Supporting Information

Oxygenation of a Benzyl Ligand in SNS-Palladium Complexes with O_2: Acceleration by Anions or Brønsted Acids

Reina Shimokawa, Yumi Kawada, Miki Hayashi, Yasutaka Kataoka, and Yasuyuki Ura*

Department of Chemistry, Faculty of Science, Nara Women's University, Kitauoyanishi-machi, Nara 630-8506, Japan

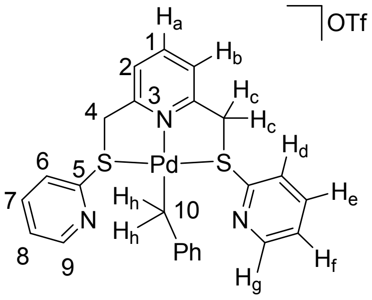
ura@cc.nara-wu.ac.jp

Experimental Section

Materials and Methods. All manipulations were performed under an argon atmosphere using standard Schlenk techniques. Dry solvents were purchased from either Wako Chemical or Nacalai. Flash column chromatography was performed using silica gel SILICYCLE SiliaFlash F60 (40-63 µm, 230-400 mesh). The SNS ligands (pysmepy[1] and phsmepy[2]) and [PdBnCl(cod)][3] were prepared as reported previously.

Physical and Analytical Measurements. NMR spectra were recorded on either a Bruker AV-300N (300 MHz (^{1}H), 75 MHz (^{13}C)) or a JEOL JNM-AL400 (400 MHz (^{1}H), 100 MHz (^{13}C)) spectrometer. Chemical shift values (δ) were expressed relative to $SiMe_4$. Elemental analysis was obtained using a J-SCIENCE LAB JM-10 analyzer. High-resolution mass spectra were recorded on a JEOL JMS-T100LC spectrometer (ESI-TOF MS) with positive ionization mode.

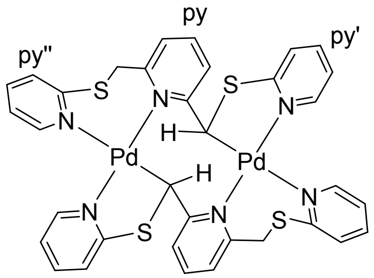
Synthesis of [PdBn(pysmepy)][OTf] (1). [PdBnCl(cod)] (0.202 g, 0.59 mmol), pysmepy (0.192 g, 0.59 mmol, 1.00 equiv.), and AgOTf (0.156 g, 0.61 mmol, 1.03 equiv.) were dissolved in dry CH_2Cl_2 (10 mL) and the reaction mixture was stirred at room temperature for 11 h under argon. After filtration, hexane was added to the filtrate to precipitate yellow solids. The supernatant solution was removed and the obtained solids were dried under vacuum to give **1** (0.391 g, 0.58 mmol, 98% yield).



^{1}H NMR (300 MHz, CD_3CN) δ 8.38 (d, J = 4.5 Hz, 2H, H_g), 7.93 (t, J = 7.8Hz, 1H, H_a), 7.70 (dt, J = 7.8, 1.5 Hz, 2H, H_e), 7.55 (d, J = 7.8 Hz, 2H, H_b), 7.35–7.31 (m, 4H, H_d, H_f), 7.23–7.09 (m, 5H, Ph), 5.05 (s, 4H, H_c), 3.32 (s, 2H, H_h). ^{13}C NMR (75 MHz, CD_3CN) δ 158.2 (C^3), 151.7 (C^9), 151.6 (C^5), 147.2 (Ph), 140.5 (C^1), 139.3 (C^7), 130.3 (Ph), 129.8 (Ph), 126.7 (C^8 or C^6), 125.7 (Ph), 125.2 (C^6 or C^8), 122.9 (C^2), 47.5 (C^4), 22.4 (C^{10}). Anal. Calcd for $C_{25}H_{22}F_3N_3O_3PdS_3 \cdot 0.5CH_2Cl_2$: C, 42.86; H, 3.24; N, 5.88. Found: C, 43.05; H, 3.38; N, 5.82.

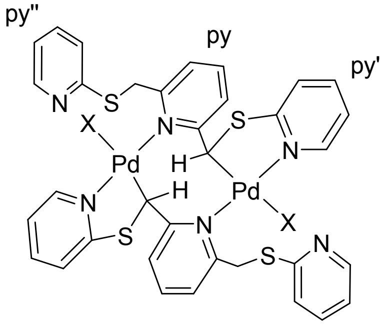
General Procedure for the Reaction of Complex 1 with O_2. All the reactions were performed in sealed J. young NMR tubes (528-LPV-8). Either dichloromethane, 1,1,2,2-tetrachloroethane, or hexamethyldisiloxane was used as an internal standard for each reaction. Complex **1** (10.0 mg, 15 µmol) was dissolved in CD_3CN (0.5 mL) under argon, and O_2 (10 mL) was passed through the solution via syringe in 1 min. Additives (either *n*-Bu_4NX in CH_3CN (0.50 M), HCl in dioxane/CH_3CN (1:7 v/v, 0.50 M), HBr in MeOH (0.40 M), AcOH in CH_3CN (0.50 M), CF_3CO_2H in CH_3CN (0.50 M), or TfOH in CH_3CN (0.50 M), 18 μmol, 1.2 equiv) were then added to the solution, and the reaction mixture was heated up to 40 °C. The reactions were monitored by ^{1}H NMR. Yields of the oxygenated compounds (PhCHO, BnOOH, and BnOH) were determined based on the integrations of corresponding aldehyde or methylene proton signals (δ 10.0, 4.90, and 4.57, respectively). The formation of complex **4a** was also confirmed based on ^{1}H NMR analysis by comparing the NMR data for the reaction mixture with those for **4a** reported previously.[1]

Isolation of Dinuclear Palladium Complex 2. Complex **1** (31.2 mg, 41 μmol) was dissolved in dry CH_3CN, and the solution was heated at 60 °C for 8 days under O_2. Et_2O was diffused slowly to the reaction mixture, and the resulted yellow needle-like crystals were collected and dried under vacuum to give **2** (16.5 mg, 14 μmol, 69% yield).



