	Ryd(7d)	0.00005	2.71731
415	Pd 23	dz2	Val(4d)	1.90885	-0.27761
416	Pd 23	dz2	Ryd(6d)	0.00190	1.12340
417	Pd 23	dz2	Ryd(5d)	0.00041	0.72291
418	Pd 23	dz2	Ryd(7d)	0.00004	2.69493
419	Pd 23	f(0)	Ryd(4f)	0.00026	1.65658
420	Pd 23	f(0)	Ryd(5f)	0.00002	4.40386
421	Pd 23	f(c1)	Ryd(4f)	0.00049	1.74350
422	Pd 23	f(c1)	Ryd(5f)	0.00002	4.50108
423	Pd 23	f(s1)	Ryd(4f)	0.00024	1.72473
424	Pd 23	f(s1)	Ryd(5f)	0.00001	4.48078
425	Pd 23	f(c2)	Ryd(4f)	0.00052	1.79183
426	Pd 23	f(c2)	Ryd(5f)	0.00003	4.54482
427	Pd 23	f(s2)	Ryd(4f)	0.00048	1.72457
428	Pd 23	f(s2)	Ryd(5f)	0.00002	4.48007
429	Pd 23	f(c3)	Ryd(4f)	0.00023	1.70805

430	Pd 23	f(c3)	Ryd(5f)	0.00001	4.46648
431	Pd 23	f(s3)	Ryd(4f)	0.00017	1.63821
432	Pd 23	f(s3)	Ryd(5f)	0.00001	4.38899
433	Pd 24	s	Cor(4s)	1.99828	-3.31114
434	Pd 24	s	Val(5s)	0.35352	0.35694
435	Pd 24	s	Ryd(7s)	0.00217	4.09255
436	Pd 24	s	Ryd(9s)	0.00073	8.46469
437	Pd 24	s	Ryd(8s)	0.00036	4.82179
438	Pd 24	s	Ryd(6s)	0.00001	3.16037
439	Pd 24	s	Ryd(10s)	0.00000	9.60336
440	Pd 24	s	Ryd(11s)	0.00000	12.25043
441	Pd 24	px	Cor(4p)	1.99894	-2.07641
442	Pd 24	px	Ryd(6p)	0.00145	1.86334
443	Pd 24	px	Ryd(5p)	0.00292	1.19282
444	Pd 24	px	Ryd(7p)	0.00029	1.95474
445	Pd 24	px	Ryd(8p)	0.00030	2.08245
446	Pd 24	px	Ryd(9p)	0.00000	9.34185
447	Pd 24	px	Ryd(10p)	0.00000	11.38699
448	Pd 24	py	Cor(4p)	1.99920	-2.05589
449	Pd 24	py	Ryd(6p)	0.00490	1.31846
450	Pd 24	py	Ryd(5p)	0.00103	1.03514
451	Pd 24	py	Ryd(8p)	0.00039	2.45236
452	Pd 24	py	Ryd(7p)	0.00007	2.26119
453	Pd 24	py	Ryd(9p)	0.00000	9.35216
454	Pd 24	py	Ryd(10p)	0.00000	11.39068
455	Pd 24	pz	Cor(4p)	1.99855	-2.07644
456	Pd 24	pz	Ryd(5p)	0.00165	1.02837
457	Pd 24	pz	Ryd(6p)	0.00186	1.07831
458	Pd 24	pz	Ryd(7p)	0.00034	1.85622
459	Pd 24	pz	Ryd(8p)	0.00035	2.15081
460	Pd 24	pz	Ryd(9p)	0.00000	9.30263
461	Pd 24	pz	Ryd(10p)	0.00000	11.38093
462	Pd 24	dxy	Val(4d)	1.94880	-0.28147
463	Pd 24	dxy	Ryd(6d)	0.00224	1.16196
464	Pd 24	dxy	Ryd(5d)	0.00091	0.95402
465	Pd 24	dxy	Ryd(7d)	0.00005	2.78880
466	Pd 24	dxz	Val(4d)	1.19995	-0.26059
467	Pd 24	dxz	Ryd(6d)	0.00245	1.79991
468	Pd 24	dxz	Ryd(5d)	0.00085	0.92714
469	Pd 24	dxz	Ryd(7d)	0.00006	2.65015
470	Pd 24	dyz	Val(4d)	1.85709	-0.27750
471	Pd 24	dyz	Ryd(6d)	0.00165	1.22091
472	Pd 24	dyz	Ryd(5d)	0.00098	0.76673
473	Pd 24	dyz	Ryd(7d)	0.00004	2.80826
474	Pd 24	dx2y2	Val(4d)	1.92668	-0.28225
475	Pd 24	dx2y2	Ryd(6d)	0.00211	1.21881
476	Pd 24	dx2y2	Ryd(5d)	0.00118	1.17015
477	Pd 24	dx2y2	Ryd(7d)	0.00006	2.87633
478	Pd 24	dz2	Val(4d)	1.92816	-0.28434

479	Pd 24	dz2	Ryd(6d)	0.00213	1.15229
480	Pd 24	dz2	Ryd(5d)	0.00080	0.94709
481	Pd 24	dz2	Ryd(7d)	0.00006	2.79110
482	Pd 24	f(0)	Ryd(4f)	0.00032	1.56624
483	Pd 24	f(0)	Ryd(5f)	0.00001	4.37407
484	Pd 24	f(c1)	Ryd(4f)	0.00078	1.72749
485	Pd 24	f(c1)	Ryd(5f)	0.00004	4.48978
486	Pd 24	f(s1)	Ryd(4f)	0.00028	1.61815
487	Pd 24	f(s1)	Ryd(5f)	0.00002	4.42114
488	Pd 24	f(c2)	Ryd(4f)	0.00062	1.75232
489	Pd 24	f(c2)	Ryd(5f)	0.00004	4.51232
490	Pd 24	f(s2)	Ryd(4f)	0.00056	1.67998
491	Pd 24	f(s2)	Ryd(5f)	0.00003	4.45582
492	Pd 24	f(c3)	Ryd(4f)	0.00025	1.60512
493	Pd 24	f(c3)	Ryd(5f)	0.00001	4.40952
494	Pd 24	f(s3)	Ryd(4f)	0.00023	1.60986
495	Pd 24	f(s3)	Ryd(5f)	0.00001	4.41078



F

H1	-3.8339841476	0.4979884017	-0.0048627135
C2	-2.7726140542	0.2799170290	0.0851854563
H3	-2.4664221535	0.2447126845	-2.0395168361
C4	-2.0141255441	0.1380534092	-1.0569755284
C5	-0.8713363372	-0.1166980065	1.5069575802
C6	-0.6430801292	-0.1520285103	-0.9536706054
C7	-2.2125338477	0.1559189638	1.3701795369
C8	-0.1007890123	-0.2803790772	0.3370835005
C9	0.2365749901	-0.3185350543	-2.0723145824
H10	-2.8332980442	0.2823792067	2.2534296317
C11	1.5545208348	-0.6029649765	-1.9111628986
H12	-0.1779623089	-0.2101655859	-3.0717163189
H13	2.2043857756	-0.7230640031	-2.7737398652
C14	2.1240908370	-0.7513086078	-0.6069179915
C15	3.4676185417	-1.0437519031	-0.3338541092
C16	1.2739410171	-0.5827988151	0.4947425166
C17	3.8956496024	-1.1467608353	0.9708005167
H18	4.1637333491	-1.1797813083	-1.1575639642
H19	4.9299044859	-1.3664408893	1.2074079426
C20	2.9831892880	-0.9589535647	2.0125069393
H21	3.2697729770	-1.0136892454	3.0589943436

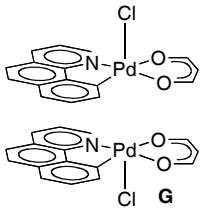
N22	1.7109330795	-0.6952687302	1.7734594667
Pd23	0.2170788385	-0.3413896371	3.1624366866
Pd24	1.4742805004	2.5984556411	3.2952361999
H25	4.8567917880	2.2876443245	-0.6542327910
C26	3.8338265077	2.4769504802	-0.3383343263
H27	3.1414686021	2.8229916011	-2.3408042721
C28	2.8798640525	2.7773189383	-1.2868649552
C29	2.2337746222	2.6344816979	1.4526062291
C30	1.5557240668	3.0309001248	-0.8905207018
C31	3.5224737568	2.4016824142	1.0319103126
C32	1.2628406419	2.9592645234	0.4826532313
C33	0.4870567663	3.3488743570	-1.7904600909
H34	4.2933757476	2.1531477872	1.7567216205
C35	-0.7746521918	3.5869984049	-1.3485050861
H36	0.7085695770	3.3952690155	-2.8540267836
H37	-1.5712918768	3.8233587312	-2.0486884146
C38	-1.0915857989	3.5319995692	0.0457517134
C39	-2.3581227510	3.7589073018	0.6020051810
C40	-0.0550411672	3.2148957376	0.9342838533
C41	-2.5369891443	3.6597802250	1.9635717190
H42	-3.1926578797	4.0042557497	-0.0498569679
H43	-3.5072820081	3.8248161292	2.4165784366
C44	-1.4502012293	3.3345189346	2.7796802933
H45	-1.5378566138	3.2307865316	3.8575201765
N46	-0.2469488918	3.1300299683	2.2739494132
O47	0.5092913558	2.7305031160	5.2084210807
O48	-1.4106794323	0.0438006409	4.3792399205
O49	1.5176204923	-0.7387883412	4.8217361843
O50	3.2953634939	2.0663287423	4.1186882862
C53	3.4324726251	1.9815753874	5.3673775267
C54	2.5160430475	2.1940056925	6.3937703845
C55	1.1642078942	2.5373450697	6.2545181201
H56	4.4456095224	1.6963784661	5.6950996433
H57	2.8864422885	2.0721959550	7.4064292120
H58	0.6079806582	2.6466695122	7.2023630975
C59	-1.3135830812	-0.0615976826	5.6301135611
C60	-0.2269227873	-0.4149932523	6.4254672321
C61	1.0705038605	-0.7142785869	5.9882807487
H62	1.7914542455	-0.9569316462	6.7887790880
H63	-0.4014638059	-0.4516280657	7.4958631856
H64	-2.2440164682	0.1588990967	6.1786641695

369	Pd 23	s	Cor(4s)	1.99474	-3.27287
370	Pd 23	s	Val(5s)	0.37988	0.50679
371	Pd 23	s	Ryd(11s)	0.00185	16.49941
372	Pd 23	s	Ryd(6s)	0.00066	1.14686
373	Pd 23	s	Ryd(7s)	0.00026	2.07602
374	Pd 23	s	Ryd(8s)	0.00004	6.76453
375	Pd 23	s	Ryd(9s)	0.00000	10.79665
376	Pd 23	s	Ryd(10s)	0.00000	16.25934
377	Pd 23	px	Cor(4p)	1.99665	-2.05855
378	Pd 23	px	Ryd(6p)	0.00144	1.30955
379	Pd 23	px	Ryd(7p)	0.00034	2.20709
380	Pd 23	px	Ryd(8p)	0.00049	2.69148
381	Pd 23	px	Ryd(5p)	0.00023	1.04864
382	Pd 23	px	Ryd(9p)	0.00001	8.52561
383	Pd 23	px	Ryd(10p)	0.00000	11.38764
384	Pd 23	py	Cor(4p)	1.99860	-2.04707
385	Pd 23	py	Ryd(7p)	0.00199	1.27758
386	Pd 23	py	Ryd(6p)	0.00087	1.12584
387	Pd 23	py	Ryd(8p)	0.00040	1.96686
388	Pd 23	py	Ryd(5p)	0.00016	1.02684
389	Pd 23	py	Ryd(9p)	0.00000	9.27157
390	Pd 23	py	Ryd(10p)	0.00000	11.46662
391	Pd 23	pz	Cor(4p)	1.99615	-2.06049
392	Pd 23	pz	Ryd(6p)	0.00180	1.47890
393	Pd 23	pz	Ryd(7p)	0.00050	2.80258
394	Pd 23	pz	Ryd(8p)	0.00054	2.82646
395	Pd 23	pz	Ryd(5p)	0.00021	1.20090
396	Pd 23	pz	Ryd(9p)	0.00001	8.69422
397	Pd 23	pz	Ryd(10p)	0.00000	11.37760
398	Pd 23	dxy	Val(4d)	1.95259	-0.26931
399	Pd 23	dxy	Ryd(6d)	0.00198	1.01104
400	Pd 23	dxy	Ryd(5d)	0.00055	0.75946
401	Pd 23	dxy	Ryd(7d)	0.00002	2.89169
402	Pd 23	dxz	Val(4d)	1.22760	-0.25142
403	Pd 23	dxz	Ryd(6d)	0.00115	1.95416
404	Pd 23	dxz	Ryd(5d)	0.00075	1.04903
405	Pd 23	dxz	Ryd(7d)	0.00005	2.67350
406	Pd 23	dyz	Val(4d)	1.90740	-0.27116
407	Pd 23	dyz	Ryd(6d)	0.00159	0.80240
408	Pd 23	dyz	Ryd(5d)	0.00058	0.72285

409	Pd 23	dyz	Ryd(7d)	0.00001	2.88461
410	Pd 23	dx2y2	Val(4d)	1.93669	-0.26841
411	Pd 23	dx2y2	Ryd(6d)	0.00286	1.49395
412	Pd 23	dx2y2	Ryd(5d)	0.00064	0.66156
413	Pd 23	dx2y2	Ryd(7d)	0.00005	2.76773
414	Pd 23	dz2	Val(4d)	1.92510	-0.28006
415	Pd 23	dz2	Ryd(6d)	0.00328	1.40982
416	Pd 23	dz2	Ryd(5d)	0.00087	0.79675
417	Pd 23	dz2	Ryd(7d)	0.00008	2.68248
418	Pd 23	f(0)	Ryd(4f)	0.00027	1.71844
419	Pd 23	f(0)	Ryd(5f)	0.00001	4.49510
420	Pd 23	f(c1)	Ryd(4f)	0.00082	1.90734
421	Pd 23	f(c1)	Ryd(5f)	0.00004	4.65817
422	Pd 23	f(s1)	Ryd(4f)	0.00016	1.59227
423	Pd 23	f(s1)	Ryd(5f)	0.00001	4.34672
424	Pd 23	f(c2)	Ryd(4f)	0.00063	1.83344
425	Pd 23	f(c2)	Ryd(5f)	0.00003	4.58355
426	Pd 23	f(s2)	Ryd(4f)	0.00033	1.65220
427	Pd 23	f(s2)	Ryd(5f)	0.00001	4.40198
428	Pd 23	f(c3)	Ryd(4f)	0.00017	1.65694
429	Pd 23	f(c3)	Ryd(5f)	0.00001	4.41794
430	Pd 23	f(s3)	Ryd(4f)	0.00015	1.62337
431	Pd 23	f(s3)	Ryd(5f)	0.00000	4.38198
432	Pd 24	s	Cor(4s)	1.99473	-3.27283
433	Pd 24	s	Val(5s)	0.37977	0.50456
434	Pd 24	s	Ryd(11s)	0.00204	16.52303
435	Pd 24	s	Ryd(6s)	0.00066	1.05848
436	Pd 24	s	Ryd(7s)	0.00028	1.82610
437	Pd 24	s	Ryd(8s)	0.00003	6.54412
438	Pd 24	s	Ryd(9s)	0.00000	10.82925
439	Pd 24	s	Ryd(10s)	0.00000	16.23048
440	Pd 24	px	Cor(4p)	1.99721	-2.05814
441	Pd 24	px	Ryd(6p)	0.00150	1.39483
442	Pd 24	px	Ryd(7p)	0.00039	2.20865
443	Pd 24	px	Ryd(8p)	0.00048	2.42650
444	Pd 24	px	Ryd(5p)	0.00025	1.08952
445	Pd 24	px	Ryd(9p)	0.00001	8.48199
446	Pd 24	px	Ryd(10p)	0.00000	11.38209
447	Pd 24	py	Cor(4p)	1.99863	-2.04720
448	Pd 24	py	Ryd(7p)	0.00202	1.27982
449	Pd 24	py	Ryd(6p)	0.00083	1.18194

450	Pd 24	py	Ryd(8p)	0.00048	1.83880
451	Pd 24	py	Ryd(5p)	0.00014	1.08085
452	Pd 24	py	Ryd(9p)	0.00001	9.28497
453	Pd 24	py	Ryd(10p)	0.00000	11.46170
454	Pd 24	pz	Cor(4p)	1.99553	-2.06068
455	Pd 24	pz	Ryd(6p)	0.00177	1.48812
456	Pd 24	pz	Ryd(8p)	0.00055	2.89606
457	Pd 24	pz	Ryd(7p)	0.00050	2.74353
458	Pd 24	pz	Ryd(5p)	0.00020	1.28081
459	Pd 24	pz	Ryd(9p)	0.00001	8.68539
460	Pd 24	pz	Ryd(10p)	0.00000	11.37856
461	Pd 24	dxy	Val(4d)	1.91668	-0.26794
462	Pd 24	dxy	Ryd(6d)	0.00184	1.06681
463	Pd 24	dxy	Ryd(5d)	0.00054	0.80376
464	Pd 24	dxy	Ryd(7d)	0.00002	2.90455
465	Pd 24	dxz	Val(4d)	1.49198	-0.26121
466	Pd 24	dxz	Ryd(6d)	0.00231	1.72245
467	Pd 24	dxz	Ryd(5d)	0.00084	0.89662
468	Pd 24	dxz	Ryd(7d)	0.00005	2.57388
469	Pd 24	dyz	Val(4d)	1.93645	-0.27209
470	Pd 24	dyz	Ryd(6d)	0.00170	0.80735
471	Pd 24	dyz	Ryd(5d)	0.00061	0.69854
472	Pd 24	dyz	Ryd(7d)	0.00002	2.90198
473	Pd 24	dx2y2	Val(4d)	1.89512	-0.26647
474	Pd 24	dx2y2	Ryd(6d)	0.00263	1.51663
475	Pd 24	dx2y2	Ryd(5d)	0.00064	0.70944
476	Pd 24	dx2y2	Ryd(7d)	0.00005	2.78153
477	Pd 24	dz2	Val(4d)	1.70956	-0.27252
478	Pd 24	dz2	Ryd(6d)	0.00240	1.52286
479	Pd 24	dz2	Ryd(5d)	0.00086	0.88457
480	Pd 24	dz2	Ryd(7d)	0.00007	2.68454
481	Pd 24	f(0)	Ryd(4f)	0.00055	1.81191
482	Pd 24	f(0)	Ryd(5f)	0.00002	4.58148
483	Pd 24	f(c1)	Ryd(4f)	0.00063	1.84555
484	Pd 24	f(c1)	Ryd(5f)	0.00004	4.60182
485	Pd 24	f(s1)	Ryd(4f)	0.00017	1.60499
486	Pd 24	f(s1)	Ryd(5f)	0.00001	4.36226
487	Pd 24	f(c2)	Ryd(4f)	0.00045	1.76506
488	Pd 24	f(c2)	Ryd(5f)	0.00002	4.51663
489	Pd 24	f(s2)	Ryd(4f)	0.00026	1.63674
490	Pd 24	f(s2)	Ryd(5f)	0.00001	4.38623

491	Pd 24	f(c3)	Ryd(4f)	0.00022	1.66645
492	Pd 24	f(c3)	Ryd(5f)	0.00001	4.42520
493	Pd 24	f(s3)	Ryd(4f)	0.00024	1.65233
494	Pd 24	f(s3)	Ryd(5f)	0.00001	4.41063



G

Pd1	1.0016249501	2.0042562346	2.8318015400
H2	3.6587435382	1.5863531374	-1.6204929553
C3	2.7189826949	1.8382950915	-1.1329593696
H4	1.7482850406	2.3412426412	-2.9826476811
C5	1.6506154608	2.2594537730	-1.9015806973
C6	1.4436614461	2.0421110183	0.8822531197
C7	0.4296989997	2.6022849325	-1.2893603354
C8	2.6356254445	1.7368035630	0.2720372459
C9	0.3498664935	2.4789857839	0.1111377061
C10	-0.7284563670	3.0820148004	-1.9876577575
H11	3.4950977359	1.4282713560	0.8629406084
C12	-1.8717694589	3.4288906951	-1.3327585341
H13	-0.6735467227	3.1753119382	-3.0712440548
H14	-2.7336910150	3.8008843227	-1.8835131995
C15	-1.9690531449	3.3189796588	0.0928200122
C16	-3.0887870347	3.6662265806	0.8686869074
C17	-0.8480527023	2.8282837129	0.7821416982
C18	-3.0486849668	3.5243478807	2.2424185263
H19	-3.9811669396	4.0538881837	0.3798194975
H20	-3.8982965090	3.7974357613	2.8604774349
C21	-1.8917652514	3.0227894622	2.8520155992
H22	-1.7950013627	2.8943624498	3.9288087719
N23	-0.8392381690	2.6729373408	2.1291813794
O24	0.2839545677	1.9222332468	4.8558353208
O25	2.8363925077	1.2179725152	3.3079123546
Cl26	1.7897751467	4.3696111074	3.0979181873
C27	1.0981179632	1.6883248003	5.7830078919
C28	2.4515078471	1.3276489454	5.6927881178
H29	2.9795659651	1.1697345207	6.6287068095
C30	3.1773090737	1.1095953610	4.5260286117
H31	4.2168253145	0.7734388863	4.6659371394

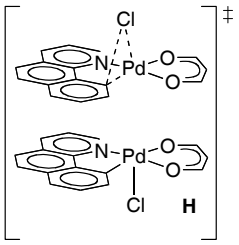
H32	0.6933096453	1.7569447955	6.8082692225

1	Pd	1	s	Cor(4s)	0.99729	-3.33462
2	Pd	1	s	Val(5s)	0.17344	0.49709
3	Pd	1	s	Ryd(11s)	0.00084	15.50416
4	Pd	1	s	Ryd(6s)	0.00067	0.85018
5	Pd	1	s	Ryd(8s)	0.00010	4.19872
6	Pd	1	s	Ryd(9s)	0.00001	10.62284
7	Pd	1	s	Ryd(7s)	0.00000	3.67103
8	Pd	1	s	Ryd(10s)	0.00000	13.46525
9	Pd	1	px	Cor(4p)	0.99899	-2.11775
10	Pd	1	px	Ryd(7p)	0.00110	1.16486
11	Pd	1	px	Ryd(6p)	0.00050	1.14063
12	Pd	1	px	Ryd(8p)	0.00025	2.83615
13	Pd	1	px	Ryd(5p)	0.00007	0.53961
14	Pd	1	px	Ryd(9p)	0.00000	9.42728
15	Pd	1	px	Ryd(10p)	0.00000	11.24271
16	Pd	1	py	Cor(4p)	0.99950	-2.12106
17	Pd	1	py	Ryd(5p)	0.00593	0.53829
18	Pd	1	py	Ryd(7p)	0.00069	0.74853
19	Pd	1	py	Ryd(8p)	0.00012	2.17276
20	Pd	1	py	Ryd(6p)	0.00004	0.55183
21	Pd	1	py	Ryd(9p)	0.00000	9.44446
22	Pd	1	py	Ryd(10p)	0.00000	11.28856
23	Pd	1	pz	Cor(4p)	0.99754	-2.11744
24	Pd	1	pz	Ryd(7p)	0.00097	2.42182
25	Pd	1	pz	Ryd(6p)	0.00060	1.55767
26	Pd	1	pz	Ryd(8p)	0.00026	2.73259
27	Pd	1	pz	Ryd(5p)	0.00007	0.56262
28	Pd	1	pz	Ryd(9p)	0.00000	9.29665
29	Pd	1	pz	Ryd(10p)	0.00000	11.26896
30	Pd	1	dxy	Val(4d)	0.95584	-0.33291
31	Pd	1	dxy	Ryd(6d)	0.00104	1.15715
32	Pd	1	dxy	Ryd(5d)	0.00037	0.38657
33	Pd	1	dxy	Ryd(7d)	0.00003	2.70939
34	Pd	1	dxz	Val(4d)	0.89854	-0.32352
35	Pd	1	dxz	Ryd(6d)	0.00164	1.48906
36	Pd	1	dxz	Ryd(5d)	0.00050	0.53786
37	Pd	1	dxz	Ryd(7d)	0.00002	2.46912
38	Pd	1	dyz	Val(4d)	0.98038	-0.33273
39	Pd	1	dyz	Ryd(6d)	0.00072	0.79745

40	Pd	1	dyz	Ryd(5d)	0.00074	0.41525
41	Pd	1	dyz	Ryd(7d)	0.00002	2.75813
42	Pd	1	dx2y2	Val(4d)	0.96243	-0.33561
43	Pd	1	dx2y2	Ryd(6d)	0.00134	1.34134
44	Pd	1	dx2y2	Ryd(5d)	0.00033	0.38438
45	Pd	1	dx2y2	Ryd(7d)	0.00003	2.71173
46	Pd	1	dz2	Val(4d)	0.76893	-0.32067
47	Pd	1	dz2	Ryd(6d)	0.00080	1.72004
48	Pd	1	dz2	Ryd(5d)	0.00031	0.57572
49	Pd	1	dz2	Ryd(7d)	0.00003	2.71568
50	Pd	1	f(0)	Ryd(4f)	0.00040	1.83330
51	Pd	1	f(0)	Ryd(5f)	0.00002	4.59235
52	Pd	1	f(c1)	Ryd(4f)	0.00029	1.70661
53	Pd	1	f(c1)	Ryd(5f)	0.00001	4.48627
54	Pd	1	f(s1)	Ryd(4f)	0.00018	1.53460
55	Pd	1	f(s1)	Ryd(5f)	0.00000	4.33357
56	Pd	1	f(c2)	Ryd(4f)	0.00014	1.59456
57	Pd	1	f(c2)	Ryd(5f)	0.00000	4.38144
58	Pd	1	f(s2)	Ryd(4f)	0.00012	1.54631
59	Pd	1	f(s2)	Ryd(5f)	0.00000	4.33613
60	Pd	1	f(c3)	Ryd(4f)	0.00019	1.53913
61	Pd	1	f(c3)	Ryd(5f)	0.00000	4.33368
62	Pd	1	f(s3)	Ryd(4f)	0.00026	1.64441
63	Pd	1	f(s3)	Ryd(5f)	0.00000	4.42841

		Natural Population				Natural
	Natural	----------				Spin
Atom	No	Charge	Core	Valence	Rydberg	Total	Density
Pd	1	0.87098	35.98537	9.10501	0.03865	45.12902	0.38026
H	2	0.20837	0.00000	0.79015	0.00148	0.79163	0.00036
C	3	-0.17573	1.99930	4.15774	0.01869	6.17573	-0.00521
H	4	0.20551	0.00000	0.79245	0.00204	0.79449	-0.00037
C	5	-0.18321	1.99899	4.16699	0.01723	6.18321	0.01019
C	6	-0.03091	1.99889	3.99099	0.04104	6.03091	0.01643
C	7	-0.07645	1.99920	4.05249	0.02476	6.07645	-0.00273
C	8	-0.22905	1.99894	4.20919	0.02093	6.22905	0.01187
C	9	-0.03979	1.99879	4.02880	0.01221	6.03979	0.00476
C	10	-0.14014	1.99900	4.12411	0.01703	6.14014	0.00281
H	11	0.23480	0.00000	0.76308	0.00213	0.76520	-0.00031
C	12	-0.19103	1.99922	4.17398	0.01783	6.19103	-0.00297

H 13	0.20875	0.00000	0.78919	0.00207	0.79125	-0.00010
H 14	0.20915	0.00000	0.78904	0.00181	0.79085	0.00026
C 15	-0.09591	1.99908	4.07895	0.01788	6.09591	0.00347
C 16	-0.09780	1.99900	4.08220	0.01660	6.09780	-0.00064
C 17	0.22079	1.99894	3.75174	0.02853	5.77921	-0.00435
C 18	-0.25051	1.99929	4.23555	0.01567	6.25051	0.00340
H 19	0.21181	0.00000	0.78617	0.00202	0.78819	0.00016
H 20	0.22181	0.00000	0.77679	0.00139	0.77819	0.00010
C 21	0.10698	1.99930	3.86985	0.02387	5.89302	-0.00046
H 22	0.23078	0.00000	0.76753	0.00168	0.76922	0.00090
N 23	-0.44121	1.99927	5.41237	0.02958	7.44121	0.04326
O 24	-0.66942	1.99978	6.65087	0.01877	8.66942	0.00775
O 25	-0.62619	1.99977	6.60647	0.01995	8.62619	0.05054
Cl 26	-0.44822	9.99989	7.44419	0.00414	17.44822	0.47731
C 27	0.39629	1.99938	3.57014	0.03419	5.60371	-0.00508
C 28	-0.50606	1.99923	4.49041	0.01642	6.50606	0.01386
H 29	0.21750	0.00000	0.78144	0.00106	0.78250	-0.00055
C 30	0.37453	1.99933	3.59254	0.03360	5.62547	-0.00833
H 31	0.14918	0.00000	0.84809	0.00273	0.85082	0.00346
H 32	0.13441	0.00000	0.86251	0.00308	0.86559	-0.00005
==========	==========	==========	==========	==========	==========	==========
* Total *	0.00001	83.96992	108.54100	0.48908	192.99999	1.00000



Pd1	0.9969589639	2.0358552046	2.8516534014
H2	3.5503921570	1.2830865583	-1.6154386763
C3	2.6595375600	1.6599466404	-1.1183008672
H4	1.6087841096	1.9832012120	-2.9724748309
C5	1.5656154686	2.0457541631	-1.8863603532
C6	1.5159797410	2.2952923914	0.9369529562
C7	0.3716837934	2.4934421495	-1.2679055304
C8	2.6540171062	1.7726194777	0.2703808235
C9	0.3512852311	2.5622527133	0.1293237832
C10	-0.8189511016	2.8423208514	-1.9813187283
H11	3.5286997174	1.5174540237	0.8645956406

C12	-1.9604095251	3.2095016230	-1.3294340674
H13	-0.8011695118	2.8056646695	-3.0693878102
H14	-2.8566323699	3.4721379781	-1.8884490887
C15	-2.0177941115	3.2207806300	0.0975458876
C16	-3.1634191319	3.5041677431	0.8647881171
C17	-0.8479155107	2.8750099521	0.8000992040
C18	-3.1077654872	3.4122801597	2.2395343191
H19	-4.0895536383	3.7821770255	0.3642936386
H20	-3.9791108777	3.6215344562	2.8524918375
C21	-1.9095805566	3.0231685782	2.8599910195
H22	-1.8192889421	2.9020915267	3.9382008026
N23	-0.8200737027	2.7655260697	2.1576577071
O24	0.2508997894	1.8815222239	4.8280755817
O25	2.8427932069	1.2644644821	3.3193556899
Cl26	2.3122418043	4.3825830025	1.3117125380
C27	0.9936363227	1.4346178676	5.7414391987
C28	2.3151304518	0.9801423196	5.6586103312
H29	2.7723121952	0.6318489615	6.5805974764
C30	3.1072269974	0.9304713358	4.5104208875
H31	4.1272105046	0.5367977049	4.6531485546
H32	0.5388453787	1.3924739679	6.7470384335

1	Pd	1	s	Cor(4s)	0.99678	-3.28498
2	Pd	1	s	Val(5s)	0.17457	0.42548
3	Pd	1	s	Ryd(11s)	0.00116	14.08277
4	Pd	1	s	Ryd(7s)	0.00024	5.14390
5	Pd	1	s	Ryd(6s)	0.00011	1.99047
6	Pd	1	s	Ryd(9s)	0.00002	6.03835
7	Pd	1	s	Ryd(8s)	0.00000	6.02424
8	Pd	1	s	Ryd(10s)	0.00000	11.78363
9	Pd	1	px	Cor(4p)	0.99883	-2.07316
10	Pd	1	px	Ryd(5p)	0.00071	0.84338
11	Pd	1	px	Ryd(7p)	0.00024	1.40231
12	Pd	1	px	Ryd(8p)	0.00014	2.35423
13	Pd	1	px	Ryd(6p)	0.00010	0.94806
14	Pd	1	px	Ryd(9p)	0.00000	9.55821
15	Pd	1	px	Ryd(10p)	0.00000	11.18805
16	Pd	1	py	Cor(4p)	0.99932	-2.06353
17	Pd	1	py	Ryd(5p)	0.00144	0.46988
18	Pd	1	py	Ryd(7p)	0.00028	1.08163
19	Pd	1	py	Ryd(8p)	0.00009	1.49131

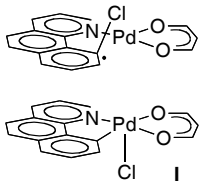
20	Pd	1	py	Ryd(6p)	0.00010	0.80447
21	Pd	1	py	Ryd(9p)	0.00000	9.60461
22	Pd	1	py	Ryd(10p)	0.00000	11.31053
23	Pd	1	pz	Cor(4p)	0.99749	-2.07527
24	Pd	1	pz	Ryd(6p)	0.00097	1.04913
25	Pd	1	pz	Ryd(7p)	0.00040	1.58911
26	Pd	1	pz	Ryd(8p)	0.00017	2.37704
27	Pd	1	pz	Ryd(5p)	0.00009	0.98819
28	Pd	1	pz	Ryd(9p)	0.00000	9.63232
29	Pd	1	pz	Ryd(10p)	0.00000	11.20976
30	Pd	1	dxy	Val(4d)	0.93010	-0.28133
31	Pd	1	dxy	Ryd(6d)	0.00076	1.23751
32	Pd	1	dxy	Ryd(5d)	0.00024	0.47486
33	Pd	1	dxy	Ryd(7d)	0.00002	2.77756
34	Pd	1	dxz	Val(4d)	0.87061	-0.28739
35	Pd	1	dxz	Ryd(6d)	0.00161	1.46850
36	Pd	1	dxz	Ryd(5d)	0.00035	0.56698
37	Pd	1	dxz	Ryd(7d)	0.00003	2.59209
38	Pd	1	dyz	Val(4d)	0.97298	-0.28900
39	Pd	1	dyz	Ryd(6d)	0.00094	0.94046
40	Pd	1	dyz	Ryd(5d)	0.00024	0.42765
41	Pd	1	dyz	Ryd(7d)	0.00001	2.78455
42	Pd	1	dx2y2	Val(4d)	0.95111	-0.28319
43	Pd	1	dx2y2	Ryd(6d)	0.00099	1.43600
44	Pd	1	dx2y2	Ryd(5d)	0.00030	0.52734
45	Pd	1	dx2y2	Ryd(7d)	0.00002	2.76624
46	Pd	1	dz2	Val(4d)	0.76538	-0.28183
47	Pd	1	dz2	Ryd(6d)	0.00075	1.65181
48	Pd	1	dz2	Ryd(5d)	0.00051	0.64097
49	Pd	1	dz2	Ryd(7d)	0.00003	2.60334
50	Pd	1	f(0)	Ryd(4f)	0.00036	1.78314
51	Pd	1	f(0)	Ryd(5f)	0.00001	4.56737
52	Pd	1	f(c1)	Ryd(4f)	0.00029	1.72866
53	Pd	1	f(c1)	Ryd(5f)	0.00002	4.51107
54	Pd	1	f(s1)	Ryd(4f)	0.00011	1.62050
55	Pd	1	f(s1)	Ryd(5f)	0.00000	4.39583
56	Pd	1	f(c2)	Ryd(4f)	0.00010	1.64258
57	Pd	1	f(c2)	Ryd(5f)	0.00000	4.41492
58	Pd	1	f(s2)	Ryd(4f)	0.00010	1.61045
59	Pd	1	f(s2)	Ryd(5f)	0.00000	4.38206
60	Pd	1	f(c3)	Ryd(4f)	0.00010	1.58211

61	Pd	1	f(c3)	Ryd(5f)	0.00000	4.34870
62	Pd	1	f(s3)	Ryd(4f)	0.00020	1.67112
63	Pd	1	f(s3)	Ryd(5f)	0.00001	4.44971

		Natural Population				Natural
	Natural	----------				Spin
Atom No	Charge	Core	Valence	Rydberg	Total	Density
Pd 1	0.70994	35.98479	9.27666	0.02861	45.29006	0.05306
H 2	0.21214	0.00000	0.78623	0.00162	0.78786	0.00375
C 3	-0.20794	1.99925	4.19134	0.01735	6.20794	-0.12763
H 4	0.20450	0.00000	0.79381	0.00168	0.79550	-0.01277
C 5	-0.13613	1.99922	4.11933	0.01758	6.13613	0.30411
C 6	-0.03019	1.99875	3.99696	0.03447	6.03019	-0.02887
C 7	-0.05303	1.99886	4.03477	0.01940	6.05303	-0.07322
C 8	-0.17077	1.99912	4.14733	0.02433	6.17077	0.29564
C 9	-0.10156	1.99879	4.07424	0.02852	6.10156	0.13487
C 10	-0.14333	1.99902	4.12616	0.01814	6.14333	0.04805
H 11	0.23547	0.00000	0.76270	0.00183	0.76453	-0.01218
C 12	-0.18293	1.99921	4.16657	0.01715	6.18293	-0.04516
H 13	0.20884	0.00000	0.78896	0.00221	0.79116	-0.00198
H 14	0.20954	0.00000	0.78874	0.00172	0.79046	0.00180
C 15	-0.11155	1.99915	4.08835	0.02404	6.11155	0.04413
C 16	-0.10377	1.99900	4.08834	0.01644	6.10377	-0.02152
C 17	0.30229	1.99889	3.68244	0.01637	5.69771	-0.03742
C 18	-0.24936	1.99928	4.23340	0.01668	6.24936	0.04269
H 19	0.21185	0.00000	0.78624	0.00192	0.78815	0.00075
H 20	0.22099	0.00000	0.77764	0.00138	0.77901	-0.00171
C 21	0.10430	1.99932	3.87062	0.02576	5.89570	-0.01558
H 22	0.22663	0.00000	0.77163	0.00174	0.77337	0.00065
N 23	-0.46325	1.99933	5.42700	0.03692	7.46325	0.04142
O 24	-0.67213	1.99978	6.65377	0.01858	8.67213	0.00867
O 25	-0.63254	1.99976	6.61237	0.02041	8.63254	0.01186
Cl 26	-0.31763	9.99988	7.31121	0.00654	17.31763	0.38575
C 27	0.38192	1.99937	3.58457	0.03414	5.61808	-0.00109
C 28	-0.51793	1.99924	4.50210	0.01659	6.51793	0.00036
H 29	0.21554	0.00000	0.78339	0.00108	0.78446	-0.00006
C 30	0.37477	1.99934	3.59188	0.03401	5.62523	-0.00132
H 31	0.14188	0.00000	0.85523	0.00290	0.85812	0.00155
H 32	0.13345	0.00000	0.86346	0.00309	0.86655	0.00140

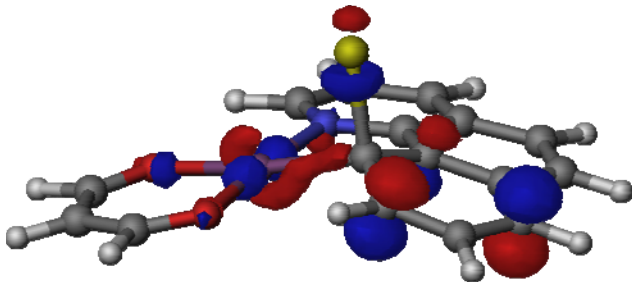
==========

* Total *	0.00000	83.96935	108.53744	0.49321	193.00000	1.00000



I

The Pd(I) fragment of complex **I** is best represented as a Pd(II) metal center with a ligand-centered radical. This formulation is supported by the SOMO orbital coefficients, illustrated below:



Pd1	1.0045652621	2.0592010358	2.8338608793
H2	3.4785735284	1.0440705665	-1.5092739932
C3	2.6268067785	1.5364487766	-1.0450067154
H4	1.5279673432	1.6702439545	-2.9070954413
C5	1.5224622284	1.8725371043	-1.8375220019
C6	1.5997424804	2.5622575110	0.9415194412
C7	0.3561934095	2.4159988525	-1.2411252551
C8	2.6859095570	1.8538431147	0.2979493016
C9	0.3722655617	2.6612276452	0.1357720769
C10	-0.8585101373	2.6582450916	-1.9597351960
H11	3.5780882796	1.6603544685	0.8892369976
C12	-1.9972919593	3.0636961123	-1.3268400758
H13	-0.8600326291	2.5006813553	-3.0372558789
H14	-2.9117819474	3.2432428249	-1.8893217253
C15	-2.0318710855	3.1851127157	0.0938733433
C16	-3.1864229834	3.4374949807	0.8567174471
C17	-0.8343635941	2.9447613832	0.8004340397
C18	-3.1239426370	3.3964428319	2.2337181390
H19	-4.1288431250	3.6369099278	0.3493169329
H20	-4.0053838248	3.5729292129	2.8424733069
C21	-1.9080828479	3.0719654024	2.8577382483
H22	-1.8178528989	2.9525051015	3.9361439965
N23	-0.8072344688	2.8562520346	2.1610215010
O24	0.2131540788	1.7373100867	4.7946201542

O25	2.8538791431	1.2499819203	3.2886265155
Cl26	2.2375941418	4.3142703574	1.3309780739
C27	0.9429977424	1.2215455487	5.6790001603
C28	2.2703484395	0.7814684228	5.5851505974
H29	2.7105235933	0.3630063629	6.4862688971
C30	3.0896323206	0.8254967025	4.4556035418
H31	4.1089489737	0.4262597947	4.5965413995
H32	0.4742871062	1.0943060951	6.6723889155

1	Pd 1 s	Cor(4s)	0.99711	-3.28369
2	Pd 1 s	Val(5s)	0.17365	0.39759
3	Pd 1 s	Ryd(11s)	0.00100	11.02474
4	Pd 1 s	Ryd(10s)	0.00021	10.64571
5	Pd 1 s	Ryd(6s)	0.00009	2.56819
6	Pd 1 s	Ryd(7s)	0.00001	3.83082
7	Pd 1 s	Ryd(8s)	0.00000	6.75389
8	Pd 1 s	Ryd(9s)	0.00000	10.43320
9	Pd 1 px	Cor(4p)	0.99885	-2.06474
10	Pd 1 px	Ryd(5p)	0.00073	0.75808
11	Pd 1 px	Ryd(7p)	0.00026	1.41802
12	Pd 1 px	Ryd(6p)	0.00015	1.08537
13	Pd 1 px	Ryd(8p)	0.00009	1.87041
14	Pd 1 px	Ryd(9p)	0.00000	9.78358
15	Pd 1 px	Ryd(10p)	0.00000	11.29528
16	Pd 1 py	Cor(4p)	0.99938	-2.05581
17	Pd 1 py	Ryd(5p)	0.00162	0.51621
18	Pd 1 py	Ryd(7p)	0.00024	1.20715
19	Pd 1 py	Ryd(6p)	0.00013	0.65513
20	Pd 1 py	Ryd(8p)	0.00007	1.53398
21	Pd 1 py	Ryd(9p)	0.00000	9.72393
22	Pd 1 py	Ryd(10p)	0.00000	11.39588
23	Pd 1 pz	Cor(4p)	0.99765	-2.06660
24	Pd 1 pz	Ryd(5p)	0.00104	0.87143
25	Pd 1 pz	Ryd(7p)	0.00042	1.40776
26	Pd 1 pz	Ryd(6p)	0.00010	1.03455
27	Pd 1 pz	Ryd(8p)	0.00005	1.92898
28	Pd 1 pz	Ryd(9p)	0.00000	9.86915
29	Pd 1 pz	Ryd(10p)	0.00000	11.32838
30	Pd 1 dxy	Val(4d)	0.92231	-0.27417
31	Pd 1 dxy	Ryd(6d)	0.00080	1.26443
32	Pd 1 dxy	Ryd(5d)	0.00019	0.45961

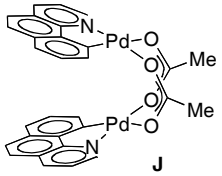
33	Pd	1	dxy	Ryd(7d)	0.00002	2.74808
34	Pd	1	dxz	Val(4d)	0.88320	-0.28110
35	Pd	1	dxz	Ryd(6d)	0.00144	1.41835
36	Pd	1	dxz	Ryd(5d)	0.00032	0.56879
37	Pd	1	dxz	Ryd(7d)	0.00002	2.61643
38	Pd	1	dyz	Val(4d)	0.97287	-0.28223
39	Pd	1	dyz	Ryd(6d)	0.00094	1.09686
40	Pd	1	dyz	Ryd(5d)	0.00026	0.43352
41	Pd	1	dyz	Ryd(7d)	0.00002	2.79257
42	Pd	1	dx2y2	Val(4d)	0.95922	-0.27731
43	Pd	1	dx2y2	Ryd(6d)	0.00101	1.33854
44	Pd	1	dx2y2	Ryd(5d)	0.00021	0.49189
45	Pd	1	dx2y2	Ryd(7d)	0.00002	2.76461
46	Pd	1	dz2	Val(4d)	0.80631	-0.27538
47	Pd	1	dz2	Ryd(6d)	0.00070	1.51735
48	Pd	1	dz2	Ryd(5d)	0.00038	0.61436
49	Pd	1	dz2	Ryd(7d)	0.00003	2.59058
50	Pd	1	f(0)	Ryd(4f)	0.00026	1.72620
51	Pd	1	f(0)	Ryd(5f)	0.00001	4.50733
52	Pd	1	f(c1)	Ryd(4f)	0.00025	1.72785
53	Pd	1	f(c1)	Ryd(5f)	0.00002	4.51249
54	Pd	1	f(s1)	Ryd(4f)	0.00013	1.67138
55	Pd	1	f(s1)	Ryd(5f)	0.00000	4.45321
56	Pd	1	f(c2)	Ryd(4f)	0.00009	1.64284
57	Pd	1	f(c2)	Ryd(5f)	0.00000	4.41130
58	Pd	1	f(s2)	Ryd(4f)	0.00012	1.64903
59	Pd	1	f(s2)	Ryd(5f)	0.00000	4.42096
60	Pd	1	f(c3)	Ryd(4f)	0.00009	1.58333
61	Pd	1	f(c3)	Ryd(5f)	0.00000	4.34724
62	Pd	1	f(s3)	Ryd(4f)	0.00019	1.68303
63	Pd	1	f(s3)	Ryd(5f)	0.00001	4.46131

		Natural	Natural Population				Natural Spin
Atom	No	Charge	Core	Valence	Rydberg	Total	Density
Pd	1	0.67211	35.98622	9.31424	0.02743	45.32789	0.12072
H	2	0.21091	0.00000	0.78733	0.00177	0.78909	0.00424
C	3	-0.22192	1.99925	4.20553	0.01714	6.22192	-0.14663
H	4	0.20228	0.00000	0.79609	0.00163	0.79772	-0.01720
C	5	-0.14871	1.99923	4.13222	0.01726	6.14871	0.40920

C 6	-0.10517	1.99867	4.07215	0.03435	6.10517	-0.06161
C 7	-0.05857	1.99885	4.04034	0.01937	6.05857	-0.09752
C 8	-0.16389	1.99914	4.14021	0.02455	6.16389	0.36315
C 9	-0.08912	1.99901	4.05882	0.03128	6.08912	0.19056
C 10	-0.14634	1.99901	4.12948	0.01784	6.14634	0.06414
H 11	0.23168	0.00000	0.76660	0.00172	0.76832	-0.01485
C 12	-0.18446	1.99921	4.16824	0.01702	6.18446	-0.06174
H 13	0.20812	0.00000	0.78970	0.00218	0.79188	-0.00264
H 14	0.20868	0.00000	0.78958	0.00174	0.79132	0.00243
C 15	-0.11381	1.99915	4.09115	0.02350	6.11381	0.06194
C 16	-0.10603	1.99900	4.09058	0.01645	6.10603	-0.03394
C 17	0.29161	1.99888	3.69340	0.01611	5.70839	-0.04599
C 18	-0.25439	1.99928	4.23821	0.01690	6.25439	0.06436
H 19	0.21065	0.00000	0.78742	0.00193	0.78935	0.00122
H 20	0.21983	0.00000	0.77877	0.00140	0.78017	-0.00251
C 21	0.10312	1.99932	3.87164	0.02593	5.89688	-0.02956
H 22	0.22406	0.00000	0.77421	0.00173	0.77594	0.00123
N 23	-0.47465	1.99934	5.43880	0.03651	7.47465	0.06687
O 24	-0.66879	1.99978	6.65022	0.01879	8.66879	0.02453
O 25	-0.64367	1.99977	6.62350	0.02041	8.64367	0.02090
Cl 26	-0.11838	9.99970	7.10431	0.01437	17.11838	0.11691
C 27	0.38078	1.99937	3.58529	0.03456	5.61922	-0.00291
C 28	-0.52085	1.99923	4.50474	0.01688	6.52085	0.00114
H 29	0.21387	0.00000	0.78506	0.00107	0.78613	-0.00013
C 30	0.37304	1.99934	3.59337	0.03425	5.62696	-0.00278
H 31	0.13795	0.00000	0.85896	0.00309	0.86205	0.00287
H 32	0.13006	0.00000	0.86666	0.00328	0.86994	0.00359

==========

* Total *	0.00000	83.97075	108.52680	0.50245	193.00000	1.00000



J

H1	-3.8063267603	0.6256319333	0.3658492198
C2	-2.7469451554	0.3710081486	0.3665470853
H3	-2.6097037673	0.3851381301	-1.7826486334
C4	-2.0849879839	0.2364745545	-0.8396046273
C5	-0.7465753485	-0.1241831579	1.6284987226
C6	-0.7175907621	-0.0973206485	-0.8526629315
C7	-2.0895112431	0.2004596629	1.6027934392

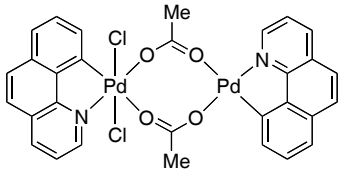
C8	-0.0776659154	-0.2788312402	0.3903563954
C9	0.0634470637	-0.2512515084	-2.0459533962
H10	-2.6372603004	0.3284954336	2.5350251101
C11	1.3847480138	-0.5785613226	-2.0021432620
H12	-0.4286030435	-0.0975211365	-3.0060860018
H13	1.9595481881	-0.6905079662	-2.9203317344
C14	2.0523046093	-0.7834696311	-0.7510724774
C15	3.4055834398	-1.1284986228	-0.6023677512
C16	1.2991359739	-0.6198347175	0.4252598203
C17	3.9362779693	-1.2916497206	0.6621241381
H18	4.0262821662	-1.2622207059	-1.4874290352
H19	4.9787477830	-1.5604859559	0.8044252535
C20	3.1200433953	-1.0959189467	1.7827013795
H21	3.4933775109	-1.1978354418	2.8000599150
N22	1.8394928509	-0.7696469254	1.6642649092
Pd23	0.5097176667	-0.2411433493	3.1543312636
Pd24	1.1169578294	2.5659272558	3.3491437809
H25	4.8892029546	2.2217941272	-0.2290649913
C26	3.8490716286	2.4596931557	-0.0086547049
H27	3.3516231863	2.7923202736	-2.0774512135
C28	2.9957314923	2.7797178279	-1.0479682956
C29	2.0974696711	2.7182234839	1.6358812264
C30	1.6507605922	3.0935806083	-0.7760300146
C31	3.4118382753	2.4190889380	1.3317420828
C32	1.2319600108	3.0625126486	0.5697278401
C33	0.6821203440	3.4280073492	-1.7798784202
H34	4.1069106936	2.1486599287	2.1249855095
C35	-0.6084834866	3.7248052786	-1.4618377949
H36	1.0032711027	3.4385935756	-2.8211868556
H37	-1.3284863926	3.9752882426	-2.2395980930
C38	-1.0530611912	3.7144868970	-0.0998234548
C39	-2.3577349411	4.0099523160	0.3283103409
C40	-0.1146643782	3.3736120297	0.8907196335
C41	-2.6658216871	3.9578126107	1.6735817232
H42	-3.1168937423	4.2755074822	-0.4063571352
H43	-3.6661606940	4.1836558512	2.0308468392
C44	-1.6749453916	3.5955813196	2.5940575828
H45	-1.8706185372	3.5248733172	3.6624910223
N46	-0.4368579801	3.3120914740	2.2105835739
C47	-0.9295813263	1.3124808340	5.2278609849
O48	-0.1704679711	2.3047433300	5.0833068310
O49	-0.9561773826	0.2528023046	4.5279532600
C50	2.8552157165	0.7043215811	4.8592215320
O51	2.0711584925	-0.2600101213	4.6679067978
O52	2.7818247074	1.8698222862	4.3591807053
C53	-1.9265393289	1.3567413097	6.3596099259
H54	-2.1477208797	2.3885820113	6.6425632790
H55	-1.4925071082	0.8479107967	7.2274122644
H56	-2.8404286439	0.8225111622	6.0875858118

C57	4.0254875137	0.4838454541	5.7853523353
H58	4.9241425173	0.9556382022	5.3776524194
H59	4.1925944251	-0.5813639994	5.9588396375
H60	3.8117083921	0.9699997968	6.7433794739

369	Pd 23	s	Cor(4s)	1.99454	-3.26926
370	Pd 23	s	Val(5s)	0.37485	0.49498
371	Pd 23	s	Ryd(11s)	0.00135	19.24017
372	Pd 23	s	Ryd(6s)	0.00064	1.16953
373	Pd 23	s	Ryd(7s)	0.00023	3.61089
374	Pd 23	s	Ryd(8s)	0.00003	5.03776
375	Pd 23	s	Ryd(9s)	0.00000	9.30681
376	Pd 23	s	Ryd(10s)	0.00000	15.77191
377	Pd 23	px	Cor(4p)	1.99619	-2.05702
378	Pd 23	px	Ryd(5p)	0.00189	0.96745
379	Pd 23	px	Ryd(7p)	0.00026	2.63891
380	Pd 23	px	Ryd(8p)	0.00040	3.14140
381	Pd 23	px	Ryd(6p)	0.00023	0.99342
382	Pd 23	px	Ryd(9p)	0.00001	8.31134
383	Pd 23	px	Ryd(10p)	0.00000	11.35530
384	Pd 23	py	Cor(4p)	1.99817	-2.04509
385	Pd 23	py	Ryd(6p)	0.00286	1.27078
386	Pd 23	py	Ryd(7p)	0.00064	1.40969
387	Pd 23	py	Ryd(8p)	0.00024	2.98922
388	Pd 23	py	Ryd(5p)	0.00028	0.67712
389	Pd 23	py	Ryd(9p)	0.00000	9.18701
390	Pd 23	py	Ryd(10p)	0.00000	11.42775
391	Pd 23	pz	Cor(4p)	1.99603	-2.05850
392	Pd 23	pz	Ryd(6p)	0.00204	1.16464
393	Pd 23	pz	Ryd(7p)	0.00051	2.82633
394	Pd 23	pz	Ryd(8p)	0.00043	2.98284
395	Pd 23	pz	Ryd(5p)	0.00023	0.88804
396	Pd 23	pz	Ryd(9p)	0.00001	8.55857
397	Pd 23	pz	Ryd(10p)	0.00000	11.37210
398	Pd 23	dxy	Val(4d)	1.94313	-0.26932
399	Pd 23	dxy	Ryd(6d)	0.00203	1.06247
400	Pd 23	dxy	Ryd(5d)	0.00046	0.67268
401	Pd 23	dxy	Ryd(7d)	0.00002	2.81419
402	Pd 23	dxz	Val(4d)	1.18870	-0.24939
403	Pd 23	dxz	Ryd(6d)	0.00070	1.99232
404	Pd 23	dxz	Ryd(5d)	0.00078	0.91073
405	Pd 23	dxz	Ryd(7d)	0.00006	2.61231
406	Pd 23	dyz	Val(4d)	1.91108	-0.27051
407	Pd 23	dyz	Ryd(6d)	0.00221	1.07976
408	Pd 23	dyz	Ryd(5d)	0.00059	0.67373
409	Pd 23	dyz	Ryd(7d)	0.00002	2.84959
410	Pd 23	dx2y2	Val(4d)	1.94526	-0.27025
411	Pd 23	dx2y2	Ryd(6d)	0.00320	1.42885
412	Pd 23	dx2y2	Ryd(5d)	0.00042	0.71562

413	Pd 23	dx2y2	Ryd(7d)	0.00004	2.71078
414	Pd 23	dz2	Val(4d)	1.95578	-0.27828
415	Pd 23	dz2	Ryd(6d)	0.00200	1.14580
416	Pd 23	dz2	Ryd(5d)	0.00045	0.59202
417	Pd 23	dz2	Ryd(7d)	0.00005	2.66425
418	Pd 23	f(0)	Ryd(4f)	0.00024	1.69872
419	Pd 23	f(0)	Ryd(5f)	0.00001	4.45925
420	Pd 23	f(c1)	Ryd(4f)	0.00075	1.89746
421	Pd 23	f(c1)	Ryd(5f)	0.00004	4.64713
422	Pd 23	f(s1)	Ryd(4f)	0.00015	1.63136
423	Pd 23	f(s1)	Ryd(5f)	0.00001	4.37642
424	Pd 23	f(c2)	Ryd(4f)	0.00062	1.86220
425	Pd 23	f(c2)	Ryd(5f)	0.00003	4.60488
426	Pd 23	f(s2)	Ryd(4f)	0.00040	1.69971
427	Pd 23	f(s2)	Ryd(5f)	0.00001	4.43817
428	Pd 23	f(c3)	Ryd(4f)	0.00013	1.68116
429	Pd 23	f(c3)	Ryd(5f)	0.00001	4.43412
430	Pd 23	f(s3)	Ryd(4f)	0.00016	1.67477
431	Pd 23	f(s3)	Ryd(5f)	0.00001	4.42670
432	Pd 24	s	Cor(4s)	1.99456	-3.27120
433	Pd 24	s	Val(5s)	0.37523	0.49618
434	Pd 24	s	Ryd(11s)	0.00123	19.69992
435	Pd 24	s	Ryd(6s)	0.00062	1.27028
436	Pd 24	s	Ryd(7s)	0.00023	3.81059
437	Pd 24	s	Ryd(8s)	0.00003	4.46343
438	Pd 24	s	Ryd(9s)	0.00000	9.00409
439	Pd 24	s	Ryd(10s)	0.00000	13.00444
440	Pd 24	px	Cor(4p)	1.99679	-2.05801
441	Pd 24	px	Ryd(5p)	0.00186	0.98775
442	Pd 24	px	Ryd(7p)	0.00026	2.34979
443	Pd 24	px	Ryd(8p)	0.00040	3.24550
444	Pd 24	px	Ryd(6p)	0.00023	1.04073
445	Pd 24	px	Ryd(9p)	0.00001	8.25795
446	Pd 24	px	Ryd(10p)	0.00000	11.34853
447	Pd 24	py	Cor(4p)	1.99826	-2.04816
448	Pd 24	py	Ryd(6p)	0.00305	1.24377
449	Pd 24	py	Ryd(7p)	0.00062	1.43910
450	Pd 24	py	Ryd(8p)	0.00026	3.07612
451	Pd 24	py	Ryd(5p)	0.00022	0.80372
452	Pd 24	py	Ryd(9p)	0.00000	9.12578
453	Pd 24	py	Ryd(10p)	0.00000	11.41891
454	Pd 24	pz	Cor(4p)	1.99533	-2.05983
455	Pd 24	pz	Ryd(6p)	0.00173	1.24208
456	Pd 24	pz	Ryd(7p)	0.00049	2.77926
457	Pd 24	pz	Ryd(8p)	0.00040	2.91509
458	Pd 24	pz	Ryd(5p)	0.00025	0.85088
459	Pd 24	pz	Ryd(9p)	0.00001	8.63927
460	Pd 24	pz	Ryd(10p)	0.00000	11.38144
461	Pd 24	dxy	Val(4d)	1.86484	-0.26756

462	Pd 24	dxy	Ryd(6d)	0.00194	1.22360
463	Pd 24	dxy	Ryd(5d)	0.00044	0.72806
464	Pd 24	dxy	Ryd(7d)	0.00002	2.79843
465	Pd 24	dxz	Val(4d)	1.36647	-0.25658
466	Pd 24	dxz	Ryd(6d)	0.00103	1.78588
467	Pd 24	dxz	Ryd(5d)	0.00077	0.81259
468	Pd 24	dxz	Ryd(7d)	0.00005	2.62984
469	Pd 24	dyz	Val(4d)	1.93688	-0.27317
470	Pd 24	dyz	Ryd(6d)	0.00215	1.10891
471	Pd 24	dyz	Ryd(5d)	0.00064	0.62227
472	Pd 24	dyz	Ryd(7d)	0.00003	2.83845
473	Pd 24	dx2y2	Val(4d)	1.94151	-0.27137
474	Pd 24	dx2y2	Ryd(6d)	0.00340	1.39274
475	Pd 24	dx2y2	Ryd(5d)	0.00046	0.76083
476	Pd 24	dx2y2	Ryd(7d)	0.00004	2.71116
477	Pd 24	dz2	Val(4d)	1.83239	-0.27577
478	Pd 24	dz2	Ryd(6d)	0.00167	1.19687
479	Pd 24	dz2	Ryd(5d)	0.00039	0.64421
480	Pd 24	dz2	Ryd(7d)	0.00006	2.71660
481	Pd 24	f(0)	Ryd(4f)	0.00037	1.72061
482	Pd 24	f(0)	Ryd(5f)	0.00002	4.47584
483	Pd 24	f(c1)	Ryd(4f)	0.00062	1.86777
484	Pd 24	f(c1)	Ryd(5f)	0.00004	4.61440
485	Pd 24	f(s1)	Ryd(4f)	0.00016	1.66819
486	Pd 24	f(s1)	Ryd(5f)	0.00001	4.42268
487	Pd 24	f(c2)	Ryd(4f)	0.00044	1.77978
488	Pd 24	f(c2)	Ryd(5f)	0.00002	4.51829
489	Pd 24	f(s2)	Ryd(4f)	0.00044	1.72997
490	Pd 24	f(s2)	Ryd(5f)	0.00002	4.47030
491	Pd 24	f(c3)	Ryd(4f)	0.00013	1.66269
492	Pd 24	f(c3)	Ryd(5f)	0.00000	4.41520
493	Pd 24	f(s3)	Ryd(4f)	0.00027	1.70689
494	Pd 24	f(s3)	Ryd(5f)	0.00001	4.46044



K

H1	2.5736229028	-4.8118259675	-3.5034698038
C2	2.8617932156	-4.0537897425	-2.7766889578
H3	4.3959507616	-5.2879006771	-1.9076917075
C4	3.8840262123	-4.3269944550	-1.8874525030
C5	2.5299723432	-1.8478010036	-1.8626659557
C6	4.2699873249	-3.3531329701	-0.9465279866
C7	2.1761883231	-2.8206246738	-2.7752244774
C8	3.5808980578	-2.1234203508	-0.9586567120
C9	5.3128147091	-3.5305878242	0.0228232557

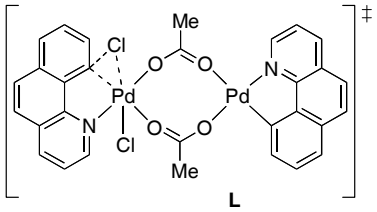
H10	1.3792898429	-2.6352830575	-3.4918891026
C11	5.6395047814	-2.5543869481	0.9148665217
H12	5.8479587519	-4.4796152471	0.0354918144
H13	6.4319733356	-2.7136461597	1.6444262000
C14	4.9517929160	-1.2973420395	0.9185096847
C15	5.2048320269	-0.2311274680	1.7984044583
C16	3.9338560492	-1.1102035701	-0.0321700966
C17	4.4629310685	0.9295301389	1.7022311869
H18	5.9834042891	-0.3313851913	2.5534057110
H19	4.6347948462	1.7637545801	2.3757165094
C20	3.4664823096	1.0337311041	0.7222261873
H21	2.8450280659	1.9196662735	0.6103365965
N22	3.2201199381	0.0418628788	-0.1208973309
Pd23	1.7546647515	-0.0530603999	-1.5913131513
Pd24	-1.7685735254	0.9635278613	0.0170520440
H25	-3.2456419028	5.0472514029	2.8738663502
C26	-3.2761786866	3.9697074212	2.7256052361
H27	-4.5221145434	3.6394445710	4.4429799175
C28	-3.9937573565	3.1847039163	3.6073046184
C29	-2.6299272167	2.0700835142	1.4649724772
C30	-4.0523007688	1.7887997335	3.4283411533
C31	-2.5747239119	3.4242150513	1.6256956968
C32	-3.3537397921	1.2451523125	2.3327794491
C33	-4.7712945389	0.8792803060	4.2739170275
H34	-2.0225002003	4.0501870539	0.9307659216
C35	-4.7893708391	-0.4625524832	4.0384352567
H36	-5.3140595891	1.2887461849	5.1244573342
H37	-5.3423204131	-1.1308375214	4.6958628243
C38	-4.0872279798	-1.0291787999	2.9249541698
C39	-4.0369218491	-2.3930155046	2.5864668433
C40	-3.3823641729	-0.1479036093	2.0919648120
C41	-3.3202669730	-2.8066470895	1.4807725143
H42	-4.5661160154	-3.1176608789	3.2031524257
H43	-3.2682836915	-3.8555493237	1.2060911137
C44	-2.6451951811	-1.8638179819	0.6930642302
H45	-2.0627595149	-2.1065590667	-0.1939281520
N46	-2.6945725360	-0.5821983236	1.0119618041
C47	-0.7954810167	-0.4798979358	-2.6728285449
O48	-1.0502263994	-0.5946415825	-1.4409615688
O49	0.3716533143	-0.3112722374	-3.1340420742
C50	0.1759868785	2.8640794016	-1.2274386556
O51	1.1120793507	2.0685178387	-1.3143324484
O52	-1.0329147565	2.6597852089	-0.8247695240
C53	-1.9215830894	-0.5579028614	-3.6648180647
H54	-2.5114306204	0.3627682948	-3.5792259213
H55	-2.5937417148	-1.3792104903	-3.3987771560
H56	-1.5539493305	-0.6714495300	-4.6864881898
C57	0.3821355450	4.3122336359	-1.6201310172
H58	0.2517593460	4.9519219716	-0.7406078315

H59	-0.3738546938	4.6077503402	-2.3533634413
H60	1.3826095318	4.4488995902	-2.0342002571
Cl61	0.0688923566	0.6894447829	1.4865177047
Cl62	-3.7508966829	1.2797162514	-1.2395465278

370	Pd 23	s	Cor(4s)	1.99498	-3.26643
371	Pd 23	s	Val(5s)	0.35194	0.45442
372	Pd 23	s	Ryd(11s)	0.00192	17.22471
373	Pd 23	s	Ryd(6s)	0.00057	0.93282
374	Pd 23	s	Ryd(7s)	0.00031	1.68963
375	Pd 23	s	Ryd(8s)	0.00003	4.76979
376	Pd 23	s	Ryd(9s)	0.00000	5.84133
377	Pd 23	s	Ryd(10s)	0.00000	12.90624
378	Pd 23	px	Cor(4p)	1.99786	-2.04467
379	Pd 23	px	Ryd(5p)	0.00125	1.09925
380	Pd 23	px	Ryd(6p)	0.00077	1.50082
381	Pd 23	px	Ryd(7p)	0.00026	1.81464
382	Pd 23	px	Ryd(8p)	0.00027	2.04329
383	Pd 23	px	Ryd(9p)	0.00001	8.83815
384	Pd 23	px	Ryd(10p)	0.00000	11.29564
385	Pd 23	py	Cor(4p)	1.99370	-2.05102
386	Pd 23	py	Ryd(5p)	0.00124	0.92196
387	Pd 23	py	Ryd(8p)	0.00035	2.36630
388	Pd 23	py	Ryd(6p)	0.00026	1.98602
389	Pd 23	py	Ryd(7p)	0.00023	2.27338
390	Pd 23	py	Ryd(9p)	0.00001	8.55673
391	Pd 23	py	Ryd(10p)	0.00000	11.23625
392	Pd 23	pz	Cor(4p)	1.99806	-2.04270
393	Pd 23	pz	Ryd(5p)	0.00116	0.84861
394	Pd 23	pz	Ryd(6p)	0.00066	1.26102
395	Pd 23	pz	Ryd(7p)	0.00032	1.79506
396	Pd 23	pz	Ryd(8p)	0.00016	1.80137
397	Pd 23	pz	Ryd(9p)	0.00001	8.83234
398	Pd 23	pz	Ryd(10p)	0.00000	11.30409
399	Pd 23	dxy	Val(4d)	1.82216	-0.26494
400	Pd 23	dxy	Ryd(6d)	0.00153	1.22529
401	Pd 23	dxy	Ryd(5d)	0.00066	0.70897
402	Pd 23	dxy	Ryd(7d)	0.00005	2.76186
403	Pd 23	dxz	Val(4d)	1.69148	-0.24935
404	Pd 23	dxz	Ryd(6d)	0.00142	1.83980
405	Pd 23	dxz	Ryd(5d)	0.00056	0.85857
406	Pd 23	dxz	Ryd(7d)	0.00005	2.78504
407	Pd 23	dyz	Val(4d)	1.95703	-0.26542
408	Pd 23	dyz	Ryd(6d)	0.00211	1.13265
409	Pd 23	dyz	Ryd(5d)	0.00058	0.55588
410	Pd 23	dyz	Ryd(7d)	0.00003	2.74221
411	Pd 23	dx2y2	Val(4d)	1.66443	-0.25653
412	Pd 23	dx2y2	Ryd(6d)	0.00161	1.43299
413	Pd 23	dx2y2	Ryd(5d)	0.00059	0.76657

414	Pd 23	dx2y2	Ryd(7d)	0.00004	2.64181
415	Pd 23	dz2	Val(4d)	1.81633	-0.25804
416	Pd 23	dz2	Ryd(6d)	0.00178	1.13099
417	Pd 23	dz2	Ryd(5d)	0.00060	0.61222
418	Pd 23	dz2	Ryd(7d)	0.00003	2.77401
419	Pd 23	f(0)	Ryd(4f)	0.00020	1.65394
420	Pd 23	f(0)	Ryd(5f)	0.00001	4.40860
421	Pd 23	f(c1)	Ryd(4f)	0.00050	1.75377
422	Pd 23	f(c1)	Ryd(5f)	0.00002	4.51493
423	Pd 23	f(s1)	Ryd(4f)	0.00021	1.69531
424	Pd 23	f(s1)	Ryd(5f)	0.00001	4.44833
425	Pd 23	f(c2)	Ryd(4f)	0.00048	1.78482
426	Pd 23	f(c2)	Ryd(5f)	0.00002	4.54141
427	Pd 23	f(s2)	Ryd(4f)	0.00023	1.66715
428	Pd 23	f(s2)	Ryd(5f)	0.00001	4.42214
429	Pd 23	f(c3)	Ryd(4f)	0.00045	1.79000
430	Pd 23	f(c3)	Ryd(5f)	0.00002	4.54725
431	Pd 23	f(s3)	Ryd(4f)	0.00028	1.68631
432	Pd 23	f(s3)	Ryd(5f)	0.00001	4.44614
433	Pd 24	s	Cor(4s)	1.99498	-3.35872
434	Pd 24	s	Val(5s)	0.35108	0.59545
435	Pd 24	s	Ryd(6s)	0.00223	1.74936
436	Pd 24	s	Ryd(11s)	0.00101	20.54162
437	Pd 24	s	Ryd(7s)	0.00030	2.58872
438	Pd 24	s	Ryd(8s)	0.00001	6.51534
439	Pd 24	s	Ryd(10s)	0.00001	16.98517
440	Pd 24	s	Ryd(9s)	0.00000	15.57152
441	Pd 24	px	Cor(4p)	1.99822	-2.15403
442	Pd 24	px	Ryd(7p)	0.01035	1.35052
443	Pd 24	px	Ryd(5p)	0.00307	0.86020
444	Pd 24	px	Ryd(8p)	0.00028	3.13230
445	Pd 24	px	Ryd(6p)	0.00019	1.24268
446	Pd 24	px	Ryd(9p)	0.00002	8.40800
447	Pd 24	px	Ryd(10p)	0.00000	11.21116
448	Pd 24	py	Cor(4p)	1.99627	-2.14736
449	Pd 24	py	Ryd(7p)	0.00139	2.01841
450	Pd 24	py	Ryd(5p)	0.00255	0.83610
451	Pd 24	py	Ryd(8p)	0.00054	3.29817
452	Pd 24	py	Ryd(6p)	0.00023	1.70965
453	Pd 24	py	Ryd(9p)	0.00001	7.60254
454	Pd 24	py	Ryd(10p)	0.00000	11.10942
455	Pd 24	pz	Cor(4p)	1.99611	-2.15063
456	Pd 24	pz	Ryd(7p)	0.00573	2.11470
457	Pd 24	pz	Ryd(5p)	0.00304	0.83303
458	Pd 24	pz	Ryd(8p)	0.00041	3.08621
459	Pd 24	pz	Ryd(6p)	0.00018	1.47303
460	Pd 24	pz	Ryd(9p)	0.00001	8.09936
461	Pd 24	pz	Ryd(10p)	0.00000	11.18322
462	Pd 24	dxy	Val(4d)	1.72817	-0.35043

463	Pd 24	dxy	Ryd(6d)	0.00229	1.19311
464	Pd 24	dxy	Ryd(5d)	0.00155	0.66119
465	Pd 24	dxy	Ryd(7d)	0.00003	2.72946
466	Pd 24	dxz	Val(4d)	1.60386	-0.35863
467	Pd 24	dxz	Ryd(6d)	0.00278	1.22874
468	Pd 24	dxz	Ryd(5d)	0.00123	0.94649
469	Pd 24	dxz	Ryd(7d)	0.00004	2.91832
470	Pd 24	dyz	Val(4d)	1.60876	-0.34751
471	Pd 24	dyz	Ryd(6d)	0.00158	1.53739
472	Pd 24	dyz	Ryd(5d)	0.00159	0.70246
473	Pd 24	dyz	Ryd(7d)	0.00004	2.58547
474	Pd 24	dx2y2	Val(4d)	1.77935	-0.35506
475	Pd 24	dx2y2	Ryd(6d)	0.00477	1.33612
476	Pd 24	dx2y2	Ryd(5d)	0.00153	1.04432
477	Pd 24	dx2y2	Ryd(7d)	0.00004	2.56784
478	Pd 24	dz2	Val(4d)	1.93860	-0.36018
479	Pd 24	dz2	Ryd(6d)	0.00252	0.94638
480	Pd 24	dz2	Ryd(5d)	0.00184	0.79324
481	Pd 24	dz2	Ryd(7d)	0.00004	2.67268
482	Pd 24	f(0)	Ryd(4f)	0.00066	1.54643
483	Pd 24	f(0)	Ryd(5f)	0.00002	4.35042
484	Pd 24	f(c1)	Ryd(4f)	0.00072	1.61320
485	Pd 24	f(c1)	Ryd(5f)	0.00001	4.40005
486	Pd 24	f(s1)	Ryd(4f)	0.00054	1.58604
487	Pd 24	f(s1)	Ryd(5f)	0.00001	4.37474
488	Pd 24	f(c2)	Ryd(4f)	0.00116	1.60114
489	Pd 24	f(c2)	Ryd(5f)	0.00003	4.40107
490	Pd 24	f(s2)	Ryd(4f)	0.00108	1.75990
491	Pd 24	f(s2)	Ryd(5f)	0.00004	4.50006
492	Pd 24	f(c3)	Ryd(4f)	0.00087	1.59474
493	Pd 24	f(c3)	Ryd(5f)	0.00003	4.37971
494	Pd 24	f(s3)	Ryd(4f)	0.00039	1.55064
495	Pd 24	f(s3)	Ryd(5f)	0.00001	4.34486

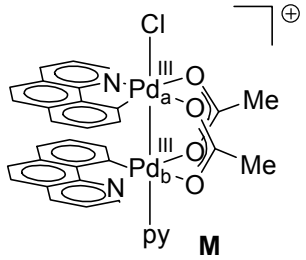


L

H1	0.7864736960	-4.9307311488	-2.2843967115
C2	1.2816022319	-4.1244751058	-1.7449161183
H3	2.1572107231	-5.4557859208	-0.2967253508
C4	2.0492223301	-4.4260853573	-0.6354365092
C5	1.7414912634	-1.7610246084	-1.5368953030
C6	2.7146818235	-3.3943050410	0.0553360975
C7	1.1223706057	-2.7997949346	-2.2062534000
C8	2.5474021530	-2.0759547290	-0.4167962711
C9	3.5502006143	-3.6011475834	1.2036246290

H10	0.5147480108	-2.6009512364	-3.0867493792
C11	4.1774620383	-2.5673367254	1.8296915769
H12	3.6789207824	-4.6190350919	1.5708559520
H13	4.8079738280	-2.7470240235	2.6990637433
C14	4.0246644484	-1.2206390494	1.3651742328
C15	4.6265266213	-0.0889672887	1.9417874097
C16	3.2039179292	-1.0058571998	0.2457062696
C17	4.3953332653	1.1606300392	1.4031954759
H18	5.2695460047	-0.2080145322	2.8127528630
H19	4.8446067393	2.0503174350	1.8337187822
C20	3.5474648987	1.2862828398	0.2950452020
H21	3.2971237164	2.2509436597	-0.1412520602
N22	2.9765545477	0.2309720702	-0.2630828471
Pd23	1.5433984718	0.1970156617	-1.7720383223
Pd24	-1.2554254047	1.0253548730	-0.0391476726
H25	-3.5077473829	4.4707976007	3.2499982731
C26	-3.3919513444	3.4308229256	2.9522583035
H27	-4.2623315813	2.6679560730	4.7641579423
C28	-3.8102568489	2.4255069363	3.8046152596
C29	-2.7327906830	1.8391202094	1.3215718347
C30	-3.6353752555	1.0765889582	3.4469611098
C31	-2.8619988567	3.1564798241	1.6790555451
C32	-3.0484097365	0.7863105251	2.1975402998
C33	-3.9944078144	-0.0298012577	4.2871900074
H34	-2.6078196227	3.9469388521	0.9796141363
C35	-3.7338895623	-1.3172136707	3.9330377242
H36	-4.4832007880	0.1874341586	5.2351726014
H37	-4.0161948114	-2.1401394544	4.5867252630
C38	-3.0277572959	-1.6202002342	2.7242266198
C39	-2.5812563177	-2.8972209793	2.3443347462
C40	-2.6814064485	-0.5466371400	1.8846838865
C41	-1.8119762815	-3.0534288560	1.2078610193
H42	-2.8284307506	-3.7556182197	2.9674302865
H43	-1.4393808558	-4.0269224868	0.9027696873
C44	-1.4606231042	-1.9303407044	0.4501665665
H45	-0.8249378034	-1.9789571123	-0.4329949175
N46	-1.8968296796	-0.7274443974	0.7960563729
C47	-0.9164871805	-0.2142513097	-3.1590596958
O48	-1.4079230996	-0.3420002633	-2.0194130672
O49	0.3114927975	-0.0011254473	-3.4182453445
C50	0.3771560380	3.1511921449	-1.3325385222
O51	1.2710895799	2.3920987268	-1.7360589034
O52	-0.7066933238	2.8614806313	-0.7076640962
C53	-1.8337917076	-0.3477282234	-4.3506177026
H54	-2.6521839499	0.3720372150	-4.2451989421
H55	-2.2835878863	-1.3464100663	-4.3470110282
H56	-1.3057663250	-0.1840076127	-5.2919710197
C57	0.5048237158	4.6345584860	-1.5951938103
H58	0.3525064304	5.1940701163	-0.6680288101

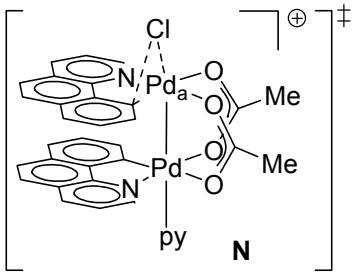
H59	-0.2779714041	4.9420780687	-2.2957841330
H60	1.4838307197	4.8598761138	-2.0219007371
Cl61	0.4978220860	0.9855510316	1.5551060007
Cl62	-3.5574198120	1.5393223639	-0.7200407619



M

Pd1	-0.3594325980	0.8476616597	-1.0073683335
Pd2	-0.4431053563	-1.7738096849	-0.8405163145
Cl3	-0.6250552234	-4.1356220683	-0.9088859841
C4	-2.7578084553	-0.3776362982	-2.1551188944
O5	0.1927222598	-1.7495132879	-2.7909412485
C6	0.7632121785	-0.7251700684	-3.2899034165
N7	1.1873243779	1.0469866409	0.3664025636
N8	-0.9348299545	-1.8574915685	1.1477288088
C9	-1.4820208937	1.2324819137	0.6112198899
C10	-2.8430430262	1.4190466908	0.6932244853
H11	-3.4797279994	1.3430277050	-0.1852748080
C12	-3.4092799876	1.7374806047	1.9485008307
H13	-4.4855770056	1.8837971562	2.0130179928
C14	-2.6372992506	1.8714040548	3.0856831663
H15	-3.0996712841	2.1175479781	4.0397279340
C16	-1.2394186900	1.7136119269	3.0136451597
C17	-0.6806715484	1.4003193388	1.7577812733
C18	0.7269719246	1.3005978988	1.6188144105
C19	1.5920275678	1.4872217829	2.7095795642
C20	2.9716383243	1.4048975838	2.4507266861
H21	3.6799736299	1.5348245791	3.2672158006
C22	3.4187412520	1.1697190884	1.1649542035
H23	4.4791062982	1.1072070741	0.9405147229
C24	2.4907388432	0.9950163555	0.1309151042
H25	2.7882556714	0.7922282339	-0.8965286540
C26	1.4182172587	-2.0748907586	-0.1239947513
C27	2.5813099668	-2.2896117218	-0.8178046726
H28	2.5922922963	-2.3714072931	-1.9018456332
C29	3.7744824649	-2.4404277673	-0.0742407277
H30	4.7036946951	-2.6073218959	-0.6150855821
C31	3.7905750436	-2.4054878718	1.3072359278
H32	4.7242854920	-2.5430715286	1.8490332945
C33	2.5882103846	-2.2457112657	2.0255179290
C34	1.4038242599	-2.0824914872	1.2797294874
C35	0.1572369162	-1.9848706808	1.9421201252
C36	0.0546662918	-2.0568684941	3.3398861150
C37	-1.2410506014	-2.0147548761	3.8845911476
H38	-1.3718660447	-2.0723068279	4.9638219627
C39	-2.3386832477	-1.9210865329	3.0503089736
H40	-3.3481695340	-1.9053802842	3.4490706171
C41	-2.1548368771	-1.8475992714	1.6641561094
H42	-2.9790765239	-1.7752954537	0.9574223476
C43	1.2722162586	-2.1874450932	4.0847983401
H44	1.2112589571	-2.2361568984	5.1702189411
C45	2.4780876275	-2.2743927283	3.4559059008
H46	3.3886257792	-2.3950020408	4.0405145168
C47	-0.3483356936	1.8694590116	4.1282314903