^{1}H NMR (300 MHz, CD_3CN) δ 9.21 (dd, *J* = 0.9, 5.7 Hz, 2H, py''), 7.98 (dd, *J* = 0.9, 8.1 Hz, 2H, py), 7.87–7.70 (m, 8H, py, py', py''), 7.56 (d, *J* = 5.7 Hz, 2H, py'), 7.48 (s, 2H, C*H*), 7.46–7.38 (m, 4H, py''), 7.14–7.06 (m, 4H, py, py'), 6.82 (d, *J* = 14.1 Hz, 2H, C*H*H), 4.30 (d, *J* = 14.1 Hz, 2H, CH*H*). ^{13}C NMR (75 MHz, CD_3CN) δ 174.2 (py'-quaternary), 166.0 (py-quaternary), 158.9 (py''-quaternary), 156.7 (py-quaternary), 152.4 (py''), 151.2 (py'), 142.6 (py), 140.4 (py'), 140.2 (py''), 129.1 (py''), 124.9 (py''), 123.1 (py), 122.5 (py), 122.3 (py'), 121.9 (py'), 44.4 (*C*H), 38.4 (*C*H_2). Anal. Calcd for $C_{36}H_{28}F_6N_6O_6Pd_2S_6$: C, 37.28; H, 2.43; N, 7.25. Found: C, 37.29; H, 2.51; N, 7.03.

Isolation of Dinuclear Palladium Complexes 3a–c. The following procedure for complex **3a** is representative. In a J. young NMR tube, complex **1** (10.1 mg, 15 μmol) was dissolved in CD_3CN (0.5 mL) under argon. Hexamethyldisiloxane (1.0 μL) was added as an internal standard, and O_2 (10 mL) was passed through the solution via syringe in 1 min. A CD_3CN solution (0.50 M) of *n*-Bu_4NCl (36 μL, 18 μmol, 1.2 equiv.) was then added to the solution, and the reaction mixture was heated up to 40 °C. Orange block crystals were observed after 6 h and were collected, washed with CH_3CN and dried under vacuum (4.5 mg, 4.8 μmol, 64% yield).



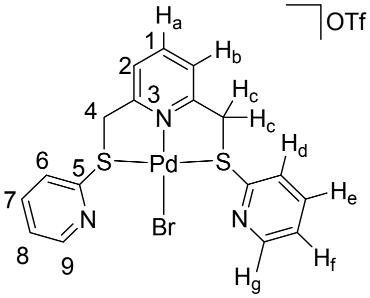
Complex **3a** (X = Cl): ^{1}H NMR (300 MHz, CDCl$_3$) δ 9.21 (ddd, *J* = 0.6, 1.5, 6.0 Hz, 2H, py'-6), 8.41 (ddd, *J* = 0.9, 1.8, 4.8 Hz, 2H, py''-6), 7.87 (s, 2H, C*H*), 7.69–7.58 (m, 6H, py-3 or py-5, py'-3 and py'-4), 7.50 (dt, *J* = 1.8, 7.5 Hz, 2H, py''-4), 7.29 (t, *J* = 7.8 Hz, 2H, py-4), 7.23 (td, *J* = 0.6, 8.1 Hz, 2H, py''-3), 7.13–7.07 (m, 4H, py-3 or py-5, and py'-5), 7.00 (ddd, *J* = 0.9, 5.1, 7.5 Hz, 2H, py''-5), 5.62 (d, *J* = 16.2 Hz, 2H, C*H*H), 5.45 (d, *J* = 16.2 Hz, 2H, CH*H*). ^{13}C NMR (75 MHz, CDCl$_3$) δ 170.5 (py'-2), 160.4 (py-2), 159.9 (py''-2), 157.7 (py-6), 153.3 (py'-6), 149.5 (py''-6), 138.6 (py'-3), 137.9, 136.5 (py''-4), 121.9 (py''-3), 120.9, 120.7, 120.5, 120.1, 119.7, 46.2 (*C*H), 36.8 (*C*H$_2$). Anal. Calcd for $C_{34}H_{28}Cl_2N_6Pd_2S_4\cdot H_2O$: C; 42.96; H, 3.18; N, 8.84. Found: C, 42.93; H, 3.16; N, 8.84.

Complex **3b** (X = Br): Orange solid (4.9 mg, 4.7 μmol, 63% yield). ^{1}H NMR (300 MHz, CDCl$_3$) δ 9.41(d, *J* = 5.4 Hz, 2H, py'-6), 8.42 (d, *J* = 4.2 Hz, 2H, py''-6), 7.88 (s, 2H, C*H*), 7.68–7.59 (m, 6H, py-3 or py-5, py'-3 and py'-4), 7.50 (dt, *J* = 1.8, 7.8 Hz, 2H, py''-4), 7.30 (t, *J* = 8.1 Hz, 2H, py-4), 7.23 (d, *J* = 8.1 Hz, 2H, py''-3), 7.12–6.99 (m, 6H, py-3 or py-5, py'-5 and py''-5), 5.61 (d, *J* = 16.5 Hz, 2H, C*H*H), 5.44 (d, *J* = 16.5 Hz, 2H, CH*H*). ^{13}C NMR (75 MHz, CDCl$_3$) δ 169.9 (py'-2), 163.8 (py-2), 159.8 (py''-2), 157.5 (py-6), 154.7 (py'-6), 149.4 (py''-6), 138.6 (py'-3), 137.7, 136.4 (py''-4), 121.7 (py''-3), 120.9, 120.7, 120.4, 119.9, 119.2, 47.2 (*C*H), 37.0 (*C*H$_2$). HRMS (ESI): *m*/*z* calcd for $C_{34}H_{28}BrN_6Pd_2S_4$ [M-Br]$^+$ 940.8516, found 940.8506.

Complex **3c** (X = I): Orange solid (4.8 mg, 4.2 μmol, 56% yield). ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.70 (d, *J* = 6.0 Hz, 2H, py'-6), 8.43 (d, *J* = 4.4 Hz, 2H, py''-6), 7.86 (s, 2H, C*H*), 7.64–7.61 (m, 4H, py'-3 and py'-4), 7.53 (d, *J* = 8.0 Hz, 2H, py-3 or py-5), 7.50 (t, *J* = 7.6 Hz, 2H, py''-4), 7.32 (t, *J* = 7.8 Hz, 2H, py-4), 7.24 (d, *J* = 8.0 Hz, 2H, py''-3), 7.11–7.00 (m, 6H, py-3 or py-5, py'-5 and py''-5), 5.58 (d, *J* = 16.2 Hz, 2H, C*H*H), 5.38 (d, *J* = 16.2 Hz, 2H, CH*H*). ^{13}C NMR (100 MHz, CDCl$_3$) δ 169.3 (Py'-2), 163.3 (Py-2), 159.9 (Py''-2), 157.7 (Py-6), 157.4 (Py'-6), 149.4 (Py''-6), 138.6 (Py'-3), 137.6, 136.4 (Py''-4), 121.8 (Py''-3), 121.1, 121.0, 120.0, 120.0, 118.8, 49.0 (*C*H), 37.6 (*C*H$_2$). HRMS (ESI): *m*/*z* calcd for $C_{34}H_{28}IN_6Pd_2S_4$ [M-I]$^+$ 988.8386, found 988.8359.

Isolation of Complex 4b. In a J. Young NMR tube, complex **1** (10.2 mg, 15 μmol) was dissolved in CD$_3$CN (0.5 mL) under argon. 1,1,2,2-Tetrachloroethane (2.0 μL) was added as an internal standard, and O$_2$ (10 mL) was passed through the solution via syringe in 1 min. A CH$_3$OH solution of HBr (0.40

M, 45 μL, 18 μmol, 1.2 equiv.) was then added to the solution, and the reaction mixture was heated up to 40 °C for 6 h. At room temperature, Et_2O was added to the reaction mixture. The supernatant solution was removed and the obtained solids were dried under vacuum to give **4b** (6.3 mg, 9.5 μmol, 63% yield). The ratio of **4b**-SNS:**4b**-NNN in CD_3CN at room temperature was ca. 17:1, determined by ^1H NMR.



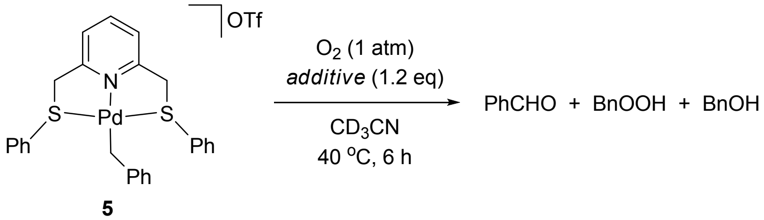
^1H NMR for **4b**-SNS (300 MHz, CD_3CN) δ 8.46 (d, J = 4.2 Hz, 2H, H_g), 8.09 (t, J = 8.0 Hz, 1H, H_a), 7.90 (br s, 4H, H_d and H_e), 7.70 (d, J = 8.1 Hz, 2H, H_b), 7.45 (br t, J = 5.0 Hz, 2H, H_f), 5.25 (br s, 4H, H_c). ^1H NMR for **4b**-NNN (300 MHz, CD_3CN, selected data) δ 9.23 (dd, J = 6.2, 1.1 Hz, 2H, H_g), 7.58 (d, J = 7.8 Hz, 2H, H_b), 7.28 (ddd, J = 7.4, 6.0, 1.4 Hz, 2H, H_f), 6.74 (d, J = 14.7 Hz, 2H, H_c), 4.64 (d, J = 14.7 Hz, 2H, H_c). ^{13}C NMR for **4b**-SNS (75 MHz, CD_3CN) δ 163.7 (C^3), 151.8 (C^9), 149.0 (C^5), 141.7 (C^1), 139.7 (C^7), 127.4 (C^6), 126.0 (C^8), 123.2 (C^2), 47.2 (C^4). HRMS (ESI): *m*/*z* calcd for $C_{17}H_{15}BrN_3PdS_2$ $[M]^+$ 511.8919, found 511.8921.

Synthesis of [PdBn(phsmepy)][OTf] (5). [PdBnCl(cod)] (29.8 mg, 87 μmol), phsmepy (28.5 mg, 88 μmol, 1.01 equiv.), and AgOTf (22.9 mg, 89 μmol, 1.02 equiv.) were dissolved in dry CH_2Cl_2 (3 mL) under argon and the reaction mixture was stirred at room temperature for 3 h. After filtration, hexane was added to the filtrate to precipitate yellow block crystals. The supernatant solution was removed and the obtained crystals were dried under vacuum to give **5** (58.5 mg, 87 μmol, >99% yield).

^1H NMR (300 MHz, $CDCl_3$) δ 7.82 (t, J = 7.8 Hz, 1H, py-4), 7.62–7.53 (m, 6H, Ph, py-3,5), 7.46–7.34 (m, 6H, Ph), 6.87 (s, 5H, Ph), 4.97 (br s, 4H, CH_2S), 3.11 (s, 2H, CH_2Ph). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.3 (Py-2,6), 145.7 (Ph), 140.2 (Py-4), 132.8 (Ph), 131.2 (Ph), 130.5 (Ph), 130.0 (Ph), 128.9 (Ph), 128.4 (Ph), 124.8 (Ph), 123.1 (Py-3,5), 52.5 (CH_2S), 22.7 (CH_2Ph). Anal. Calcd for $C_{27}H_{24}F_3NO_3PdS_3$: C; 48.39; H, 3.61; N, 2.09. Found: C, 48.01; H, 3.61; N, 2.08.