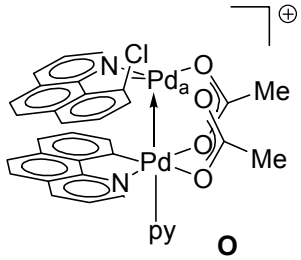
H48	-0.7770873137	2.0953695421	5.1032157676
C49	1.0018518698	1.7585754415	3.9871682511
H50	1.6600791970	1.8914477318	4.8435821116
O51	-2.5163394916	-1.4101833758	-1.4919120684
O52	0.9339871269	0.3770577529	-2.7058679580
O53	-2.0182475500	0.6697023220	-2.2036758851
C54	-4.0297022053	-0.3136208207	-2.9494763144
H55	-4.0623852659	-1.1573502852	-3.6446247555
H56	-4.8780441067	-0.4299658380	-2.2662422877
C57	1.2838112695	-0.8853922065	-4.6873969074
H58	0.8178350852	-0.1339293584	-5.3320169894
H59	2.3621157034	-0.6945415439	-4.6920212157
C60	0.6332761636	5.7615230371	-1.9080852874
C61	-0.2727471522	5.4386387469	-0.9051537784
C62	-0.6083090134	4.1059217551	-0.7173089600
N63	-0.0918154299	3.1267094794	-1.4669846452
C64	0.7791049658	3.4344581397	-2.4360825921
C65	1.1656626012	4.7432813991	-2.6893863778
H66	0.9208380959	6.7958740517	-2.0787339913
H67	-0.7141663163	6.2036136937	-0.2730497732
H68	-1.3133806928	3.8042150949	0.0575984468
H69	1.1659114098	2.5944520663	-3.0121747124
H70	1.8739588423	4.9539199724	-3.4852467995
H71	1.0815340147	-1.8851744354	-5.0733773705
H72	-4.1180997019	0.6281385426	-3.4927747054



N

Pd1	-0.2863625554	0.8376964598	-0.9899940688
Pd2	-0.6559480192	-1.7886485631	-0.8636328500
Cl3	-0.2709543440	-4.2069726519	-0.7257445898
C4	-2.8080203095	-0.0599682644	-2.1902658588
O5	0.0205572998	-1.7947115515	-2.7932437303
C6	0.7451103564	-0.8485245546	-3.2463013936
N7	1.2797179292	0.8309841606	0.3960583679
N8	-1.2271807031	-1.8424295613	1.1095562980
C9	-1.3469783551	1.3899442108	0.6127671328
C10	-2.6754045043	1.7452186752	0.6877164635
H11	-3.3210543796	1.6995861745	-0.1866445743
C12	-3.1899623411	2.2063838239	1.9196442591
H13	-4.2399281033	2.4869844902	1.9753695017
C14	-2.3965495239	2.3217260116	3.0443199312
H15	-2.8159068596	2.6895984753	3.9791125682
C16	-1.0293453259	1.9894101644	2.9821263779
C17	-0.5234215425	1.5222703098	1.7505765206
C18	0.8606699732	1.2344379239	1.6243333698
C19	1.7492029948	1.4006477109	2.7001829258
C20	3.1097305279	1.1467352038	2.4502780581
H21	3.8347215652	1.2707958372	3.2532525135
C22	3.5173148311	0.7570434856	1.1897177436
H23	4.5632740750	0.5623266410	0.9726003083
C24	2.5668156246	0.6059493593	0.1713516983
H25	2.8312451671	0.2916951502	-0.8372123461
C26	1.0948056466	-2.7347315554	-0.0608871125

C27	2.3141701196	-2.8973253237	-0.6974428507
H28	2.3495997431	-3.1410986070	-1.7564957656
C29	3.4878816634	-2.8374844171	0.0686036855
H30	4.4425950058	-2.9787582100	-0.4334831303
C31	3.4566637851	-2.6677325946	1.4427991551
H32	4.3767206967	-2.6867513683	2.0228035511
C33	2.2273021598	-2.4772351041	2.1014834064
C34	1.0461733761	-2.4632896199	1.3292600918
C35	-0.1817390111	-2.1017252721	1.9386259540
C36	-0.2891793471	-1.9316665561	3.3305964858
C37	-1.5564641885	-1.5991643708	3.8390107985
H38	-1.6843552769	-1.4696671807	4.9125298928
C39	-2.6239611418	-1.4269418454	2.9792231607
H40	-3.6121553292	-1.1751334003	3.3511846312
C41	-2.4204565668	-1.5287628261	1.5985246238
H42	-3.2024622118	-1.3367340880	0.8671276445
C43	0.9064613153	-2.0448553465	4.1111656329
H44	0.8368089804	-1.9073806290	5.1885312861
C45	2.1096495504	-2.2706352185	3.5166289241
H46	3.0179982740	-2.3074873838	4.1160551304
C47	-0.1181188820	2.1221038785	4.0826614780
H48	-0.5092393130	2.4749962185	5.0357420626
C49	1.2081291581	1.8419096472	3.9514962965
H50	1.8857567149	1.9671818071	4.7940079367
O51	-2.7196415748	-1.1225942789	-1.5410689085
O52	1.0110682972	0.2215532691	-2.6420424494
O53	-1.9389725021	0.8813978129	-2.2191107257
C54	-4.0521544218	0.1879314905	-3.0002991902
H55	-4.2308495186	-0.6678663747	-3.6568303863
H56	-4.9072567304	0.2535804375	-2.3185487644
C57	1.0821472538	5.6744153894	-2.0518503450
C58	1.3259627808	-1.0627154426	-4.6127079271
H59	0.9394316755	-0.2935894306	-5.2888039386
N60	0.2360371142	3.1013478371	-1.4777110571
C61	0.0474744711	5.4578989883	-1.1498807308
H62	2.4122886288	-0.9352148985	-4.5645482080
C63	-0.3437975454	4.1520882443	-0.8901986488
C64	1.2300975565	3.3074163975	-2.3491874966
C65	1.6836245708	4.5811801421	-2.6637950744
H66	1.4148028055	6.6847727674	-2.2766765211
H67	-0.4516683672	6.2842983429	-0.6520502329
H68	-1.1493177764	3.9320880550	-0.1887398697
H69	1.6557526702	2.4134102492	-2.8049031035
H70	2.4926083605	4.7087270929	-3.3772083625
H71	1.0813374259	-2.0525292955	-5.0003973108
H72	-3.9780038685	1.1062080355	-3.5839979579

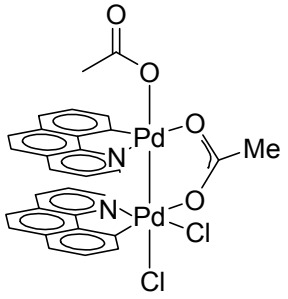


O

Pd1	-0.4181409152	0.8655587473	-1.0108246664
C2	-2.8390863793	-0.0689431234	-2.3776918770
O3	0.1246232672	-1.7862465205	-2.7110753950
C4	0.8053748696	-0.8115842940	-3.1686600197
N5	1.0379541793	0.8092113671	0.5003459850

C6	-1.5823134611	1.4432036132	0.5003047294
C7	-2.9066294366	1.8257705441	0.4728740636
H8	-3.4877338255	1.7603651426	-0.4445050676
C9	-3.4967543612	2.3397576761	1.6477103420
H10	-4.5423589617	2.6407052627	1.6207116522
C11	-2.7812237717	2.4817180578	2.8212053425
H12	-3.2555740147	2.8915255081	3.7113174901
C13	-1.4219041691	2.1171673698	2.8665211045
C14	-0.8404954703	1.5974099106	1.6911989397
C15	0.5405834576	1.2632054358	1.6799018430
C16	1.3467126524	1.4192672970	2.8217400160
C17	2.7023202770	1.0673691640	2.7001802811
H18	3.3618475979	1.1667919296	3.5616197175
C19	3.1890291465	0.6057123210	1.4920618313
H20	4.2327073178	0.3294341250	1.3756248978
C21	2.3224922892	0.4921717670	0.3977171135
H22	2.6526590074	0.1449099578	-0.5799449455
C23	-0.5905097430	2.2619409766	4.0275901335
H24	-1.0390979418	2.6633457002	4.9348135151
C25	0.7294867797	1.9281448721	4.0106484490
H26	1.3439887218	2.0543202243	4.9005871969
O27	-2.7883133364	-1.1254697881	-1.7257958586
O28	0.9920289010	0.2828330774	-2.5777578630
O29	-1.9813124844	0.8882634757	-2.3511953233
C30	-4.0291663513	0.1855319654	-3.2697886586
H31	-4.2830487682	-0.7282243197	-3.8121574220
H32	-4.8875651613	0.4379003893	-2.6360740172
C33	1.0557033839	5.7337510678	-1.9744468089
C34	1.4096121576	-1.0071812920	-4.5264965174
H35	0.8036627613	-0.4598677500	-5.2564789870
N36	0.1485179556	3.1645964257	-1.4661811800
C37	-0.0448611677	5.5248455642	-1.1523285244
H38	2.4160457559	-0.5813221023	-4.5497607650
C39	-0.4632784007	4.2213508619	-0.9246442794
C40	1.2060746557	3.3651336275	-2.2601821709
C41	1.6924743541	4.6354303724	-2.5396550087
H42	1.4116406549	6.7415880081	-2.1739337562
H43	-0.5739226525	6.3548472548	-0.6926344626
H44	-1.3206178603	4.0086769878	-0.2850680274
H45	1.6576241117	2.4678572762	-2.6836095127
H46	2.5534216284	4.7567332923	-3.1907754597
Pd47	-0.6199551460	-1.7691487578	-0.8222110199
H48	4.6244870446	-3.6621896851	1.9362575983
C49	3.5806199415	-3.3661667966	1.9924825722
H50	3.7310309830	-2.5289876056	3.9595100822
C51	3.0879642650	-2.7296430647	3.1046921106
C52	1.3858402600	-3.3176692527	1.0120806295
C53	1.7338440792	-2.3479935979	3.1836193875
C54	2.7077444728	-3.6973598215	0.9484729886
C55	0.8519754237	-2.5566785391	2.0832312059
C56	1.2434269521	-1.8046485834	4.4103240349
H57	3.0526437107	-4.2850380243	0.1022721819
C58	-0.0694335578	-1.5215409810	4.5709580928
H59	1.9482526658	-1.6780139862	5.2300583389
H60	-0.4613039557	-1.1722890992	5.5241097538
C61	-0.9660382726	-1.6229002493	3.4671965246
C62	-2.3192163006	-1.2659655625	3.6128338332
C63	-0.4971429771	-2.0331701906	2.1941799245
C64	-3.1585749262	-1.2850239598	2.5276569169
H65	-2.6781890823	-0.9700985444	4.5973294000
H66	-4.2094348234	-1.0262532748	2.6070920113
C67	-2.6028698708	-1.5472045941	1.2732199766

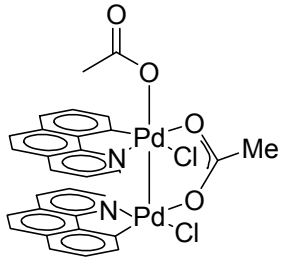
H68	-3.1752819002	-1.4410274192	0.3529649299
N69	-1.3229464495	-1.8806354845	1.1156745574
Cl70	0.3595416914	-3.9965791578	-0.2560769446
H71	-3.8472746792	1.0084715831	-3.9622468412
H72	1.4307603784	-2.0619811303	-4.8040256913



S1A

Pd1	6.6432377215	3.8544951500	5.9499216797
Pd2	6.4461937303	1.1824033252	5.9928543079
O3	7.0872848286	6.0612768944	5.3214628220
O4	4.9747639351	3.7927262853	4.7687251050
O5	4.3730651989	1.7140129563	5.4240194116
C6	4.2160374898	2.7640822095	4.7601897921
C7	3.0277686997	2.8602483689	3.8446277385
H8	3.3036671240	2.3869453261	2.8955226186
H9	2.7570736078	3.9000576194	3.6509633100
H10	2.1862264313	2.3034389054	4.2638318478
N11	8.2028751557	3.9179600127	7.3022403247
N12	6.0110643622	0.9836028003	8.0342733934
C13	5.5403746124	4.0001860503	7.6203750188
C14	4.1811490506	4.1709686659	7.7575738149
H15	3.5228418828	4.1563344419	6.8932522432
C16	3.6440919442	4.3824969152	9.0451740761
H17	2.5684608940	4.5163815058	9.1457834738
C18	4.4400450854	4.4212374193	10.1735242454
H19	3.9996581559	4.5777141951	11.1569962107
C20	5.8360321806	4.2849194708	10.0536268731
C21	6.3648975306	4.0935832424	8.7604212891
C22	7.7703208376	4.0315564239	8.5824277140
C23	8.6607721907	4.1118556975	9.6655687365
C24	10.0334288916	4.0479662802	9.3679014500
H25	10.7601401094	4.0931033686	10.1777906048
C26	10.4496533129	3.9337890233	8.0563645120
H27	11.5039912267	3.8809076254	7.8025027921
C28	9.4976144370	3.8769108463	7.0293660480
H29	9.7560251969	3.7959509466	5.9741888056
C30	8.3175139877	0.8111133651	6.6371732630
C31	9.4703110974	0.6851630281	5.9013214796
H32	9.4488628076	0.7668935444	4.8178943647
C33	10.6804887541	0.4472906811	6.5875165207
H34	11.5946461823	0.3500044602	6.0048744396
C35	10.7333727855	0.3267976332	7.9621923829
H36	11.6788466302	0.1332085943	8.4653883768
C37	9.5529228450	0.4253840224	8.7225450239
C38	8.3449556588	0.6701394961	8.0359807386
C39	7.1277355984	0.7473388221	8.7615222597
C40	7.0845442172	0.5685696499	10.1544435430
C41	5.8175405673	0.6164520003	10.7617399908
H42	5.7355864598	0.4862671716	11.8398678384
C43	4.6890666957	0.8150147330	9.9909068448
H44	3.7000187524	0.8445104662	10.4379314761

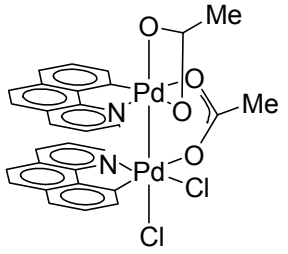
C45	4.8196675776	0.9954910668	8.6072849961
H46	3.9715723811	1.1670108779	7.9470099237
C47	7.8744260777	5.6093051049	4.4430877485
C48	8.5539992239	6.5670617284	3.5046988399
H49	7.8609434110	6.8116775383	2.6925483130
H50	9.4476782473	6.1128497424	3.0701535583
H51	8.8036862046	7.4973599730	4.0219234646
O52	8.0924591048	4.3640551701	4.3197547830
C53	8.3250246930	0.3468345693	10.8352514443
H54	8.3073018757	0.2199241377	11.9163553321
C55	9.4995069762	0.2817261898	10.1487907177
H56	10.4325199223	0.1004344679	10.6809534259
C57	6.7525730346	4.3475629647	11.1558129256
H58	6.3444483638	4.4804496118	12.1569575246
C59	8.0997017632	4.2575752527	10.9753520162
H60	8.7777442402	4.3112560008	11.8249078567
Cl61	7.0763636773	1.3561411582	3.7714354650
Cl62	6.1578990546	-1.1860758816	5.8398853946



S1B

Pd1	6.9491106143	3.6865369255	4.2801261877
Pd2	6.7728043715	0.9765360774	4.5559032387
O3	6.6506601817	5.6575594771	3.8552016927
O4	5.3537704666	3.4710530997	3.0208763870
O5	4.7273834418	1.5011670583	3.9385249257
C6	4.5986013159	2.4438345197	3.1246622547
C7	3.4593010326	2.4100534167	2.1467802251
H8	3.7846532752	1.8075283026	1.2908769003
H9	3.2044495953	3.4108011778	1.7931243713
H10	2.5959485950	1.9170359404	2.6004784623
N11	8.4302974465	3.8559463853	5.7208624749
N12	6.3616051333	1.0583395417	6.6174891192
C13	5.7421763609	4.0694558279	5.8848853078
C14	4.3879093110	4.2915623502	5.9127426816
H15	3.7870248253	4.2255905667	5.0090244259
C16	3.7845205397	4.6246268827	7.1449039405
H17	2.7088748303	4.7893435084	7.1742094849
C18	4.5231749311	4.7542909275	8.3050568539
H19	4.0360516624	5.0167228122	9.2430975223
C20	5.9203698045	4.5795088678	8.2789320857
C21	6.5144044632	4.2460311725	7.0441537658
C22	7.9236673569	4.1154699193	6.9509690899
C23	8.7516077966	4.2872990449	8.0705487398
C24	10.1373571261	4.1694408446	7.8657760582
H25	10.8152715297	4.2900556570	8.7096797591
C26	10.6246961518	3.9153453577	6.6014256221
H27	11.6903863892	3.8268552905	6.4135615623
C28	9.7366860389	3.7757899945	5.5266081668
H29	10.0506085014	3.6088652221	4.4956516925
C30	8.6284384014	0.6388358016	5.2200958034
C31	9.7909157697	0.4660026350	4.5008030998

H32	9.7694465029	0.4759246249	3.4136997653
C33	11.0059695785	0.2906153487	5.1955700507
H34	11.9182102719	0.1488708983	4.6191272481
C35	11.0685102929	0.2946865618	6.5762984970
H36	12.0188621229	0.1536273295	7.0881427304
C37	9.8950095342	0.4763811332	7.3324862923
C38	8.6821943597	0.6526374156	6.6310751276
C39	7.4805079311	0.8603729816	7.3593113062
C40	7.4549337466	0.8516017250	8.7654323587
C41	6.2018784779	1.0196119361	9.3803627427
H42	6.1356150228	1.0194011216	10.4675604882
C43	5.0684244445	1.1766466883	8.6067536933
H44	4.0903133594	1.3057373895	9.0603010061
C45	5.1852251226	1.1998181072	7.2108686001
H46	4.3322068315	1.3572857157	6.5535023630
C47	7.4607254743	6.5838801234	4.3003684610
C48	7.1381780324	7.8964276548	3.5973640007
H49	7.6751886952	7.9035486027	2.6438740446
H50	7.4955787317	8.7169651849	4.2235923218
H51	6.0714581308	7.9976415183	3.3894907016
O52	8.3504221328	6.4884895299	5.1205519220
C53	8.6960419167	0.6657271314	9.4550768515
H54	8.6895747836	0.6611910492	10.5438226300
C55	9.8582892251	0.4920142313	8.7663077321
H56	10.7944468392	0.3496912763	9.3052136132
C57	6.7749461938	4.7280614184	9.4211687934
H58	6.3180973115	4.9717152730	10.3795835704
C59	8.1253656676	4.5836460327	9.3240339253
H60	8.7600813035	4.7063901026	10.1998018315
Cl61	8.6236948806	3.5904624838	2.4950487958
Cl62	7.2334446634	0.3627060069	2.3853978205



S1C

Pd1	6.6964164182	3.6445183184	5.7695658890
Pd2	6.3997040737	1.0015351766	6.1069684569
O3	7.2110410509	5.7617968051	4.9245587146
O4	5.0048525226	3.5329928341	4.6266911422
O5	4.3441083548	1.5496049834	5.4882998994
C6	4.2093339821	2.5382865675	4.7319010784
C7	3.0006374539	2.5965530421	3.8397577374
H8	3.2215877014	2.0083786666	2.9420538336
H9	2.7764513219	3.6223688806	3.5407603662
H10	2.1452220348	2.1346276004	4.3389210156
N11	8.2817544821	3.7772059721	7.0829201776
N12	5.9613156626	1.0340392671	8.1571003712
C13	5.6330087434	4.0081114589	7.4322609488
C14	4.2856336870	4.2529223783	7.5713439402
H15	3.6105357040	4.1806972310	6.7229608034
C16	3.7834701008	4.6169488004	8.8387939018
H17	2.7167413106	4.8083489590	8.9414238849
C18	4.6018818879	4.7329806347	9.9455857078
H19	4.1875205131	5.0057880495	10.9149313400
C20	5.9883823863	4.5233739164	9.8190773106

C21	6.4827737769	4.1800355236	8.5439981195
C22	7.8804590332	4.0387732996	8.3514841226
C23	8.7950075159	4.1860421888	9.4068216500
C24	10.1571552051	4.0305346146	9.0950243550
H25	10.9014688428	4.1224983957	9.8848023401
C26	10.5415749726	3.7671503906	7.7951911512
H27	11.5873568758	3.6408826365	7.5315679430
C28	9.5673356137	3.6502732989	6.7943232270
H29	9.7998693123	3.4506962877	5.7487536227
C30	8.2552260904	0.6198790419	6.7913555706
C31	9.3978571508	0.3587997474	6.0752857461
H32	9.3753166593	0.3176891920	4.9894159164
C33	10.5990681286	0.1464280577	6.7855846718
H34	11.5053844953	-0.0579543632	6.2183842735
C35	10.6527426790	0.1819653841	8.1653021213
H36	11.5912601898	0.0044597474	8.6871863591
C37	9.4808874060	0.4168111867	8.9095209256
C38	8.2817262695	0.6333253311	8.1974886741
C39	7.0695925036	0.8337536709	8.9077782684
C40	7.0215442384	0.8021853139	10.3115708322
C41	5.7578310017	0.9587470031	10.9072635622
H42	5.6724049114	0.9428347749	11.9928434184
C43	4.6365593459	1.1183605210	10.1171756551
H44	3.6498129086	1.2303930384	10.5560738671
C45	4.7721644791	1.1497195877	8.7227309622
H46	3.9301476078	1.2823178235	8.0459619432
C47	8.2536840687	0.6065678050	11.0152520163
H48	8.2321002227	0.5929684610	12.1035987433
C49	9.4242478265	0.4267926180	10.3427594771
H50	10.3502544159	0.2662096827	10.8936226399
C51	6.9285112981	4.6531441765	10.8954436963
H52	6.5462479600	4.9018299548	11.8847341348
C53	8.2667505892	4.4853056934	10.7042594310
H54	8.9630280106	4.5910923990	11.5340553962
Cl55	7.0339577103	0.9278599985	3.8813384593
Cl56	6.0156476772	-1.3566025226	6.1987359129
O57	8.1282140047	3.9387666663	4.0699749446
C58	7.9579050702	5.1976078236	4.0769356443
C59	8.6509700555	6.0253949044	3.0312422815
H60	8.7295030253	7.0679389053	3.3477732042
H61	9.6391685568	5.6105607827	2.8144165111
H62	8.0636962729	5.9838382125	2.1076120186

Evaluation of Kinetic Advantage of Bimetallic Reductive Elimination (Data Pertaining to Eq 6)

An in silico experiment was performed where the solvent corrected electronic energy for activation for the C-Cl reductive elimination from Pd(III)-Pd(III) structure (**A**) was examined as a function of Pd-Pd distance. The following distances were chosen 2.62 Å (equilibrium distance found in **A**), 2.95 Å (about halfway between the sum of the covalent and vdW radii), 3.30 Å (about the sum of the vdW radii), 3.65 Å (longer than the sum of the vdW radii).[25]

Geometries were optimized with each Pd-Pd distance constraint and, as well as the respective transition structures at the M06/LACVP** level. Energies were calculated using the LACV3P++**(2f) basis set.

XYZ Coordinates for in silico experiment

Pd-Pd 2.95 Å

H1	-3.7840792335	0.6332995689	0.3316083904
C2	-2.7234541179	0.3874269375	0.3405482364
H3	-2.5738211770	0.3817565015	-1.8050455681
C4	-2.0503507492	0.2494207768	-0.8596112074
C5	-0.7424829791	-0.0806150526	1.5890151218
C6	-0.6844793752	-0.0934176776	-0.8670382423
C7	-2.0826771509	0.2146986886	1.5870854912
C8	-0.0456998178	-0.2490758940	0.3792668361
C9	0.0983958773	-0.3074827333	-2.0501349352
H10	-2.6329162714	0.3069773201	2.5203705444
C11	1.4072937744	-0.6801498653	-1.9895446261
H12	-0.3858815734	-0.1770152808	-3.0164866382
H13	1.9767284411	-0.8514624791	-2.9009477524
C14	2.0672780036	-0.8636641199	-0.7311272666
C15	3.4002564065	-1.2723301333	-0.5560558917
C16	1.3204572808	-0.6195486624	0.4324565726
C17	3.9119809480	-1.4277200593	0.7178406738
H18	4.0197353883	-1.4728907207	-1.4288176114
H19	4.9338954135	-1.7581217643	0.8767828416
C20	3.1027893271	-1.1551601477	1.8277769335
H21	3.4461550513	-1.2684823107	2.8539841542
N22	1.8533773158	-0.7450160345	1.6712485332
Pd23	0.4752002581	-0.3021665335	3.1484214037
Pd24	1.2082778869	2.5501178720	3.3203810390
H25	4.8880323781	2.1891363352	-0.3212118757
C26	3.8469090541	2.4021693546	-0.0846599356
H27	3.3139216949	2.7419254422	-2.1392033721
C28	2.9688711111	2.7105507448	-1.1069451296
C29	2.1228730276	2.6125347453	1.5538676629
C30	1.6243803212	3.0116818746	-0.8175546469
C31	3.4400773080	2.3595551086	1.2662978751
C32	1.2206535456	2.9527141845	0.5309582563
C33	0.6413261036	3.3844193446	-1.7938964202
H34	4.1483842809	2.1343534019	2.0600960996
C35	-0.6348497509	3.7073928700	-1.4430888287
H36	0.9434543865	3.4160903334	-2.8394850765
H37	-1.3598946997	3.9996505592	-2.2006794811
C38	-1.0552172449	3.6788435745	-0.0733197838
C39	-2.3334520307	4.0198923584	0.4000001950
C40	-0.1110876425	3.2778323617	0.8854858314
C41	-2.6052079304	3.9644509196	1.7535537412
H42	-3.1010012079	4.3339384846	-0.3056264390
H43	-3.5810669317	4.2382904367	2.1426421057
C44	-1.6088694371	3.5460382339	2.6443254430
H45	-1.7609501098	3.4893324749	3.7201978412
N46	-0.4096284956	3.1975565812	2.2042346553
C47	-0.8651750510	1.2749260880	5.2491869228

O48	-0.0917532818	2.2460861364	5.1108950683
O49	-0.9652725174	0.2370067380	4.5065184049
C50	2.8908346440	0.6654396774	4.8449466966
O51	2.0868801678	-0.2789192043	4.6954153236
O52	2.8649818100	1.8170018813	4.2864906318
C53	-1.8164104584	1.2756327899	6.4191987668
H54	-1.9924788562	2.2949858990	6.7689837228
H55	-1.3571718940	0.7020664124	7.2316110609
H56	-2.7533543883	0.7789391132	6.1565528476
C57	4.0524440304	0.4760310634	5.7879151659
H58	4.9382099197	0.9986407174	5.4188521669
H59	4.2542212871	-0.5866064123	5.9378354647
H60	3.7873287537	0.9227650046	6.7521249104
Cl61	1.8508482732	4.8804881884	3.6882439320
Cl62	-0.1248986355	-2.6712397100	3.2449768697

Transition state for Pd-Pd 2.95 Å

H1	-3.9427344843	0.4883543526	0.4340041975
C2	-2.8721279492	0.2910203420	0.4079364769
H3	-2.8016394773	0.2460112799	-1.7411027034
C4	-2.2375231281	0.1599227202	-0.8135018378
C5	-0.8279285371	-0.0767981776	1.5903094036
C6	-0.8596289791	-0.1223929951	-0.8668530849
C7	-2.1801050566	0.1616723353	1.6304568350
C8	-0.1677054497	-0.2278494968	0.3565424163
C9	-0.1205225331	-0.3443202127	-2.0764480473
H10	-2.7015992553	0.2304337789	2.5821053478
C11	1.1989158936	-0.6823647906	-2.0604719289
H12	-0.6486135650	-0.2555157076	-3.0251518371
H13	1.7348391721	-0.8669929198	-2.9897530906
C14	1.9125771722	-0.8169105973	-0.8257123307
C15	3.2606480253	-1.1920151133	-0.6996658534
C16	1.2096060013	-0.5607638191	0.3628942144
C17	3.8290267690	-1.3048167777	0.5536174097
H18	3.8456267674	-1.4014576744	-1.5942309809
H19	4.8645449419	-1.6077078792	0.6765984877
C20	3.0580789321	-1.0276397680	1.6899343135
H21	3.4466362816	-1.1196328646	2.7020459187
N22	1.7936701990	-0.6496988481	1.5823442840
Pd23	0.4219195712	-0.3017427956	3.1164195737
Pd24	1.2276612380	2.5224428394	3.3943613168
H25	4.9259407894	1.9419283140	-0.1770142659
C26	3.9212003327	2.2988149486	0.0424021470
H27	3.3170807378	2.3007169899	-2.0298673796
C28	3.0230891174	2.4903609943	-0.9988234374
C29	2.3125564512	3.0539769894	1.6690704258
C30	1.7128768673	2.9154495225	-0.7208255011
C31	3.5938309488	2.5936678636	1.3676125827

C32	1.3469991638	3.1417452060	0.6228475956
C33	0.7100909189	3.1012129814	-1.7310242246
H34	4.3339040045	2.5239628629	2.1606562628
C35	-0.5669824306	3.4533416281	-1.4228719107
H36	0.9993119368	2.9455318686	-2.7693995742
H37	-1.3101839362	3.5924146422	-2.2065250763
C38	-0.9837190851	3.5730702782	-0.0585984690
C39	-2.3032325933	3.7932688679	0.3632352894
C40	-0.0147845005	3.3640912015	0.9432200829
C41	-2.6115535592	3.7708519583	1.7103564065
H42	-3.0815547871	3.9577703390	-0.3808142847
H43	-3.6263175727	3.9366996021	2.0589874835
C44	-1.6079736276	3.4708229688	2.6373449827
H45	-1.8038144958	3.3722328612	3.7033269785
N46	-0.3558562761	3.2628782735	2.2542982943
C47	-0.9469417528	1.2050200951	5.2556666566
O48	-0.1468285885	2.1601444746	5.1715566544
O49	-1.0289909960	0.1763555704	4.5051582603
C50	2.8478786886	0.5455454575	4.8788078009
O51	2.0474358863	-0.3830644871	4.6459872365
O52	2.8326827497	1.7317695680	4.3999312134
C53	-1.9594607734	1.2313653173	6.3780395369
H54	-2.2757547446	2.2592972568	6.5742541875
H55	-1.4734873115	0.8528031015	7.2837562458
H56	-2.8149036178	0.5908087494	6.1558880908
C57	3.9866722520	0.2829825283	5.8343150229
H58	4.8536139286	0.9008534881	5.5890119090
H59	4.2461083009	-0.7781828435	5.8319632892
H60	3.6575721889	0.5519010716	6.8440770742
Cl61	2.4382938448	4.7360832014	2.8601638307
Cl62	-0.1617061820	-2.6975402867	3.1043907172

Pd-Pd 3.30 Å

H1	-3.7917674868	0.6564386817	0.4171520116
C2	-2.7369752695	0.3867276830	0.4081362164
H3	-2.5921303662	0.5010408924	-1.7348819918
C4	-2.0697279003	0.3030386567	-0.8001132282
C5	-0.7640120190	-0.1932664283	1.6197195679
C6	-0.7104648649	-0.0640568565	-0.8319942454
C7	-2.0973443917	0.1301723856	1.6409958501
C8	-0.0707957450	-0.3020571516	0.4010173264
C9	0.0678695463	-0.2122451534	-2.0283646831
H10	-2.6419770403	0.1826327707	2.5803229931
C11	1.3764865965	-0.5892320908	-1.9931779091
H12	-0.4188941637	-0.0208410897	-2.9839362023
H13	1.9440339420	-0.7052605016	-2.9145709876
C14	2.0405352291	-0.8428198261	-0.7488819155
C15	3.3802680332	-1.2403325023	-0.6001439666

C16	1.2951522059	-0.6759307289	0.4289527320
C17	3.9003796729	-1.4520976442	0.6620987452
H18	3.9993320220	-1.3829754274	-1.4846318166
H19	4.9297990730	-1.7687406974	0.7995892489
C20	3.0908724107	-1.2535217392	1.7882326530
H21	3.4436590489	-1.4025903167	2.8069062737
N22	1.8318916597	-0.8646254156	1.6579456185
Pd23	0.4549555548	-0.4814597849	3.1626781389
Pd24	1.2306879840	2.7203557127	3.3540351494
H25	4.9210435967	2.1886147511	-0.2436828704
C26	3.8797762424	2.4175423382	-0.0231118540
H27	3.3526820083	2.6386362218	-2.0956882230
C28	3.0053630250	2.6681311492	-1.0639461238
C29	2.1511816234	2.7240788674	1.5939112927
C30	1.6594060325	2.9832171584	-0.7971790581
C31	3.4688741074	2.4519732125	1.3270876204
C32	1.2502289869	3.0017365577	0.5509806254
C33	0.6778752793	3.2885248137	-1.7983391468
H34	4.1728793372	2.2691768218	2.1351605402
C35	-0.6036966227	3.6162159016	-1.4724171207
H36	0.9849118325	3.2600444853	-2.8431452826
H37	-1.3287976759	3.8535072945	-2.2491405054
C38	-1.0312607754	3.6595376561	-0.1051339956
C39	-2.3197726424	3.9988907531	0.3412019434
C40	-0.0873353376	3.3299076141	0.8803711063
C41	-2.6021770345	4.0030386670	1.6936483352
H42	-3.0876912520	4.2602374529	-0.3853496145
H43	-3.5881443207	4.2712078752	2.0606464344
C44	-1.6045596762	3.6500996287	2.6119393248
H45	-1.7679393851	3.6301310229	3.6876947655
N46	-0.3921986005	3.3134059885	2.1999593833
C47	-0.9130451291	1.2219163686	5.2014936793
O48	-0.1748097404	2.2149931499	5.0470245394
O49	-0.9540796092	0.1330037909	4.5273165187
C50	2.9315439903	0.7230355435	4.7942045122
O51	2.1579485995	-0.2411158172	4.6278367398
O52	2.8591269308	1.9094212815	4.3157047704
C53	-1.9150577705	1.2521271245	6.3329392718
H54	-2.1380243356	2.2823771859	6.6186438709
H55	-1.4723871859	0.7400372422	7.1940924139
H56	-2.8241881351	0.7110641485	6.0608481204
C57	4.1394590460	0.5179998085	5.6801074046
H58	4.9919471356	1.0935780534	5.3118455794
H59	4.3826239500	-0.5441357714	5.7547516006
H60	3.8982488075	0.8923330410	6.6807312578
Cl61	1.9072164554	5.0426515502	3.6804037733
Cl62	-0.1940674643	-2.8342313963	3.2193806520

Transition state for Pd-Pd 3.30 Å

H1	-3.9971478178	0.3784241011	0.4948233819
C2	-2.9270514075	0.1817860370	0.4504456619
H3	-2.8737990443	0.2462470314	-1.6989088310
C4	-2.3021811338	0.1123194409	-0.7813868120
C5	-0.8732463836	-0.2430973885	1.5954175194
C6	-0.9243201898	-0.1651108944	-0.8599114161
C7	-2.2257405817	-0.0091031783	1.6595391137
C8	-0.2216516733	-0.3311016095	0.3506357099
C9	-0.1933451241	-0.3185874138	-2.0848106686
H10	-2.7371852283	0.0159920140	2.6183955359
C11	1.1309661310	-0.6375956142	-2.0979728370
H12	-0.7312657950	-0.1866714166	-3.0227201705
H13	1.6581904797	-0.7658850908	-3.0423394584
C14	1.8591810540	-0.8176562615	-0.8767587892
C15	3.2192346986	-1.1578315262	-0.7781383752
C16	1.1614552862	-0.6388720517	0.3290173590
C17	3.8032768636	-1.3069474288	0.4644631373
H18	3.8021820424	-1.3083914690	-1.6858197085
H19	4.8495426717	-1.5799156518	0.5646793463
C20	3.0350523126	-1.1056986785	1.6188950242
H21	3.4374037445	-1.2202393570	2.6237963894
N22	1.7573271810	-0.7691512190	1.5390049226
Pd23	0.3909536996	-0.4776423339	3.0990508425
Pd24	1.2636646916	2.6859400298	3.4454895979
H25	4.9907064022	1.9589848592	-0.0485414146
C26	3.9820198813	2.3200756159	0.1437016717
H27	3.4077690695	2.2483698562	-1.9348257441
C28	3.0982793848	2.4728822109	-0.9152355371
C29	2.3450249103	3.1180660063	1.7182808690
C30	1.7816563905	2.9016381300	-0.6725083633
C31	3.6330990767	2.6594942743	1.4530455000
C32	1.3961049672	3.1738999295	0.6571574078
C33	0.7922179316	3.0377552873	-1.7030532761
H34	4.3592088296	2.6158136055	2.2604782069
C35	-0.4956795373	3.3734701378	-1.4229144560
H36	1.0975525872	2.8498131273	-2.7317706361
H37	-1.2325720238	3.4650099322	-2.2195643809
C38	-0.9311487645	3.5372984975	-0.0694212465
C39	-2.2624187614	3.7383813338	0.3262399579
C40	0.0284219149	3.3977859920	0.9518226098
C41	-2.5885768596	3.7645650689	1.6683263973
H42	-3.0336275428	3.8493465295	-0.4343474679
H43	-3.6127156911	3.9141511064	1.9962635075
C44	-1.5873154809	3.5431695313	2.6205411471
H45	-1.7941167863	3.4898959330	3.6876778276
N46	-0.3245889531	3.3591261580	2.2627571799
C47	-0.9654005390	1.1964676224	5.1810254314

O48	-0.1689817866	2.1571247036	5.0904751667
O49	-1.0270238166	0.1296552619	4.4885718799
C50	2.8803084718	0.6077303966	4.8326494577
O51	2.0925531700	-0.3222732481	4.5746705410
O52	2.8433239632	1.8272210843	4.4426342076
C53	-2.0170541594	1.2857570926	6.2670760933
H54	-2.3637784822	2.3179231645	6.3691315083
H55	-1.5542246665	0.9967103046	7.2166003039
H56	-2.8498407503	0.6090420641	6.0684169945
C57	4.0543879664	0.2966043302	5.7347509428
H58	4.8561422479	1.0276946536	5.6141359704
H59	4.4145442553	-0.7169714980	5.5397448068
H60	3.7075177175	0.3304287819	6.7731986320
Cl61	2.4718904230	4.8864459804	2.8659905703
Cl62	-0.2159103695	-2.8689509471	3.1299796895

Pd-Pd 3.65 Å

H1	-3.8578656897	0.5419903937	0.5492068916
C2	-2.8008246761	0.2837402315	0.5149741938
H3	-2.6812642751	0.5108260526	-1.6193290747
C4	-2.1459533823	0.2673717720	-0.7023940231
C5	-0.8094668680	-0.3357555177	1.6667928047
C6	-0.7830785057	-0.0795276884	-0.7705970720
C7	-2.1451955364	-0.0290340492	1.7255289041
C8	-0.1259030621	-0.3799470306	0.4392256466
C9	-0.0156576896	-0.1439080370	-1.9815979812
H10	-2.6753398768	-0.0302625064	2.6742527443
C11	1.3004522521	-0.4952098907	-1.9811698494
H12	-0.5160366560	0.0980723600	-2.9187050337
H13	1.8614151817	-0.5402317338	-2.9130955504
C14	1.9822121697	-0.8102944577	-0.7604710071
C15	3.3344710689	-1.1762728679	-0.6473789305
C16	1.2454891619	-0.7364131257	0.4321704107
C17	3.8741979123	-1.4458073845	0.5954503629
H18	3.9487753338	-1.2441840011	-1.5441486464
H19	4.9152535725	-1.7341534883	0.7051473437
C20	3.0697990939	-1.3402884116	1.7381022009
H21	3.4418709607	-1.5258656392	2.7440255341
N22	1.7971985809	-0.9894543386	1.6425112803
Pd23	0.4228345103	-0.6614735496	3.1833862992
Pd24	1.2677348982	2.8842195048	3.3749750503
H25	4.9896068867	2.2143176137	-0.1464890355
C26	3.9471738015	2.4568363973	0.0525242082
H27	3.4452825851	2.5926181494	-2.0331467641
C28	3.0857882903	2.6677596686	-1.0078408898
C29	2.2023550466	2.8390886509	1.6290434451
C30	1.7375834848	2.9982528965	-0.7721349642
C31	3.5227251200	2.5493608691	1.3955919352

C32	1.3113322440	3.0782704913	0.5683500298
C33	0.7674166265	3.2547208589	-1.7977887043
H34	4.2135353027	2.3990214382	2.2208804301
C35	-0.5224663768	3.5800603297	-1.5034422109
H36	1.0888692586	3.1831615955	-2.8362182216
H37	-1.2399638865	3.7728706539	-2.2994996059
C38	-0.9703015824	3.6739996333	-0.1451811633
C39	-2.2740486284	3.9975403507	0.2686642477
C40	-0.0336008655	3.4096200263	0.8664924014
C41	-2.5777916831	4.0466993067	1.6153014349
H42	-3.0377213468	4.2081162502	-0.4786515583
H43	-3.5772234648	4.2990109095	1.9567786419
C44	-1.5839029434	3.7603265444	2.5608256365
H45	-1.7666834235	3.7683401620	3.6336744879
N46	-0.3554663081	3.4464011128	2.1811688763
C47	-0.9620727790	1.1495426267	5.1373075509
O48	-0.2410236373	2.1422445051	4.9358168053
O49	-0.9604763045	0.0054226048	4.5568353263
C50	2.9642368754	0.8051670713	4.7387269067
O51	2.1965937704	-0.1534319354	4.5433267617
O52	2.8712838206	2.0216159426	4.3439962736
C53	-2.0092932671	1.2424928216	6.2286243264
H54	-2.2513531935	2.2871112833	6.4370090129
H55	-1.5965247175	0.7932671031	7.1383172464
H56	-2.9037731470	0.6759962693	5.9591188264
C57	4.2052967392	0.5592190606	5.5730281130
H58	5.0357566683	1.1807861092	5.2304311547
H59	4.4717443970	-0.5000214801	5.5558245330
H60	3.9843144862	0.8434833762	6.6072880978
Cl61	2.0194941907	5.1922437348	3.6638821902
Cl62	-0.3105591014	-2.9932357784	3.2084342094

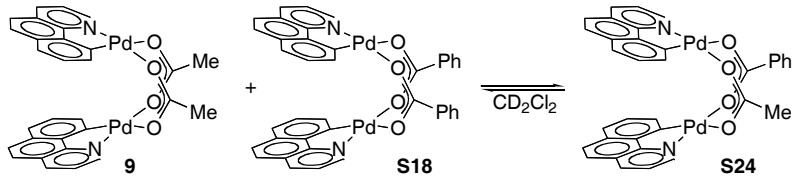
Transition state for Pd-Pd 3.65 Å

H1	-4.2977246448	-0.0719151001	0.7138324542
C2	-3.2307040585	-0.2009024108	0.5390208297
H3	-3.4685043080	-0.3408822785	-1.5933780065
C4	-2.7709187878	-0.3470455598	-0.7570053999
C5	-1.0192387602	-0.3949131669	1.4233261966
C6	-1.3979483429	-0.5444644864	-1.0008107033
C7	-2.3651446600	-0.2382836997	1.6524524526
C8	-0.5316139805	-0.5508854056	0.1112820347
C9	-0.8241860012	-0.7676514524	-2.2972654354
H10	-2.7456246171	-0.1625435901	2.6677928769
C11	0.5098040411	-0.9908647009	-2.4647133604
H12	-1.4888831130	-0.7729527555	-3.1605760078
H13	0.9187022561	-1.1755282479	-3.4569860804
C14	1.4049973986	-0.9943515619	-1.3453568716
C15	2.7918203319	-1.2212071071	-1.4042559874

C16	0.8574837719	-0.7558002959	-0.0741205408
C17	3.5415786231	-1.2035695024	-0.2441654458
H18	3.2635980860	-1.4172400623	-2.3663814381
H19	4.6135848884	-1.3775663103	-0.2670198071
C20	2.9141184265	-0.9461533460	0.9835060802
H21	3.4532046427	-0.9055754181	1.9285779662
N22	1.6131273550	-0.7189392275	1.0498461181
Pd23	0.4152204172	-0.4303637698	2.7683413307
Pd24	1.3339677802	2.9807983140	3.6861514019
H25	5.4251557165	2.0216664828	0.6574840831
C26	4.3809553760	2.3225243488	0.7147204548
H27	4.0058192303	1.9440907281	-1.3723850102
C28	3.5902470080	2.2740055855	-0.4217839627
C29	2.5553882351	3.1849263518	2.0098403345
C30	2.2294937479	2.6235052986	-0.3524165421
C31	3.8834880097	2.7909436151	1.9356226849
C32	1.7061641070	3.0648344529	0.8817556106
C33	1.3335337033	2.4979933319	-1.4655676773
H34	4.5241739482	2.8981063241	2.8064071026
C35	0.0015794526	2.7425961853	-1.3443610201
H36	1.7456733976	2.1708591838	-2.4195501083
H37	-0.6661820734	2.6163201852	-2.1953386603
C38	-0.5649706957	3.0972499574	-0.0788929757
C39	-1.9421754515	3.2223604913	0.1651846438
C40	0.3031104366	3.2379329911	1.0215861996
C41	-2.3960544876	3.4487826726	1.4489891502
H42	-2.6430695006	3.1079418868	-0.6603763296
H43	-3.4564455777	3.5372201032	1.6652115404
C44	-1.4716358604	3.5175663592	2.4973618384
H45	-1.7775390737	3.6321357954	3.5355709945
N46	-0.1694802259	3.4145827823	2.2807534358
C47	-0.9198498140	1.2233067356	5.0539612688
O48	-0.1709374832	2.2336938570	5.0826570785
O49	-0.9114152507	0.2250526968	4.2798052442
C50	2.9233367027	0.8359938669	4.7673232393
O51	2.3195204382	0.0434188463	4.0262103931
O52	2.8017210935	2.1147848229	4.8327036675
C53	-2.0014988265	1.1959263791	6.1167093050
H54	-2.4903963480	2.1727634862	6.1776611198
H55	-1.5291680038	1.0080179315	7.0862647983
H56	-2.7289089251	0.4078031643	5.9157451441
C57	3.9458309734	0.2759664885	5.7309927781
H58	4.5690240046	1.0583613782	6.1668892985
H59	4.5605757522	-0.4678270151	5.2166947254
H60	3.4090260494	-0.2449666428	6.5306187427
Cl61	2.5233526730	5.1107821901	3.0049329933
Cl62	-0.0064455082	-2.8868474694	3.0131306094

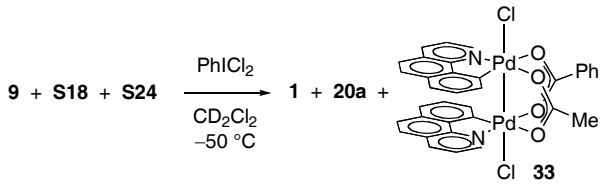
Cross-Over Experiments (Data Pertaining Scheme 6)

Cross-Over Between Acetate-Bridged 9 and Benzoate Bridged S18



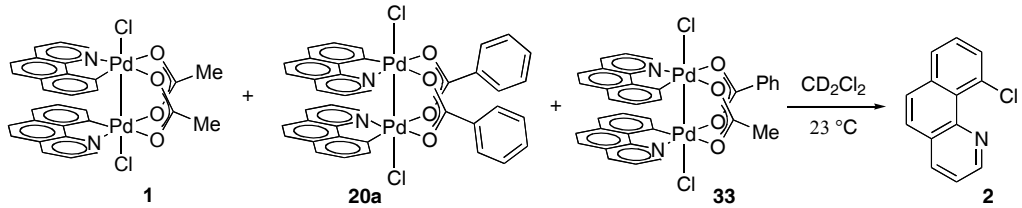
A solution of benzo[*h*]quinolinyl palladium acetate dimer (**9**) (8.7 mg, 1.3×10^{-5} mol, 1.0 equiv) in CD_2Cl_2 (1.0 mL) was added to a solution of benzo[*h*]quinolinyl palladium benzoate dimer (**S18**) (10.3 mg, 1.27×10^{-5} mol, 1.00 equiv) in CD_2Cl_2 (1.0 mL) at 23 °C. A ^{1}H NMR spectrum of the reaction mixture was obtained which contained the ^{1}H NMR signals of **9** and **S18** as well as an additional species, assigned as **S24**. The ratio of **9** and **S24** can be assayed by comparison of the ^{1}H NMR signal at 2.38 ppm (**9**) and at 2.34 ppm (**S24**). The ^{1}H NMR spectrum of the crude reaction mixture is reproduced below.

Synthesis of Cross-over Intermediate 33



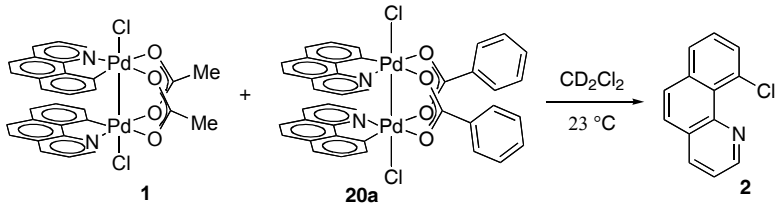
A solution of benzo[*h*]quinolinyl palladium acetate dimer (**9**) (14.9 mg, 2.17×10^{-5} mol, 0.50 equiv) and benzo[*h*]quinolinyl palladium benzoate dimer (**S18**) (17.6 mg, 2.17×10^{-5} mol, 0.50 equiv) in CD_2Cl_2 (3.0 mL) was prepared at 23 °C. The reaction mixture was cooled to –50 °C at which temperature $PhICl_2$ (11.9 mg, 4.34×10^{-5} mol, 1.00 equiv) is added to the reaction mixture as a solid. A ^{1}H NMR spectrum of the reaction mixture was obtained at –50 °C which contained the ^{1}H NMR signals of **1** and **20a** as well as an additional species, assigned as **33**. The presence of **33** in the reaction mixture was assayed by the ^{1}H NMR signal at 2.64 ppm and the ratio of **1** and **33** could be determined by the ratio of the ^{1}H NMR signals at 2.70 ppm (**1**) and 2.64 ppm (**33**). The ^{1}H NMR spectrum of the crude reaction mixture is reproduced below.

Thermolysis of Mixture of 1, 20a, and 33



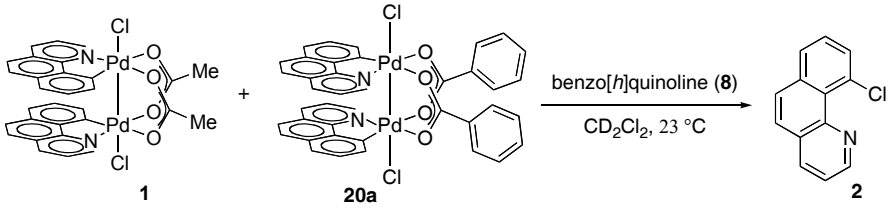
A solution of **1**, **20a**, and **33** (prepared above) was warmed from –50 °C to 23 °C at which temperature it was maintained for 5 minutes. Subsequently, the reaction solution was cooled to –50 °C and a ^{1}H NMR spectrum was obtained. The ^{1}H NMR showed the formation of **2** and that the ratio of **1** and **33** did not change. Subsequent cycles of warming to 23 °C followed by cooling to –50 °C for ^{1}H NMR analysis showed gradual increase in the yield of **2** with no change in the ratio of **1** and **33**. The reaction was monitored in this fashion until 20% yield in **2** based the combined amount of **1**, **20a**, and **33**. A ^{1}H NMR spectrum is reproduced below showing **1**, **20a**, **33**, and **2**.

Thermolysis of Mixture of 1 and 20a



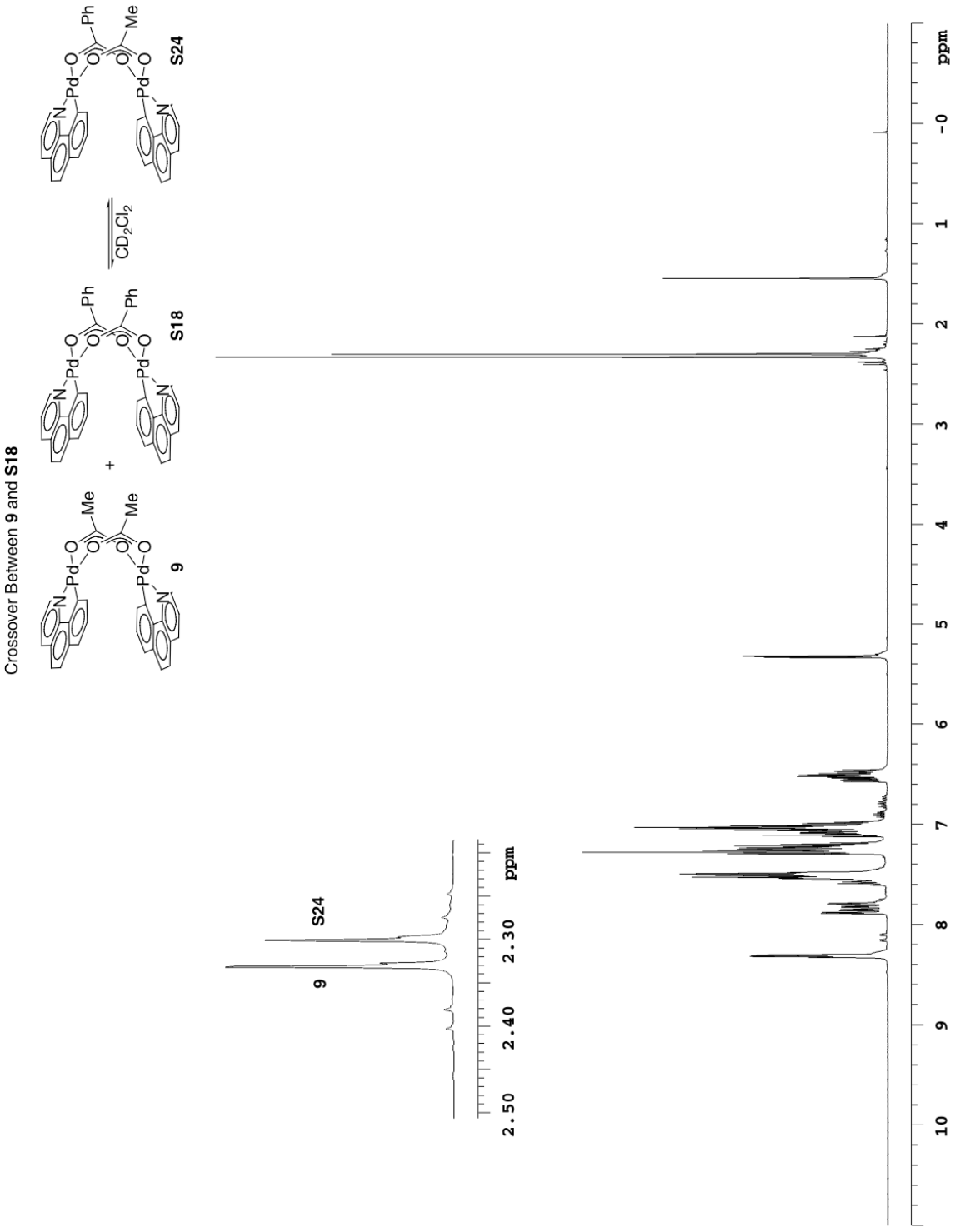
A solution of **1** was prepared by addition of $PhICl_2$ (3.9 mg, 1.4×10^{-5}, 1.0 equiv) to benzo[*h*]quinolinyl palladium acetate dimer (**9**) (9.8 mg, 1.4×10^{-5}, 1.0 equiv) in CD_2Cl_2 (0.7 mL) at –50 °C. This solution was added (at –50 °C) to a solution of **20a**, prepared by addition of $PhICl_2$ (3.9 mg, 1.4×10^{-5}, 1.0 equiv) to benzo[*h*]quinolinyl palladium benzoate dimer (**S18**) (11.5 mg, 1.42×10^{-5}, 1.00 equiv) in CD_2Cl_2 (0.7 mL) at –50 °C. The solution of **1** and **20a** was warmed from –50 °C to 23 °C at which temperature it was maintained for 5 minutes. Subsequently, the reaction solution was cooled to –50 °C and a ^{1}H NMR spectrum was obtained. The ^{1}H NMR showed the formation of **2**. Compound **2** was observed without the formation of detectable amounts of **33**. Subsequent cycles of warming to 23 °C followed by cooling to –50 °C for ^{1}H NMR analysis showed gradual increase in the yield of **2** without the evolution of **33**. ^{1}H NMR spectra at later times in the reaction (approximately 20% yield of **2** based on the combined amount of **1** and **20a**) showed the evolution of a small amount of **33**, likely due to exchange with the Pd(II) complexes generated during reductive elimination. A ^{1}H NMR spectrum is reproduced below showing the formation of **2** and the absence of **33**.

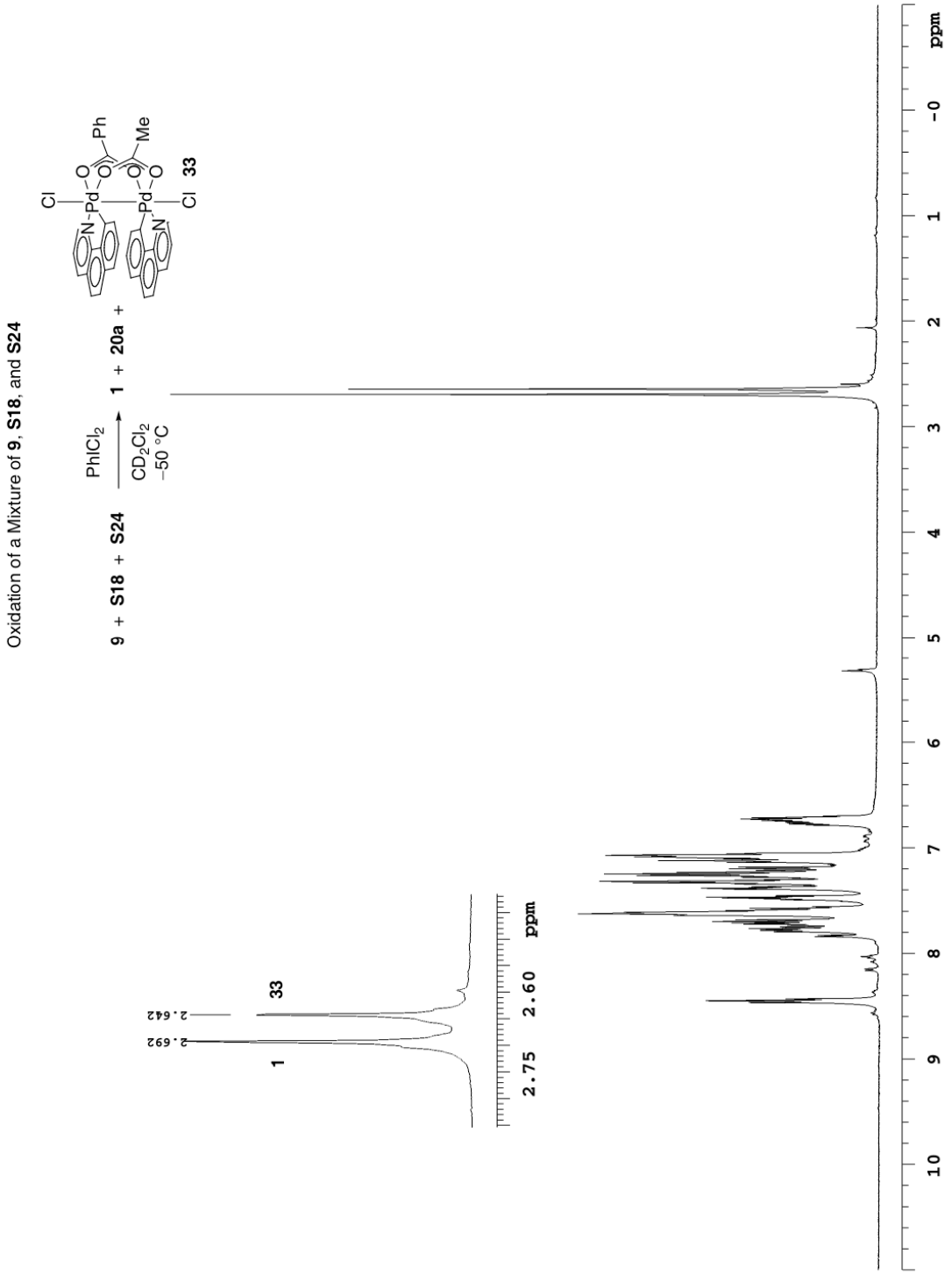
Thermolysis of Mixture of 1 and 20a with Added Benzo[*h*]quinoline (8)

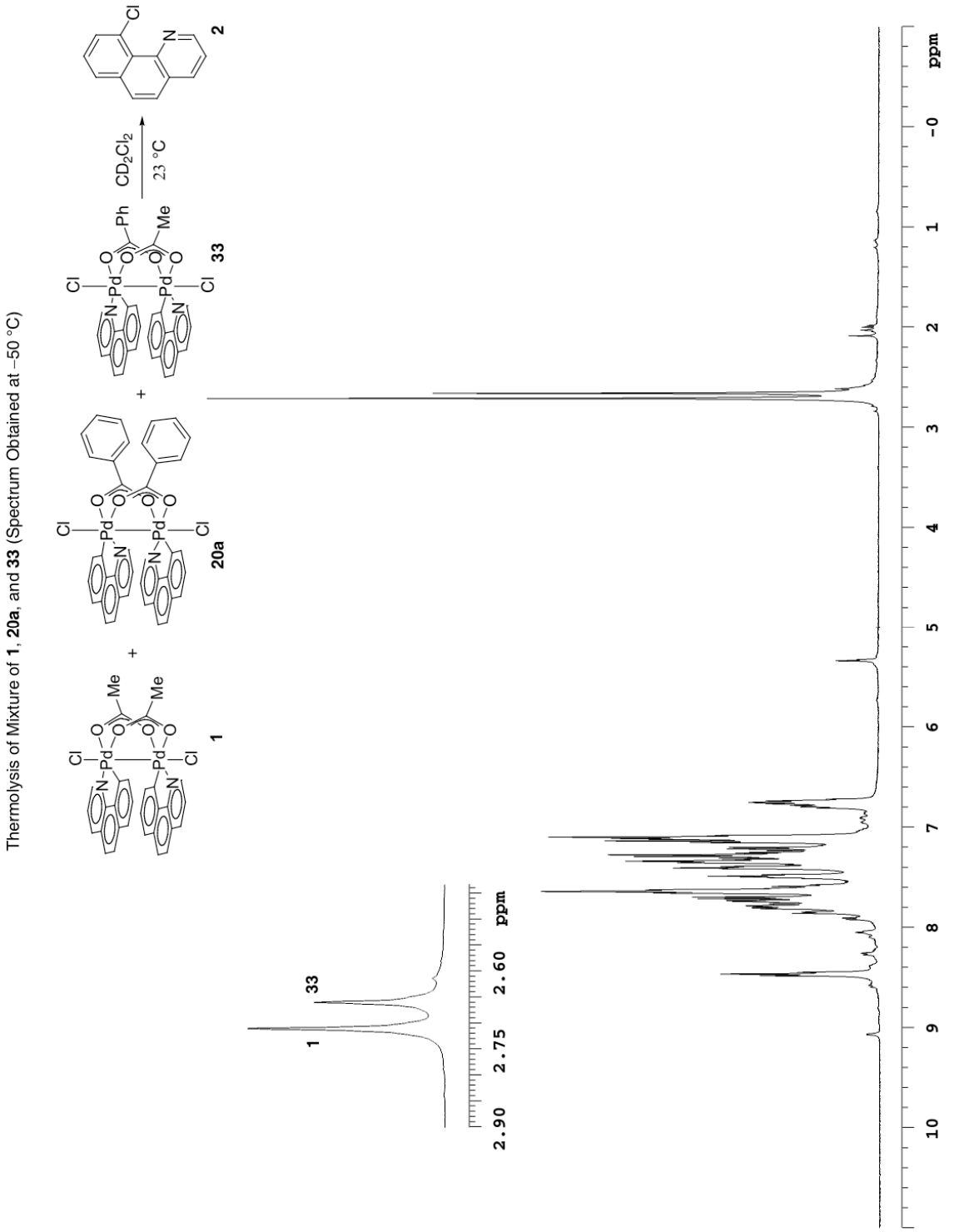


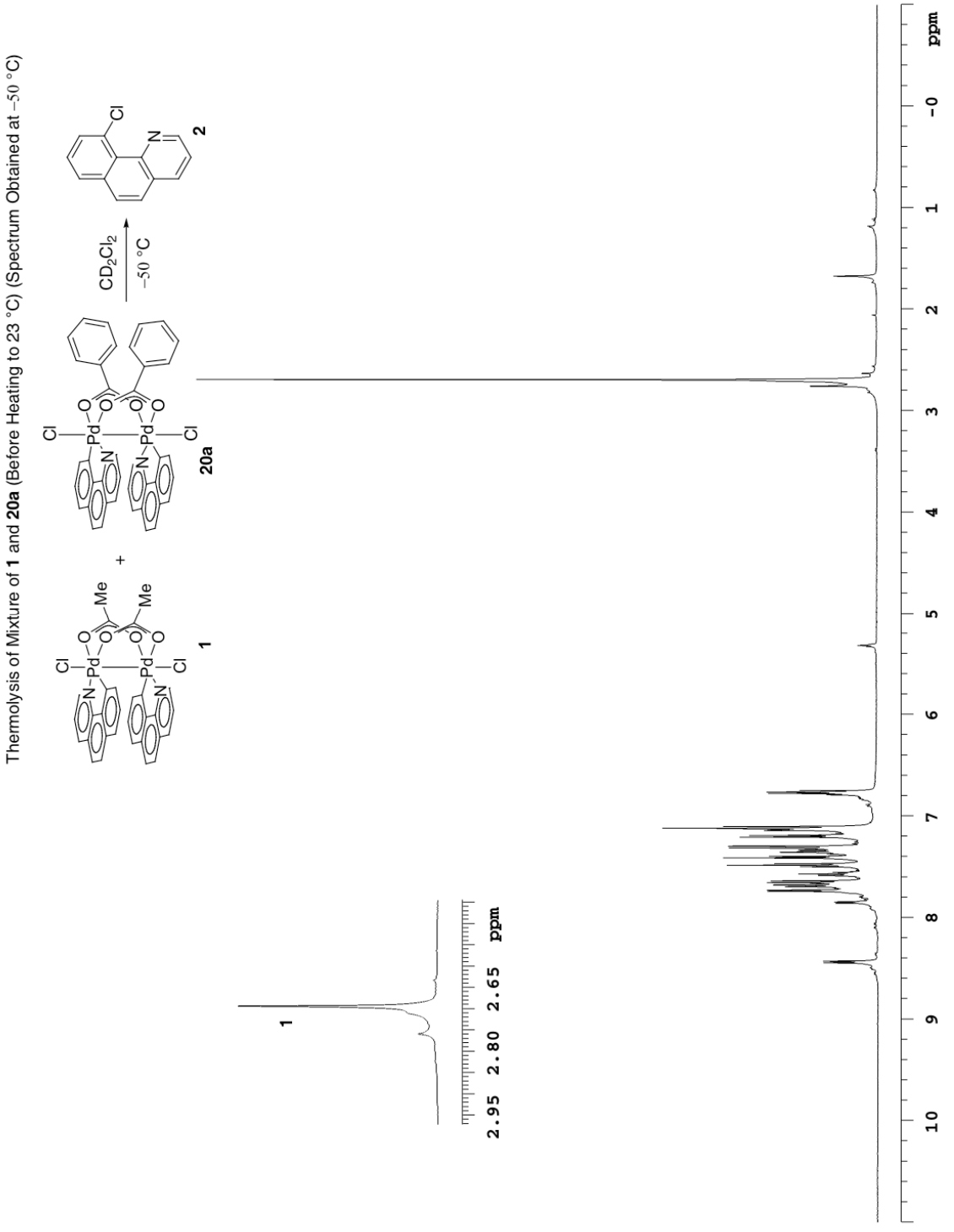
A solution of **1** was prepared by addition of $PhICl_2$ (3.6 mg, 1.4×10^{-5}, 1.0 equiv) to benzo[*h*]quinolinyl palladium acetate dimer (**9**) (9.0 mg, 1.3×10^{-5}, 1.0 equiv) in CD_2Cl_2 (0.7 mL) at –50 °C. This solution was added (at –50 °C) to a solution of **20a**, prepared by addition of $PhICl_2$ (3.6 mg, 1.4×10^{-5}, 1.0 equiv)

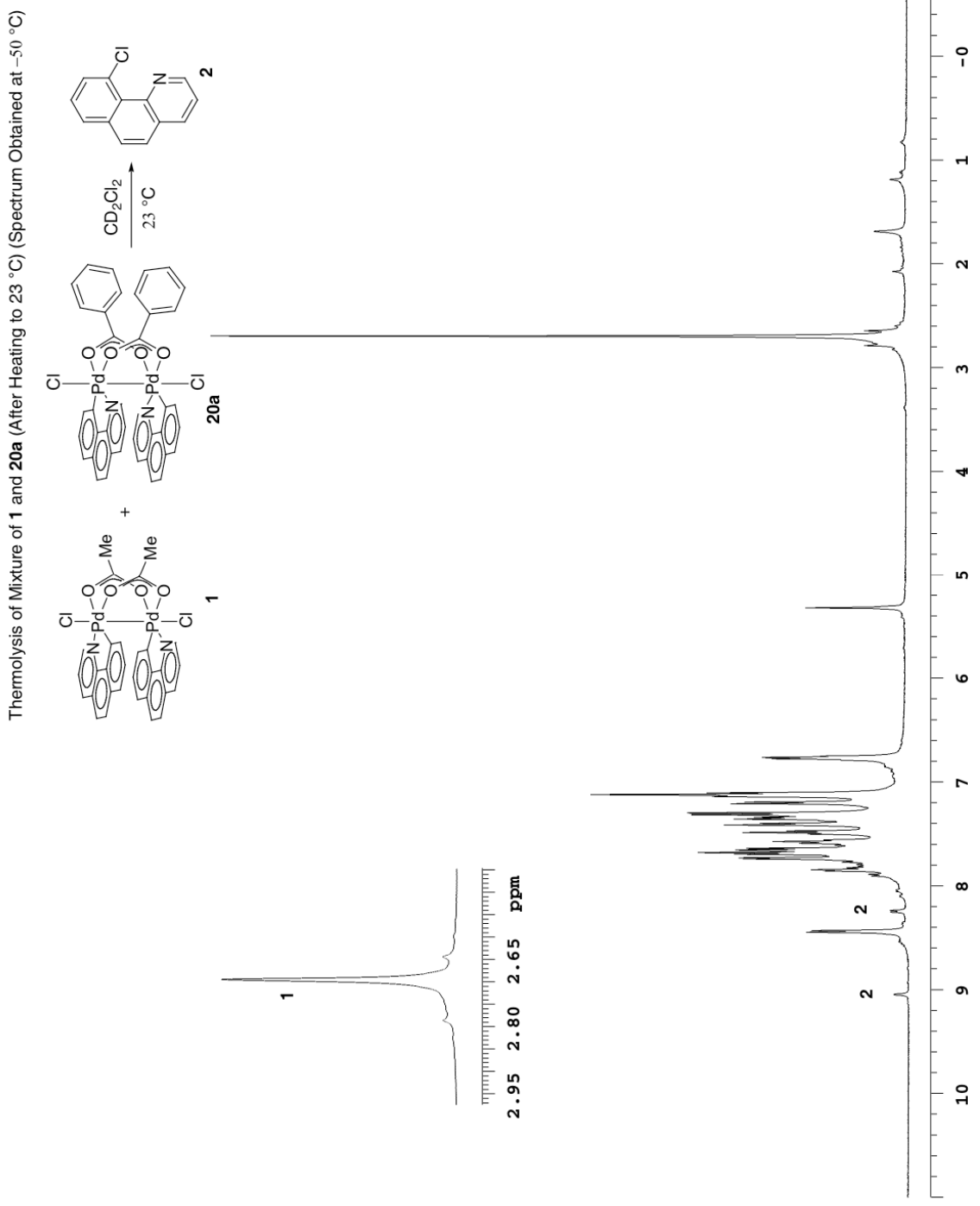
to benzo[*h*]quinolinyl palladium benzoate dimer (**S18**) (10.6 mg, 1.31×10^{-5}, 1.00 equiv) in CD_2Cl_2 (0.7 mL) at –50 °C. Benzo[*h*]quinoline (**8**) (4.7 mg, 2.6×10^{-5}, 2.0 equiv) was added to the combined solution of **1** and **20a** at –50 °C. The solution of **1**, **20a**, and **8** was warmed from –50 °C to 23 °C at which temperature it was maintained for 5 minutes. Subsequently, the reaction solution was cooled to –50 °C and a ^{1}H NMR spectrum was obtained. The ^{1}H NMR showed the formation of **2**. Compound **2** was observed without the formation of detectable amounts of **33**. Subsequent cycles of warming to 23 °C followed by cooling to –50 °C for ^{1}H NMR analysis showed gradual increase in the yield of **2** without the evolution of **33**. ^{1}H NMR spectra at later times in the reaction (approximately 20% yield of **2** based on the combined amount of **1** and **20a**) showed the evolution of a small amount of **33**, likely due to exchange with the Pd(II) complexes generated during reductive elimination. A ^{1}H NMR spectrum is reproduced below showing the formation of **2** and the absence of **33**.

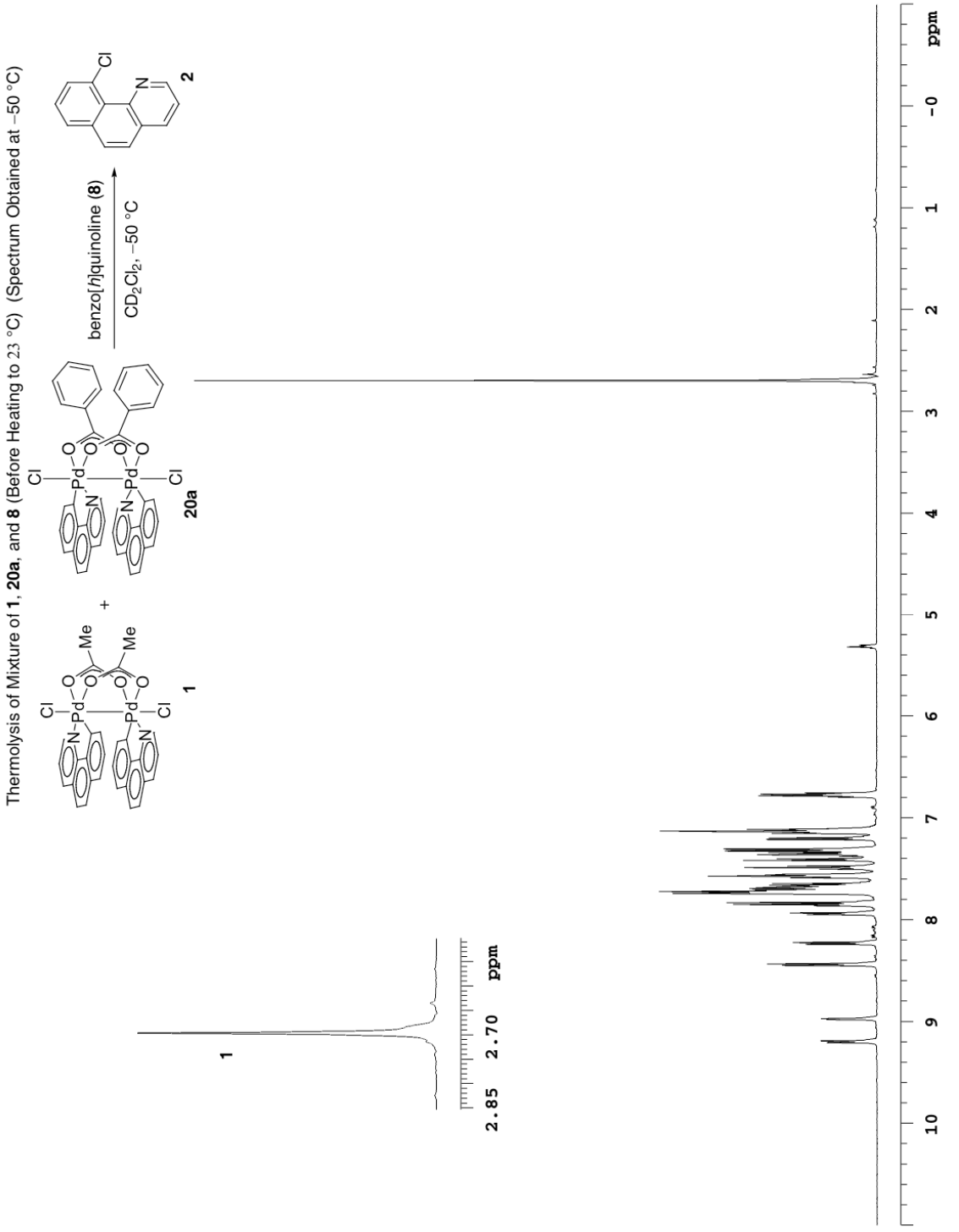

Crossover Between 9 and S18
9
+
S18
CD2Cl2
S24
S24
9
2.50
2.40
2.30
ppm
ppm

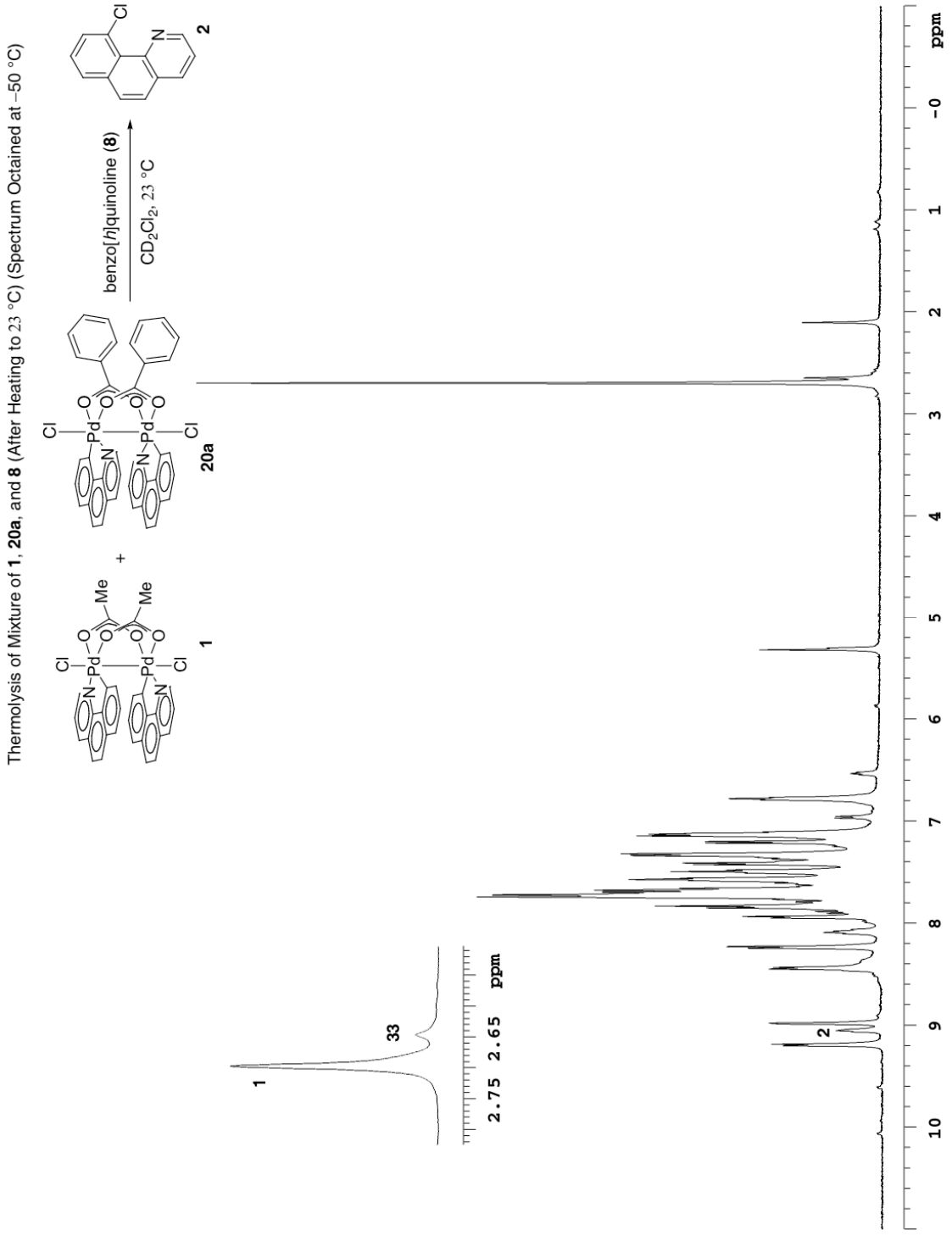

Oxidation of a Mixture of 9, S18, and S24
9 + S18 + S24
PhICl2
CD2Cl2
–50 °C
1 + 20a +
33
Ph
Me
Cl
Pd
N
O
2.642
2.692
33
1
2.75
2.60
ppm
ppm


Thermolysis of Mixture of 1, 20a, and 33 (Spectrum Obtained at –50 °C)
Me
Me
Cl
Pd
O
N
1
+
20a
Ph
Me
33
CD2Cl2
23 °C
2
33
1
2.90
2.75
2.60
ppm
10
9
8
7
6
5
4
3
2
1
–0
ppm


Thermolysis of Mixture of 1 and 20a (Before Heating to 23 °C) (Spectrum Obtained at –50 °C)
Me
Me
Cl
Pd
O
N
Cl
1
+
20a
CD2Cl2
–50 °C
Cl
N
2
1
2.95 2.80 2.65 ppm
10 9 8 7 6 5 4 3 2 1 –0 ppm

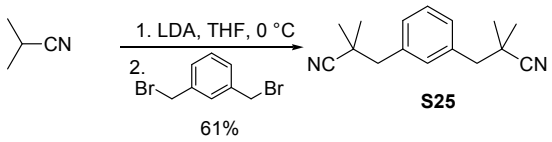

Thermolysis of Mixture of 1 and 20a (After Heating to 23 °C) (Spectrum Obtained at –50 °C)
Me
Me
Cl
Pd
O
N
1
+
20a
CD2Cl2
23 °C
Cl
N
2
1
2.95 2.80 2.65 ppm
2
2
10 9 8 7 6 5 4 3 2 1 -0 ppm


Thermolysis of Mixture of 1, 20a, and 8 (Before Heating to 23 °C) (Spectrum Obtained at −50 °C)
benzo[h]quinoline (8)
CD2Cl2, −50 °C
1
20a
2
2.85
2.70
ppm


Thermolysis of Mixture of 1, 20a, and 8 (After Heating to 23 °C) (Spectrum Octained at –50 °C)
benzo[h]quinoline (8)
CD2Cl2, 23 °C
1
20a
2
33
2.75 2.65 ppm
ppm

Synthesis and Thermolysis of 34 (Data Pertaining to Eq 5)

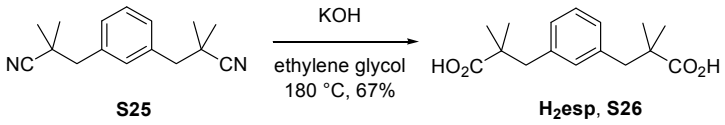
1,3-Bis(2-methyl-2-cyanopropyl)benzene (S25)



To a THF solution of LDA, prepared by treating *i*Pr_2NH (8.00 mL, 57.0 mmol, 3.50 equiv) in THF (50 mL) with 2.70 M *n*-BuLi (15.8 mL, 42.7 mmol, 2.63 equiv) at 0 ºC, was added isobutyronitrile (2.96 mL, 32.5 mmol, 2.00 equiv). After 10 minutes at 0 ºC, xylylene dibromide (4.30 g, 16.3 mmol, 1.00 equiv) in THF (10 mL) was added. The reaction was allowed to stir at 0 ºC for 20 minutes, at which time the solution was poured into 1 N HCl (100 mL). The phases were separated and the aqueous phase was extracted with EtOAc (3 × 40 mL). The organic phases were combined, washed with brine, and concentrated *in vacuo*. The residue was purified by chromatography on silica gel eluting with benzene to afford 2.40 g of the title compound as a pale yellow oil (61% yield).