Reaction of Complex 5 with O_2. The procedure was same as that for complex **1**. The results were summarized in Table S1.

Table S1. Reaction of 5 with O_2[a]



5

entry	additive	yield (%)[b]		
		PhCHO	BnOOH	BnOH
1	none	<1	0	1
2[c]	none	6	0	1
3	^{n}Bu$_4$NCl	49	0	0
4	HCl	12	69	0

[a] Reaction conditions: **5** (15 μmol), additive (18 μmol), and CD_3CN (0.5 mL). [b] NMR yield. [c] 70 °C, 72 h.

Isolation of Benzyl Hydroperoxide. Complex **1** (88 mg, 0.13 mmol) was placed in a 20 mL two-neck flask under argon, and oxygen was then purged. CH_3CN (5 mL) was added to give a yellow solution. HCl in Et_2O (1 M, 130 μL, 0.13 mmol) was added to the solution, and the reaction mixture was stirred at room temperature for 5 h. Et_2O (15 mL) was added to the solution to precipitate the formed complex **4** (orange yellow solid). The colorless supernatant was transferred to 50 mL flask and the solvent was removed under vacuum. The obtained yellow oil was purified by silica gel column chromatography (eluent: CH_2Cl_2/hexane = 7 : 2 to 5 : 1) to give benzyl hydroperoxide (11.2 mg, 0.09 mmol, 69% yield) after removal of the solvents. The spectral data were consistent with those reported previously.[4]

Conversion of Benzyl Hydroperoxide into Benzaldehyde and Benzyl Alcohol. In a J. young NMR tube, benzyl hydroperoxide in CD_3CN (30 mM, 0.50 mL, 15 μmol) and 1,1,2,2-tetrachloroethane (2.0 μL, 19 μmol) as an internal standard were placed under argon (for the reaction under O_2, O_2 gas was passed through the solution for 10 min at a rate of 10 mL/min). An additive in solution (0.50 M, 30 μL, 15 μmol, either *n*-Bu$_4$NCl in CH_3CN or HCl in dioxane/CH_3CN) was added and the reaction mixture was heated at 40 °C for 2 h. The conversion of benzyl hydroperoxide and yields of benzaldehyde and benzyl alcohol were determined by ^{1}H NMR analysis.

Crystallographic Study of Complexes 1, 2, 3a, and 5. Crystals suitable for X-ray diffraction measurements were obtained by recrystallization from CH_2Cl_2/hexane for **1** (yellow block crystals), CH_3CN/Et_2O for **2** (yellow needle crystals), CD_3CN only for **3a** (orange block crystals), and CH_3CN/Et_2O for **5** (yellow block crystals), respectively. The crystals were mounted using a cryoloop.

The diffraction data were collected with a Rigaku Mercury detector or a Rigaku Saturn CCD detector ($\mathrm{Mo}_{\mathrm{K}\alpha}$, $\lambda = 0.71073$ Å). Crystal data and experimental data are listed in Table S2. The structures were solved by direct methods using SHELXS-97 and refined by least squares on F^2, SHELXL-97.[5, 6] Non-hydrogen atoms were anisotropically refined. Refinements were continued until all shifts were smaller than one-tenth of the standard deviations of the parameters involved. Atomic scattering factors and anomalous dispersion terms were taken from the International Tables for X-ray Crystallography.[7] CCDC reference numbers: 1491453 (**1**), 1491480 (**2**), 1491481 (**3a**), and 1491479 (**5**).

Table S2. Summary of Crystal Data, Collection Data, and Refinement of 1, 2, 3a, and 5

	1	**2**	**3a**	**5**
formula	$C_{26}H_{24}Cl_2F_3N_3O_3PdS_3$	$C_{40}H_{34}F_6N_8O_6Pd_2S_6$	$C_{36}H_{31}Cl_2N_7Pd_2S_4$	$C_{27}H_{24}F_3NO_3PdS_3$
fw	756.96	1241.91	973.62	670.05
cryst size, mm	0.20 × 0.20 × 0.20	0.20 × 0.05 × 0.03	0.12 × 0.10 × 0.08	0.10 × 0.10 × 0.10
cryst syst	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/c$	P-1	P-1	$P2_1/n$
a, Å	9.995(3)	11.8556(15)	11.028(2)	10.224(2)
b, Å	26.900(7)	12.2946(14)	11.8922(19)	13.422(3)
c, Å	11.989(3)	16.8688(19)	14.942(3)	20.061(4)
α, deg	90	74.287(4)	73.820(4)	90
β, deg	113.816(3)	85.564(5)	89.554(5)	102.936(4)
γ, deg	90	81.418(4)	88.613(6)	90
V, Å^3	2949.1(13)	2338.6(5)	1881.4(6)	2682.9(9)
Z	4	2	2	4
D (calcd), g cm^{-3}	1.705	1.764	1.719	1.659
data collection temp, K	293(2)	153(2)	153(2)	153(2)
μ (Mo Kα), mm^{-1}	1.077	1.116	1.358	0.977
$2\theta_{\max}$, deg	55.0	55.0	55.0	55.0
no. of measd reflns	22131	28245	30679	31792
no. of unique reflns	6753	10659	8611	6140
no. of obsd reflns ($I > 2\sigma(I)$)	6019	9426	7396	5409
no. of variables	371	615	461	343
$R_1{}^a$ ($I > 2\sigma(I)$)	0.0532	0.0367	0.0475	0.0474
$wR_2{}^a$ ($I > 2\sigma(I)$)	0.1297	0.0898	0.1245	0.1232
$R_1{}^a$ (all data)	0.0591	0.0416	0.0558	0.0533
$wR_2{}^a$ (all data)	0.1356	0.0942	0.1325	0.1292
GOF	1.050	1.058	1.058	1.036

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{1/2}$.

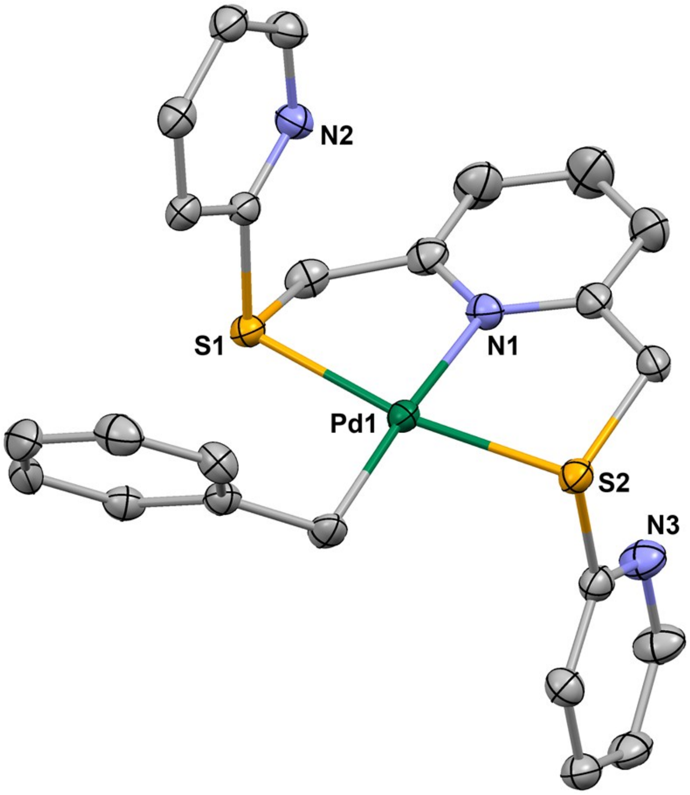


Figure S1. Molecular Structure of **1**. Thermal ellipsoids are shown at the 50% probability level. A counter anion, a solvent molecule (CH_2Cl_2), and hydrogen atoms are omitted for clarity.