R_f = 0.18 (benzene). ^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.32 (dd, *J* = 8.1 Hz, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 1.5 Hz, 1H), 7.18 (d, *J* = 10.2 Hz, 2H), 2.82 (s, 4H), 1.36 (s, 12H). ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 135.85, 132.11, 129.21, 128.44, 124.69, 46.51, 33.59, 26.56. These spectroscopic data correspond to those reported in the literature.[26]

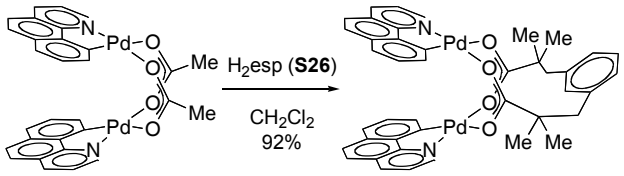
α,α,α',α'-Tetramethyl-1,3-benzenedipropionic acid (H_2esp) (S26)



1,3-Bis(2-methyl-2-cyanopropyl)benzene (**S25**) (2.40 g, 10.0 mmol, 1.00 equiv) was dissolved in ethylene glycol (13 mL). KOH (2.81 g, 50.0 mmol, 2.50 equiv) was added and the reaction was heated to 180 ºC. After six hours, the reaction mixture was cooled to room temperature and $CHCl_3$ (15 mL) and water (15 mL) were added. The aqueous layer was isolated and was acidified (pH = 1) with 6 N HCl. The aqueous phase was then extracted with EtOAc (3 × 60 mL). The organic phases were combined and washed sequentially with water (2 × 20 mL) and brine (2 × 20 mL) before being dried with Na_2SO_4. Solvent was removed *in vacuo* to afford 1.85 g of the title compound as a colorless solid (67% yield.)

^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC, δ): 7.19 (t, *J* = 7.6 Hz, 1H), 7.03 (s, 1H), 7.01 (t, *J* = 7.3 Hz, 2H), 2.84 (s, 4H), 1.18 (s, 12H). ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC, δ): 184.04, 137.32, 131.40, 128.70, 127.57, 46.13, 43.55, 24.39. These spectroscopic data correspond to those reported in the literature.[27]

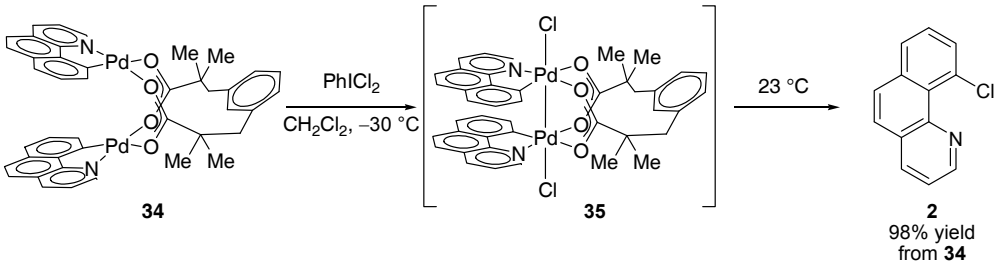
[Pd$_2$(bhq)$_2$]esp (34)



To a solution of benzo[*h*]quinolinyl palladium acetate dimer (**9**) (388 mg, 0.565 mmol, 1.00 equiv) in CH_2Cl_2 (10 mL) at 23 ºC was added α,α,α',α'-tetramethyl-1,3-benzenedipropionic acid (H_2esp, **S26**) (157 mg, 0.565 mmol, 1.00 eq). After stirring for 30 minutes, solvent was removed *in vacuo*. Trituration with Et_2O (5 mL) and isolation by filtration afforded 438 mg of the title compound as a yellow solid (92% yield) in a 20:1 ratio of isomers (benzo[*h*]quinolinyl ligand head to tail vs. head to head).

R_f = 0.29 (hexanes/EtOAc 7:3 (v/v)). Melting Point: >250 ˚C. ^{1}H-NMR (500 MHz, $CDCl_3$, 23 ºC, δ): Major Isomer: 7.79 (dd, *J* = 5.4 Hz, *J* = 1.5 Hz, 2H), 7.52 (s, 1H), 7.44 (dd, *J* = 7.8 Hz, *J* = 1.0 Hz, 2H), 7.23–7.14 (m, 7H), 7.07 (d, *J* = 7.3 Hz, 2H), 7.00 (dd, *J* = 7.3 Hz, *J* = 1.5 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.50 (dd, *J* = 7.8 Hz, *J* = 4.9 Hz, 2H) 2.99 (d, *J* = 12.2 Hz, 2H), 2.88 (d, *J* = 12.2 Hz, 2H), 1.50 (s, 6H), 1.39 (s, 6H). Minor Isomer: 8.07 (dd, *J* = 6.3 Hz, *J* = 1.5 Hz, 2H), 7.71 (dd, *J* = 7.8 Hz, *J* = 1.5 Hz, 2H), 7.50 (s, 1H), 6.93–6.87 (m, 7H), 6.78 (d, *J* = 6.8 Hz, 2H), 1.48 (s, 6H), 1.41 (s, 6H). ^{13}C-NMR (125 MHz, $CDCl_3$, 23 ºC, δ): Major Isomer: 186.82, 153.06, 149.08, 148.37, 139.80, 138.76, 135.01, 132.05, 131.42, 128.13, 127.93, 127.41, 127.38, 126.68, 124.65, 122.64, 121.59, 119.72, 47.62, 46.19, 27.12, 26.67. UV-VIS Spectroscopy (CH_2Cl_2, 23 ˚C): 425 nm (ε = 2.07 × 10^3 M^{-1} cm^{-1}); 381 nm (ε = 4.13 × 10^3 M^{-1} cm^{-1}); 277 nm (ε = 1.97 × 10^4 M^{-1} cm^{-1}). Mass Spectrometry: LRMS-FIA (m/z): calcd for [$C_{42}H_{36}N_2O_4Pd_2$+H], 845.1. Found, 845.0. Anal: calcd for $C_{42}H_{36}N_2O_4Pd_2$: C, 59.66; H, 4.29; N, 3.31; found: C, 59.60; H, 4.31; N, 3.23.

[Pd$_2$(bhq)$_2$Cl$_2$]esp (35)



To [Pd$_2$(bhq)$_2$]esp complex (**34**) (73.4 mg, 8.68 × 10^{-5} mol, 1.00 equiv) in CH_2Cl_2 (5 mL) was added iodobenzene dichloride (23.9 mg, 8.68 × 10^{-5} mol, 1.00 eq) at –30 ºC. The reaction mixture immediately turned from pale yellow to dark red. The formation of [Pd$_2$(bhq)$_2$Cl$_2$]esp (**35**) as a 10:1 mixture of isomers (benzo[*h*]quinolinyl ligand head to tail vs. head to head) was confirmed spectroscopically (see below); compound **35** was not isolated. The reaction was allowed to warm to room temperature and was

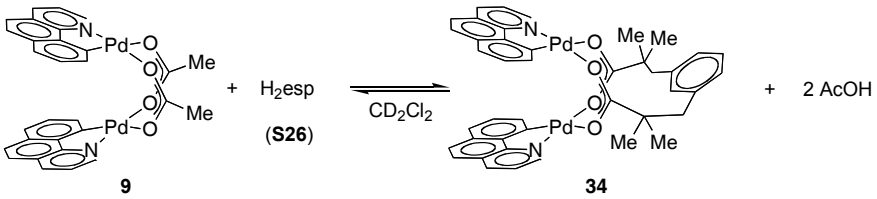
stirred for 6 hours, at which time the reaction mixture was yellow. Solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel eluting with hexanes / diethyl ether (9:1) to afford 18.2 mg of **2** as a colorless solid (98% yield).

Characterization of $[Pd_2(bhq)_2Cl_2]$esp (**35**):

^{1}H-NMR (500 MHz, $CDCl_3$, –30 ºC, δ): Major Isomer: 7.86 (d, *J* = 5.4 Hz, 2H), 7.77 (s, 1H), 7.70 (dd, *J* = 8.3 Hz, *J* = 1.0 Hz, 2H), 7.28–7.21 (m, 8H), 7.08 (dd, *J* = 7.3 Hz, *J* = 1.0 Hz, 2H)**,** 7.03 (d, *J* = 8.8 Hz, 2H)**,** 6.78 (dd, *J* = 7.8 Hz, *J* = 5.4 Hz, 2H)**,** 3.16 (d, *J* = 12.7 Hz, 2H), 3.11 (d, *J* = 12.7 Hz, 2H), 1.60 (s, 6H), 1.59 (s, 6H). Minor Isomer: 8.17 (d, *J* = 7.3 Hz, 2H), 8.04 (d, *J* = 5.4 Hz, 2H), 7.80 (s, 1H), 7.49 (dd, *J* = 8.3 Hz, *J* = 8.3 Hz, 2H), 7.00 (dd, *J* = 8.8 Hz, *J* = 8.8 Hz, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$, –30 ºC, δ): 193.16, 155.44, 149.12, 148.42, 138.12, 136.43, 135.75, 133.26, 131.35, 130.39, 128.39, 127.71, 127.43, 126.34, 125.91, 124.14, 123.93, 122.08,47.58, 47.13, 26.67, 26.44. UV-VIS Spectroscopy (CH_2Cl_2, 0 ˚C): 570 nm (ε = 3.41 × 10^3 M^{-1} cm^{-1}); 418 nm (ε = 2.26 × 10^4 M^{-1} cm^{-1}); 277 nm (ε = 3.54 × 10^4 M^{-1} cm^{-1}).

Compound **2** obtained from this procedure is spectroscopically identical to that reported above.

Determination of H_2esp (S26) vs. AcOH Equilibrium Constant



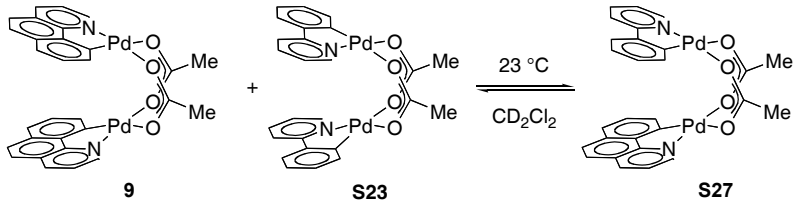
To $[Pd_2(bhq)_2]$esp complex (**34**) (9.0 mg, 1.1 × 10^{-5} mol, 1.0 equiv) in CD_2Cl_2 (0.7 mL) was added AcOH (10 μL mg, 1.8 × 10^{-4} mol, 16 equiv) at 23 ºC. The ^{1}H NMR spectrum was obtained after 5 minutes, 30 minutes, and 90 minutes and showed no change over time in the relative intensities of signals attributable to **9**, **S26**, **34**, and AcOH. Diagnostic peaks for **34** (1.48 and 1.41 ppm), **9** (2.38 ppm), H_2esp (**S26**) (1.18 ppm), and AcOH (2.10 ppm) were used to measure the relative amount of the four species. The integration of each of these signals was adjusted for the number of protons represented by that signal, and the equilibrium constant was calculated using the following equation:

K_{eq} = [**34**][AcOH]^2/[**9**][**S26**]

Evaluating this expression, K_{eq} = 1.2 x 10^5.

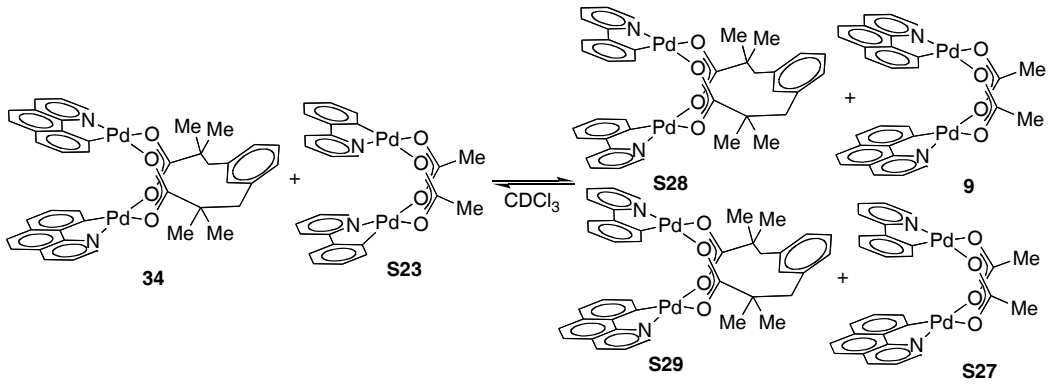
Evaluation of the Relative Rates of Dissociation of Acetate and esp-Bridged Complexes

Exchange Between 9 and S23



A solution of benzo[*h*]quinolinyl palladium acetate dimer (**9**) (10.3 mg, 1.50×10^{-5} mol, 1.0 equiv) in CD_2Cl_2 (0.7 mL) was prepared. At 23 °C a solution of 2-phenylpyridyl palladium acetate dimer (**S23**) (9.6 mg, 1.5×10^{-5} mol, 1.0 equiv) in CD_2Cl_2 (0.7 mL) was added. A ^{1}H-NMR was obtained immediately upon preparing the solution (2 min following combination of the two solutions). The spectrum contained only peaks assigned to **9**, **S23**, and a third species, **S27**. The ^{1}H NMR spectrum of the mixture was obtained again following 3 h at 23 °C and showed no change in the integrations of the peaks attributable to **9**, **S23**, and **S27**.

Exchange Between 34 and S23



A solution of 2-phenylpyridyl palladium acetate dimer (**S23**) (4.2 mg, 6.6×10^{-6} mol, 1.0 equiv) and complex **34** (5.6 mg, 6.6×10^{-6} mol, 1.0 equiv) in $CDCl_3$ (0.7 mL) was prepared. A ^{1}H-NMR was obtained immediately upon preparation of the solution. The spectrum contained only peaks assigned to complexes **34** and **S23**. The solution was stirred for 1 h at 23 °C. A ^{1}H-NMR spectrum was obtained and, based on the integration of the signals for the bridging acetate ligands in **S23** as compared to the residual proton signal in $CDCl_3$ it was determined that <2% exchange had occurred during this time. The solution was heated for 4 h at 50 °C. ^{1}H-NMR analysis after this period revealed that 68% exchange had occurred under these conditions. The percentages of scrambling are based on an equilibrated samples, obtained after prolonged (>24 h) heating. The ^{1}H-NMR after this time contains only peaks assignable to compounds **34** and **S23** as well as two new compounds.

Comparison of Acetate and esp-Bridged Complexes

In 2 minutes, scrambling between **9** and **S23** was complete. In 1 h, 2% scrambling between **34** and **S23** was observed. Assuming a simplified model of percent scrambling as a linear function of time, **34** undergoes dimer monomer cleavage atleast 1500 times slower than **9**. This approximation is conservative estimate as the rate of cleavage of **34** was assayed using an initial rate (2% scrambling) and the rate of cleavage of **9** was assayed following complete scrambling.

Comparison of variable temperature ^{1}H NMR spectra of 9 and 34

Qualitative information concerning the relative fluxionalities of **9** and **34** can be obtained by examining the ^{1}H NMR spectra of **9** and **34** at elevated temperatures. These experiments are outlined below.

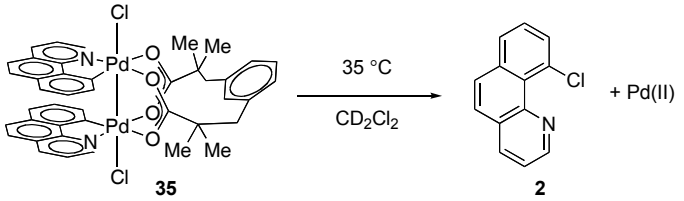
Temperature Dependent ^{1}H NMR of 9 in Presence of Benzo[*h*]quinoline (8)

A solution of benzo[*h*]quinoline (**8)** (13 mg, 7.3×10^{-5} mol, 1.0 equiv) and $Pd(OAc)_2$ (1.6 mg, 7.1×10^{-6} mol, 0.10 equiv) in CD_3CN (0.7 mL) was prepared. A ^{1}H NMR of the solution was obtained at 23 °C. The sample was warmed to 80 °C at which temperature a ^{1}H NMR was obtained. The sample was subsequently cooled to 23 °C at which temperature the ^{1}H NMR was observed again. The spectrum exhibits temperature-dependent reversible line broadening for the signals corresponding to **9** while no line broadening is observed for the signals corresponding to exogenous benzo[*h*]quinoline (**8**).

Temperature Dependent ^{1}H NMR of 33 in Presence of Benzo[*h*]quinoline (8)

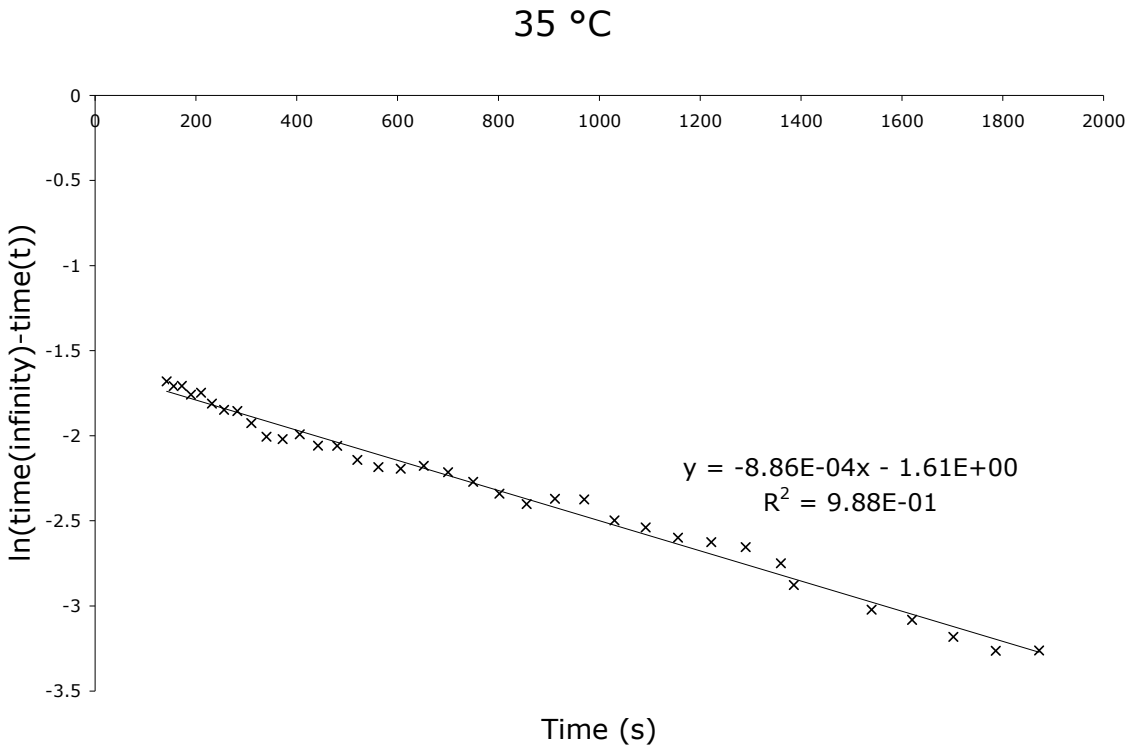
A solution of benzo[*h*]quinoline (**8**) (16 mg, 8.9×10^{-5} mol, 1.0 equiv) and complex **34** (5.0 mg, 5.9×10^{-6} mol, 0.067 equiv) in CD_3CN (0.7 mL) was prepared. A ^{1}H NMR of the solution was obtained at 23 °C. The sample was warmed to 80 °C at which temperature a ^{1}H NMR was obtained. The sample was subsequently cooled to 23 °C at which temperature the ^{1}H NMR was observed again. No change in any signal was observed with changing temperature.

Rate of C–Cl Reductive Elimination from esp-Bridged 35



Solutions (20 mM) of compound **34** and $PhICl_2$ in CD_2Cl_2 were prepared and stored at –30 ˚C. An NMR tube was purged with N_2 and cooled to –45 ˚C. Compound **34** in CD_2Cl_2 (300 μL) and $PhICl_2$ in CD_2Cl_2 (300 μL) were combined. ^{1}H NMR spectra were obtained; the evolution of **2** was monitored by the ^{1}H NMR signal at 9.12 ppm. These signals were integrated relative the residual proton signal from CD_2Cl_2. These ratios were converted to concentrations based on the integration of a 20 mM solution of **2** in

CD_2Cl_2. Since evolution of product was measured, linear natural log plots were obtained by using an infinite time point set to 100% yield (20 mM in **2**). The reactions was followed to greater than 3 half-lives. Data were fitted to a first order regression; plot, slope, and R^2 value are reported below.



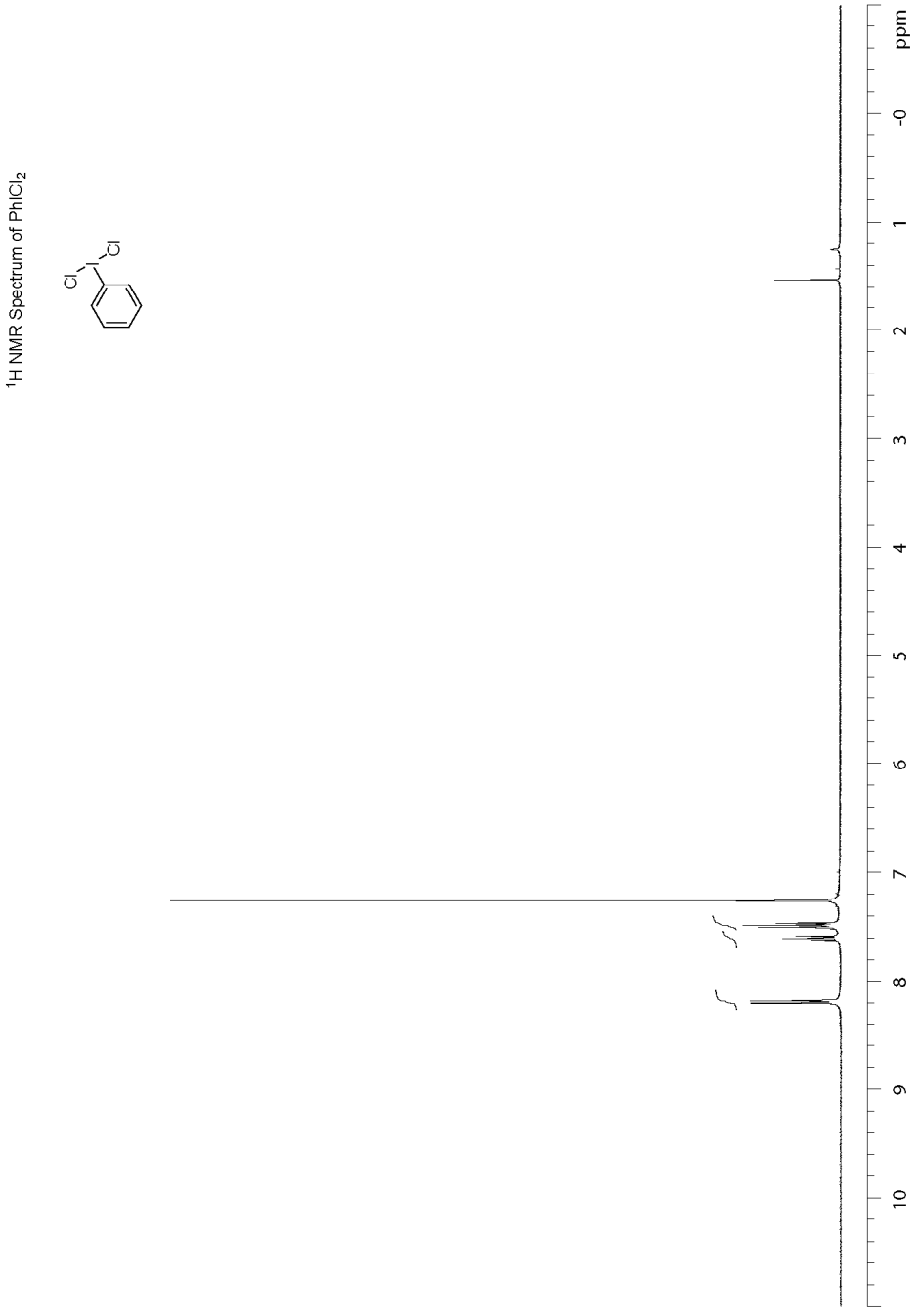
Comparison of the rate constant for C–Cl reductive elimination from **1** ($k = 1.33 \times 10^{-2}$ s^{-1}) and **35** ($k = 8.33\times 10^{-2}$ s^{-1}) shows that reductive elimination from **1** proceeds 16 times faster than from **35**. This is consistent with our Hammett analysis of the bridging carboxylate ligands, which revealed that electron-deficient carboxylate bridged complexes undergo reductive elimination more rapidly than electron-rich carboxylates. The relative rates may also be a reflection of differing ligand rigidities of bridging acetate and bridging esp ligands.

References

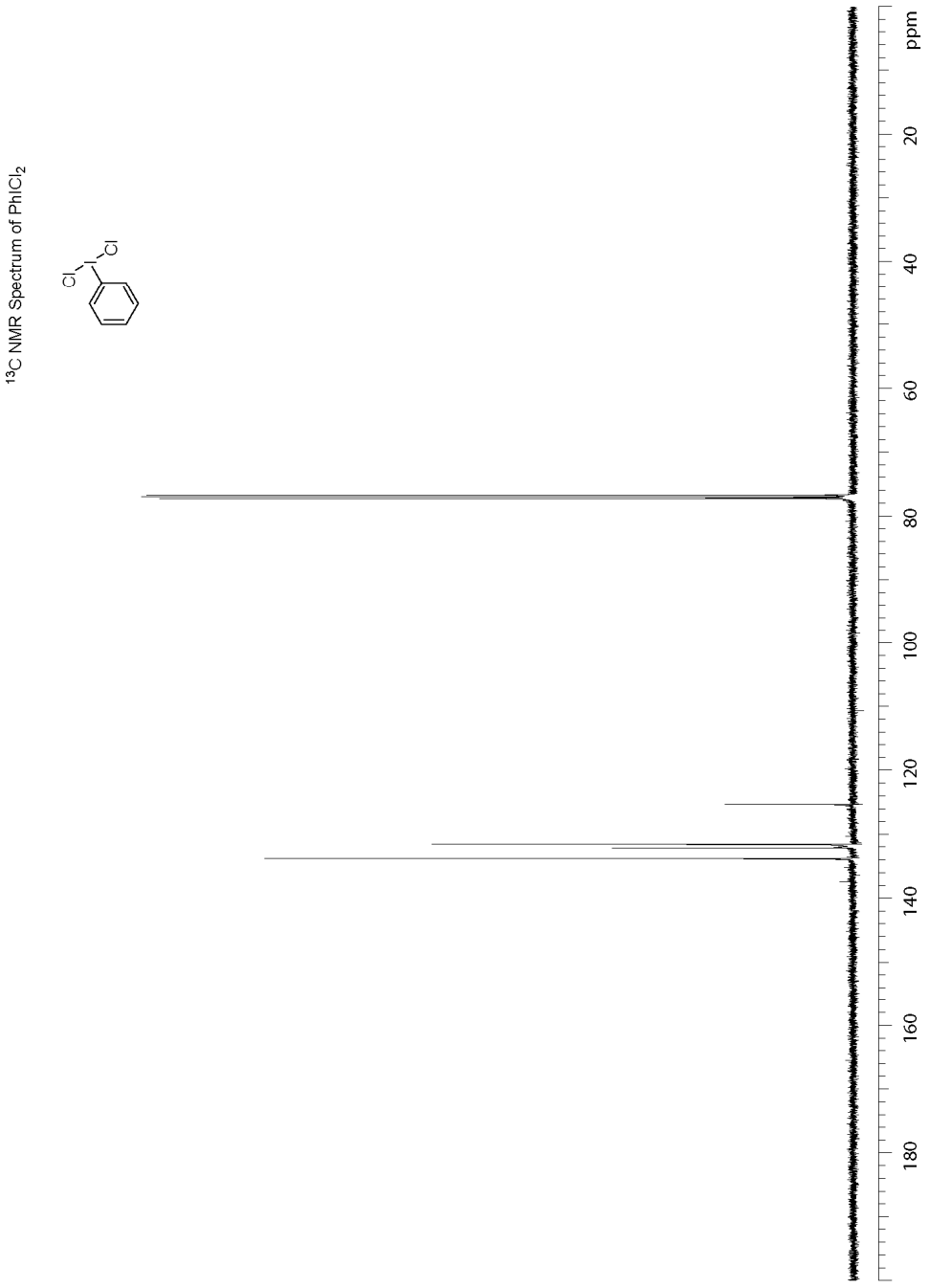
(1) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.
(2) Taylor, R. T.; Stevenson, T. A. *Tetrahedron Lett.* **1988**, *29*, 2033–2036.
(3) Dick, A. R.; Hull, K. L.; Sanford, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 2300–2301.
(4) Rotzoll, S.; Ullah, E.; Görls, H.; Fischer, C.; Langer, P. *Tetrahedron* **2007**, *63*, 2647–2656.
(5) Rajput, J.; Moss, J. R.; Hutton, A. T.; Hendricks, D. T.; Arendse, C. E.; Imrie, C. *J. Organomet. Chem.* **2004**, *689*, 1553–1568.
(6) Zhang, Y. H.; Shi, B. F.; Yu, J. Q. *J. Am. Chem. Soc.* **2009**, *131*, 5072–5074.
(7) Hartwell, G. E.; Lawrence, R. V.; Smas, M. J. *J. Chem. Soc. Chem. Comm.* **1970**, 912.
(8) Cockburn, B. N.; Howe, D. V.; Keating, T.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc. Dalton* **1973**, 404–410.
(9) Barltrop, J. A.; Macphee, K. E. *J. Chem. Soc.* **1952**, 638–642.
(10) Furuya, T.; Benitez, D.; Tkatchouk, E.; Strom, A. E.; Tang, P.; Goddard, W. A., III; Ritter, T. *J. Am. Chem. Soc.* **2010**, *132*, 3793–3807.

(11) Constable, E. C.; Thompson, A.; Leese, T. A.; Reese, D. G. F.; Tocher, D. A. *Inorg. Chim. Acta* **1991**, *182*, 93–100.
(12) Dick, A. R.; Kampf, J. W.; Sanford, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 12790–12791.
(13) Yu, W. Y.; Sit, W. N.; Zhou, Z. Y.; Chan, A. S. C. *Org. Lett.* **2009**, *11*, 3174–3177.
(14) Staab, H. A.; Rohr, W.; Graf, F. *Chem. Ber.* **1965**, *98*, 1122–1127.
(15) Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157–167.
(16) Jaguar 7.6, Schrodinger, LLC, New York, NY (2006).
(17) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299–310.
(18) Martin, J. M. L.; Sundermann, A. *J. Chem. Phys.* **2001**, *114*, 3408–3420.
(19) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650–654.
(20) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265–3269.
(21) Tannor, D. J.; Marten, B.; Murphy, R.; Friesner, R. A.; Sitkoff, D.; Nicholls, A.; Ringnalda, M.; Goddard, W. A., III; Honig, B. *J. Am. Chem. Soc.* **1994**, *116*, 11875–11882.
(22) Weinhold, F.; Landis, C. R. *Valency and Bonding: A Natural Bond Orbital Donor-Acceptor Perspective*; Cambridge University Press, 2005.
(23) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899–926.
(24) *NBO 5.0.* Glendening, E. D.; Badenhoop, J, K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F.; Theoretical Chemistry Institute, University of Wisconsin, Madison (2001).
(25) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441–451.
(26) Fukazawa, Y.; Usui, S.; Tanimoto, K.; Hirai, Y. *J. Am. Chem. Soc.* **1994**, *116*, 8169–8175.
(27) Espino, C. G.; Fiori, K. W.; Kim, M.; Du Bois, J. *J. Am. Chem. Soc.* **2004**, *126*, 15378–15379.

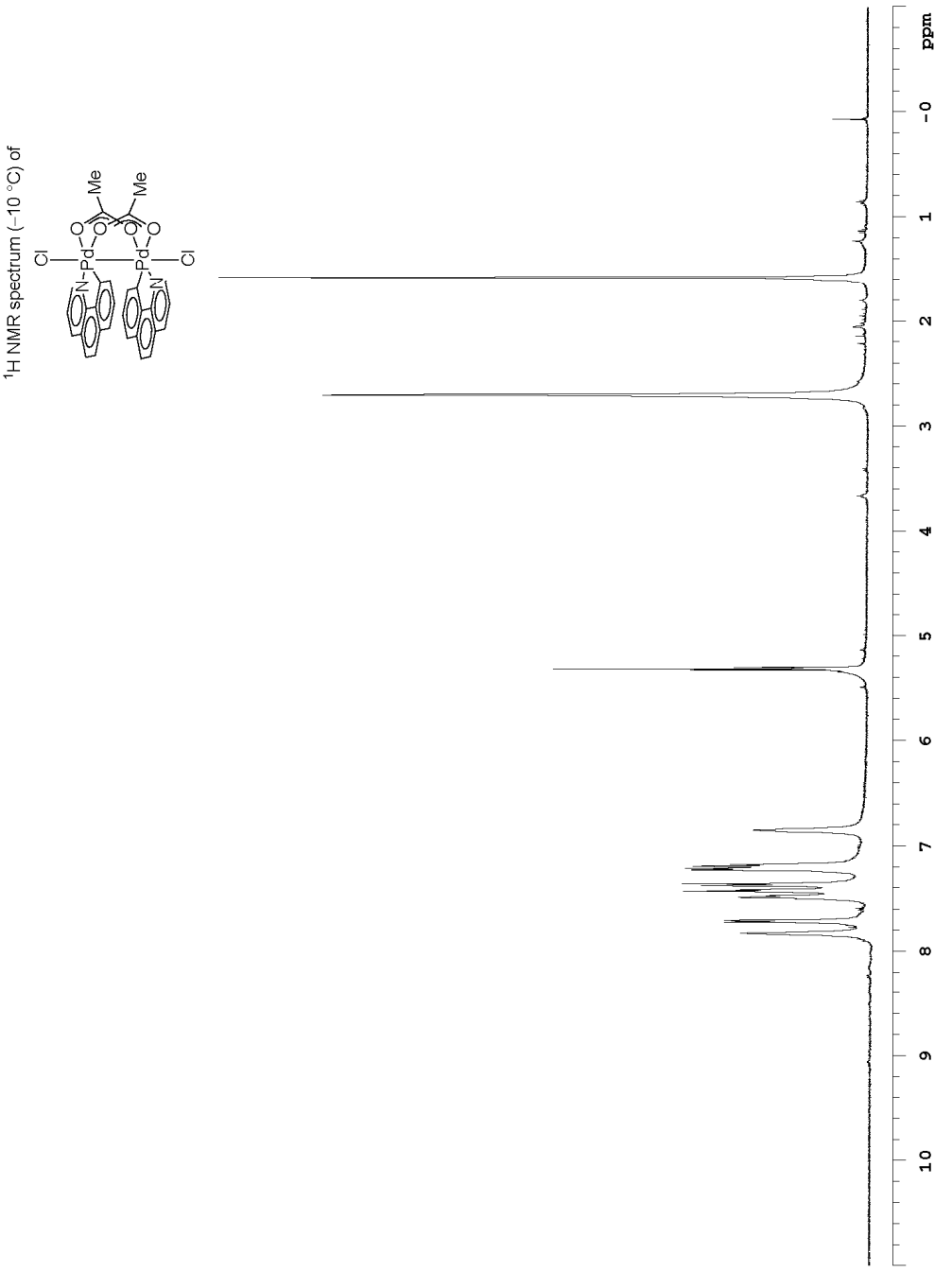
Appendix A: NMR Data



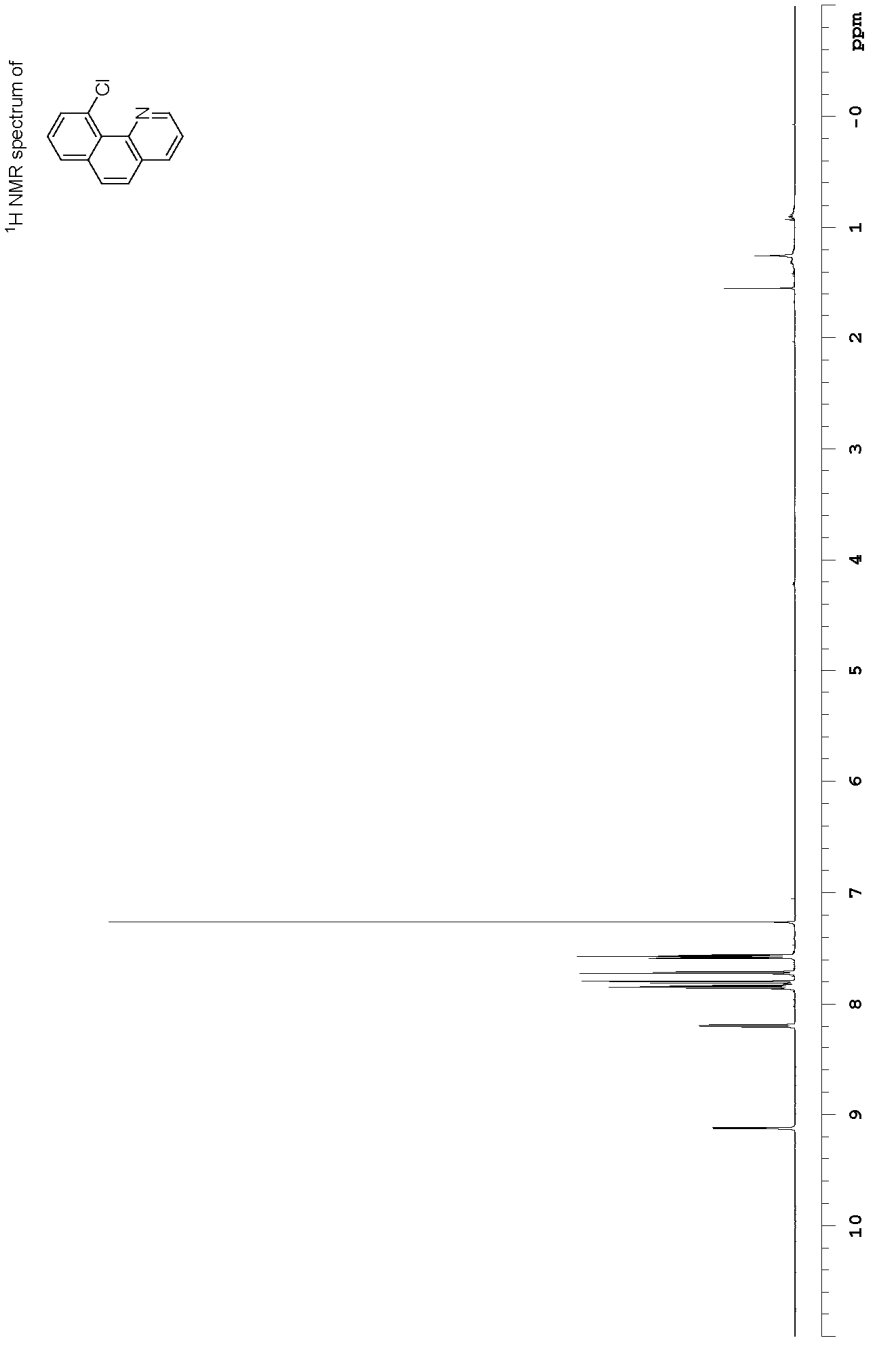
^{1}H NMR spectrum of $PhICl_2$ in $CDCl_3$ at 23 °C.



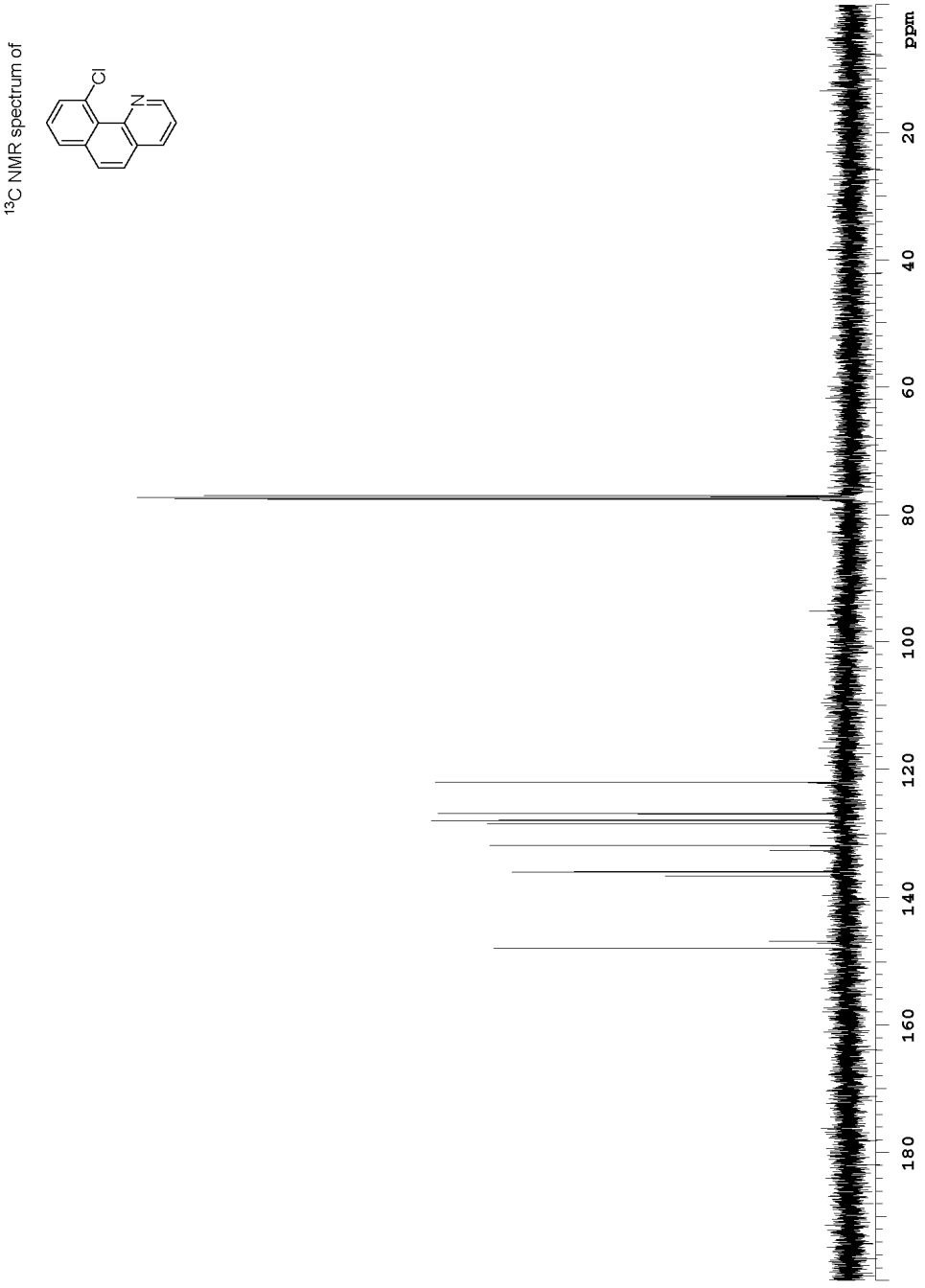
^{13}C NMR spectrum of $PhICl_2$ in $CDCl_3$ at 23 °C.



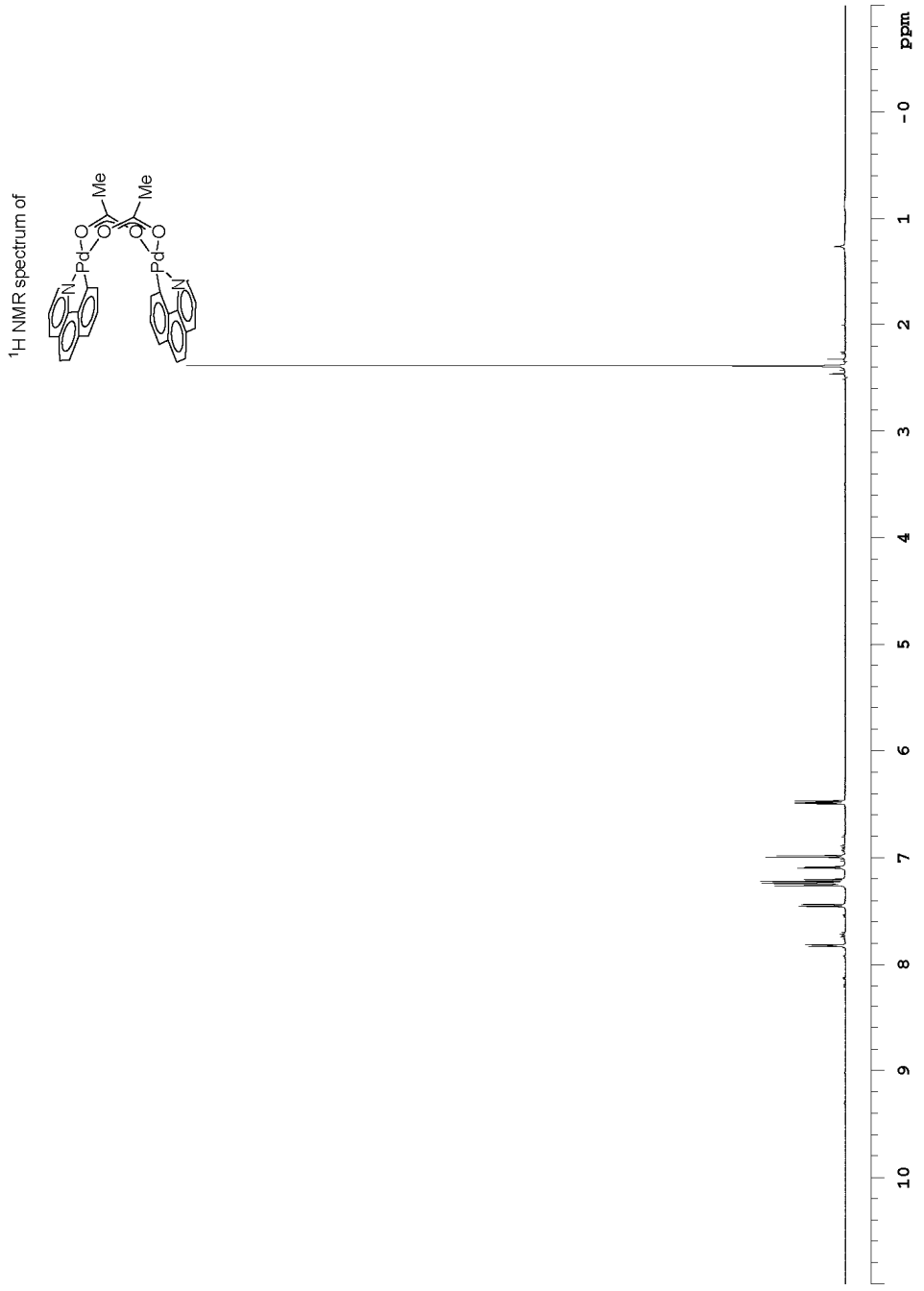
^{1}H NMR spectrum of **1** in CD_2Cl_2 at –10 °C.



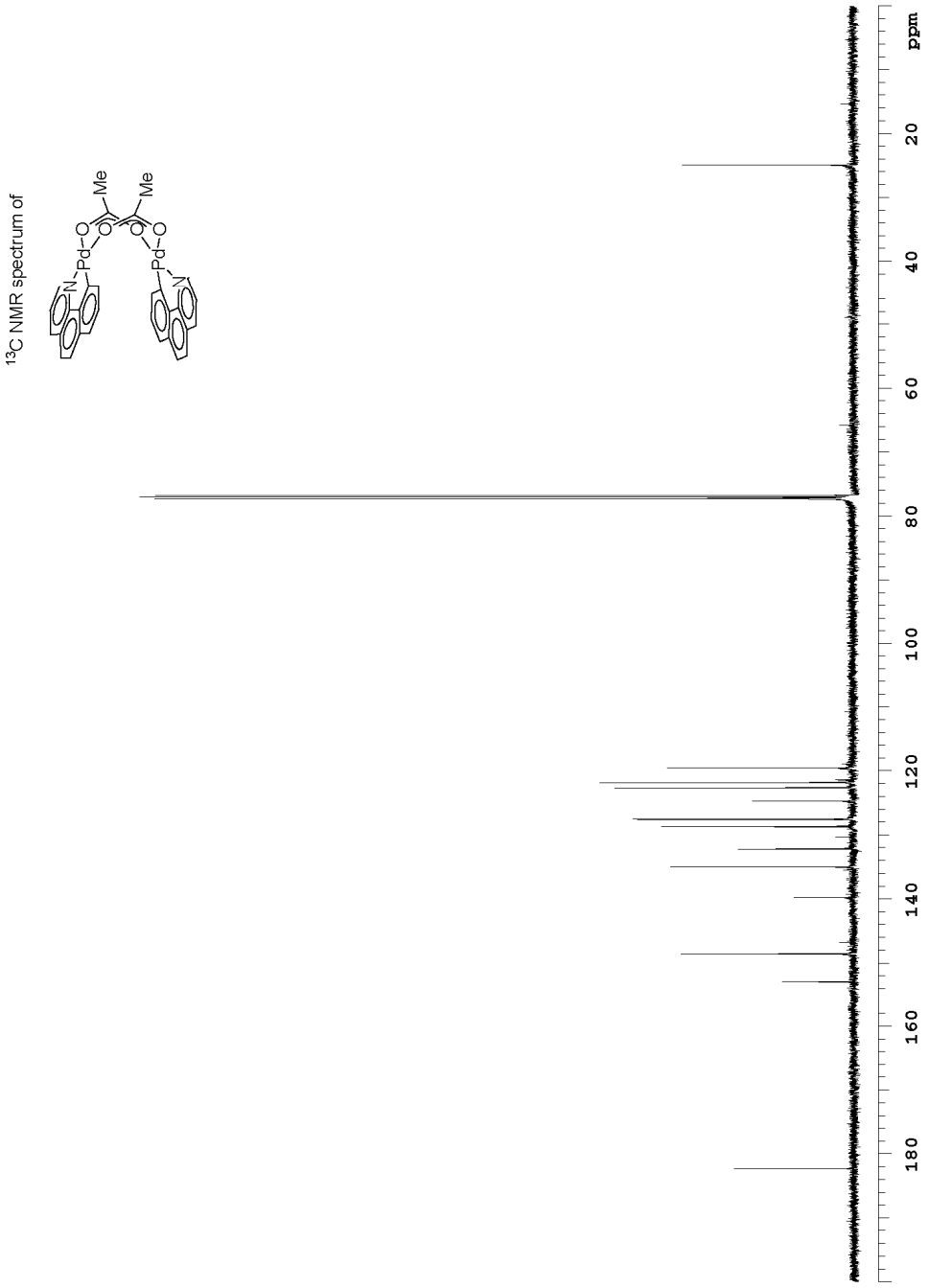
^{1}H NMR spectrum of **2** in $CDCl_3$ at 23 °C.



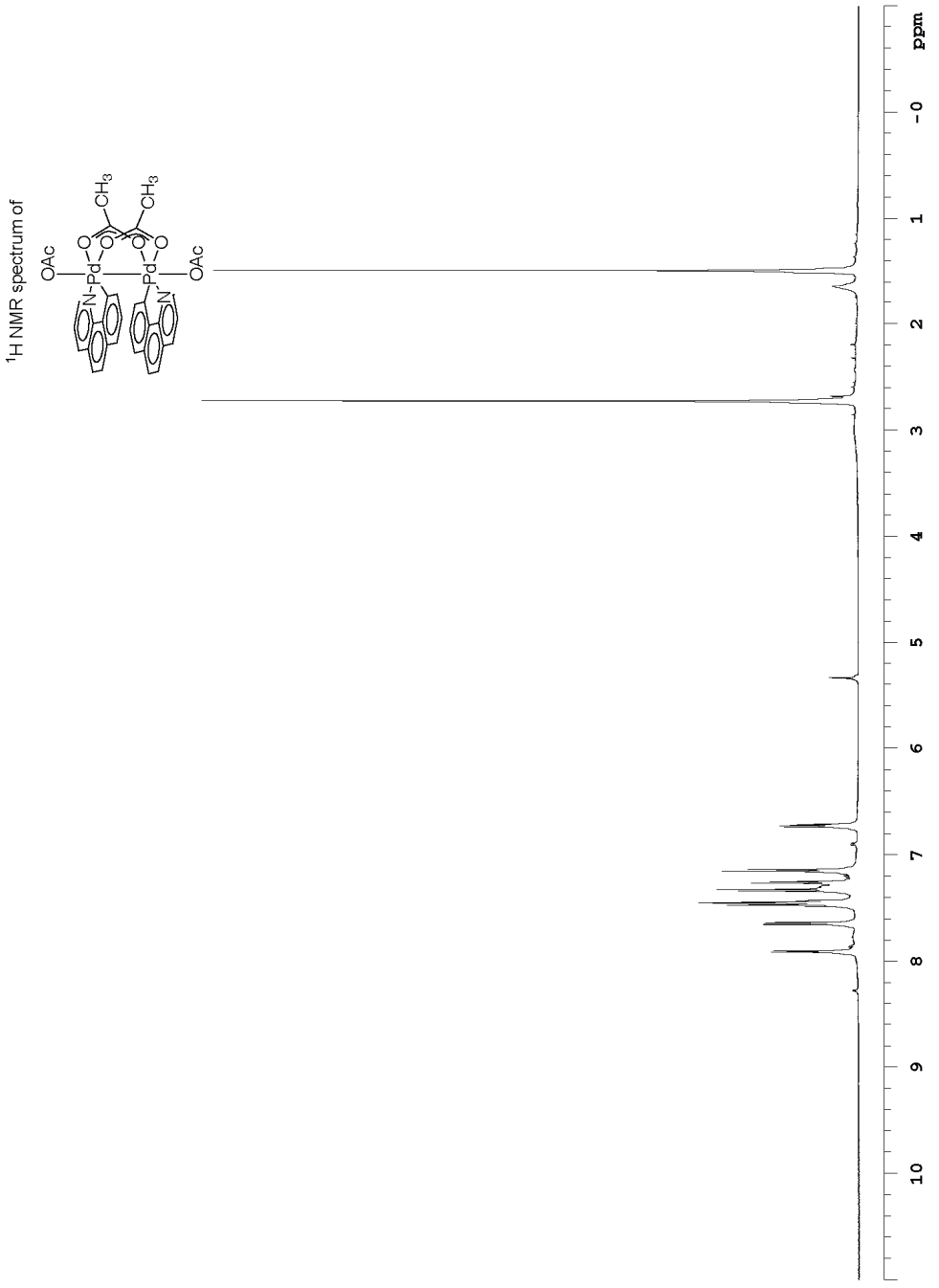
^{13}C NMR spectrum of **2** in $CDCl_3$ at 23 °C.



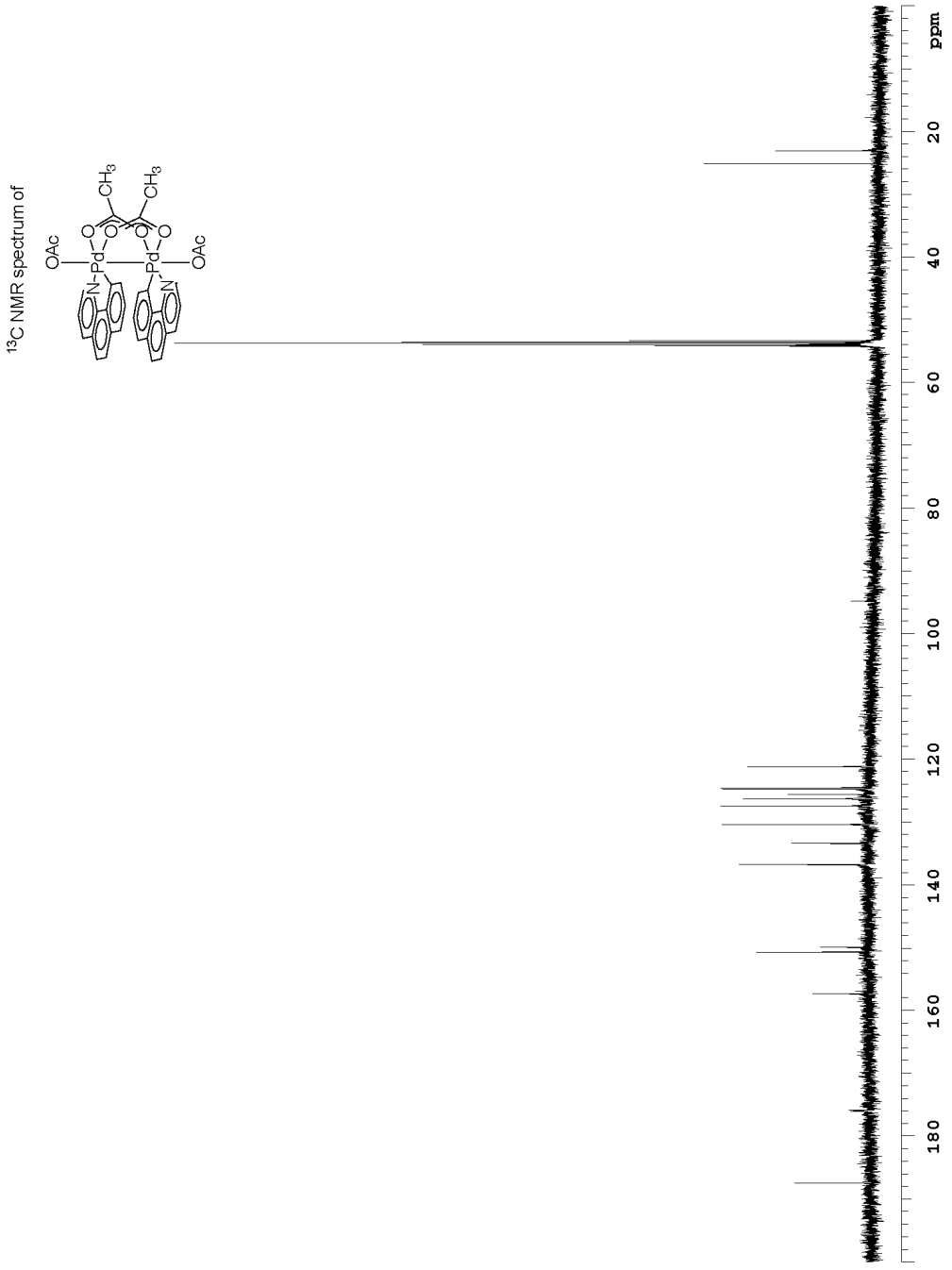
^{1}H NMR spectrum of **9** in $CDCl_3$ at 23 °C.



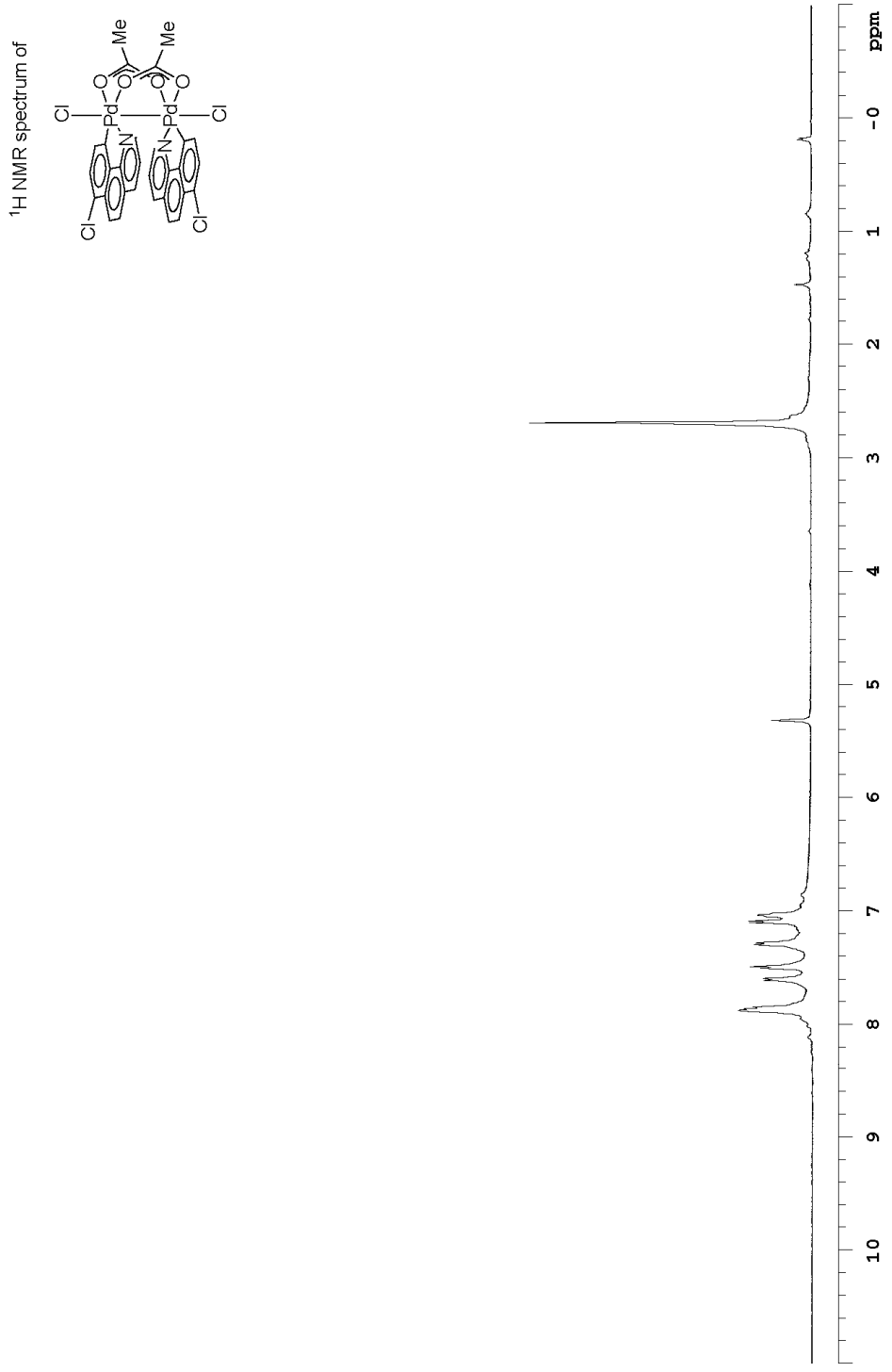
^{13}C NMR spectrum of **9** in $CDCl_3$ at 23 °C.



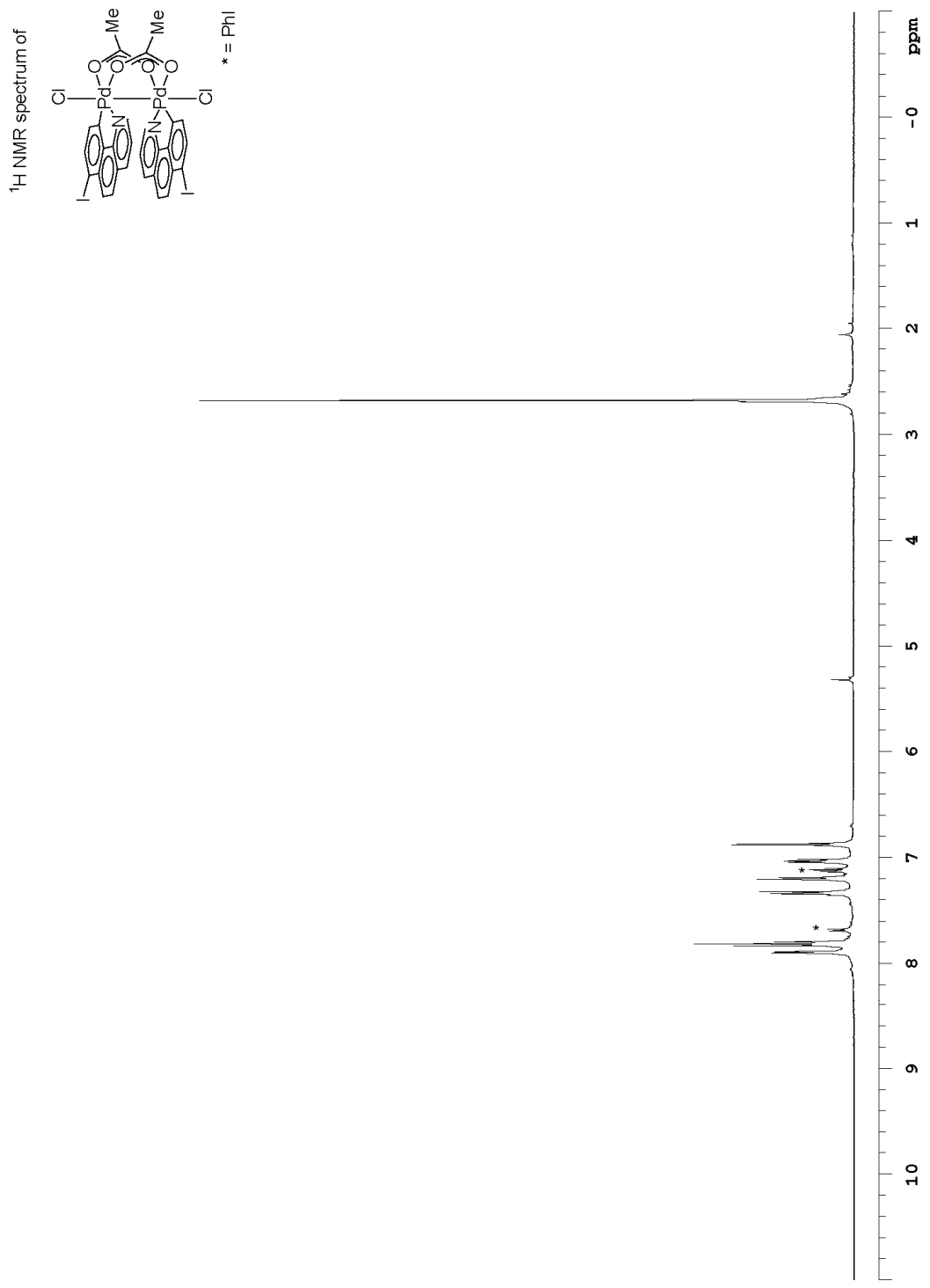
^{1}H NMR spectrum of **10** in CD_2Cl_2 at –30 °C.



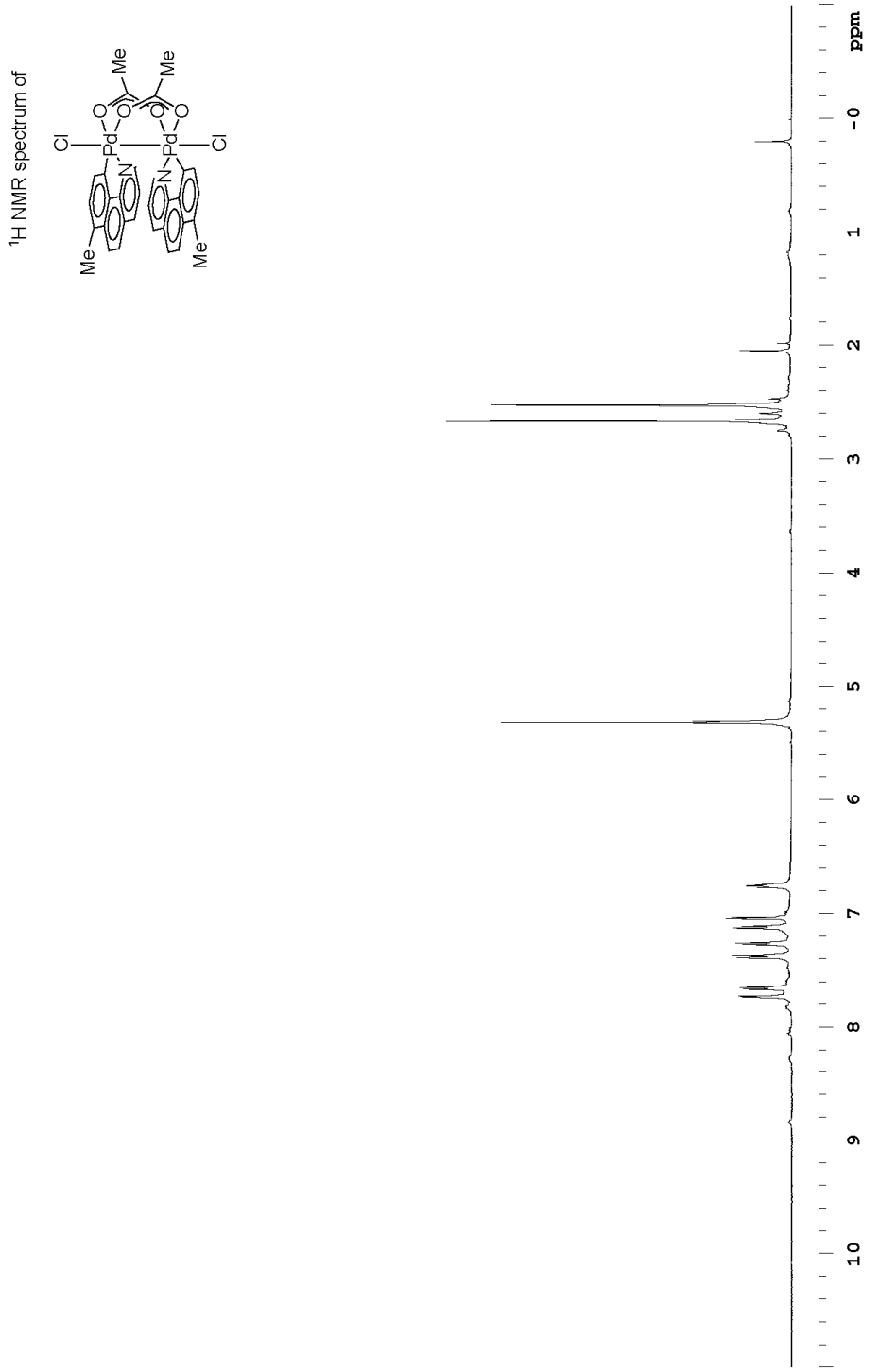
^{13}C NMR spectrum of **10** in CD_2Cl_2 at –30 °C.



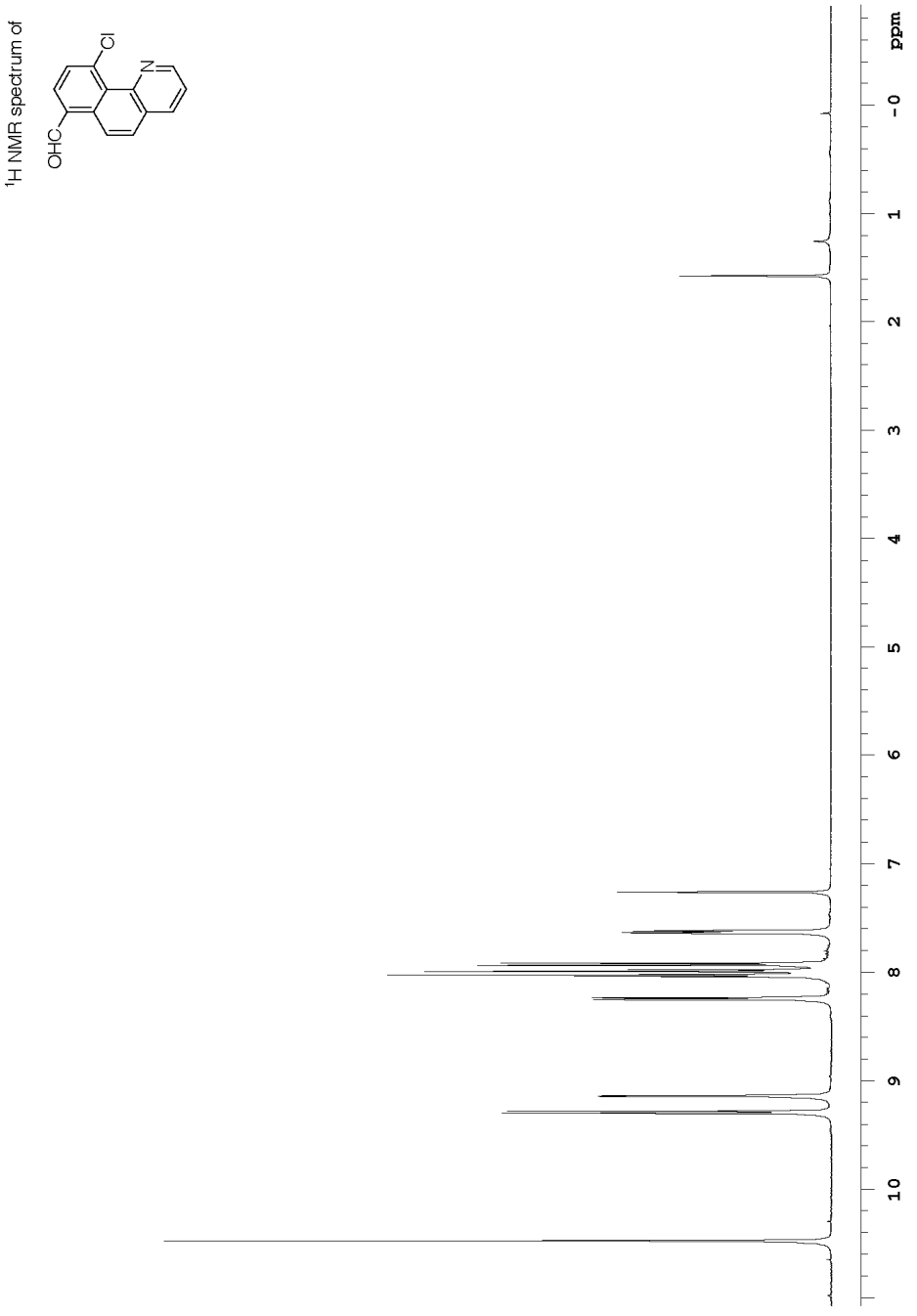
^{1}H NMR spectrum of **18c** in CD_2Cl_2 at –50 °C.



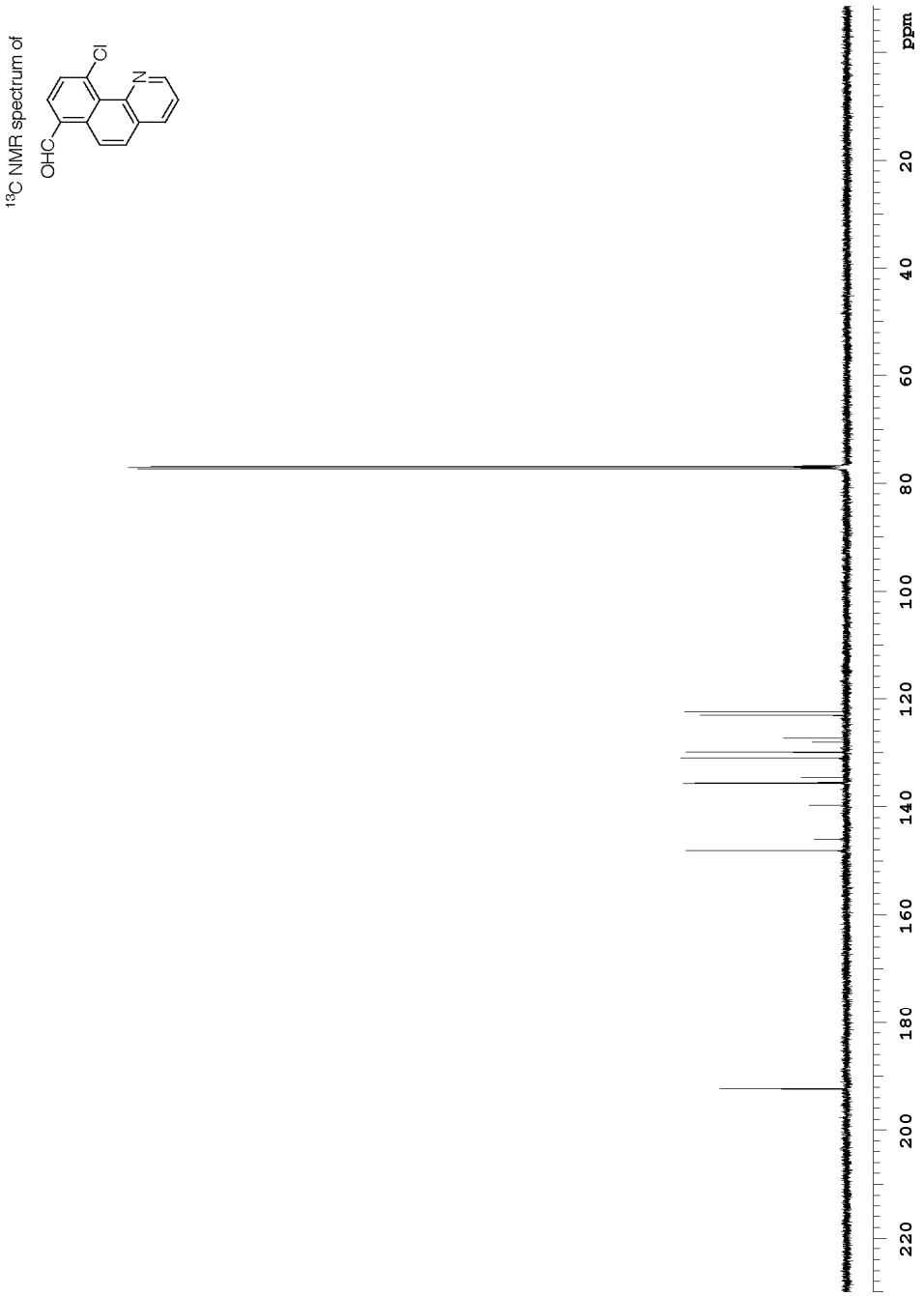
^{1}H NMR spectrum of **18d** in CD_2Cl_2 at –50 °C.