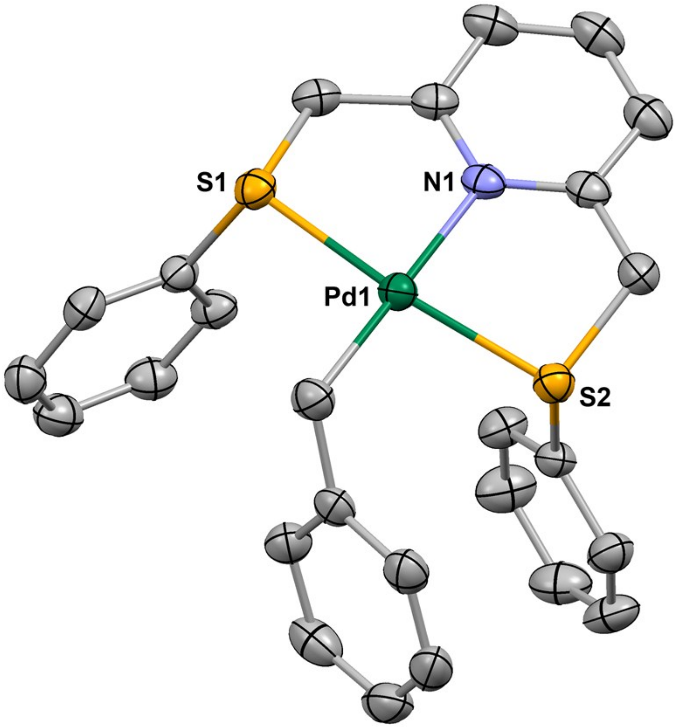
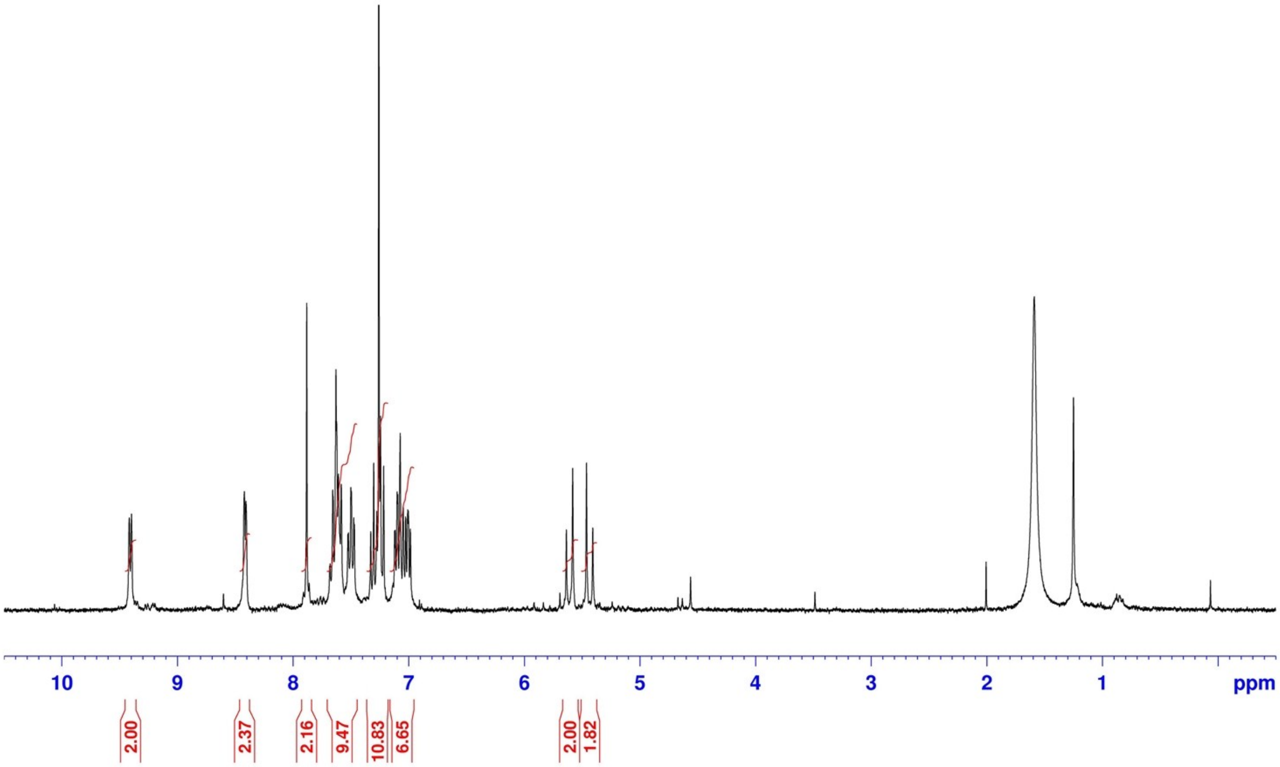
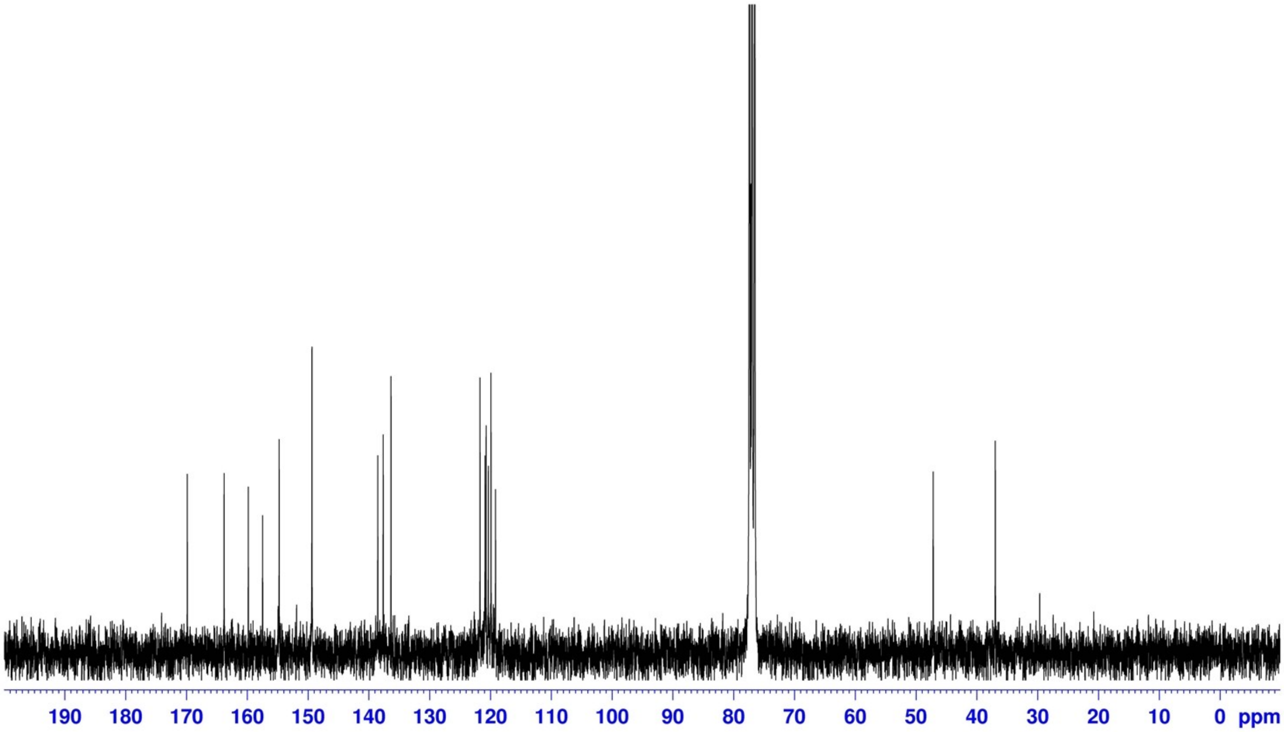


Figure S2. Molecular Structure of **5**. Thermal ellipsoids are shown at the 50% probability level. A counter anion and hydrogen atoms are omitted for clarity.