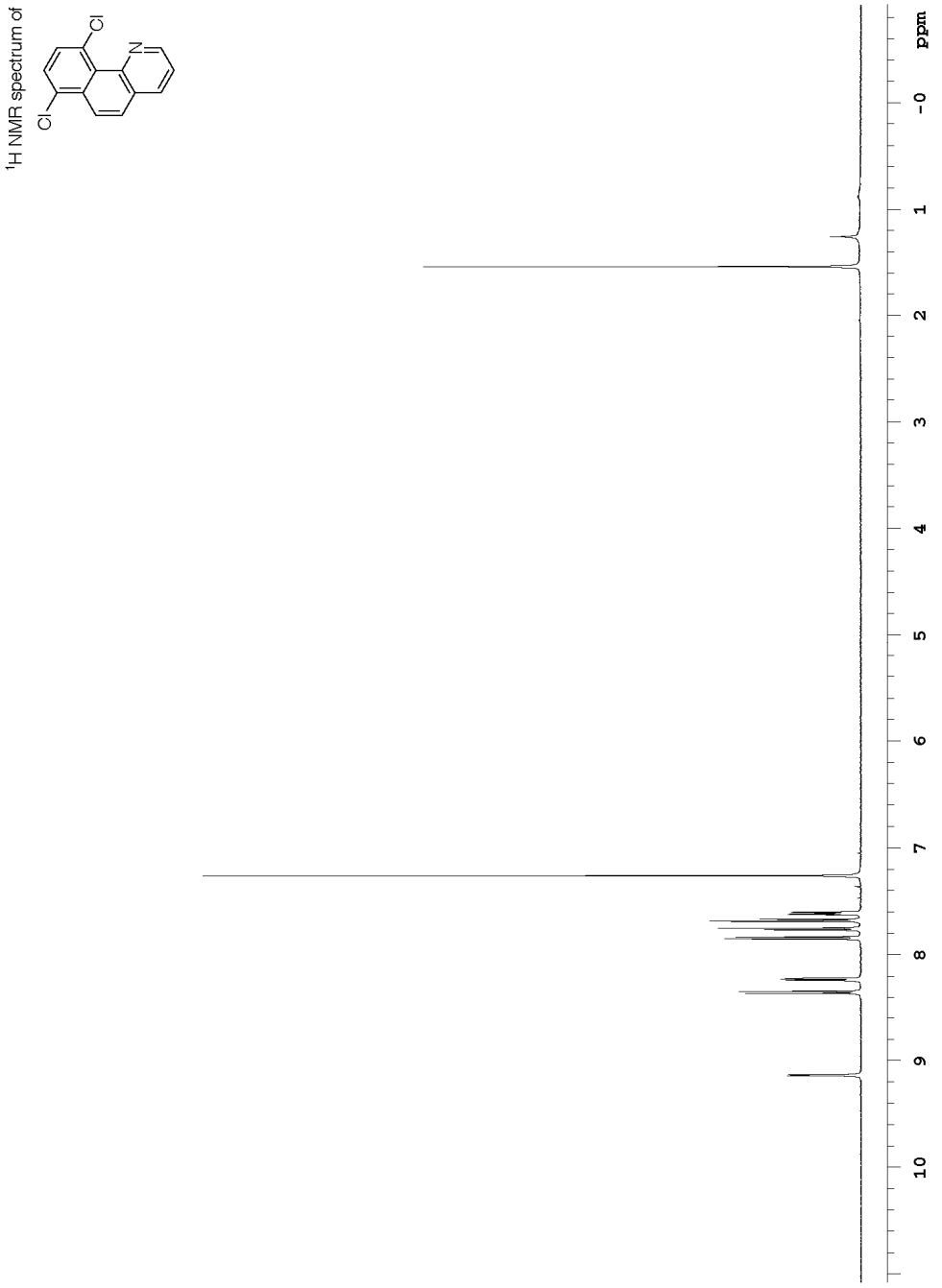
^{1}H NMR spectrum of **18e** in CD_2Cl_2 at –50 °C.



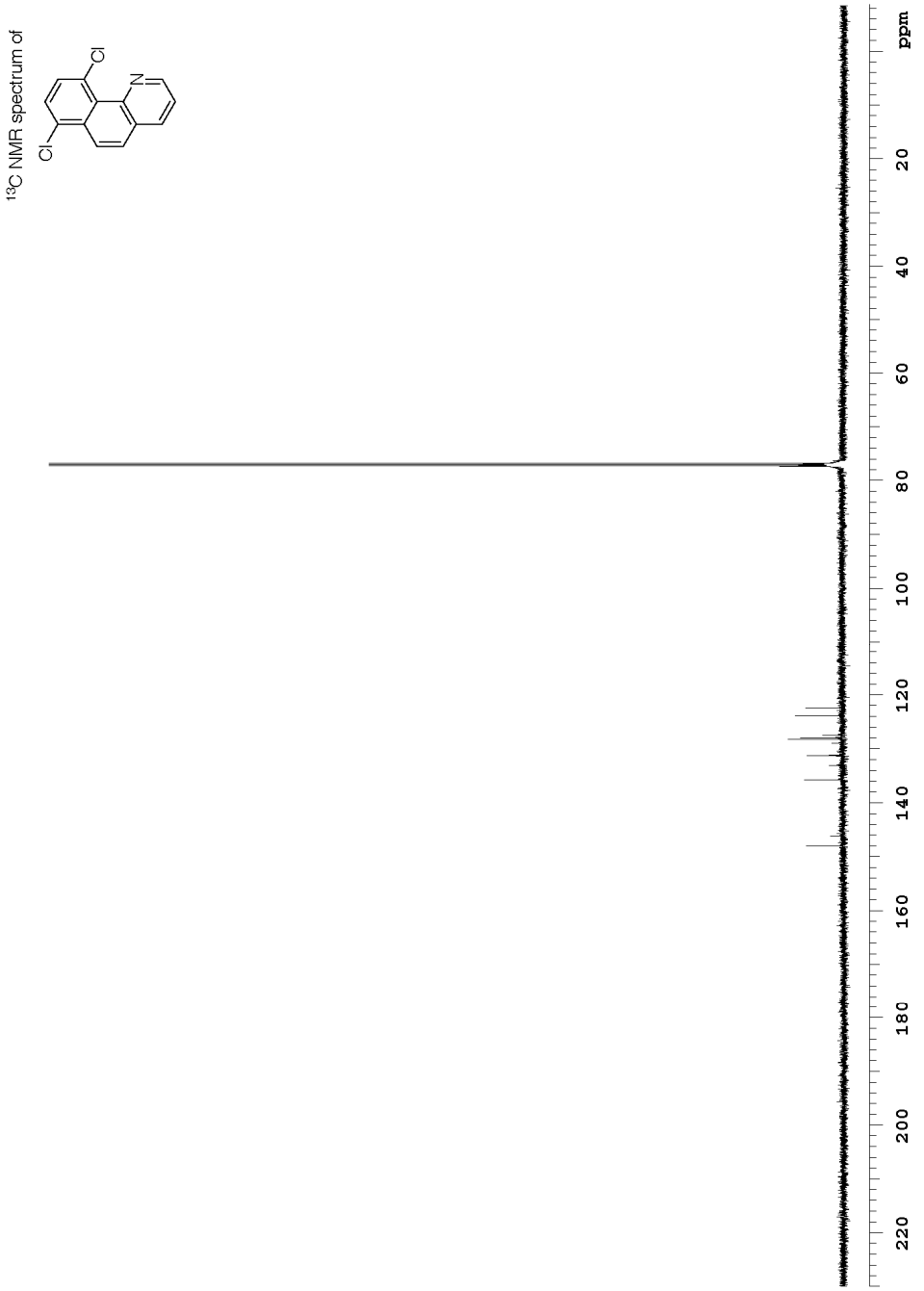
^{1}H NMR spectrum of **19b** in $CDCl_3$ at 23 °C.



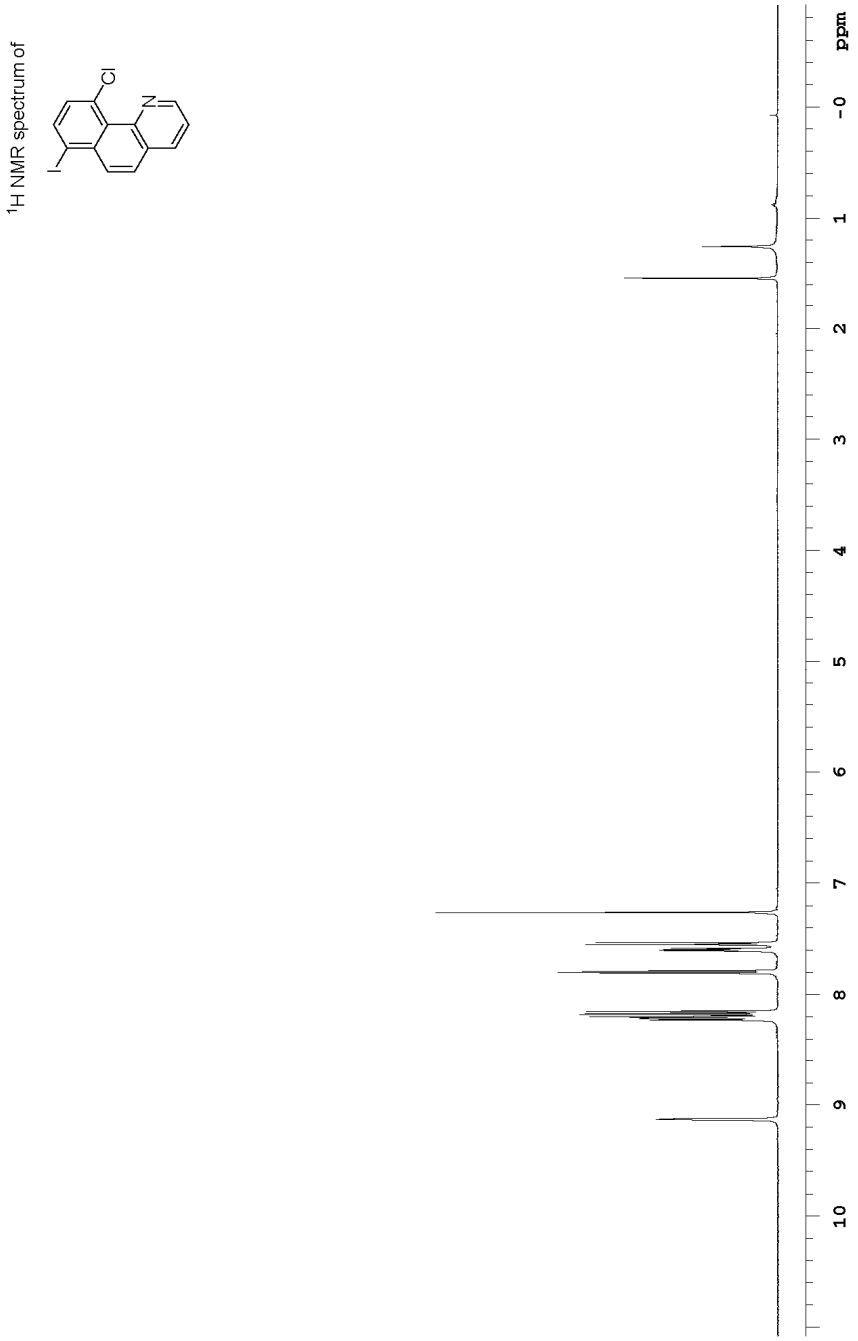
^{13}C NMR spectrum of **19b** in $CDCl_3$ at 23 °C.



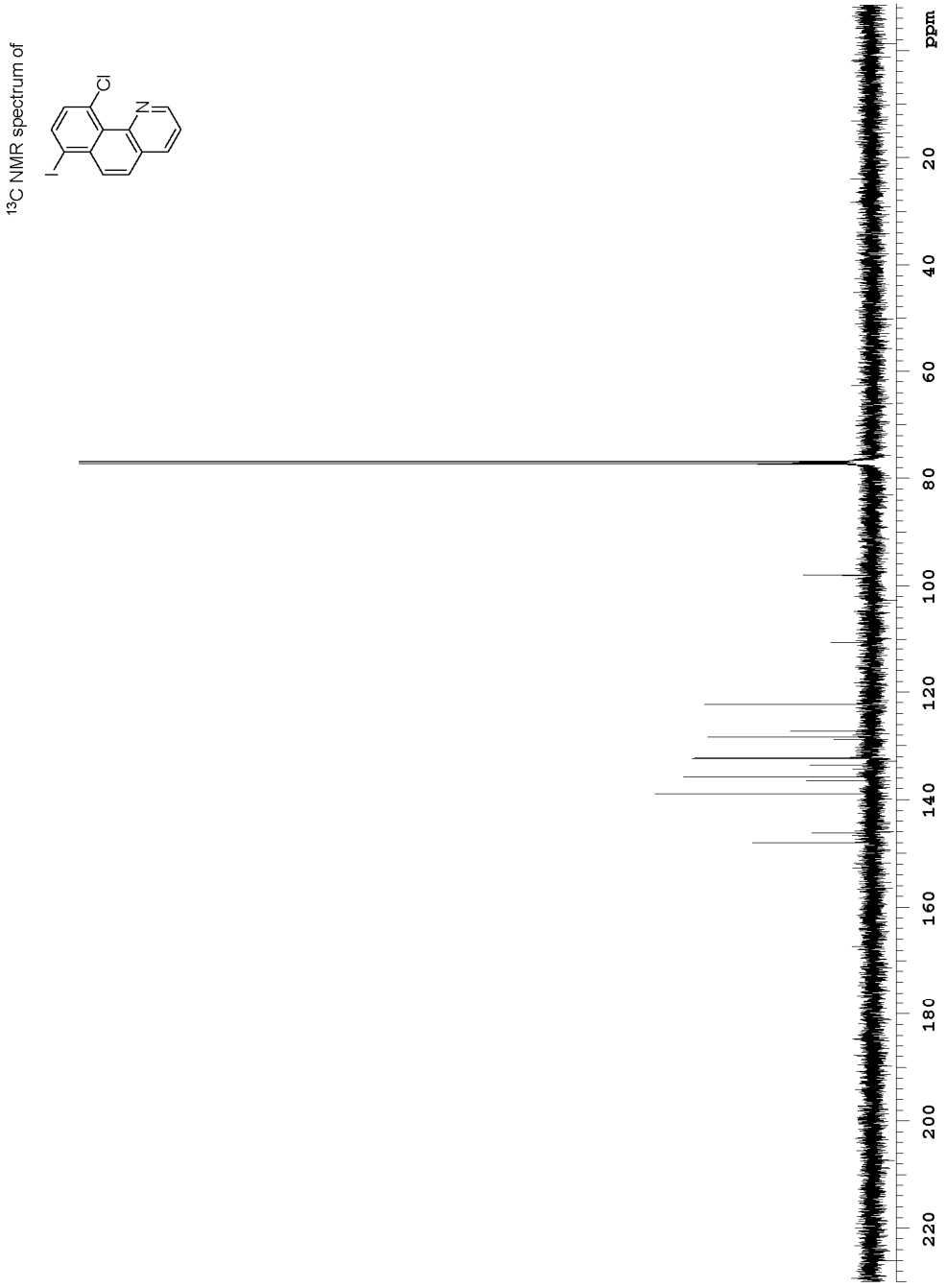
^{1}H NMR spectrum of **19c** in $CDCl_3$ at 23 °C.



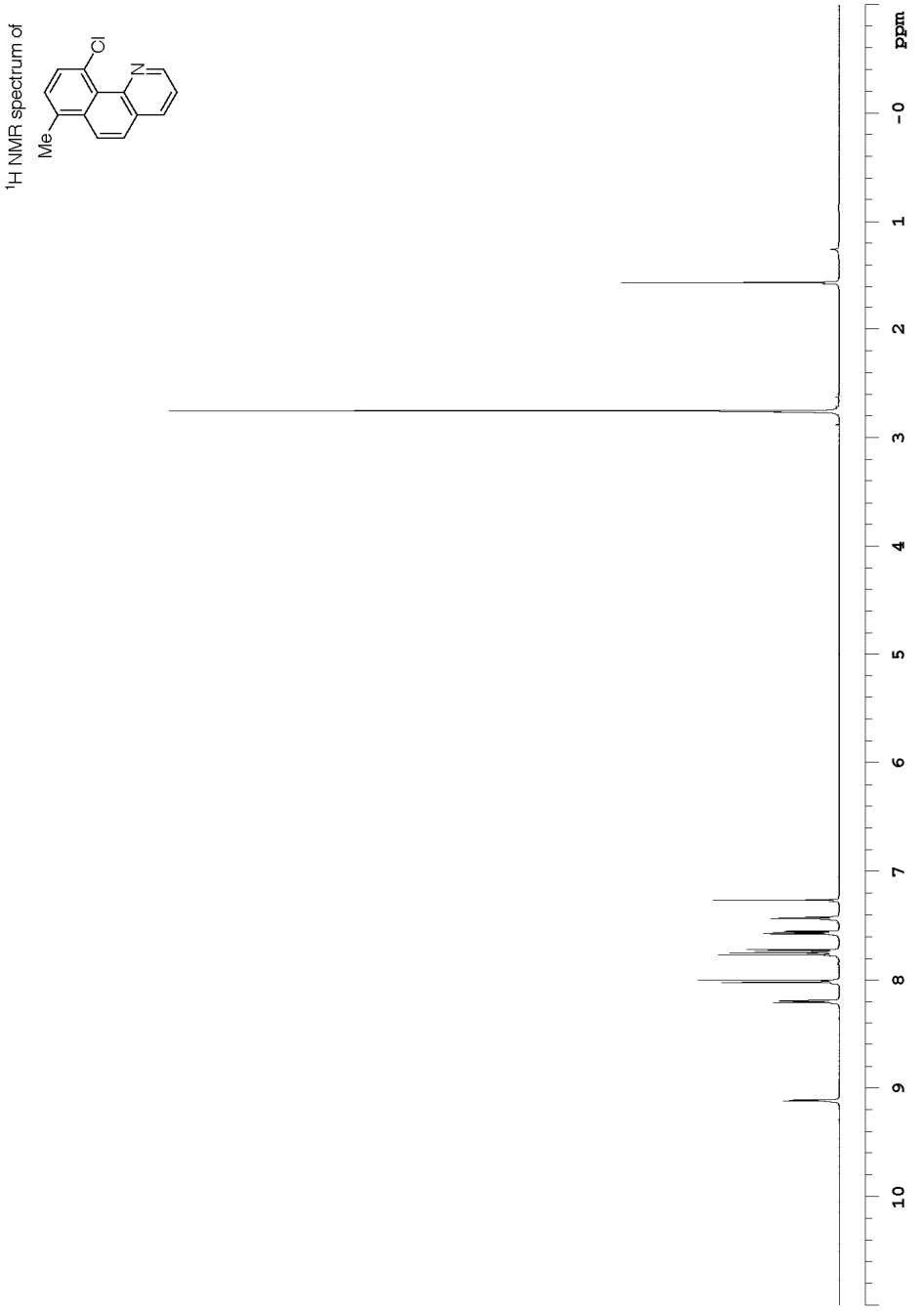
^{13}C NMR spectrum of **19c** in $CDCl_3$ at 23 °C.



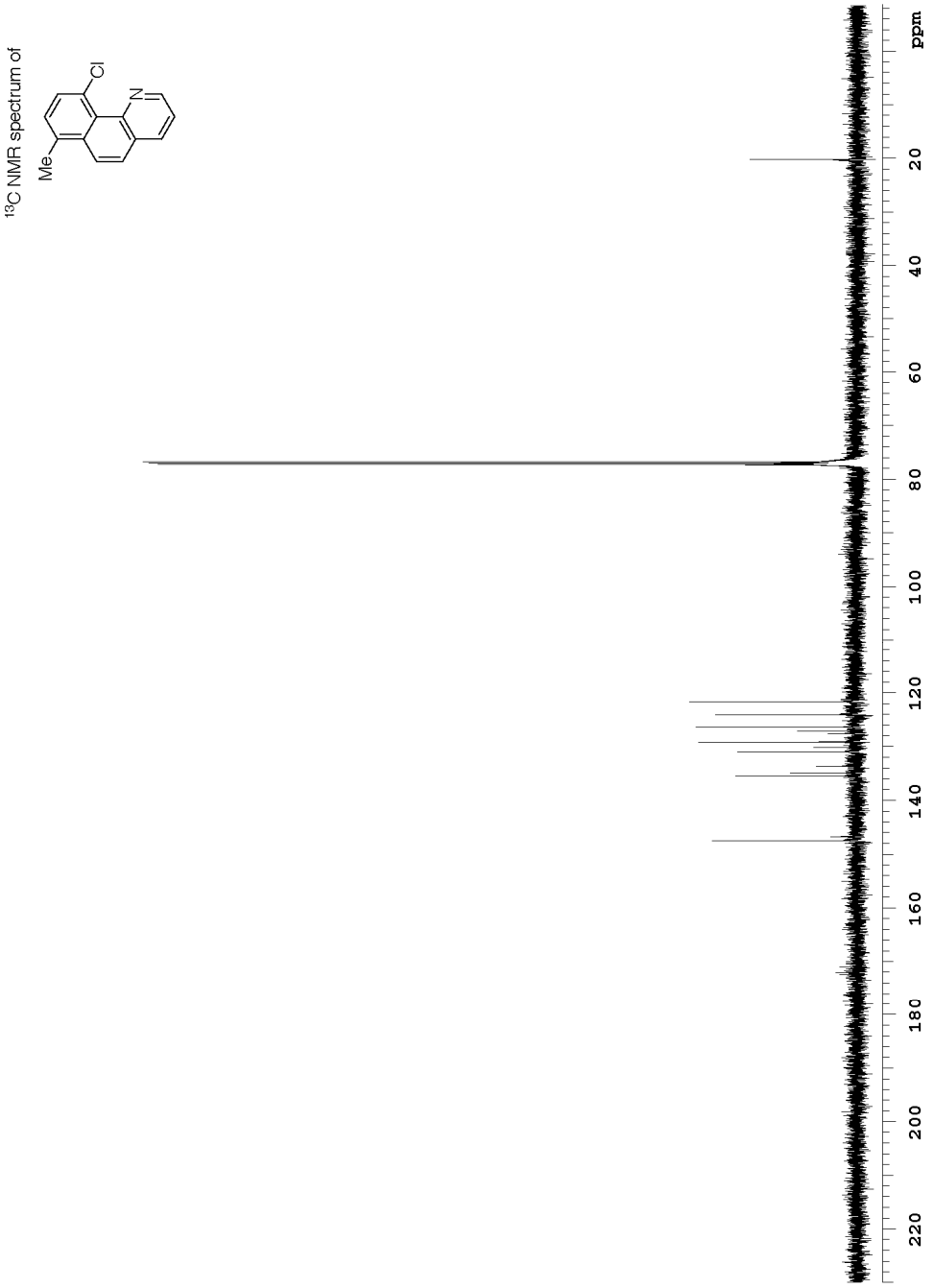
^{1}H NMR spectrum of **19d** in $CDCl_3$ at 23 °C.



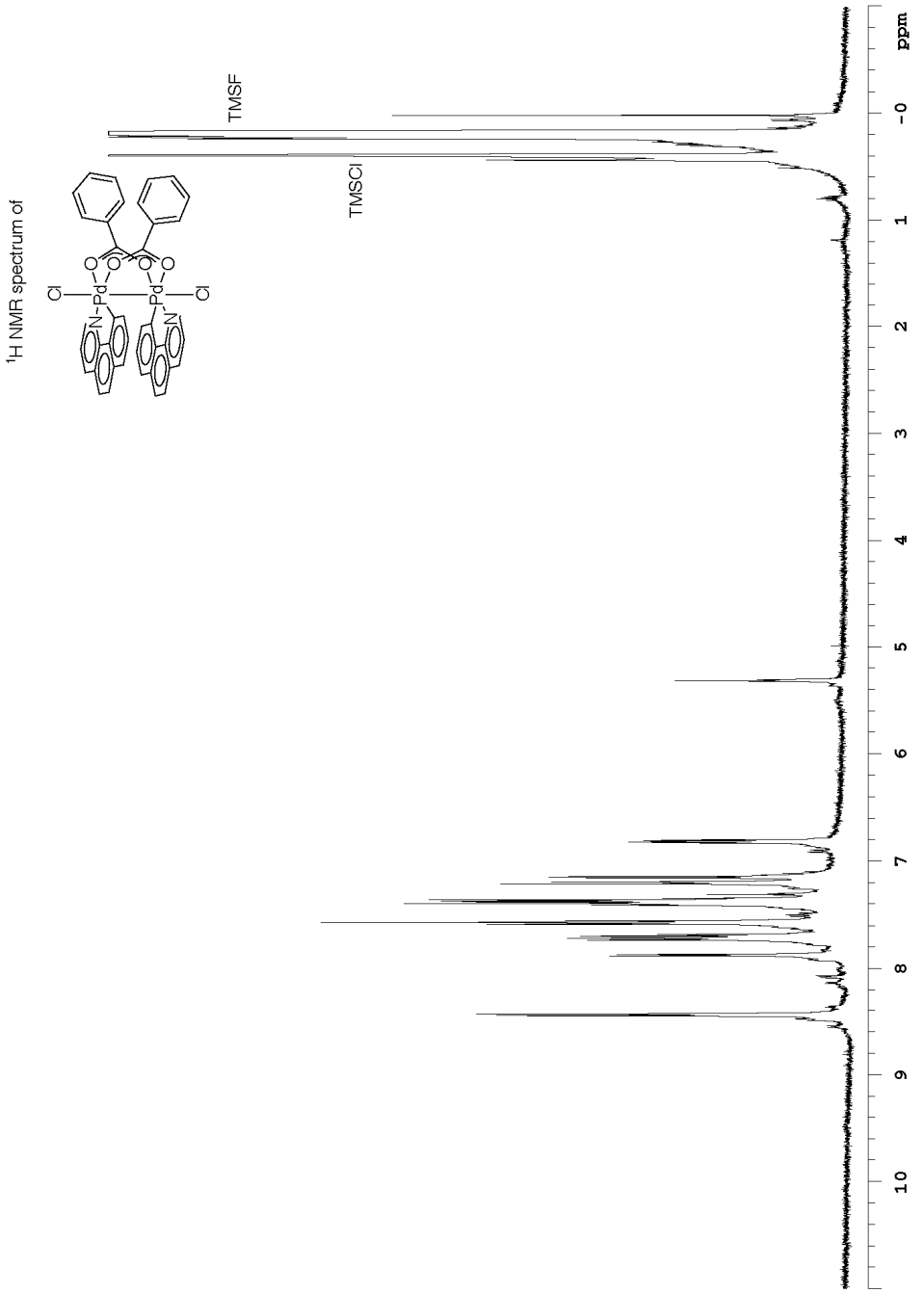
^{13}C NMR spectrum of **19d** in $CDCl_3$ at 23 °C.



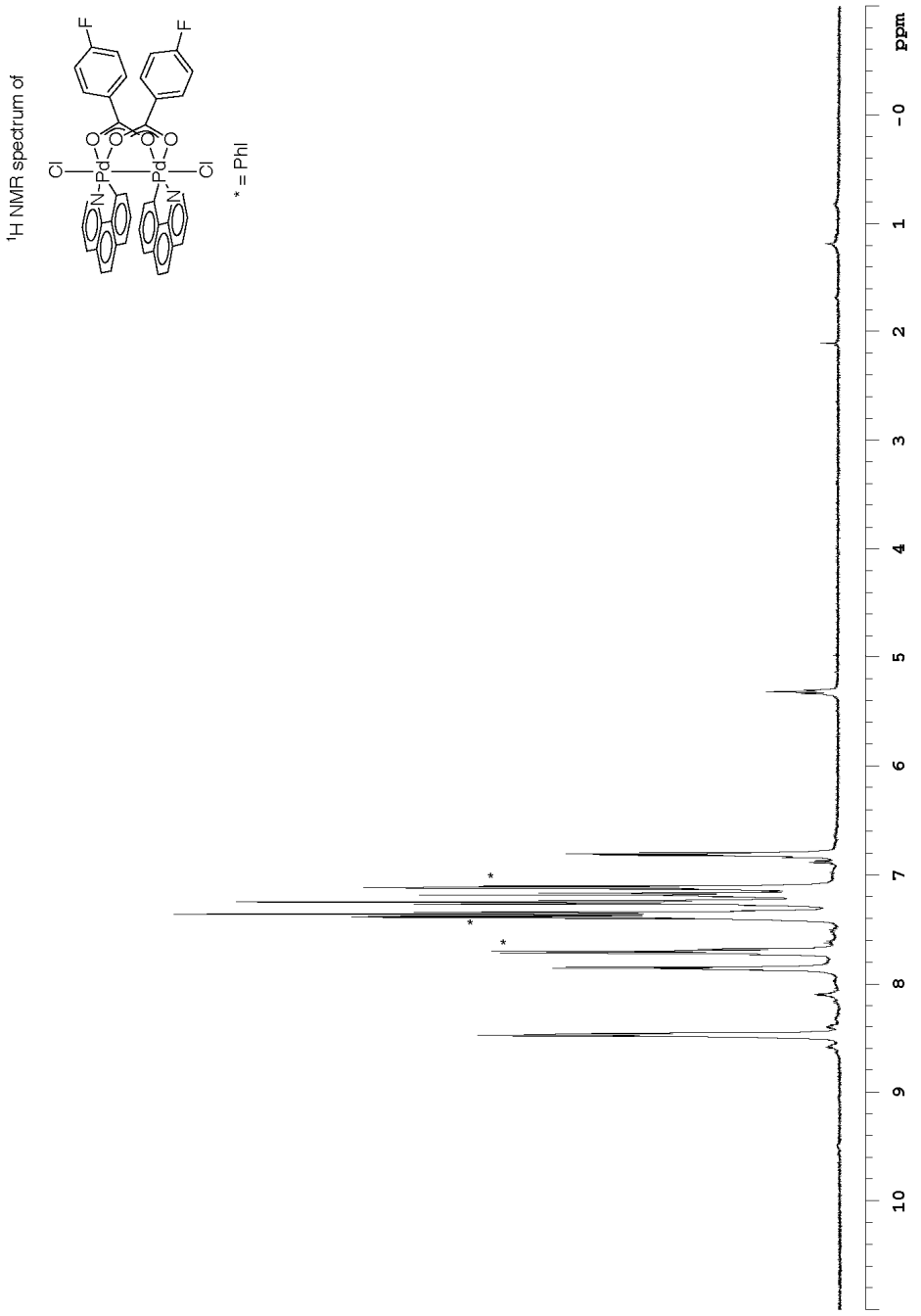
^{1}H NMR spectrum of **19e** in $CDCl_3$ at 23 °C.



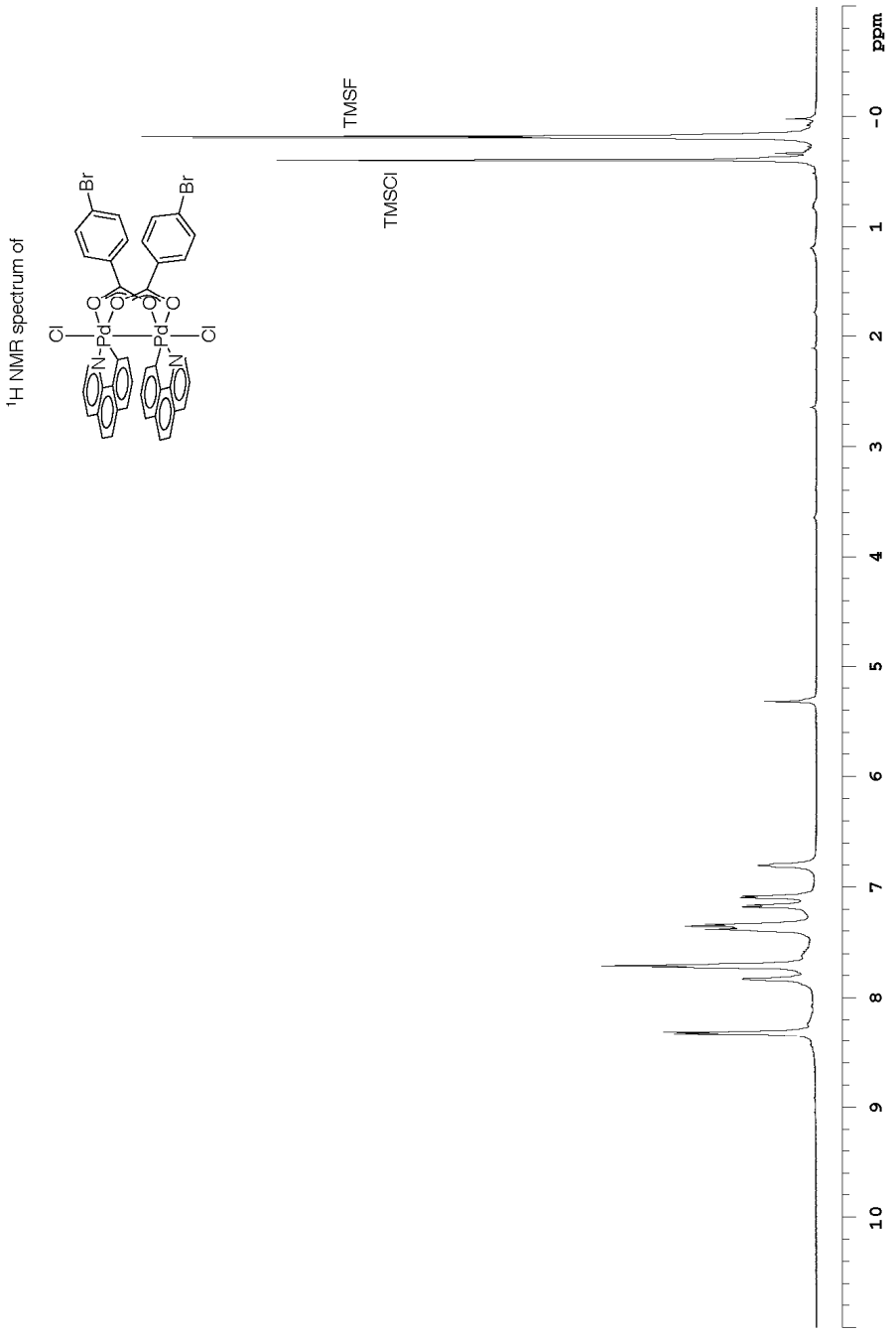
^{13}C NMR spectrum of **19e** in $CDCl_3$ at 23 °C.



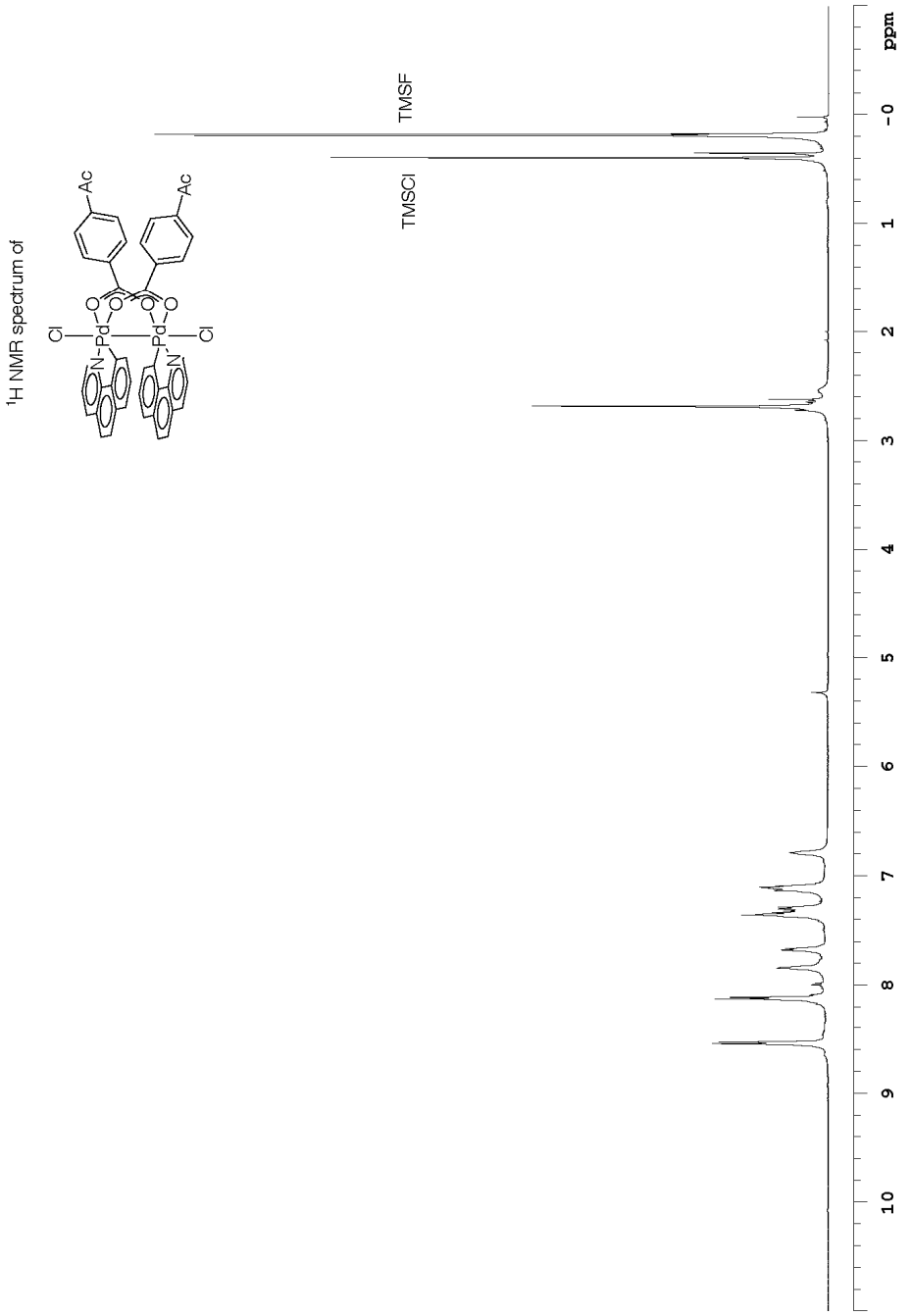
^{1}H NMR spectrum of **20a** in CD_2Cl_2 at –50 °C.



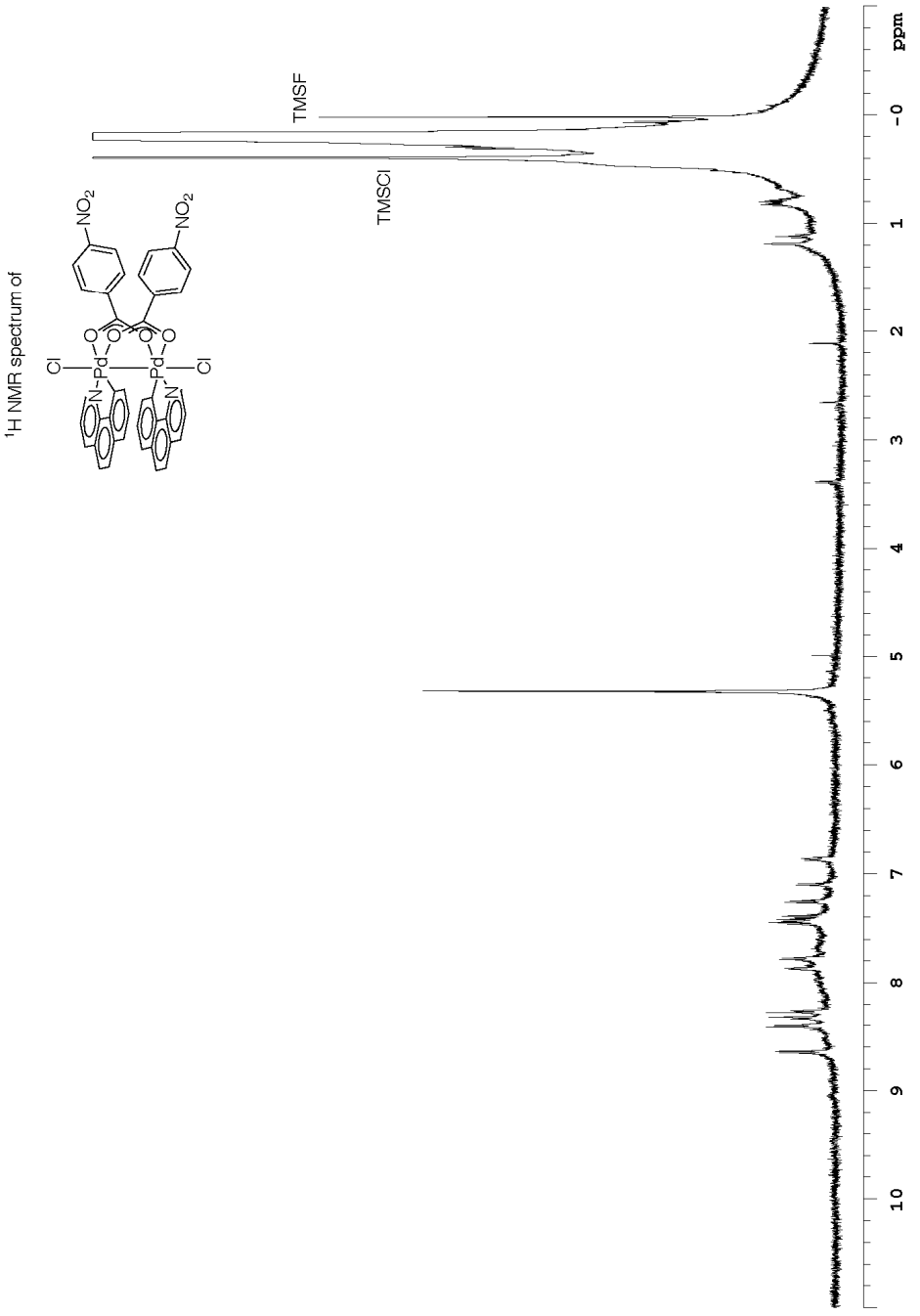
^{1}H NMR spectrum of **20b** in CD_2Cl_2 at –50 °C.



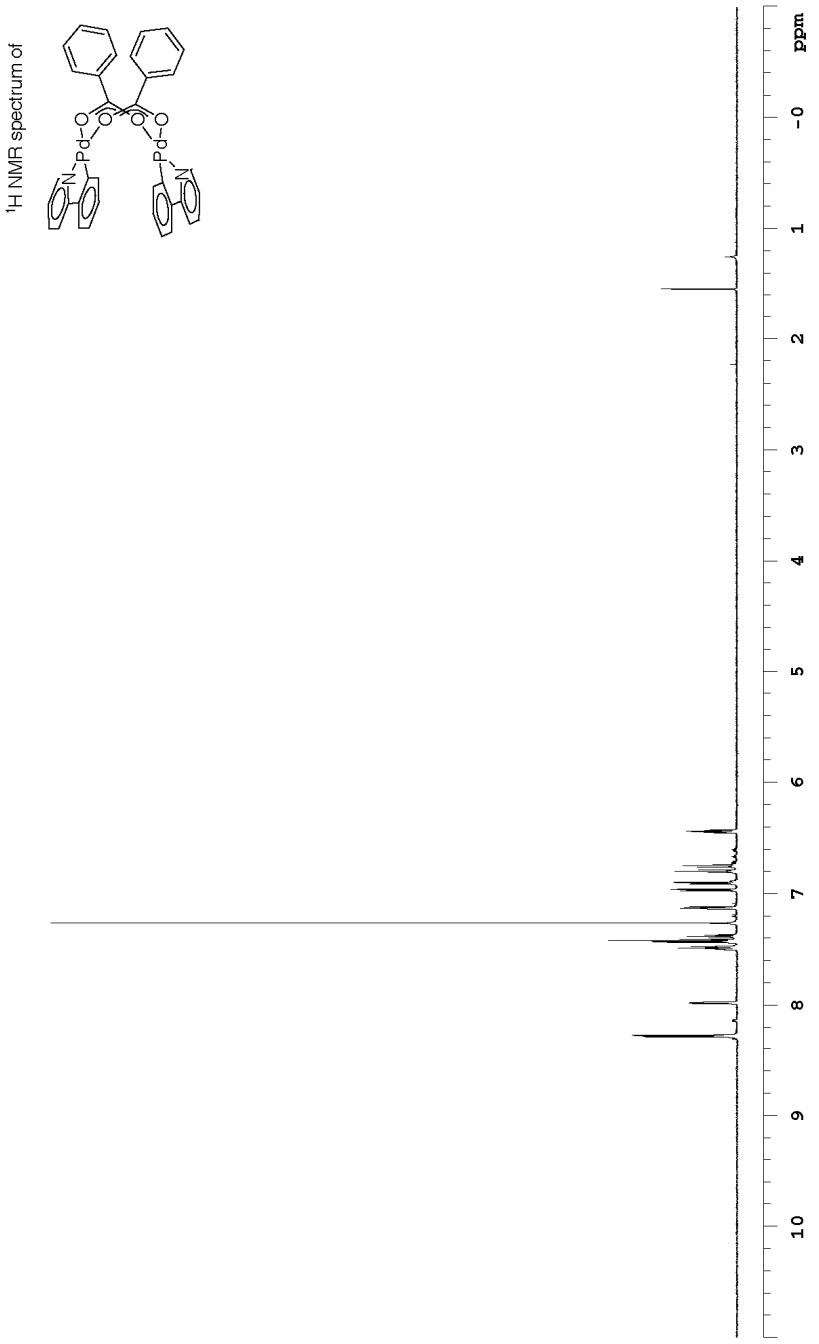
^{1}H NMR spectrum of **20c** in CD_2Cl_2 at –50 °C.



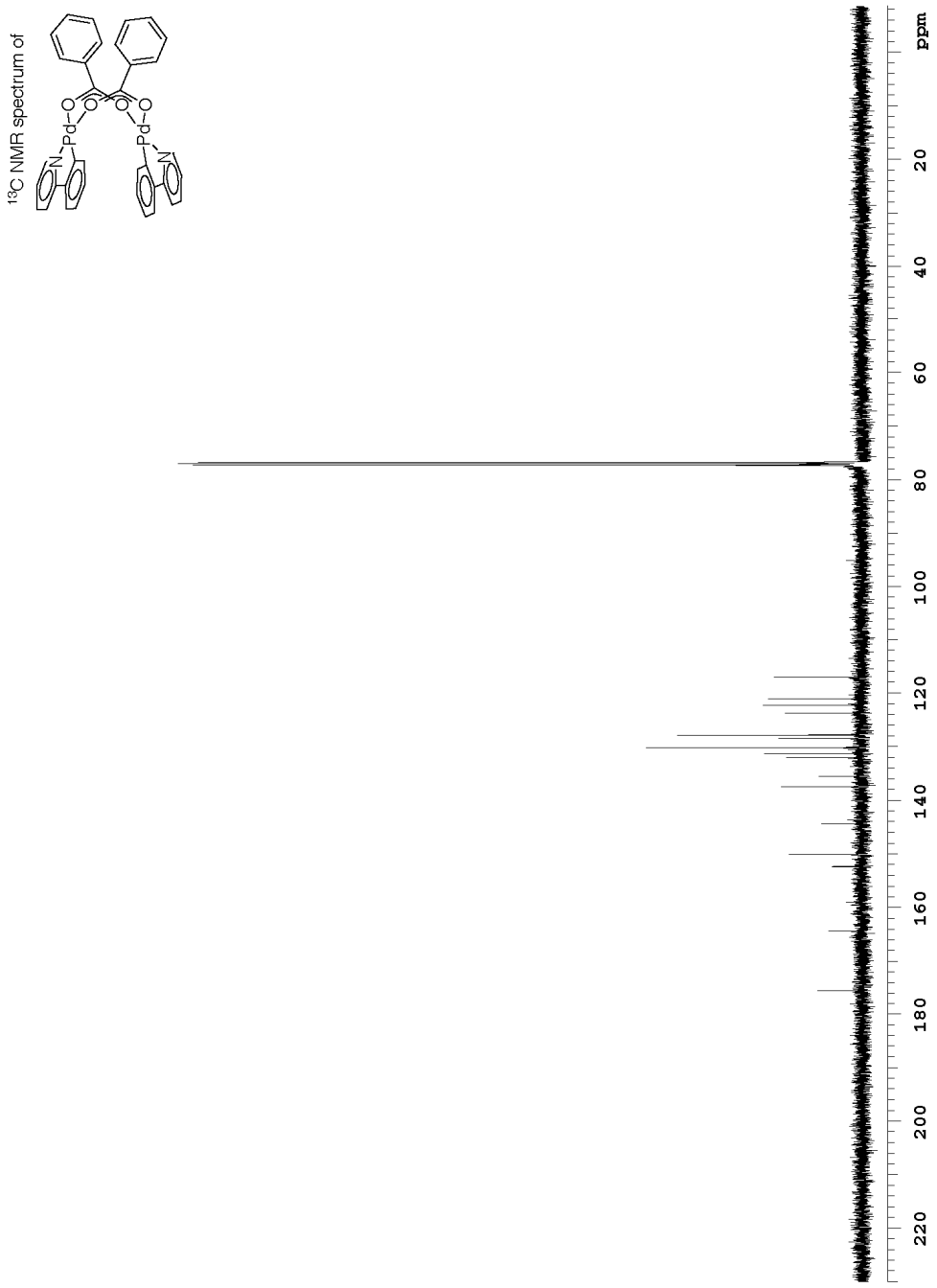
^{1}H NMR spectrum of **20d** in CD_2Cl_2 at –50 °C.



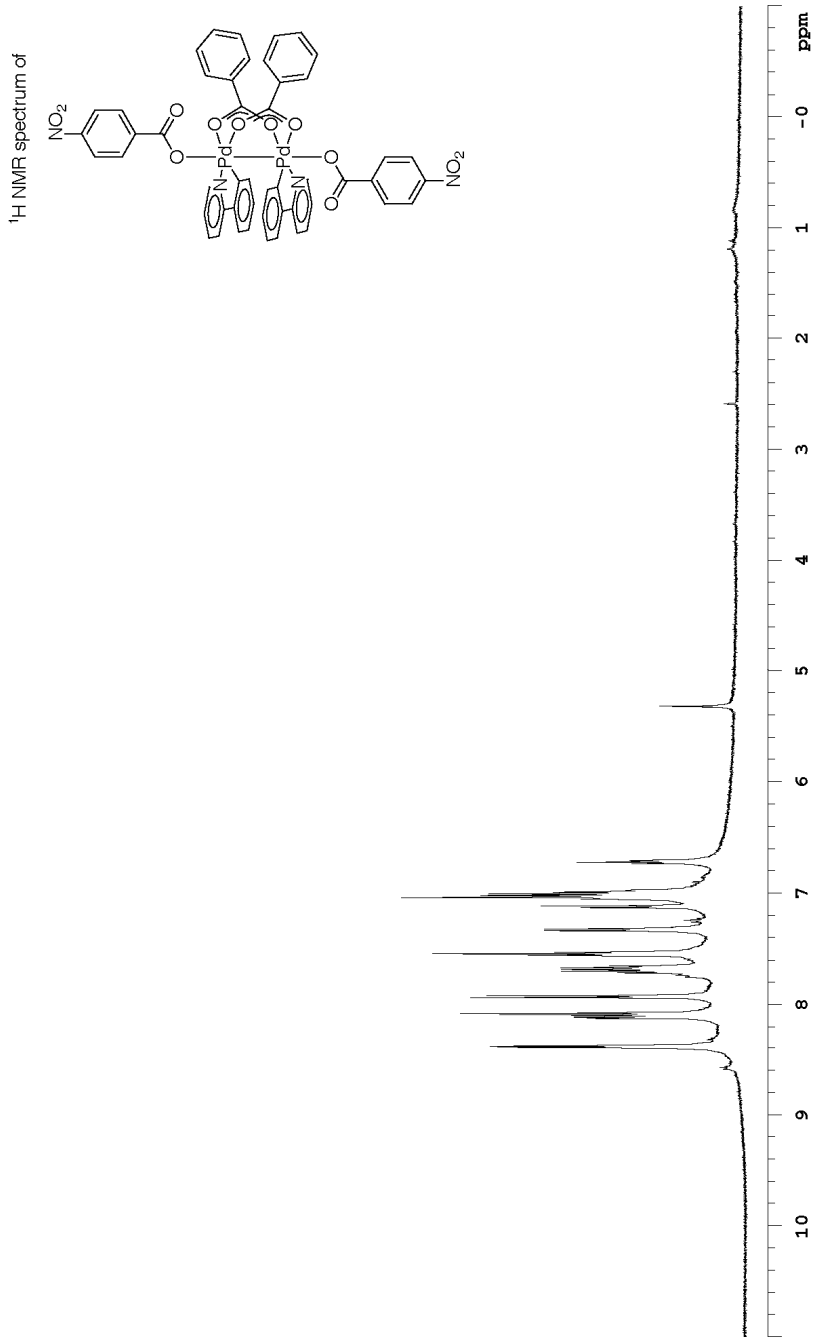
^{1}H NMR spectrum of **20e** in CD_2Cl_2 at –50 °C.



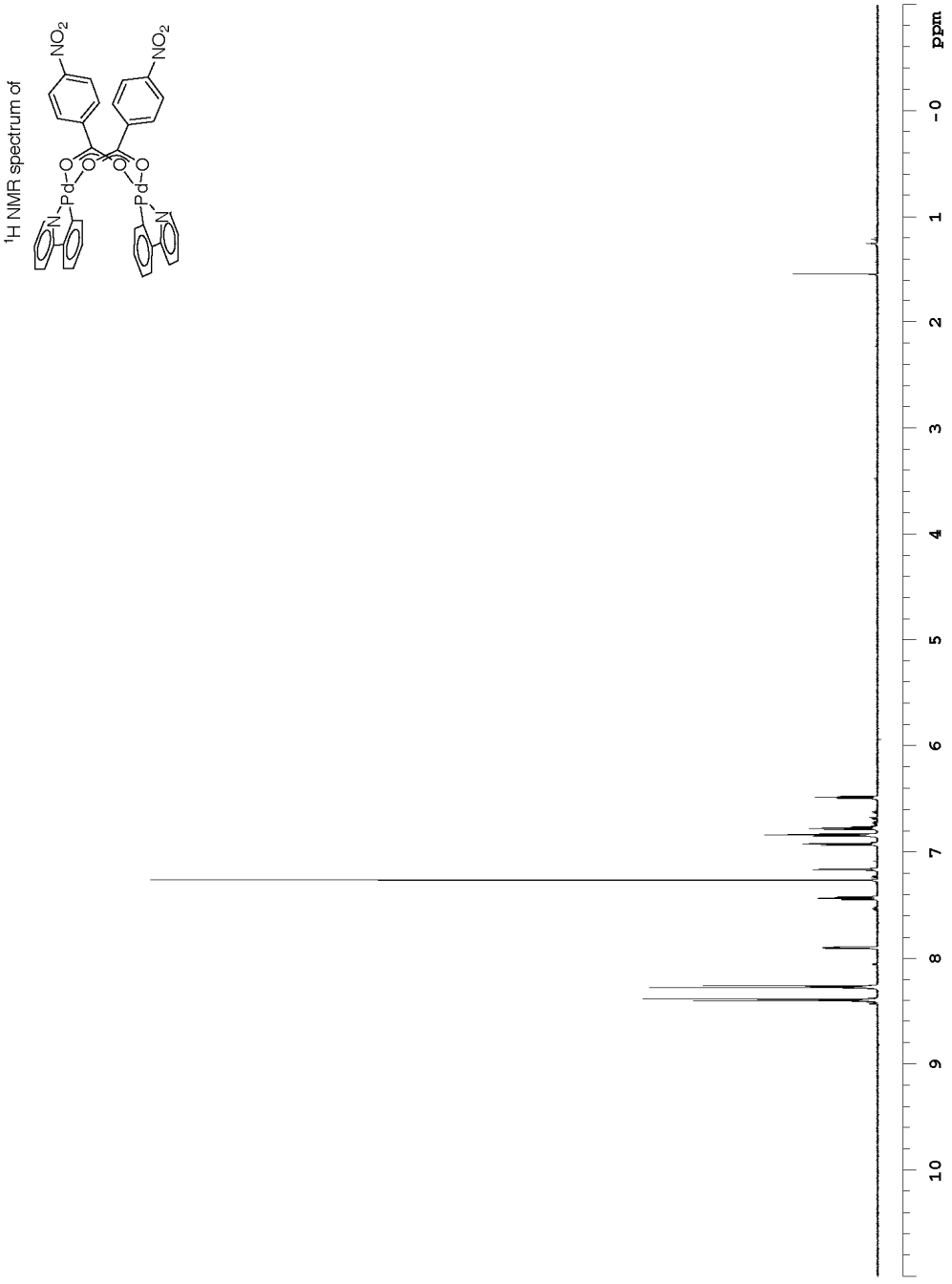
^{1}H NMR spectrum of **21** in $CDCl_3$ at 23 °C.



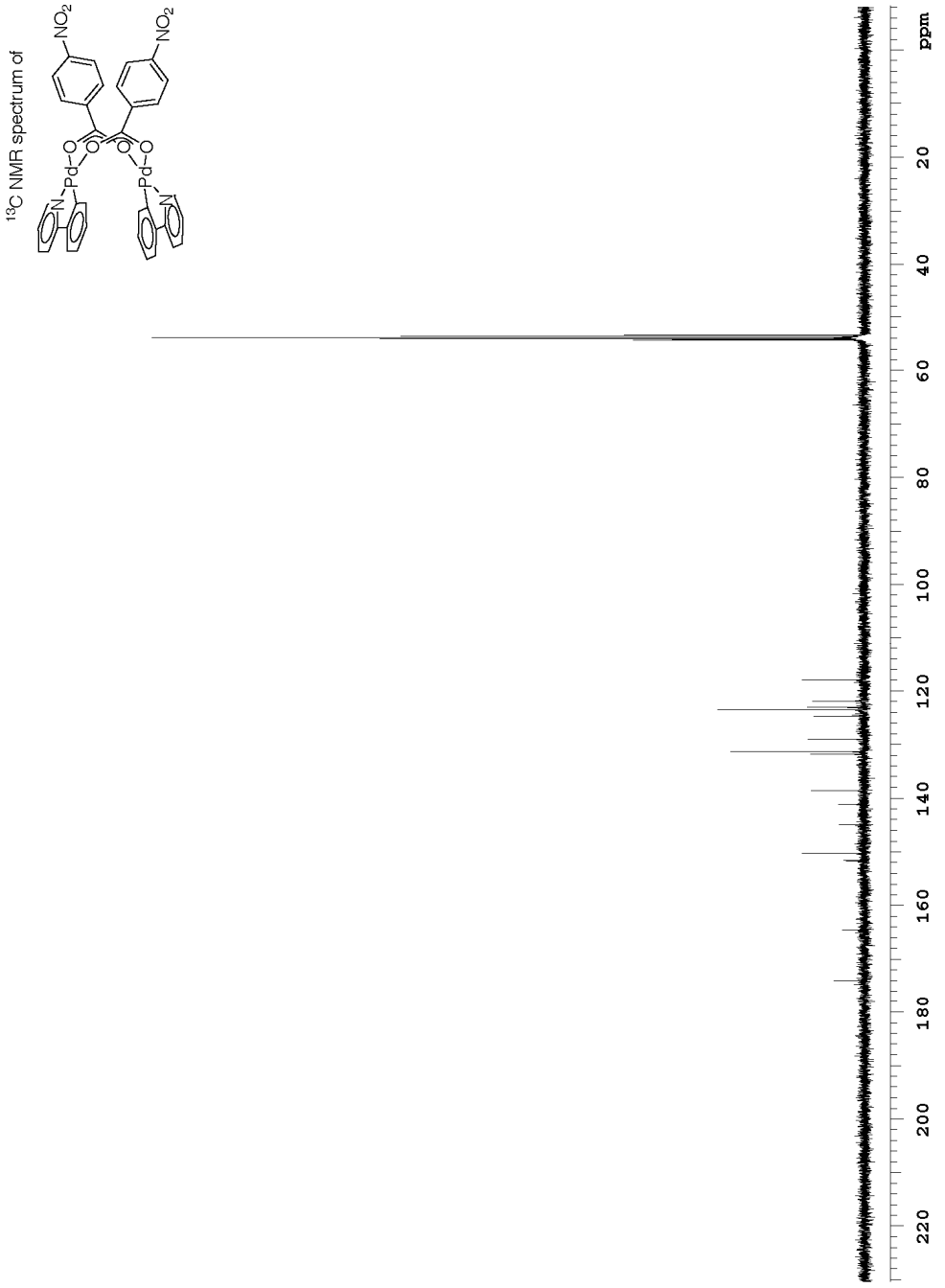
^{13}C NMR spectrum of **21** in $CDCl_3$ at 23 °C.



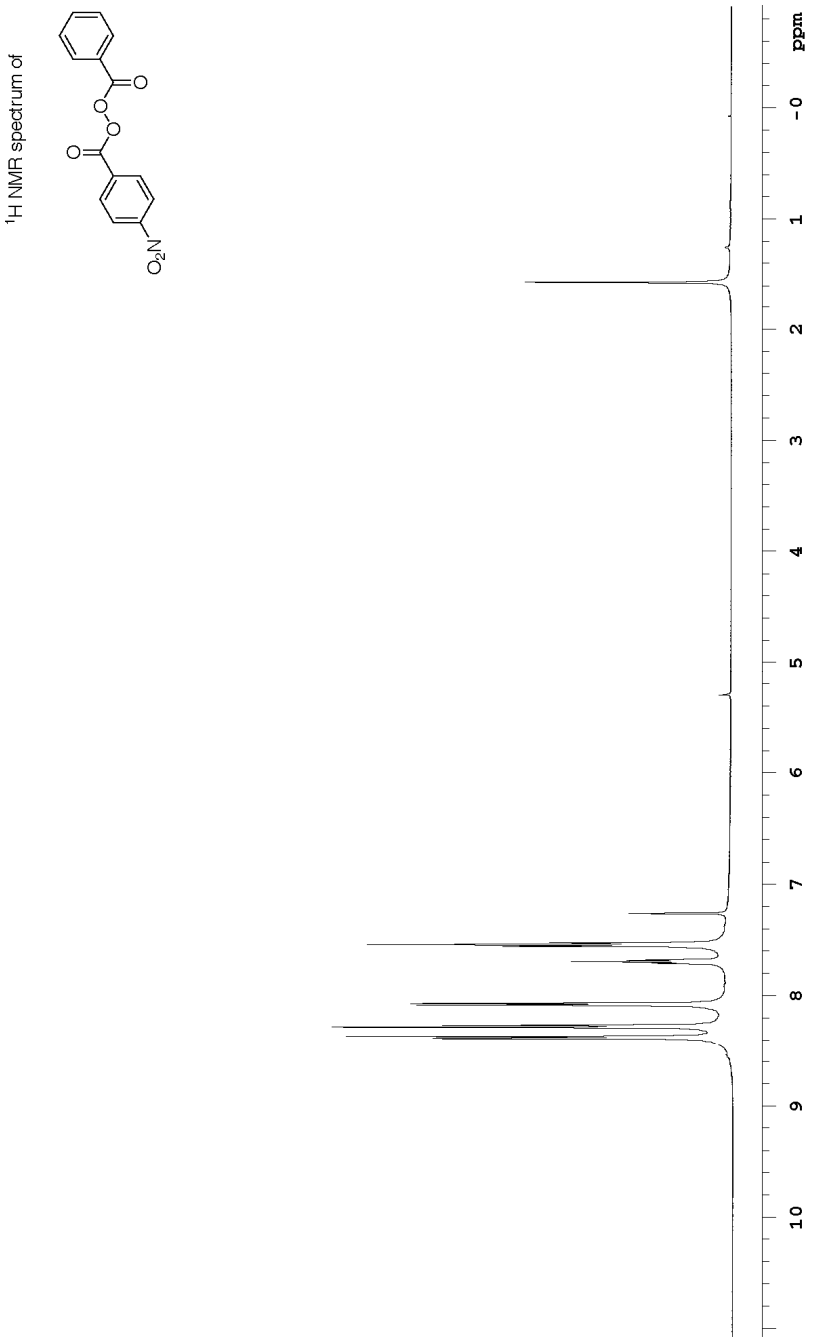
^{1}H NMR spectrum of **22** in CD_2Cl_2 at –50 °C.



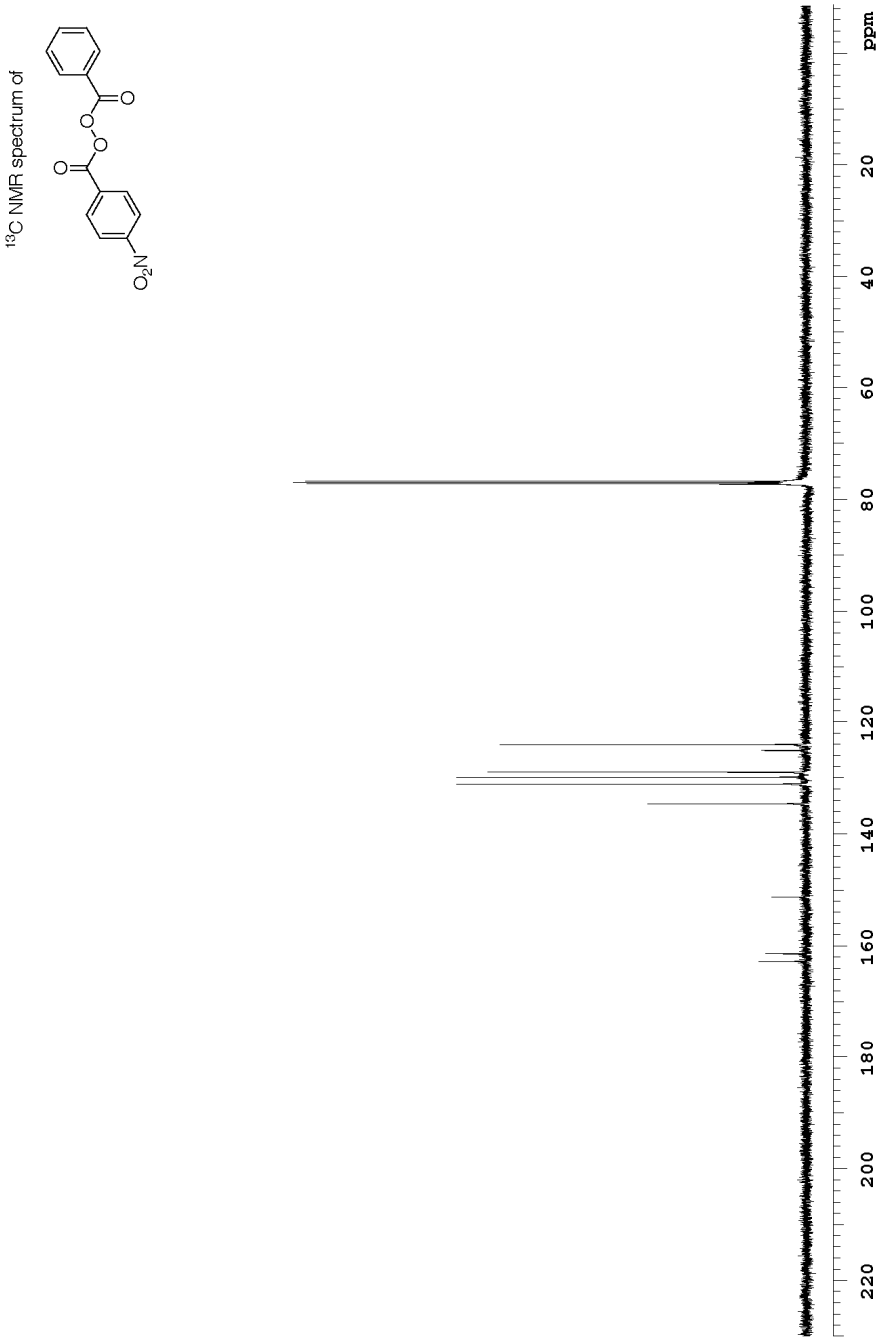
^{1}H NMR spectrum of **23** in $CDCl_3$ at 23 °C.



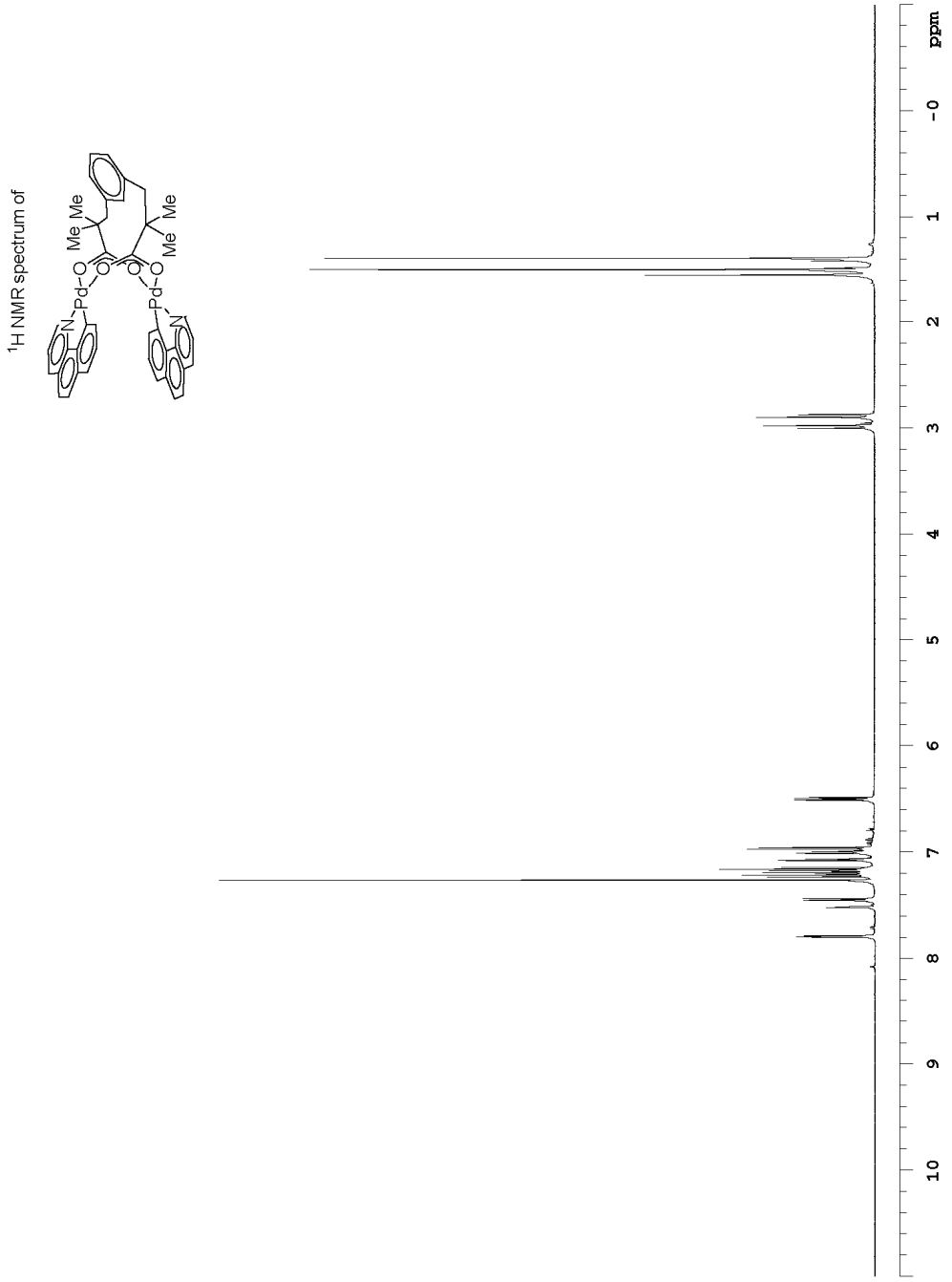
^{13}C NMR spectrum of **23** in CD_2Cl_2 at 23 °C.



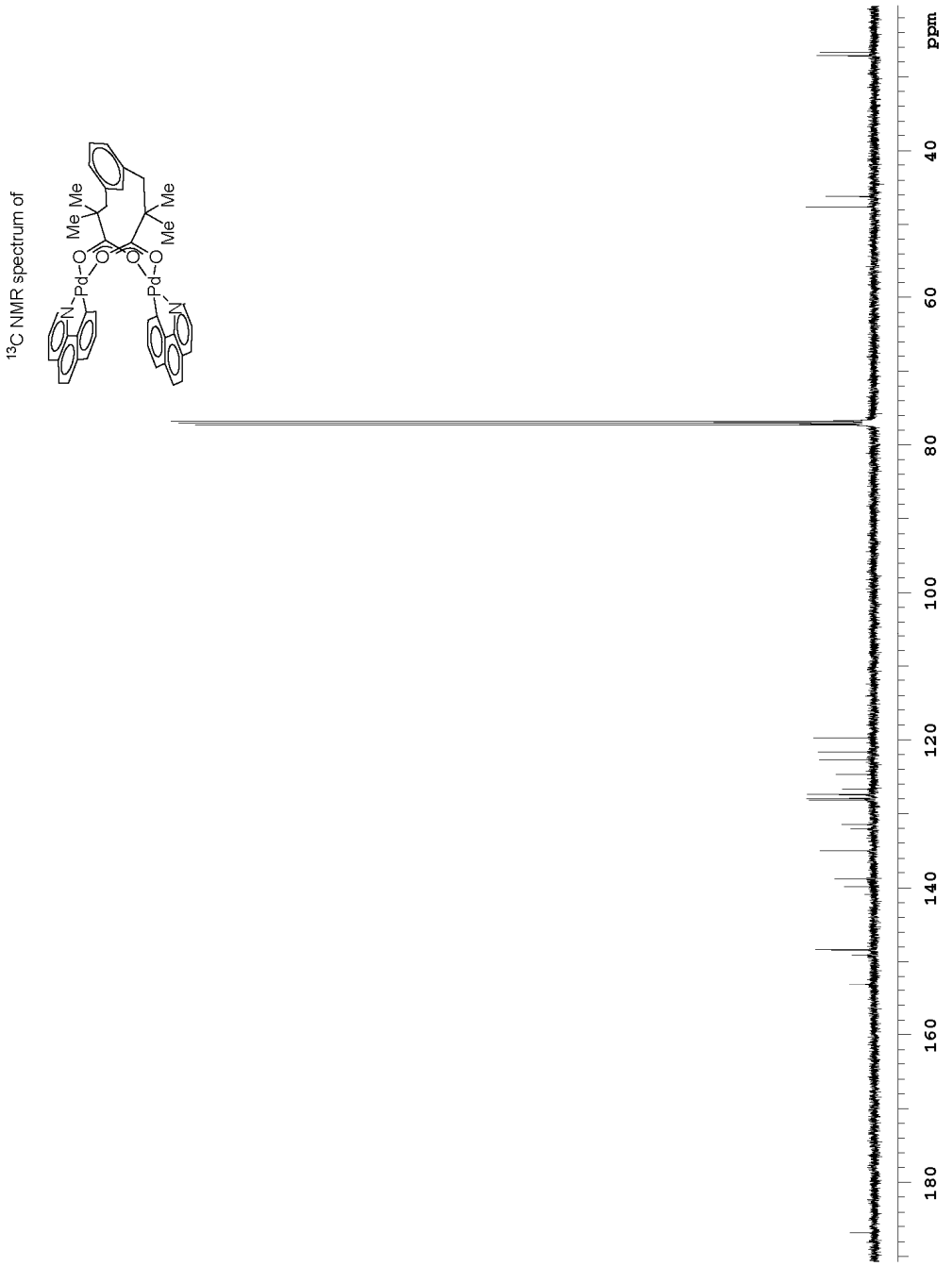
^{1}H NMR spectrum of **30** in $CDCl_3$ at 23 °C.



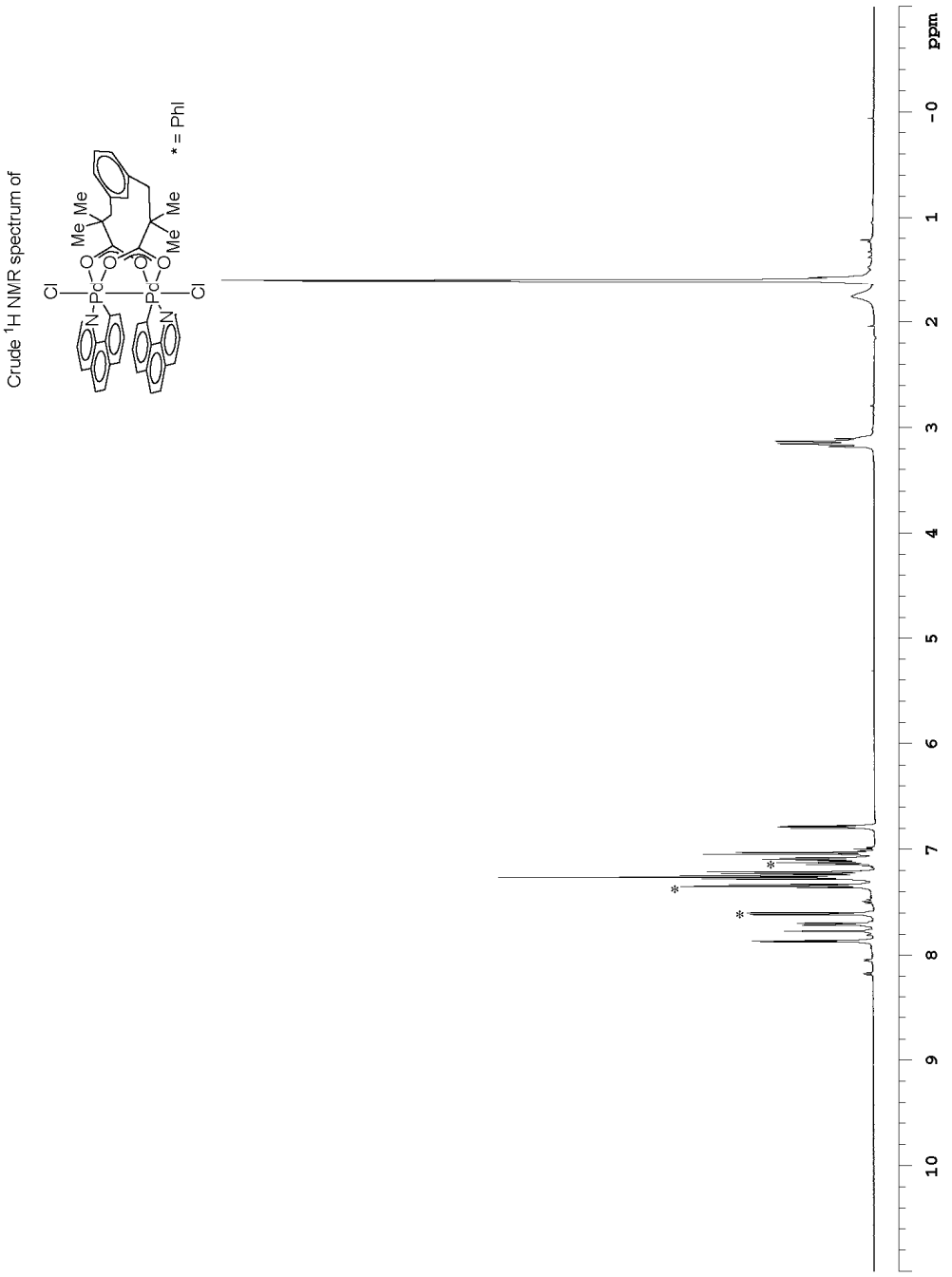
^{13}C NMR spectrum of **30** in $CDCl_3$ at 23 °C.



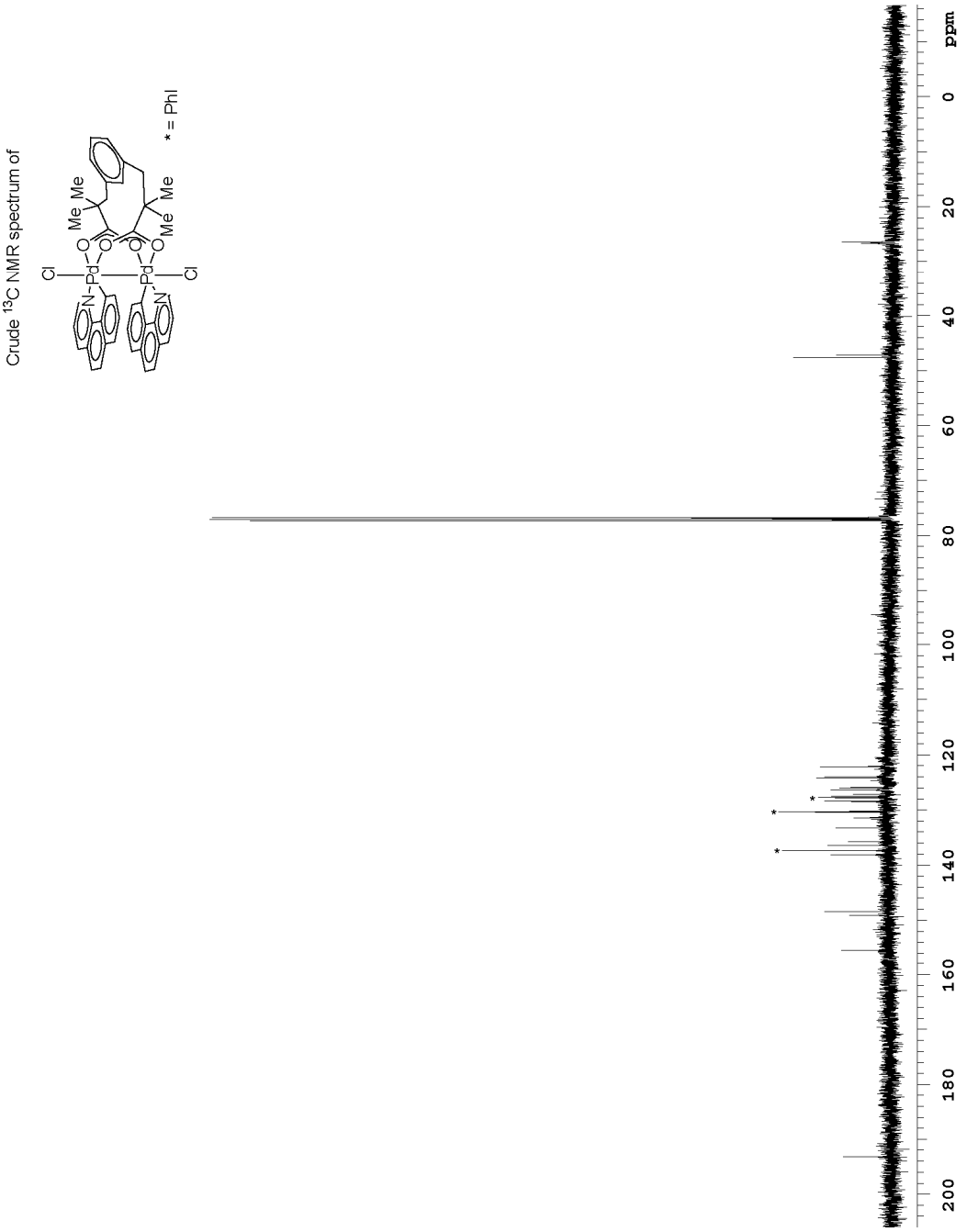
^{1}H NMR spectrum of **34** in $CDCl_3$ at 23 °C.



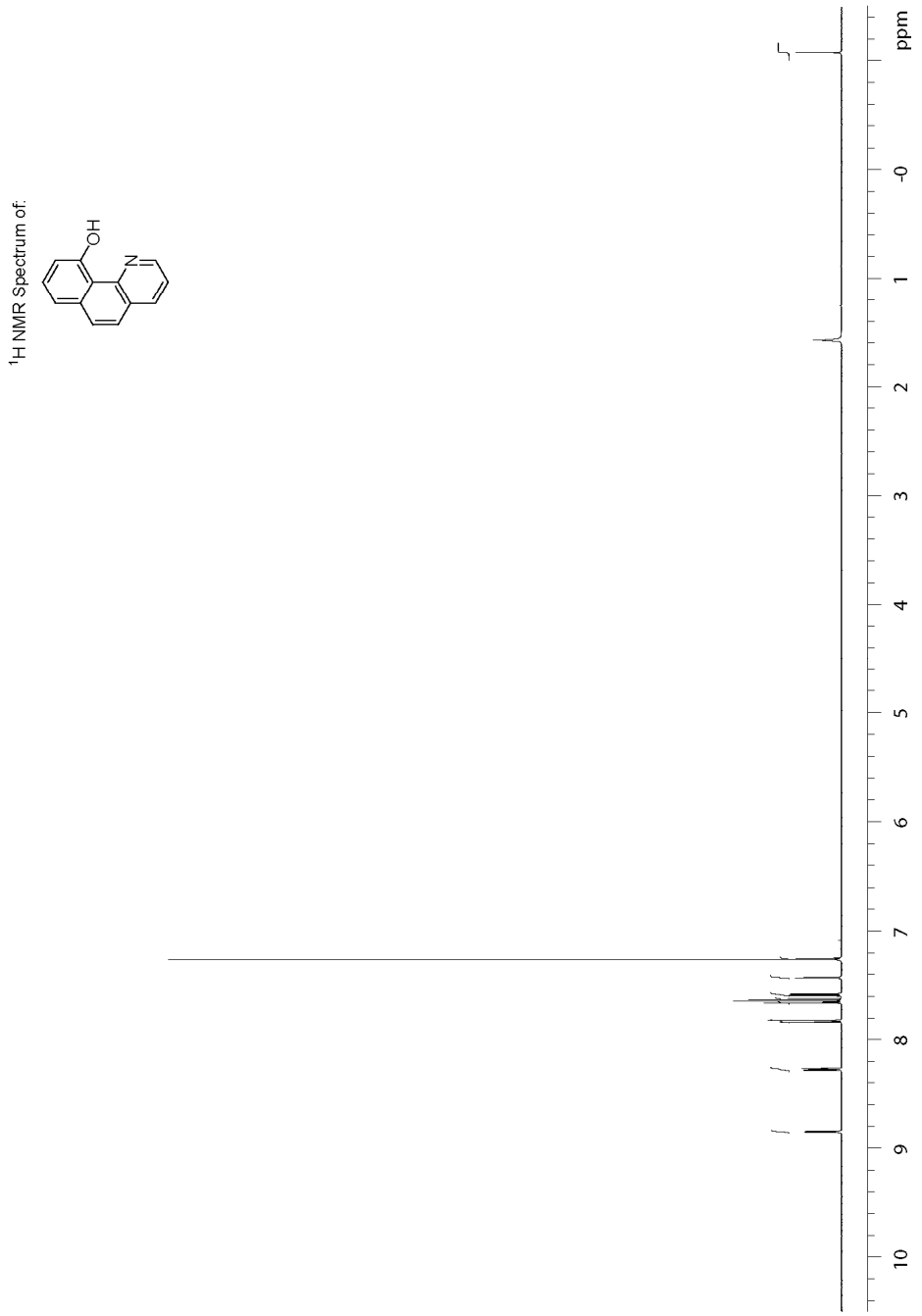
^{13}C NMR spectrum of **34** in $CDCl_3$ at 23 °C.



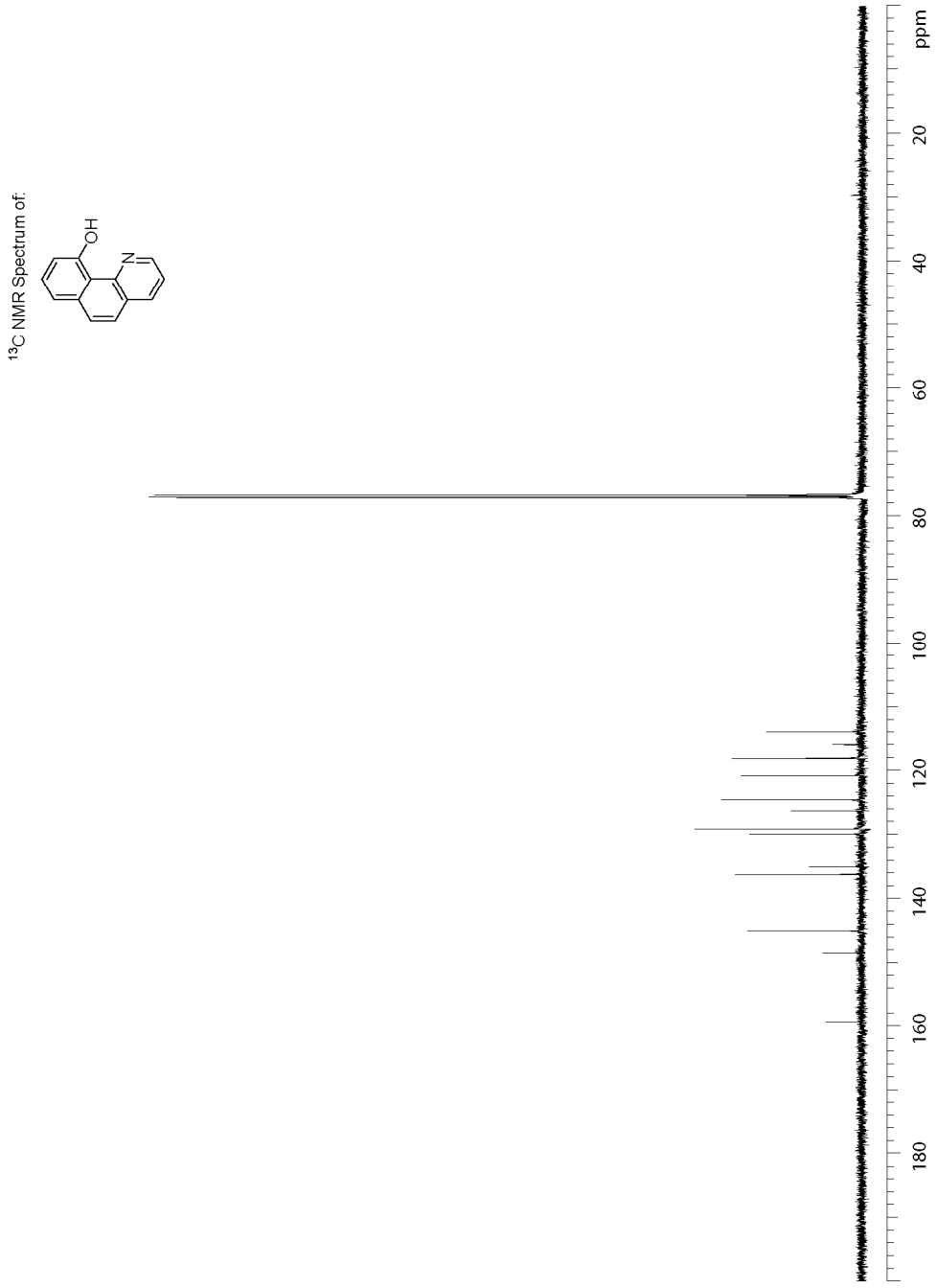
^{1}H NMR spectrum of **35** in $CDCl_3$ at –30 °C.



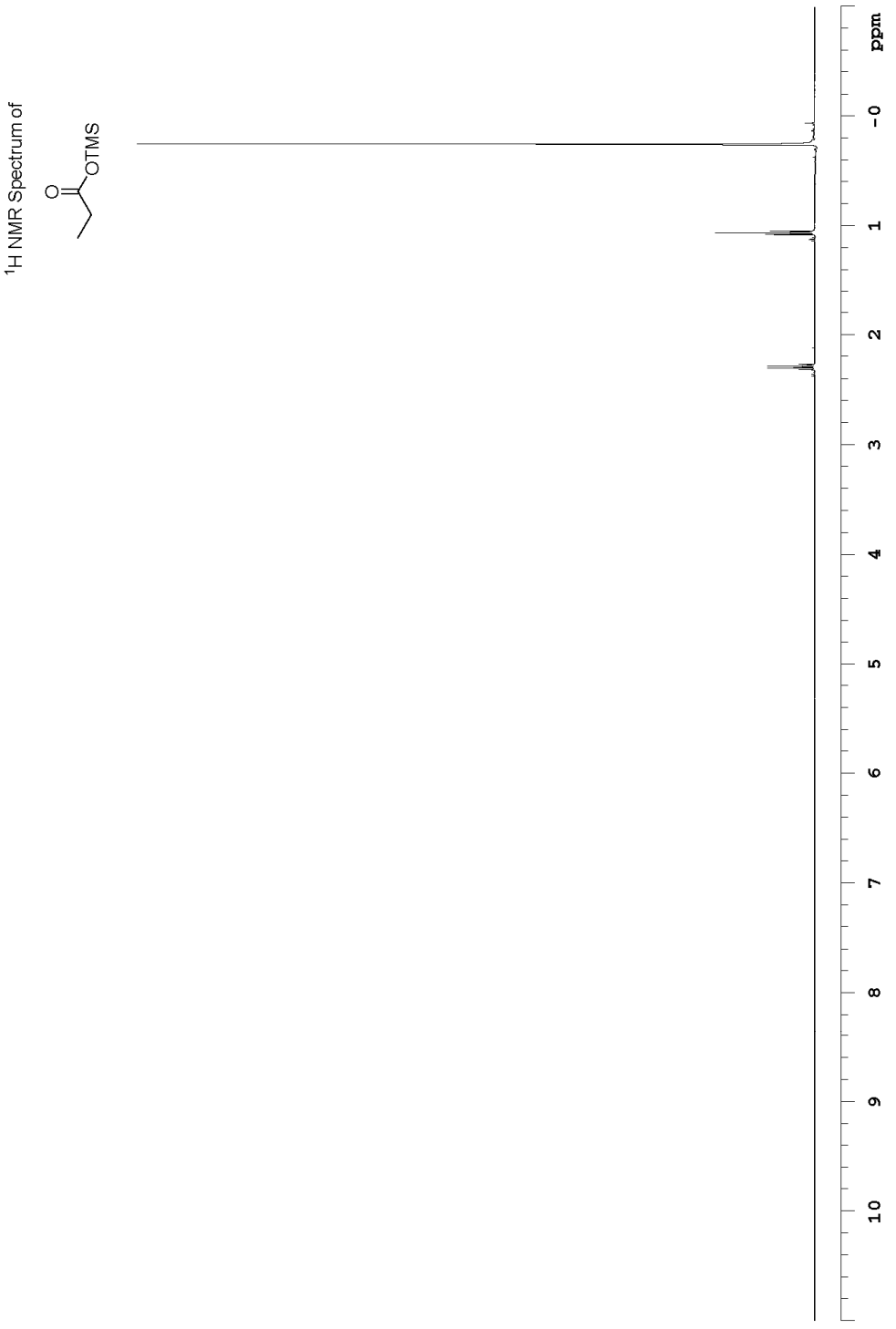
^{13}C NMR spectrum of **35** in $CDCl_3$ at –30 °C.



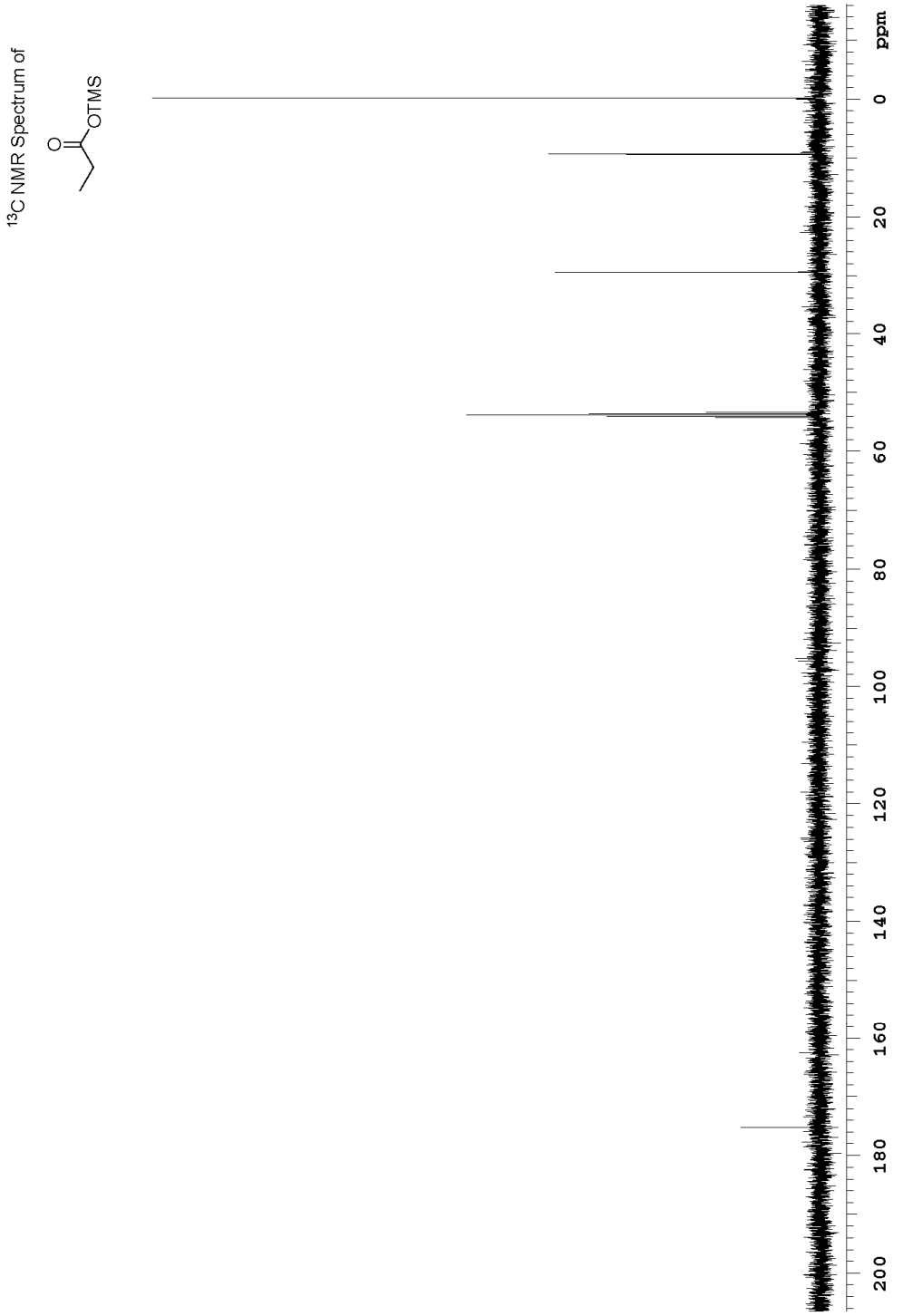
^{1}H NMR spectrum of **S1** in $CDCl_3$ at 23 °C.



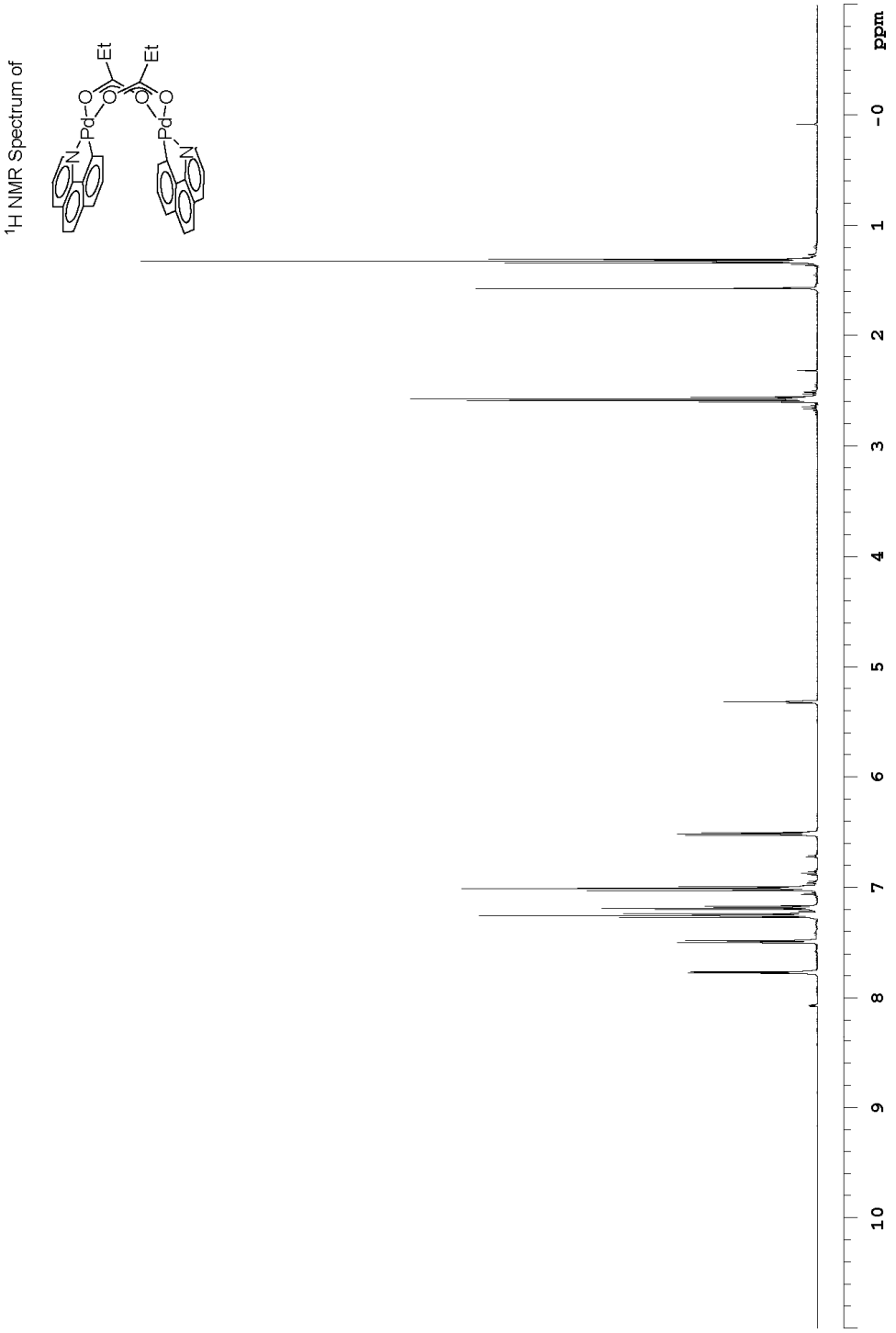
^{13}C NMR spectrum of **S1** in $CDCl_3$ at 23 °C.



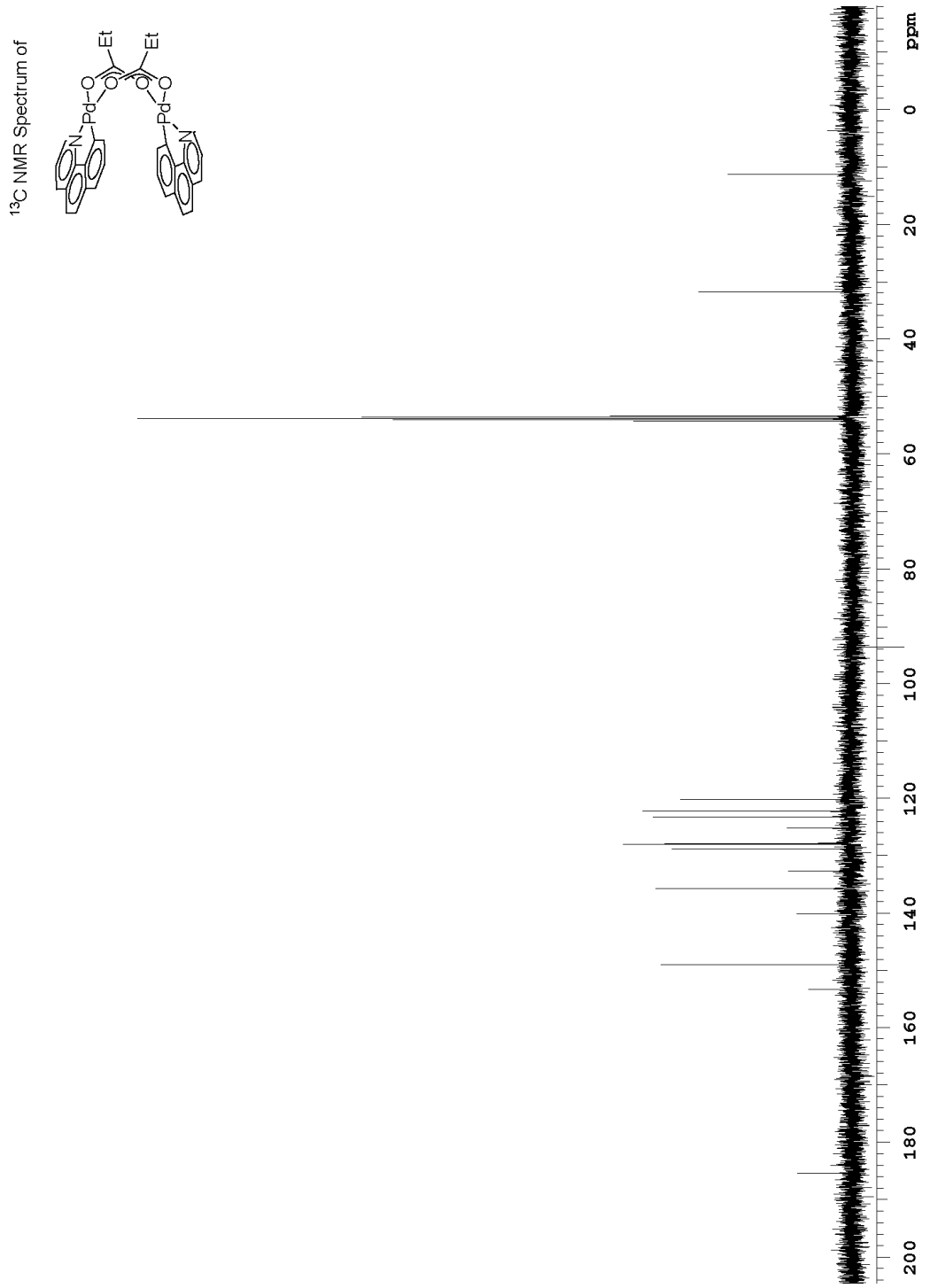
^{1}H NMR spectrum of **S2** in CD_2Cl_2 at 23 °C.



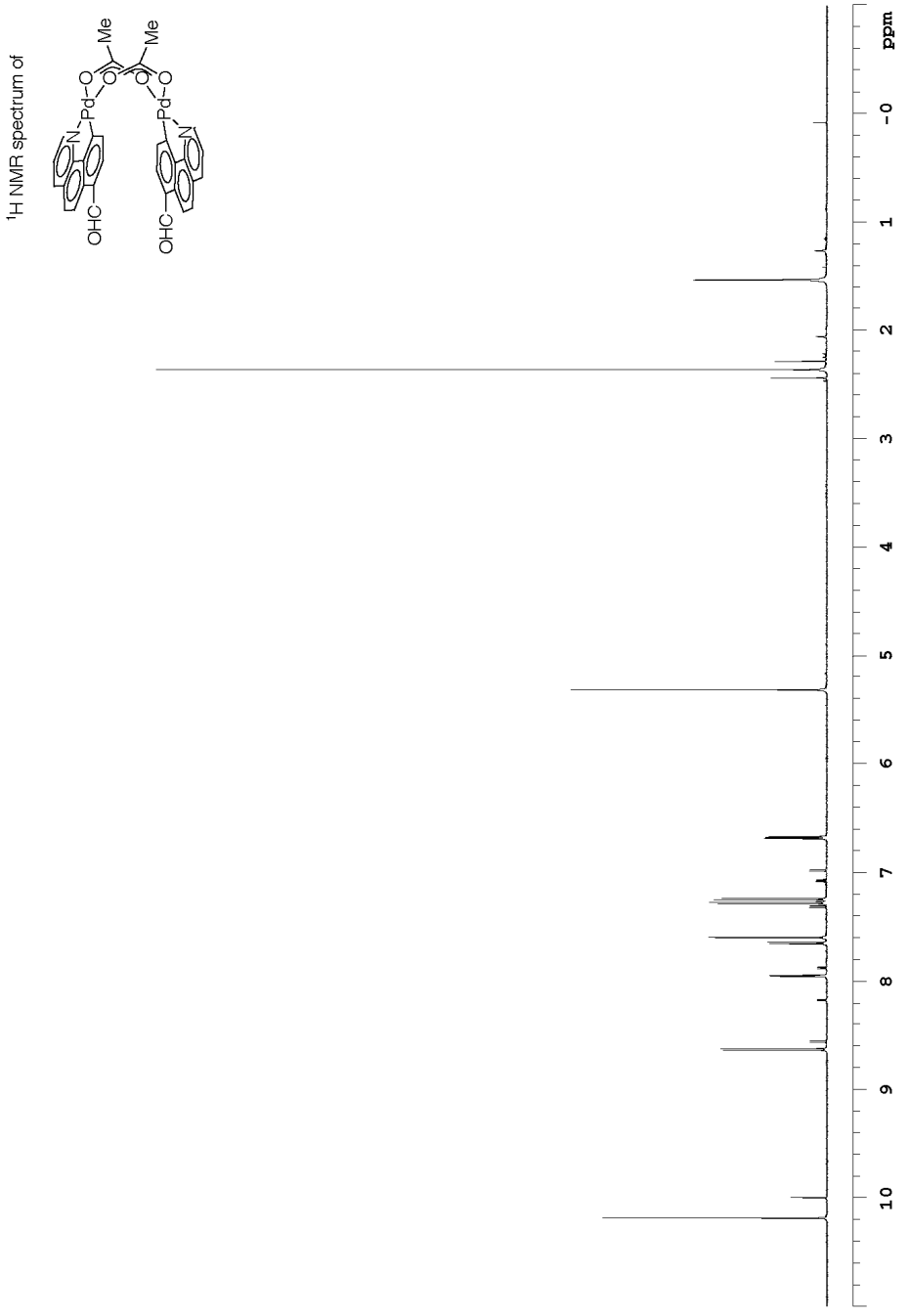
^{13}C NMR spectrum of **S2** in CD_2Cl_2 at 23 °C.



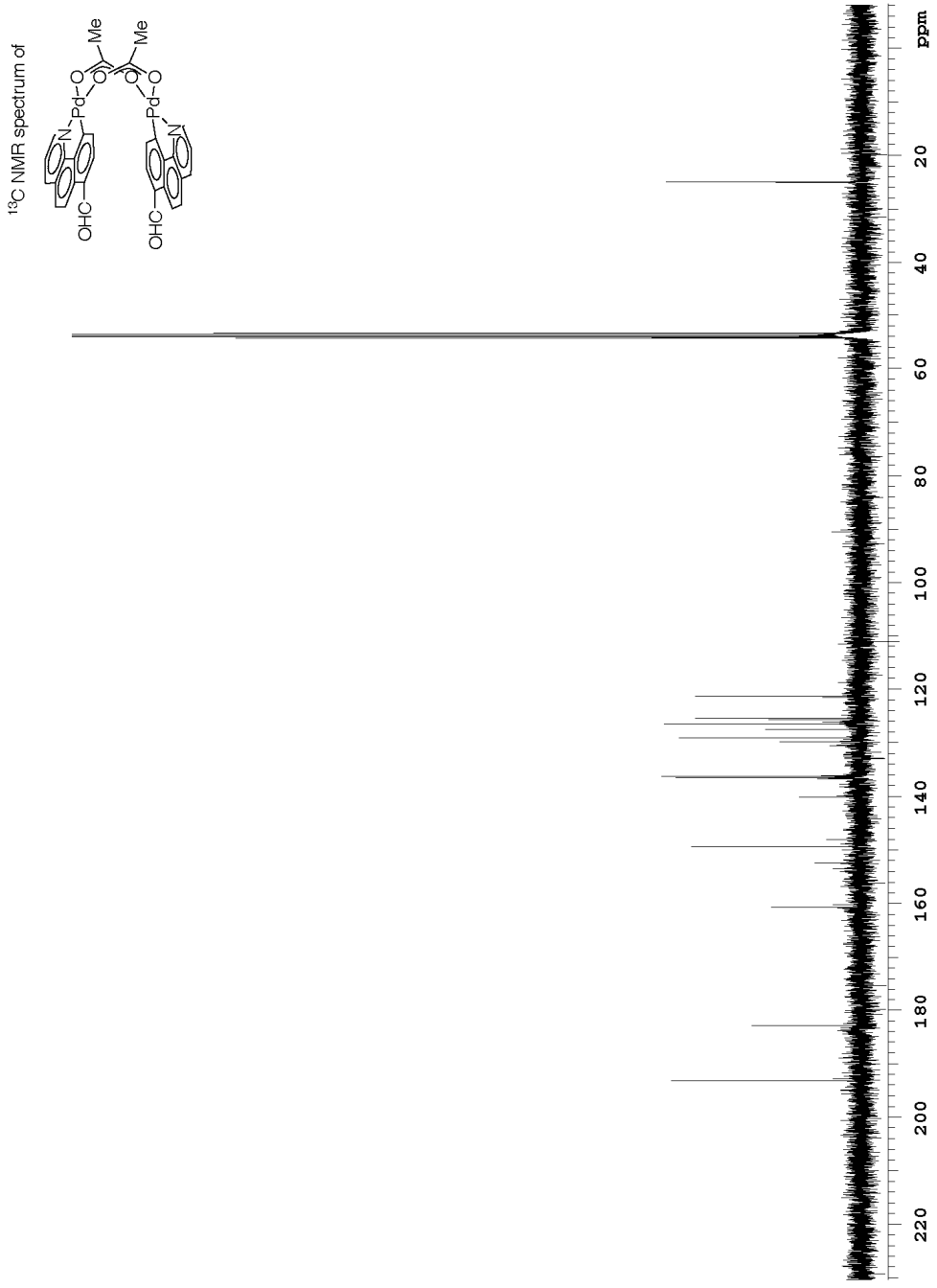
^{1}H NMR spectrum of **S3** in CD_2Cl_2 at 23 °C.



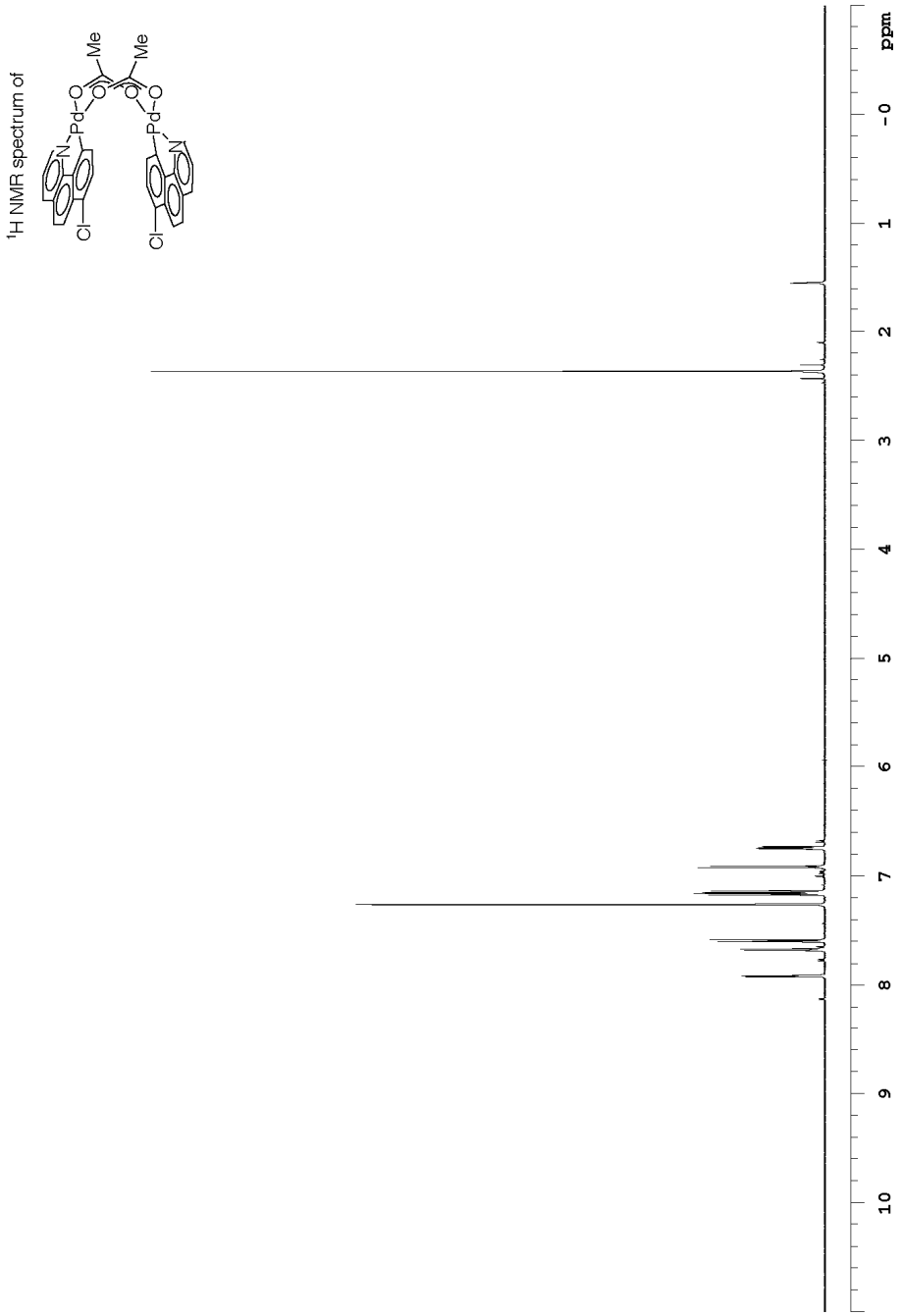
^{13}C NMR spectrum of **S3** in CD_2Cl_2 at 23 °C.



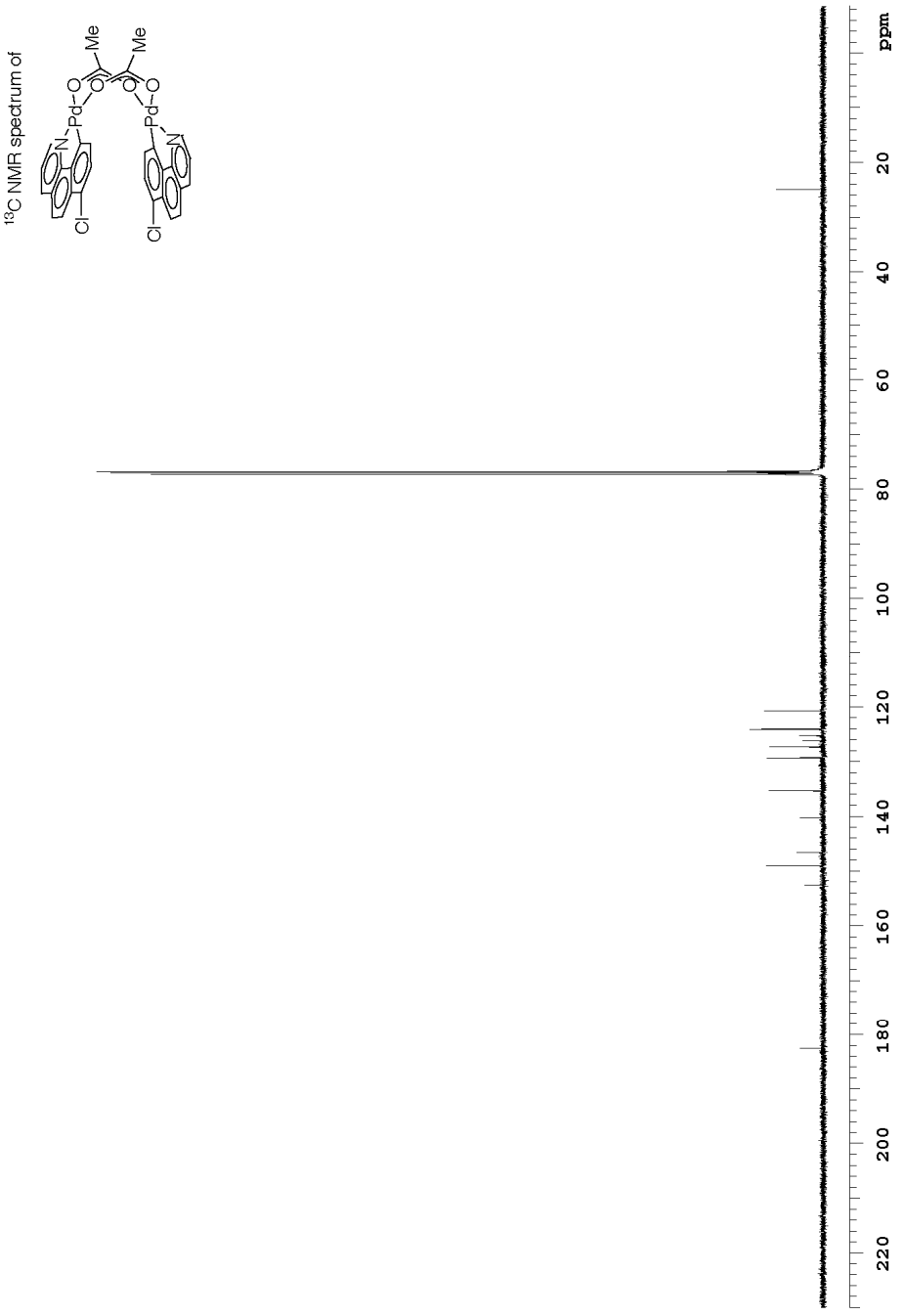
^{1}H NMR spectrum of **S14** in CD_2Cl_2 at 23 °C.



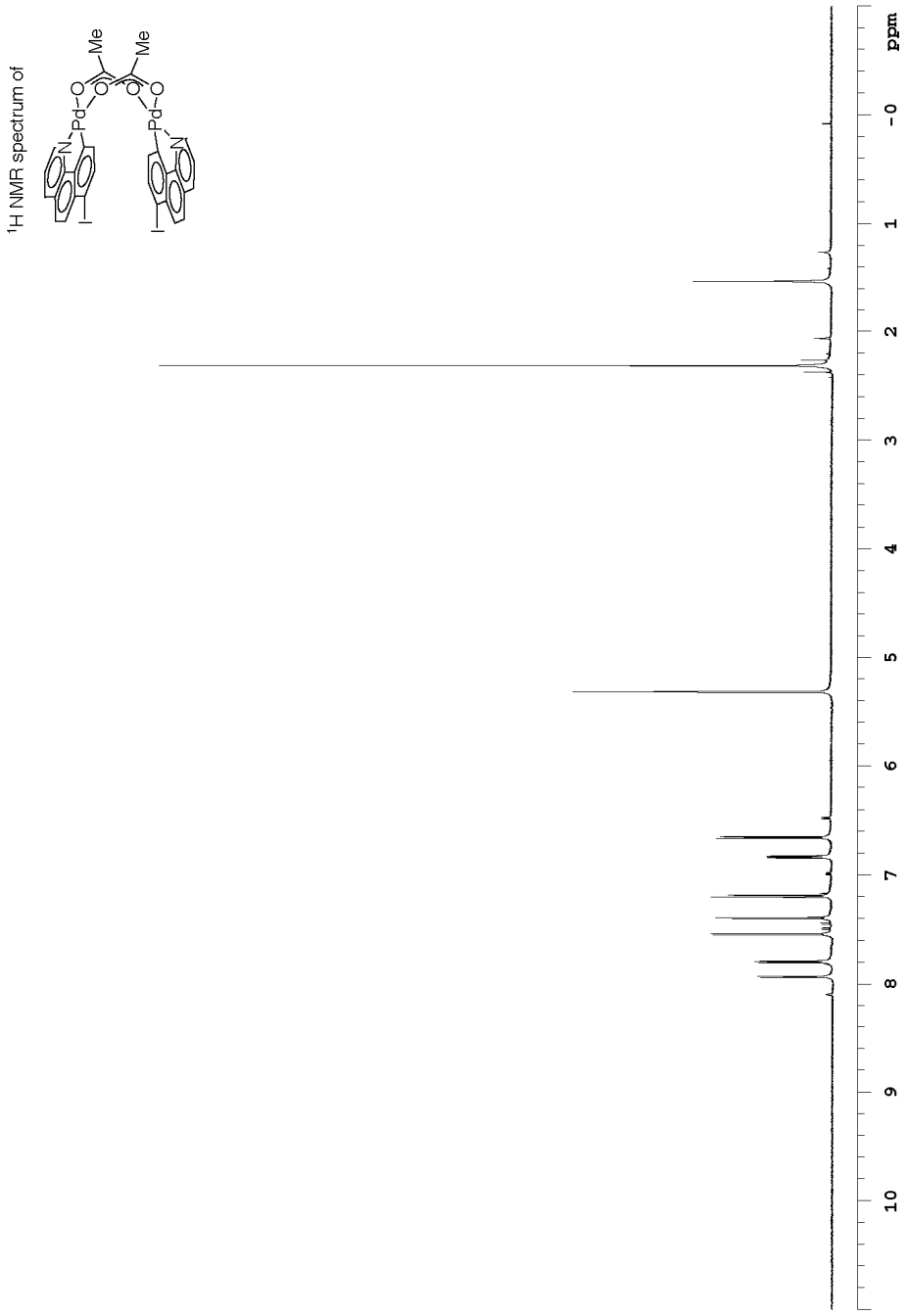
^{13}C NMR spectrum of **S14** in CD_2Cl_2 at 23 °C.



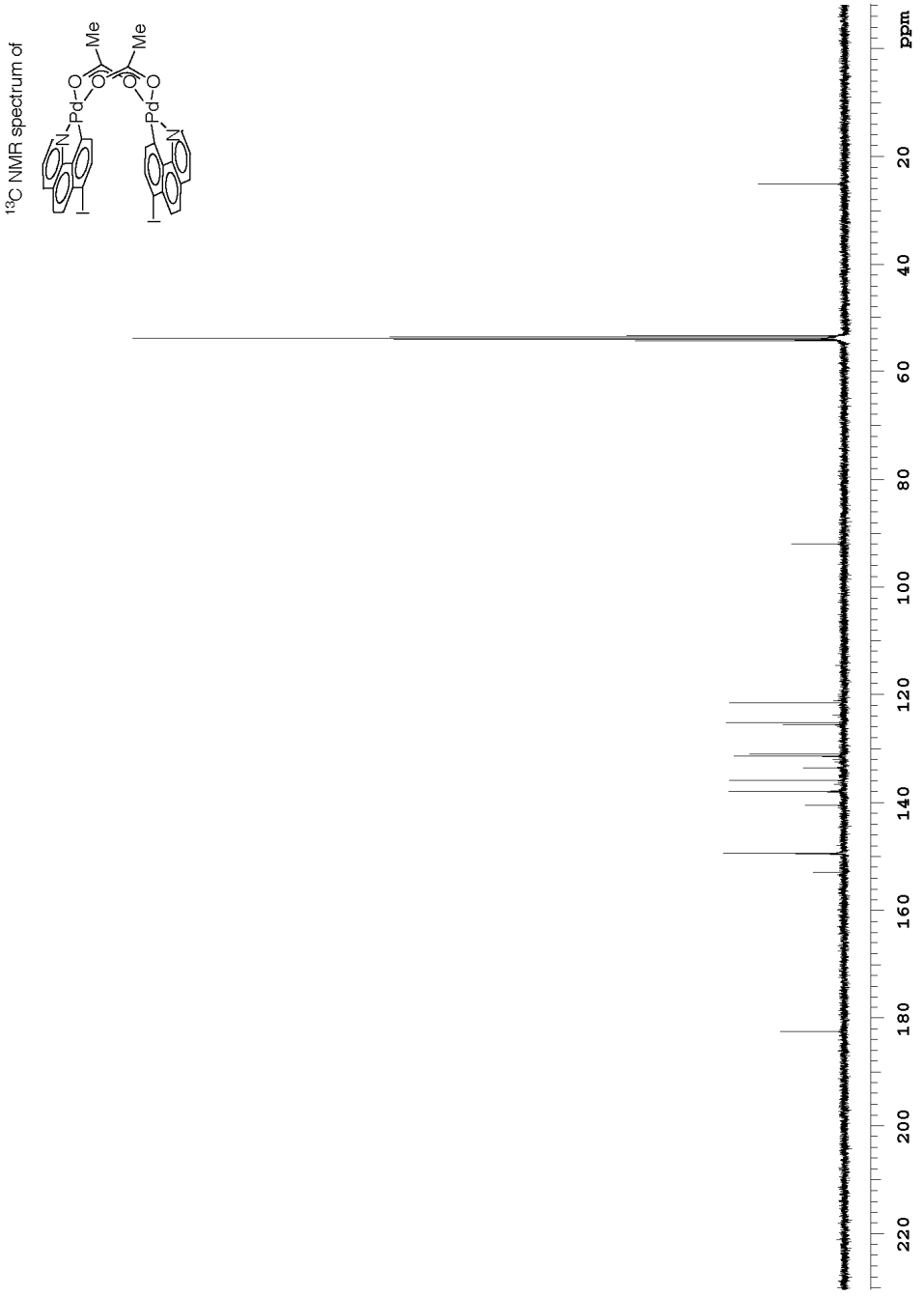
^{1}H NMR spectrum of **S15** in $CDCl_3$ at 23 °C.



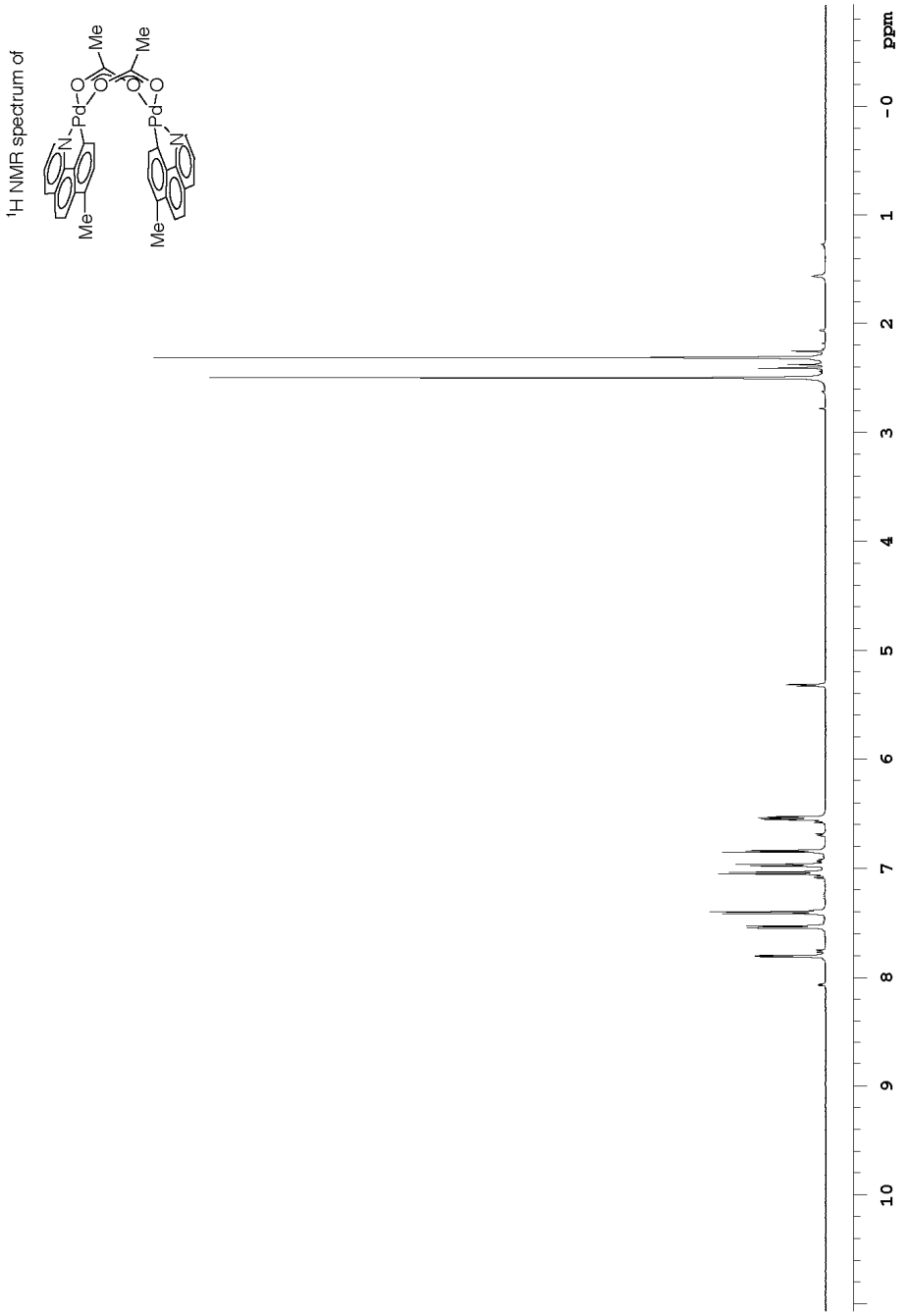
^{13}C NMR spectrum of **S15** in $CDCl_3$ at 23 °C.



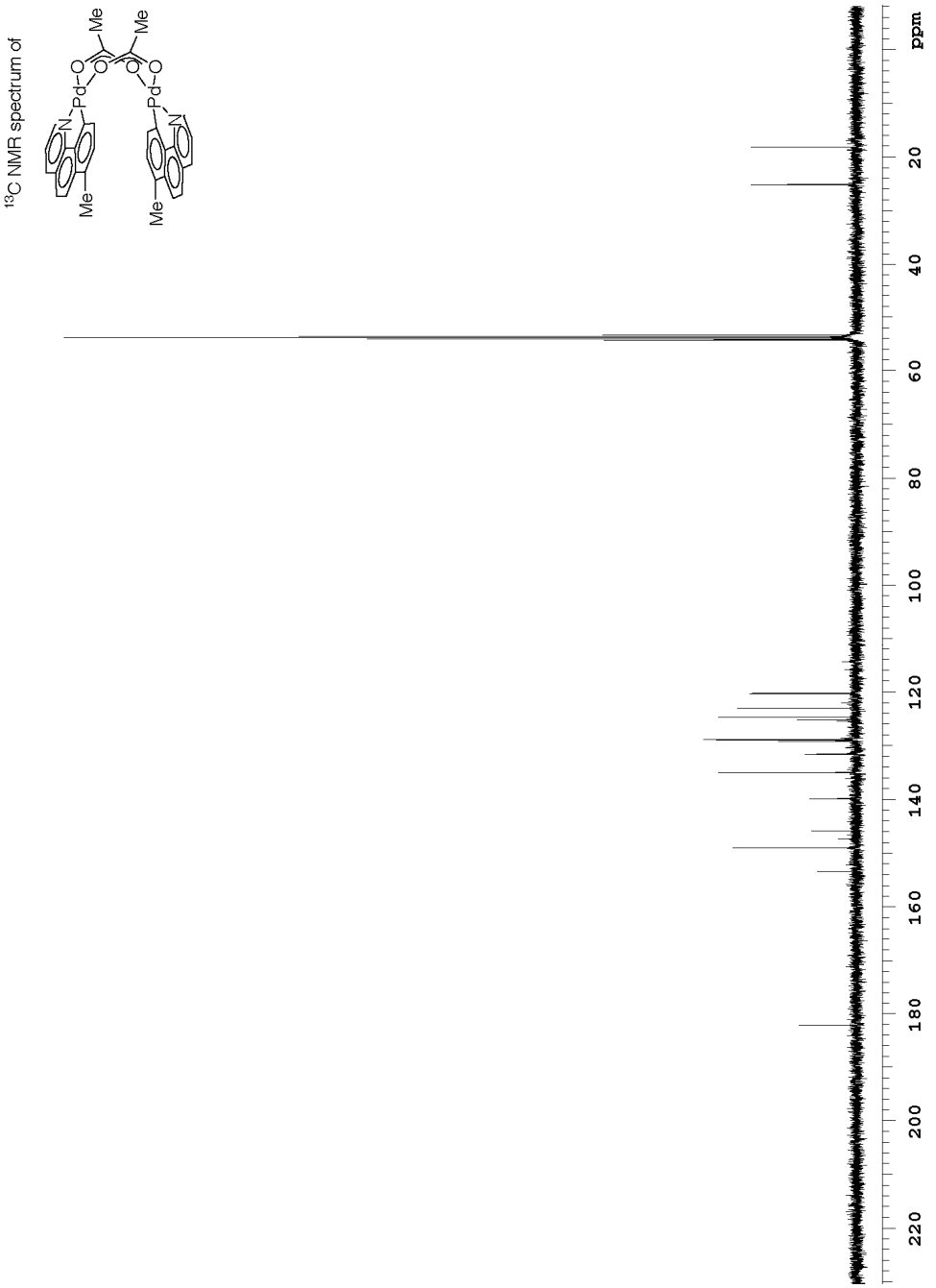
^{1}H NMR spectrum of **S16** in CD_2Cl_2 at 23 °C.



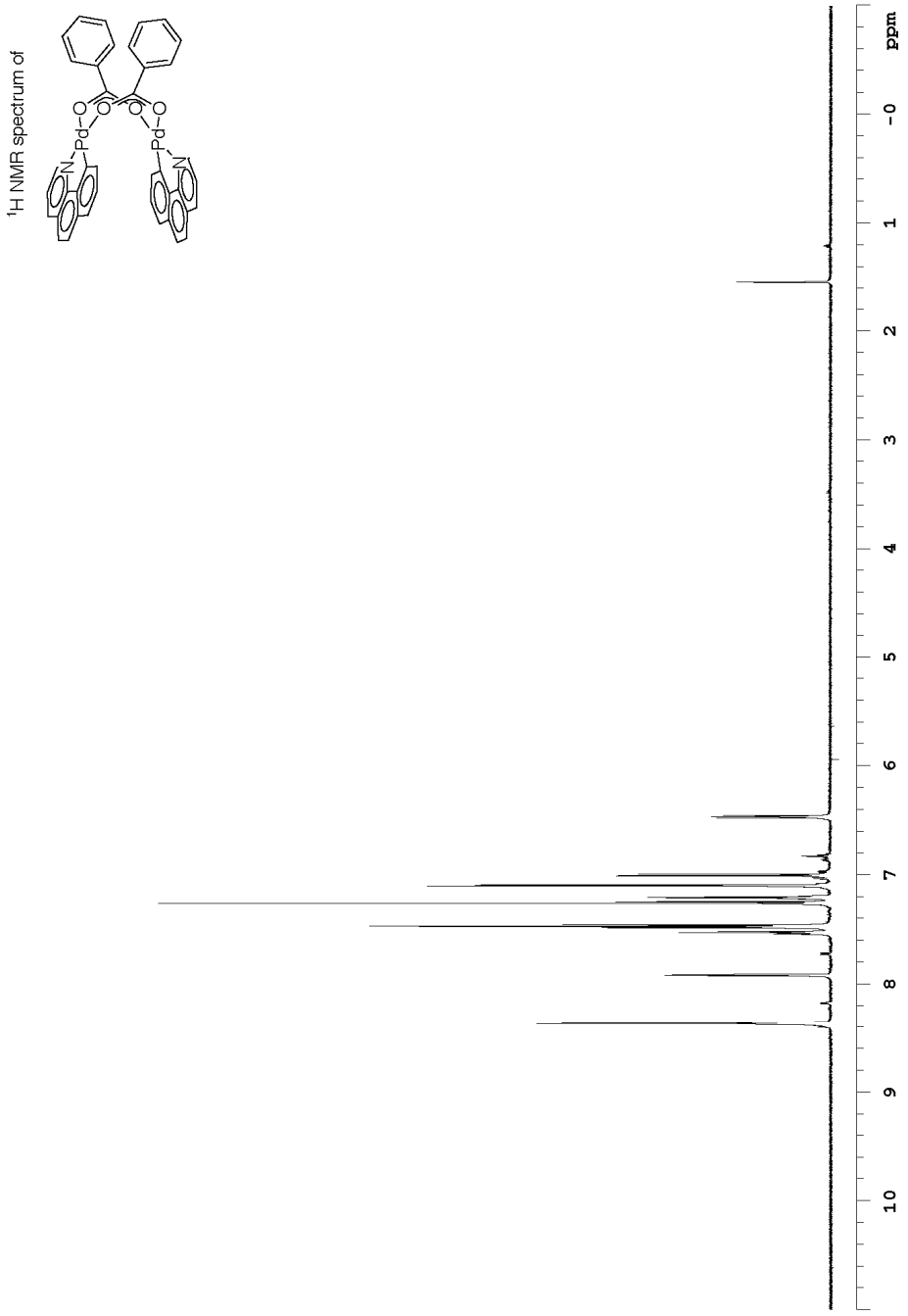
^{13}C NMR spectrum of **S16** in CD_2Cl_2 at 23 °C.



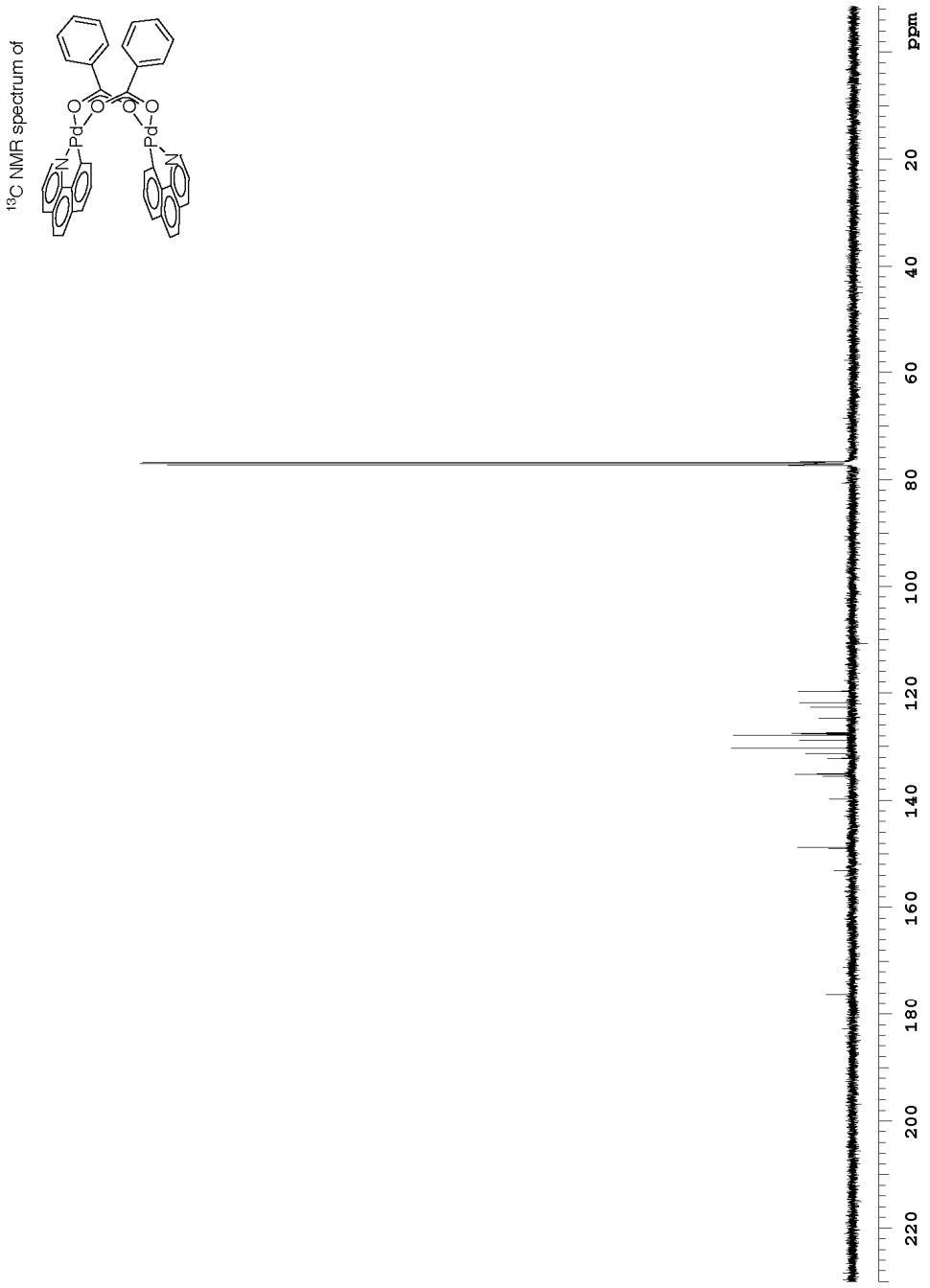
^{1}H NMR spectrum of **S17** in CD_2Cl_2 at 23 °C.



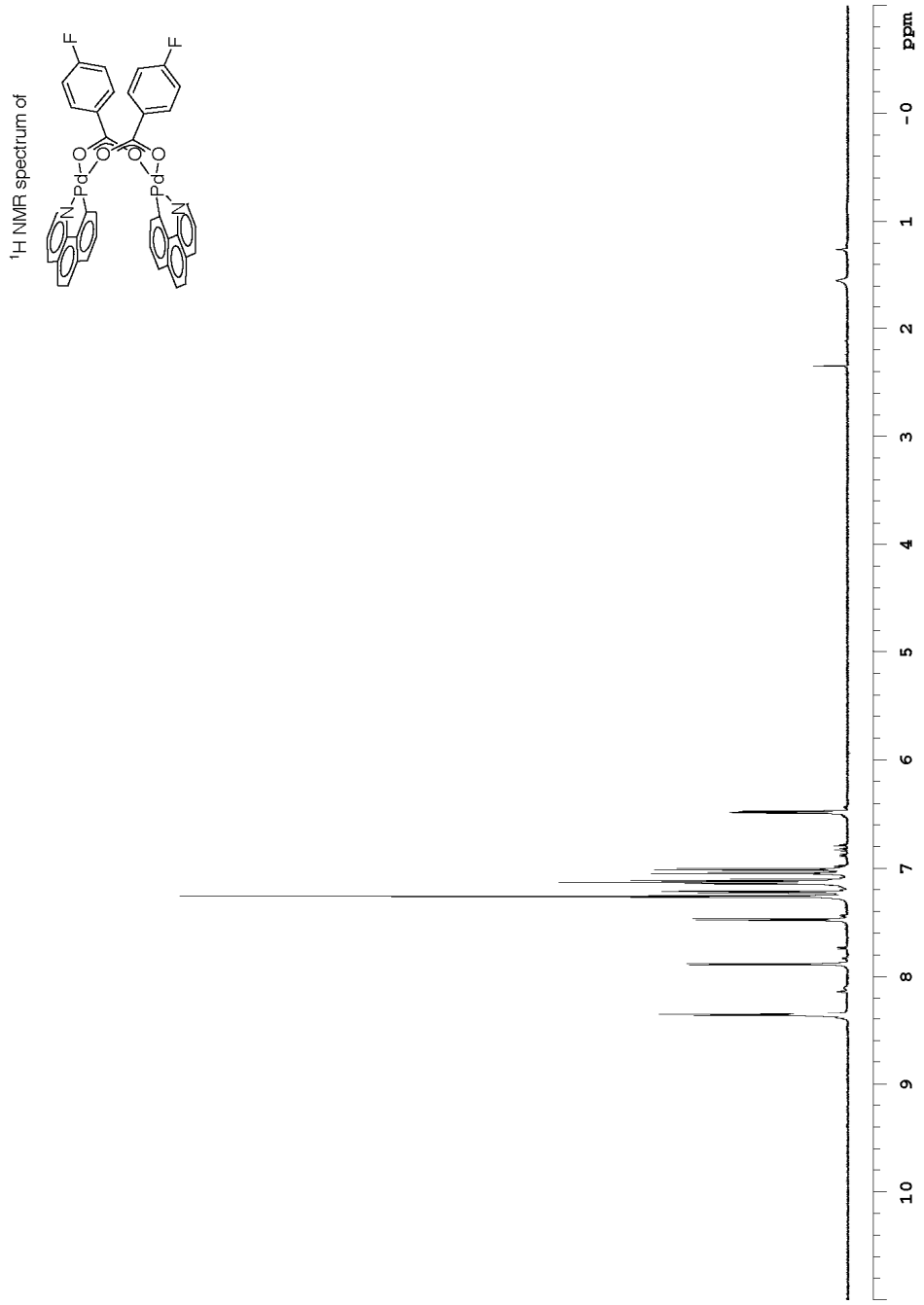
^{13}C NMR spectrum of **S17** in CD_2Cl_2 at 23 °C.



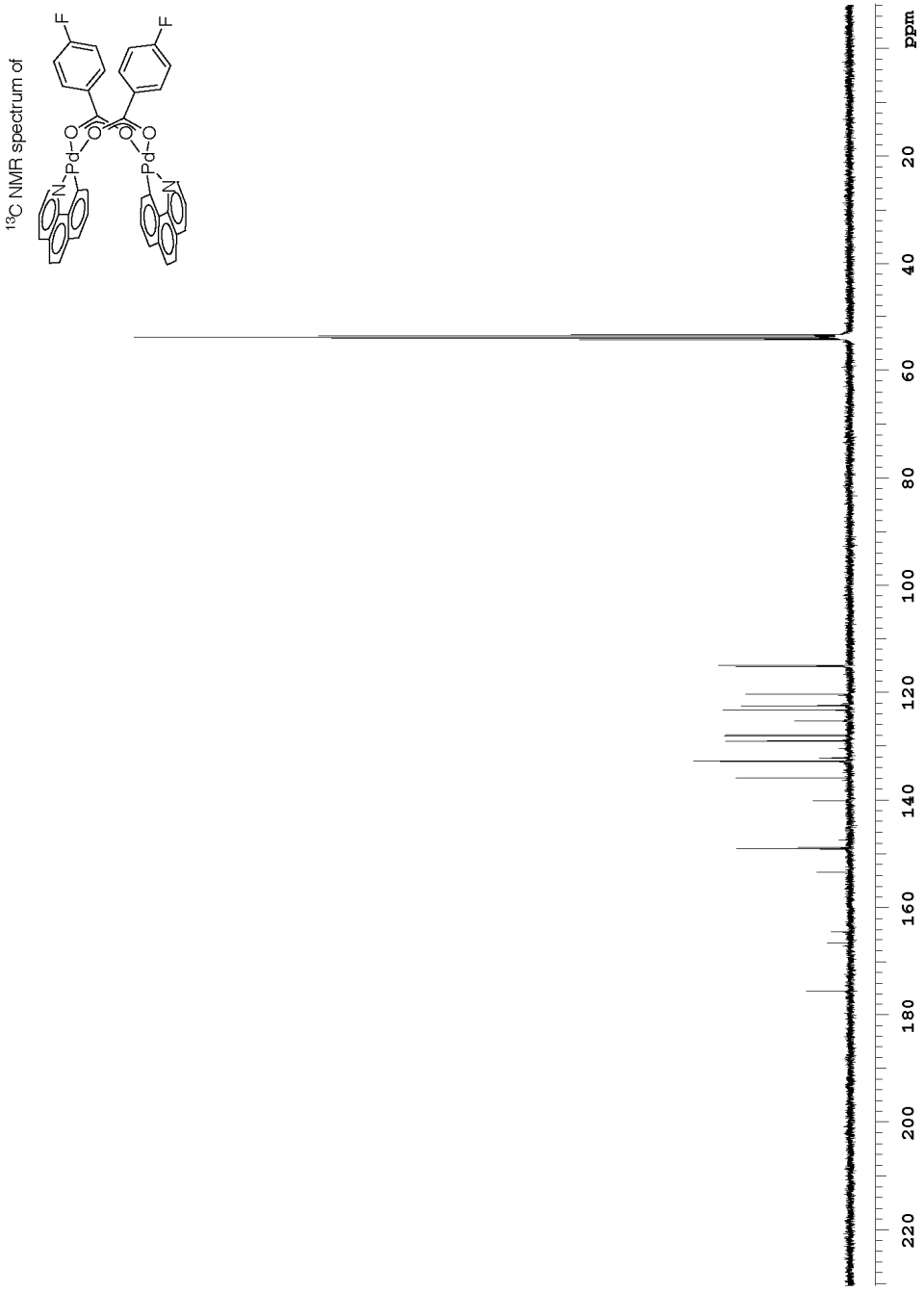
^{1}H NMR spectrum of **S18** in $CDCl_3$ at 23 °C.



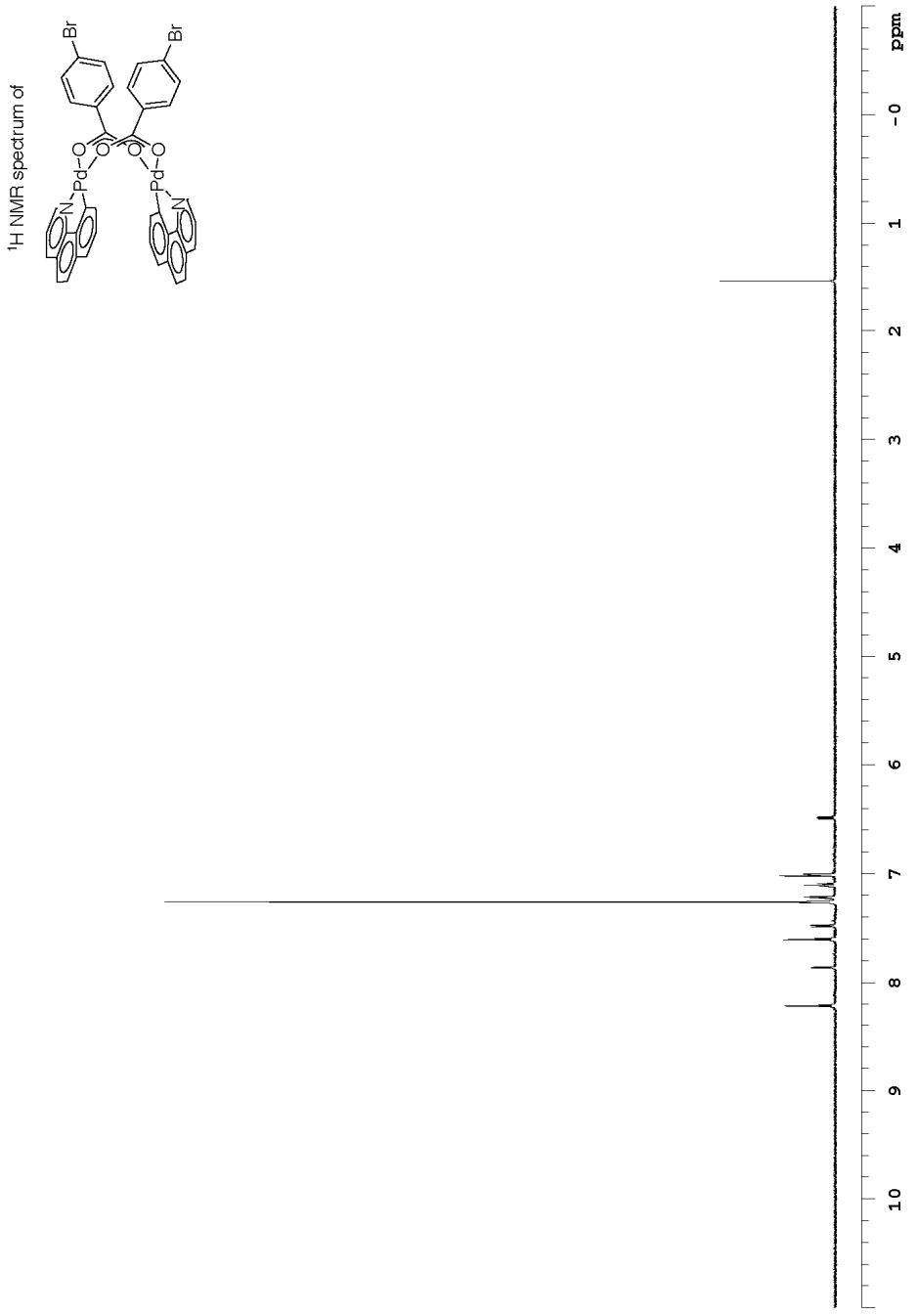
^{13}C NMR spectrum of **S18** in $CDCl_3$ at 23 °C.



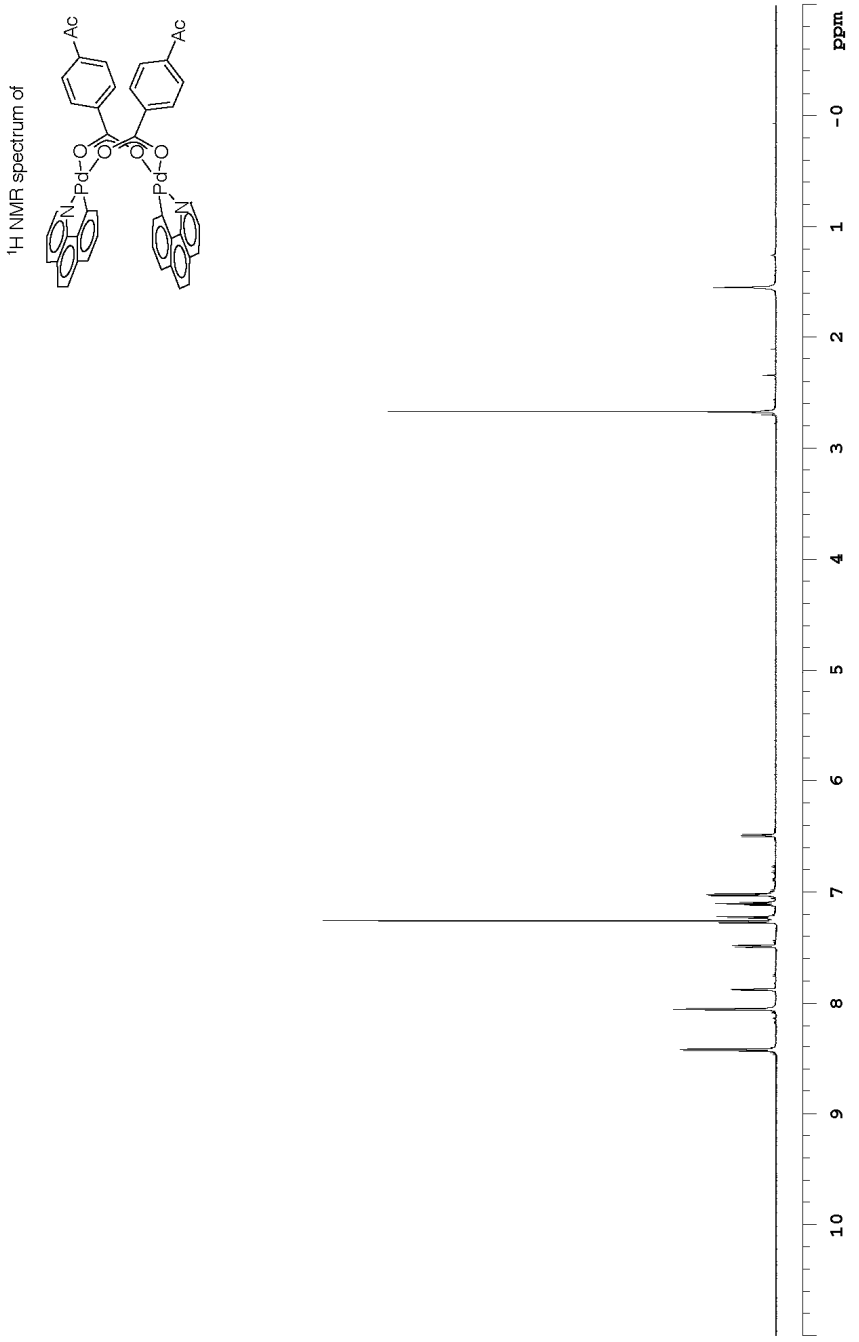
^{1}H NMR spectrum of **S19** in $CDCl_3$ at 23 °C.



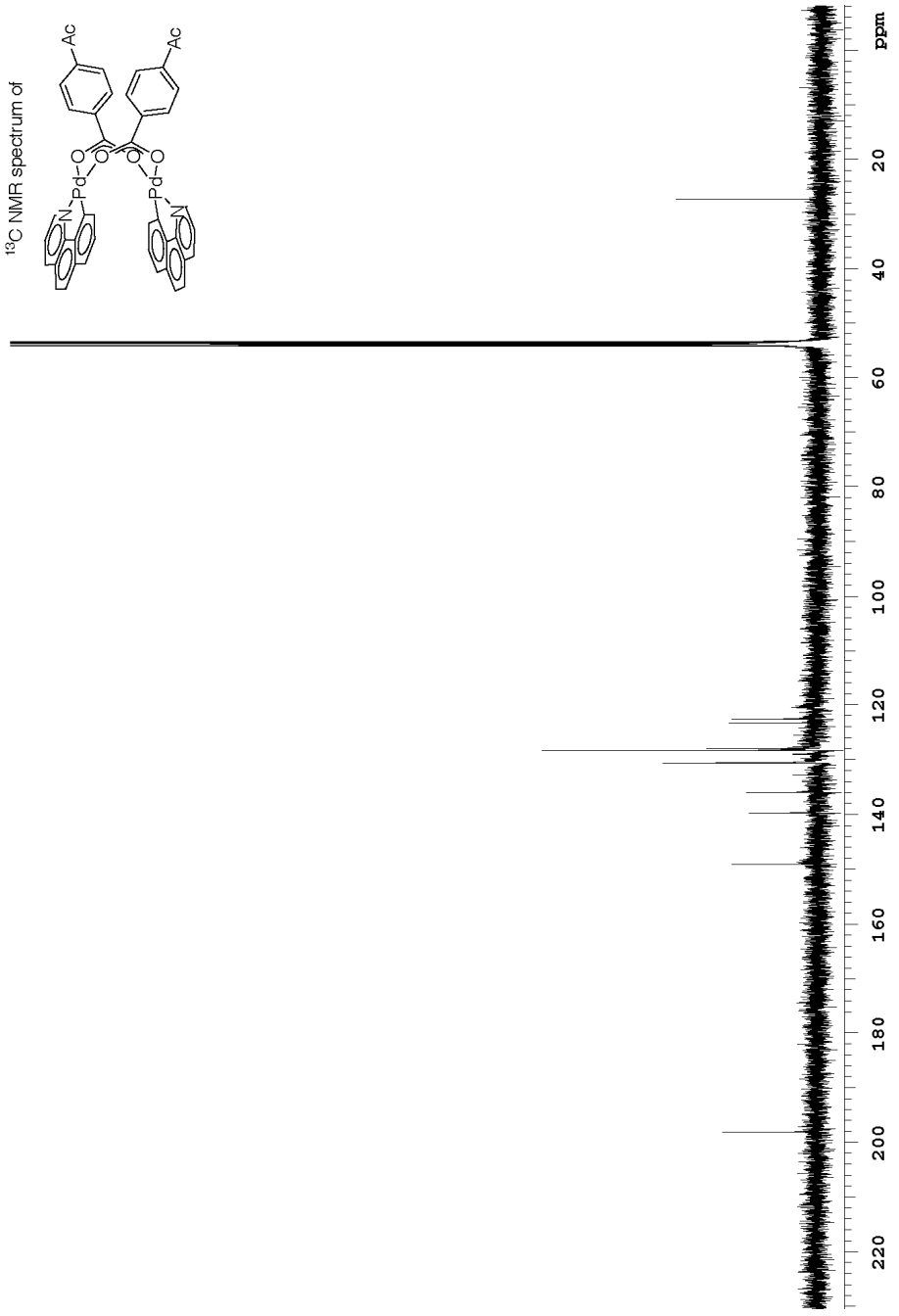
^{13}C NMR spectrum of **S19** in CD_2Cl_2 at 23 °C.