Complex 3b

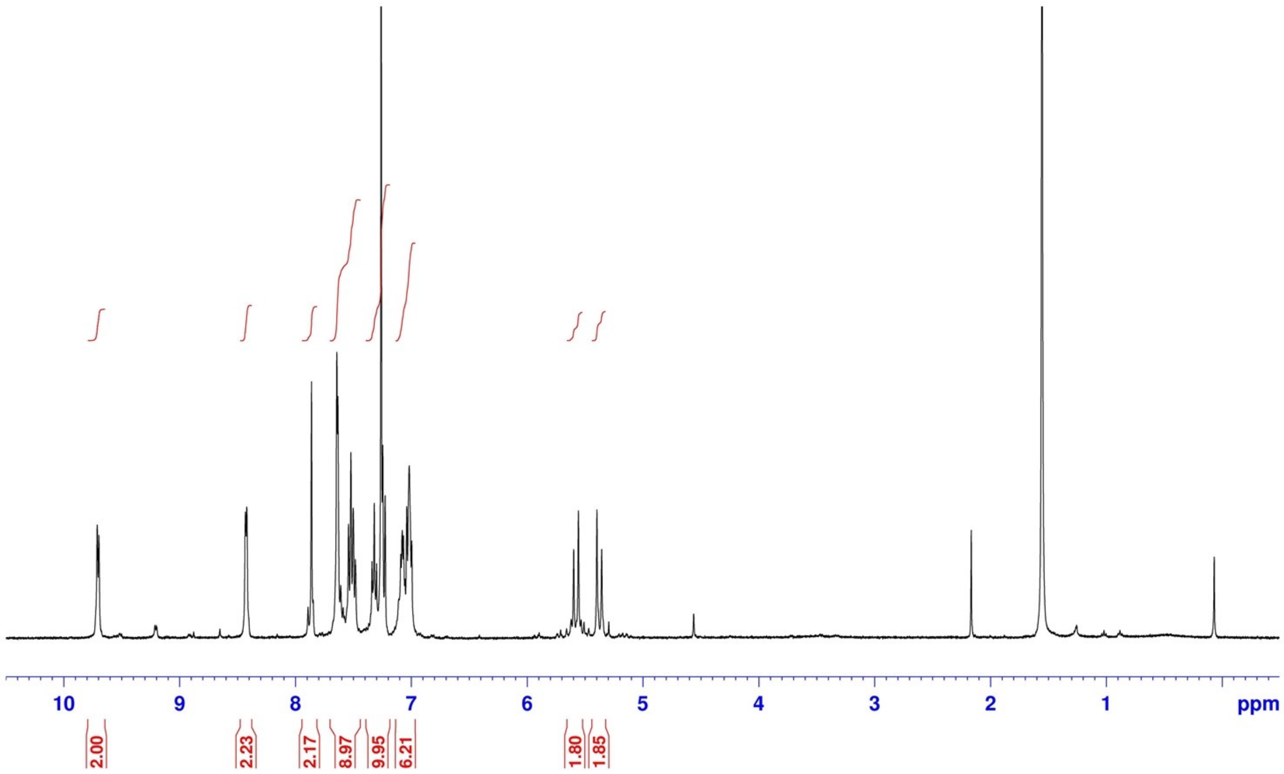


^{1}H NMR (300 MHz, CDCl$_3$)

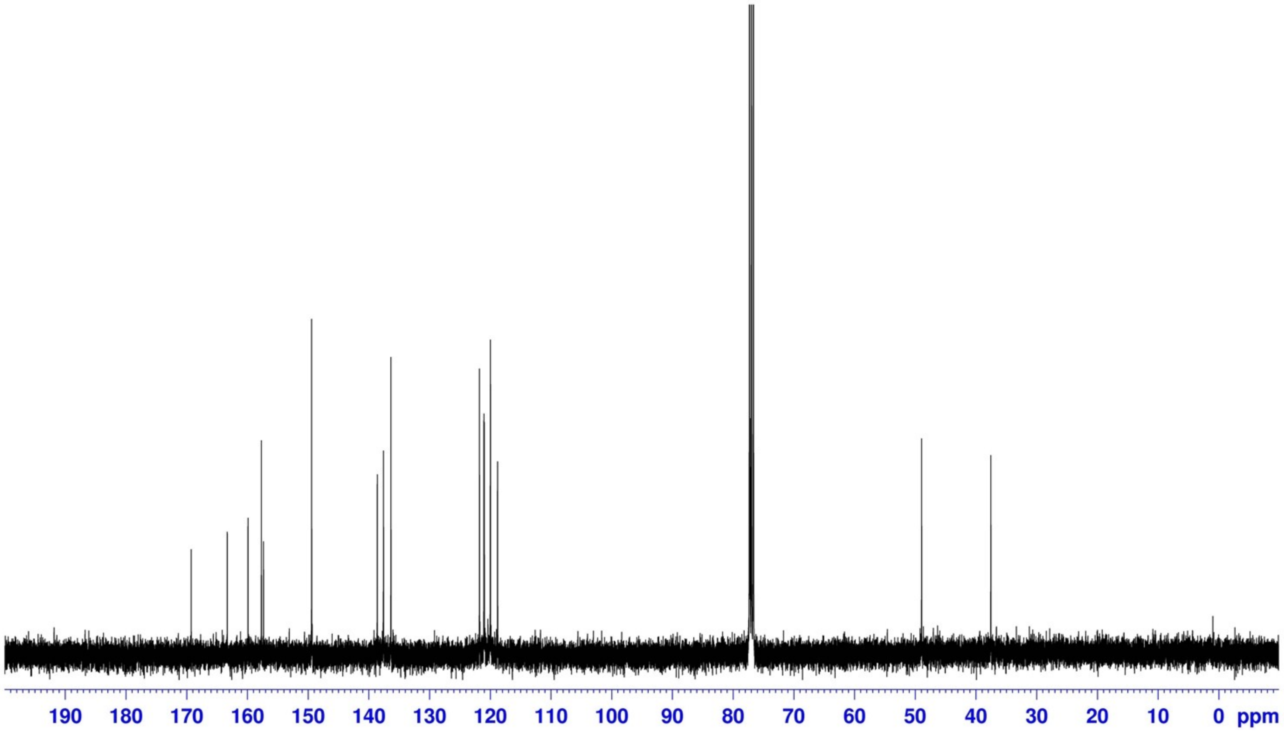


^{13}C NMR (75 MHz, CDCl$_3$)