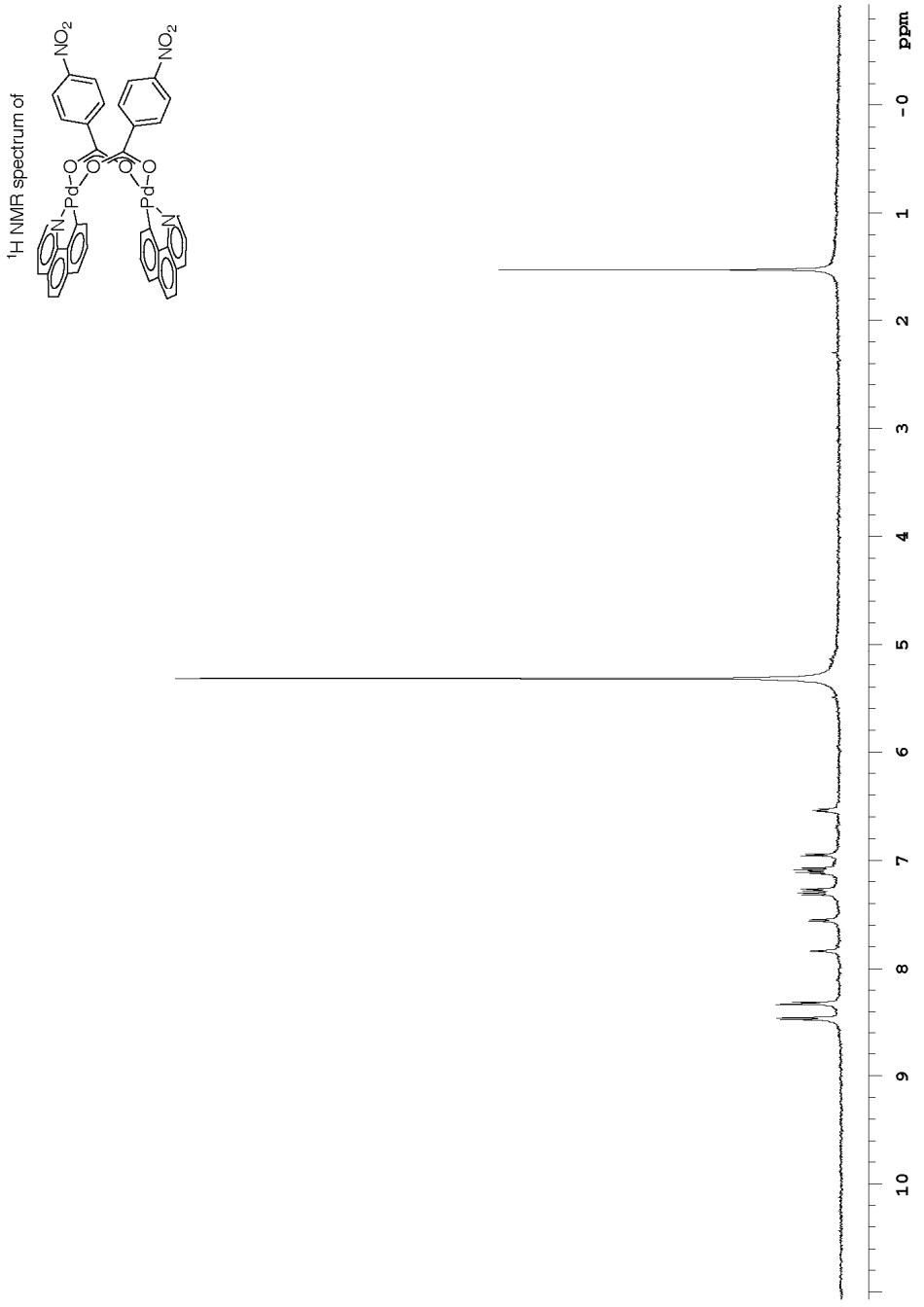
^{1}H NMR spectrum of **S20** in $CDCl_3$ at 23 °C.



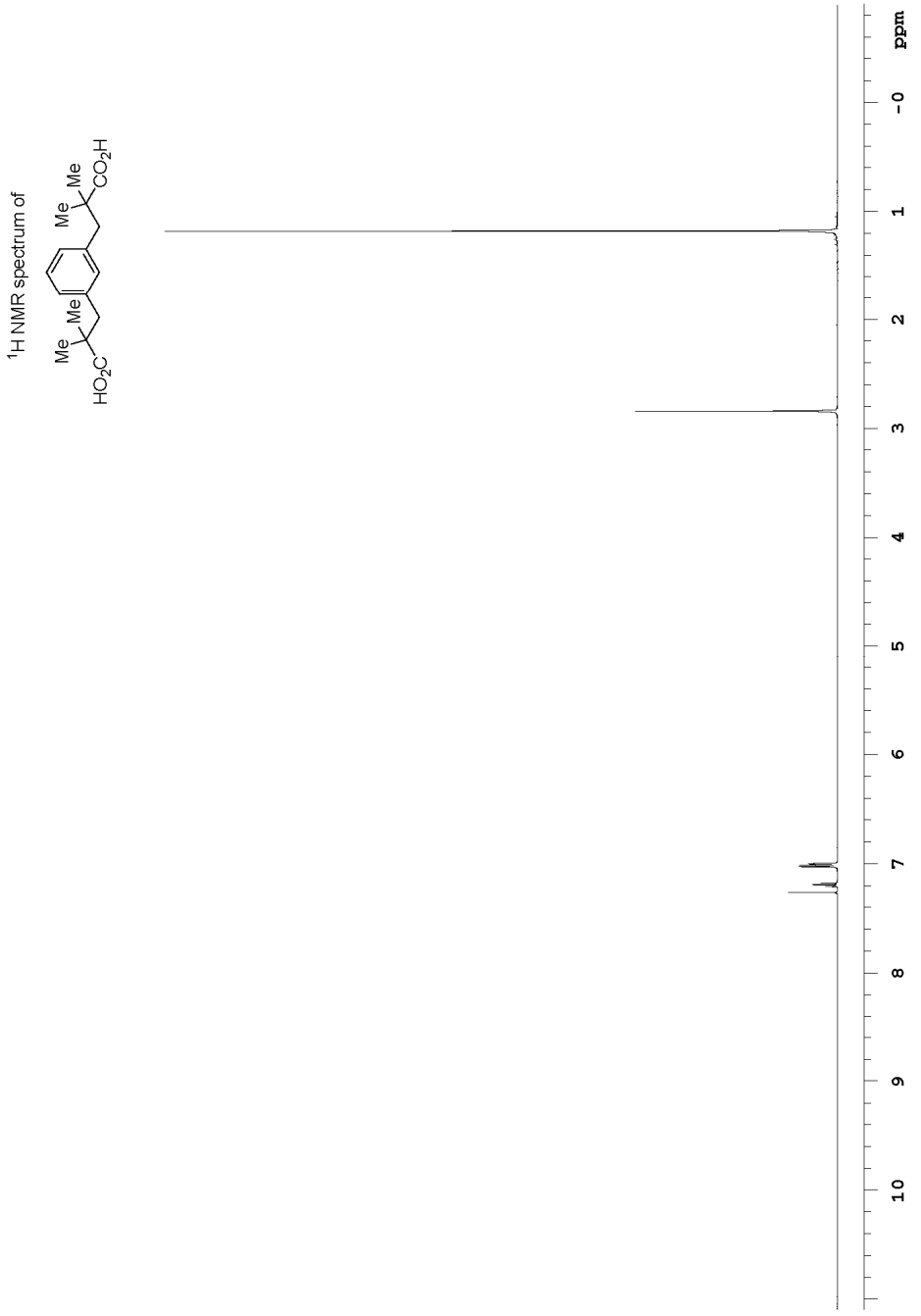
^{1}H NMR spectrum of **S21** in $CDCl_3$ at 23 °C.



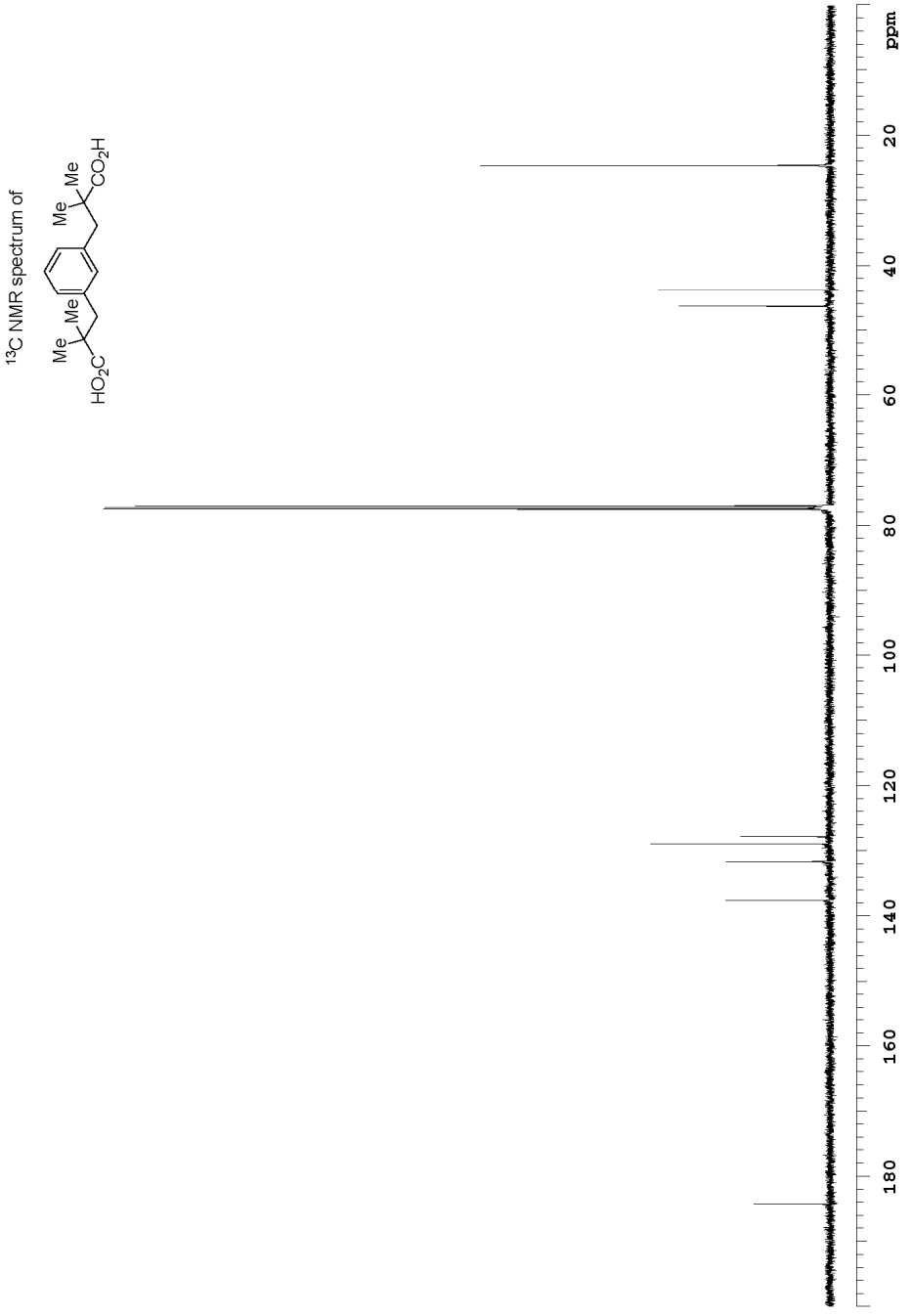
^{13}C NMR spectrum of **S21** in CD_2Cl_2 at 23 °C.



^{1}H NMR spectrum of **S22** in CD_2Cl_2 at 23 °C.



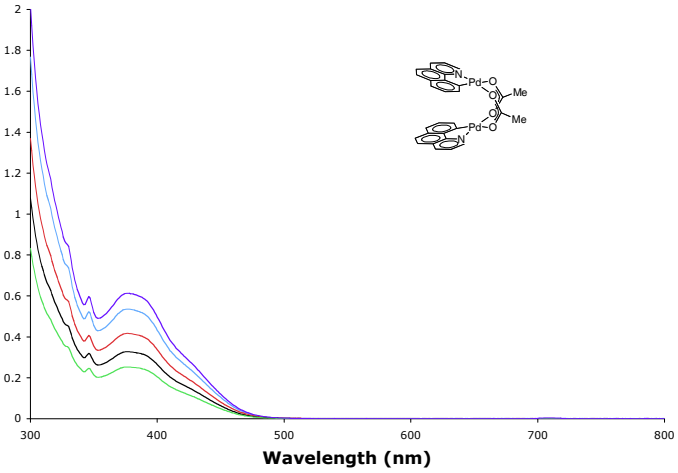
^{1}H NMR spectrum of **S26** in $CDCl_3$ at 23 °C.



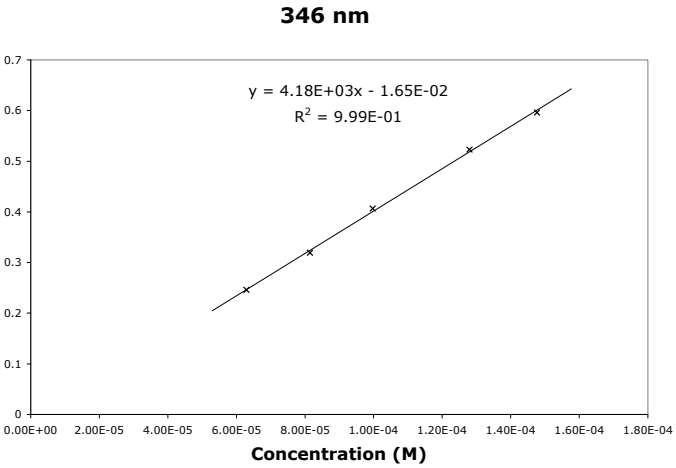
^{13}C NMR spectrum of **S26** in $CDCl_3$ at 23 °C.

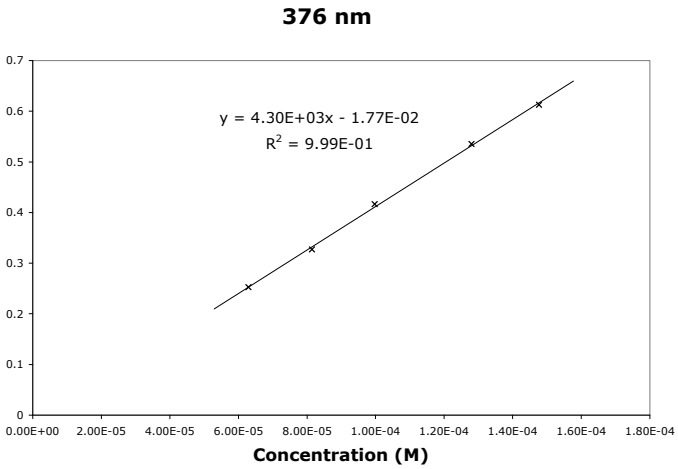
Appendix B: UV vis Data

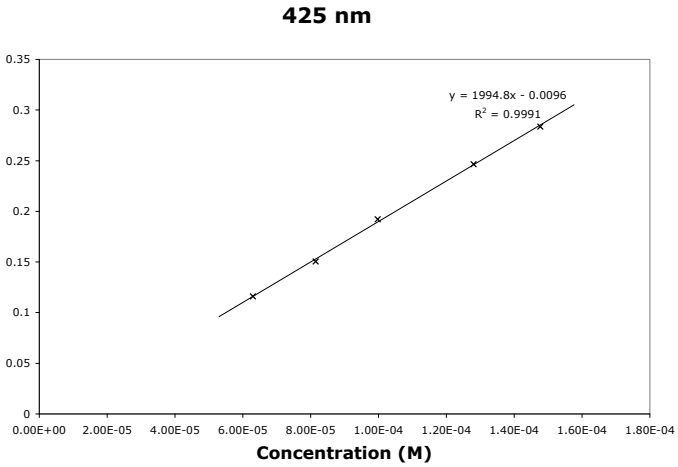
UV-VIS Spectrum of **9**



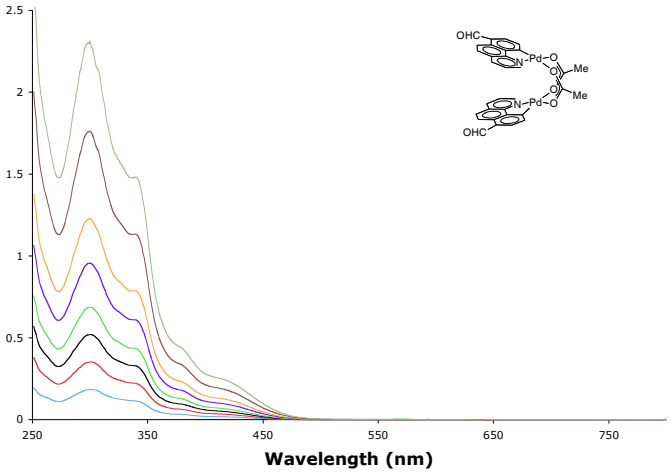
Molar Absorptivity Determinations





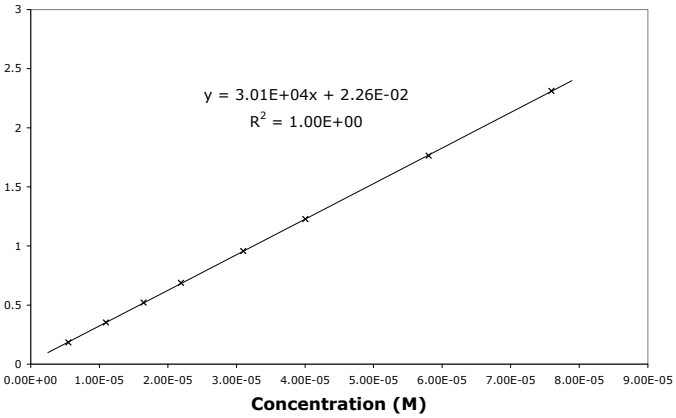


UV-VIS Spectrum of **S14**

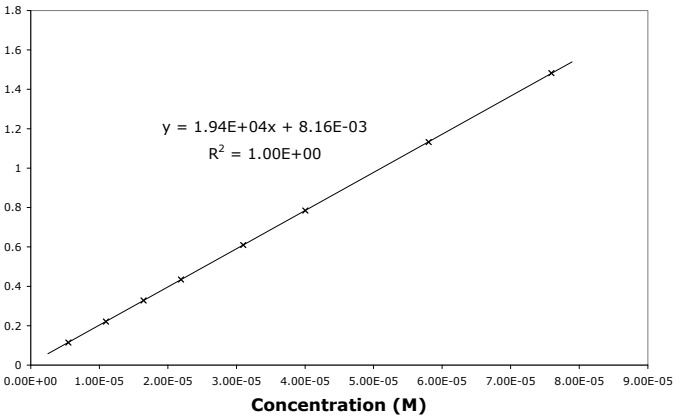


Molar Absorptivity Determinations

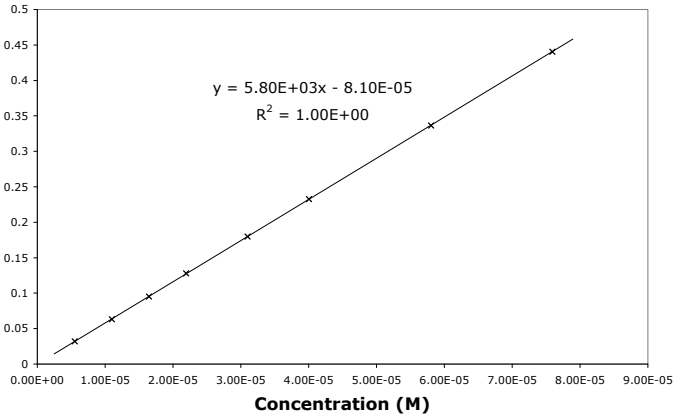
300 nm

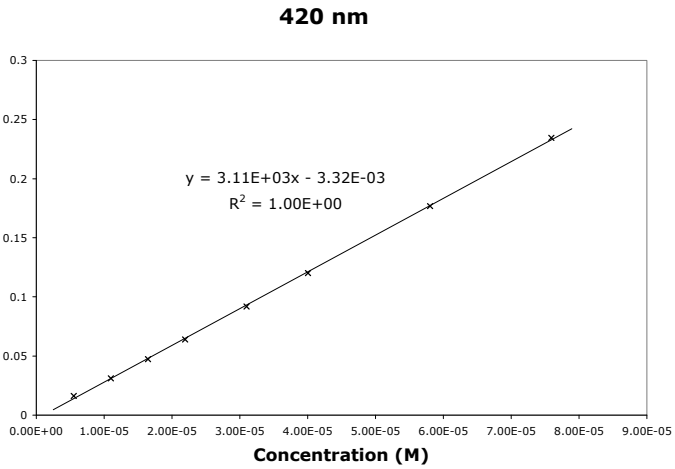


340 nm

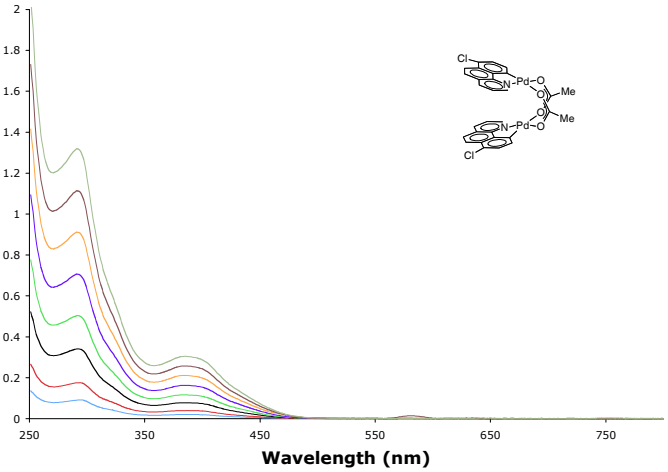


379 nm

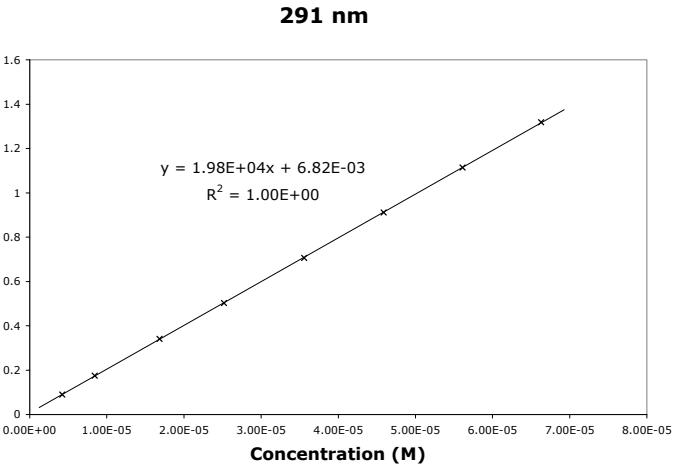


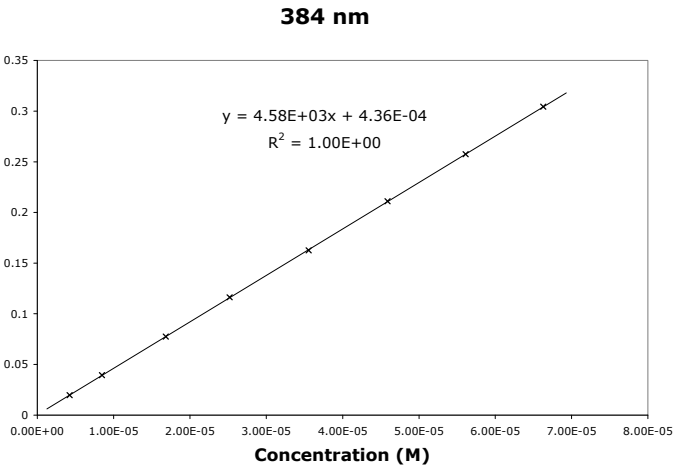


UV VIS Spectrum of **S15**

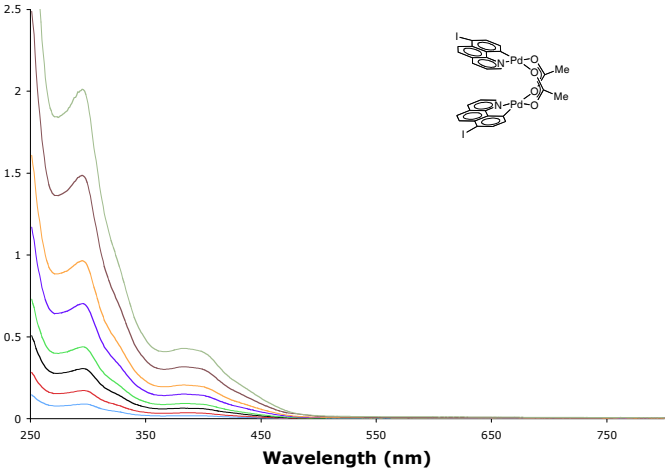


Molar Absorptivity Determinations

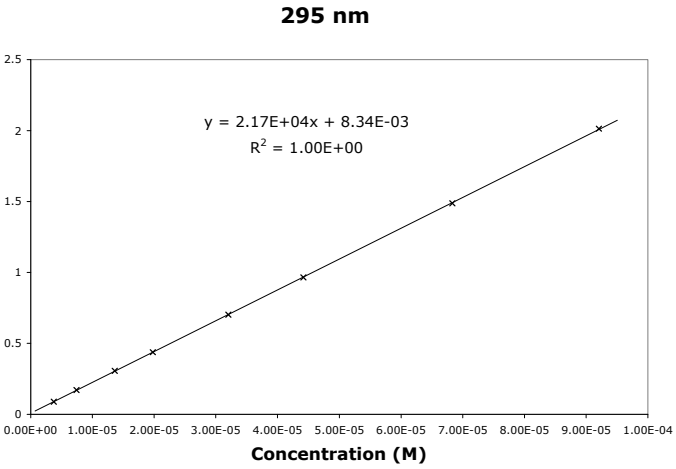


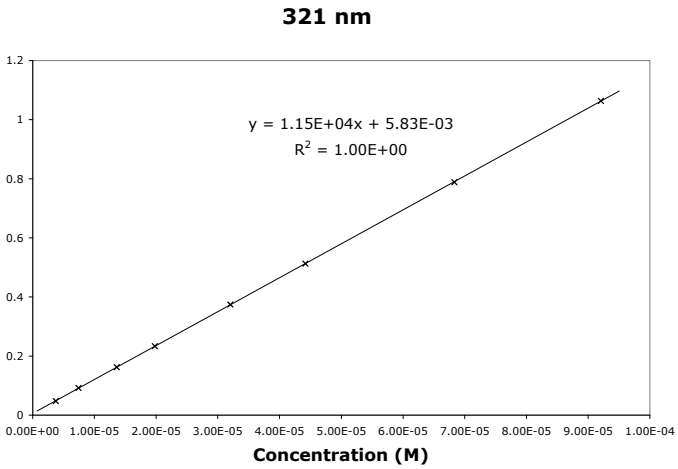


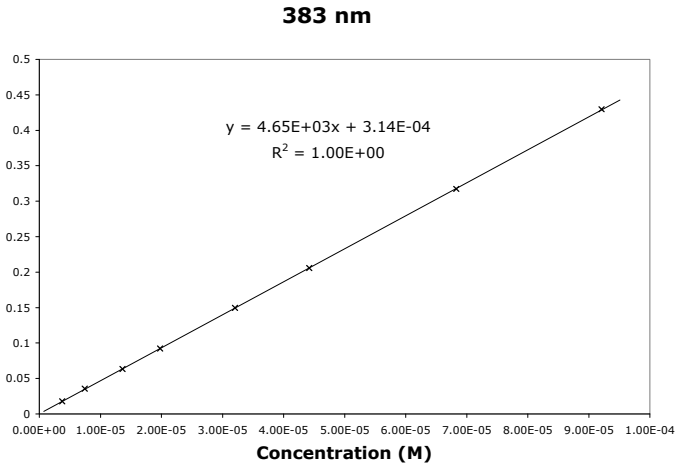
UV VIS Spectrum of **S16**



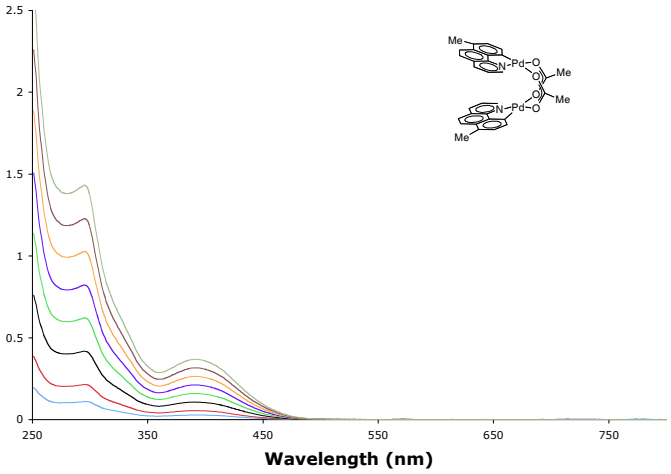
Molar Absorptivity Determinations



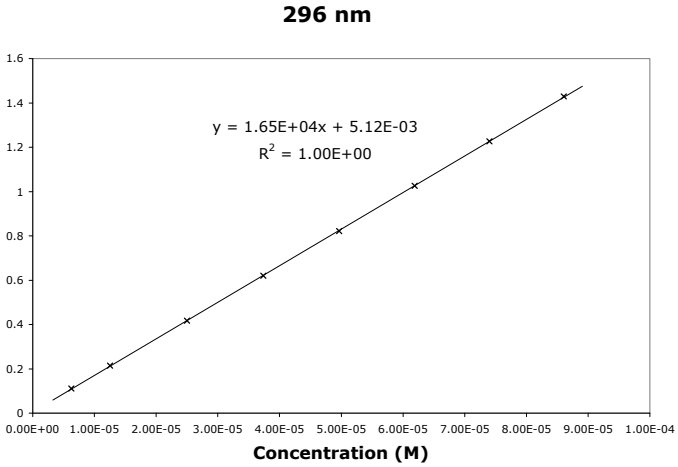


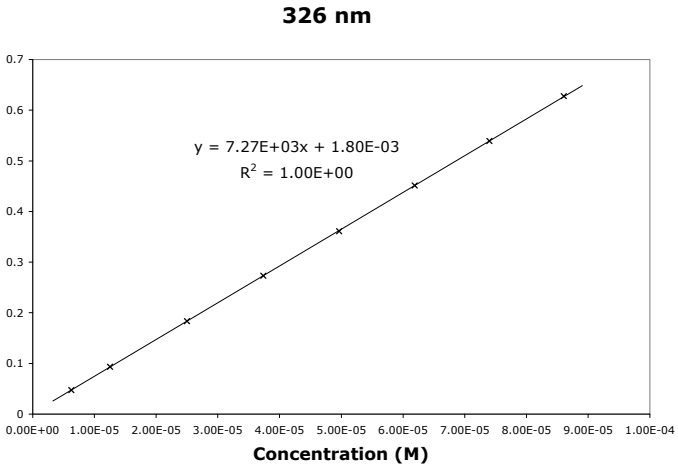


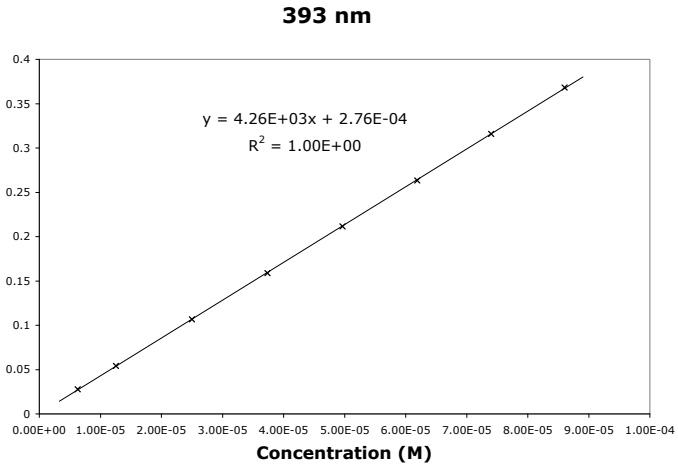
UV VIS Spectrum of **S17**



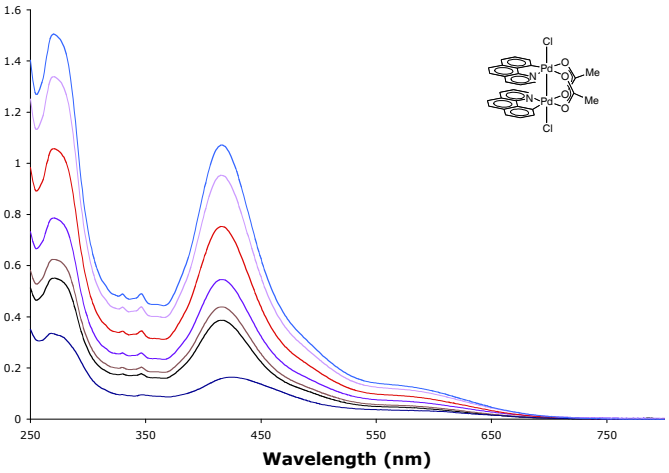
Molar Absorptivity Determinations



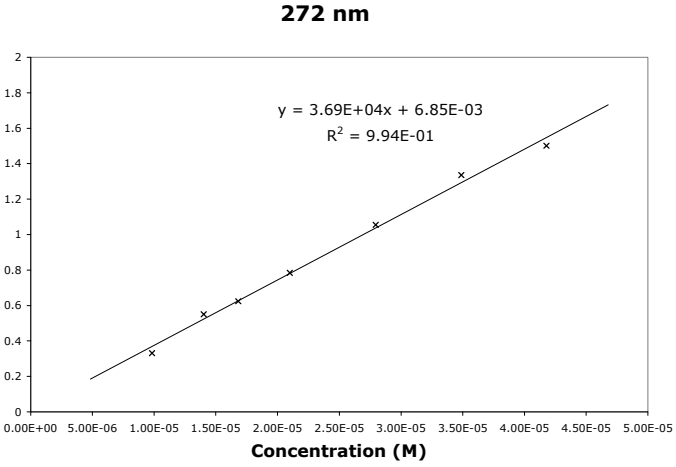


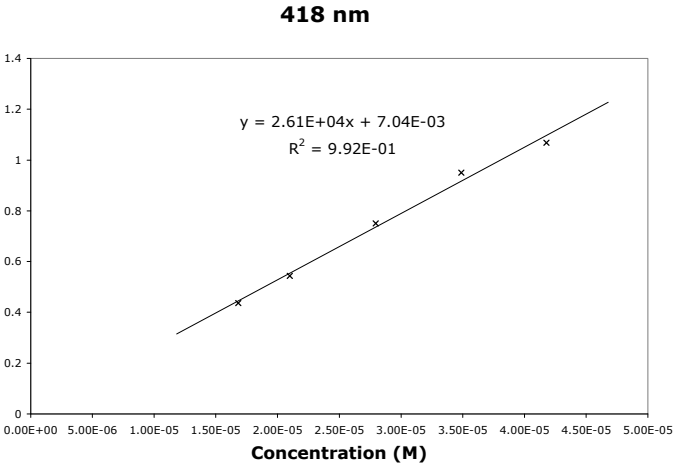


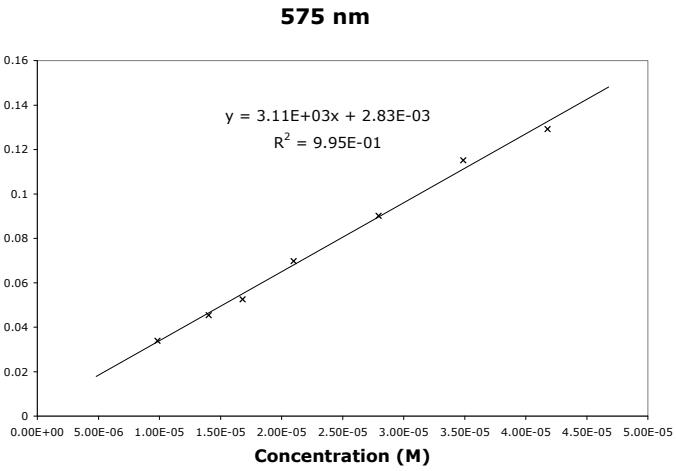
UV VIS Spectrum of **1** (**18a**)



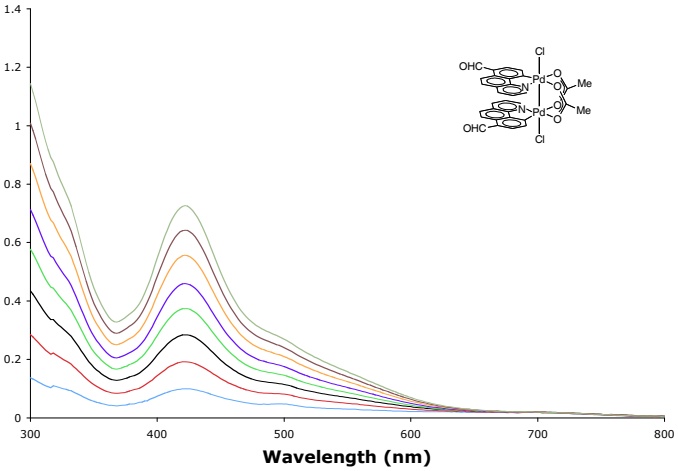
Molar Absorptivity Determinations



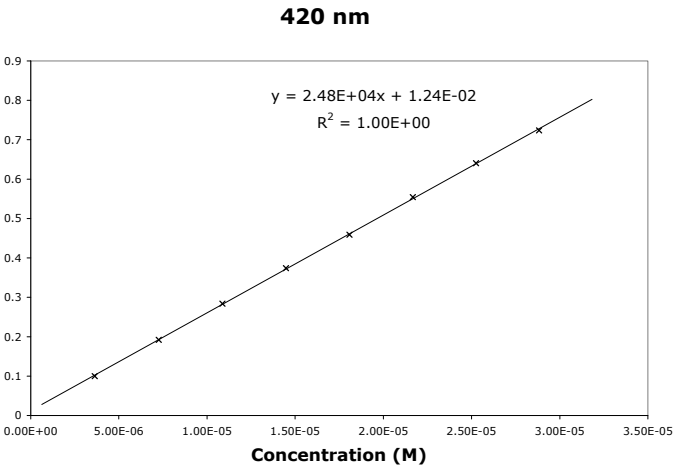


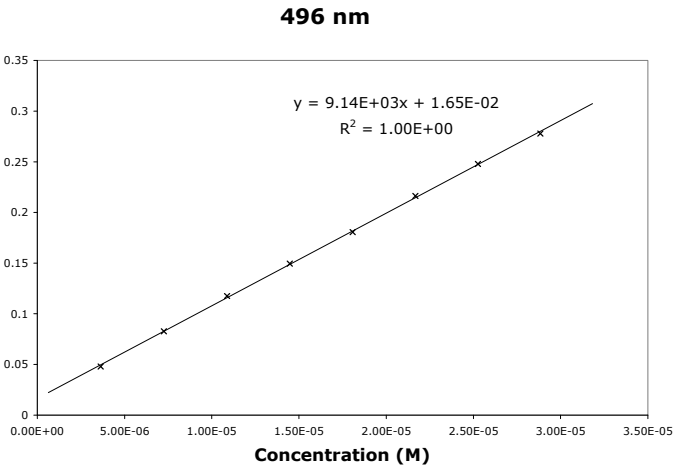


UV VIS Spectrum of **18b**

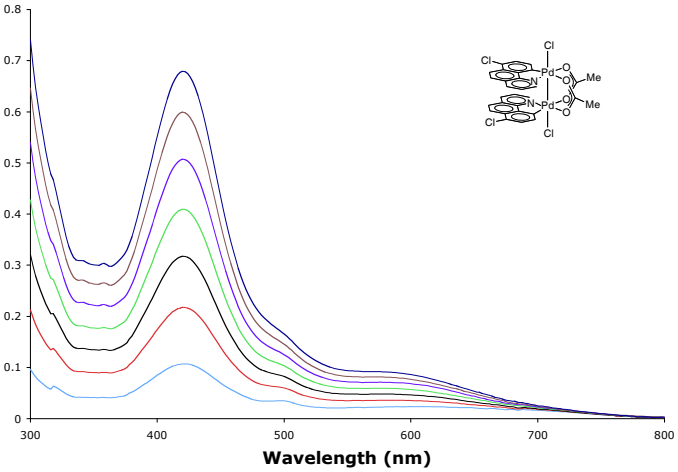


Molar Absorptivity Determinations

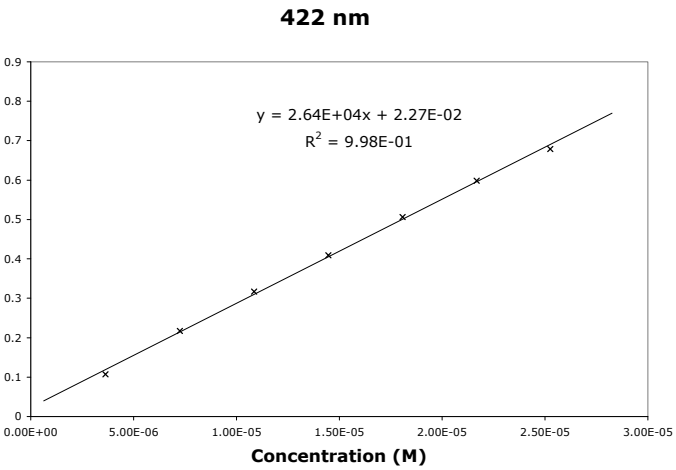


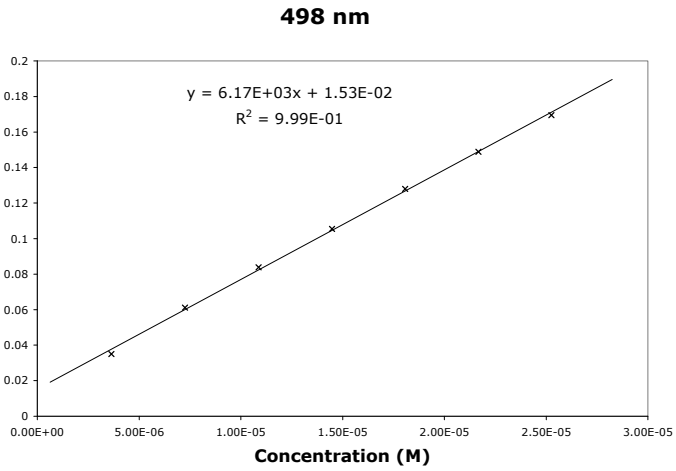


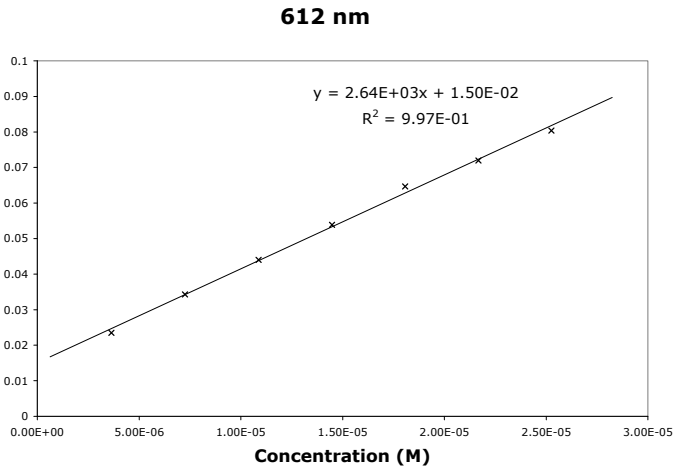
UV VIS Spectrum of **18c**



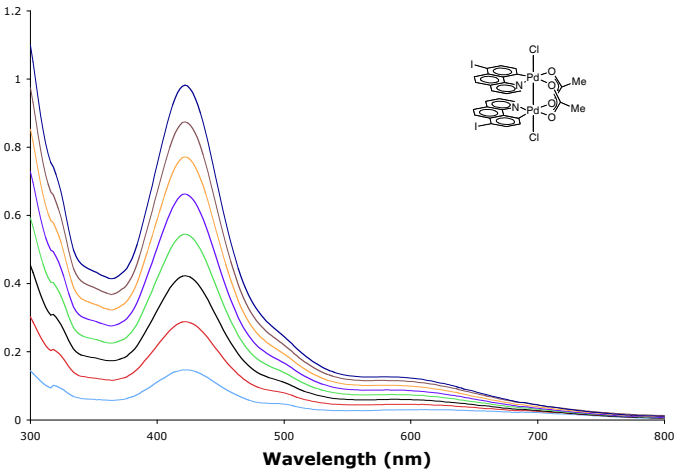
Molar Absorptivity Determinations





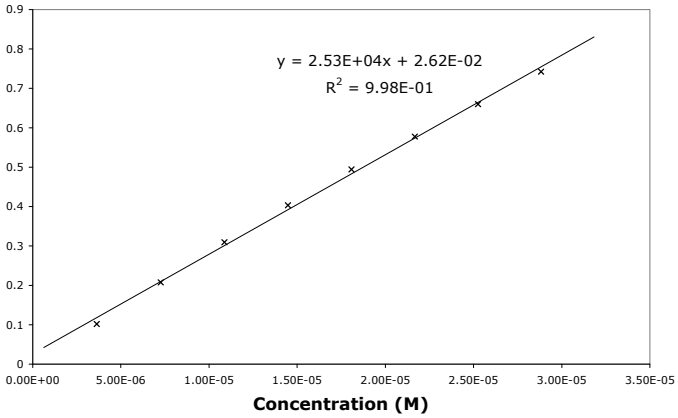


UV VIS Spectrum of **18d**

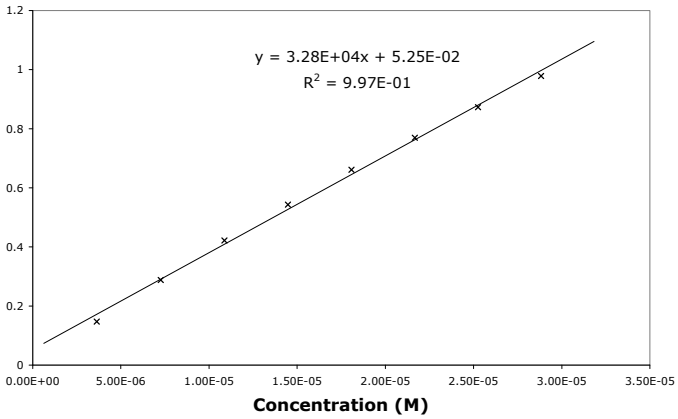


Molar Absorptivity Determinations

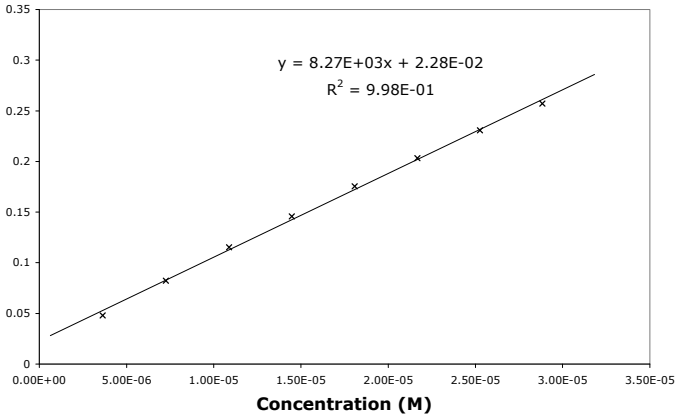
318 nm

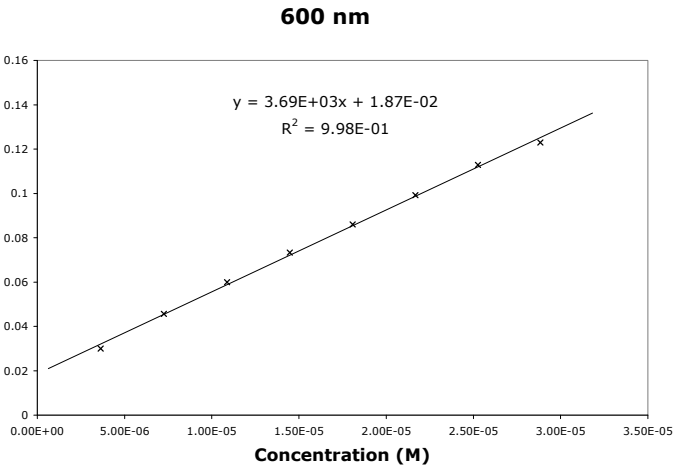


420 nm

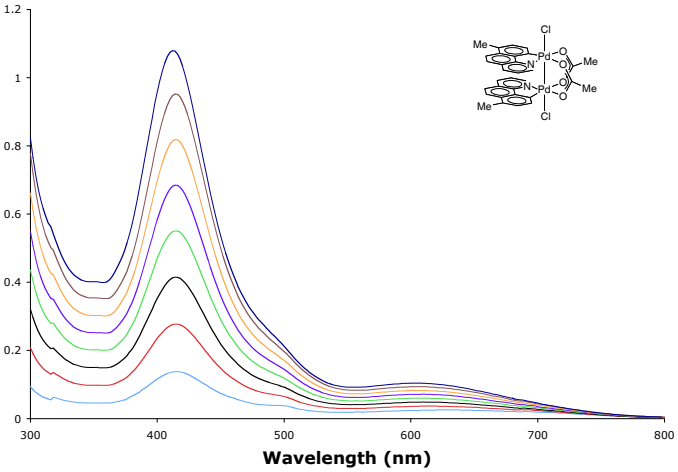


496 nm

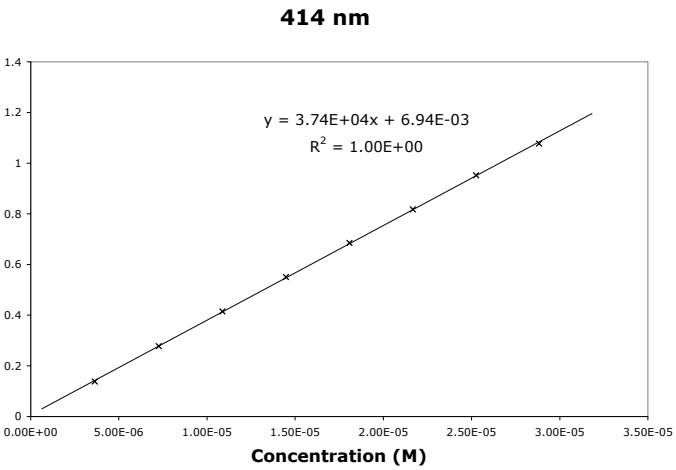


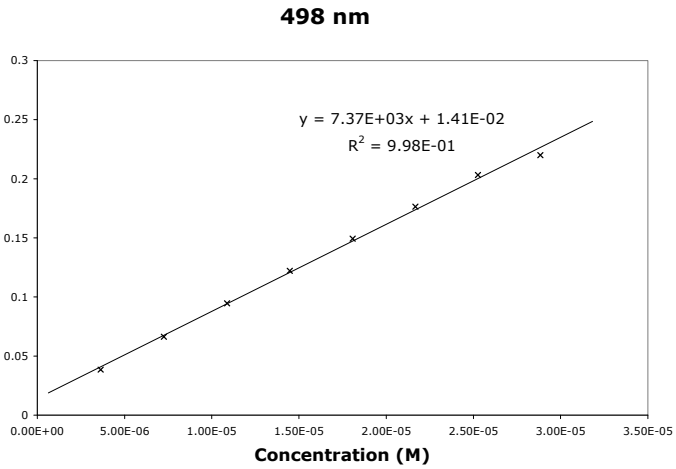


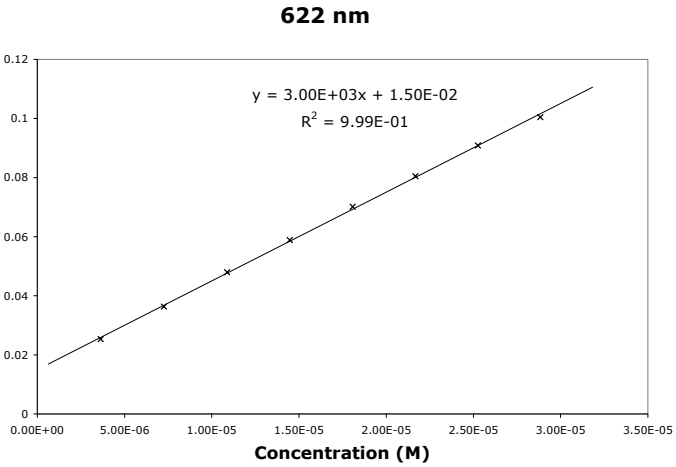
UV VIS Spectrum of **18e**



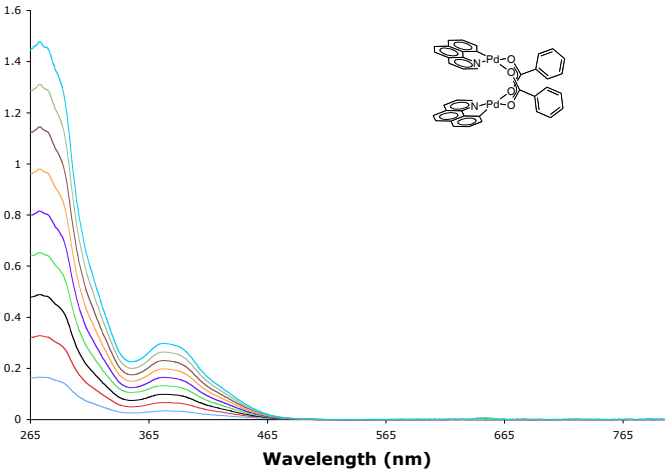
Molar Absorptivity Determinations



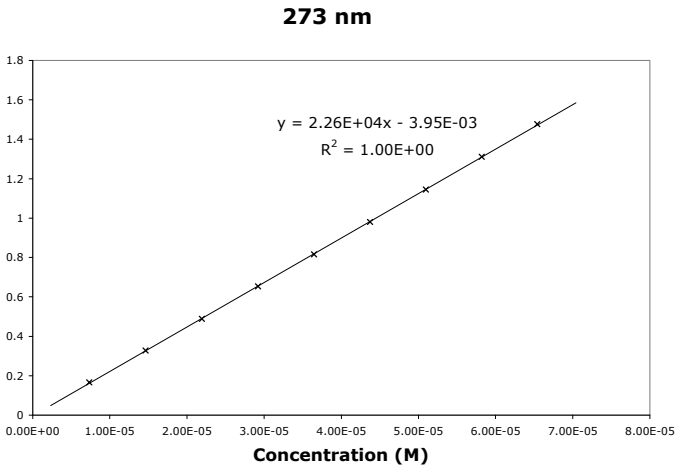


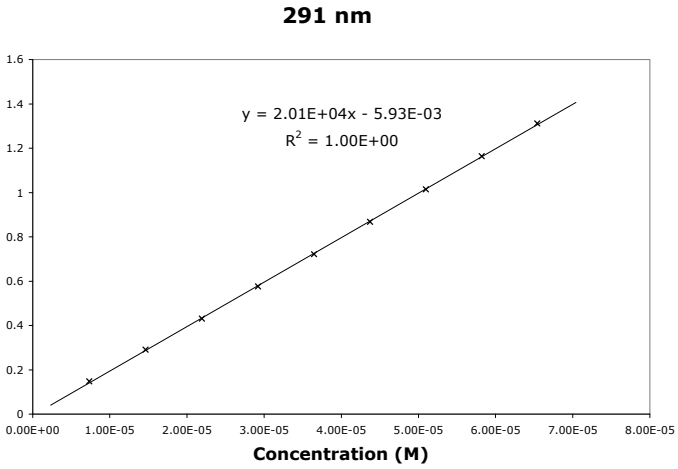


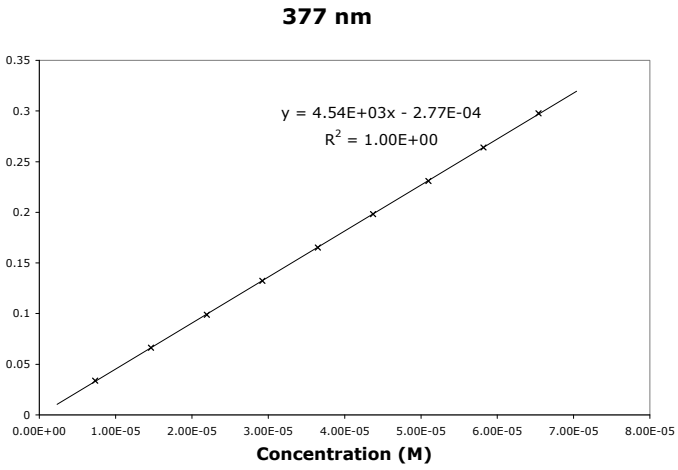
UV VIS Spectrum of **S18**



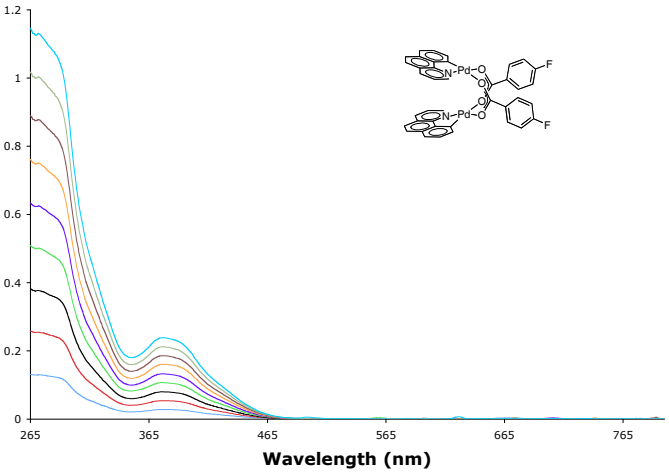
Molar Absorptivity Determinations



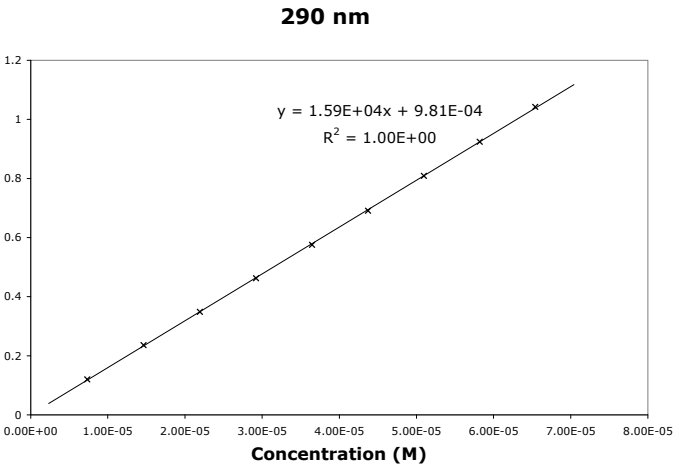


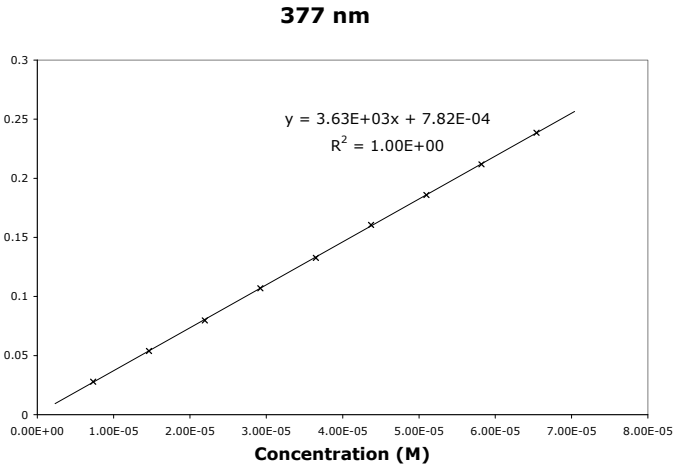


UV VIS Spectrum of **S19**

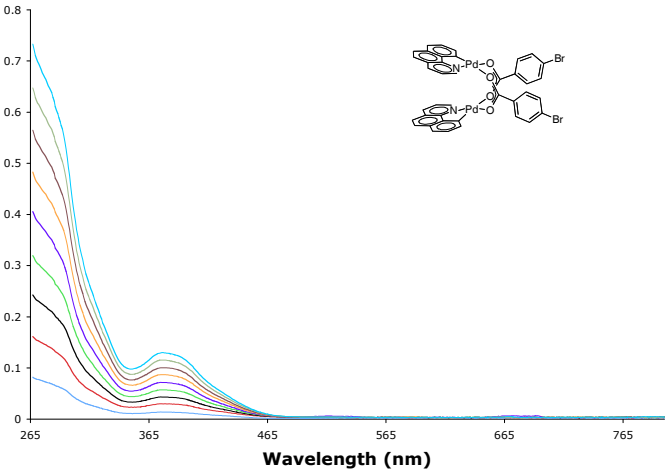


Molar Absorptivity Determinations

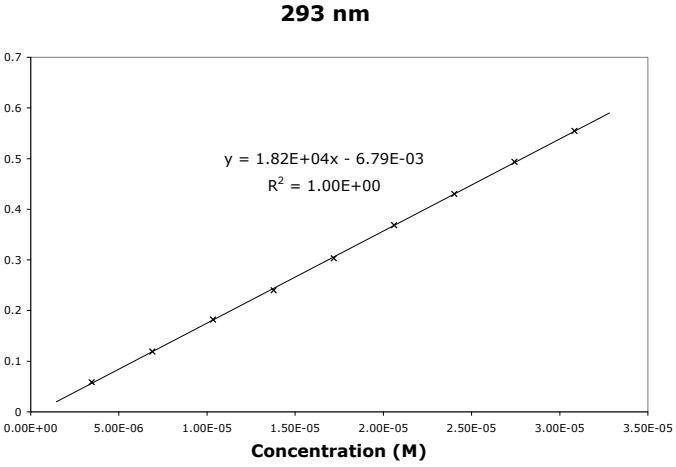


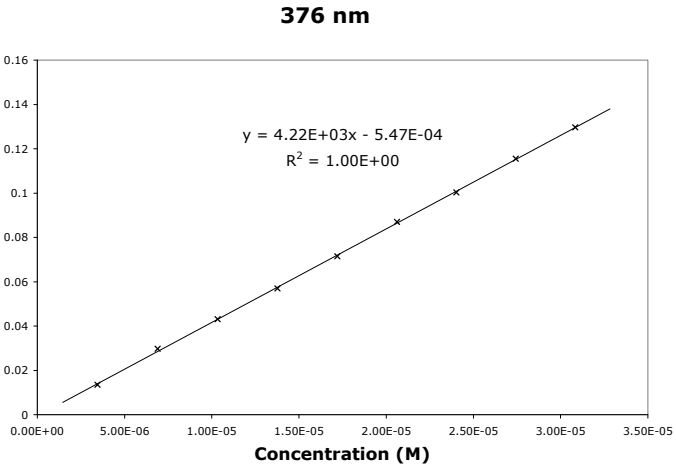


UV VIS Spectrum of **S20**

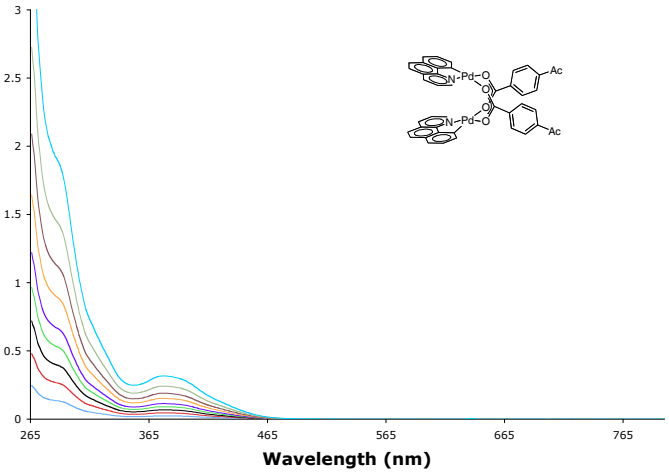


Molar Absorptivity Determinations

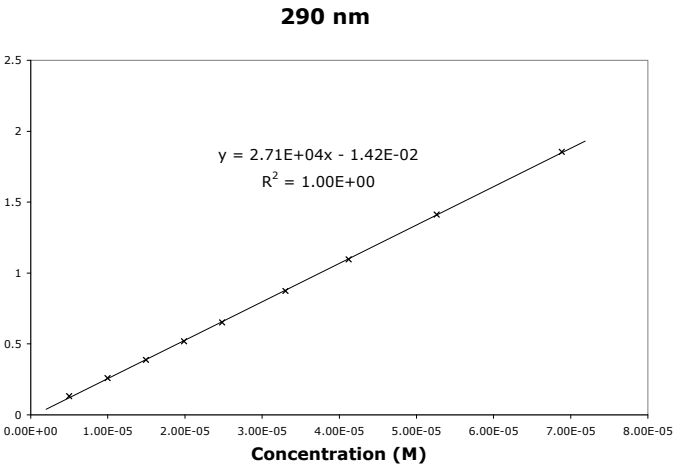


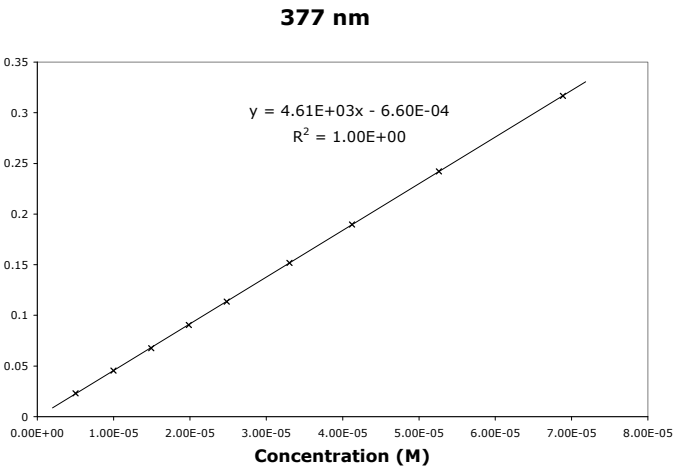


UV VIS Spectrum of **S21**

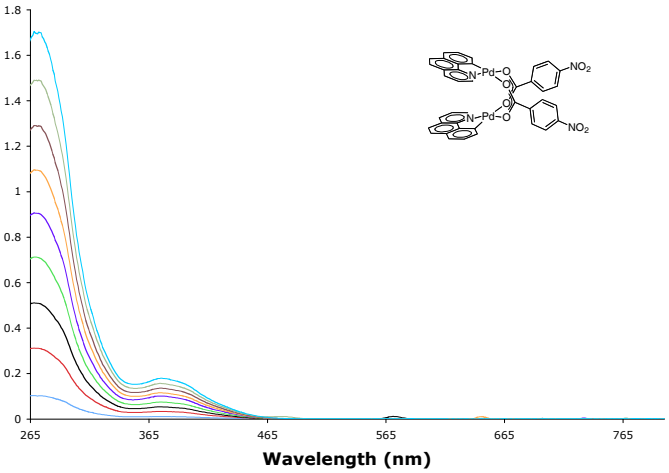


Molar Absorptivity Determinations

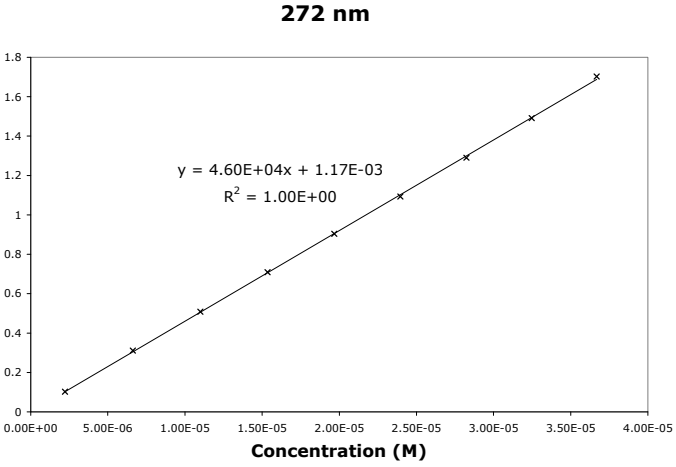


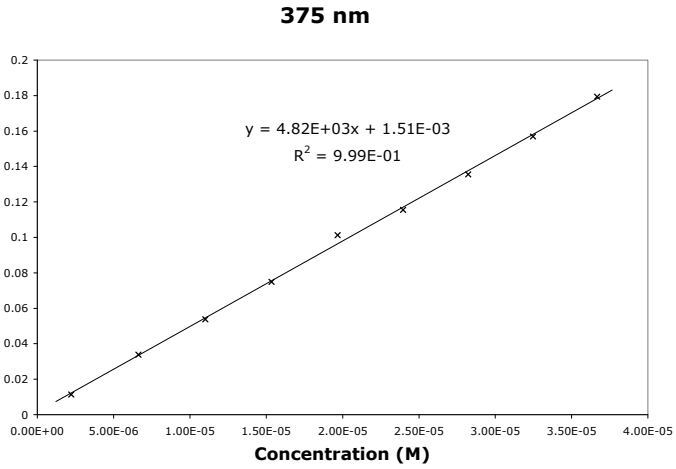


UV VIS Spectrum of **S22**

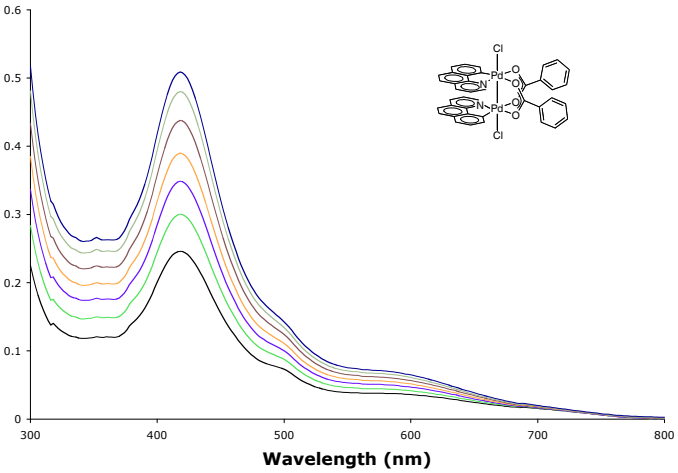


Molar Absorptivity Determinations

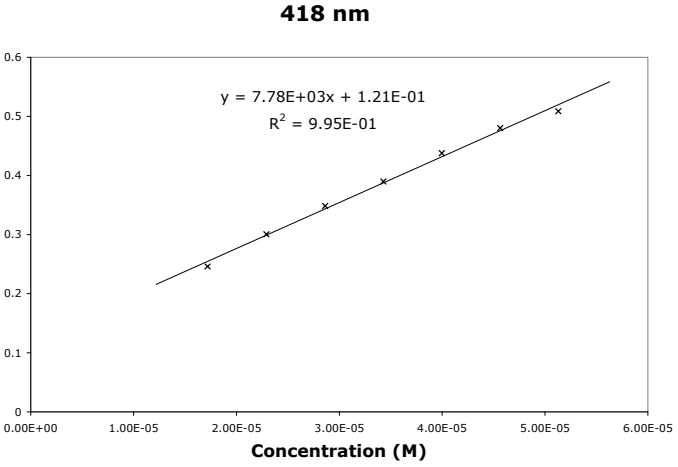


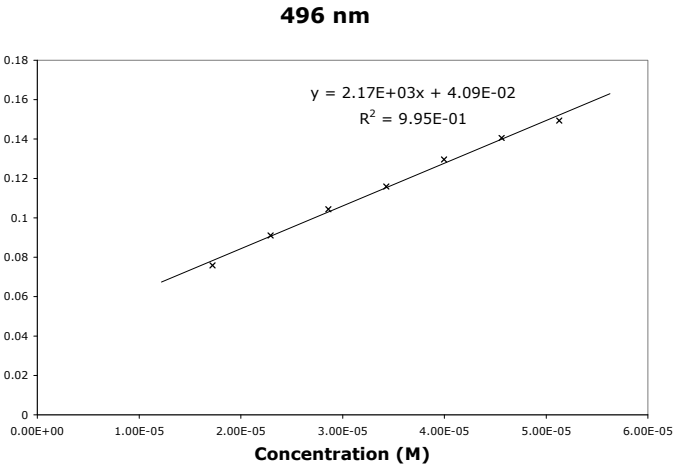


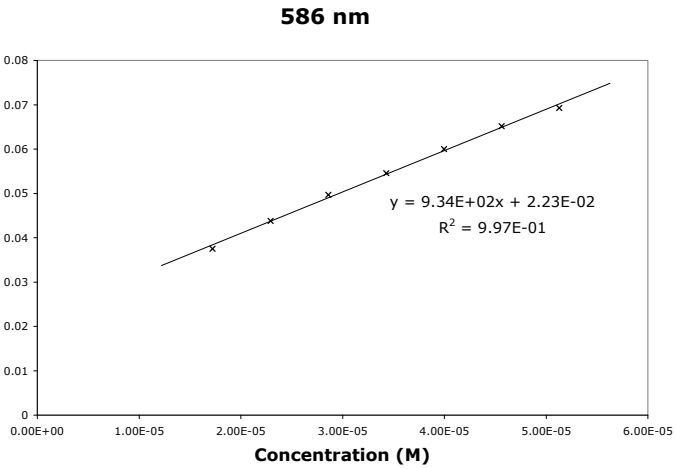
UV VIS Spectrum of **20a**



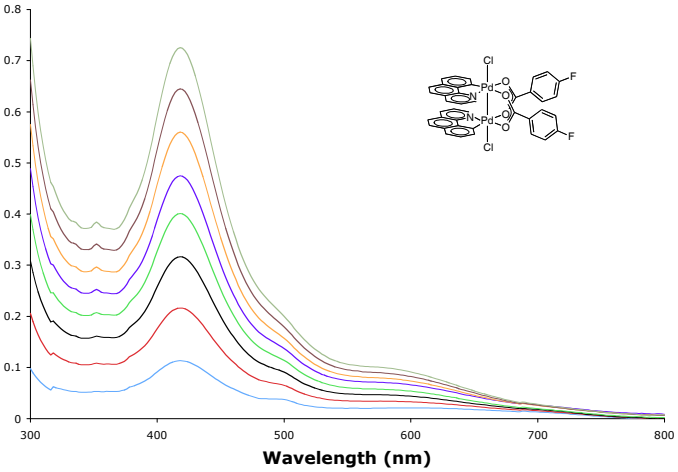
Molar Absorptivity Determinations



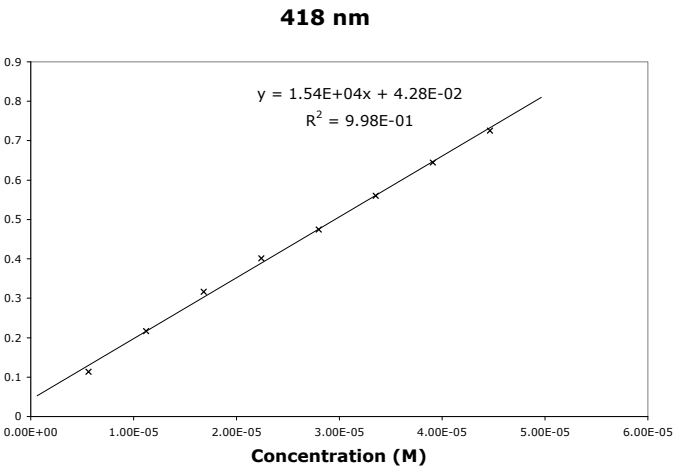


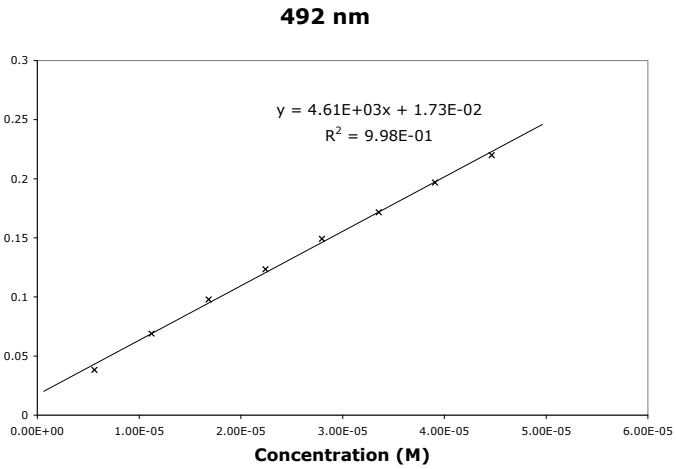


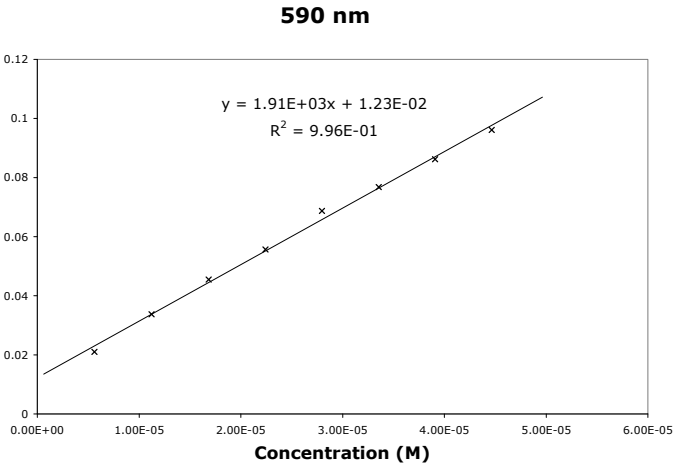
UV VIS Spectrum of **20b**



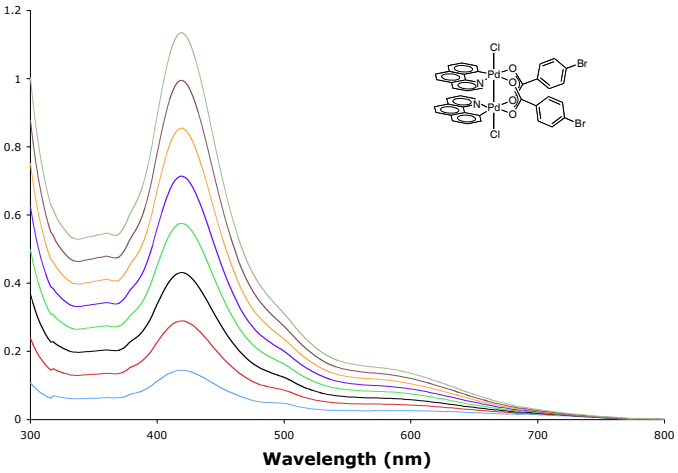
Molar Absorptivity Determinations



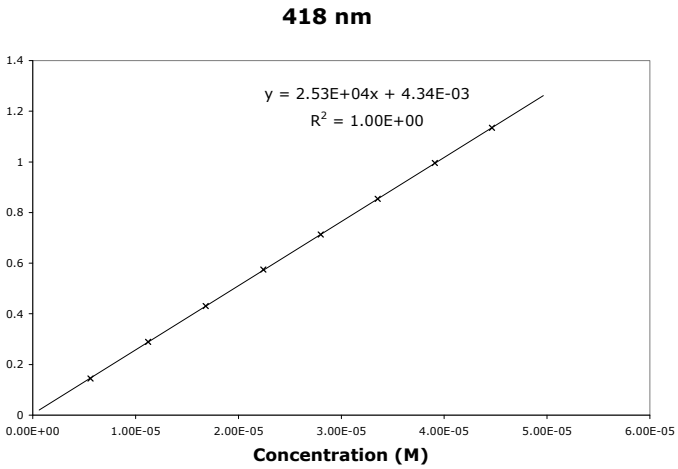


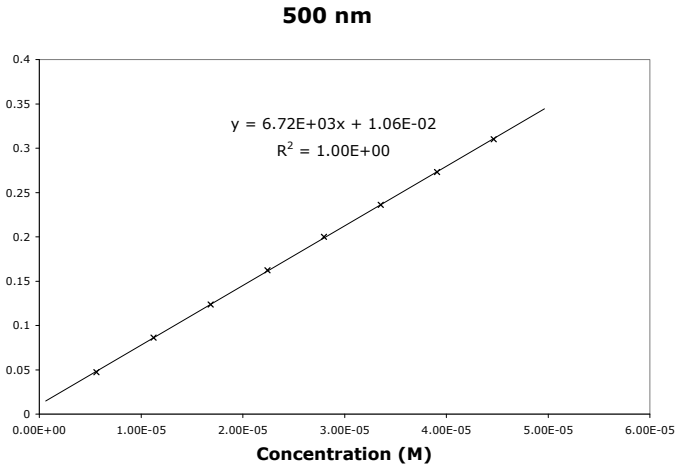


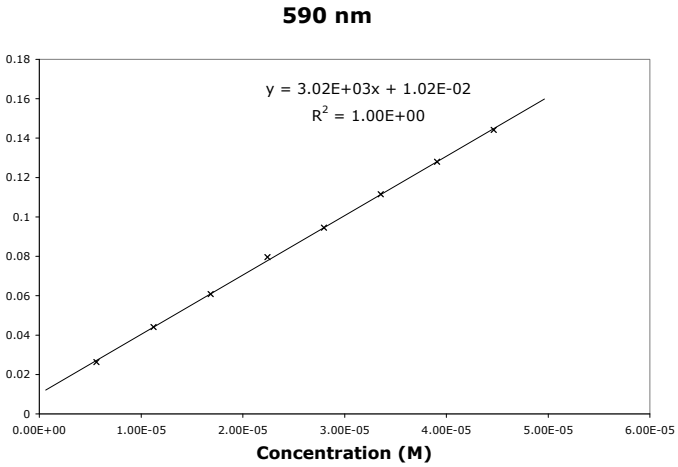
UV VIS Spectrum of **20c**



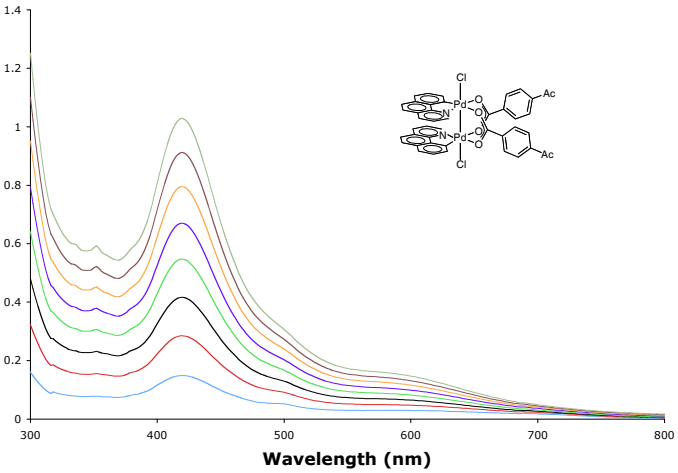
Molar Absorptivity Determinations





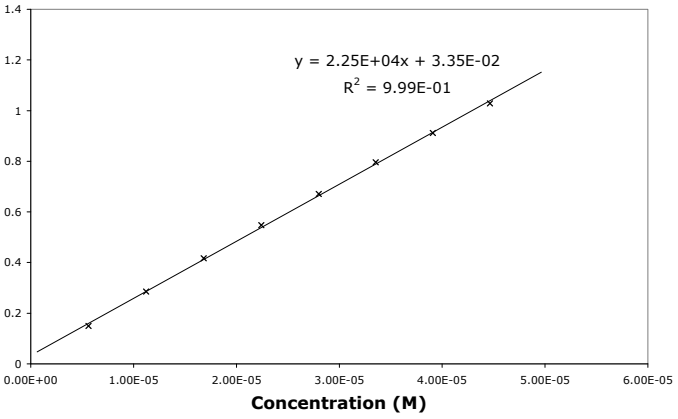


UV VIS Spectrum of **20d**

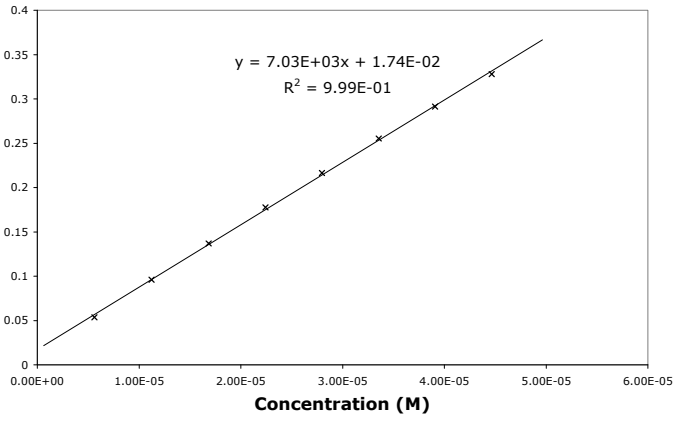


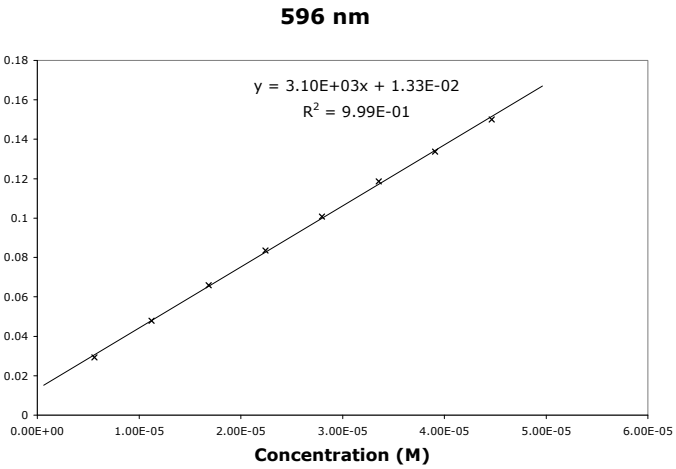
Molar Absorptivity Determinations

420 nm

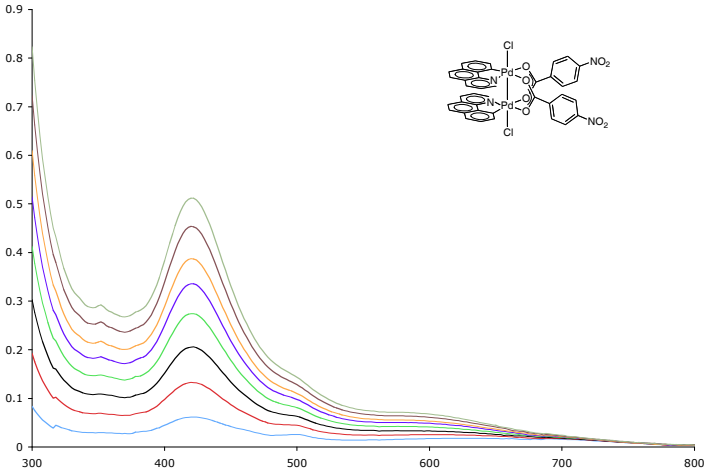


494 nm

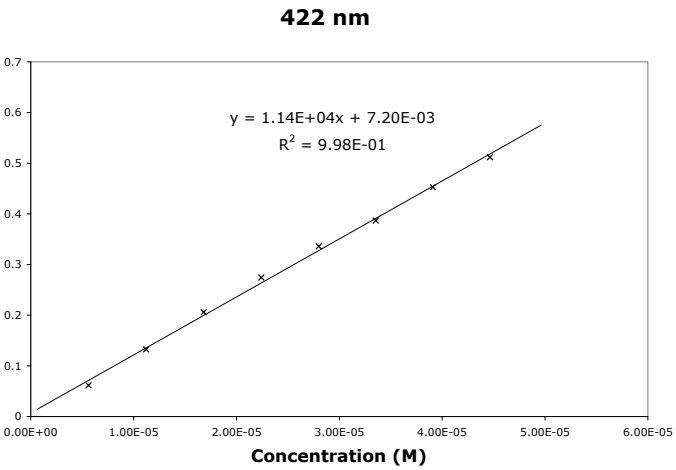


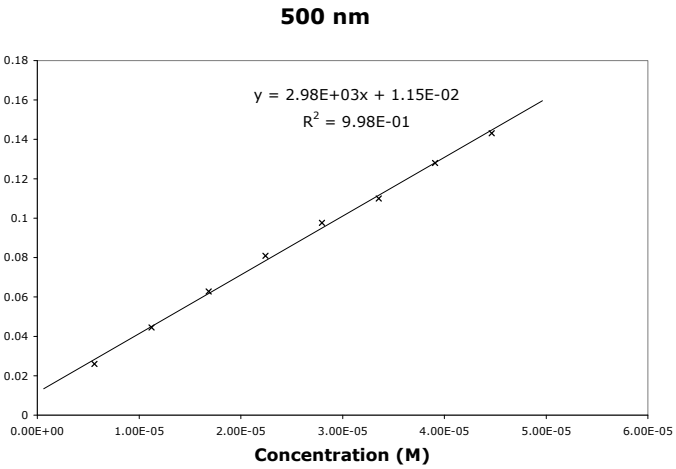


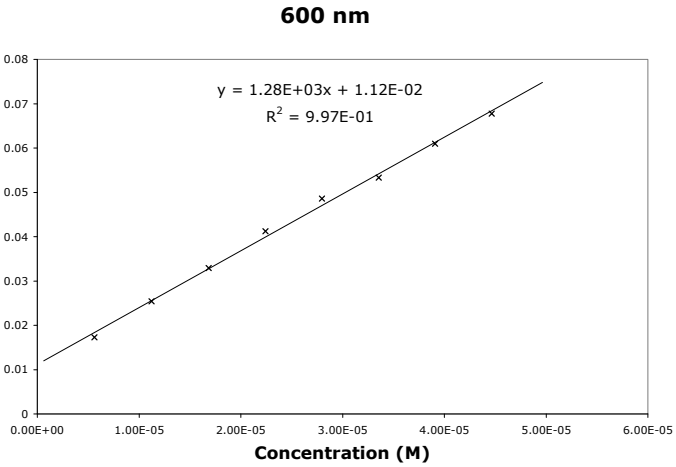
UV VIS Spectrum of **20e**



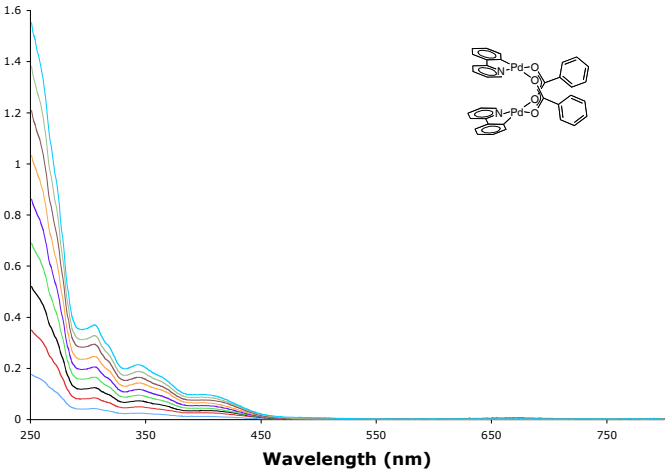
Molar Absorptivity Determinations





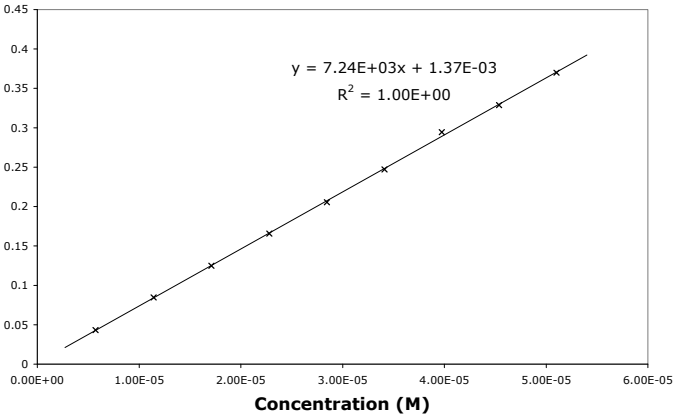


UV VIS Spectrum of **21**

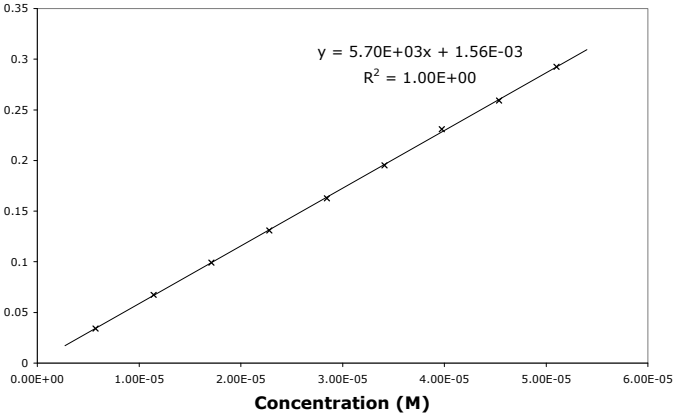


Molar Absorptivity Determinations

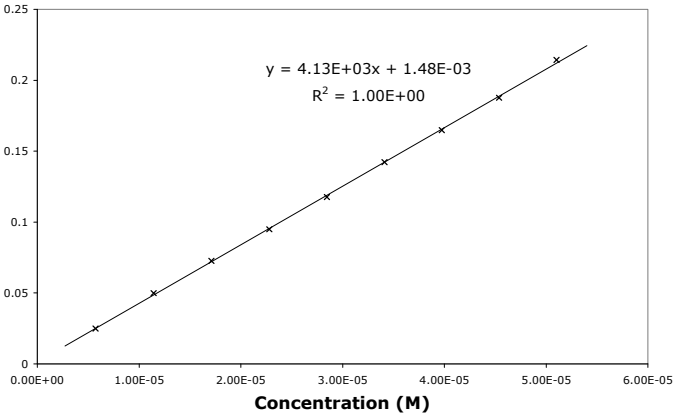
306 nm

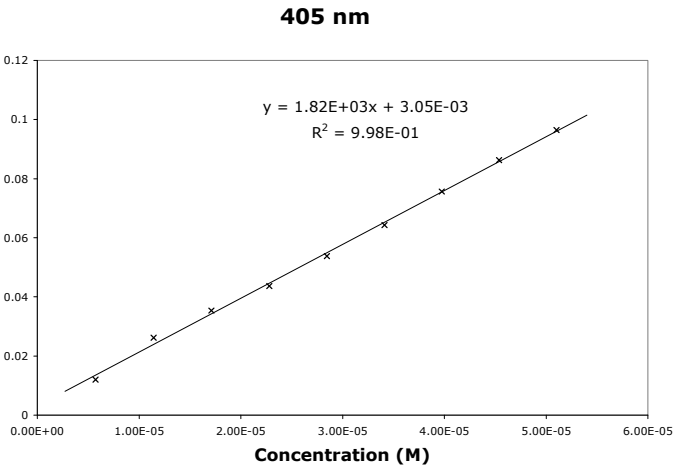


317 nm

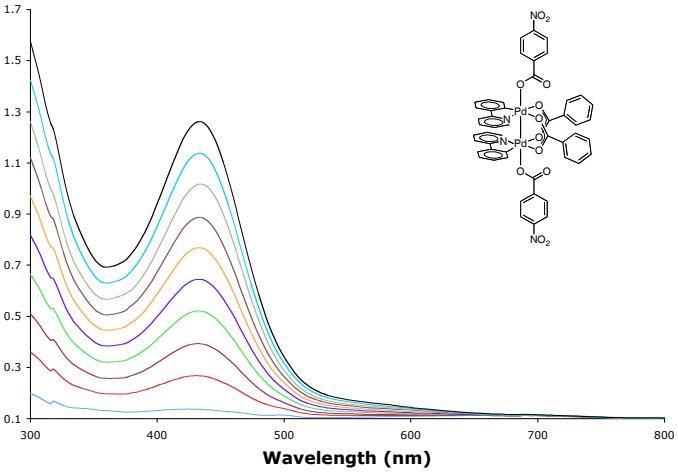


343 nm

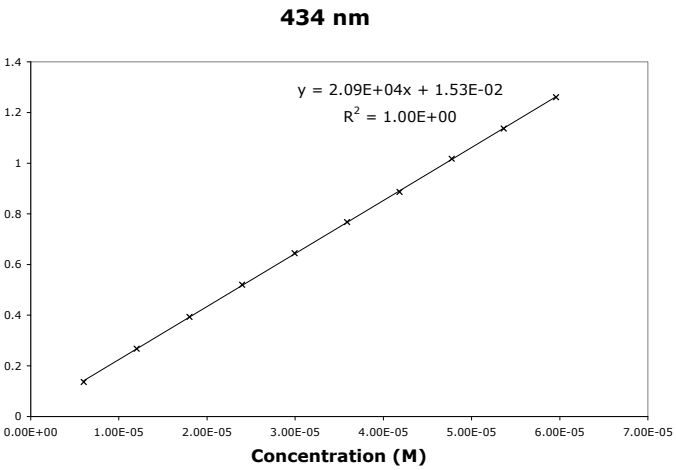




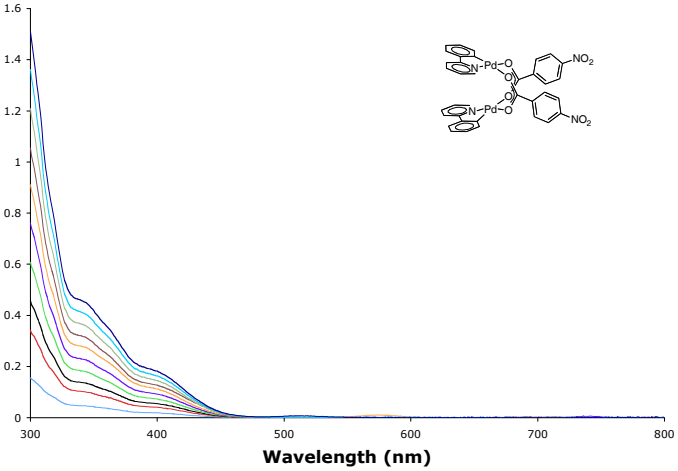
UV VIS Spectrum of **22**



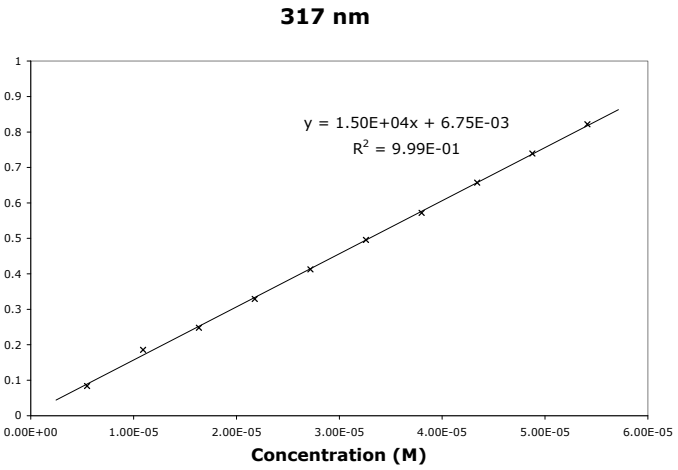
Molar Absorptivity Determinations

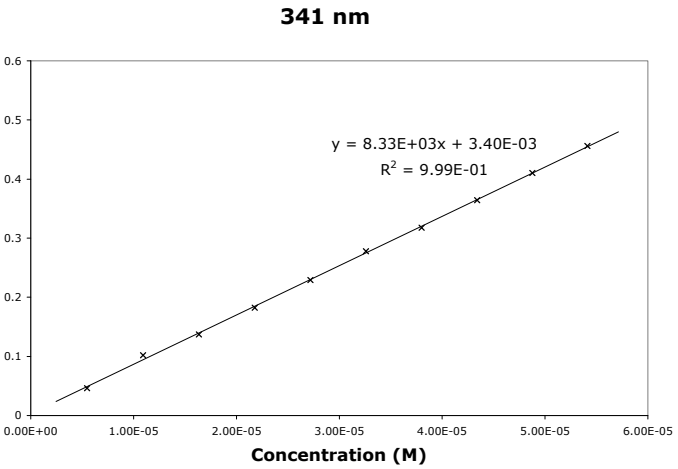


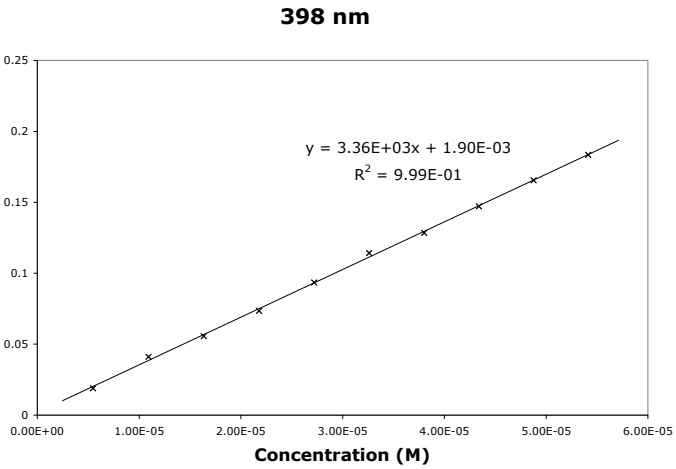
UV VIS Spectrum of **23**



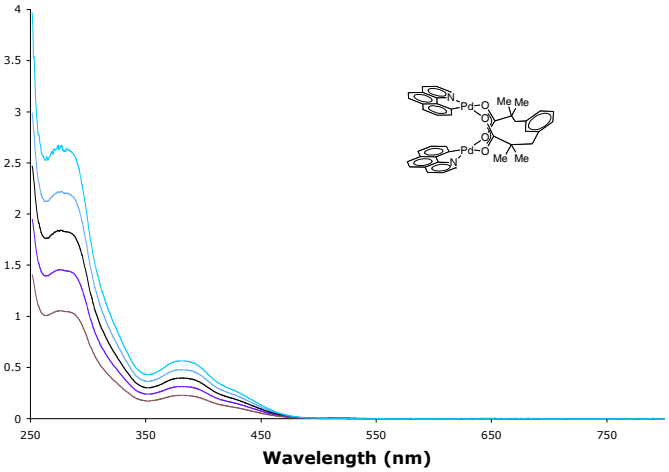
Molar Absorptivity Determinations



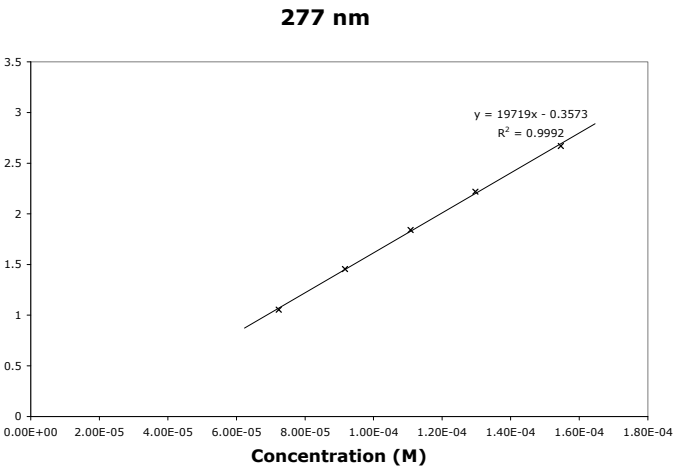


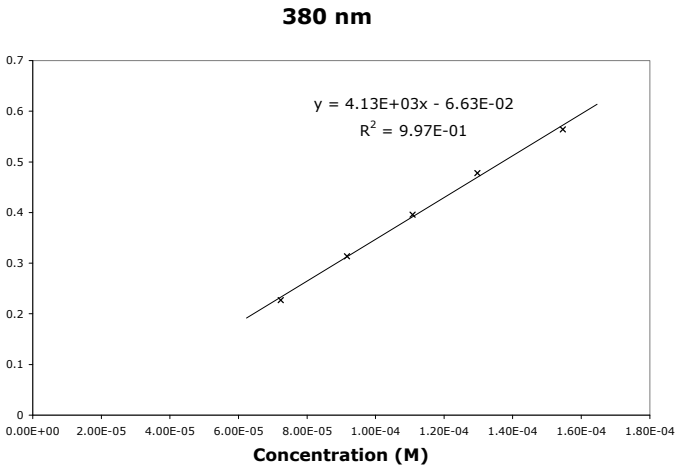


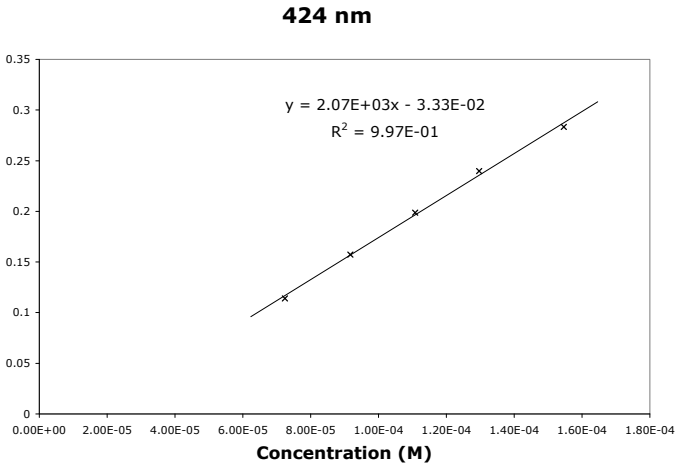
UV VIS Spectrum of **34**



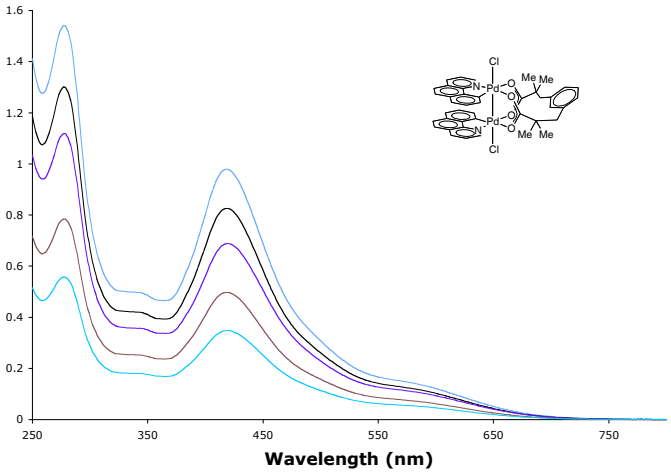
Molar Absorptivity Determinations





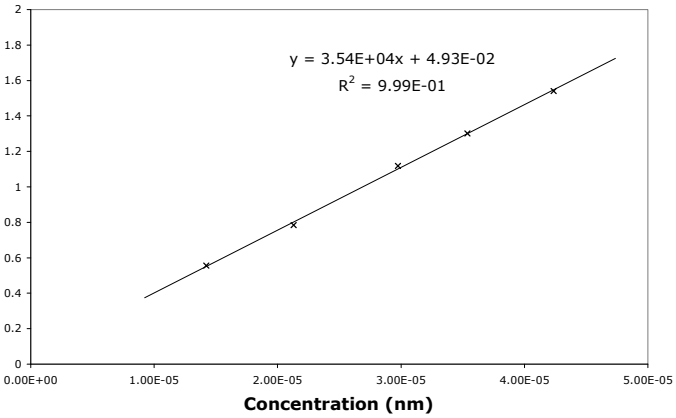


UV VIS Spectrum of **35**

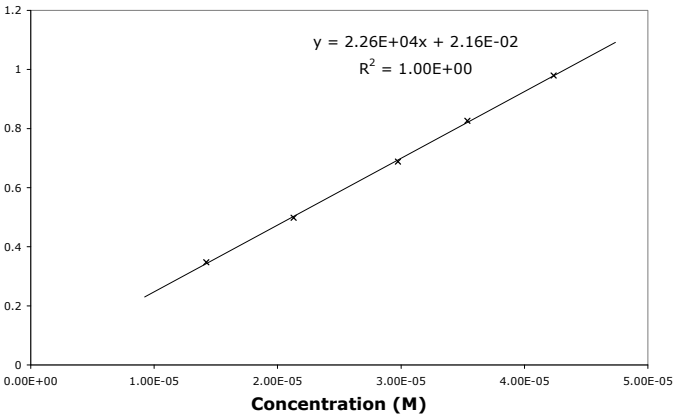


Molar Absorptivity Determinations

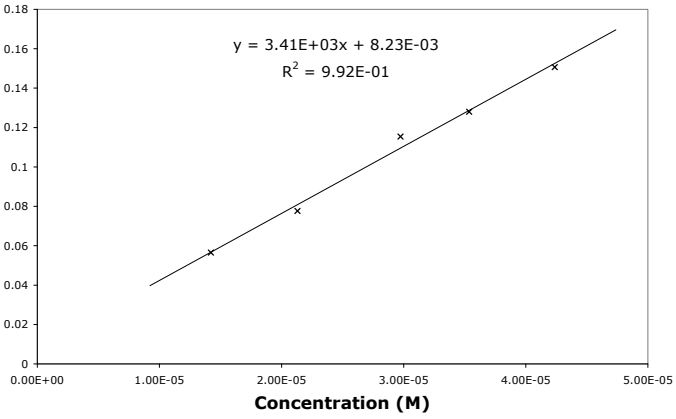
277 nm



418 nm

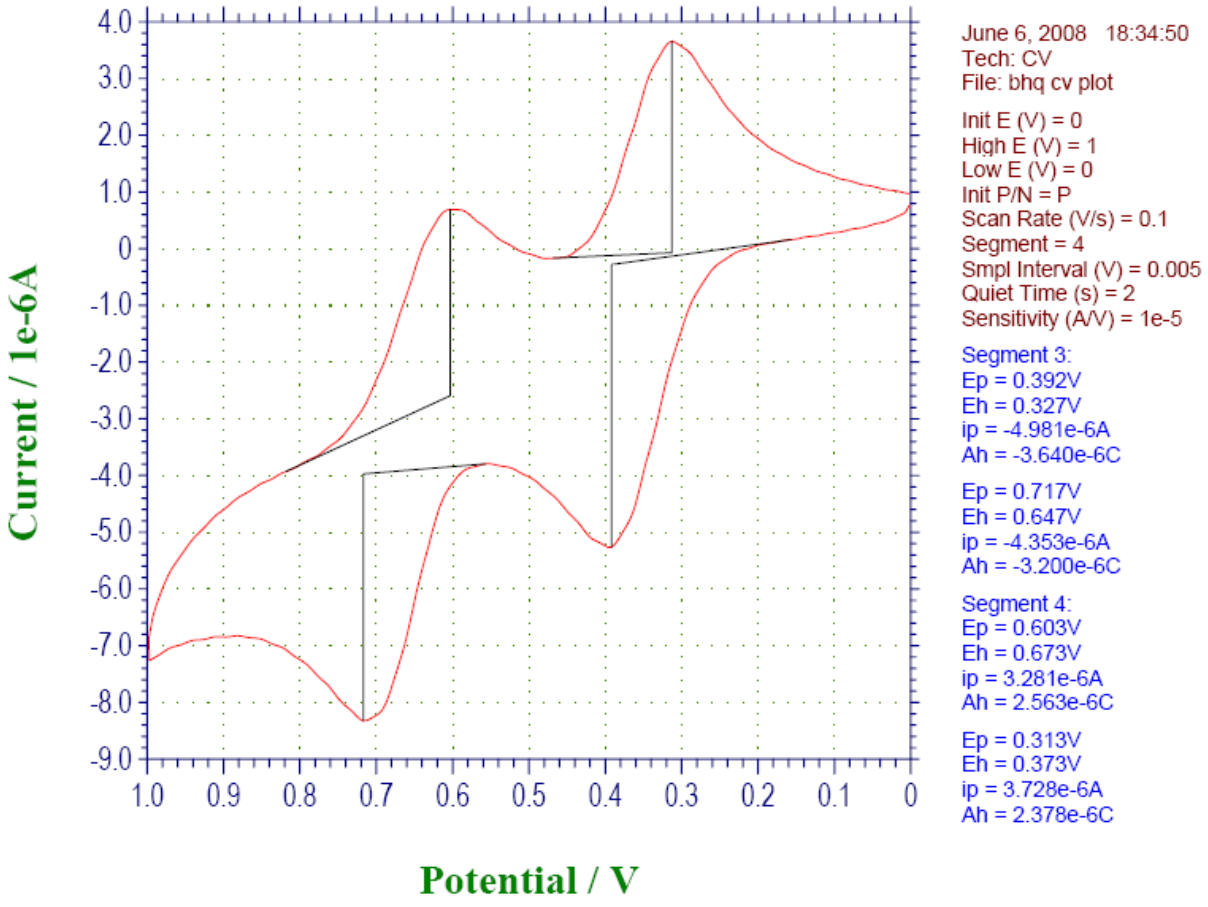


570 nm



Appendix C: Electrochemical Data

Benzo[*h*]quinolinyl Palladium Acetate Dimer (9)



The CV of **9** was obtained from a 1 mM solution of **9** in THF with a glassy carbon working electrode. $NBu_4 \cdot PF_6$ (3.0 M) was used as the electrolyte. The CV was obtained at a scan rate of 0.1 V/s against Ag/AgCl and was confirmed versus added ferrocene.

The oxidation wave at 420 mV (vs Fc/Fc^+) is due to the Pd(II)–Pd(II) to Pd(II)–Pd(III) redox couple while the oxidation wave at 720 mV (vs. Fc/Fc^+) is due to the Pd(II)–Pd(III) to Pd(III)–Pd(III) redox couple.

Appendix D: X-ray Crystallographic Analysis

Benzo[*h*]quinolinyl Palladium Acetate Dimer (9) (CCDC 705005)

The compound was crystallized from a dichloromethane / pentane solution as yellow needles. A crystal 0.250 mm x 0.100 mm x 0.075 mm in size was selected, mounted on a nylon loop with Paratone-N oil, and transferred to a Bruker SMART APEX diffractometer equipped with an Oxford Cryosystems 600 Series Cryostream Cooler and Mo Kα radiation (λ = 0.71073 Å). A total of 3840 frames were collected at 193 (2) K to θ_{max} = 27.5° with an oscillation range of 0.3°/frame, and an exposure time of 10 s/frame using SMART software. (Bruker AXS, 2001a) Unit cell refinement on all observed reflections, and data reduction with corrections for Lp and decay were performed using SAINT. (Bruker AXS, 2006) Scaling and a multi-scan absorption correction were done using SADABS. (Bruker AXS, 2004) The minimum and maximum transmission factors were 0.7132 and 0.8990, respectively. A total of 51012 reflections were collected, 3144 were unique (R_{int} = 0.0453), and 3033 had $I > 2\sigma(I)$. Systematic absences were consistent with the compound having crystallized in the orthorhombic space group $Pmn2_1$ or Pmmn. The observed mean $|E^2-1|$ value was 0.786 (versus the expectation values of 0.968 and 0.736 for centric and noncentric data, respectively). The E^2 statistics and figures of merit were ascertained to be unreliable due to the presence of two palladium atoms in the asymmetric unit and the presence of twinning. The centrosymmetric space group Pmmn (No. 59) was selected, and confirmed to be the correct choice by successful refinement of the structure.

The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL. (Bruker AXS, 2001b) The asymmetric unit was found to contain two quarter-molecules of (Acetato) (10-benzo[*h*]quinolinato)palladium(II) dimer, i.e., there are four dimers in the unit cell, each with crystallographic *mm*2 symmetry, and located at Wyckoff positions 2*a* and 2*b*. Since the ligating atoms of the 10-benzo[*h*]quinolinato ligands are required by symmetry to be compositionally disordered, the N(1) and C(1) atoms were assigned site occupancy factors of 0.5 and their coordinates were refined to the same values. The N(1') and C(1') atoms were treated similarly. All of the nonhydrogen atoms were refined with anisotropic displacement coefficients. The hydrogen atoms were assigned isotropic displacement coefficients $U(H) = 1.2U(C)$ or $1.5U(C_{methyl})$, and their coordinates were allowed to ride on their respective carbons. This model refined to $R(F) = 0.2773$, at which point it was obvious that the data were twinned. A Platon/TwinRotMat test indicated 50:50 twinning about [1-10]. (Spek, 2003) Inclusion of the twin law (0-10, -100, 00-1) in all subsequent cycles of least-squares led to a dramatic lowering of $R(F)$ from 0.28 to under 0.03. The refinement converged to $R(F) = 0.0282$, $wR(F^2) = 0.0701$, and $S = 1.120$ for 3033 reflections with $I > 2\sigma(I)$, and $R(F) = 0.0297$, $wR(F^2) = 0.0713$, and $S = 1.120$ for 3144 unique reflections and 183 parameters. The maximum $|\Delta/\sigma|$ in the final cycle of least-squares was 0.001, and the residual peaks on the final difference-Fourier map ranged from -0.487 to 1.091 eÅ^{-3}. Scattering factors were taken from the International Tables for Crystallography, Volume C. (Maslen *et al.*, 1992, and Creagh & McAuley, 1992)

Table 1. Crystal data and structure refinement for **9**.

Identification code	**9** (CCDC 705005)	
Empirical formula	C30 H22 N2 O4 Pd2	
Formula weight	687.30	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pmmn	
Unit cell dimensions	a = 16.039(2) Å	α= 90°.
	b = 16.038(2) Å	β= 90°.

	c = 9.9156(13) Å γ = 90°.
Volume	2550.6(6) Å^3
Z	4
Density (calculated)	1.790 Mg/m^3
Absorption coefficient	1.450 mm^{-1}
F(000)	1360
Crystal size	0.25 x 0.10 x 0.08 mm^3
Theta range for data collection	1.27 to 27.50°.
Index ranges	-20<=h<=20, -20<=k<=20, -12<=l<=12
Reflections collected	51012
Independent reflections	3144 [R(int) = 0.0453]
Completeness to theta = 27.50°	100.0 %
Max. and min. transmission	0.8990 and 0.7132
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3144 / 0 / 183
Goodness-of-fit on F^2	1.120
Final R indices [I>2sigma(I)]	R1 = 0.0282, wR2 = 0.0701
R indices (all data)	R1 = 0.0297, wR2 = 0.0713
Largest diff. peak and hole	1.091 and -0.487 e.Å^{-3}

Table 2. Bond lengths [Å] and angles [°] for **9**.

Pd(1)-N(1)	2.000(3)	N(1')-C(6')	1.380(5)
Pd(1)-C(1)#1	2.000(3)	C(2')-C(3')	1.407(6)
Pd(1)-N(1)#1	2.000(3)	C(2')-H(2')	0.9500
Pd(1)-O(1)#1	2.090(2)	C(3')-C(4')	1.367(6)
Pd(1)-O(1)	2.090(2)	C(3')-H(3')	0.9500
Pd(1)-Pd(1)#2	2.8419(8)	C(4')-C(5')	1.406(6)
O(1)-C(8)	1.249(3)	C(4')-H(4')	0.9500
N(1)-C(2)	1.367(5)	C(5')-C(6')	1.408(5)
N(1)-C(6)	1.394(5)	C(5')-C(7')	1.429(5)
C(2)-C(3)	1.396(6)	C(6')-C(6')#4	1.432(6)
C(2)-H(2)	0.9500	C(7')-C(7')#4	1.377(8)
C(3)-C(4)	1.368(6)	C(7')-H(7')	0.9500
C(3)-H(3)	0.9500	C(8')-O(1')#1	1.261(4)
C(4)-C(5)	1.418(6)	C(8')-C(9')	1.510(6)
C(4)-H(4)	0.9500	C(9')-H(9A')	0.9800
C(5)-C(6)	1.407(5)	C(9')-H(9B')	0.9800
C(5)-C(7)	1.442(6)	C(9')-H(9C')	0.9800
C(6)-C(6)#1	1.404(7)		
C(7)-C(7)#1	1.350(9)	N(1)-Pd(1)-C(1)#1	83.04(19)
C(7)-H(7)	0.9500	N(1)-Pd(1)-N(1)#1	83.04(19)
C(8)-O(1)#3	1.249(3)	C(1)#1-Pd(1)-N(1)#1	0.0(3)
C(8)-C(9)	1.512(7)	N(1)-Pd(1)-O(1)#1	176.69(12)
C(9)-H(9A)	0.9800	C(1)#1-Pd(1)-O(1)#1	93.66(12)
C(9)-H(9B)	0.9800	N(1)#1-Pd(1)-O(1)#1	93.66(12)
C(9)-H(9C)	0.9800	N(1)-Pd(1)-O(1)	93.66(12)
Pd(1')-N(1')	1.999(3)	C(1)#1-Pd(1)-O(1)	176.70(12)
Pd(1')-C(1')#4	1.999(3)	N(1)#1-Pd(1)-O(1)	176.70(12)
Pd(1')-N(1')#4	1.999(3)	O(1)#1-Pd(1)-O(1)	89.64(14)
Pd(1')-O(1')#4	2.086(3)	N(1)-Pd(1)-Pd(1)#2	98.90(10)
Pd(1')-O(1')	2.086(3)	C(1)#1-Pd(1)-Pd(1)#2	98.90(10)
Pd(1')-Pd(1')#5	2.8819(9)	N(1)#1-Pd(1)-Pd(1)#2	98.90(10)
O(1')-C(8')	1.261(4)	O(1)#1-Pd(1)-Pd(1)#2	81.76(7)
N(1')-C(2')	1.351(5)	O(1)-Pd(1)-Pd(1)#2	81.76(7)

C(8)-O(1)-Pd(1)	124.4(2)	N(1')#4-Pd(1')-O(1')	176.01(12)
C(2)-N(1)-C(6)	119.0(3)	O(1')#4-Pd(1')-O(1')	90.47(14)
C(2)-N(1)-Pd(1)	129.3(3)	N(1')-Pd(1')-Pd(1')#5	99.18(10)
C(6)-N(1)-Pd(1)	111.7(2)	C(1')#4-Pd(1')-Pd(1')#5	99.18(10)
N(1)-C(2)-C(3)	120.2(4)	N(1')#4-Pd(1')-Pd(1')#5	99.18(10)
N(1)-C(2)-H(2)	119.9	O(1')#4-Pd(1')-Pd(1')#5	81.39(8)
C(3)-C(2)-H(2)	119.9	O(1')-Pd(1')-Pd(1')#5	81.39(8)
C(4)-C(3)-C(2)	121.6(4)	C(8')-O(1')-Pd(1')	125.1(3)
C(4)-C(3)-H(3)	119.2	C(2')-N(1')-C(6')	118.3(3)
C(2)-C(3)-H(3)	119.2	C(2')-N(1')-Pd(1')	129.1(3)
C(3)-C(4)-C(5)	119.9(4)	C(6')-N(1')-Pd(1')	112.5(2)
C(3)-C(4)-H(4)	120.1	N(1')-C(2')-C(3')	120.5(4)
C(5)-C(4)-H(4)	120.1	N(1')-C(2')-H(2')	119.8
C(6)-C(5)-C(4)	117.2(4)	C(3')-C(2')-H(2')	119.8
C(6)-C(5)-C(7)	117.4(3)	C(4')-C(3')-C(2')	121.1(4)
C(4)-C(5)-C(7)	125.4(4)	C(4')-C(3')-H(3')	119.4
N(1)-C(6)-C(6)#1	116.6(2)	C(2')-C(3')-H(3')	119.4
N(1)-C(6)-C(5)	122.2(3)	C(3')-C(4')-C(5')	120.1(4)
C(6)#1-C(6)-C(5)	121.1(2)	C(3')-C(4')-H(4')	119.9
C(7)#1-C(7)-C(5)	121.5(2)	C(5')-C(4')-H(4')	119.9
C(7)#1-C(7)-H(7)	119.2	C(4')-C(5')-C(6')	116.3(3)
C(5)-C(7)-H(7)	119.2	C(4')-C(5')-C(7')	125.4(3)
O(1)-C(8)-O(1)#3	127.7(4)	C(6')-C(5')-C(7')	118.3(3)
O(1)-C(8)-C(9)	116.2(2)	N(1')-C(6')-C(5')	123.6(3)
O(1)#3-C(8)-C(9)	116.2(2)	N(1')-C(6')-C(6')#4	115.86(19)
C(8)-C(9)-H(9A)	109.5	C(5')-C(6')-C(6')#4	120.5(2)
C(8)-C(9)-H(9B)	109.5	C(7')#4-C(7')-C(5')	121.3(2)
C(8)-C(9)-H(9C)	109.5	C(7')#4-C(7')-H(7')	119.4
N(1')-Pd(1')-C(1')#4	82.49(19)	C(5')-C(7')-H(7')	119.4
N(1')-Pd(1')-N(1')#4	82.49(19)	O(1')-C(8')-O(1')#1	126.9(4)
C(1')#4-Pd(1')-N(1')#4	0.0(2)	O(1')-C(8')-C(9')	116.5(2)
N(1')-Pd(1')-O(1')#4	176.01(12)	O(1')#1-C(8')-C(9')	116.5(2)
C(1')#4-Pd(1')-O(1')#4	93.52(12)	C(8')-C(9')-H(9A')	109.5
N(1')#4-Pd(1')-O(1')#4	93.52(12)	C(8')-C(9')-H(9B')	109.5
N(1')-Pd(1')-O(1')	93.52(12)	C(8')-C(9')-H(9C')	109.5
C(1')#4-Pd(1')-O(1')	176.01(12)		

Symmetry transformations used to generate equivalent atoms:
#1 x,-y+1/2,z #2 -x+3/2,-y+1/2,z #3 -x+3/2,y,z
#4 -x+1/2,y,z #5 -x+1/2,-y+1/2,z

(Acetato)(10-benzo[*h*]quinolinato)-chloropalladium(III) Dimer (1) (CCDC 705506)

The compound was crystallized from a dichloromethane / pentane solution at -35 ˚C as orange prisms. A crystal 0.03 mm x 0.03 mm x 0.15 mm in size was selected, mounted on a nylon loop with Paratone-N oil, and transferred to a Bruker SMART APEX II diffractometer equipped with an Oxford Cryosystems 700 Series Cryostream Cooler and Mo Kα radiation (λ = 0.71073 Å). A total of 2762 frames were collected at 193 (2) K to θ_{max} = 25.00° with an oscillation range of 0.5°/frame, and an exposure time of 20 s/frame using the APEX2 suite of software. (Bruker AXS, 2006a) Data were collected to θ_{max} = 25.00° rather than the routine value of θ_{max} = 27.50° because the crystal examined did not exhibit usable diffraction beyond 25.00°. Unit cell refinement on all observed reflections, and data reduction with corrections for Lp and decay were performed using SAINT. (Bruker AXS, 2006b) Scaling and a numerical absorption correction were done using SADABS. (Bruker AXS, 2004) The minimum and maximum transmission factors were 0.7430 and 0.9395, respectively. A total of 37194 reflections were collected, 3313 were unique (R_{int} = 0.0770), and 2701 had $I > 2\sigma(I)$. Systematic absences were consistent with the compound having

crystallized in the monoclinic space group Cc or C2/c. The latter centrosymmetric space group C2/c (No. 15) was selected based on an observed mean $|E^2-1|$ value of 0.927 (versus the expectation values of 0.968 and 0.736 for centric and noncentric data, respectively).

The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL. (Bruker AXS, 2001) The asymmetric unit was found to contain a half molecule of the desired (acetato)(10-benzo[*h*]quinolinato)chloropalladium(III) dimer plus a disordered iodobenzene molecule, and an even more severely disordered solvent molecule that we believe to be dichloromethane. The palladium(III) dimer resides on Wyckoff position 4*e* and possesses crystallographically imposed two-fold symmetry. To the best of our knowledge, based on various models and occupancy tests, the chemical formulation for the compound is $[Pd(C_2H_3O_2)(C_{13}H_8N)Cl]_2 \cdot C_6H_5I \cdot CH_2Cl_2$.

All of the nonhydrogen atoms were refined with anisotropic displacement coefficients. The hydrogen atoms were assigned isotropic displacement coefficients $U(H) = 1.2U(C)$ or $1.5U(C_{methyl})$, and their coordinates were allowed to ride on their respective carbons. The disordered iodobenzene molecule was treated with a two-site model [I(1), C(13), C(14), C(15), C(16), C(17), C(18)] and [I(1*), C(13*), C(14*), C(15*), C(16*), C(17*), C(18*)] with refined site occupancy factors of 0.466 (3) and 0.034 (3), respectively. That two-site model also included rigid bond, similar U_{ij}, common plane, and distance restraints. The benzene rings were treated as idealized regular hexagons with C-C = 1.39 Å. Attempts to model the dichloromethane were without success. The best discrete-atom model for the disordered dichloromethane converged to $wR(F^2) = 0.0860$. However, due to nonsensical bond distances and angles, and unjustifiable occupancy factors, that discrete-atom model for the dichloromethane was ultimately abandoned in favor of the solvent-free model contained in this CIF file. The dichloromethane contributions to the intensity data were removed by the Squeeze/Bypass procedure (van der Sluis & Spek, 1990) implemented in Platon (Spek, 2003). The refinement converged to $R(F) = 0.0336$, $wR(F^2) = 0.0761$, and $S = 1.075$ for 2701 reflections with $I > 2\sigma(I)$, and $R(F) = 0.0491$, $wR(F^2) = 0.0804$, and $S = 1.075$ for 3313 unique reflections, 285 parameters, and 246 restraints. The maximum $|\Delta/\sigma|$ in the final cycle of least-squares was 0.001, and the residual peaks on the final difference-Fourier map ranged from -0.816 to 0.355 eÅ^{-3}. Scattering factors were taken from the International Tables for Crystallography, Volume C. (Maslen *et al.*, 1992, and Creagh & McAuley, 1992)

Table 1. Crystal data and structure refinement for **1**.

Identification code	**1** (CCDC 705006)	
Formula	C37 H29 Cl4 I N2 O4 Pd2	
Formula weight	1047.12	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c (No. 15)	
Unit cell dimensions	a = 16.7605(5) Å	α= 90°
	b = 17.7508(5) Å	β= 117.053(2)°
	c = 14.1762(4) Å	γ = 90°
Volume	3756.13(19) Å^3	
Z	4	
Density (calculated)	1.852 Mg/m^3	
Absorption coefficient	2.106 mm^{-1}	
F(000)	2040	
Crystal size	0.15 x 0.03 x 0.03 mm^3	
Theta range for data collection	1.78 to 25.00°	
Index ranges	-19<=h<=19, -21<=k<=21, -16<=l<=16	
Reflections collected	37194	
Independent reflections	3313 [R(int) = 0.0770]	
Completeness to theta = 25.00°	100.0 %	

Absorption correction	Numerical
Max. and min. transmission	0.9395 and 0.7430
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3313 / 246 / 285
Goodness-of-fit on F^2	1.075
Final R indices [I>2sigma(I)]	R1 = 0.0336, wR2 = 0.0761
R indices (all data)	R1 = 0.0491, wR2 = 0.0804
Largest diff. peak and hole	0.355 and -0.816 e.Å^{-3}

Table 2. Bond lengths [Å] and angles [°] for **1**.

Pd(1)-C(10)	2.000(4)	C(16)-H(16)	0.9500
Pd(1)-N(1)	2.016(3)	C(17)-C(18)	1.3900
Pd(1)-O(1)	2.042(3)	C(17)-H(17)	0.9500
Pd(1)-O(2)#1	2.133(3)	C(18)-H(18)	0.9500
Pd(1)-Cl(1)	2.4167(10)	I(1*)-C(13*)	2.067(15)
Pd(1)-Pd(1)#1	2.5672(5)	C(13*)-C(14*)	1.3900
N(1)-C(2)	1.344(5)	C(13*)-C(18*)	1.3900
N(1)-C(10B)	1.362(5)	C(14*)-C(15*)	1.3900
C(2)-C(3)	1.397(6)	C(14*)-H(14*)	0.9500
C(2)-H(2)	0.9500	C(15*)-C(16*)	1.3900
C(3)-C(4)	1.367(6)	C(15*)-H(15*)	0.9500
C(3)-H(3)	0.9500	C(16*)-C(17*)	1.3900
C(4)-C(4A)	1.401(6)	C(16*)-H(16*)	0.9500
C(4)-H(4)	0.9500	C(17*)-C(18*)	1.3900
C(4A)-C(10B)	1.414(5)	C(17*)-H(17*)	0.9500
C(4A)-C(5)	1.425(6)	C(18*)-H(18*)	0.9500
C(5)-C(6)	1.356(6)	C(10)-Pd(1)-O(1)	92.55(13)
C(5)-H(5)	0.9500	N(1)-Pd(1)-O(1)	175.39(12)
C(6)-C(6A)	1.433(6)	C(10)-Pd(1)-O(2)#1	177.37(13)
C(6)-H(6)	0.9500	N(1)-Pd(1)-O(2)#1	94.61(12)
C(6A)-C(7)	1.396(6)	O(1)-Pd(1)-O(2)#1	89.94(11)
C(6A)-C(10A)	1.408(5)	C(10)-Pd(1)-Cl(1)	88.88(10)
C(7)-C(8)	1.389(6)	N(1)-Pd(1)-Cl(1)	90.48(9)
C(7)-H(7)	0.9500	O(1)-Pd(1)-Cl(1)	90.06(8)
C(8)-C(9)	1.401(6)	O(2)#1-Pd(1)-Cl(1)	91.94(7)
C(8)-H(8)	0.9500	C(10)-Pd(1)-Pd(1)#1	96.24(10)
C(9)-C(10)	1.360(5)	N(1)-Pd(1)-Pd(1)#1	95.66(8)
C(9)-H(9)	0.9500	O(1)-Pd(1)-Pd(1)#1	84.18(7)
C(10)-C(10A)	1.398(5)	O(2)#1-Pd(1)-Pd(1)#1	83.19(7)
C(10A)-C(10B)	1.407(5)	Cl(1)-Pd(1)-Pd(1)#1	172.44(2)
O(1)-C(11)	1.275(5)	C(2)-N(1)-C(10B)	119.9(3)
O(2)-C(11)	1.254(5)	C(2)-N(1)-Pd(1)	127.8(3)
O(2)-Pd(1)#1	2.133(3)	C(10B)-N(1)-Pd(1)	112.3(2)
C(11)-C(12)	1.494(6)	N(1)-C(2)-C(3)	120.0(4)
C(12)-H(12A)	0.9800	N(1)-C(2)-H(2)	120.0
C(12)-H(12B)	0.9800	C(3)-C(2)-H(2)	120.0
C(12)-H(12C)	0.9800	C(4)-C(3)-C(2)	121.0(4)
I(1)-C(13)	2.064(5)	C(4)-C(3)-H(3)	119.5
C(13)-C(14)	1.3900	C(2)-C(3)-H(3)	119.5
C(13)-C(18)	1.3900	C(3)-C(4)-C(4A)	120.0(4)
C(14)-C(15)	1.3900	C(3)-C(4)-H(4)	120.0
C(14)-H(14)	0.9500	C(4A)-C(4)-H(4)	120.0
C(15)-C(16)	1.3900	C(4)-C(4A)-C(10B)	116.8(4)
C(15)-H(15)	0.9500	C(4)-C(4A)-C(5)	126.5(4)
C(16)-C(17)	1.3900	C(10B)-C(4A)-C(5)	116.6(4)

C(6)-C(5)-C(4A)	122.2(4)	H(12B)-C(12)-H(12C)	109.5
C(6)-C(5)-H(5)	118.9	C(14)-C(13)-C(18)	120.0
C(4A)-C(5)-H(5)	118.9	C(14)-C(13)-I(1)	118.9(3)
C(5)-C(6)-C(6A)	121.6(4)	C(18)-C(13)-I(1)	121.1(3)
C(5)-C(6)-H(6)	119.2	C(15)-C(14)-C(13)	120.0
C(6A)-C(6)-H(6)	119.2	C(15)-C(14)-H(14)	120.0
C(7)-C(6A)-C(10A)	117.5(4)	C(13)-C(14)-H(14)	120.0
C(7)-C(6A)-C(6)	125.2(4)	C(14)-C(15)-C(16)	120.0
C(10A)-C(6A)-C(6)	117.3(4)	C(14)-C(15)-H(15)	120.0
C(8)-C(7)-C(6A)	120.4(4)	C(16)-C(15)-H(15)	120.0
C(8)-C(7)-H(7)	119.8	C(17)-C(16)-C(15)	120.0
C(6A)-C(7)-H(7)	119.8	C(17)-C(16)-H(16)	120.0
C(7)-C(8)-C(9)	120.8(4)	C(15)-C(16)-H(16)	120.0
C(7)-C(8)-H(8)	119.6	C(16)-C(17)-C(18)	120.0
C(9)-C(8)-H(8)	119.6	C(16)-C(17)-H(17)	120.0
C(10)-C(9)-C(8)	119.7(4)	C(18)-C(17)-H(17)	120.0
C(10)-C(9)-H(9)	120.2	C(17)-C(18)-C(13)	120.0
C(8)-C(9)-H(9)	120.2	C(17)-C(18)-H(18)	120.0
C(9)-C(10)-C(10A)	119.9(3)	C(13)-C(18)-H(18)	120.0
C(9)-C(10)-Pd(1)	129.3(3)	C(14*)-C(13*)-C(18*)	120.0
C(10A)-C(10)-Pd(1)	110.8(3)	C(14*)-C(13*)-I(1*)	119.8(10)
C(10)-C(10A)-C(10B)	117.6(3)	C(18*)-C(13*)-I(1*)	120.2(10)
C(10)-C(10A)-C(6A)	121.6(4)	C(15*)-C(14*)-C(13*)	120.0
C(10B)-C(10A)-C(6A)	120.7(4)	C(15*)-C(14*)-H(14*)	120.0
N(1)-C(10B)-C(10A)	116.2(3)	C(13*)-C(14*)-H(14*)	120.0
N(1)-C(10B)-C(4A)	122.2(3)	C(16*)-C(15*)-C(14*)	120.0
C(10A)-C(10B)-C(4A)	121.5(4)	C(16*)-C(15*)-H(15*)	120.0
C(11)-O(1)-Pd(1)	121.3(2)	C(14*)-C(15*)-H(15*)	120.0
C(11)-O(2)-Pd(1)#1	117.9(2)	C(15*)-C(16*)-C(17*)	120.0
O(2)-C(11)-O(1)	124.4(4)	C(15*)-C(16*)-H(16*)	120.0
O(2)-C(11)-C(12)	119.3(4)	C(17*)-C(16*)-H(16*)	120.0
O(1)-C(11)-C(12)	116.2(4)	C(18*)-C(17*)-C(16*)	120.0
C(11)-C(12)-H(12A)	109.5	C(18*)-C(17*)-H(17*)	120.0
C(11)-C(12)-H(12B)	109.5	C(16*)-C(17*)-H(17*)	120.0
H(12A)-C(12)-H(12B)	109.5	C(17*)-C(18*)-C(13*)	120.0
C(11)-C(12)-H(12C)	109.5	C(17*)-C(18*)-H(18*)	120.0
H(12A)-C(12)-H(12C)	109.5	C(13*)-C(18*)-H(18*)	120.0

Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+3/2

Tris(μ2-acetato)-bis(benzo[h]quinolinato)- (μ2-chloro)-tripalladium(II) (3a) (CCDC 705007)

The compound was crystallized from a dichloromethane / pentane solution as orange plates. A crystal 0.030 mm x 0.095 mm x 0.150 mm in size was selected, mounted on a nylon loop with Paratone-N oil, and transferred to a Bruker SMART APEX II diffractometer equipped with an Oxford Cryosystems 700 Series Cryostream Cooler and Mo Kα radiation (λ = 0.71073 Å). A total of 2580 frames were collected at 193 (2) K to θ_{max} = 30.0° with an oscillation range of 0.5°/frame, and an exposure time of 30 s/frame using the APEX2 suite of software. (Bruker AXS, 2001a) Unit cell refinement on all observed reflections, and data reduction with corrections for Lp and decay were performed using SAINT. (Bruker AXS, 2006b) Scaling and a numerical absorption correction were done using SADABS. (Bruker AXS, 2004) The minimum and maximum transmission factors were 0.7571 and 0.9434, respectively. A total of 36302 reflections were collected, 8529 were unique (R_{int} = 0.029), and 7147 had I > 2σ(I). A lack of systematic absences were consistent with the compound having crystallized in the triclinic space group P1 or $P\bar{1}$. The latter centrosymmetric space group $P\bar{1}$ (No. 2) was selected based on an observed mean $|E^2-1|$ value of 0.924 (versus the expectation values of 0.968 and 0.736 for centric and noncentric data, respectively).

The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL. (Bruker AXS, 2001) The centrosymmetric unit was found to contain one molecule of tris (μ_2-acetato)-bis(benzo[*h*]quinolato)-(μ_2-chloro)- tripalladium(II). All of the nonhydrogen atoms were refined with anisotropic displacement coefficients. The hydrogen atoms were assigned isotropic displacement coefficients U(H) = 1.2U(C) or 1.5U(Cmethyl), and their coordinates were allowed to ride on their respective carbons. During refinement, a residual peak was observed between the oxygen atoms of one of the bridging acetato ligands (O(5), O(6)), so attempts were made to treat that bridging site as compositionally disordered (i.e. partially occupied by an acetate and by a chloride). However, even with restraints, this model yielded Pd−Cl distances that were too long and a miniscule Cl site occupancy factor of 0.036 (4). Therefore, the residual peak was left unassigned and the refinement was completed with all atoms fully occupied. The refinement converged to $R(F)$ = 0.0369, $wR(F^2)$ = 0.0792, and S = 1.091 for 7147 reflections with I > 2σ(I), and $R(F)$ = 0.0479, $wR(F^2)$ = 0.0834, and S = 1.091 for 8529 unique reflections and 400 parameters. The maximum |Δ/σ| in the final cycle of least-squares was less than 0.001, and the residual peaks on the final difference-Fourier map ranged from -1.375 to 1.876 eÅ^{-3}. Scattering factors were taken from the International Tables for Crystallography, Volume C. (Maslen *et al*., 1992, and Creagh & McAuley, 1992)

Table 1. Crystal data and structure refinement for **3a**.

Identification code	**3a** (CCDC 705007)	
Empirical formula	C32 H25 Cl N2 O6 Pd3	
Formula weight	888.19	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$ (No. 2)	
Unit cell dimensions	a = 10.0632(2) Å	α= 96.989(1)°
	b = 11.2475(2) Å	β= 95.423(1)°
	c = 13.9230(2) Å	γ = 108.992(1)°
Volume	1463.85(5) Å^3	
Z	2	
Density (calculated)	2.015 mg/m^3	
Absorption coefficient	1.964 mm^{-1}	
F(000)	868	
Crystal size	0.150 x 0.095 x 0.030 mm^3	
Theta range for data collection	1.94 to 30.00°.	
Index ranges	-14<=h<=14, -15<=k<=15, -19<=l<=19	
Reflections collected	36302	
Independent reflections	8529 [R(int) = 0.0289]	
Completeness to theta = 30.00°	99.9 %	
Absorption correction	Numerical	
Max. and min. transmission	0.9434 and 0.7571	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8529 / 0 / 400	
Goodness-of-fit on F^2	1.091	
Final R indices [I>2sigma(I)]	R1 = 0.0369, wR2 = 0.0792	
R indices (all data)	R1 = 0.0479, wR2 = 0.0834	
Largest diff. peak and hole	1.876 and -1.375 e.Å^{-3}	

Table 2. Bond lengths [Å] and angles [°] for **3a**.

Pd(1)-C(10)	1.969(3)	Pd(1)-O(1)	2.140(3)
Pd(1)-N(1)	2.022(3)	Pd(1)-Pd(2)	2.9168(4)
Pd(1)-O(3)	2.052(2)	Pd(2)-O(5)	2.003(3)

Pd(2)-O(2)	2.005(3)	C(4')-C(4A')	1.401(7)
Pd(2)-O(4)	2.021(3)	C(4')-H(4')	0.9500
Pd(2)-Cl(1)	2.2822(10)	C(4A')-C(10D)	1.408(5)
Pd(3)-C(10')	1.974(4)	C(4A')-C(5')	1.434(6)
Pd(3)-N(1')	2.039(3)	C(5')-C(6')	1.343(7)
Pd(3)-O(6)	2.106(3)	C(5')-H(5')	0.9500
Pd(3)-Cl(1)	2.3068(10)	C(6')-C(6A')	1.437(6)
N(1)-C(2)	1.328(5)	C(6')-H(6')	0.9500
N(1)-C(10B)	1.368(4)	C(6A')-C(7')	1.389(7)
C(2)-C(3)	1.392(5)	C(6A')-C(10C)	1.414(5)
C(2)-H(2)	0.9500	C(7')-C(8')	1.366(7)
C(3)-C(4)	1.369(6)	C(7')-H(7')	0.9500
C(3)-H(3)	0.9500	C(8')-C(9')	1.416(6)
C(4)-C(4A)	1.398(6)	C(8')-H(8')	0.9500
C(4)-H(4)	0.9500	C(9')-C(10')	1.366(6)
C(4A)-C(10B)	1.401(5)	C(9')-H(9')	0.9500
C(4A)-C(5)	1.436(6)	C(10')-C(10C)	1.418(5)
C(5)-C(6)	1.334(7)	C(10C)-C(10D)	1.407(6)
C(5)-H(5)	0.9500	O(1)-C(11)	1.247(4)
C(6)-C(6A)	1.436(6)	O(2)-C(11)	1.260(4)
C(6)-H(6)	0.9500	C(11)-C(12)	1.507(5)
C(6A)-C(7)	1.400(7)	C(12)-H(12C)	0.9800
C(6A)-C(10A)	1.405(5)	C(12)-H(12B)	0.9800
C(7)-C(8)	1.370(7)	C(12)-H(12A)	0.9800
C(7)-H(7)	0.9500	O(3)-C(13)	1.254(4)
C(8)-C(9)	1.401(6)	O(4)-C(13)	1.256(4)
C(8)-H(8)	0.9500	C(13)-C(14)	1.509(5)
C(9)-C(10)	1.377(6)	C(14)-H(14A)	0.9800
C(9)-H(9)	0.9500	C(14)-H(14B)	0.9800
C(10)-C(10A)	1.406(5)	C(14)-H(14C)	0.9800
C(10A)-C(10B)	1.412(5)	O(5)-C(15)	1.256(5)
N(1')-C(2')	1.322(5)	O(6)-C(15)	1.246(5)
N(1')-C(10D)	1.364(5)	C(15)-C(16)	1.524(6)
C(2')-C(3')	1.404(6)	C(16)-H(16A)	0.9800
C(2')-H(2')	0.9500	C(16)-H(16B)	0.9800
C(3')-C(4')	1.356(7)	C(16)-H(16C)	0.9800
C(3')-H(3')	0.9500		

C(10)-Pd(1)-N(1)	82.71(14)	O(4)-Pd(2)-Pd(1)	83.07(7)
C(10)-Pd(1)-O(3)	91.09(13)	Cl(1)-Pd(2)-Pd(1)	101.82(3)
N(1)-Pd(1)-O(3)	171.31(11)	C(10')-Pd(3)-N(1')	82.61(15)
C(10)-Pd(1)-O(1)	174.02(13)	C(10')-Pd(3)-O(6)	170.51(14)
N(1)-Pd(1)-O(1)	92.10(11)	N(1')-Pd(3)-O(6)	87.94(12)
O(3)-Pd(1)-O(1)	93.74(11)	C(10')-Pd(3)-Cl(1)	93.57(12)
C(10)-Pd(1)-Pd(2)	108.68(10)	N(1')-Pd(3)-Cl(1)	175.55(9)
N(1)-Pd(1)-Pd(2)	109.92(8)	O(6)-Pd(3)-Cl(1)	95.91(8)
O(3)-Pd(1)-Pd(2)	77.80(7)	Pd(2)-Cl(1)-Pd(3)	106.27(4)
O(1)-Pd(1)-Pd(2)	75.84(7)	C(2)-N(1)-C(10B)	118.9(3)
O(5)-Pd(2)-O(2)	172.05(11)	C(2)-N(1)-Pd(1)	128.2(2)
O(5)-Pd(2)-O(4)	84.22(12)	C(10B)-N(1)-Pd(1)	112.9(2)
O(2)-Pd(2)-O(4)	90.26(11)	N(1)-C(2)-C(3)	121.3(4)
O(5)-Pd(2)-Cl(1)	97.12(9)	N(1)-C(2)-H(2)	119.3
O(2)-Pd(2)-Cl(1)	87.86(8)	C(3)-C(2)-H(2)	119.3
O(4)-Pd(2)-Cl(1)	174.57(8)	C(4)-C(3)-C(2)	120.5(4)
O(5)-Pd(2)-Pd(1)	100.16(8)	C(4)-C(3)-H(3)	119.7
O(2)-Pd(2)-Pd(1)	84.80(7)	C(2)-C(3)-H(3)	119.7

C(3)-C(4)-C(4A)	119.5(3)	C(7')-C(6A')-C(10C)	117.1(4)
C(3)-C(4)-H(4)	120.2	C(7')-C(6A')-C(6')	124.6(4)
C(4A)-C(4)-H(4)	120.2	C(10C)-C(6A')-C(6')	118.3(4)
C(4)-C(4A)-C(10B)	117.1(3)	C(8')-C(7')-C(6A')	120.6(4)
C(4)-C(4A)-C(5)	126.3(4)	C(8')-C(7')-H(7')	119.7
C(10B)-C(4A)-C(5)	116.6(4)	C(6A')-C(7')-H(7')	119.7
C(6)-C(5)-C(4A)	121.8(4)	C(7')-C(8')-C(9')	121.7(4)
C(6)-C(5)-H(5)	119.1	C(7')-C(8')-H(8')	119.2
C(4A)-C(5)-H(5)	119.1	C(9')-C(8')-H(8')	119.2
C(5)-C(6)-C(6A)	122.2(4)	C(10')-C(9')-C(8')	120.3(4)
C(5)-C(6)-H(6)	118.9	C(10')-C(9')-H(9')	119.9
C(6A)-C(6)-H(6)	118.9	C(8')-C(9')-H(9')	119.9
C(7)-C(6A)-C(10A)	117.3(4)	C(9')-C(10')-C(10C)	117.3(4)
C(7)-C(6A)-C(6)	125.3(4)	C(9')-C(10')-Pd(3)	131.2(3)
C(10A)-C(6A)-C(6)	117.4(4)	C(10C)-C(10')-Pd(3)	111.5(3)
C(8)-C(7)-C(6A)	120.0(4)	C(10D)-C(10C)-C(6A')	119.2(4)
C(8)-C(7)-H(7)	120.0	C(10D)-C(10C)-C(10')	117.7(3)
C(6A)-C(7)-H(7)	120.0	C(6A')-C(10C)-C(10')	123.1(4)
C(7)-C(8)-C(9)	122.1(4)	N(1')-C(10D)-C(10C)	115.2(3)
C(7)-C(8)-H(8)	118.9	N(1')-C(10D)-C(4A')	122.3(4)
C(9)-C(8)-H(8)	118.9	C(10C)-C(10D)-C(4A')	122.4(4)
C(10)-C(9)-C(8)	119.8(4)	C(11)-O(1)-Pd(1)	127.8(2)
C(10)-C(9)-H(9)	120.1	C(11)-O(2)-Pd(2)	122.6(2)
C(8)-C(9)-H(9)	120.1	O(1)-C(11)-O(2)	126.8(3)
C(9)-C(10)-C(10A)	117.8(3)	O(1)-C(11)-C(12)	117.3(3)
C(9)-C(10)-Pd(1)	130.2(3)	O(2)-C(11)-C(12)	115.9(3)
C(10A)-C(10)-Pd(1)	112.0(3)	C(11)-C(12)-H(12C)	109.5
C(6A)-C(10A)-C(10)	123.0(4)	C(11)-C(12)-H(12B)	109.5
C(6A)-C(10A)-C(10B)	119.7(3)	H(12C)-C(12)-H(12B)	109.5
C(10)-C(10A)-C(10B)	117.3(3)	C(11)-C(12)-H(12A)	109.5
N(1)-C(10B)-C(4A)	122.6(3)	H(12C)-C(12)-H(12A)	109.5
N(1)-C(10B)-C(10A)	115.1(3)	H(12B)-C(12)-H(12A)	109.5
C(4A)-C(10B)-C(10A)	122.2(3)	C(13)-O(3)-Pd(1)	128.4(2)
C(2')-N(1')-C(10D)	119.0(3)	C(13)-O(4)-Pd(2)	123.4(2)
C(2')-N(1')-Pd(3)	128.1(3)	O(3)-C(13)-O(4)	126.7(3)
C(10D)-N(1')-Pd(3)	112.8(3)	O(3)-C(13)-C(14)	116.9(3)
N(1')-C(2')-C(3')	121.5(4)	O(4)-C(13)-C(14)	116.4(3)
N(1')-C(2')-H(2')	119.3	C(13)-C(14)-H(14A)	109.5
C(3')-C(2')-H(2')	119.3	C(13)-C(14)-H(14B)	109.5
C(4')-C(3')-C(2')	120.3(4)	H(14A)-C(14)-H(14B)	109.5
C(4')-C(3')-H(3')	119.8	C(13)-C(14)-H(14C)	109.5
C(2')-C(3')-H(3')	119.8	H(14A)-C(14)-H(14C)	109.5
C(3')-C(4')-C(4A')	119.7(4)	H(14B)-C(14)-H(14C)	109.5
C(3')-C(4')-H(4')	120.2	C(15)-O(5)-Pd(2)	129.0(3)
C(4A')-C(4')-H(4')	120.2	C(15)-O(6)-Pd(3)	137.3(3)
C(4')-C(4A')-C(10D)	117.2(4)	O(6)-C(15)-O(5)	128.1(4)
C(4')-C(4A')-C(5')	126.1(4)	O(6)-C(15)-C(16)	117.0(4)
C(10D)-C(4A')-C(5')	116.8(4)	O(5)-C(15)-C(16)	115.0(4)
C(6')-C(5')-C(4A')	121.9(4)	C(15)-C(16)-H(16A)	109.5
C(6')-C(5')-H(5')	119.1	C(15)-C(16)-H(16B)	109.5
C(4A')-C(5')-H(5')	119.1	H(16A)-C(16)-H(16B)	109.5
C(5')-C(6')-C(6A')	121.5(4)	C(15)-C(16)-H(16C)	109.5
C(5')-C(6')-H(6')	119.3	H(16A)-C(16)-H(16C)	109.5
C(6A')-C(6')-H(6')	119.3	H(16B)-C(16)-H(16C)	109.5

Bis(μ2-acetato)-bis(benzo[h]quinolinato)-bis(acetatopalladium(III)) (10) CCDC 705008)

The compound was crystallized from a dichloromethane solution at -35 °C as dark red plates. A crystal 0.010 mm x 0.125 mm x 0.125 mm in size was selected, mounted on a nylon loop with Paratone-N oil, and transferred to a Bruker SMART APEX II diffractometer equipped with an Oxford Cryosystems 700 Series Cryostream Cooler and Mo Kα radiation (λ = 0.71073 Å). A total of 694 frames were collected at 193 (2) K to θ_{max} = 25.0° with an oscillation range of 0.5°/frame, and an exposure time of 90 s/frame using the APEX2 suite of software. (Bruker AXS, 2001a) Unit cell refinement on all observed reflections and data reduction with corrections for Lp and decay were performed using SAINT. (Bruker AXS, 2006b) Scaling and a numerical absorption correction were done using SADABS. (Bruker AXS, 2004) The minimum and maximum transmission factors were 0.8536 and 0.9870, respectively. A total of 36560 reflections were collected, 6548 were unique (R_{int} = 0.102), and 4318 had $I > 2\sigma(I)$. Systematic absences were consistent with the compound having crystallized in the orthorhombic space group Pbca (No. 61). The observed mean $|E^2-1|$ value was 0.958 (versus the expectation values of 0.968 and 0.736 for centric and noncentric data, respectively).

The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL. (Bruker AXS, 2001) The centrosymmetric unit was found to contain one molecule of Bis(acetato)bis(μ_2-acetato)-bis(10-benzo[*h*]quinolato)- dipalladium(III) and two molecules of dichloromethane. All of the nonhydrogen atoms were refined with anisotropic displacement coefficients. All of the hydrogen atoms were assigned isotropic displacement coefficients U(H) = 1.2U(C) or 1.5U(C_{methyl}), and their coordinates were allowed to ride on their respective carbons. The ligating atoms of the 10-benzo[*h*] quinolinato ligands exhibited signs of compositional disorder. This was treated with a two-site model [N(1), C(12)], [N(1'), C(12')] and [C(1), N(12)], [C(1'), N(12')] with refined site occupancy factors of 0.78 (3) and 0.22 (3), respectively. The dichloromethane molecules were disordered and were treated with three-site models, i.e., [C(1S), Cl(1), Cl(2)], [C(1S'), Cl(1'), Cl(2')], [C(1S"), Cl(1"), Cl(2")], [C(2S), Cl(3), Cl(4)], [C(2S'), Cl(3'), Cl(4')], [C(2S"), Cl(3"), Cl(4")] with fixed site occupancy factors of 0.763 (4), 0.125 (5), 0.112 (4), 0.352 (4), 0.29 (4), and 0.36 (3) based on population refinement tests and included in the least-squares refinement with 1,2-distance, 1,3-distance, rigid-bond, and similar U_{ij} restraints. The refinement converged to $R(F)$ = 0.0428, $wR(F^2)$ = 0.0819, and S = 1.005 for 4318 reflections with $I > 2\sigma(I)$, and $R(F)$ = 0.0866, $wR(F^2)$ = 0.0969, and S = 1.005 for 6548 unique reflections, 582 parameters, and 444 restraints. The maximum $|\Delta/\sigma|$ in the final cycle of least-squares was 0.002, and the residual peaks on the final difference-Fourier map ranged from -0.504 to 0.630 eÅ^{-3}. Scattering factors were taken from the International Tables for Crystallography, Volume C. (Maslen et al., 1992, and Creagh & McAuley, 1992)

References

Bruker AXS (2001). *SHELXTL v6.12*. Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, USA.

Bruker AXS (2004). *SADABS*. Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, USA.

Bruker AXS (2006a). *APEX2 v2.1-0*. Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, USA.

Bruker AXS (2006b). *SAINT V7.34A*. Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, USA.

Creagh, D. C. & McAuley, W. J. (1992). *International Tables for Crystallography: Mathematical, Physical and Chemical Tables*, Vol C, edited by A. J. C. Wilson, pp. 206-222. Dordrecht, The Netherlands: Kluwer.

Maslen, E. N., Fox, A. G. & O'Keefe, M. A. (1992). *International Tables for Crystallography: Mathematical, Physical and Chemical Tables*, Vol C, edited by A. J. C. Wilson, pp. 476-516. Dordrecht, The Netherlands: Kluwer.

$R(F) = R1 = \Sigma\ ||F_o|-|F_c|| / \Sigma|F_o|$, $wR(F^2) = wR2 = [\ \Sigma\ w\ (F_o^2-F_c^2)^2 / \Sigma\ w\ (F_o^2)^2\ ]^{1/2}$, and S = Goodness-of-fit on $F^2 = [\ \Sigma\ w\ (F_o^2-F_c^2)^2 / (n-p)\ ]^{1/2}$, where n is the number of reflections and p is the number of parameters refined.

Table 1. Crystal data and structure refinement for **10**.

Identification code	**10** (CCDC 705008)
Formula	C36 H32 Cl4 N2 O8 Pd2

Formula weight	975.24	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca (No. 16)	
Unit cell dimensions	a = 16.3668(4) Å	α= 90°
	b = 17.4864(4) Å	β= 90°
	c = 26.0050(6) Å	γ = 90°
Volume	7442.5(3) $Å^3$	
Z	8	
Density (calculated)	1.741 mg/m^3	
Absorption coefficient	1.308 mm^{-1}	
F(000)	3888	
Crystal size	0.125 x 0.125 x 0.010 mm^3	
Theta range for data collection	1.88 to 25.00°.	
Index ranges	-19<=h<=17, -20<=k<=20, -23<=l<=30	
Reflections collected	36560	
Independent reflections	6548 [R(int) = 0.1022]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Numerical	
Max. and min. transmission	0.9870 and 0.8536	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6548 / 444 / 582	
Goodness-of-fit on F^2	1.005	
Final R indices [I>2sigma(I)]	R1 = 0.0428, wR2 = 0.0819	
R indices (all data)	R1 = 0.0866, wR2 = 0.0969	
Largest diff. peak and hole	0.630 and -0.504 e.$Å^{-3}$	

Table 2. Bond lengths [Å] and angles [°] for **10**.