Complex 3c

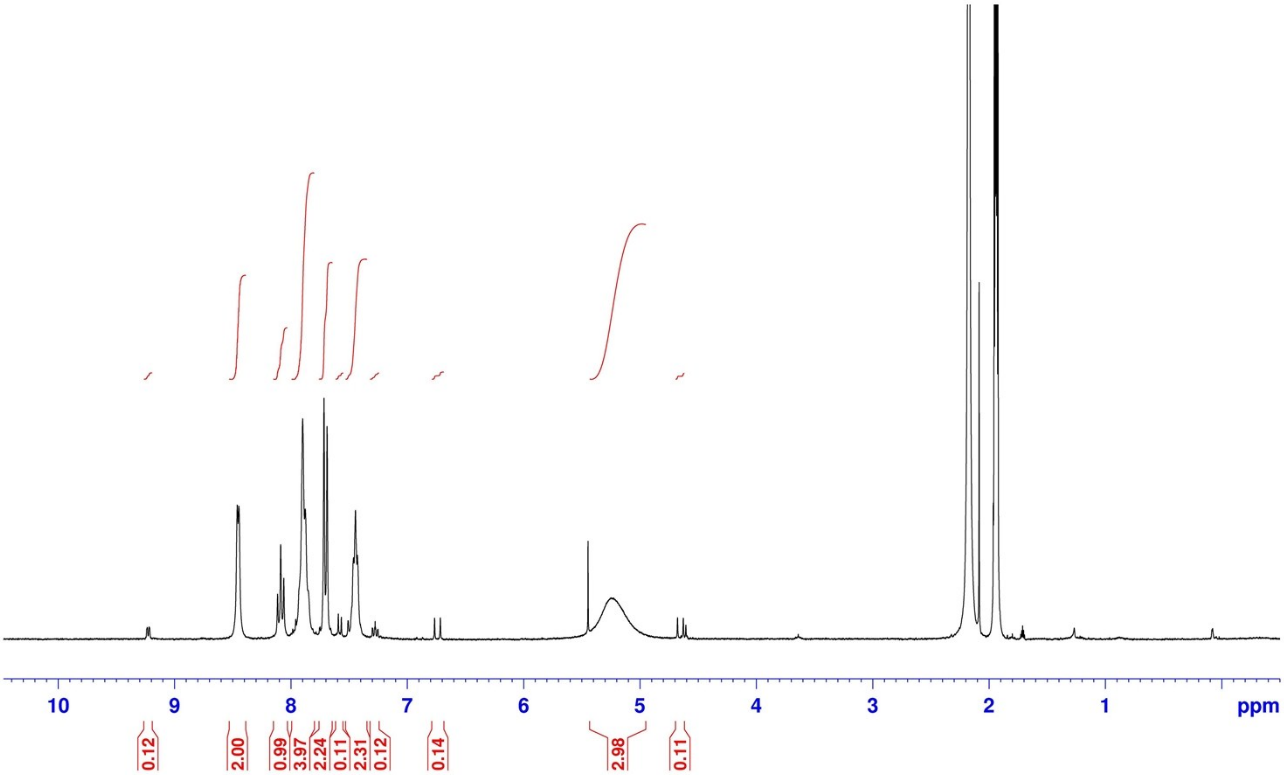


^{1}H NMR (400 MHz, $CDCl_3$)

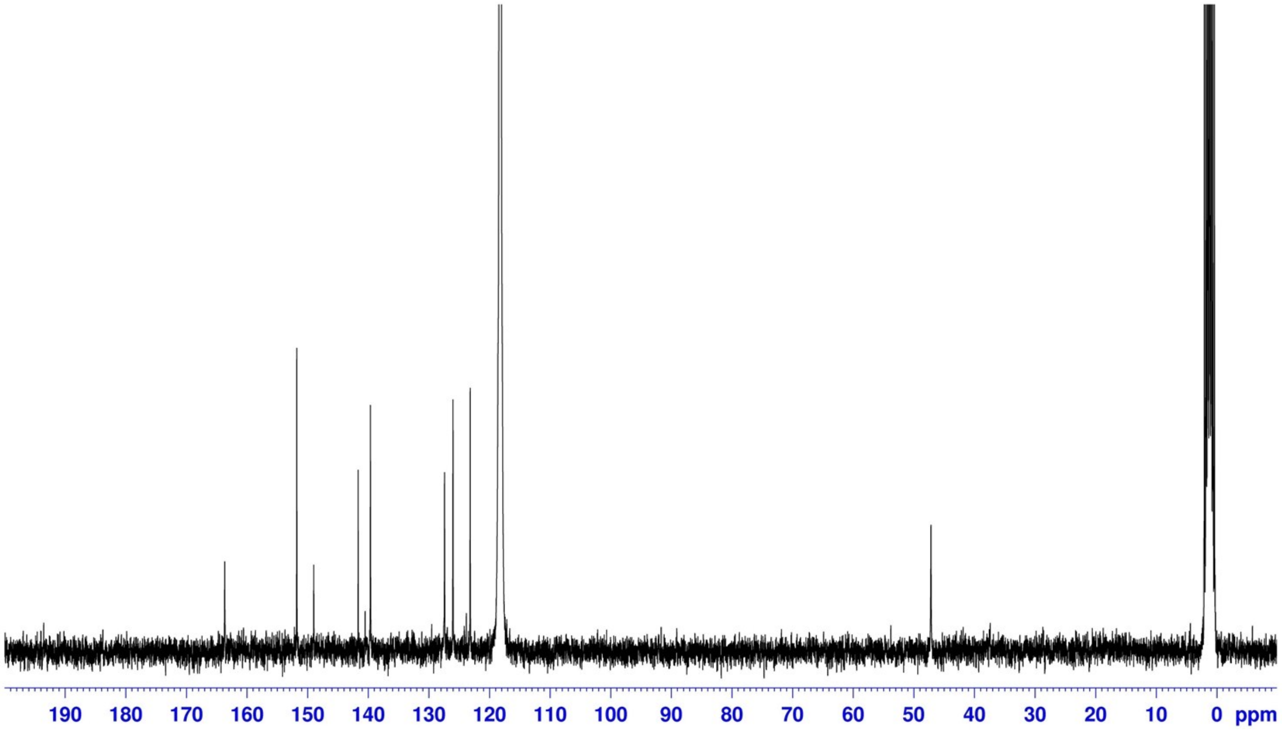


^{13}C NMR (100 MHz, $CDCl_3$)

Complex 4b (a mixture of 4b-SNS and 4b-NNN)



^{1}H NMR (300 MHz, CD$_3$CN)



^{13}C NMR (75 MHz, CD$_3$CN)

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