Pd-N(1)	2.002(5)	C(8)-C(13)	1.401(7)
Pd-C(12)	2.006(5)	C(8)-C(9)	1.409(8)
Pd-O(5)	2.042(4)	C(9)-C(10)	1.356(8)
Pd-O(3)	2.108(4)	C(9)-H(9)	0.9500
Pd-O(1)	2.120(4)	C(10)-C(11)	1.411(8)
Pd-Pd'	2.5681(5)	C(10)-H(10)	0.9500
Pd'-C(12')	1.988(5)	C(11)-C(12)	1.360(7)
Pd'-N(1')	2.009(4)	C(11)-H(11)	0.9500
Pd'-O(4)	2.043(4)	C(12)-C(13)	1.379(7)
Pd'-O(7)	2.107(4)	C(13)-C(14)	1.422(8)
Pd'-O(6)	2.118(4)	N(1')-C(2')	1.349(7)
N(1)-C(2)	1.340(7)	N(1')-C(14')	1.361(7)
N(1)-C(14)	1.367(7)	C(2')-C(3')	1.394(8)
C(2)-C(3)	1.391(8)	C(2')-H(2')	0.9500
C(2)-H(2)	0.9500	C(3')-C(4')	1.371(8)
C(3)-C(4)	1.355(9)	C(3')-H(3')	0.9500
C(3)-H(3)	0.9500	C(4')-C(5')	1.402(8)
C(4)-C(5)	1.391(8)	C(4')-H(4')	0.9500
C(4)-H(4)	0.9500	C(5')-C(14')	1.391(7)
C(5)-C(14)	1.398(8)	C(5')-C(6')	1.423(8)
C(5)-C(6)	1.444(8)	C(6')-C(7')	1.348(8)
C(6)-C(7)	1.349(9)	C(6')-H(6')	0.9500
C(6)-H(6)	0.9500	C(7')-C(8')	1.429(8)
C(7)-C(8)	1.427(8)	C(7')-H(7')	0.9500
C(7)-H(7)	0.9500	C(8')-C(13')	1.402(7)

C(8')-C(9')	1.416(8)	C(21)-C(22)	1.495(8)
C(9')-C(10')	1.365(8)	C(22)-H(22A)	0.9800
C(9')-H(9')	0.9500	C(22)-H(22B)	0.9800
C(10')-C(11')	1.392(8)	C(22)-H(22C)	0.9800
C(10')-H(10')	0.9500	C(1S)-Cl(1)	1.756(7)
C(11')-C(12')	1.367(7)	C(1S)-Cl(2)	1.765(6)
C(11')-H(11')	0.9500	C(1S)-H(1SA)	0.9900
C(12')-C(13')	1.387(7)	C(1S)-H(1SB)	0.9900
C(13')-C(14')	1.421(7)	C(1S')-Cl(2')	1.761(7)
O(1)-C(15)	1.285(7)	C(1S')-Cl(1')	1.761(7)
O(2)-C(15)	1.215(7)	C(1S')-H(1SC)	0.9900
C(15)-C(16)	1.517(7)	C(1S')-H(1SD)	0.9900
C(16)-H(16A)	0.9800	C(1S")-Cl(2")	1.759(7)
C(16)-H(16B)	0.9800	C(1S")-Cl(1")	1.762(7)
C(16)-H(16C)	0.9800	C(1S")-H(1SE)	0.9900
O(3)-C(17)	1.253(6)	C(1S")-H(1SF)	0.9900
O(4)-C(17)	1.272(6)	C(2S)-Cl(4)	1.760(7)
C(17)-C(18)	1.493(8)	C(2S)-Cl(3)	1.762(7)
C(18)-H(18A)	0.9800	C(2S)-H(2SA)	0.9900
C(18)-H(18B)	0.9800	C(2S)-H(2SB)	0.9900
C(18)-H(18C)	0.9800	C(2S')-Cl(4')	1.760(7)
O(5)-C(19)	1.269(6)	C(2S')-Cl(3')	1.764(7)
O(6)-C(19)	1.252(6)	C(2S')-H(2SC)	0.9900
C(19)-C(20)	1.490(8)	C(2S')-H(2SD)	0.9900
C(20)-H(20A)	0.9800	C(2S")-Cl(4")	1.761(7)
C(20)-H(20B)	0.9800	C(2S")-Cl(3")	1.764(7)
C(20)-H(20C)	0.9800	C(2S")-H(2SE)	0.9900
O(7)-C(21)	1.303(6)	C(2S")-H(2SF)	0.9900
O(8)-C(21)	1.219(6)		

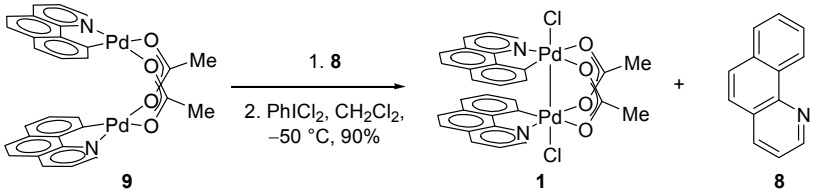
N(1)-Pd-C(12)	82.8(2)	N(1')-Pd'-Pd	96.42(12)
N(1)-Pd-O(5)	177.54(17)	O(4)-Pd'-Pd	83.73(10)
C(12)-Pd-O(5)	94.74(19)	O(7)-Pd'-Pd	163.64(11)
N(1)-Pd-O(3)	93.96(17)	O(6)-Pd'-Pd	83.87(10)
C(12)-Pd-O(3)	176.69(18)	C(2)-N(1)-C(14)	118.9(5)
O(5)-Pd-O(3)	88.49(15)	C(2)-N(1)-Pd	128.4(4)
N(1)-Pd-O(1)	85.97(16)	C(14)-N(1)-Pd	112.7(4)
C(12)-Pd-O(1)	92.24(17)	N(1)-C(2)-C(3)	121.0(6)
O(5)-Pd-O(1)	94.14(15)	N(1)-C(2)-H(2)	119.5
O(3)-Pd-O(1)	86.83(15)	C(3)-C(2)-H(2)	119.5
N(1)-Pd-Pd'	96.80(12)	C(4)-C(3)-C(2)	120.3(6)
C(12)-Pd-Pd'	96.93(14)	C(4)-C(3)-H(3)	119.9
O(5)-Pd-Pd'	83.48(10)	C(2)-C(3)-H(3)	119.9
O(3)-Pd-Pd'	84.11(10)	C(3)-C(4)-C(5)	120.5(6)
O(1)-Pd-Pd'	170.68(11)	C(3)-C(4)-H(4)	119.8
C(12')-Pd'-N(1')	82.25(19)	C(5)-C(4)-H(4)	119.8
C(12')-Pd'-O(4)	93.89(18)	C(4)-C(5)-C(14)	117.1(6)
N(1')-Pd'-O(4)	176.13(17)	C(4)-C(5)-C(6)	126.4(6)
C(12')-Pd'-O(7)	97.03(17)	C(14)-C(5)-C(6)	116.5(6)
N(1')-Pd'-O(7)	95.29(16)	C(7)-C(6)-C(5)	122.1(6)
O(4)-Pd'-O(7)	85.35(15)	C(7)-C(6)-H(6)	118.9
C(12')-Pd'-O(6)	176.55(18)	C(5)-C(6)-H(6)	118.9
N(1')-Pd'-O(6)	94.36(17)	C(6)-C(7)-C(8)	121.3(6)
O(4)-Pd'-O(6)	89.50(15)	C(6)-C(7)-H(7)	119.4
O(7)-Pd'-O(6)	83.89(15)	C(8)-C(7)-H(7)	119.4
C(12')-Pd'-Pd	95.83(13)	C(13)-C(8)-C(9)	117.0(6)

C(13)-C(8)-C(7)	118.4(6)	C(12')-C(13')-C(8')	123.6(5)
C(9)-C(8)-C(7)	124.5(6)	C(12')-C(13')-C(14')	116.8(5)
C(10)-C(9)-C(8)	119.3(6)	C(8')-C(13')-C(14')	119.7(5)
C(10)-C(9)-H(9)	120.3	N(1')-C(14')-C(5')	122.9(5)
C(8)-C(9)-H(9)	120.3	N(1')-C(14')-C(13')	115.4(5)
C(9)-C(10)-C(11)	122.9(6)	C(5')-C(14')-C(13')	121.7(5)
C(9)-C(10)-H(10)	118.5	C(15)-O(1)-Pd	123.4(4)
C(11)-C(10)-H(10)	118.5	O(2)-C(15)-O(1)	126.3(5)
C(12)-C(11)-C(10)	118.1(6)	O(2)-C(15)-C(16)	119.4(6)
C(12)-C(11)-H(11)	121.0	O(1)-C(15)-C(16)	114.3(5)
C(10)-C(11)-H(11)	121.0	C(15)-C(16)-H(16A)	109.5
C(11)-C(12)-C(13)	119.8(5)	C(15)-C(16)-H(16B)	109.5
C(11)-C(12)-Pd	128.9(4)	H(16A)-C(16)-H(16B)	109.5
C(13)-C(12)-Pd	111.3(4)	C(15)-C(16)-H(16C)	109.5
C(12)-C(13)-C(8)	122.8(5)	H(16A)-C(16)-H(16C)	109.5
C(12)-C(13)-C(14)	117.4(5)	H(16B)-C(16)-H(16C)	109.5
C(8)-C(13)-C(14)	119.8(5)	C(17)-O(3)-Pd	117.9(3)
N(1)-C(14)-C(5)	122.3(5)	C(17)-O(4)-Pd'	122.0(4)
N(1)-C(14)-C(13)	115.8(5)	O(3)-C(17)-O(4)	124.6(5)
C(5)-C(14)-C(13)	121.9(5)	O(3)-C(17)-C(18)	119.4(5)
C(2')-N(1')-C(14')	120.1(5)	O(4)-C(17)-C(18)	116.0(5)
C(2')-N(1')-Pd'	126.6(4)	C(17)-C(18)-H(18A)	109.5
C(14')-N(1')-Pd'	113.3(3)	C(17)-C(18)-H(18B)	109.5
N(1')-C(2')-C(3')	118.9(5)	H(18A)-C(18)-H(18B)	109.5
N(1')-C(2')-H(2')	120.6	C(17)-C(18)-H(18C)	109.5
C(3')-C(2')-H(2')	120.6	H(18A)-C(18)-H(18C)	109.5
C(4')-C(3')-C(2')	121.7(6)	H(18B)-C(18)-H(18C)	109.5
C(4')-C(3')-H(3')	119.1	C(19)-O(5)-Pd	122.2(3)
C(2')-C(3')-H(3')	119.1	C(19)-O(6)-Pd'	117.5(3)
C(3')-C(4')-C(5')	119.4(5)	O(6)-C(19)-O(5)	124.5(5)
C(3')-C(4')-H(4')	120.3	O(6)-C(19)-C(20)	118.7(5)
C(5')-C(4')-H(4')	120.3	O(5)-C(19)-C(20)	116.8(5)
C(14')-C(5')-C(4')	117.0(5)	C(19)-C(20)-H(20A)	109.5
C(14')-C(5')-C(6')	117.6(5)	C(19)-C(20)-H(20B)	109.5
C(4')-C(5')-C(6')	125.5(6)	H(20A)-C(20)-H(20B)	109.5
C(7')-C(6')-C(5')	121.3(6)	C(19)-C(20)-H(20C)	109.5
C(7')-C(6')-H(6')	119.4	H(20A)-C(20)-H(20C)	109.5
C(5')-C(6')-H(6')	119.4	H(20B)-C(20)-H(20C)	109.5
C(6')-C(7')-C(8')	122.1(5)	C(21)-O(7)-Pd'	127.0(4)
C(6')-C(7')-H(7')	118.9	O(8)-C(21)-O(7)	124.9(5)
C(8')-C(7')-H(7')	118.9	O(8)-C(21)-C(22)	120.8(5)
C(13')-C(8')-C(9')	115.8(5)	O(7)-C(21)-C(22)	114.2(5)
C(13')-C(8')-C(7')	117.6(5)	C(21)-C(22)-H(22A)	109.5
C(9')-C(8')-C(7')	126.5(5)	C(21)-C(22)-H(22B)	109.5
C(10')-C(9')-C(8')	120.0(6)	H(22A)-C(22)-H(22B)	109.5
C(10')-C(9')-H(9')	120.0	C(21)-C(22)-H(22C)	109.5
C(8')-C(9')-H(9')	120.0	H(22A)-C(22)-H(22C)	109.5
C(9')-C(10')-C(11')	122.6(6)	H(22B)-C(22)-H(22C)	109.5
C(9')-C(10')-H(10')	118.7	Cl(1)-C(1S)-Cl(2)	113.5(6)
C(11')-C(10')-H(10')	118.7	Cl(1)-C(1S)-H(1SA)	108.9
C(12')-C(11')-C(10')	118.9(6)	Cl(2)-C(1S)-H(1SA)	108.9
C(12')-C(11')-H(11')	120.6	Cl(1)-C(1S)-H(1SB)	108.9
C(10')-C(11')-H(11')	120.6	Cl(2)-C(1S)-H(1SB)	108.9
C(11')-C(12')-C(13')	119.0(5)	H(1SA)-C(1S)-H(1SB)	107.7
C(11')-C(12')-Pd'	128.8(4)	Cl(2')-C(1S')-Cl(1')	112.6(9)
C(13')-C(12')-Pd'	112.2(4)	Cl(2')-C(1S')-H(1SC)	109.1

Cl(1')-C(1S')-H(1SC)	109.1	Cl(3)-C(2S)-H(2SB)	109.2
Cl(2')-C(1S')-H(1SD)	109.1	H(2SA)-C(2S)-H(2SB)	107.9
Cl(1')-C(1S')-H(1SD)	109.1	Cl(4')-C(2S')-Cl(3')	111.9(8)
H(1SC)-C(1S')-H(1SD)	107.8	Cl(4')-C(2S')-H(2SC)	109.2
Cl(2")-C(1S")-Cl(1")	112.9(9)	Cl(3')-C(2S')-H(2SC)	109.2
Cl(2")-C(1S")-H(1SE)	109.0	Cl(4')-C(2S')-H(2SD)	109.2
Cl(1")-C(1S")-H(1SE)	109.0	Cl(3')-C(2S')-H(2SD)	109.2
Cl(2")-C(1S")-H(1SF)	109.0	H(2SC)-C(2S')-H(2SD)	107.9
Cl(1")-C(1S")-H(1SF)	109.0	Cl(4")-C(2S")-Cl(3")	110.4(8)
H(1SE)-C(1S")-H(1SF)	107.8	Cl(4")-C(2S")-H(2SE)	109.6
Cl(4)-C(2S)-Cl(3)	112.0(8)	Cl(3")-C(2S")-H(2SE)	109.6
Cl(4)-C(2S)-H(2SA)	109.2	Cl(4")-C(2S")-H(2SF)	109.6
Cl(3)-C(2S)-H(2SA)	109.2	Cl(3")-C(2S")-H(2SF)	109.6
Cl(4)-C(2S)-H(2SB)	109.2	H(2SE)-C(2S")-H(2SF)	108.1

Appendix E: Reactivity of 1 with Exogenous Benzo[*h*]quinoline (8)[8]

Synthesis of 1 in the Presence of Benzo[*h*]quinoline (8)

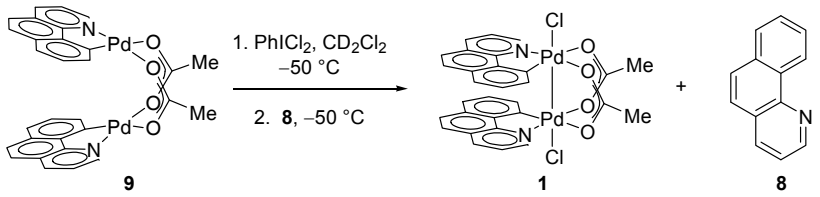


To a solution of benzo[*h*]quinolinyl palladium acetate dimer (**9**) (17.3 mg, 2.51×10^{-5} mol, 1.00 equiv) and benzo[*h*]quinoline (**8**) (18.0 mg, 1.04×10^{-4} mol, 4.00 equiv) in CH_2Cl_2 (3.0 mL) at –50˚C was added $PhICl_2$ (6.9 mg, 2.5×10^{-5} mol, 1.0 equiv). The color of the solution immediately changed from pale yellow to dark red-brown. After stirring at –50˚C for 10 minutes, solvent was removed *in vacuo* at –50˚C. The residue was washed with cold Et_2O (–50˚C) three times. The remaining solid was dried under vacuum at –50˚C to afford 17 mg of the title compound as a dark red solid (90% yield.). Alternatively, the reaction could be carried out in CD_2Cl_2 to allow the reaction mixture to be directly analyzed.

Spectral properties of **1** obtained by this procedure were identical to those reported above.

[8] We have previously reported data regarding the reactivity of complex **1** in the presence of exogenous **8** (*Nat. Chem*. **2009**, *1*, 302–309.). Based on a reinvestigation of the reactivity of the **1** with **8**, we have revised our original proposal that **8** can serve as a ligand for **1**. As is detailed below, no interaction between **1** and **8** can be detected by either ^{1}H NMR or UV-vis spectroscopy (spectra below). The reproducible acceleration of C–Cl bond formation from **1** that has been observed in the presence of **8** is now believed to be a function of acidity (see above) and not *N*-ligation, as we proposed.

Addition of Benzo[*h*]quinoline (8) to Complex 1

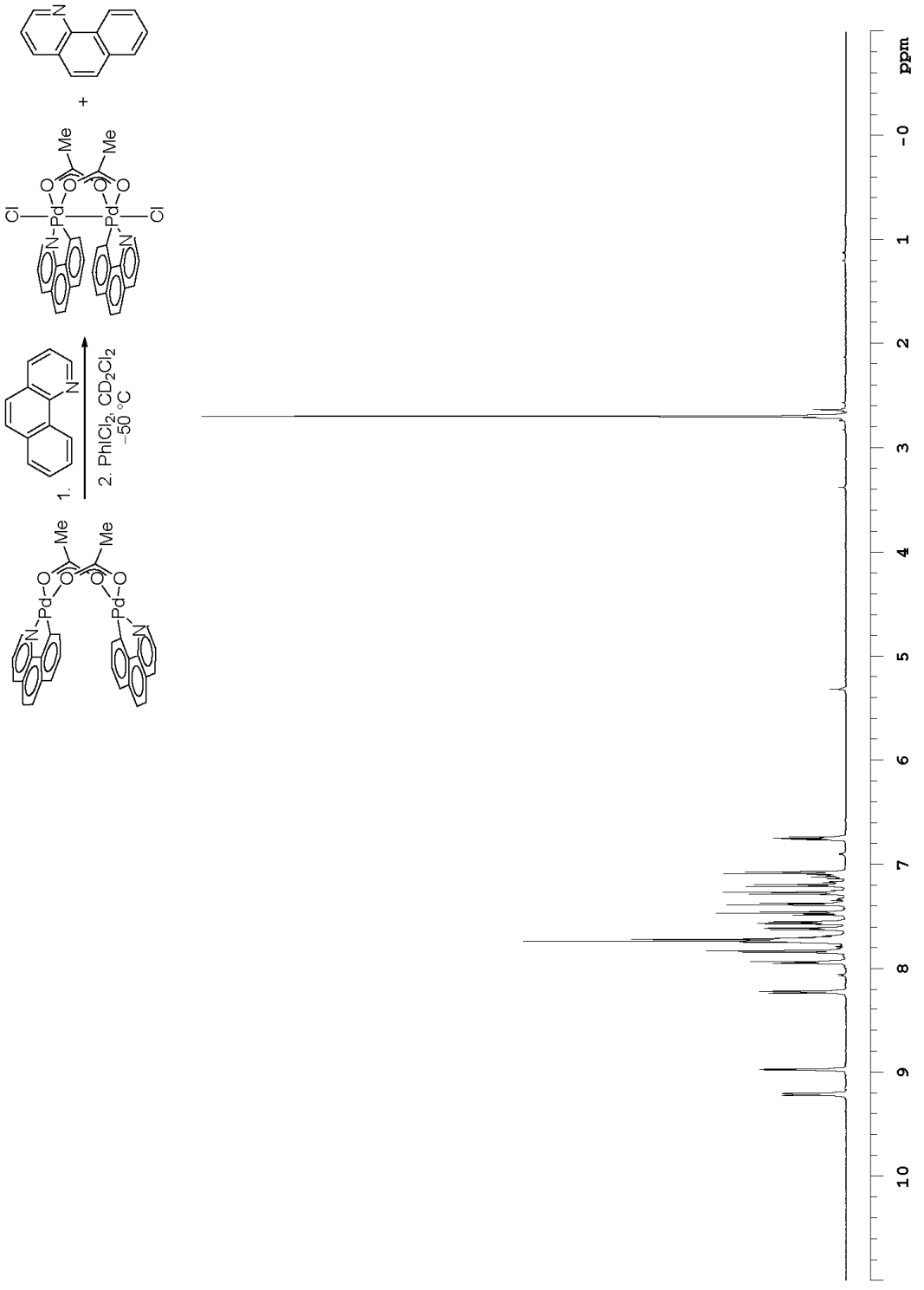


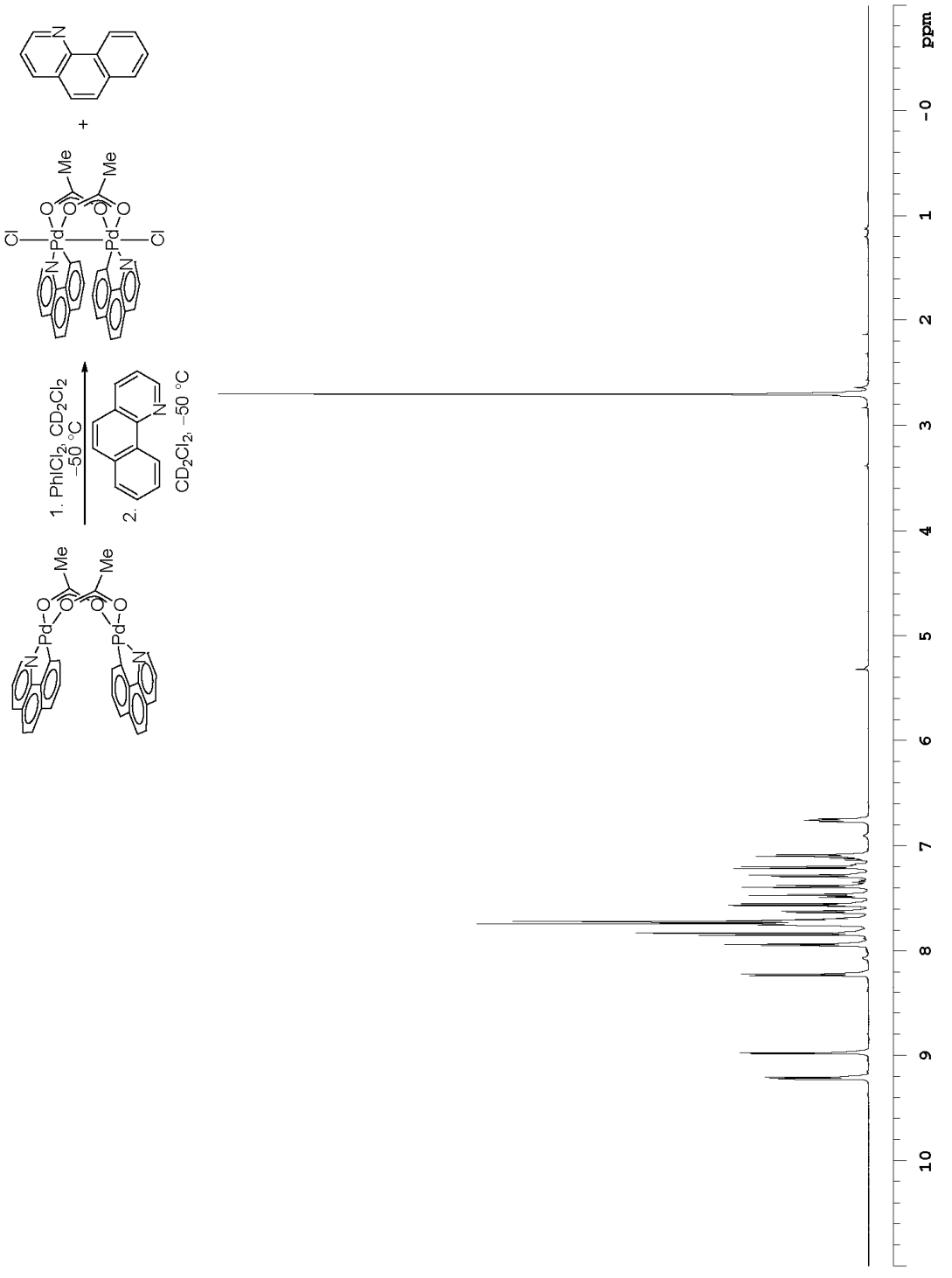
9 **1** **8**

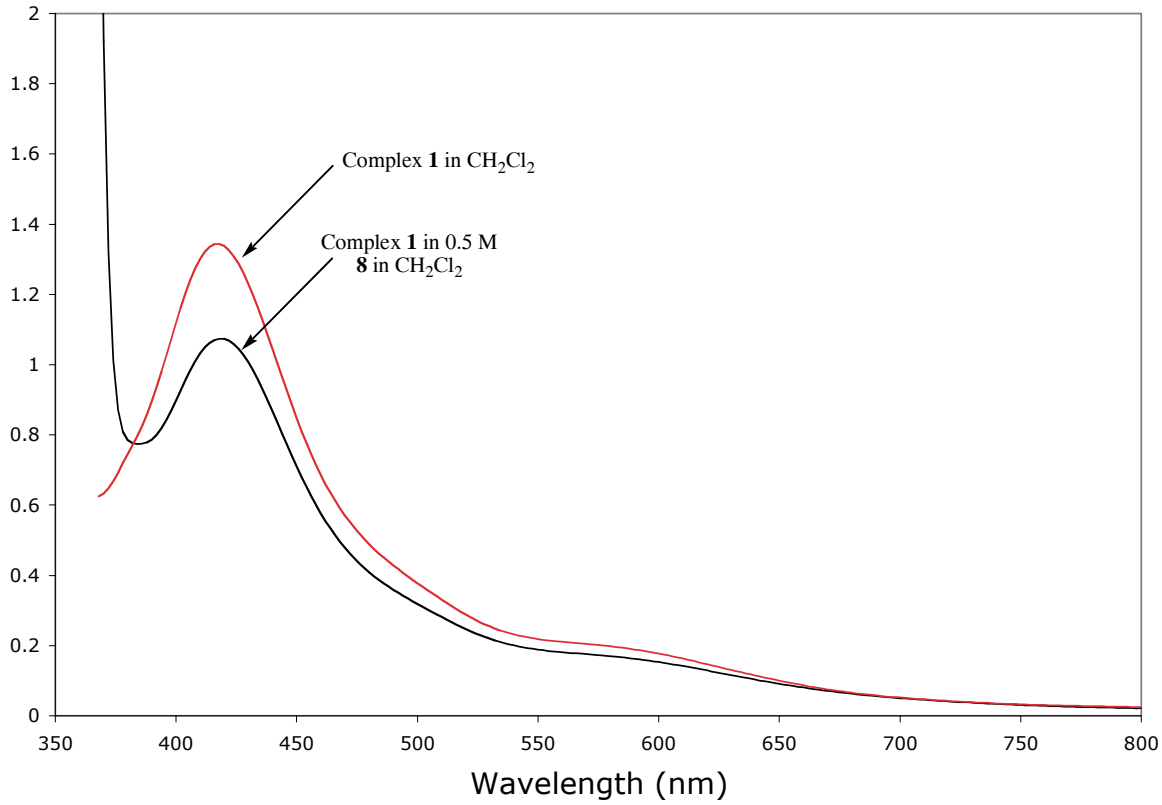
To a solution of benzo[*h*]quinolinyl palladium acetate dimer (**9**) (6.8 mg, 9.8×10^{-6} mol, 1.0 equiv) in CD_2Cl_2 (1.0 mL) was added $PhICl_2$ (2.7 mg, 9.8×10^{-6} mol, 1.0 equiv) in one portion as a solid at –50˚C. After five minutes, benzo[*h*]quinoline (**8**) (7.0 mg, 3.9×10^{-5} mol, 4.0 equiv) was added at –50 ˚C.

^{1}H NMR and UV-vis[9] spectroscopies provided no evidence of interaction between **1** and **8**.

[9] The UV-vis spectrum of **1** in the presence of **8** was also unchanged if acquired immediately following sample preparation at 23 ˚C. Further, UV-vis spectra obtained of **1** in a 0.5 M solution of **8** also did not show evidence of interaction between **1** and **8** (reproduced below).

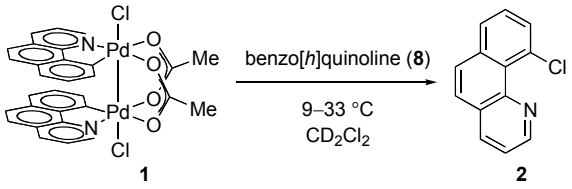

Me
Me
Cl
Pd
Pd
Cl
N
N
1.
2. PhICl2, CD2Cl2
−50 °C
Me
Me
Pd
Pd
N
N
ppm
10
9
8
7
6
5
4
3
2
1
0


1. PhICl2, CD2Cl2
–50 °C
2.
CD2Cl2, –50 °C
ppm



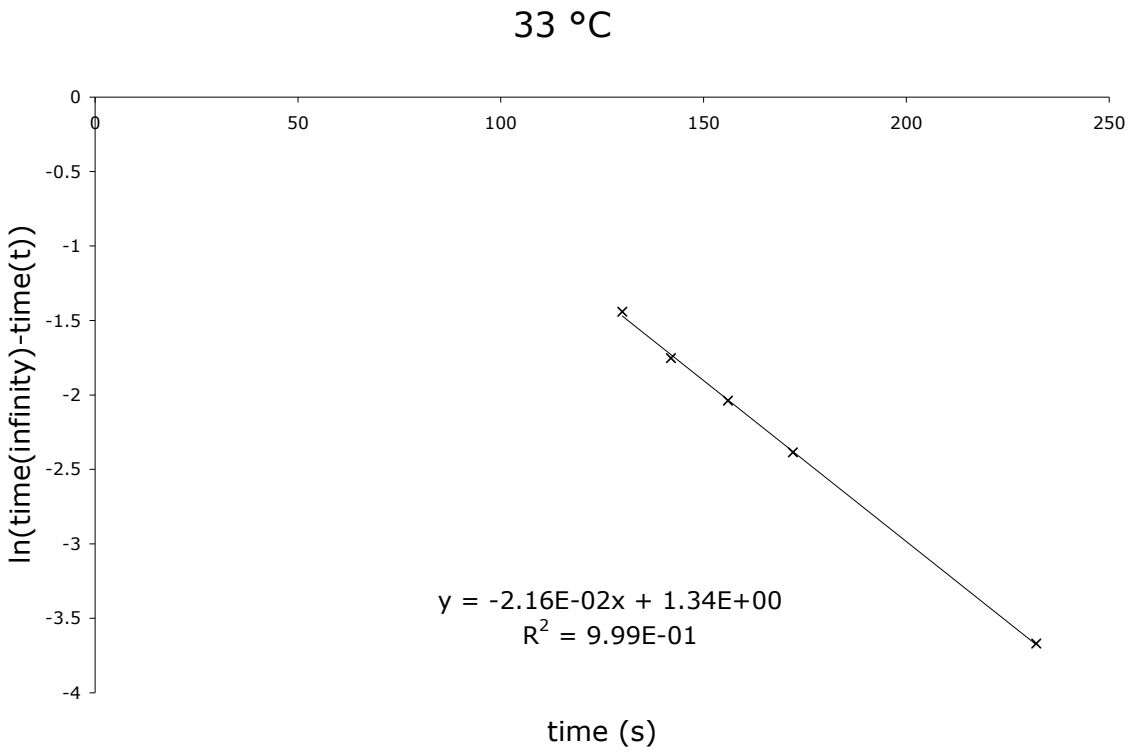
Above is a plot of the UV-vis spectra of **1** in CH_2Cl_2 and in 0.5 M **8** in CH_2Cl_2. No change in the λ_{max} above 400 nm can be observed. The plots deviate below 380 nm due to absorbances of the concentrated solution of **8** and thus this region can not be used to compare the UV-vis spectra of **1** in the different media employed.

Rate of C–Cl Reductive Elimination from 1 in Presence of Exogenous 8

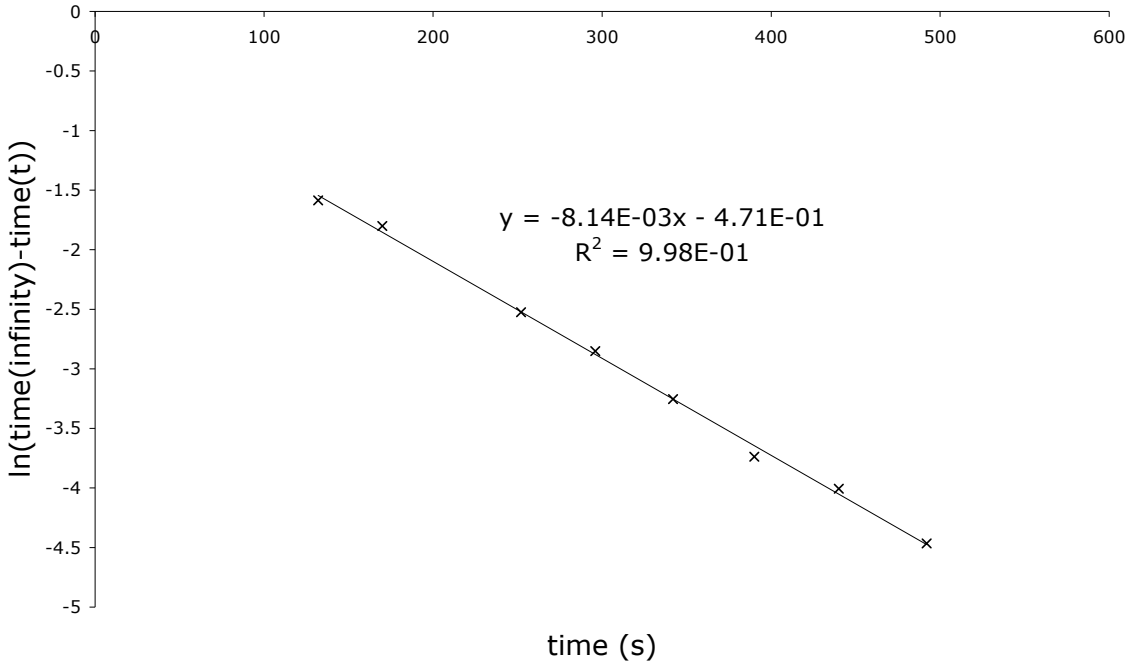


Stock solutions of compound **11** (29.2 mM) and benzo[*h*]quinoline (**8**) (104 mM) were prepared in CD_2Cl_2. In a nitrogen-filled dry box, compound **9** (350 µL) was diluted with 250 µL CD_2Cl_2 in an NMR tube before 100 µL of benzo[*h*]quinoline (**8**) solution was added to the NMR tube. $PhICl_2$ (2.8 mg, 1.00 equiv) was added to the NMR tube as a solid. ^{1}H NMR spectra were obtained; the evolution of **2** was monitored by the ^{1}H NMR signal at 9.12 ppm. These signals were integrated relative the residual proton signal from CD_2Cl_2. Time points were excluded for those spectra in which the monitored peak overlapped with other peaks. Since evolution of product was measured, linear natural log plots were

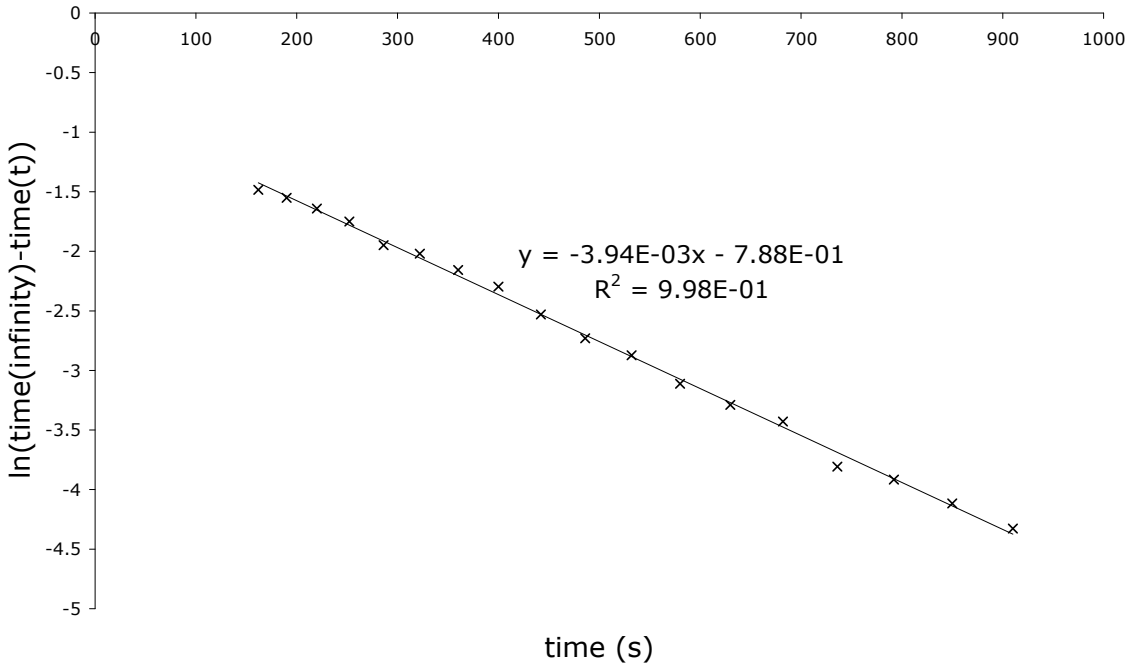
obtained by using an infinite time point set to 100% yield. In each case, the reactions were followed to greater than 3 half-lives. Data were fitted to a first order regression; plots, slopes, and R^2 values are reported below.



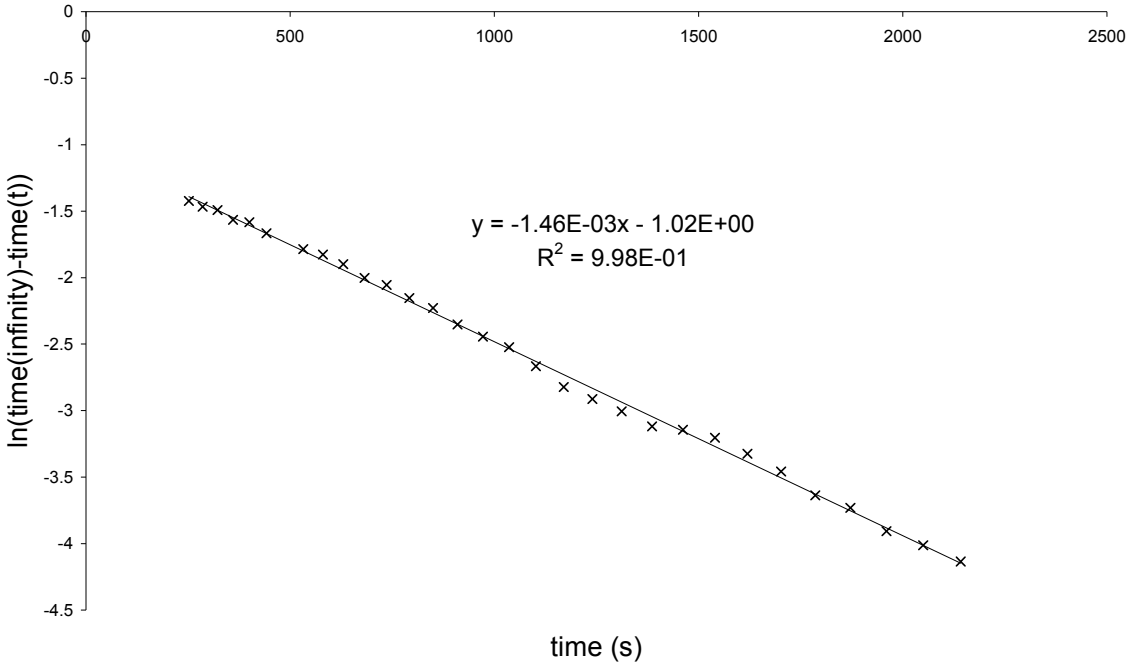
25 °C


y = -8.14E-03x - 4.71E-01
R2 = 9.98E-01
ln(time(infinity)-time(t))
time (s)
0
100
200
300
400
500
600
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
-4.5
-5

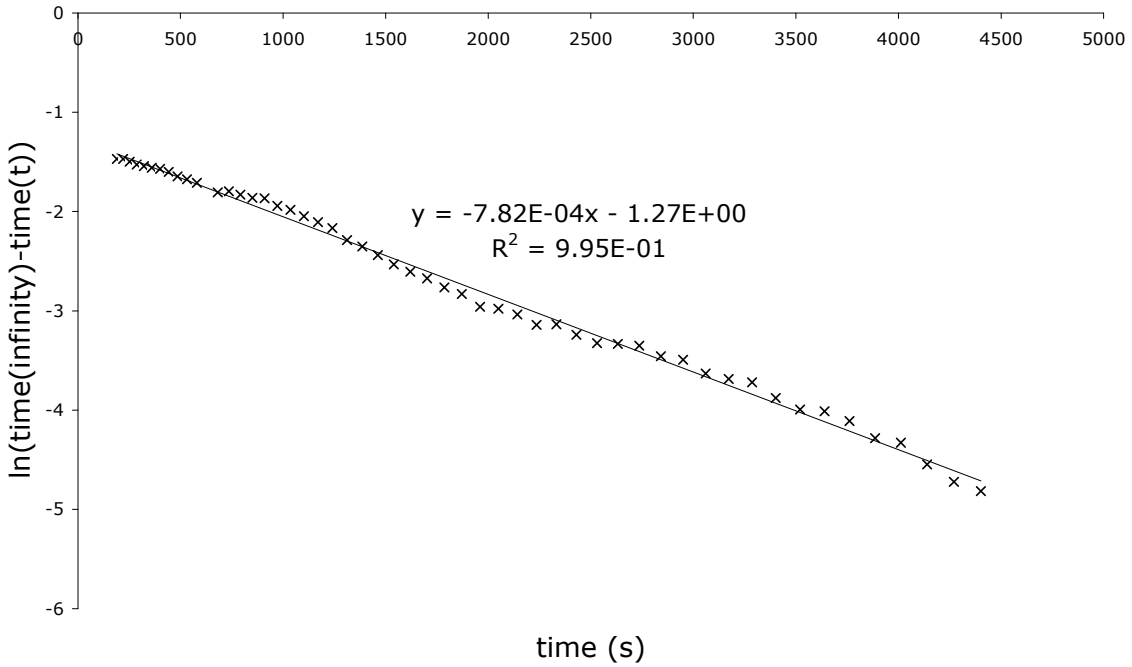
19 °C


y = -3.94E-03x - 7.88E-01
R2 = 9.98E-01
ln(time(infinity)-time(t))
time (s)
0
100
200
300
400
500
600
700
800
900
1000
-0.5
-1
-1.5
-2
-2.5
-3
-3.5
-4
-4.5
-5

13 °C

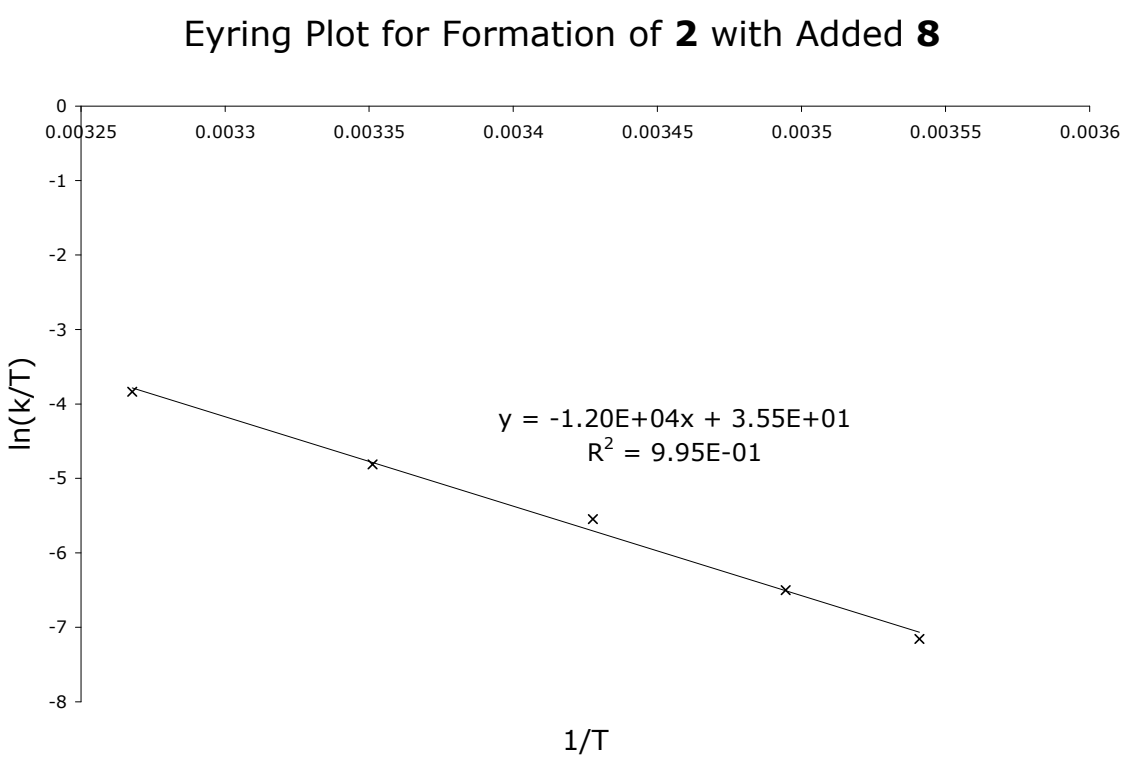

y = -1.46E-03x - 1.02E+00
R2 = 9.98E-01
ln(time(infinity)-time(t))
time (s)

9 °C


y = -7.82E-04x - 1.27E+00
R2 = 9.95E-01
ln(time(infinity)-time(t))
time (s)

Eyring Analysis

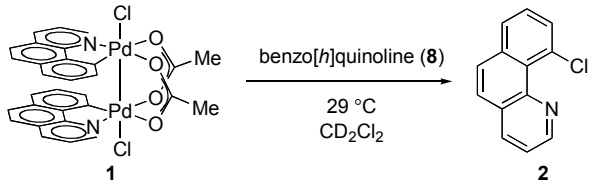
Temperature (K)	k (s^{-1}), R^2
282.41	7.82×10^{-4}; 0.995
286.16	1.46×10^{-3}; 0.998
291.75	3.94×10^{-3}; 0.998
298.40	8.14×10^{-3}; 0.998
306.02	2.16×10^{-2}; 0.999



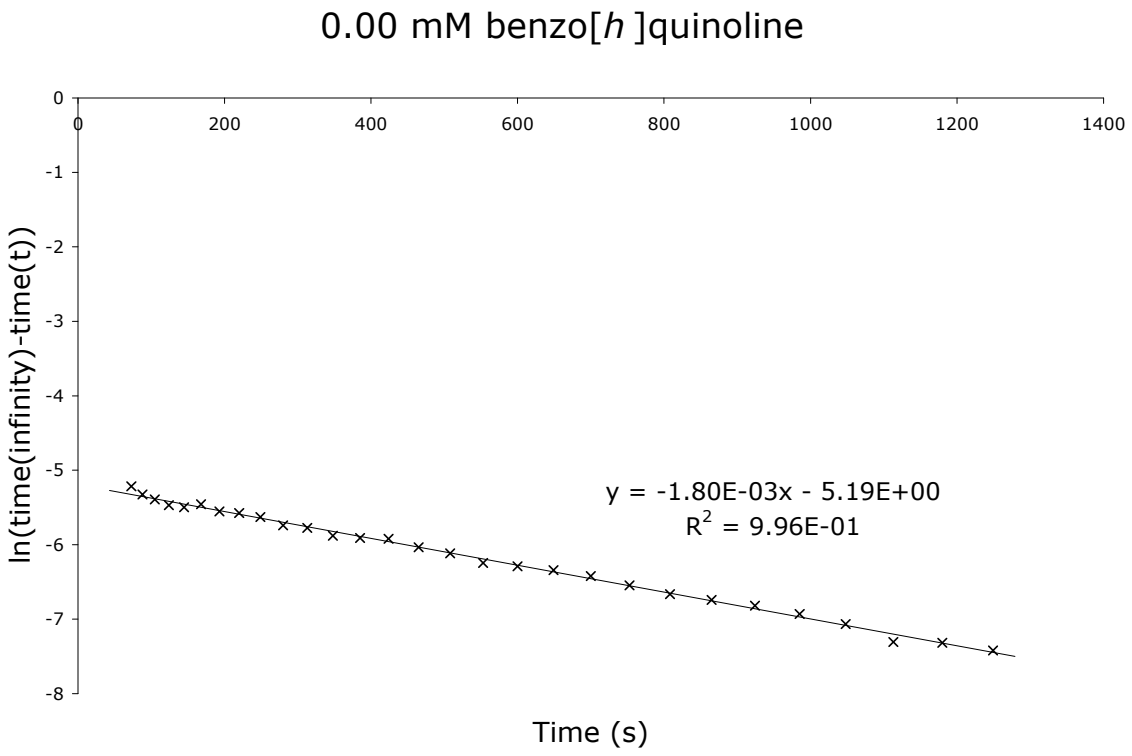
Error Analysis for Eyring Data

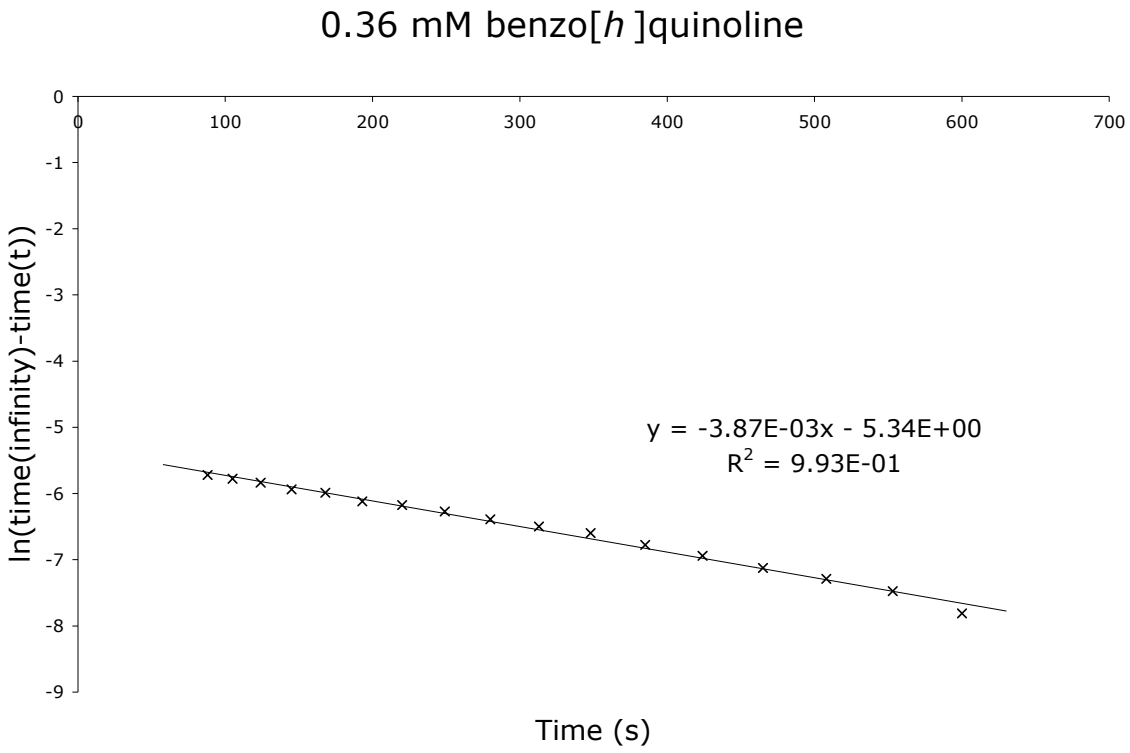
	Slope	Intercept	$\Delta H^{\ddagger}$	Difference	$\Delta S^{\ddagger}$	Difference	$\Delta G^{\ddagger}$	Difference
calcd + error	–10083	23.19	20.0	–3.4	–1.1	–11.3	20.3	–0.1
calcd	–11754	28.90	23.4	0.0	10.2	0.0	20.4	0.0
calcd – error	–13424	34.61	26.7	3.3	21.6	11.4	20.5	0.1

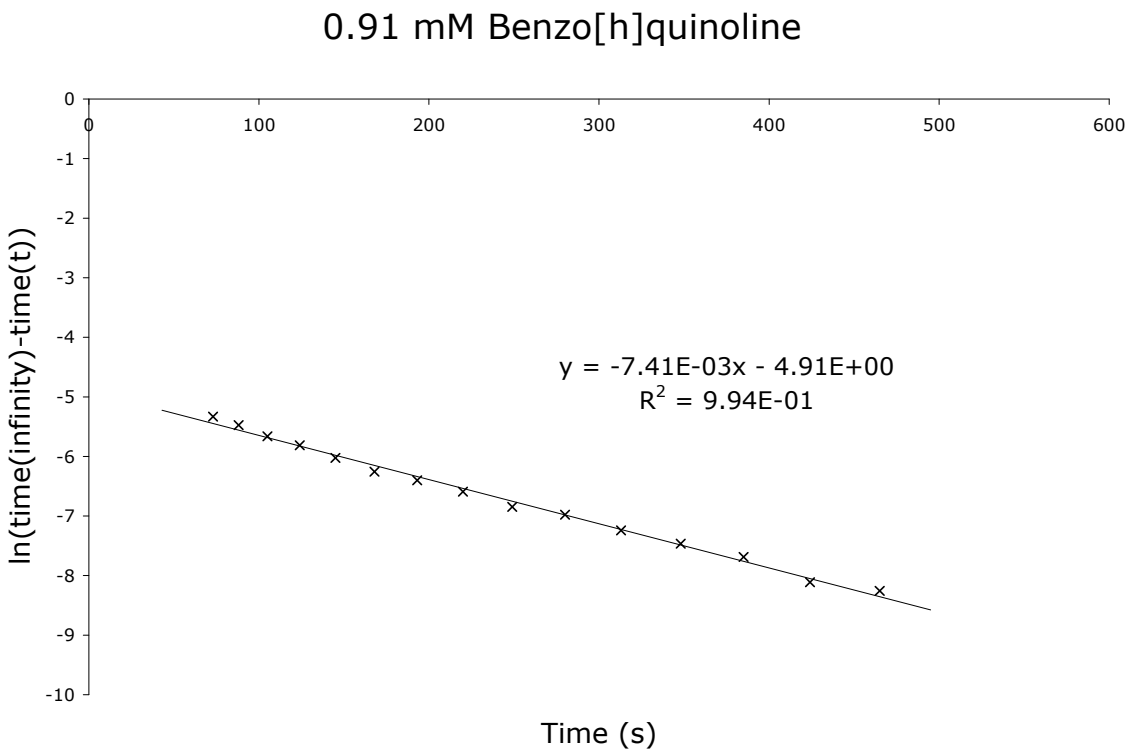
Rate of C–Cl Reductive Elimination from 1 as a Function of Concentration of 8

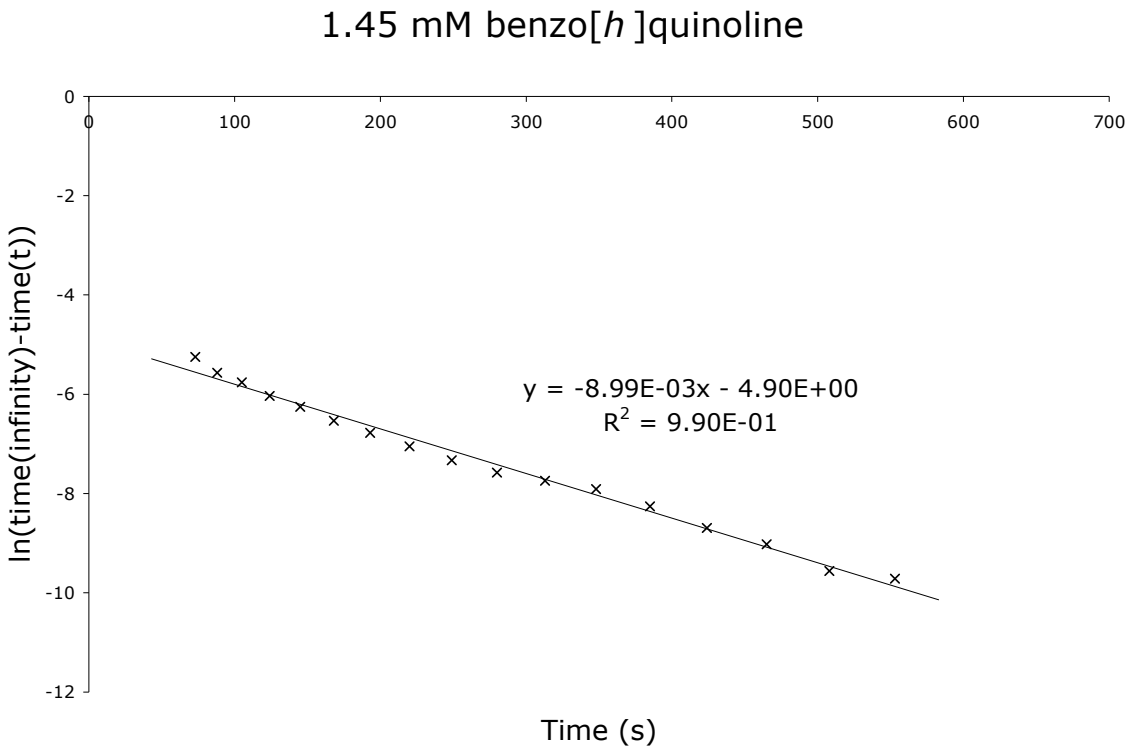


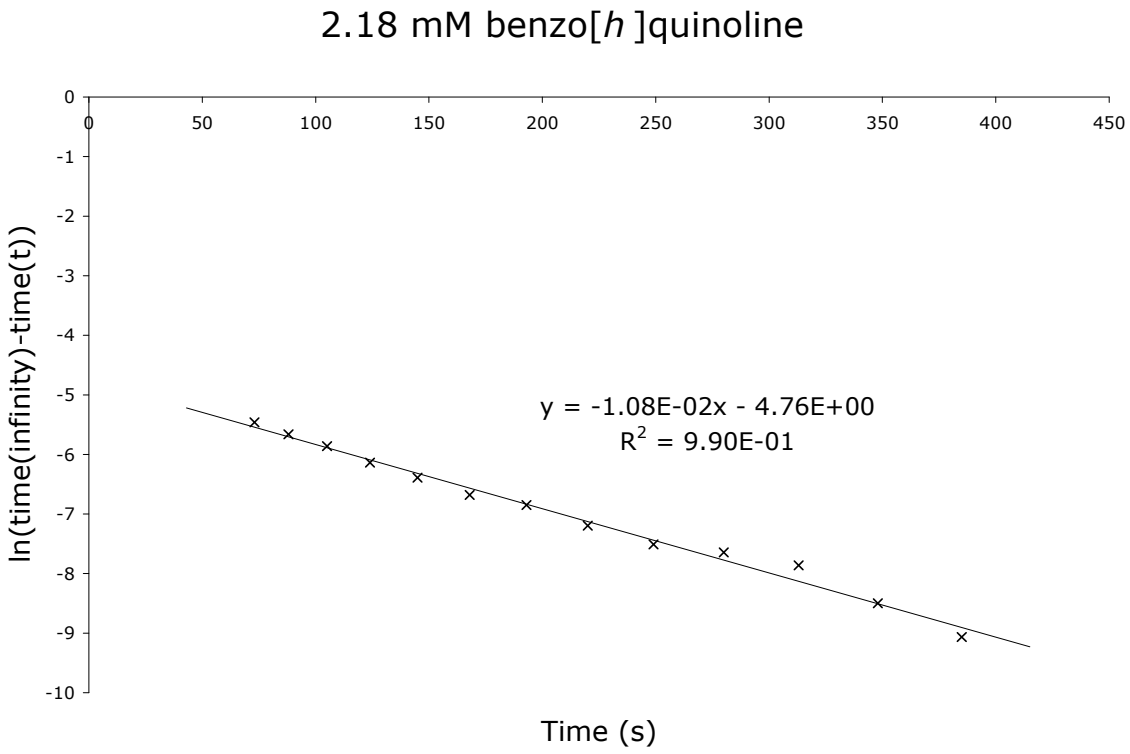
Stock solutions of compound **9** (19.4 mM), benzo[*h*]quinoline (**8**) (58.3 mM), and $PhICl_2$ (29.1 mM) were prepared in CD_2Cl_2. Samples were prepared by combining compound **9** solution (300 μL), $PhICl_2$ solution (200 μL), benzo[*h*]quinoline (**8**) solution (*n* μL), and CD_2Cl_2 (300–*n*) in a nitrogen-purged NMR tube. ^1H NMR spectra were obtained; the evolution of **2** was monitored by the ^1H NMR signal at 9.12 ppm. These signals were integrated relative the residual proton signal from CD_2Cl_2. Time points were excluded for those spectra in which the monitored peak overlapped with other peaks. Since evolution of product was measured, linear natural log plots were obtained by using an infinite time point set to 100% yield. In each case, the reactions were followed to greater than 3 half-lives. Data were fitted to a first order regression; plots, slopes, and R^2 values are reported below.

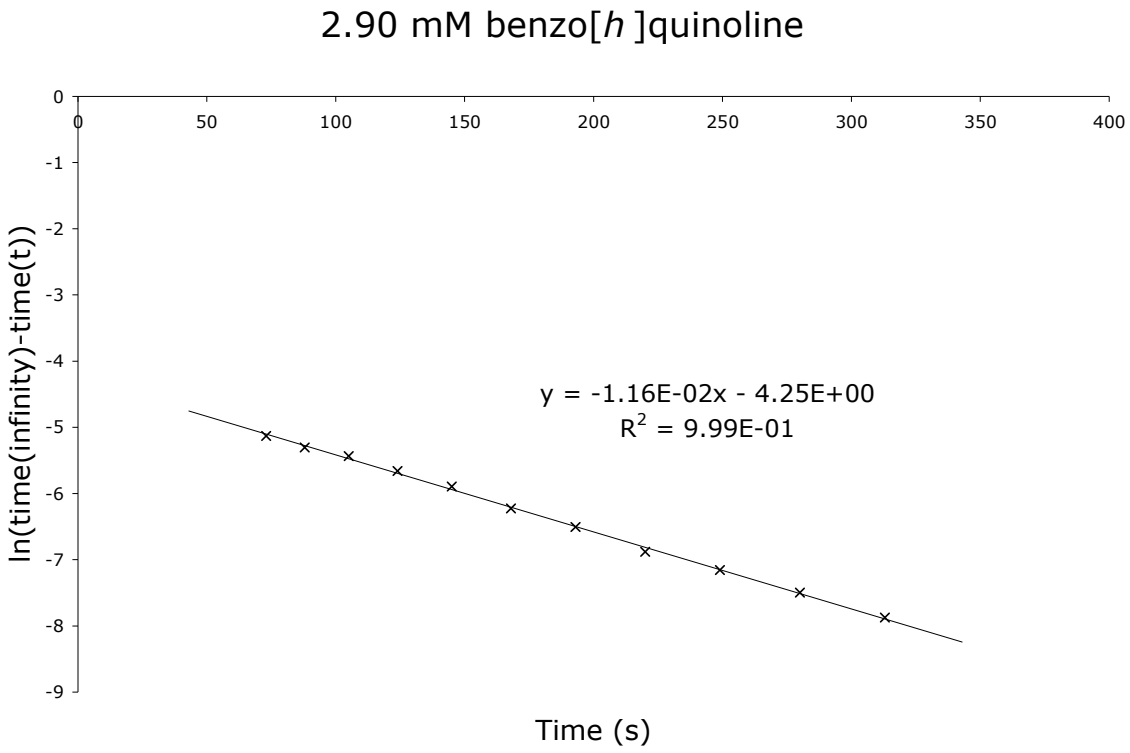


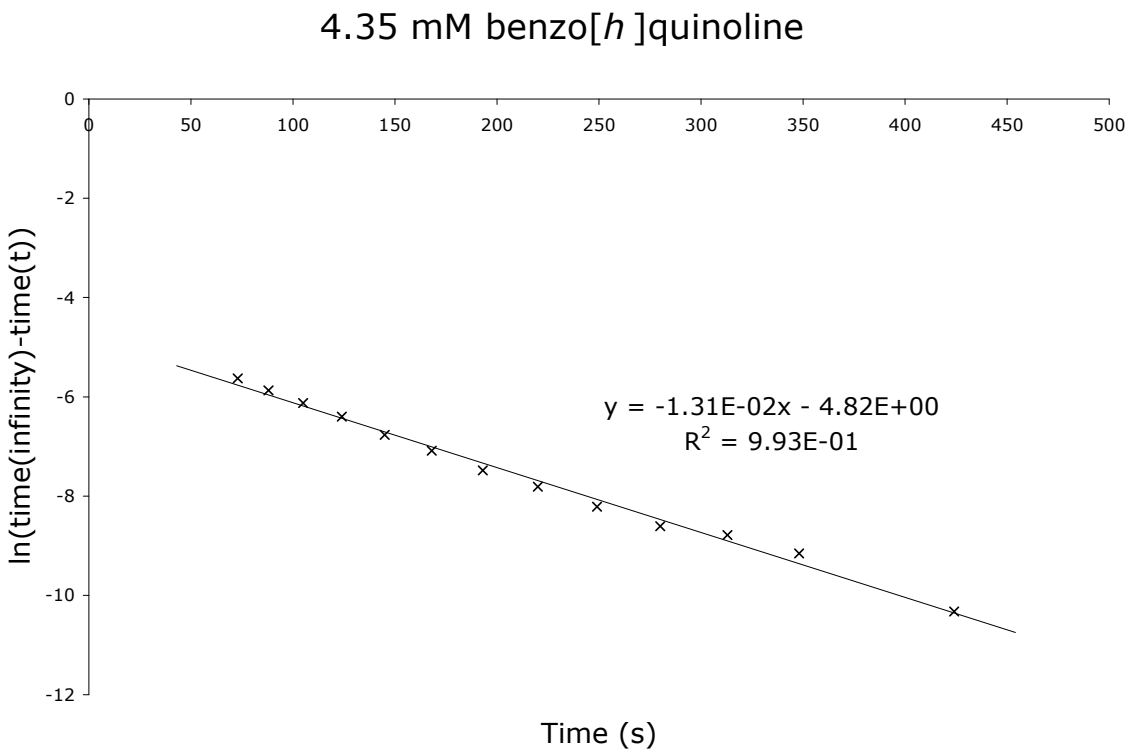

0.36 mM benzo[h]quinoline
ln(time(infinity)-time(t))
Time (s)
y = -3.87E-03x - 5.34E+00
R2 = 9.93E-01
0
100
200
300
400
500
600
700
-1
-2
-3
-4
-5
-6
-7
-8
-9

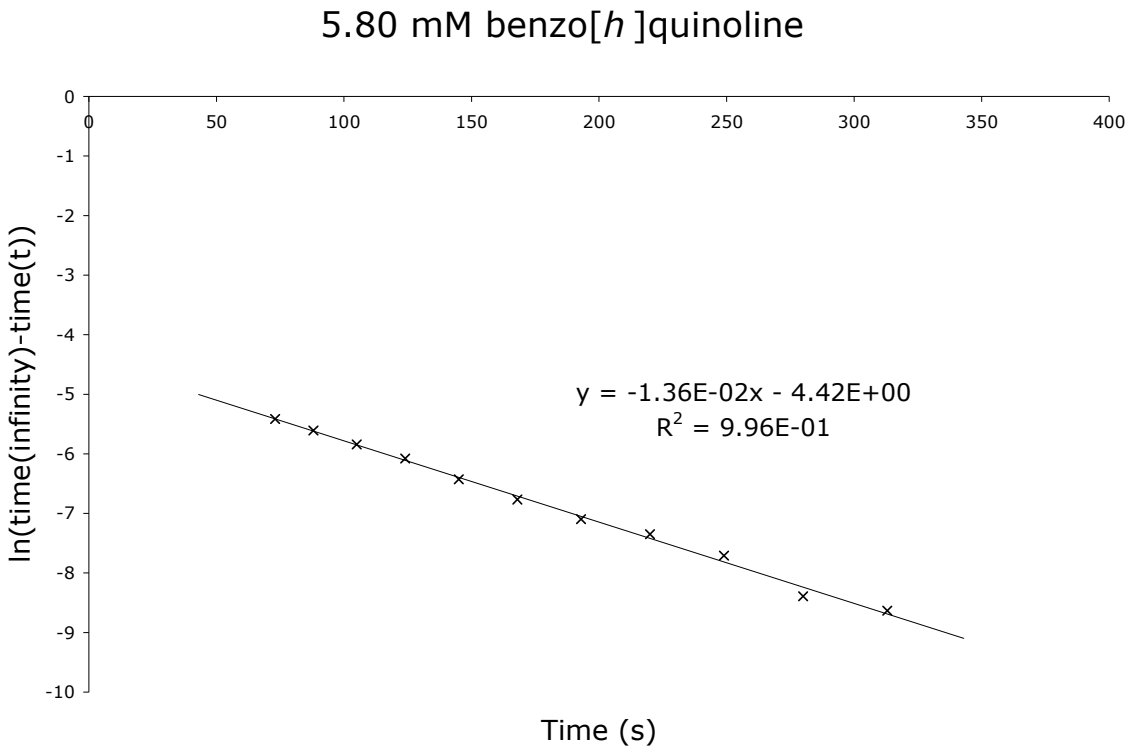

0.91 mM Benzo[h]quinoline
ln(time(infinity)-time(t))
Time (s)
y = -7.41E-03x - 4.91E+00
R2 = 9.94E-01
0
100
200
300
400
500
600
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10

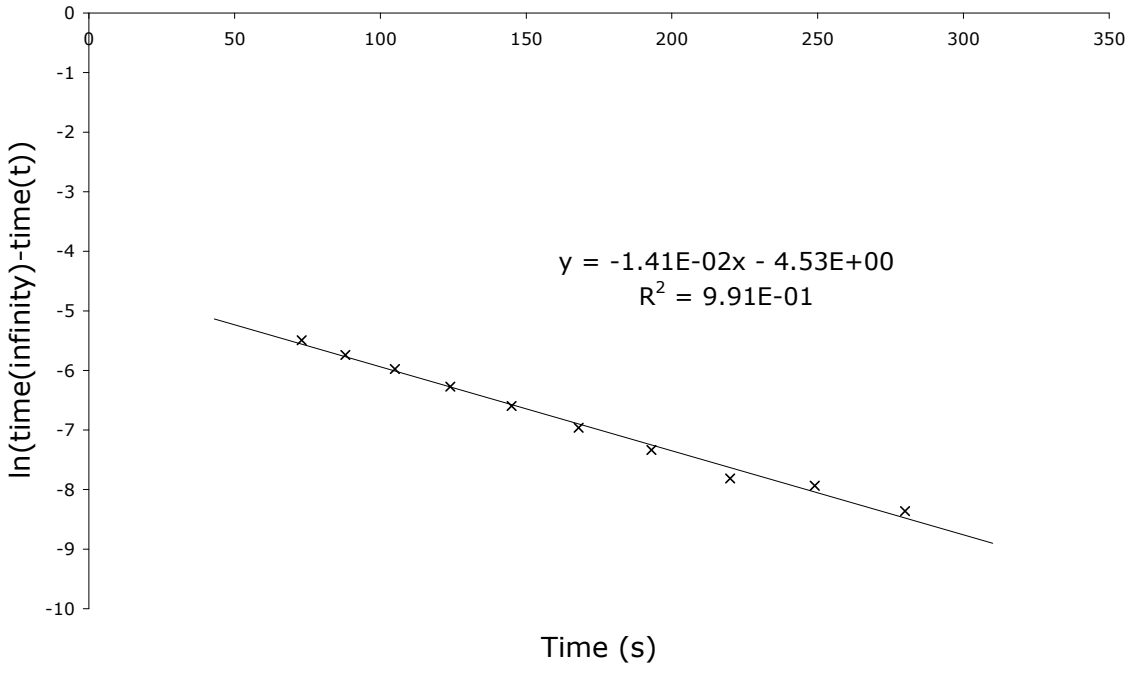

1.45 mM benzo[h]quinoline
ln(time(infinity)-time(t))
Time (s)
y = -8.99E-03x - 4.90E+00
R2 = 9.90E-01
0
-2
-4
-6
-8
-10
-12
0
100
200
300
400
500
600
700

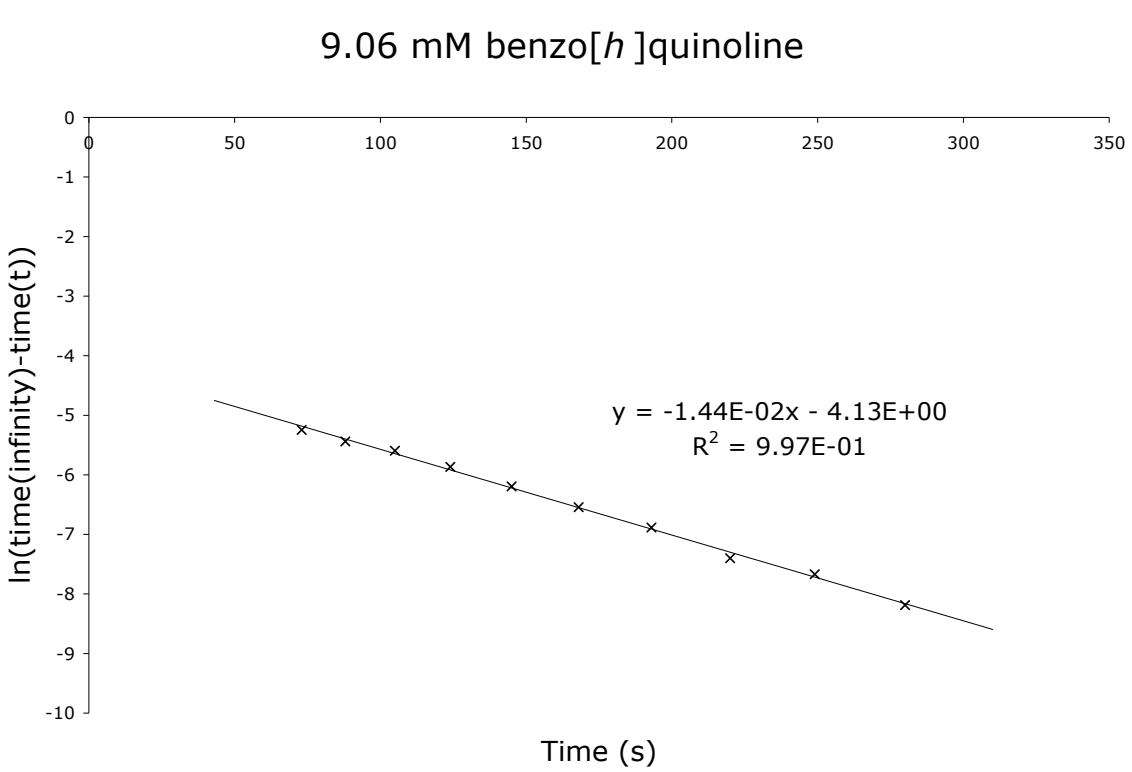

2.18 mM benzo[h]quinoline
ln(time(infinity)-time(t))
Time (s)
y = -1.08E-02x - 4.76E+00
R2 = 9.90E-01
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
0
50
100
150
200
250
300
350
400
450


2.90 mM benzo[h]quinoline
ln(time(infinity)-time(t))
Time (s)
y = -1.16E-02x - 4.25E+00
R2 = 9.99E-01
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
0
50
100
150
200
250
300
350
400

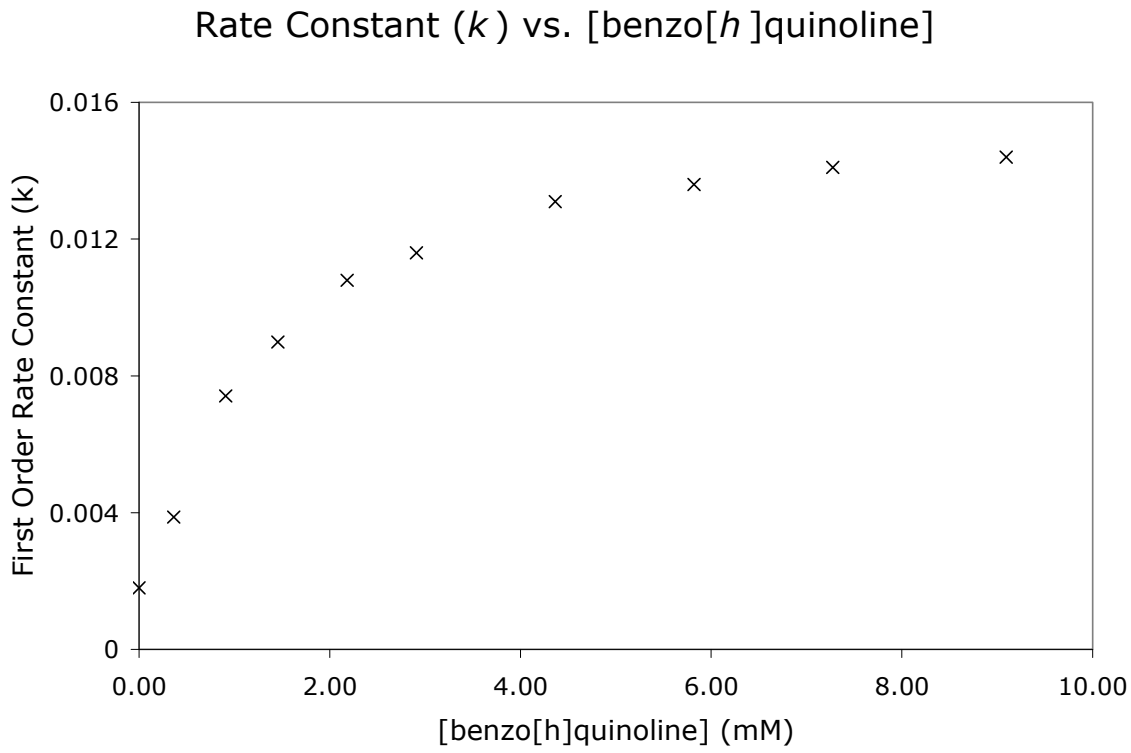

4.35 mM benzo[h]quinoline
ln(time(infinity)-time(t))
Time (s)
y = -1.31E-02x - 4.82E+00
R2 = 9.93E-01
0
-2
-4
-6
-8
-10
-12
0
50
100
150
200
250
300
350
400
450
500

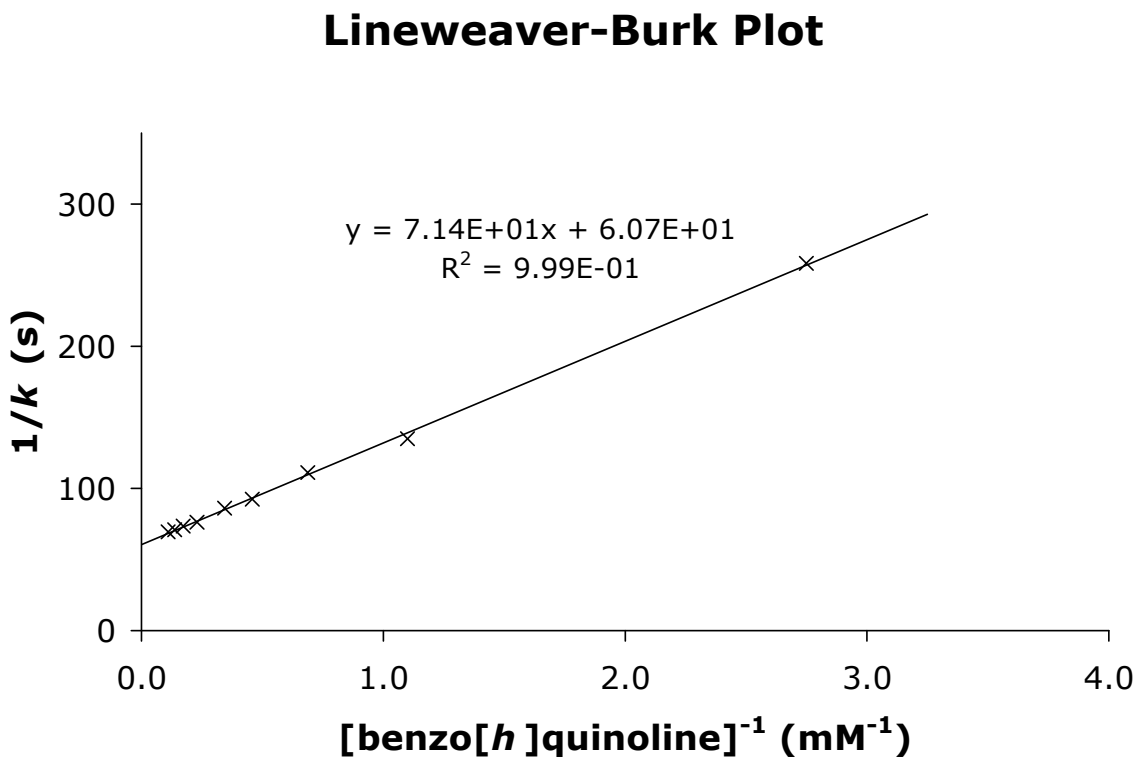

5.80 mM benzo[h]quinoline
ln(time(infinity)-time(t))
Time (s)
y = -1.36E-02x - 4.42E+00
R2 = 9.96E-01
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
0
50
100
150
200
250
300
350
400


7.25 mM benzo[h]quinoline
ln(time(infinity)-time(t))
Time (s)
y = -1.41E-02x - 4.53E+00
R2 = 9.91E-01
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
0
50
100
150
200
250
300
350



Concentration (mM)	k (s^{-1}), R^2
0.00	1.80×10^{-3}; 0.996
0.36	3.87×10^{-3}; 0.993
0.91	7.41×10^{-3}; 0.994
1.45	8.99×10^{-3}; 0.990
2.18	1.08×10^{-2}; 0.990
2.90	1.16×10^{-2}; 0.999
4.35	1.31×10^{-2}; 0.993
5.80	1.36×10^{-2}; 0.996
7.25	1.41×10^{-2}; 0.991
9.06	1.44×10^{-2}; 0.997


Rate Constant (k) vs. [benzo[h]quinoline]
First Order Rate Constant (k)
0.016
0.012
0.008
0.004
0
0.00
2.00
4.00
6.00
8.00
10.00
[benzo[h]quinoline] (mM)


Lineweaver-Burk Plot
y = 7.14E+01x + 6.07E+01
R2 = 9.99E-01
1/k (s)
300
200
100
0
0.0
1.0
2.0
3.0
4.0
[benzo[h]quinoline]-1 (mM-1)